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THE THEORY AND PRACTICE OF

SEMIMICRO QUALITATIVE ANALYSIS

By

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Second Edition, Illustrated

PHILADELPHIA & LONDON

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1950

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Preface to the Second Edition

IN THE SECOND EDITION of "The Theory and Practice of Semimicro Qualitative Analysis" discussions have been modified to conform with present accepted modern views. The subject of chemical equilibrium has been emphasized by including a discussion of the deduction of equilibrium constants of chemical reactions, the method of evaluating the equilibrium constants and the qualitative and quantitative use of the expressions.

The procedures have been revised to include specific directions for separating precipitates by using either centrifuges or filter tubes. The amount of each ion present in the sample is 0.1 mg. The volumes of the solutions used vary from 2 drops to 1.5 ml.

The periodic table on end sheets in the front of the book is used through the courtesy of Dr. Joseph A. Babor and taken from his "Basic College Chemistry," published by Thomas Y. Crowell Company.

G. B. HEISIG

April, 1950

Preface to the First Edition

THE AUTHOR believes that a course in qualitative analysis should accomplish several objects. It should serve as a means of reviewing and extending a student's knowledge of the principles and descriptive matter of general chemistry. On the experimental side its aim should be to train the beginner to acquire methods of careful manipulation and to do exact, dependable and intelligent work. To this end an attempt has been made to present the experimental material in a concise form, and to give laws and theories in such a way that the student may understand and correctly interpret his observations and results.

This book is designed for the use of students who have had a thorough course in general inorganic chemistry. It is intended to serve as a basis for two quarters of five credits each, or two semesters of three credits each, of qualitative analysis, but is so divided that the analysis of cations can be used alone when only one term of qualitative analysis is taught. The material is presented in the light of the theory of ionization, the law of mass action and the concepts of Debye, Brønsted and Werner.

Many preliminary experiments are given so that each instructor can select those most suited to the needs of his class. The size of the sample used for the analysis has been reduced to 1 mg. The small volumes (2 drops to 1.5 ml.) are filtered through plugs of glass wool held in filtering tubes. The liquid is blown through the glass wool by compressing the air in a rubber bulb (an ear syringe) held tightly against the top of the tube. If centrifuges are available they may be used instead of filtering tubes.

A decided improvement in laboratory technique has followed the use of smaller samples. The smaller quantity of precipitates and of solutions has also materially reduced the time consumed in filtering. The use of smaller amounts of ions reduces the quantities of chemicals required for the course, and thus effects a considerable saving in cost.

Since the primary objective of an elementary course in qualitative analysis is to acquaint the student with the properties and reactions of the ions of the twenty-four common metals and the anions of the twenty-four common acids, inorganic reagents, with

three exceptions, are used in the separation and identification of the ions. The three organic reagents are used where there are no satisfactory confirmatory inorganic tests. The use of organic reagents remains to be considered in advanced courses in qualitative analysis or to be taken up as the occasion demands after the student has had organic chemistry.

The chapter on the activity concept has been placed so that it can be omitted if a short course is given. Questions and problems have been placed at the end of each chapter to enable the student to determine whether or not he has grasped the material presented.

In writing this text, information has been secured from many sources, especially from the books on qualitative analysis by Treadwell and Hall, and Prescott and Johnson revised by MacAlpine and Soule. Permission to use portions of tables from Oxidation Potentials by Latimer, and to use the equipment for filtering by H. H. Barber is acknowledged. The author also wishes to thank the many people who have helped perfect the procedures by their suggestions and criticisms, and wishes especially to acknowledge the aid of L. M. H. for much help in preparing the manuscript and in reading proof.

It is hoped that this book will prove to be a real aid to the student who wishes to develop his talents to the utmost.

G. B. Heisig

Suggestions to Instructors

THIS TEXT is divided into two parts. The theory of qualitative analysis is discussed in the first part. Problems of varying difficulty have been placed at the close of each chapter. Some answers are given to permit the student to check his work. The systematic analysis of cations and anions is considered in Part II. A short discussion of the properties of the ions of each group is followed by a sufficient number of preliminary experiments to enable the instructor to select those he thinks are necessary to round out the student's knowledge of the properties of the ions. Partially completed equations follow each part of the preliminary experiments. To test the knowledge of the properties of the ions and to furnish practice in balancing equations, each student should complete all of the equations whether the preliminary experiments are performed or not. At the end of each chapter in Part II there are questions to test the student's knowledge of the principles and reactions involved in the analysis.

It is well to require a student to bring the completed and balanced equations for the preliminary experiments to his laboratory instructor when he applies for an oral quiz on the general principles involved in the analysis. When the analysis of the known has been carried out satisfactorily, the student may be required to bring to his laboratory instructor the equations for the action of each ion toward each reagent with which it is treated. If the equations are satisfactory and the student passes the detailed oral quiz on the analysis of the group, he is given the unknown.

The first term's work in qualitative analysis should include Chapters I–VI and the systematic analysis of the cations. Some of the mathematical sections can be omitted if the students are not being trained to be chemists. The number of unknowns analyzed should be adjusted to the number of hours of laboratory work and the ability of the students.

The second term's work should include a review of the work of the first term and involve more complicated problems and the systematic analysis of the anions. Chapter VII, The Activity Concept, was included to acquaint the student who is majoring in chemistry with the activity concept early in his studies. Further-

more, the use of activities enables the instructor to review the subjects considered in the first six chapters without the necessity of referring students to portions of the text which have been studied previously. The chapter may be omitted without breaking the continuity.

In a one semester course the laboratory work must be very carefully planned if the analysis of both cations and anions are to be studied. Only a minimum number of preliminary experiments and relatively simple unknowns can be included.

The reagents required to carry out the preliminary experiments and analyses are so listed in the Appendix that the instructor can tell whether they are required for carrying out the preliminary experiments or for the analyses of the cations or anions. The ideal arrangement would be for each student to have a set of reagents. However, by locating the sets of reagents properly, as many as 25–30 students can use a single set without appreciable waste of time. The dropping bottles should have a capacity of one ounce. Screw top dropping bottles or tincture bottles fitted with droppers can be used. These bottles can be obtained from the laboratory supply houses. An extra supply of the rubber bulbs should be ordered, since the vapors from some of the solutions shorten the life of the bulbs.

A convenient method of grading unknowns so that an average grade can be computed easily, is to place a fraction on the report, the numerator of which is the number of ions correctly reported and the denominator, the sum of the number of ions reported correctly, incorrectly and missed. At the end of the course add the numerators and denominators and calculate the percentage of ions correctly reported.

There are many advantages in providing for the students a schedule of the dates on which the analyses of the known and unknown solutions should be completed. A penalty should be imposed if the unknowns are not completed and handed in on or before the time set.

THE AUTHOR

Table of Contents

PREFACE TO THE SECOND EDITION 3

PREFACE TO THE FIRST EDITION 5

SUGGESTIONS TO INSTRUCTORS 7

INTRODUCTION 13

PART I. THEORETICAL

I. SOLUTION AND IONIZATION 19

II. CHEMICAL EQUILIBRIUM 42

III. APPLICATION OF THE LAW OF MASS ACTION TO SATURATED SOLUTIONS 58

IV. OXIDATION AND REDUCTION, COMPLEX IONS, AND THE COLLOIDAL STATE 72

V. HYDROGEN SULFIDE AS A PRECIPITATING AGENT AND THE SOLUTION OF SULFIDES 93

VI. HYDROLYSIS AND AMPHIPROTIC SUBSTANCES 103

VII. THE ACTIVITY CONCEPT 116

PART II. EXPERIMENTAL

THE CATIONS

VIII. GENERAL LABORATORY DIRECTIONS 139

IX. IONS OF GROUP I. SILVER, MERCURY (OUS) AND LEAD. 157

Properties of Metals and Ions 157
Reactions of the Ions 161

Analysis 163
Discussion of the Analysis 165
Exercises 167

X. Ions of Group II. Lead, Bismuth, Copper, Cadmium, Mercury (ic), Arsenic, Antimony and Tin 168

Properties of Metals and Ions 168
Reactions of the Ions 172
Analysis 177
Discussion of the Analysis 181
Exercises 191

XI. Ions of Group III. Cobalt, Nickel, Zinc, Manganese, Iron, Aluminum and Chromium 193

Properties of Metals and Ions 193
Reactions of the Ions 199
Analysis 204
Discussion of the Analysis 209
Exercises 216

XII. Ions of Group IV. Barium, Strontium, Calcium and Magnesium 218

Properties of Metals and Ions 218
Reactions of the Ions
Analysis 222
Discussion of the Analysis 224
Exercises 228

XIII. Ions of Group V. Potassium, Sodium and Ammonium 229

Properties of Metals and Ions 229
Reactions of the Ions 230
Analysis 232
Discussion of the Analysis 233
Exercises 235

THE ANIONS

XIV. General Discussion 237

XV. Anions of Group I. Carbonate, Sulfite, Fluoride, Phosphate and Arsenate 243

Properties of Acids and Ions 243

Reactions of the Ions 246
Analysis 250
Discussion of the Analysis 253
Exercises 255

XVI. Anions of Group II. Sulfate, Chromate-Dichromate and Iodate 257

Properties of Acids and Ions 257
Reactions of the Ions 258
Analysis 260
Discussion of the Analysis 263
Exercises 268

XVII. Anions of Group III. Ferrocyanide, Ferricyanide, and Sulfide 270

Properties of Acids and Ions 270
Reactions of the Ions 271
Analysis 273
Discussion of the Analysis 274
Exercises 275

XVIII. Anions of Group IV. Cyanide, Thiosulfate, Thiocyanate, Chloride, Bromide, and Iodide 276

Properties of Acids and Ions 276
Reactions of the Ions 279
Analysis 283
Discussion of the Analysis 288
Exercises 290

XIX. Anions of Group V. Hypochlorite, Chlorate, Bromate, Iodate, Perchlorate, Borate, Nitrite and Nitrate 292

Properties of Acids and Ions 292
Reactions of the Ions 295
Analysis 298
Discussion of the Analysis 303
Exercises 304

XX. Complete Analysis 306

Systematic Analysis of a Solid or Liquid Sample .. 306
Preliminary Examination 307
Analysis of a Metallic Substance 310
Analysis of Non-metallic Samples 313

Method of Changing Very Insoluble Substances into More Soluble Ones 316
Rules of Solubility 317
Colors of Inorganic Compounds 318

APPENDIX

Reference Books 319
Degree of Ionization of Acids, Bases and Salts (According to Arrhenius) 320
Equilibrium Constants 321
Oxidation-Reduction Potentials—Acid Solutions 324
Oxidation-Reduction Potentials—Basic Solutions 325
Mathematical Operations Used in Qualitative Analysis 326
Reagents 328
Special Reagents 332
Preparation of Solutions 333
Equipment 336
Logarithm Tables 337

INDEX 339

END SHEETS

The Representative Elements ..... *Inside Front Cover*
The Related or Transitional Metals ..... *Inside Front Cover*
The Rare Earth Elements ..... *Inside Front Cover*
International Atomic Weights, 1947 ..... *Inside Back Cover*
Periodic Table of the Elements ..... *Inside Back Cover*

Introduction

QUALITATIVE ANALYSIS is the determination of the ingredients in a material. To do intelligent analytical work, it is necessary to be familiar with the chemical reactions and properties of ions and substances. In most cases more time and energy are saved by following a systematic procedure for identifying ions and substances than by attacking the problem in a haphazard manner. Accordingly a course in qualitative analysis may be divided into three parts: first, the study of chemical reactions and characteristic tests by which an ion or substance is identified; second, the systematic analytical procedures; and third, a discussion of the laws and theories which give an interpretation of the procedures used.

SCOPE OF THE BOOK. Qualitative analysis in its broadest sense includes the analysis of all natural and manufactured products. Since the subject is so extensive it is necessary to limit the material presented in a beginning course. In this book, therefore, the analytical procedures provide for the detection of twenty-four common inorganic cations and an equal number of anions. This limitation of the subject gives the student time to study the scientific principles which raise the subject above a mere group of mechanical manipulations.

QUALITATIVE GROUPS. In a systematic scheme of analysis, separate solutions are used for the identification of the cations (metal ions) and the anions (acid ions). The identification of the cations usually precedes that of the anions. The ions are divided into analytical groups. The basis for such grouping depends largely, though not entirely, upon the solubility of certain salts which these ions form. The cations (NH_4^+ excepted) are grouped in the order in which they are separated and identified according to the scheme used.

Remember that the ions of a lower group, if present, must be removed before the precipitation of the next group is undertaken. Thus, if all the groups are present in solution, the ions of Group I should be removed before further separation of groups is made. *At the beginning of the analysis a test should be made on a separate portion of the sample for the ammonium ion.*

1. CATIONS

Group I. Ions whose chlorides are difficultly soluble in water and acids. The reagent for precipitating this group is *hydrochloric acid.* The ions of this group are:

Lead ion, Pb^{++} (high concentrations) Mercurous ion, Hg_2^{++} Silver ion, Ag^{+}

Group II. Ions whose sulfides are sparingly soluble in water and dilute acids. The reagent for precipitating this group is *hydrogen sulfide in acid solution.* The ions are:

A. Lead ion, Pb^{++}
Bismuth ion, Bi^{+++}
Cupric ion, Cu^{++}
Cadmium ion, Cd^{++}

B. Mercuric ion, Hg^{++}
Arsenious and arsenate ions, As^{+++} and As^{+5} ($AsO_4^{\equiv}$)
Antimonous and antimonic ions, Sb^{+++} and Sb^{+5} ($SbO_4^{\equiv}$ and $SbCl_6^{-}$)
Stannous and stannic ions, Sn^{++} and Sn^{+4} ($SnCl_6^{=}$)

Group III. Ions whose sulfides are not precipitated from dilute acid solutions but are almost insoluble in water and slightly alkaline solutions or are hydrolyzed by water forming insoluble hydroxides. The reagents for precipitating this group are *hydrogen sulfide, ammonium chloride, and ammonia, frequently called ammonium hydroxide.*

Nickel ion, Ni^{++}
Cobalt ion, Co^{++}
Manganous ion, Mn^{++}
Ferrous and ferric ions, Fe^{++} and Fe^{+++}
Aluminum ion, Al^{+++}
Chromium ion, Cr^{+++}
Zinc ion, Zn^{++}

Group IV. Ions whose carbonates are difficultly soluble in water. The reagents for precipitating this group, with the exception of magnesium, are *ammonium chloride, ammonia and ammonium carbonate.* The ions of this group are:

Barium ion, Ba^{++}
Magnesium ion, Mg^{++}
Calcium ion, Ca^{++}
Strontium ion, Sr^{++}

Group V. Ions whose chlorides, sulfides, carbonates and phosphates are soluble in water. The ions of this group are:

Ammonium ion, NH_4^{+} Sodium ion, Na^{+} Potassium ion, K^{+}

2. ANIONS

Group I. Ions whose calcium salts are insoluble in neutral solutions. The ions of this group are:

Carbonate ion, $CO_3^=$
Phosphate ion, $PO_4^=$
Arsenate ion, $AsO_4^=$
Sulfite ion, $SO_3^=$
Fluoride ion, F^-

Group II. Ions whose calcium salts are soluble, but whose barium salts are insoluble in neutral solutions containing 20 per cent acetone by volume. The ions of this group are:

Sulfate ion, $SO_4^=$
Sulfite ion, $SO_3^=$
Chromate ion, $CrO_4^=$
Iodate ion, IO_3^-
Bromate ion, BrO_3^- (in high concentration)

Group III. Ions whose calcium and barium salts are soluble, but whose cadmium salts are insoluble in neutral solutions. The ions of this group are:

Sulfide ion, $S^=$
Ferricyanide ion, $Fe(CN)_6^{\equiv}$
Ferrocyanide ion, $Fe(CN)_6^{\equiv}$

Group IV. Ions whose calcium, barium and cadmium salts are soluble, but whose nickel or silver salts are insoluble in solutions slightly acid with nitric acid. These ions are:

Cyanide ion, CN^-
Chloride ion, Cl^-
Bromide ion, Br^-
Iodide ion, I^-
Thiocyanate ion, CNS^-
Thiosulfate ion, $S_2O_3^=$

Group V. Ions whose calcium, barium, cadmium, nickel and silver salts are soluble. These ions are:

Hypochlorite ion, ClO^-
Chlorate ion, ClO_3^-
Perchlorate ion, ClO_4^-
Iodate ion, IO_3^-
Bromate ion, BrO_3^-
Borate ion, BO_2^- or $B_4O_7^=$
Nitrate ion, NO_3^-
Nitrite ion, NO_2^-

PART I

THEORETICAL

W. D. LEAVITT

CHAPTER I

Solution and Ionization

A SOLUTION is a homogeneous mixture. The proportion of the components may vary to a greater or less degree. This implies that the solubility of one substance in another may be limited, and by experiment we learn that this is true. However certain liquids (for example water and sulfuric acid) are miscible in all proportions. On the other hand, at the temperature of the laboratory nearly all inorganic solids dissolve in liquids only to a certain extent. Thus, at 20°, 100 g. of pure water dissolve only 0.0000003 g. of silver iodide, while under the same conditions 446.4 g. of zinc bromide, 74.5 g. of calcium chloride, 19.4 g. of sodium sulfate or 0.00024 g. of barium sulfate will dissolve.

The amounts of various substances which are soluble in a liter of a given liquid may vary from a barely perceptible amount up to a large quantity. Account must be taken of these facts in qualitative analysis, for we generally make use of differences in solubilities to separate one substance from another. In analytical work we have to consider not only the solvent action of pure water but also the influence of various reagents upon solution and precipitation.

Methods of Expressing Concentration. In order to use solutions intelligently, we must know how much of a solute is present in a given volume of solution; in other words, we must know the concentration of the solutions. There are a number of ways of expressing concentration. In qualitative analysis the units of weight used are the gram equivalent weight and the gram formula weight (mole). The *gram formula weight* of a substance is the sum of the gram atomic weights of all the atoms appearing in the chemical formula of the substance. In the case of substances which exist as molecules, for example, many organic compounds, the gram formula weight and the gram molecular weight are identical. There are no molecules in substances which are built up of ions but the term *molecular weight* of an ionic substance is still used, however, to denote the sum of the atomic weights in

the formula used to represent the compound. This formula is usually the simplest one which corresponds to the per cent composition of the substance. The commonly used unit of volume is the liter.

A *normal solution* is a solution which contains a *gram equivalent weight* of the solute in a liter of the solution. A gram equivalent weight of a compound in a reaction which does not involve a transfer of electrons is that weight which reacts with a gram formula weight of a univalent ion. Thus a gram equivalent weight of sodium chloride is its gram formula weight (58.5 g.) since one mole of sodium chloride reacts with one gram formula weight of the univalent silver ion. The gram equivalent weight of barium chloride is one-half of its gram formula weight (208.4 g.) since a mole reacts with a gram formula weight of sulfate ion, which in turn reacts with two hydronium ions. The gram equivalent weight of a compound is not a fixed quantity. The gram equivalent weight of sodium hydrogen sulfate ($NaHSO_4$) depends on the reaction in which it is used. If the compound is used to neutralize a base, then a gram equivalent weight is the gram formula weight since a mole reacts with a gram formula weight of a univalent hydroxide ion. If the compound is used to precipitate barium as the sulfate, then a mole reacts with a gram formula weight of barium ion, which reacts with two gram formula weights of the chloride ion. The gram equivalent weight of sodium hydrogen sulfate in the reaction to precipitate barium sulfate is one-half of its gram formula weight. The number of gram equivalent weights of the solute in a liter of the solution is known as the normality of the solution. Thus the normality of a solution containing a gram formula weight (208.4 g.) of barium chloride in a liter of the solution is two. The normality of the solution containing one-hundredth of a gram formula weight (2.084 g.) of barium chloride in a liter of the solution is one-fiftieth. These concentrations are usually written 2-*N* and *N*/50 or 0.02-*N* respectively.

An *equivalent weight of an oxidizing or reducing agent* is the gram formula weight of the oxidizing or reducing agent divided by the number of units of change in the oxidation state of the active element in the oxidation-reduction reaction being considered. Thus an equivalent weight of the ferrous ion which is oxidized to the ferric ion is its gram formula weight. An equivalent weight of a ferrous compound to be used for this purpose is that weight which contains a formula weight of ferrous ion. The equivalent weight of potassium permanganate will depend upon the reaction in which it takes part. For a reaction in an alkaline solution in which the manganese is reduced to manganese dioxide, an equivalent weight

of the compound is one-third of its gram formula weight. For reactions in which the manganese is reduced to manganous ion, an equivalent weight is one-fifth of the gram formula weight.

A *molar solution* is a solution which contains a gram formula weight (mole) of the solute in a liter of the solution. The molarity of a solution is the number of moles of solute in a liter of the solution. Thus, the molarity of a solution containing a mole (58.5 g.) of sodium chloride in a liter of the solution is one, usually written 1-*M*. The molarity of a liter of a solution containing one-hundredth of a mole (2.08 g.) of barium chloride is one-hundredth and is usually written 0.01-*M* or *M*/100.

The *molar or molecular concentration* is the number of gram formula weights of an ion or the undissociated part of a solute in a liter of solution. Thus the molar or molecular concentration of the undissociated acetic acid in a 0.1-*M* solution which is 1.34 per cent ionized is 0.9866 × 0.1 or 0.09866. Since a hydronium ion and an acetate ion are formed when a molecule of acetic acid ionizes, the molar or molecular concentration of each of these ions is 0.0134 × 0.1 or 0.00134. Solutions of barium chloride are ionized completely and consequently the molar concentration of the undissociated barium chloride is zero. The molar concentration of the barium ion in a 1-*M* solution of barium chloride is one and that of the chloride ion is two. *Unless otherwise stated,* in this book, the term *concentration means molar concentration.*

Other Methods of Expressing the Amount of Solute in a Solution. The amount of solute in a solution may be expressed by molal solutions. A *molal solution* contains one mole of solute dissolved in 1000 g. of solvent. The molality of the solution is the number of moles of solute dissolved in 1000 g. of solvent.

Per cent solutions are also used to express the content of solute in a solution. Per cent solutions may be on the weight-weight, the weight-volume, or the volume-volume basis. Weight-weight per cent is defined as the weight of solute in 100 g. of a solution. Weight-volume per cent is the number of grams of solute in 100 ml. of a solution. Volume-volume per cent is the number of volumes of a liquid solute dissolved in 100 volumes of the solution.

Effect of the Solute on the Physical Properties of the Solvent. The vapor pressure, boiling point and freezing point of a solvent are changed by the addition of a solute. The greater the concentration of the solution, the greater is the effect. Furthermore, a gram molecular weight of any solute which is not an electrolyte—

that is, one which does not ionize—causes the same effect when added to a given weight of solvent. A gram molecular weight of a solute without an appreciable vapor pressure of its own dissolved in 1000 g. of water raises the boiling point 0.52°, and lowers the freezing point 1.86°. This is true because solutions which contain the same number of moles of non-electrolytes contain the same number of molecules of solute. The molecular weight of a non-electrolyte may be determined by adding a convenient weight to a suitable weight of water and determining the elevation of the boiling point or the lowering of the freezing point. The weight of the solute which, when dissolved in 1000 g. of water, would lower the freezing point or elevate the boiling point 1.86° or 0.52° respectively, can be calculated and is the gram molecular weight. Due to inherent difficulties, the molecular weights thus obt ined may differ as much as 10 to 15% from the correct values. Other solvents may be used but the lowering of the freezing point or elevation of the boiling point produced by a mole of the solute dissolved in 1000 g. of solvent must be known.

Attempts to Determine the Molecular Weights of Acids, Bases and Salts. The weights of acids, bases and salts which lower the freezing point of water 1.86° are very much less than expected. Furthermore the amount of solute required to give this effect

Table I. Gram Formula Weights of Some Salts from the Depression of the Freezing Point

Molality	KCl	K_2SO_4	$MgSO_4$	$K_3Fe(CN)_6$
0.005	38.1	57.6	72.8	89.3
.01	38.5	58.6	76.4	91.3
.05	39.6	64.0	81.0	109.0
.10	40.1	67.0	93.0	115.0
.50	41.5	71.0	113.9	134.4
	Accepted Formula Weights			
	74.6	164.2	120.3	329.2

increases as the molality of the solutions increase. Typical values are given in Table I. Since the weight of potassium chloride required to lower the freezing point of 1000 g. of water 1.86° is only about one-half of that calculated from the accepted formula

(KCl), about twice the expected number of particles must be present. Similarly, three times the expected number of particles must be present in a solution of potassium sulfate.

Other Characteristics of Acids, Bases and Salts. When aqueous solutions of these substances react with one another, the reaction is practically instantaneous and unless oxidation and reduction take place, an insoluble or slightly ionized substance is formed. They also give in aqueous solution abnormally large values for osmotic pressures, elevation of the boiling points and depression of the freezing points. This indicates that there are more particles which can affect the boiling point or freezing point in a solution of an acid, base or salt than are present in a solution of a non-electrolyte of the same concentration. Furthermore these solutions are sharply distinguished from other solutions in that they are incomparably better conductors of electricity and undergo decomposition at the electrodes when a current passes through them. Such solutions are called *electrolytes*, and their decomposition by the action of an electric current is known as *electrolysis*.

There are two classes of conductors of electricity: electrolytes, solutions which conduct the electric current, and conductors proper, such as metals and graphite. The first are decomposed by the current; the second suffer no apparent change except a rise in temperature. It should be noted that substances which in aqueous solution conduct electricity are, in the anhydrous state at ordinary temperatures, non-conductors. Also, water is an exceedingly feeble conductor. Thus, solid sodium chloride does not conduct an electric current but, when it is dissolved in water the resulting solution is a good conductor.

Electrolysis. Since the early years of the nineteenth century the idea has prevailed that the constituent elements of chemical compounds are held together by electrical forces. This conception is supported by the fact that in a compound such as potassium chloride the potassium is the positive radical and the chloride the negative one, as is evident when an electric current is passed through the fused salt. Metallic potassium collects at the negative electrode while gaseous chlorine is liberated at the positive electrode. This practically proves that these radicals are positive and negative respectively. Since the potassium and chlorine are set free at opposite electrodes, there must be a movement of the radicals through the fused material. Because of their property of migrating

toward one electrode or the other these radicals of the solute are called ions. The *ions* that travel toward the cathode are positive, or *cations*, while those that travel toward the anode are negative, or *anions*. The total charge on the positive ions is numerically equal to the total charge on the negative ions. The charge of an ion is the same as its valence. If an electric current is passed through an aqueous solution of potassium chloride using platinum or graphite electrodes, hydrogen and chlorine are liberated at the cathode and the anode respectively. Around the cathode a solution of potassium hydroxide is formed. The complete reaction is represented by the equation

$$2K^+ + 2Cl^- + 2H_2O \xrightarrow{\text{el. cur.}} H_2 + 2K^+ + 2OH^- + Cl_2$$

The reactions at the electrodes are represented by the following equations:

$$2H_3O^+ \text{ (from water)} + 2\epsilon^* \rightarrow H_2 + 2H_2O$$
$$2Cl^- \qquad\qquad - 2\epsilon \rightarrow Cl_2$$

Since electrons are removed from ions at the anode and given to ions at the cathode, it is clear that oxidation and reduction take place at the anode and cathode respectively. If inert electrodes are not used, electrons may be removed from or taken up by the material comprising the anode and cathode. In general it may be said that the lower the position of a metal in the activity or electromotive force series, the greater is the ease of depositing the free metal at the cathode. Similarly, the difficulty of removing electrons from simple ions at the anode increases with the activity of the free element.

In the body of the solution during electrolysis there is a migration of positive and negative ions toward the cathode and anode respectively. In the example just cited both the potassium and the hydronium ions (from water) migrate toward the cathode, while the chloride and the hydroxide ions (from water) migrate toward the anode. There are very few hydronium and hyoxide ions to migrate. If this migration is prevented by the introduction of a non-conducting partition, the action stops.

Experimental Facts Regarding Electrolytes. The experimentally established facts concerning electrolytes may be summarized as follows:

1. The weights of acids, bases and salts in aqueous solution re-

* The symbol ϵ is used to denote an electron.

quired to lower the freezing point or to elevate the boiling point of 1000 g. of water, 1.86° and 0.52° respectively, are abnormally low.

2. The reactions between most electrolytes in aqueous solutions are almost instantaneous.

3. Their aqueous solutions are conductors of electricity.

4. Except for fused systems, both the solvent and the solute are necessary components of the conducting system.

5. The substances which are liberated at inert electrodes during electrolysis come from the electrolyte or the solvent.

Assumptions of Arrhenius. The main assumptions of the Arrhenius theory of electrolytic dissociation or *ionization*, may be summarized as follows:

1. The solution of an electrolyte in water is attended by a more or less complete ionization of the solute into new, charged particles—cations and anions.

2. The cations are positively charged, and the anions are negatively charged. The sum of the unit charges on the cations in each case is equal but of opposite sign to those on the anions. Thus the solution is electrically neutral.

3. Ionization is a reversible reaction. The degree of ionization is increased by dilution, and consequently all electrolytes are completely dissociated at infinite dilution.

4. Save for the slight attraction and repulsion of the ions, due to their charges, they may be considered as independent molecules with their own specific chemical and physical properties.

5. The undissociated molecules of an electrolyte take no part in conveying an electrical current, the current being the migration of the electrically charged ions.

6. When two highly ionized electrolytes react with each other, they give reactions of the component ions.

The degree of ionization of a number of electrolytes according to the theory of Arrhenius is given in the Appendix.

Classes of Electrolytes. Electrolytes are substances which, when dissolved or fused, break up into ions. They may be classified into acids, bases and salts. An *acid* has been defined as a substance whose aqueous solution contains a concentration of hydronium ions greater than that in pure water, namely 10^{-7}, at 25°. Similarly, a *base* has been defined as a substance whose aqueous solution has a higher concentration of hydroxide ions than water (10^{-7}). The solution is alkaline. A *salt* is the product formed when an acid and a base react. More general definitions of acids and bases will be discussed later.

Origin of the Charges on Ions. Arrhenius stated that molecules of acids, bases and salts break up into charged particles when dissolved in an ionizing medium. Recent studies in atomic structure have clarified the problem. According to our present ideas an *atom* consists of a very small positively charged nucleus about which electrons revolve. With the exception of the hydrogen atom the nuclei contain *neutrons*—particles whose mass is somewhat more than that of the hydrogen atom and whose charge is zero—and protons. A *proton* is a hydrogen atom from which the electron has been removed. Since the mass of an electron is very nearly one-eighteen hundred and fiftieth (1/1850) of the mass of hydrogen atom, the mass of the proton is essentially that of the hydrogen atom. The positive charge on the nucleus is numerically equal to the atomic number of the element. Since atoms are electrically neutral, the number of electrons outside of the nucleus must be equal to the number of protons in the nucleus. The number of protons in the nucleus and the number of electrons outside of the nucleus of an atom of each element is known, since the atomic numbers of the elements are known. In an atom of lithium whose atomic weight, or more exactly mass number, is six and whose atomic number is three, there are three protons and three neutrons in the nucleus. Outside the nucleus there are three electrons. The symbol for this isotope of lithium is ${}^{6}_{3}\mathrm{Li}$. Atoms of lithium having a mass number of seven, that is ${}^{7}_{3}\mathrm{Li}$, have the same number of protons and electrons as an atom having a mass number of six. The increase in the mass of the atom is accounted for by the presence of four neutrons in the nucleus instead of three.

Arrangement of Electrons in Atoms. The electrons are grouped according to their energies into seven shells or levels. These shells or levels are differentiated by numbers 1, 2, . . . , 7 or letters K, L, . . . , Q. The maximum number of electrons in the outermost shell is found in the rare or inert gases as is shown in Table II. One electron is added to those present in the rare gas for each element succeeding the rare gas. Thus all of the elements in Group I of the periodic table have one valence electron; i.e., one electron in the outermost shell, in Group II two valence electrons, etc. The rare gases are very inert because the electrons in their outermost shells have a very stable arrangement—one which all other atoms except hydrogen in metallic hydrides tend to assume by the transfer or sharing of electrons.

The number of electrons in an atom is equal to the atomic number of the element; that is, an electron is added when the atomic number increases one unit. The electron that is added

frequently is called the differentiating electron and usually goes into the outermost shell or starts a new shell. In the periodic table on the inside of the back cover, the elements in the vertical columns correspond to the elements in the groups or subgroups in analogous columns in the Mendeleef periodic table. The elements included in the boxes or frames are the transition elements. With few exceptions they are elements which have valence electrons in two shells instead of only the outermost.* A more complete form of the periodic table showing the arrangement of electrons in the atoms is inside the front cover.

Table II. Distribution of Electrons in the Rare Gases

Shell	1 or *K*	2 or *L*	3 or *M*	4 or *N*	5 or *O*	6 or *P*
He	2					
Ne	2	8				
A	2	8	8			
Kr	2	8	18	8		
Xe	2	8	18	18	8	
Rn	2	8	18	32	18	8

The first transition group consists of the elements between scandium and zinc inclusive. The transition elements of this group have two valence electrons in the N shell, except chromium and copper, which have one. The arrangement of the electrons in scandium, the first element in this transition group, is 2, 8, 9, 2 and that in the last, zinc, is 2, 8, 18, 2. In forming compounds, electrons can be lost from the next to the outermost or M shell as well as from the outermost shell.

The second transition group starts with yttrium and ends with cadmium. The differentiating electrons go into the N or 4 shell instead of the outermost or O shell. The electron arrangement of yttrium, the first element in the transition group, is 2, 8, 18, 9, 2, and that of the last, cadmium, is 2, 8, 18, 18, 2. Yttrium, zirconium, technecium, and cadmium have two valence electrons in the O shell. Palladium has eighteen electrons in the N shell and none in the O shell. The other members of the group have one valence electron in the O shell. Electrons may be lost from the next to the outermost or N shell as well as from the O shell.

The third transition group consists of the related element

* Zinc, cadmium and mercury are not classified as transition elements by many chemists.

lanthanum,* atomic number 57, the lanthanides, more generally known as the rare earth elements whose atomic numbers are 58 to 71 inclusive, and the elements whose atomic numbers are 72 to 80. The rare earth elements are in the double box or frame. With the exception of iridium, which has no valence electron in the P shell, and platinum and gold which have one electron, the elements in the third transition group have two valence electrons in the P shell. The differentiating electrons in the related elements are in the next to the outermost or O shell. Thus the electronic structure of hafnium is 2, 8, 18, 32, 10, 2 and that of mercury, the last, is 2, 8, 18, 32, 18, 2. The differentiating electrons in the lanthanides or rare earth elements which follow lanthanum are in the third from the outermost or N shell. Thus, the structure of cerium, the first of the rare earths, is 2, 8, 18, 19, 9, 2 and that of lutecium, the last, is 2, 8, 18, 32, 9, 2.

The fourth transition group is incomplete, but it is analogous to the third transition group. Actinium, the only known member of the related elements of the group, has the electronic arrangement 2, 8, 18, 32, 18, 9, 2, in which the differentiating electron is in the P or next to the outermost shell. The actinides, analogs of the lanthanides, start with the next element, thorium, whose electronic structure is 2, 8, 18, 32, 19, 9, 2. The differentiating electrons in these elements are in the third from the outermost shell. Curium, the last known member of the actinides, has the electronic structure 2, 8, 18, 32, 25, 9, 2.

Since the differentiating electrons in the transition elements are not in the outermost shell, it is not surprising that these elements should have many properties in common. The variable valence of the transition elements is accounted for by the fact that under proper conditions electrons from the next to the outermost shell, or in the case of the rare earths, the second from the outermost shell, may also act as valence electrons. The partially completed inner shell of electrons in these elements causes the ions to be colored.

The extremely close identity of the properties of the rare earths is accounted for by the fact that the differences in electron arrangement are largely minimized because the differentiating electrons are in the third to the outermost shell.

Types of Valence. A stable outer shell of eight electrons may be obtained either by the loss or gain of electrons, or by the

* Note: The electron configuration of lanthanum is such as to place it as the first of the related elements; however, in chemical properties it resembles very closely the rare earths.

sharing of pairs of electrons by two atoms. Many of the metals have one, two or three electrons in the outermost shell. These elements may form a stable arrangement by losing these electrons, thus leaving the atom positively charged and exposing the next to the outermost shell of eight electrons. The non-metallic elements have from four to seven electrons in their outermost shell. A stable arrangement of eight electrons may be obtained if one or more electrons are donated to such atoms. When electrons are added, the atom becomes negative. Even in the solid state substances formed by the loss and gain of electrons are ionic; i.e., they are built up of ions and the valences are electrostatic or ionic. The *valence* of an ion is the number of electrons lost or gained. The valence is positive if electrons have been lost and

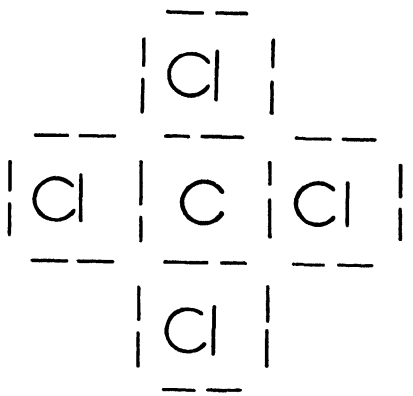
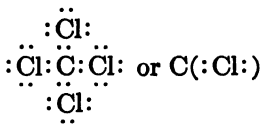


Fig. 1

negative if they have been gained. Thus a piece of solid sodium chloride is built up of Na^+ and Cl^-. In a similar way the solid nitrates, sulfates and most other common salts are built up of ions. Since these salts are ionized in the solid state there is no reason to believe that neutral molecules would be formed on dissolving the solid in water—a liquid with a high dielectric constant. The development of modern atomic structure makes it necessary to modify the original ideas of Arrhenius. These modifications are discussed in a succeeding paragraph.

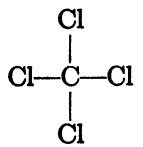
A stable arrangement of the outermost shell of electrons may also be attained by the sharing of one or more pairs of electrons by two atoms, thus forming a *covalence*. The four chlorine atoms in carbon tetrachloride are held to the carbon by four covalences. The covalence of carbon is four and that of chlorine is one. For

the sake of clearness the electrons supplied by the carbon atom have been indicated by four short dashes. Actually there is no difference between the electrons from the carbon and the chlorine. By sharing electrons both the carbon and chlorine atoms have eight electrons in their outermost shells. If dots are used to represent electrons, the structural formula of carbon tetrachloride is



or $C(:Cl:)_4$

Frequently a line is used to designate a covalence or covalent bond and the electrons not participating in the formation of the covalent bonds are not shown. The formula is then



The atoms of a non-electrolyte, such as sugar or glycerine, are held together by covalences and are called covalent compounds. There are also some inorganic compounds whose atoms are held together by covalences, for example the hydrogen halides, aluminum, stannic and ferric chlorides. These substances in the absence of water melt, boil, or sublime at low temperatures—properties typical of covalent compounds. Crystals of their anhydrous compounds are built up of molecules rather than ions. The conductivity and other properties, however, force us to conclude that in aqueous solutions they are ionized. Experiments show that in aqueous solutions many inorganic acids and nearly all salts are ionized completely. These apparently contradictory statements are explained by the reaction of the anhydrous substances with water to form hydrated ions. Thus

$$AlCl_3 + 12H_2O \rightarrow Al(H_2O)_6^{+++} + 3Cl(H_2O)_6^-$$

(usually written Al^{+++} and Cl^-)

$$HCl + 11H_2O \rightarrow H_3O(H_2O)_4^+ + Cl(H_2O)_6^-$$

(usually written H_3O^+ and Cl^-)

Free protons do not exist to an appreciable extent in an aqueous solution but react with water to form hydronium ions (H_3O^+).

$$H^+ + H_2O \rightleftharpoons H_3O^+ + 258 \text{ Kg. Cal.}$$

It has been calculated that the concentration of protons in an aqueous solution of an acid at ordinary temperatures is of the order of 10^{-15}. The hydronium ion, like other cations in aqueous solutions, is further hydrated and a more exact representation in an aqueous solution is $H_3O(H_2O)_x^+$ where x may be four or possibly six. Since all ions are hydrated and the number of molecules of water is not usually indicated, many chemists still prefer to use H^+ to denote the hydronium ion. However, we will be consistent and use the unhydrated formula of the hydronium ion (H_3O^+) just as we ordinarily use the unhydrated formulas of other ions.

It is not necessary that each atom sharing a pair of electrons furnish an electron to make the pair which is shared. Thus nitrogen furnishes both electrons for the formation of the ammonium ion.

$$:N(:H)_3 + H^+ \rightarrow [H:N(:H)_3]^+$$

A covalence in which both of the electrons are furnished by one atom is known as a coordinate covalence. The use of this type of valence in explaining the formation of complex ammonia compounds is considered in Chapter IV. There is no hard and fast line of demarcation between electrostatic or ionic valences and covalences. In many cases it is hard to decide whether a valence is ionic or covalent.

In the case of covalent compounds it is really meaningless to speak of the valence of the elements of which it is composed, for the electrons are shared by the atoms and have not been transferred from one atom to another. However, as we shall see later in considering the method of balancing oxidation-reduction equations, it is convenient to regard compounds or ions, in which the atoms are held by covalences, as being composed of atoms which have actually lost or gained electrons, and to designate the number of electrons apparently lost or gained as the valence number, or as the oxidation state. Thus in the covalent compound sulfur dioxide, the sulfur appears to have a valence of four positive and each oxygen a valence of two negative whereas actually no electrons have been lost or gained. The sulfur is said to have an oxidation state of positive four. This is usually written S^{+4}. The oxygen has an oxidation state of negative two and is represented by O^{-2}.

Objections to the Theory of Arrhenius. While the general explanation of the abnormally low apparent molecular weights of acids, bases and salts (electrolytes) and the conduction of the electric current by their solutions as formulated by Arrhenius is universally accepted, several objections to the theory as stated have been raised. The law of mass action cannot be applied quantitatively to the equilibrium which is supposed to exist between the ions and the un-ionized molecules of many electrolytes. The degree of ionization for a given electrolyte varies in many cases with the experimental method used. The solubility of difficultly soluble electrolytes increases in the presence or salts. Solids, although built up of ions, are considered to be partly molecular when dissolved in an ionizing medium.

Theory of Complete Ionization. To overcome these difficulties, Sutherland suggested that the electrolytes which were thought to be highly ionized are actually ionized completely at finite dilutions. The work of Debye and Hückel confirms Sutherland's hypothesis, and the complete ionization of strong electrolytes is now generally accepted. The picture presented by Arrhenius for the weak electrolytes remains unchanged. If strong electrolytes are really ionized completely, why is the freezing point of a molal solution of sodium chloride $-3.26°$ and not $-3.7°$ ($2 \times -1.85°$)? A lowering of the freezing point of 3.26° would be expected if the percentage of ionization were 75. Under this condition the number of moles in the solution according to Arrhenius would be 1.75 (0.25 mole of undissociated sodium chloride + 0.75 mole of chloride ion, + 0.75 mole of sodium ion) and the lowering would be $1.75 \times 1.85° = 3.26°$. Similar discrepancies are noted when other strong electrolytes are used. Calculations by Debye and Hückel show that the activity of an ion, that is, its ability to lower the freezing point or raise the boiling point of a solvent, is the same as a molecule when the concentration of the ions in the solution is small and that the activity decreases as the concentration of the ions increases. The activity of an ion rather than its concentration should be used in calculations. The activity of an ion is the product of the concentration and the activity coefficient. The activity coefficients may be calculated by means of equations derived by Debye and Hückel on the assumption that a single ion, because of the accumulation of ions of the opposite sign in its vicinity, does not have the freedom of motion or the energy of neutral molecules. The ionization of dilute solutions of strong

electrolytes will be considered complete. In dilute solutions of weak electrolytes the concentration of undissociated solute and ions is so low that the theory of Arrhenius and the law of mass action hold with sufficient accuracy.

It should be noted that if the complete ionization of strong electrolytes is assumed, the use of molecular concentrations of the ions instead of their activities may introduce large errors. Thus the concentration of the zinc and sulfate ions in a 0.1 molal solution of zinc sulfate is very close to 0.1 if the ionization is complete. The activity of these ions, however, is only 0.015. On the other hand, if the theory of Arrhenius is accepted the ionization is 45%, and the molecular concentration is 0.045 which is more nearly the correct value. Since the calculation of activities of ions is somewhat complicated and confusing to the beginning student, the concentrations of ions are used in the beginning calculations although at times the errors may be large. The calculations and use of activities of ions are discussed in Chapter VII.

Solution of a Solid Electrolyte. When such an electrolyte—sodium chloride for example—comes into contact with the polar solvent, water, the water molecules become attached to the sodium and chloride ions and weaken the attractive forces between these ions and the rest of the solid. Finally, the attractive forces between the hydrated and unhydrated ions become so small that the hydrated ions are free to move away from the solid, and we say that some sodium chloride has dissolved. The forces holding the water to the ions are greater the smaller the ion and the larger its charge. Other factors enter but cannot be considered in this course. The number of molecules of water associated with an ion is usually four or six. Ordinarily, the water molecules do not participate in reactions and the formula for the unhydrated ion is used in writing equations. However, there is considerable evidence that hydrated ions are involved in the precipitation of hydroxides and the solution of some hydroxides in an excess of a base, as well as the hydrolysis of salts.

Brønsted Concept of Acids and Bases. Since reactions analogous to neutralization occur in other solvents, the definitions of acids and bases have been broadened to include these cases. According to Brønsted, an acid is a substance which may lose one or more protons, while a base is capable of reacting with one or more pro-

tons. The fundamental relationship between an acid and a base is given by the equation

$$\text{Acid}' \rightleftarrows \text{H}^+ \text{ (proton)} + \text{Base}' \qquad (1)$$

Under appropriate conditions the following substances are proton donors and therefore acids:

$$\begin{aligned}
&\text{HCl} && \leftharpoondown \text{H}^+ + \text{Cl}^- \\
&\text{HSO}_4^- && \leftharpoondown \text{H}^+ + \text{SO}_4^- \\
&\text{NH}_4^+ && \leftharpoondown \text{H}^+ + \text{NH}_3 \\
&\text{H}_3\text{O}^+ && \leftharpoondown \text{H}^+ + \text{H}_2\text{O} \\
&\text{H}_2\text{O} && \leftharpoondown \text{H}^+ + \text{OH}^- \\
&[\text{Al} \cdot (\text{H}_2\text{O})_6]^{+++} && \rightleftharpoons \text{H}^+ + [\text{Al} \cdot (\text{H}_2\text{O})_5 \cdot (\text{OH})_1]^{++}
\end{aligned}$$

The difference in length of the arrows indicates whether reactants or products predominate after equilibrium has been established. The stronger an acid, the greater is its tendency to lose protons. Free protons do not exist to an appreciable extent in an aqueous solution but react with water to form hydronium ions (H_3O^+). An acid which can lose one proton is a monoprotic acid. If the acid can lose two protons, it is diprotic, etc.

A base, according to Brønsted, is a substance which takes up a proton. In this class are included the substances generally considered bases as well as the anions of the weak acids. The relationship involved is given by the equation

$$\text{Base} + \text{H}^+ \text{ (proton)} \rightleftarrows \text{Acid} \qquad (2)$$

A few examples may be given to clarify the relationship:

$$\begin{aligned}
\text{OH}^- + \text{H}^+ &\rightleftharpoons \text{H}_2\text{O} \\
\text{H}_2\text{O} + \text{H}^+ &\rightleftharpoons \text{H}_3\text{O}^+ \\
\text{OAc}^- + \text{H}^+ &\rightleftharpoons \text{HOAc} \\
\text{Cu(OH)}_2(\text{H}_2\text{O})_2 + 2\text{H}^+ &\rightleftharpoons \text{Cu}(\text{H}_2\text{O})_4^{++} \\
\text{Ag}(\text{NH}_3)_2^+ + 2\text{H}^+ &\rightleftharpoons \text{Ag}^+ + 2\text{NH}_4^+ \\
[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4]^- + \text{H}^+ &\rightleftharpoons \text{Al}(\text{H}_2\text{O})_3(\text{OH})_3
\end{aligned}$$

A base is monoprotic if it can accept one proton. It is diprotic if it can accept two protons, etc. The stronger a base, the greater is its tendency to gain protons.

The addition of equations 1 and 2 and simplification gives the relationship

$$\text{Acid}' + \text{Base} \rightleftarrows \text{Base}' + \text{Acid}$$

Some examples are cited below:

$$H_3O^+ + OH^- \rightleftarrows H_2O + H_2O$$
$$H_3O^+ + OAc^- \rightleftarrows HOAc + H_2O$$
$$HCO_3^- + OH^- \rightleftarrows H_2O + CO_3^=$$
$$NH_4^+ + OH^- \rightleftarrows H_2O + NH_3$$
$$Fe(H_2O)_6^{+++} + 3NH_3 \rightleftarrows 3NH_4^+ + Fe(OH)_3(H_2O)_3$$

The base formed from an acid by the loss of a proton is its conjugate. According to these views the strength of an acid or base is determined by two factors: the degree of ionization of the substance and the number and stability of the ions formed by the reaction of the proton with the solvent. The strength of acetic acid, then, depends on the values of the equilibrium constants for the following equilibria:

$$HOAc \leftrightarrows H^+ + OAc^-$$
$$H^+ + H_2O \rightleftarrows H_3O^+$$

Since the equilibrium constant (page 54) for the reaction is small, acetic acid is a weak acid. The strength of the acid should be affected by changing the solvent, since the equilibrium between protons and various solvents differs. These conclusions are amply confirmed by experiment.

Although the terms acid and base are used in both the older sense and in the newer Brønsted one, ordinarily there is no confusion as to the meaning.

SUMMARY OF THE MODERN VIEW OF IONIZATION

1. Electrolytes when dissolved in an ionizing medium conduct an electric current, lower the freezing point and elevate the boiling points of solvents to a greater extent than non-electrolytes, the molality of the solutions being the same.
2. The abnormally large effect of electrolytes on the boiling and freezing points of solvents is due to the presence of ions. The ionization of acids and hydroxides varies from zero to one hundred per cent. Salts, with few exceptions, are ionized completely.
3. Ions are atoms or groups of atoms bearing an electric charge numerically equal to the valence.
4. The molecules of the solvent become attached to the ions, thus separating them so that in dilute solutions the ions have little effect on each other.
5. In dilute solutions of electrolytes, ions affect the freezing and

boiling points of the solvent the same as molecules of non-electrolytes; that is, the activity of the ions and molecules in dilute solutions is essentially the same.

6. The activity of ions in solutions having a high concentration of ions is less than that of molecules. At very high concentrations, however, the activity in some cases is greater than that of molecules.
7. An acid is an ion or molecule which can lose one or more protons. A base is an ion or molecule which can react with protons.
8. A strong acid has a greater tendency to lose protons than a weak acid.
9. A strong base has a greater tendency to gain protons than a weak base.
10. The weaker an acid is, the stronger is the base which is formed when the acid loses a proton.
11. The fundamental relationship between acids and bases is expressed by the equation:

$$\text{Acid}' + \text{Base} \rightleftarrows \text{Base}' + \text{Acid}$$

12. Ionization of an acid in an aqueous solution is the transfer of a proton from the acid to a molecule of the base, water, to form a hydronium ion and an acid radical.
13. In the ionization of other covalent substances, such as aluminum chloride, the groups combine with water; that is, become hydrated. During the process one of the groups loses one or more electrons and becomes a positive ion. The other group gains one or more electrons and becomes a negative ion. The process may or may not take place completely.

Application in Qualitative Chemical Analysis. By far the majority of reactions of qualitative analysis are carried out in aqueous solutions. One reason for this is that usually the simplest and most rapid chemical changes take place between dissolved substances. Again, almost all aqueous solutions of inorganic substances give reactions which are characteristic of the ions present in the solution. This behavior makes it possible for the analyst to detect the ions instead of the numerous compounds which may be produced by their union. For example, it is much simpler to provide a scheme of analysis for the detection of the twenty-four cations, together with an equal number of anions than for the identification of more than five hundred compounds which these ions are capable of forming.

A solution of silver nitrate reacts with solutions of soluble

chlorides such as sodium chloride, forming a precipitate of silver chloride. No precipitate forms, however, when silver nitrate is added to a solution of a chlorate. According to the theory of ionization this is explained by assuming that chlorates yield no chloride ions. Many metallic ions form complex ions some of which are very stable. In many cases, a precipitate reacts with ions or molecules to form a complex ion. Thus silver chloride dissolves in ammonia because of the formation of the relatively stable complex silver-ammonia ion. Potassium ferrocyanide and ferricyanide contain iron in the ferrous and ferric states respectively, and both substances are electrolytes. The ferrocyanide, however, gives no precipitate with ammonium sulfide which precipitates ferrous iron quantitatively; neither does the ferricyanide respond to the most delicate tests for the ferric ion. For example, freshly prepared potassium ferricyanide gives no red coloration when treated with a thiocyanate, even though the formation of ferric thiocyanate ion is an exceedingly delicate test for the ferric ion. If we subject a solution of either of these complex cyanides to electrolysis, we find that the iron is a part of the negative ion. Each of these negative ions, $Fe(CN)_6^{\blacksquare}$ and $Fe(CN)_6^{\equiv}$, must be exceedingly stable, since they give reactions for neither ferrous nor ferric ions. Many organic substances are objectionable in qualitative analysis because of their tendency to form complexes with the cations. These organic substances must be removed before the analysis is attempted.

The chemical reactivity of electrolytes is closely related to their ionization. The most active acids are those which, at the same concentration, yield the largest number of hydronium ions. The method of qualitative analysis depends to no small degree upon the ionization of the reagents employed. A study of ionic interactions and the influence of ions upon one another leads to a clear and logical interpretation of many facts in qualitative analysis. Hence we shall consider these reactions more fully, both from a qualitative and from a quantitative point of view.

Ionic Equations. An inspection of equations shows that, in many cases, the ions present in the solutions of the reacting substances still remain after the reaction has taken place. Equations containing only the ions and the slightly ionized and insoluble substances involved in the reaction are known as ionic equations. Thus the reaction between a strong base and a strong acid is represented by the ionic equation

$$H_3O^+ + OH^- \rightleftarrows 2H_2O$$

The reaction between a weak acid, such as acetic acid, and a strong base, such as sodium hydroxide, is given by the expression

$$HOAc + OH^- \rightleftarrows H_2O + OAc^-$$

and the reaction between a weak base and a weak acid

$$Fe(OH)_3 + 3HOAc \rightleftarrows Fe^{+++} + 3\,OAc^- + 3H_2O$$

Oxidation-reduction reactions may also be represented by ionic equations as can be seen from the following cases:

$$2MnO_4^- + 5H_2S + 6H_3O^+ \rightleftarrows 2Mn^{++} + 5S + 14H_2O$$
$$IO_3^- + 3SO_2 + 9H_2O \rightleftarrows 3SO_4^{=} + I^- + 6H_3O^+$$
$$6Fe^{++} + Cr_2O_7^{=} + 14H_3O^+ \rightleftarrows 6Fe^{+++} + 2Cr^{+++} + 21H_2O$$

In every correctly balanced ionic equation the net charge of the reacting ions and the ionic products must be the same. Methods of balancing oxidation and reduction equations are given on page 73. Double arrows are placed between the substances brought together, that is, the reactants, and those formed as a result of the chemical change, the products. This is the logical outcome of the present idea that reactions are reversible to a greater or lesser extent and if carried out under suitable conditions, will proceed until equilibrium is established. The length and intensity of the arrows may be used to indicate the relative amounts of reactants and products present when equilibrium is established.

Modern Nomenclature of Simple Inorganic Compounds. According to conventions recently adopted, the oxidation state of an element which has more than one positive oxidation state is indicated by the appropriate Roman numeral in parentheses following the name of the metal from which the ion was derived. For example, the names of the compounds corresponding to the formulas given are:

CuCl	Copper (I) chloride
$Fe_2(SO_4)_3$	Iron (III) sulfate

For the most part the names of the common acids are retained, including the prefixes *ortho*, *meta* and *pyro*. The conventional relationship between the ending *ic* and *ous* of acids and the corresponding endings *ate* and *ite* for the salts of the acids is retained.

According to these rules the names of acid salts are formed by stating the number of hydrogens in the formula of the anion or salt. For example, the name of the HCO_3^- is the hydrogen carbo-

nate ion, and that of $H_2PO_4^-$ is the dihydrogen phosphate ion. Basic salts are hydroxy or oxy salts depending on whether the formula has OH or O in addition to the acid radicals. For example, the name of the compound which has the formula Zn(OH)Cl is zinc hydroxychloride, that of BiOCl is bismuth oxychloride, and that of $UO_2(NO_3)_2$ is uranium (VI) dioxynitrate.

The names of hydrates and similar compounds are obtained by adding to the name of the anhydrous compound the word hydrate preceded by the arabic number which corresponds to the number of molecules of water associated with the formula of the anhydrous compound. For example, the name of the compound which has the formula $CuSO_4 \cdot 5H_2O$ is copper (II) sulfate 5-hydrate; that of $Fe(NH_4)_2SO_4 \cdot 6H_2O$ is iron (II) ammonium sulfate 6-hydrate. In the compound $CaCl_2 \cdot 8NH_3$ the ammonia is analogous to water in a hydrate. The name of the compound is calcium chloride 8-ammoniate. For a more detailed discussion, consult the articles given in the footnote.*

EXERCISES

1. Define the terms: normality, molarity, molecular concentration, gram formula weight, equivalent weight of a compound.
2. How many milliliters of 0.1-normal (0.1-*N* or *N*/10)sulfuric acid are required to neutralize 15 ml. of 0.3-*M* sodium hydroxide? *Ans.* 45 ml.
3. Calculate the molarity of a 17.6 per cent solution of calcium chloride having a density of 1.15.
4. Given the following compounds:
   a. Hydrochloric acid
   b. Sulfuric acid
   c. Barium hydroxide
   d. Ferric sulfate
   e. Sodium sulfate
   f. Aluminum nitrate
   g. Potassium orthophosphate (normal)

   What fraction of the gram formula weights of each:
   a. Is a mole?
   b. Contains an equivalent weight of cation and of anion?
   c. Is an equivalent weight of the compound?
   d. Contains a gram formula weight of cation?
   e. Contains a gram formula weight of anion?
5. If 0.1 gram formula weight of each of the compounds named in question 4 is dissolved in sufficient water to make a liter of solution, what will be the:
   a. Molarity of each solution?
   b. Molecular concentration of the anion and of the cation assuming 100% ionization and no complications?
   c. Normality of each solution?

* Jorissen *et al.*: Rules for Naming Inorganic Compounds. J. Am. Chem. Soc *63:* 889, 1941.

Fernelius: Some Problems of Inorganic Nomenclature. Chem. and Eng. News *26:* 161–3, 1948.

Scott: Inorganic Synthesis *2:* 257–9, 1946.

Introduction to the yearly subject indices of Chemical Abstracts.

Answers to—	Exercise 4					Exercise 5			
	Mole	Equivalent weight of anion and cation	Equivalent weight of the compound	Contains formula weight of cation	Contains formula weight of anion	Molarity	Molecular concentration of cation	Molecular concentration of anion	Normality
a. Hydrochloric acid	1	1	1	1	1	0.1	0.1	0.1	0.1
b. Sulfuric acid									
c. Barium hydroxide	1	1/2	1/2	1	1/2	0.1	0.1	0.2	0.2
d. Ferric sulfate									
e. Sodium sulfate	1	1/2	1/2	1/2	1	0.1	0.2	0.1	0.2
f. Aluminum nitrate									
g. Potassium orthophosphate (normal)	1	1/3	1/3	1/3	1	0.1	0.3	0.1	0.3

	Answers to Exercise 6			
	Molarity	C_{M^+}	C_{X^-}	Normality
6. Given the following solutions:				
a. 0.10 gram equivalent weight of aluminum sulfate in 250 ml. of solution.	0.067	0.134	0.20	0.4
b. 5 g. of sodium carbonate in 200 ml. of solution.				
c. 0.006 formula weight barium nitrate in 100 ml. of solution.	0.06	0.06	0.12	0.12
d. 10% of silver nitrate, sp. gr. of solution 1.05.				
e. 11.2 liters of hydrogen chloride measured at 30° and 700 mm. in 400 ml. of solution.	1.04	1.04	1.04	1.04
f. 3.03×10^{23} molecules of hydrogen sulfate in 500 ml. of solution.				
g. Enough lead nitrate in 500 ml. of solution to react with 5 g. of potassium chromate.	0.051	0.051	0.102	0.102
h. Enough silver nitrate in 250 ml. of solution to neutralize 400 ml. of 2-*N* of sodium hydroxide.				
i. Enough mercuric chloride dissolved in 200 ml. of solution to be precipitated by 100 ml. of a molar solution of ammonium iodide.	0.25	0.25	0.50	0.50
j. Enough ferric sulfate in 100 ml. of solution to precipitate 1 g. of barium sulfate.				

What is the molarity of each of the above solutions?
What is the molar concentration of the cations and anions?
Assume 100% ionization unless otherwise stated and that no side reactions take place.
What is the normality of each of the above solutions?

7. How many milliliters of 2-*N* hydroxide will be required to precipitate completely the iron in 10 ml. of a solution containing 1 mole of ferric chloride per liter? *Ans.* 15 ml.
8. A solution contains 10 ml. of 0.1-*N* magnesium chloride and 5 ml. of 0.5-*N* hydrochloric acid. How many milliliters of 2-*N* sodium hydroxide will be required to react with the two solutes?
9. A solution contains 100 mg. of each of the following ions: mercurous ions, silver ions and lead ion. Assuming complete precipitation in each case, how many milliliters of 4-*N* hydrochloric acid will be required? *Ans.* 0.6 ml.
10. A solution contains 50 mg. of each of the following ions: lead ion, barium ions and copper ions. How many milliliters of 2-*N* sulfuric acid will be required to precipitate the appropriate ions if a 10% excess of precipitating agent is to be added?
11. Name three properties of a solvent which are affected by the addition of a solute.
12. What facts lead to the conclusion that sodium chloride is dissociated in aqueous solution?
13. Five milliliters of water dissolve 0.171 g. of cane sugar ($C_{12}H_{22}O_{11}$). If the solution freezes at $-0.186°$, what is the molecular weight of this sugar? *Ans.* 342.
14. At what temperature will a solution of ethyl alcohol (C_2H_5OH) made by dissolving equal volumes of alcohol and water freeze? The density of ethyl alcohol is 0.78.
15. At what temperature will a 50% solution of ethylene glycol ($C_2H_4(OH)_2$) by volume freeze? The specific gravity of ethylene glycol is 1.113. *Ans.* $-33.4°$.
16. What conclusion may be drawn from the fact that the molecular weight of sodium chloride calculated from the lowering of the freezing point of a dilute solution is about 29.3?
17. Define: ion, electrolyte, electrolysis, ionization.
18. State six characteristics of electrolytes.
19. State the theory of Arrhenius.
20. Show the origin of the charges on the ions present in a solution of calcium chloride.
21. Distinguish between the hydrogen ion and the hydronium ion.
22. Into what classes may ions be divided?
23. Distinguish between an acid and a base.
24. What is Brønsted's conception of an acid and a base?
25. State some of the defects of the theory of Arrhenius.
26. What is an ionic equation? What are the advantages of their use?
27. Why must the net charge of the reacting ions be equal to that on the products?
28. Summarize the modern view of ionization.

CHAPTER II

Chemical Equilibrium

THE THEORY OF ionization gives an interpretation of many of the processes and reactions of qualitative analysis. A further elaboration of the theoretical aspect of the subject is, however, necessary. To this end we shall consider the law of mass action.

Reversible Reactions. Phosphorus pentachloride, when heated, dissociates into phosphorus trichloride and chlorine. With a continuous rise in temperature up to 300°, the fraction decomposed increases rapidly once dissociation begins. If the pentachloride is kept at 200°, the progress of the action seemingly ceases when 51.7% of the substance is unchanged. The undissociated pentachloride is as capable of undergoing decomposition as the part which dissociated. The explanation of this phenomenon is that the reaction is reversible; that is, chlorine and phosphorus trichloride unite to regenerate the original material. Such reactions are more or less incomplete. When equilibrium is reached, some of the reactants are present in the mixture.

A kinetic-molecular explanation of these facts gives us a clear understanding of this variety of chemical change. When dissociation begins, $PCl_5 \rightleftarrows PCl_3 + Cl_2$, the molecules of phosphorus trichloride and chlorine are few in number; but as the dissociation proceeds, these new molecules increase in number, while the number of molecules of the reactant diminish. The increase in the number of molecules of the two products of the forward action is accompanied by more frequent collisions between these molecules and more rapid union of them to form the pentachloride. The result is an increase in the speed of the reverse action. As the concentration of the molecules of the pentachloride diminishes, the speed of the forward action will become less and less. The speed of the forward action begins at a maximum, at a given temperature, and progressively decreases; the reverse action begins at a minimum and progressively increases. Finally, a condition of equilibrium is reached when the speeds of the two opposing actions are equal. In a homogeneous system, such as we have considered,

the rate at which a chemical change takes place is defined as the decrease in the concentration of the reacting substance per unit time.

Effect of Concentration. According to the kinetic-molecular explanation, the speed of the reaction depends upon the frequency of collisions between the molecules of the reacting substances. The logical inference is that if the concentration of any one of the interacting molecular species is increased, the frequency of encounter between the molecules will become greater, and the speed at which they combine will increase correspondingly.

The Law of Mass Action or Molecular Concentration. The temperature remaining constant, the speed of a reaction is proportional to the molecular concentration of the reacting substances, each raised to the power numerically equal to the number of molecules of the substance appearing in the balanced equation. This law of molecular concentration, or of mass action, was definitely formulated by Guldberg and Waage, and applies to reactions which take place in one step as expressed by the equation. If the reaction takes place in a number of steps then the law applies rigidly to the reaction which determines the speed of the overall reaction. Usually the slowest reaction in a series determines the rate at which the reaction takes place.

MATHEMATICAL EXPRESSION OF THE LAW. If A and B interact to produce E and D, according to the equation

$$A + 3B \rightleftarrows 2E + D$$

then in agreement with the law of mass action, or molecular concentration,

$$k_1(C_A \times C_B^3) = S \text{ (the speed of the forward action is } S) \quad (3)$$

and

$$k_2(C_E^2 \times C_D) = S_1 \text{ (the speed of the reverse action is } S_1) \quad (4)$$

When equilibrium is established, $S = S_1$; thus, dividing equation 4 by equation 3 and rearranging the terms, we have,

$$\frac{C_E^2 \times C_D}{C_A \times C_B^3} = \frac{k_1}{k_2} = K_{\text{equilibrium}} \quad (5)$$

where C_A and C_B, etc. represent the concentrations of the substances A and B, etc. Equation 5 is a mathematical expression

derived from the law of mass action. It is sometimes called the law of chemical equilibrium.

Even if the law is applied to a reversible reaction that really takes place in a series of steps and not in one step as the equation indicates, the expression for the equilibrium constant is correct, since independent thermodynamic methods of deriving the equilibrium constant give the same expression as was obtained by applying the law of mass action. The derivation of the expression from the law of mass action is justified because it enables beginning students to visualize the processes involved.

The time required for equilibrium to be established varies greatly. Since there is no way of predicting the time, a system must be allowed to stand until equilibrium is reached if discrepancies in the values of concentrations and equilibrium constants are to be avoided.

The value of the equilibrium constant depends upon the nature of the substances taking part in the reaction, the presence or absence of a solvent and the temperature at which the chemical change takes place. The relative amounts of reactants and products may be varied to a greater or less extent. An inspection of equation 5 shows that an increase in the concentration of one of the substances, say B, would cause a decrease in the concentration of A, for K remains unchanged. But since A and B react to produce E and D, the concentration of the latter two substances must increase. After equilibrium has been reestablished, the concentration of B will be less than the sum of the concentration originally present and that added. If a reaction which takes place in a homogeneous system is expressed by the equation

$$a\mathrm{A} + b\mathrm{B} \rightleftarrows m\mathrm{E} + n\mathrm{D}$$

then,

$$\frac{C_{\mathrm{E}}^{m} \times C_{\mathrm{D}}^{n}}{C_{\mathrm{A}}^{a} \times C_{\mathrm{B}}^{b}} = K_{\text{equilibrium}} \tag{6}$$

A typical example of a system in equilibrium is afforded by the decomposition of hydrogen iodide as represented by the equation

$$2\mathrm{HI} \rightleftarrows \mathrm{H_2} + \mathrm{I_2}$$

Bodenstein found that equilibrium is established quickly at the temperature of boiling sulfur, 444.6°, and at this temperature the mixture contained 79% of hydrogen iodide and 10.5% of each of the two elements by volume. The system is homogene-

ous, and in a liter of the equilibrium mixture calculated to standard conditions there are 0.105 liters of hydrogen $\left(\frac{0.105}{22.4} \text{ moles}\right)$, 0.105 liters of iodine $\left(\frac{0.105}{22.4} \text{ moles}\right)$ and 0.79 liters of hydrogen iodide $\left(\frac{0.79}{22.4} \text{ moles}\right)$. Substituting these values in the expression for the equilibrium constant, we have

$$\frac{C_{H_2} \times C_{I_2}}{C_{HI}^2} = \frac{\frac{0.105}{22.4} \times \frac{0.105}{22.4}}{\left(\frac{0.79}{22.4}\right)^2} = \frac{0.105 \times 0.105}{0.79^2}$$

$$= 0.01767 = 1.8 \times 10^{-2} = 1/57 = K \qquad (7)$$

According to this, if the initial concentration of H_2, I_2 and HI are the same, then the initial velocity of the union of H_2 and I_2 will be 57 times the initial velocity of the dissociation of HI.

Ionic Equilibrium. The ionization of a weak electrolyte is a reversible, homogeneous reaction. Consequently, the law of mass action applies to such reactions. The qualitative analyst is interested chiefly in ionic reactions which proceed very nearly to completion; hence in dealing with reversible reactions he needs to know which are almost complete and why. Under five conditions ionic reactions proceed very nearly to completion: first, when a difficultly soluble substance is formed; second, when a gaseous product is evolved; third, when a very slightly ionized substance is a product; fourth, when an ionic substance is removed by formation of a complex ion; and fifth, when an ion changes its charge. The completeness of the reaction in any of these cases depends upon the extent of removal of one or more of the products. To illustrate, consider the neutralization of hydrochloric acid by sodium hydroxide. The equations for their ionization and interaction at 18° are

$$\begin{aligned} NaOH &\rightarrow Na^+ + OH^- && (100\%) \\ HCl + H_2O &\rightarrow Cl^- + H_3O^+ && (100\%) \\ & \quad \downarrow\uparrow \\ & \quad 2H_2O && (99.9+\ \%) \end{aligned}$$

The equation for the action is

$$H_3O^+ + OH^- \rightleftarrows 2H_2O$$

since these are the only ions whose concentration changes. The amounts of the reactants and products are shown by the lengths of the arrows. Examples illustrating each of the five types of reaction will be given as the occasion demands.

Ionization Constant of Weak Monoprotic (Monobasic) Acids. Acetic acid ionizes to give hydronium ions and acetate ions. The abbreviation HOAc is commonly used for acetic acid whose formula is CH_3COOH. Its ionization is given by the equation $HOAc + H_2O \leftrightharpoons H_3O^+ + OAc^-$. Application of the law of mass action to the system gives the expression

$$\frac{C_{H_3O^+} \times C_{OAc^-}}{C_{HOAc}\ (\text{undissociated}) \times C_{H_2O}} = K$$

Since the concentration of water in a dilute solution is practically constant and is very nearly 55.6, that is 1000 ÷ 18,

$$\frac{C_{H_3O^+} \times C_{OAc^-}}{C_{HOAc}} = K \times 55.6 = K_{\text{equilibrium}} = K_{\text{ionization}} = K_i$$

The equilibrium constant of a system in which the undissociated molecules of an electrolyte are in equilibrium with the ions has been given the name *ionization constant.* If the molarity and the per cent of ionization of the acid are known, the concentration of the hydronium and acetate ions, as well as that of the undissociated acetic acid, can be calculated. At 18°, 1.34% of acetic acid in a 0.1-*N* solution is ionized. Since there is one-tenth of a gram-molecular weight of the acid in a liter, the solution is 0.1-*M*. The concentrations of the three substances in the solution are as follows: undissociated acetic acid, $0.1 \times 0.9866 = 0.09866$, hydronium and acetate ions, $0.1 \times 0.0134 = 0.00134$ each. By substitution of these values, the preceding equation becomes

$$\frac{0.00134 \times 0.00134}{0.09866} = K_{\text{ionization}} = 0.0000182 = 1.82 \times 10^{-5}$$

The ionization constant expresses quantitatively the tendency of acetic acid to ionize. The more highly ionized acids are in solutions of equivalent concentrations, the more active they will be as acids. Inspection of the expression for the ionization constant of

acetic acid shows that for the various monoprotic acids, the greater the degree of ionization the greater is the value of their ionization constants. There is a wide range in the value of the ionization constants of the various acids. Many of these constants are given or may be calculated from data given in the Appendix.

Effect of Dilution. A tenth-normal solution of acetic acid at 18° is 1.34% ionized. If the solution is diluted to ten times its original volume, and if the equilibrium should remain undisturbed, then the ratio would have the value of 1.82×10^{-6}.

$$\frac{0.000134 \times 0.000134}{0.009866} = 0.00000182 = 1.82 \times 10^{-6}$$

This value, however, is only one-tenth that of the ionization constant for acetic acid. The acid must be more highly ionized in 0.01-normal solution than in 0.1-normal since the value of K_i is the same in each case. As a matter of fact, 0.01-normal acetic acid is 4.17% ionized. The ratio then has a value of 1.81×10^{-5},

$$\frac{0.000417 \times 0.000417}{0.009583} = 0.0000181 = 1.81 \times 10^{-5}$$

which is the same as the value of the ratio for 0.1-*N* acetic acid.

Ionization of Polyprotic (Polybasic) Acids. For the dissociation of a diprotic acid we should be inclined to assume that the equation

$$H_2B + H_2O \rightleftarrows 2H_3O^+ + B^= \qquad (8)$$

would represent its ionization. Experiment, however, shows that this is an incomplete representation of facts, since a diprotic acid dissociates according to the equation

$$H_2B + H_2O \rightleftarrows H_3O^+ + HB^- \qquad (9)$$

and the resulting univalent ion, HB^-, undergoes a further dissociation,

$$HB^- + H_2O \leftrightarrows H_3O^+ + B^= \qquad (10)$$

The dissociation expressed by equation 9 is called the primary ionization; by equation 10, the secondary ionization. The ioniza-

tion constants for the equilibria expressed by equations 8, 9 and 10 are, respectively:

$$\frac{C^2_{H_3O^+} \times C_{B^-}}{C_{H_2B}} = K_{\text{ionization}} \tag{11}$$

$$\frac{C_{H_3O^+} \times C_{HB^-}}{C_{H_2B}} = K_1 \text{ (primary ionization constant) or } Ki_{H_2B} \tag{12}$$

and

$$\frac{C_{H_3O^+} \times C_{B^=}}{C_{HB^-}} = K_2 \text{ (secondary ionization constant) or } Ki_{HB^-} \tag{13}$$

The primary ionization constant is much greater than the secondary. It follows that the major portion of the hydronium ions which polyprotic acids yield at usual concentrations is to be attributed to the primary ionization; that is, the primary ionization is greater than the secondary. The tertiary and quaternary dissociations diminish in the same order. The ratio of the successive ionization constants of polyprotic acids is of the order of 10^5.

These facts may be illustrated by an example. Hydrogen sulfide is a diprotic acid. Its primary ionization constant at 25° is

$$\frac{C_{H_3O^+} \times C_{HS^-}}{C_{H_2S}} = 1.2 \times 10^{-7} = K_1 \tag{14}$$

and the constant for its secondary ionization at 25° is

$$\frac{C_{H_3O^+} \times C_{S^=}}{C_{HS^-}} = 1.0 \times 10^{-15} = K_2 \tag{15}$$

While equation 8 does not represent all the equilibria involved in the ionization of a diprotic acid, the corresponding ionization constant is sometimes useful. It cannot be determined directly, but for hydrogen sulfide it is derived by combining the equations 14 and 15 for the primary and secondary ionization constants. Solving equation 15 for the concentration of hydrogen sulfide ion (C_{HS^-}) and substituting this value in equation 14, the expression becomes

$$\frac{C^2_{H_3O^+} \times C_{S^=}}{C_{H_2S}} = 1.0 \times 10^{-15} \times 1.2 \times 10^{-7} = 1.2 \times 10^{-22} \tag{16}$$

The law of mass action holds when applied to the ionic equilibrium of weak acids. It is not valid, however, for the strong acids since they are ionized completely.

Ionization of Bases. The same general relations hold for the bases as were developed for the acids. The weak bases give consistent ionization constants; the strong bases fail to do so. Polyprotic (polyacid) bases ionize in steps analogous to polyprotic (polybasic) acids. Of the hydroxides of the common metals those of sodium, potassium, barium, strontium and calcium are soluble and completely ionized.

Equilibrium Constants of Solutions of Ammonia. Ammonia gas is very soluble in water, and the solution is a weak alkali. Until recently it was thought that the following equilibria were present

$$NH_{3(gas)} \leftrightharpoons NH_{3(dis.)} + H_2O \rightleftarrows NH_4OH \leftrightharpoons NH_4^+ + OH^-$$

The small concentration of hydroxide ions was assumed to be due to the small fraction of ionization of ammonium hydroxide. The expression for the ionization constant was given as

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_4OH}} = 1.8 \times 10^{-5}$$

However, ammonia, like water, is a base and reacts with protons to form the ammonium ion analogous to the hydronium ion. In an aqueous solution, ammonia can react with the acid, water, according to the equation

$$\underset{B'}{NH_{3(dis.)}} + \underset{A}{H_2O} \leftrightharpoons \underset{A'}{NH_4^+} + \underset{B}{OH^-}$$

Only a small amount of the dissolved ammonia reacts with water, hence, the concentration of hydroxide ion is small. The Brønsted mechanism to account for the alkalinity of a solution of ammonia will be used. An aqueous solution of gaseous ammonia is called ammonium hydroxide by some chemists but many prefer to call it ammonia. The expression for the constant of the system is

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_{3(dis.)}} \times C_{H_2O}} = K$$

The concentration of water is constant and the above equation becomes

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_{3(dis.)}}} = K_{eq} = 1.8 \times 10^{-5} = K_{base,\ NH_3} \text{ or } K_{b,\ NH_3} \qquad (17)$$

The equilibrium constant for an aqueous solution of ammonia, $K_{b,\ NH_3}$, is also known as the ionization constant of ammonia, $K_{i,\ NH_3}$.

For any aqueous solution $C_{H_3O^+} \times C_{OH^-} = 10^{-14}$ (see page 59) and $C_{OH^-} = \frac{10^{-14}}{C_{H_3O^+}}$. Substitution of the value of the concentration of hydroxide ion in equation 17 gives

$$\frac{C_{NH_4^+} \times \frac{10^{-14}}{C_{H_3O^+}}}{C_{NH_3}} = 1.8 \times 10^{-5} \tag{18}$$

which when arranged is

$$\frac{C_{NH_4^+}}{C_{NH_3} \times C_{H_3O^+}} = \frac{1.8 \times 10^{-5}}{1 \times 10^{-14}} = 1.8 \times 10^{9} \tag{19}$$

On inverting equation 19 we have

$$\frac{C_{NH_3} \times C_{H_3O^+}}{C_{NH_4^+}} = 5.6 \times 10^{-10} \tag{20}$$

This is the equilibrium constant for the action of the ammonium ion as an acid

$$NH_4^+ + H_2O \leftrightharpoons NH_3 + H_3O^+$$

which is given in Table III. The constant for this equilibrium is written $K_{i,\ NH_4^+}$, $K_{(acid)\ NH_4^+}$ or $K_{a,\ NH_4^+}$.

Ionization of Salts. With few exceptions, salts are ionized completely in dilute solutions. Cadmium chloride, mercuric cyanide, mercuric chloride and lead acetate are important exceptions to this general statement. Lead acetate is so little ionized that lead sulfate, a very slightly soluble salt, dissolves on the addition of a soluble acetate.

$$PbSO_4 + 2\ OAc^- \rightleftarrows Pb(OAc)_2 + SO_4^=$$

Repression of Ionization by a Common Ion. One of the most important practical results of a consideration of ionic equilibrium is to provide a mechanism to account for the diminished reactivity of a weak electrolyte after the addition of a highly ionized substance which yields a common ion. Thus, if the concentration of the acetate ion is increased by the addition of solid ammonium, sodium or potassium acetate to acetic acid, the concentration

of the hydronium ion is reduced. This can be shown by adding a few crystals of ammonium acetate to a solution of acetic acid containing a few drops of methyl orange. The pink color of the solution changes to a straw color, showing that the concentration of hydronium ions has decreased. This effect can be qualitatively deduced from Le Chatelier's Law. Since the equilibrium was disturbed by the increase in the concentration of acetate ions, a change must take place which will reduce the concentration of acetate ions. This is accomplished by the union of hydronium ions and acetate ions to form undissociated acetic acid. The effect may be quantitatively deduced from the expression for the ionization constant.

Suppose, for example, that one-tenth of a gram formula weight of ammonium acetate is added to a liter of 0.1-*N* acetic acid. The salt is completely ionized and the acid 1.34%. The concentration of acetate ion added is 0.1 and if no change should take place, the expression for the ionization constant of acetic acid would be

$$\frac{0.00134 \times (0.1 + 0.00134)}{0.09866} = 0.00136 = 1.36 \times 10^{-3}$$

The value of the ratio (1.36×10^{-3}) is greater than the ionization constant of acetic acid (1.82×10^{-5}), and the assumption that no change takes place in the concentration of the ions is untenable. Since there is an excess of acetate ions, it is reasonable to assume that a greater number of collisions between hydronium ions and acetate ions takes place than in the solution of acetic acid, and consequently, that a greater number of molecules of undissociated acid are formed. Thus the concentrations of the hydronium and acetate ions must diminish and the concentration of the undissociated molecules increase. For every acetate and hydronium ion which combine, one molecule of undissociated acetic acid forms. If we let x equal the decrease in the concentration of the hydronium ion, x will also represent the decrease in the total concentration of the acetate ion and the increase in the concentration of the undissociated acetic acid. The concentration of hydronium ions when equilibrium is established will be $0.00134 - x$; that of the acetate ions will be $0.1 + 0.00134 - x$; and that of the un-ionized acetic acid, $0.09866 + x$. The expression for the ionization constant is

$$\frac{(0.00134 - x)(0.1 + 0.00134 - x)}{0.09866 + x} = 1.82 \times 10^{-5}$$

The value of x calculated by solving the quadratic equation obtained by simplifying the above is

$$0.00132 = 1.32 \times 10^{-3}$$

The final concentration of hydronium ion, $0.00134 - x$, is $0.00134 - 0.00132 = 0.00002 = 2 \times 10^{-5}$. The solution of the quadratic equation is given in the footnote.*

A quantity, x, may be dropped without changing the value appreciably when it is added to or subtracted from a number which is large in comparison with the largest value which x may have. The largest value which x may have in this problem is 0.00134, and since this value is small in comparison with the total concentration of acetate ion (0.10134), x may be dropped without markedly changing the value of the quantity $(0.10134 - x)$ and the previous equation becomes

$$\frac{(0.00134 - x)(0.10134)}{0.09866 + x} = 1.82 \times 10^{-5}$$

The final concentration of hydronium ion, $0.00134 - x$, is 0.00002 or 2×10^{-5}.

While this method of calculation gives a concrete picture of the changes which result from the addition of a common ion, the equation is complicated and difficult to solve. A more usual method of calculating the effect of adding a common ion is to

Let y = concentration acetic acid ionized after the addition of the sodium acetate.
y = final concentratoin of hydronium ion.
y = concentration of acetate ion from the acetic acid still ionized after adding sodium acetate.
0.1 = number of formula weights of sodium acetate added.
0.1 = concentration of acetate ion from sodium acetate.
0.1 = molarity of the acetic acid.
$0.1 + y$ = final concentration of acetate ion.
$0.1 - y$ = final concentration of the undissociated acetic acid.

* $\frac{(0.00134 - x)\ (0.10134 - x)}{0.09866 + x} = 1.82 \times 10^{-5}$

$x^2 - 0.1027x + 0.0001358 = 1.796 \times 10^{-6} + 1.82 \times 10^{-5}x$

$x^2 - 10{,}270 \times 10^{-5}x - 1.8 \times 10^{-5}x = -135.8 \times 10^{-6} + 1.796 \times 10^{-6}$

$x^2 - 10{,}272 \times 10^{-5}x = -134 \times 10^{-6}$

$x^2 - 0.10272x + 0.002642 = -134 \times 10^{-6} + 2642 \times 10^{-6} = 2508 \times 10^{-6}$

$x - 0.0514 = -50.08 \times 10^{-3} = -.05008$

$x = 0.00132$

$0.00134 - x = 0.00134 - 0.00134 = 0.00002$

By substituting these values in the expression for the ionization constant of acetic acid, we have

$$\frac{y(0.1 + y)}{0.1 - y} = 1.82 \times 10^{-5}$$

On solving this equation, $y = 0.00002$, the same value obtained by the previous method.

If the value of y is very small compared to the concentration of the anion and also to the molarity of the original acid, the quantities ($C_{\text{anion}} + y$) and (molarity of weak electrolyte $- y$) are very nearly equal to C_{anion} and the molarity of the weak electrolyte respectively. For the case under consideration, the equation

$$\frac{y(0.1 + y)}{0.1 - y} = 1.82 \times 10^{-5}$$

reduces to

$$\frac{0.1y}{0.1} = 1.82 \times 10^{-5}$$

and

$$y = 1.82 \times 10^{-5}$$

This value does not differ greatly from that obtained by the more exact method of calculation used in the preceding paragraph. While comparatively small quantities added or subtracted may be eliminated without making an appreciable error, they cannot be eliminated when they are used in multiplication or division. The effect of increasing the concentration of the ammonium ion on the concentration of hydroxide ion may be calculated by using equation 17.

Ionization Constants and the Strength of Acids and Bases (Brønsted). According to Brønsted an acid is a proton donor. The ionization of proton donors of the types HB, H_2B and HB^- is given by the following equations:

$$HB + H_2O \rightleftarrows B^- + H_3O^+$$
$$H_2B + H_2O \rightleftarrows HB^- + H_3O^+$$
$$HB^- + H_2O \leftrightarrows B^- + H_3O^+$$

The expression for the ionization constants is of the general type

$$\frac{C_{H_3O^+} \times C_{B^-}}{C_{HB}} = K_i$$

where B, with the appropriate charge, designates the base (a proton acceptor) which is formed by the ionization of the acid. The smaller the value of the ionization constant, the greater is

Table III. Weak Acids Arranged According to Increase in Strength. Strength of Anions as Bases Arranged According to Decrease in Strength

Acids		Bases			$K_{\text{ionization}}$ of Acids
$Sn(OH)_2(H_2O)_2$	+ H_2O ⇄	$[Sn(OH)_3(H_2O)]^-$	+ H_3O^+		6.0×10^{-18}
H_2O	+ " "	OH^-	+ "		3.3×10^{-18}
$Cr(OH)_3(H_2O)_3$	+ " "	$[Cr(OH)_4(H_2O)_2]^-$	+ "		9.0×10^{-17}
$Pb(OH)_2(H_2O)_2$	+ " "	$[Pb(OH)_3(H_2O)]^-$	+ "		2.1×10^{-16}
HS^-	+ " "	$S^=$	+ "		1.0×10^{-15}
$HAsO_4^=$	+ " "	$AsO_4^{\equiv}$	+ "		10^{-13}
$Al(OH)_3(H_2O)_3$	+ " "	$[Al(OH)_4(H_2O)_2]^-$	+ "		4.0×10^{-13}
$HPO_4^=$	+ " "	$PO_4^{\equiv}$	+ "		10^{-12}
H_2O_2	+ " "	HO_2^-	+ "		2.4×10^{-12}
HCO_3^-	+ " "	$CO_3^=$	+ "		4.7×10^{-11}
H_2SiO_3	+ " "	$HSiO_3^-$	+ "		1.0×10^{-10}
HCN	+ " "	CN^-	+ "		4.0×10^{-10}
NH_4^+	+ " "	NH_3	+ "		5.6×10^{-10}
H_3BO_3	+ " "	$H_2BO_3^-$	+ "		5.8×10^{-10}
H_3AsO_3	+ " "	$H_2AsO_3^-$	+ "		6.0×10^{-10}
$HOBr$	+ " "	OBr^-	+ "		2.1×10^{-9}
$HOCl$	+ " "	OCl^-	+ "		5.6×10^{-8}
$H_2PO_4^-$	+ " "	$HPO_4^=$	+ "		6.2×10^{-8}
$H_2AsO_4^-$	+ " "	$HAsO_4^=$	+ "		10^{-7}
HSO_3^-	+ " "	$SO_3^=$	+ "		1.0×10^{-7}
H_2S	+ " "	HS^-	+ "		1.2×10^{-7}
H_2CO_3	+ " "	HCO_3^-	+ "		4.3×10^{-7}
$HOAc$	+ " "	OAc^-	+ "		1.8×10^{-5}
$HC_2O_4^-$	+ " "	$C_2O_4^=$	+ "		6.4×10^{-5}
$Al(H_2O)_6^{+++}$	+ " "	$[Al(OH)(H_2O)_5]^{++}$	+ "		1.4×10^{-5}
HNO_2	+ " "	NO_2^-	+ "		4.5×10^{-4}
HF	+ " "	F^-	+ "		7.2×10^{-4}
$Fe(H_2O)_6^{+++}$	+ " "	$[Fe(OH)(H_2O)_5]^{++}$	+ "		6.0×10^{-3}
H_3AsO_4	+ " "	$H_2AsO_4^-$	+ "		4.8×10^{-3}
H_3PO_4	+ " "	$H_2PO_4^-$	+ "		7.5×10^{-3}
HSO_4^-	+ " "	$SO_4^=$	+ "		1.2×10^{-2}
H_2SO_3	+ " "	HSO_3^-	+ "		1.2×10^{-2}
$H_2C_2O_4$	+ " "	$HC_2O_4^-$	+ "		5.9×10^{-2}

Increase in Strength of Acids ↓ Increase in Strength of Bases ↑

the concentration of the undissociated acid. The greater the concentration of undissociated acid, the less is the tendency of the acid to act as a proton donor. The ionization constants of a number of acids are given in Table III. The proton donors at

the top of the list have a smaller tendency to ionize than those lower in the column and are weaker acids.

The anions of the acids are bases (proton acceptors). The weaker the base, the larger can be the concentration of hydronium ion in the solution. Hence the weak bases are the anions of the strong acids.

Limitations of the Law of Mass Action. The expression for the ionization constant holds for dilute solutions of weak electrolytes but does not hold for strong electrolytes, as is clear from Table IV, or for concentrated solutions of weak electrolytes. The concentrations in Table IV were calculated using the apparent degree of ionization of potassium chloride and the degree of ionization of acetic acid. The ionization constant of acetic acid de-

Table IV. Application of the Mass Law to Equilibria in Solutions

Molarity	$\frac{C_{M^+} \times C_{X^-}}{C_{MX}}$	
	KCl	HOAc
0.0001	0.143	1.78×10^{-5}
.0010	.046	1.80×10^{-5}
.0100	.152	1.83×10^{-5}
0.1000	0.536	1.85×10^{-5}

creases with the increase in the concentration of salts in the solution. This may be due to the fact that the law of mass action tacitly assumes the independence of the reacting particles; i.e., that they are far enough apart so that the forces between them are negligible. In concentrated solutions, however, these forces cannot be neglected, since the particles are so much closer together, and the force varies inversely as the square of the distance. The forces between ions are more pronounced than those between neutral molecules, and, as a result, the effective concentration of the ions is less than their concentrations. Furthermore, the presence of charged particles may change the dielectric constant of water, thus changing the degree of ionization of a weak electrolyte. Many of these difficulties may be eliminated by using the activities of the ions instead of their concentrations. The numerical value of the activities of ions

and their concentrations are nearly identical in dilute solutions but their values diverge with an increase in concentration of the solute or the total concentration of ions.

Since the activity of an ion depends not only upon its concentration but also on the concentration of all other ions in the solution, the relationship between the concentration and activity of an ion is complicated. The use of concentrations makes the calculations somewhat inaccurate but the usefulness of the results is beyond question. A discussion of the use of the activities of ions in making calculations is found in Chapter VII.

EXERCISES

1. What are the characteristics of a system in equilibrium?
2. By means of the kinetic molecular theory explain the effect of increasing the concentration of one of the substances present in a system at equilibrium.
3. State the law of mass action.
4. Derive the expression for the equilibrium constant for the system: $B + 2F \rightleftarrows D + 3E$.
5. Upon what does the numerical value of the equilibrium constant for any system depend?
6. By means of the expression for the equilibrium constant of hydrogen iodide predict the effect of increasing the concentration of iodine. Of hydrogen iodide.
7. Make a list of ionic reactions which are practically non-reversible and state reasons why these reactions proceed almost to completion.
8. Derive the ionization constant of acetic acid from the law of mass action.
9. Calculate the ionization constant for 0.1-*M* hydrocyanic acid which is 0.0063% ionized. *Ans.* 4×10^{-10}.
10. Calculate the ionization constant for 0.1-*M*
    a. Ammonia if 1.34% reacts with water.
    b. Hydrofluoric acid (HF) which is 8.13% ionized.
11. The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the per cent of ionization of a 0.1-*M* solution. *Ans.* 6.5% if the quadratic equation is solved or 6.7% if approximated.
12. Calculate the per cent of ionization of *M*/20 acetic acid. The ionization constant of acetic acid is 1.8×10^{-5}.
13. Calculate the hydronium ion concentration in 0.5-*M* acetic acid. The ionization constant for acetic acid is 1.8×10^{-5}.
    Ans. 3×10^{-3} moles per liter.
14. Calculate the concentration of hydroxide ion in 0.05-*M* ammonia. The ionization constant for ammonia is 1.8×10^{-5}.
15. Calculate the concentration of hydronium ion in 0.2-*M* hydrocyanic acid. The ionization constant is 4.0×10^{-10}. *Ans.* 8.9×10^{-6} moles per liter.
16. What is the molarity of a solution of nitrous acid that is 2.2% ionized? The ionization constant of nitrous acid is 4.5×10^{-4}.
17. Calculate the per cent of ionization of a solution of hydrocyanic acid made by adding sufficient water to 0.27 g. of solute to make a liter of solution. The ionization constant of hydrocyanic acid is 4×10^{-10}. *Ans.* 2×10^{-2}.

18. If the ionization constant of ammonia is 1.8×10^{-5}, at 25°, what per cent of the ammonia in a 0.1-*N* solution has reacted with water?
19. If the ionization constant for nitrous acid is 4.5×10^{-4} and it is 6.7% ionized, what is the normality of the solution? *Ans.* 0.1-*N*.
20. Give the mathematical expression for the primary and secondary ionization of carbonic acid.
21. By means of the expression for the ionization constant, show qualitatively how the equilibrium between ammonia and ammonium and hydroxide ions will be affected by the addition of a substance having a common ion.
22. One hundredth mole of solid ammonium acetate is added to a liter of 0.1 molar acetic acid. The 0.1 molar acetic acid is 1.34% ionized. Calculate the new value of the hydronium ion concentration.
23. If 7.7 g. of ammonium acetate is added to 400 ml. of a solution containing 8 ml. of acetic acid, sp. gr. 1.04, which analyzes 29% by weight of acetic acid, what is the concentration of hydronium ion? The dilute acetic acid is 1.34% ionized. *Ans.* 7.2×10^{-6}.
24. Calculate the concentration of hydronium ions in a solution made by adding 0.01 mole of sodium acetate to a liter of 0.01-*M* acetic acid. A 0.01-*M* solution of acetic acid is 4.1% ionized. The ionization constant for acetic acid is 1.8×10^{-5}.
25. Equal volumes of 0.2-*M* acetic acid and 1-*M* sodium acetate are mixed. A 0.1-*M* solution of pure acetic acid is 1.34% ionized. What is the concentration of the hydronium ion in the solution?
26. Calculate the concentration of hydroxide ions in a solution made by adding 10.69 g. of solid ammonium chloride to a liter of a 0.2-*M* solution of ammonia. The 0.2-*M* ammonia is 0.95% ionized. The K_i of ammonia is 1.8×10^{-5}.
27. State the limitations of the law of mass action when applied to the equilibrium between an electrolyte and its ions.
28. If 0.05 of a mole of hydrogen sulfide is dissolved in a liter of 1-*N* hydrochloric acid, calculate the concentration of the sulfide ion. The ionization constant of hydrogen sulfide is 1.2×10^{-22}.

CHAPTER III

Application of the Law of Mass Action to Saturated Solutions

SOLUBILITY PRODUCT. The application of the law of mass action to a saturated solution leads to very interesting and important conclusions. Consider a saturated solution of A_2B in which an excess of A_2B is suspended, the temperature being constant. If the solute is ionized completely, $A_2B_{solid} \rightleftarrows 2\ A^+ + B^=$. The speed of solution of $A_2B_{solid} = k' \times C_{A_2B_{solid}}$, and the speed of deposition of A^+ and $B^= = k'' \times C_A^2 \times C_{B^=}$. When equilibrium is established, the speed of solution is equal to the speed of deposition and

$$k' \times C_{A_2B_{solid}} = k'' \times C_{A^+}^2 \times C_{B^=}$$

Since only the surface of a solid is active chemically, and since the surface of a solid suspended in its saturated solution is constant, the product $k' \times C_{A_2B_{solid}}$ equals k''' and, therefore,

$$\frac{k'''}{k''} = C_{A^+}^2 \times C_{B^=}$$

The ratio $\frac{k'''}{k''}$ is a constant and is known as the solubility product or ion product constant. It will be designated as SP_{A_2B} or K_{A_2B}.

$$C_A^2 \times C_{B^=} = SP_{A_2B} \quad \text{or} \quad K_{A_2B} \tag{21}$$

In general the solubility product of a slightly soluble substance is not quite constant. The calculated values of the molar solubilities are somewhat lower than those determined experimentally. The discrepancy increases as the concentration of either the reacting or the non-reacting ions increases. The values of the molar solubilities calculated are those which would be obtained were the concentration of ions in the solution small. The increased solubility due to the presence of other ions is known as the "salt effect" and is discussed in Chapter VII. Another

inaccuracy in the calculation of solubilities from the solubility product results from the failure to take into account the reaction of the ions with water. This introduces a large error in many cases. The method of calculating the solubilities of slightly soluble sulfides in which the effect of the hydrolysis of the sulfide ion is taken into consideration is illustrated in Chapter VII.

An expression analogous to that of the solubility product of a slightly soluble substance can be derived for water or for a saturated solution of a slightly soluble gas, hydrogen sulfide for example. The equation for the ionization of water is: $2\ H_2O \leftrightarrows H_3O^+ + OH^-$ and the expression for the ionization constant (Table III, page 54) is

$$\frac{C_{H_3O^+} \times C_{OH^-}}{C^2_{H_2O}} = K_i = 3.3 \times 10^{-18}$$

By rearranging this equation and substituting the value of 55.3 for the concentration of the un-ionized water, we have

$$C_{H_3O^+} \times C_{OH^-} = K_i \times C^2_{H_2O} = 3.3 \times 10^{-18} \times 55.3^2 = 1 \times 10^{-14} = K_w \qquad (22)$$

The numerical value of the concentration of pure water at 25° is calculated by dividing the weight of a liter of pure water (997.02 g.) by the gram molecular weight of water (18.02 g.). The mathematical expression for the constant of water, K_w, states that the product of the concentration of the hydronium ion and that of the hydroxide ion in any aqueous solution must always equal the numerical value of the constant at the temperature when equilibrium is established.

From the expression for the solubility product, $C^2_{A^+} \times C_{B^-} = SP_{A_2B}$, it follows that if the product of the concentrations of a pair of ions, raised to the proper power, is less than the value of the SP_{A_2B}, the solution is unsaturated. If the value of the product is equal to the solubility product, the solution is saturated, and if its value is greater, the solution is supersaturated. Experience shows that a supersaturated solution is usually unstable and becomes a saturated solution when the excess solute precipitates from the solution. These considerations lead directly to the so-called rules for the precipitation and solution of slightly soluble substances.

Precipitation of a Slightly Soluble Substance. Precipitation will occur on mixing two solutions whenever the products of the concen-

tration of the ions, each raised to the power numerically equal to the number of each ion combining to form the slightly soluble substance, is greater than the solubility product of the compound formed. This follows logically from an understanding of the derivation and meaning of the solubility product. For a saturated solution of calcium carbonate the equation for the equilibrium between the solid calcium carbonate and the calcium and carbonate ions is

$$Ca(CO_3)_{solid} \rightleftharpoons Ca^{++} + CO_3^{=}$$

The solubility product of the salt at 25° is given by the expression

$$C_{Ca^{++}} \times C_{CO_3^{=}} = SP_{CaCO_3} = 4.8 \times 10^{-9}$$

If solid sodium carbonate is added to a solution of calcium chloride, will calcium carbonate always precipitate? To answer this question the concentration of the ions in the solution must be known or data must be available from which the concentrations can be calculated. If to a liter of a solution in which the concentration of calcium ion is 0.0001, sufficient solid sodium carbonate is added to give a concentration of carbonate ion of 0.01, will precipitation occur? The product of the concentrations of the carbonate and calcium ions is

$$0.01 \times 0.0001 = 0.000001 = 1 \times 10^{-6}$$

Since 1×10^{-6} is greater than 4.8×10^{-9}, precipitation of calcium carbonate over and above that required to form a saturated solution takes place. Solid sodium carbonate instead of a solution of the salt is added to keep the volume nearly constant. If solutions containing the ions are used, the change in the concentration due to the increased volume must be taken into consideration. If equal volumes of solutions are mixed, the concentrations are one-half the original values.

If the amount of solid sodium carbonate added would have given a concentration of carbonate ion of 1×10^{-6}, the product of the concentrations of the ions would have been

$$1 \times 10^{-6} \times 1 \times 10^{-4} = 1 \times 10^{-10}$$

and the solution would have been unsaturated.

For a salt whose positive and negative radicals have different valences, the concentrations of the ions must be raised to the proper powers. The solubility product of silver chromate at 25° is

$$C^2_{Ag^+} \times C_{CrO_4^{=}} = 1.1 \times 10^{-12}$$

Suppose that to a solution having a concentration of silver ion of 0.003 sufficient solid sodium chromate is added to give a $C_{CrO_4^-}$ of 0.0002. Precipitation of silver chromate will take place since the product

$$C^2_{Ag^+} \times C_{CrO_4^-} = (0.003)^2 \times (0.0002) = 1.8 \times 10^{-9}$$

is greater than the solubility product of silver chromate, (1.1×10^{-12}).

Solution of a Slightly Soluble Substance. Solution of a slightly soluble substance will take place if the product of the concentrations of the ions raised to the appropriate power is less than the solubility product of the substance. This follows from the fact that a solution is unsaturated if the product of the concentrations of the ions is less than the value of the solubility product. Calcium carbonate suspended in a saturated solution will dissolve if either or both carbonate ions and calcium ions are removed. Since the product of the concentrations is less than the value of the solubility product, momentarily the solution is unsaturated. Solid calcium carbonate will dissolve to increase the value of the product of the concentration of the ions to that of the solubility product. However, if the removal of the ions is continued, the suspended solid will continue to dissolve. It is not necessary to remove the ions from the solution as an insoluble substance. Their concentrations may be decreased by becoming part of a soluble, un-ionized compound, a complex ion or by being changed to a different ion as a result of a change of oxidation state.

If an acid is added to a suspension of calcium carbonate, carbonate ions will be removed according to one of the following equations:

$$CO_3^= + H_3O^+ \rightleftarrows HCO_3^- + H_2O$$

if one equivalent of acid is added to one mole of carbonate, or

$$CO_3^= + 2\,H_3O^+ \rightleftarrows 2\,H_2O + H_2CO_3 \rightleftarrows CO_2 + H_2O$$

if an excess of acid is added. The carbonate ion is removed by converting it to the little ionized hydrogen carbonate ion, or to the very weak carbonic acid, which in turn decomposes to form carbon dioxide and water. The product $C_{Ca^{++}} \times C_{CO_3^=}$ becomes less than the solubility product of calcium carbonate and some of the solid dissolves. This continues until the supply of either the hydronium ions or calcium carbonate is depleted.

The action of acids on barium chromate is of interest. If hydrochloric acid is added, the solid dissolves, whereas if it is treated with dilute acetic acid, only a little of the solid dissolves.

$$BaCrO_{4solid} \rightleftarrows Ba^{++} + CrO_4^{=}$$

The concentration of chromate ion is dependent on the concentration of the hydronium ion for

$$2\,H_3O^+ + 2\,CrO_4^{=} \rightleftarrows 3\,H_2O + Cr_2O_7^{=}$$

and

$$\frac{C^3_{H_2O} \times C_{Cr_2O_7^{=}}}{C^2_{H_3O^+} \times C^2_{CrO_4^{=}}} = K$$

An increase in the concentration of the hydronium ion must be followed by an increase in the concentration of the dichromate ion and a decrease in $C_{CrO_4^{=}}$. If acetic acid, a weak acid, is added, only a relatively small amount of chromate ion is converted to the dichromate ion before a new equilibrium is established. Consequently, little solid barium chromate must dissolve to reestablish the equilibrium. However, if a strong acid is added, there is a tremendous decrease in the concentration of the chromate ion and usually all of the barium chromate dissolves before equilibrium is established.

Another case is the solution of a slightly soluble hydroxide, magnesium hydroxide, for example, in an acid. In any aqueous solution the

$$C_{H_3O^+} \times C_{OH^-} = K_w = 10^{-14}$$

If an acid is added, hydroxide ions formed by the ionization of magnesium hydroxide will be removed until the constant for water is satisfied. But the product of the concentrations of the magnesium ion and the square of the concentration of the hydroxide ion will momentarily be less than the value of the solubility product. The solution will be unsaturated and more hydroxide will dissolve. This process will continue until the hydronium ions are removed or until the solid magnesium hydroxide has been dissolved.

Calculation of the Value of the Solubility Product. A saturated solution of magnesium hydroxide contains 0.000111 (1.11×10^{-4}), moles of the base per liter of solution at 25°. The equilibrium involved is given by the expression

$$Mg(OH)_2 \rightleftarrows Mg^{++} + 2\,OH^-$$

Assume that the hydroxide in this solution is completely ionized; then, the concentration of magnesium ion is 1.11×10^{-4} and the concentration of hydroxide ion is $2(1.11 \times 10^{-4})$. The value of the solubility product is given by the expression $SP_{Mg(OH)_2} = C_{Mg^{++}} \times C^2_{OH^-} = 1.11 \times 10^{-4} \times (2.22 \times 10^{-4})^2 = 5.5 \times 10^{-12}$. If the base were only 80% ionized, the concentration of the magnesium ion would be 0.8 (1.11×10^{-4}) and the concentration of the hydroxide ion would be 0.8 (2.22×10^{-4}). The value for the solubility product would be

$$SP_{Mg(OH)_2} = C_{Mg^{++}} \times C^2_{OH^-}$$
$$= 0.8(1.11 \times 10^{-4}) \times [0.8(2.22 \times 10^{-4})]^2 = 2.78 \times 10^{-12}$$

Calculation of the Molar Solubility from the Solubility Product. The *molar solubility* is the molarity of a saturated solution of a substance. If the solubility product of a substance and the per cent of ionization are known, the molar solubility can be calculated. Silver chromate is completely ionized and its solubility product is 1.1×10^{-12} at 25°. The equilibrium is given by the equation $Ag_2CrO_{4solid} \rightleftarrows 2\,Ag^+ + CrO_4^=$. Two methods may be used for the calculation.

Method A. Let x = the molar solubility (MS) of the solute. Then

$$x = C_{CrO_4^=} \text{ and } 2x = C_{Ag^+} \text{ and}$$
$$x \times (2x)^2 = 1.1 \times 10^{-12}$$
$$4x^3 = 1.1 \times 10^{-12}$$
$$x = 6.5 \times 10^{-5}$$

Method B. Let $x = C_{Ag^+}$. Then

$$x/2 = C_{CrO_4^=} \text{ and}$$
$$x^2 \times x/2 = 1.1 \times 10^{-12}$$
$$x^3/2 = 1.1 \times 10^{-12}$$
$$x = 13.0 \times 10^{-5}$$

but the concentration of silver ion is twice the molar solubility of silver chromate. The molar solubility then is $1/2 \times 13.0 \times 10^{-5} = 6.5 \times 10^{-5}$.

The solubility in grams per liter is $6.5 \times 10^{-5} \times 331.8$ g. $= 2.2 \times 10^{-2}$ g. since the gram formula weight of silver chromate is 331.8 g. The hydrolysis of the anion is not taken into account in making the above calculation. The effect is, however, appreciable in many cases and should be taken into account for greater accuracy. The method of calculation is discussed on page 134.

Effect of the Addition of a Common Ion. If a solute is added to a saturated solution and the two have an ion in common, a

change must take place in the solution to reduce the concentration of the ions so that the product of the new concentrations will equal the solubility product. Thus, in a saturated solution of calcium carbonate containing an excess of solute the following equilibrium exists:

$$CaCO_{3solid} \leftrightharpoons Ca^{++} + CO_3^{=}$$

The addition of carbonate ions will decrease the concentration of calcium ions present and increase the amount of undissolved calcium carbonate. The net effect is, then, to decrease the solubility of the solute. Advantage is taken of this fact in adding a slight excess of precipitating agent to reduce the solubility of a precipitate. A calculation will show the importance of the effect. Assume that an equivalent amount of concentrated hydrochloric acid is added to 0.002-*N* silver nitrate to precipitate the silver ion present, and that the acid added does not appreciably change the total volume of the solution. The concentration of the silver ions remaining in the solution will be that present in a saturated solution of silver chloride. This concentration may be calculated from the solubility product of silver chloride.

Let $x = C_{Ag^+} = C_{Cl^-}$ then

$$C_{Ag^+} \times C_{Cl^-} = x \cdot x = SP_{AgCl} = 1.7 \times 10^{-10}$$

$$x = 1.3 \times 10^{-5}$$

The number of grams of silver ion in a liter of solution is $1.3 \times 10^{-5} \times 108.9$ g. $= 1.4 \times 10^{-3}$ g. A second calculation will give the concentration of silver ion left in the solution when a 10% excess of hydrochloric acid is added to a 0.002-*N* solution of silver nitrate.

Let $y = C_{Ag^+}$ in the solution after equilibrium is established.
$0.002 - y$ = moles of Ag^+ and Cl^- precipitated as AgCl
0.0022 = moles of chloride ion added
$0.0022 - (0.002 - y) = 0.0002 + y$ = moles of Cl^- in the solution when equilibrium is established.

Substituting these values for the C_{Ag^+} and C_{Cl^-}, we have

$$(0.0002 + y)y = 1.7 \times 10^{-10}$$

Since y has a relatively small value, the y within the parenthesis may be dropped, and

$$0.0002\,y = 1.7 \times 10^{-10}$$

$$= 8.5 \times 10^{-7}$$

In a liter of solution there are $8.5 \times 10^{-7} \times 107.9$ g. $= 9.16 \times 10^{-5}$ g. of silver ion which is sixty-five thousandths of the concentration of the silver ion when equivalent amounts of the ions were mixed.

If a compound is produced by the union of two groups having different valences, the calculation is more complicated. Suppose an equivalent amount of potassium chromate is added to a liter of 0.002-*M* silver nitrate. The concentration of silver ions in the solution after precipitation was found to be 13.0×10^{-5} (see page 63). If 10% excess of potassium chromate is added to the 0.002-*M* silver nitrate, the C_{Ag^+} can be calculated as follows:

Let z = final C_{Ag^+}
0.002 = moles of Ag^+ in a liter of the $AgNO_3$
$0.002 - z$ = moles of Ag^+ precipitated as Ag_2CrO_4
0.001 = moles of $CrO_4^=$ equivalent to Ag^+ originally present
$1/2(0.002 - z)$ = moles of $CrO_4^=$ precipitated
0.0011 = moles of $CrO_4^=$ added + 10% excess
$0.0011 - (0.001 - 0.5\,z) = 0.0001 + 0.5\,z$ = final $C_{CrO_4^=}$
$z^2(0.0001 + 0.5\,z) = 1.1 \times 10^{-12}$

To avoid a cubic equation, $0.5\,z$ may be dropped without appreciable loss of accuracy.

$$0.0001\,z^2 = 1.1 \times 10^{-12}$$
$$z^2 = 1.1 \times 10^{-8}$$
$$z = 1.05 \times 10^{-4}$$

The concentration of silver ion left in the solution when a 10% excess of precipitating agent is added is about eight-thousandths of that when equivalent amounts are added.

There are some instances in which the addition of a common ion does not decrease the solubility of the solute as would be expected. However, it has been found that in such cases a chemical reaction takes place between the precipitating agent and the precipitate. An example of such a reaction is

$$Al\begin{matrix}(H_2O)_3\\(OH)_3\end{matrix} + OH^-_{excess} \rightleftarrows Al\begin{matrix}(H_2O)_2^-\\(OH)_4\end{matrix} + H_2O$$

These reactions will be discussed later under complex ions and amphiprotic substances. Attention will be called to other insoluble compounds which dissolve in an excess of the precipitating agent, as the occasion occurs.

The equilibrium constants given in the Appendix involve the activities of the substances rather than the concentrations. Con-

centrations of ions are the same as the activities when the solutions are very dilute and in the absence of strong electrolytes, but the values diverge at higher concentrations. The use of concentrations instead of activities introduces errors into the calculations, but the use of concentrations instead of activities is justified by the greater simplicity of the calculations and the fact that in dilute solutions the errors are not large. The limitations of the calculations have been pointed out.

Coprecipitation and Postprecipitation Precipitates as they form from a solution usually contain greater or lesser amounts of impurities. This is caused by the coprecipitation of the impurities from the solution. Coprecipitation may result from: (1) the adsorption of foreign ions on the surface of the precipitate as it remains in contact with the mother liquor; (2) the occlusion of foreign ions of solution during the period of growth of the small particles; (3) the formation of solid solutions—a solid solution of potassium permanganate and potassium perchlorate precipitates from a solution containing the two salts; (4) the formation of chemical compounds of which the undesired ions are a part. The nitrate ion is found in barium sulfate precipitated from a solution containing a nitrate. This has been attributed to the formation of a compound of the type $BaSO_4 \cdot Ba(NO_3)_2$.

Sometimes the concentration of impurities in a precipitate increases on allowing the precipitate to stand in contact with the mother liquor. This phenomenon is caused by postprecipitation. Long standing may result in the precipitation of a substance which does not ordinarily take place. Thus zinc sulfide, which does not precipitate immediately from dilute solutions of zinc salts in 0.1-*N* hydrochloric acid, will precipitate on standing. The failure of the sulfide to precipitate is probably due to the formation of a supersaturated solution. Its precipitation is hastened by the presence of a finely divided solid. The sulfides of Group II are quite efficient in breaking down the supersaturated condition. Thus, on saturating with hydrogen sulfide scarcely any zinc sulfide is precipitated from a 0.35-*N* solution of sulfuric acid containing zinc sulfate even after standing 30 minutes. However, 90% of the zinc is precipitated as zinc sulfide from 0.35-*N* sulfuric acid containing an equivalent amount of zinc sulfate and mercuric chloride after standing but 10 minutes.

Unless otherwise stated, a precipitate should not be allowed to stand in contact with the mother liquor longer than is necessary for the particles to become so large that they will not pass through

the filter and to insure the conversion of a gelatinous or amorphous precipitate into a form which will filter fairly rapidly.

Application of Law of Mass Action to Other Reversible Systems. Since all reactions are reversible, the law of mass action can be applied to the system to derive an equilibrium constant. Thus, when a solution containing zinc ion is saturated with hydrogen sulfide, we have the equation

$$Zn^{++} + 2H_2O + H_2S^{xs} \rightleftharpoons ZnS + 2H_3O^+$$

and the constant for the reaction obtained by applying the law of mass action is

$$\frac{C^2_{H_3O^+} \times C_{ZnS}}{C_{Zn^{++}} \times C^2_{H_2O} \times C_{H_2S}} = K \tag{23}$$

It is usual to eliminate all constant terms in the expression by combining them to obtain the equilibrium constant of the system, K_{eq}. In the above system the C_{ZnS}, a solid, $C^2_{H_2O}$, and the C_{H_2S} (about 0.1 at 25° and 760 mm.) are constant; hence the expression becomes

$$\frac{C^2_{H_3O^+}}{C_{Zn^{++}}} = K \times \frac{C^2_{H_2O} \times C_{H_2S}}{C_{ZnS}} = K_{eq} \tag{24}$$

Even though the reaction takes place in a series of steps and not in one step as is implied by the equation, the expression for the equilibrium constant which is obtained by the use of the law of mass action is correct. This can be shown by deriving the equilibrium constant by the application of the principles of thermodynamics. If the value of K_{eq} is small, then the $C_{Zn^{++}}$ is large and the reaction does not proceed to any great extent. If the value is large, then the $C_{Zn^{++}}$ is small and the reaction takes place extensively. Furthermore, the $C_{Zn^{++}}$ is directly proportional to the $C^2_{H_3O^+}$; hence the greater the $C_{H_3O^+}$ the greater will be the $C_{Zn^{++}}$ and the less will be the amount of ZnS which precipitates. The equilibrium constant, K_{eq}, may be evaluated; i.e., it can be expressed in terms of constants available in reference tables. This is done by multiplying the expression for the equilibrium constant by one expressed in terms of appropriate concentrations of ions, so that one obtains ratios or products of ions whose values are known. In this case equation 24 multiplied by $\frac{C_{S^-}}{C_{S^-}}$ becomes

$$\frac{C^2_{H_3O^+} \times C_{S^-}}{C_{Zn^{++}} \times C_{S^-}} = K_{eq} \tag{25}$$

The product $C^2_{H_3O^+} \times C_{S^-}$ in a saturated solution is the K_{H_2S} whose value is 1.2×10^{-23} (page 93), and the product $C_{Zn^{++}} \times C_{S^-}$ is the SP_{ZnS} whose value is 4.5×10^{-24}; hence,

$$K_{eq} = \frac{K_{H_2S}}{SP_{ZnS}} = \frac{1.2 \times 10^{-23}}{4.5 \times 10^{-24}} = 2.65 \qquad (26)$$

A reaction between zinc ion and hydrogen sulfide takes place until the ratio of the $C^2_{H_3O^+}$ to the $C_{Zn^{++}}$ is 2.65.

Calculations involving the $C_{Cu^{++}}$, C_{H_2S} and $C_{H_3O^+}$ can be made very easily. Suppose a liter of a solution in which the $C_{Cu^{++}}$ is 0.1 is saturated with hydrogen sulfide, what will be the concentration of cupric ions remaining in the solution when equilibrium is established?

The equation for the reaction is

$$Cu^{++} + H_2S^{xs} + 2H_2O \rightleftharpoons CuS + 2H_3O^+$$

The expression for the equilibrium constant is

$$\frac{C^2_{H_3O^+}}{C_{Cu^{++}}} = K_{eq} = \frac{C^2_{H_3O^+} \times C_{S^-}}{C_{Cu^{++}} \times C_{S^-}} = \frac{K_{H_2S}}{SP_{CuS}} = \frac{1.2 \times 10^{-23}}{4 \times 10^{-38}} = 3 \times 10^{14} \qquad (29)$$

Let x = number of moles of cupric ions left in 1 liter of the solution.
$0.1 - x$ = number of moles of cupric sulfide precipitated.
$2(0.1 - x)$ = number of moles of hydronium ion formed in 1 liter of the solution. By substitution in equation 29 we have

$$\frac{C^2_{H_3O^+}}{C_{Cu^{++}}} = K_{eq} = 3 \times 10^{14} = \frac{[2(0.1 - x)]^2}{x} \qquad (30)$$

Since the value of the equilibrium constant, 3×10^{14}, is large, the value of x must be small; i.e., the concentration of cupric ions when equilibrium is established will be small compared to the original concentration of these ions. Since the final $C_{Cu^{++}}$ is small compared to the initial $C_{Cu^{++}}$, $0.1 - x$ is very nearly equal to 0.1 and by dropping x a quadratic equation is avoided. On solving equation 30, $x = 1.3 \times 10^{-12}$. Similarly, other problems may be solved.

An exact solution of the expression for the equilibrium constant frequently necessitates solving a quadratic equation or an equation of higher order. In most cases the values of the concentrations involved may be expressed so that an approximate solution can be made easily. This can be done by letting the un-

known equal a concentration or change in concentration whose value will be small when equilibrium is established. The unknown then can be dropped when it is added to or subtracted from a number which is large in comparison, thus simplifying the calculations without an appreciable loss of accuracy.

In some cases it may be necessary to multiply the expression for the equilibrium constant by more than one term to evaluate the equilibrium constant. For example, for the reaction

$$NH_4^+ + OAc^- \rightleftharpoons NH_3 + HOAc$$

The expression for the K_{eq} is

$$\frac{C_{NH_3} \times C_{HOAc}}{C_{NH_4^+} \times C_{OAc^-}} = K_{eq} \tag{27}$$

The K_{eq} may be evaluated by multiplying by $\frac{C_{OH^-}}{C_{OH^-}}$ and $\frac{C_{H_3O^+}}{C_{H_3O^+}}$ which gives

$$\frac{C_{NH_3}}{C_{NH_4^+} \times C_{OH^-}} \times C_{OH^-} \times C_{H_3O^+} \times \frac{C_{HOAc}}{C_{H_3O^+} \times C_{OAc^-}} = K_{eq} \tag{28}$$

$$= \frac{1}{K_{iNH_3}} \times K_w \times \frac{1}{K_{iHOAc}} = \frac{K_w}{K_{iNH_3} \times K_{iHOAc}}$$

$$\frac{10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}} = 3.1 \times 10^{-3}$$

EXERCISES

Note: It is assumed that no complicating side reactions such as hydrolysis etc., take place.

1. Starting with the law of mass action, derive the expression for the solubility of product of silver chromate.
2. The solubility of calcium sulfate increases with a decrease in temperature. How will the value of the solubility product (SP_{CaSO_4}) change with the temperature?
3. By means of the expression for the solubility product, predict the effect of the addition of a small amount of sodium sulfate on the solubility of barium sulfate.
4. What is the expression for the constant of water (K_w)?
5. If the product of the concentrations of the ions in a solution is less than the solubility product of the substance formed by the union of the ions, what is the nature of the solution?
6. The product of the concentrations of the ions in a solution is greater than the solubility product of the substance formed by their union. If a small fragment of the solute is added to the solution, what change will take place?

7. State the rule for the precipitation and for the solution of a difficultly soluble substance.
8. The solubility product of silver bromide is 3.3×10^{-13}. If to a liter of a solution containing 10^{-3} formula weights of silver ion is added sufficient solid sodium bromide to give 10^{-10} formula weights of bromide ion, will any precipitate of silver bromide form?
   Ans. No precipitation since $3.3 \times 10^{-13} > 10^{-13}$.
9. The molarity of a saturated solution of silver iodide is 9.2×10^{-9}. Calculate the value of the solubility product.
10. The solubility of strontium carbonate is 0.00452 g. per liter. Calculate the value of the solubility product. *Ans.* 9.4×10^{-10}.
11. The molar solubility of magnesium hydroxide is 1.12×10^{-4}. Calculate the value of the solubility product.
12. The molar solubility of silver manganate is 2.0×10^{-4}. What is the value of its solubility product? *Ans.* 3.2×10^{-11}.
13. The solubility product of silver sulfide is 1.0×10^{-51}. Calculate the solubility in grams per liter.
14. The solubility of magnesium carbonate in water is 4.3×10^{-1} g. per liter. Calculate the solubility product of magnesium carbonate.
    Ans. 2.6×10^{-5}.
15. If the solubility of tertiary silver phosphate is 6.5×10^{-3} g. per liter, calculate the solubility product.
16. The solubility product of lead sulfate is 1.80×10^{-8}. Calculate the solubility of lead sulfate in grams per liter. *Ans.* 4.06×10^{-3}.
17. If there are 1.87×10^{-4} g. of silver chloride in 100 ml. of a saturated solution what is the value of the solubility product?
18. The molar solubility of silver chromate is 6.5×10^{-5}. What is the value of the solubility product? *Ans.* 1.1×10^{-12}.
19. Calculate the solubility product of tertiary silver orthophosphate if 100 ml. of a saturated solution contains 6.5×10^{-4} g. of solute.
20. The solubility product of silver carbonate is 8.2×10^{-12}. What is its solubility in grams per 100 ml.? *Ans.* 3.5×10^{-3}.
21. The solubility product of silver carbonate is 8.2×10^{-12}. What is its molar solubility?
22. Calculate the concentration of calcium ions required to start the precipitation of calcium fluoride from a solution containing 40 milligrams of fluoride ion in 10 ml. of solution. The solubility product of calcium fluoride is 3.9×10^{-11}. *Ans.* Greater than 8.9×10^{-10}.
23. To 100 ml. of a solution containing 40 mg. of silver ions is added an equal number of equivalents of chloride ion and 10% excess. How many milligrams of silver ions remain in the solution? The solubility product of silver chloride is 1.7×10^{-10}.
24. Calculate the maximum concentration of silver ion in a solution in which the molecular concentration of phosphate ions is 1. The solubility product of tertiary silver phosphate is about 1.55×10^{-18}. *Ans.* 1.16×10^{-6}.
25. What is the maximum concentration of magnesium ion that can be present in a solution, 1 liter of which contains 0.5 mole of ammonium chloride and 0.1 mole of ammonia?
26. If 9.8 g. of sodium cyanide is added to a liter of a 0.1-*N* hydrocyanic acid, which is 0.0063% ionized, what will be the concentration of the hydronium ions? The ionization constant of hydrocyanic acid is 4×10^{-10}.
    Ans. 2×10^{-10}.

27. If the concentration of hydronium ions in a solution of 1-*M* acetic acid to which ammonium acetate has been added is 1.9×10^{-5}, how many moles of ammonium acetate were added to a liter of the acid? The ionization constant of acetic acid is 1.8×10^{-5}.
28. Differentiate between coprecipitation and postprecipitation.
29. Account for the fact that the solubility of some difficultly soluble substances increases instead of decreases on the addition of a substance containing a common ion.
30. Set up the expression for the equilibrium constant of the reaction which takes place in each of the following systems. Then evaluate the constant and make the necessary calculations.
    a. To a liter of a 0.01-*N* solution of potassium chloride is added 0.001 mole of solid silver nitrate. Calculate the concentration of silver ion in the solution when equilibrium is established.
    b. How many formula weights of ammonium chloride must be added to 50 ml. of 0.1-*M* NH_3 to prevent the precipitation of magnesium hydroxide when the above solution is added to 50 ml. of a 0.02-*M* solution of magnesium chloride?
    c. The concentrations of silver and bromide ions in a saturated solution are 5.7×10^{-7}. If the concentration of silver ion is increased to 1.2×10^{-3}, what will be the concentration of bromide ion?
    d. If solid silver chloride is added to a 0.1-*N* solution of potassium thiocyanate, what will be the ratio of the concentrations of chloride ion to thiocyanate ions in the solution?
    e. How many grams of silver acetate will dissolve in 100 ml. of a 0.01-*N* solution of nitric acid?
    f. Calculate the maximum concentration of silver ions which can be in a liter of a 0.1-*N* solution of acetic acid to which has been added 0.1 mole of hydrogen nitrate without a precipitate forming.

CHAPTER IV

Oxidation and Reduction, Complex Ions, and the Colloidal State

OXIDATION AND REDUCTION

Oxidation is defined as the loss of electrons and reduction as the gain of electrons.

An oxidizing agent brings about the oxidation of the reducing agent by acquiring the electrons which are lost by the reducing agent. The oxidizing agent is thus reduced and the reducing agent is oxidized. In the reaction between chlorine and iodide ions $Cl_2 + 2\,I^- = 2\,Cl^- + I_2$, the chlorine is the oxidizing agent because it acquires electrons. The iodide ion is a reducing agent because it loses an electron. A change in either the valence or the oxidation state always accompanies oxidation and reduction. The valence of an element or radical is the number of electrons actually lost or gained. Thus the atoms of oxygen and sulfur in the sulfate ion have acquired two electrons and the valence of the sulfate ion is two negative (2 −). In the equation above, the iodide ion changes from a valence of one negative to the valence of a free element, which is zero. The iodide ion is therefore oxidized. Oxidation is associated with a decrease in the negative or an increase in the positive valence or the oxidation state of an element. The oxidation state is the apparent number of electrons lost or gained by an atom in becoming a part of a radical or covalent compound. A positive oxidation state indicates that electrons apparently have been lost by the atom, while a negative value indicates that electrons apparently have been gained.

To calculate the oxidation state of an element, the following generalizations will be of value:

1. The oxidation state of oxygen except in peroxides, molecular oxygen and ozone is negative two (−2).
2. The oxidation state of hydrogen is positive one (+1) except in metallic hydrides in which it is negative one (−1).

3. The sum of the valences and oxidation states in a molecule is zero.
4. The sum of the oxidation states of the elements in an ion is the same as the charge on the ion; i.e., the valence of the ion.

For example, the oxidation state of the sulfur in the sulfate ion whose valence is two negative (2−) is the number (+6) which must be added to the total oxidation state of oxygen [4(−2)] to give the sum (2−). The oxidation state of nitrogen in the nitrate ion is the number (+5) which when added to the total oxidation state of oxygen [3(−2)] gives the sum (1−). In the ammonium ion, whose valence is one positive, the oxidation state of the nitrogen is negative three (−3). The valence or oxidation state of a free element is zero.

The principle used in balancing oxidation-reduction equations is this: the total loss of electrons by the reducing agent must equal the total gain of electrons by the oxidizing agent. If the reaction is essentially non-ionic, molecular formulas are used. If the reactions take place between ions, ionic formulas are used. An example will make clear the method of balancing an equation for the action between non-ionic substances.

Skeletal Equation:

$$H_2SO_4 \text{ conc.} + Al \rightleftarrows Al_2(SO_4)_3 + SO_2 + H_2O$$

$1\ S^{+6} \rightarrow 1\ S^{+4}$ gain of 2 electrons (2 ϵ) $2\ Al^{\circ} \rightarrow 2\ Al^{3+}$ loss of 6 electrons (6 ϵ)	6 is the number of electrons lost and gained	×3. ×1	These are the number of units necessary to have the same loss and gain of electrons.

Balanced Equation:

$$3\ H_2SO_4 \text{ conc.} + 3\ H_2SO_4 \text{ conc.} + 2\ Al \rightleftarrows Al_2(SO_4)_3 + 3\ SO_2 + 6\ H_2O$$

The lines connecting the sulfuric acid with the products show that sulfuric acid has two functions: first it acts as an oxidizing agent and the sulfur is reduced to the sulfur in sulfur dioxide. Second, it furnishes sulfate radicals to form aluminum sulfate. The acid which furnishes the acid radicals for the aluminum sulfate acts neither as an oxidizing nor as a reducing agent. The following precedure is recommended for balancing oxidation-reduction equations when the products are known:

1. Write the correct formulas of the reactants and products.
2. Determine which elements have been oxidized and reduced.

3. Indicate the total gain or loss of electrons by each formula of the oxidizing and of the reducing agent.
4. Determine the total number of electrons lost and the total gained.
5. Take such quantities of oxidizing and reducing agents as will make the total gain equal the total loss of electrons.
6. Indicate the number of formula weights of the products formed by the reduction and oxidation of the oxidizing and reducing agents respectively.
7. Take sufficient acid or base to furnish negative radicals for the un-ionized compounds formed from the oxidizing and reducing agents, or if the equation is ionic, adjust the number of non-oxidizing or reducing positive or negative ions so that the net charge of the ionic reactants is equal to the net charge of the ionic products.
8. Use a sufficient number of molecules of water to balance the equation.

Ionic equations are used for oxidation-reduction reactions in which the reaction takes place between highly ionized substances. These equations have the advantage that only those ions or undissociated substances which actually participate in the action or are necessary to maintain the proper concentration of the hydronium ions appear in the equation. Thus, the ionic reaction for the reduction of the permanganate ion in an acid solution is $MnO_4^- + H_3O^+ + 5\,\epsilon \rightleftarrows Mn^{++} + H_2O$ and the reaction for the oxidation of concentrated hydrochloric acid is $2\,Cl^- (+ H_3O^+ \text{ conc.}) \rightleftarrows Cl_2 + 2\,\epsilon$. The unbalanced ionic equation for the action of concentrated hydrochloric acid and potassium permanganate is

$$MnO_4^- + Cl^- + H_3O^+ \text{ conc.} \rightleftarrows Mn^{++} + Cl_2 + H_2O$$

$$\begin{array}{llll} 1\,Mn^{+7} \rightarrow 1\,Mn^{2+} & \text{gain of } 5\,\epsilon & 10 & \times 2 \\ 2\,Cl^- \rightarrow 1\,Cl_2 & \text{loss of } 2\,\epsilon & & \times 5 \end{array}$$

When the number of hydronium ions is adjusted so that the net charge of the reactants is equal to the net charge of the products—four positive in this equation, the balanced equation is

$$2\,MnO_4^- + 10\,Cl^- + 16\,H_3O^+(\text{conc.}) \rightleftarrows 2\,Mn^{++} + 5\,Cl_2 + 24\,H_2O$$

An example of a reaction in which the hydronium ion must be present in high concentration, but is not necessary to balance the equation, is the precipitation of manganese dioxide from concentrated nitric acid upon the addition of solid potassium chlorate. The equation for the action is

$$2\,ClO_3^- + Mn^{++} + (H_3O^+ \text{ conc.}) \rightleftarrows MnO_2 + 2\,ClO_2$$

By convention, substances which must be present for the reaction to take place but which are not needed to balance the equation are placed in parentheses and do not appear among the products.

Prediction of the Products of an Oxidation-Reduction Reaction. The prediction of the products formed by the action of an oxidizing and a reducing agent is difficult. If an oxidizing and reducing agent are mixed, usually a reaction will take place which can be expressed by the general equation

Oxidizing Agent + Reducing Agent $\rightleftarrows$ Reduction Products of Oxidizing Agent + Oxidation Products of the Reducing Agent.

Thus if the reduction products of the oxidizing agent and the oxidation products of the reducing agent are known, they can be substituted in the general equation and the equation can than be balanced.

The following list of the reduction products of oxidizing agents and the oxidation products of reducing agents will be a material aid:

Oxidizing Agents	*Reduction Products*
$MnO_2 + H_3O^+ + 2\,\epsilon$	$Mn^{++} + H_2O$
$MnO_4^- + H_3O^+ + 5\,\epsilon$	$Mn^{++} + H_2O$
$MnO_4^- + OH^- + 3\,\epsilon$	$MnO_2 + H_2O$
$Cr_2O_7^= + H_3O^+ + 6\,\epsilon$	$2\,Cr^{+++} + H_2O$
$NO_3^- + H_3O^+ + 3\,\epsilon$	$NO + H_2O$
$NO_3^- + H_3O^+$ conc. $+ 1\,\epsilon$	$NO_2 + H_2O$
$HOX^* + 2\,\epsilon$	$X^- + H_2O$
H_2SO_4 conc. + 2, 6, or 8 ϵ	SO_2, S, or H_2S (depending on the strength of the reducing agents)†
$HNO_2 + 1\,\epsilon$	NO
$H_2O_2 + H_3O^+ + 2\,\epsilon$	H_2O
$O_2^= + H_2O(+ OH^-) + 2\,\epsilon$	OH^-

Reducing Agents	*Oxidation Products*
$H_2O_2 + H_3O^+$	$O_2 + H_2O + 2\,\epsilon$
H_2S	$S + H_2O + 2\,\epsilon$
H_2SO_3	$HSO_4^- + 2\,\epsilon$
HNO_2	$NO_3^- + 2\,\epsilon$
X^-(H_3O^+ must be conc. for Cl^-)	$X_2 + H_2O + 1\,\epsilon$ (for each X^-)
Fe^{++}	$Fe^{+++} + 1\,\epsilon$
Sn^{++}	$Sn^{++++} + 2\,\epsilon$
Hg_2^{++}	$2\,Hg^{++} + 2\,\epsilon$
Metals (The most active metals are the strongest reducing agents.)	Metallic ions $+ x\,\epsilon$

* X represents any halogen except fluorine.

† With weak reducing agents such as the metals below hydrogen the chief reduction product is SO_2. With strong reducing agents such as the metals above hydrogen or an iodide, the main reduction product is a sulfide.

In some cases a single substance may function both as an oxidizing and a reducing agent. Thus, in the equation

$$OCl^- + 2\,OCl^- \rightleftarrows ClO_3^- + 2\,Cl^-$$

one hypochlorite ion acts as a reducing agent and the other two act as oxidizing agents. If oxidation-reduction reactions actually involve the transfer of electrons from one group to another, it should be possible to arrange the oxidizing and reducing agents in such a way that the electrons transferred from one group to another must pass over an external circuit. This can be done by placing the oxidizing and reducing agents in porous cells containing an inert electrode, platinum or graphite, for example, and immersing the cells in a solution of an electrolyte with which they do not react.. When the electrodes are connected by a conductor, there will be a flow of electrons which can be detected by a suitable measuring instrument. Appropriate analytical tests of the contents of the porous cells show that the oxidizing agent has been reduced and that the reducing agent has been oxidized—characteristics of oxidation-reduction reactions. If the connection between the electrodes is maintained until no electrons pass from one electrode to the other, the reaction has taken place to the same extent as it would have if the two solutions had been mixed.

It is possible to predict the extent to which oxidizing and reducing agents react if the value of the equilibrium constant for the generalized reaction

$$\text{Oxidizing agent} + \text{reducing agent} \leftrightarrows \text{reduction products} + \text{oxidation products}$$

can be calculated. The expression for the equilibrium constant is

$$\frac{C_{\text{red prod}} \times C_{\text{ox prod}}}{C_{\text{ox ag}} \times C_{\text{red ag}}} = K$$

If the value of K is one, the reaction goes half way to completion. If the value of K is large then the value of the denominator is small and the reaction takes place to an appreciable extent. If the value of the constant is small then the value of the denominator must be large and only a small amount of the oxidizing and reducing agent react.

The value of the equilibrium constant may be calculated by using standard oxidation-reduction potentials. These potentials are found experimentally by determining the electromotive force

of battery cells arranged as shown in Figure 2. The cell may be represented

$$\text{Pt} \left| \begin{matrix} \text{1-}M \text{ ox ag} \\ \text{1-}M \text{ red prod} \end{matrix} \right\| \text{1-}M\ H_3O^+ \left| H_2(1\ \text{At.})\text{Pt} \right.$$

The platinum immersed in a solution in which the effective concentration or activity of hydronium ions is one and over which bubbles of hydrogen stream under a pressure of one atmosphere is known as a standard hydrogen electrode. The hydronium and other ions which are a part of a standard electrode must have, by convention, an effective concentration or activity of

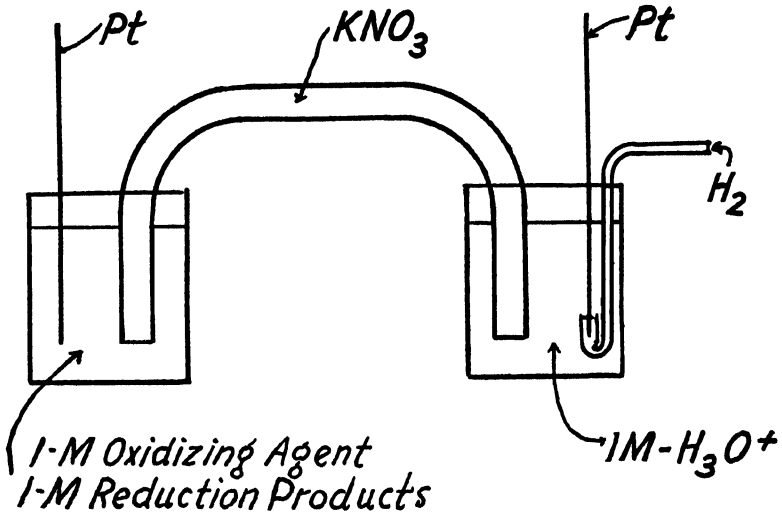


Fig. 2.

one. A gas which is a part of a standard electrode must be at a pressure of one atmosphere. If the oxidized and reduced forms in a standard electrode are ions or dissolved substances, they do not have to be at unit activity. It is only necessary that they have the same activity. However, since the activity of an ion has not yet been discussed, ordinary concentrations (molar) will be used. In dilute solutions the activity of an ion and its concentration (molar) differ but little. It is not possible to determine the potential between an electrode and a liquid, but if it is assumed that the potential between the hydrogenized platinum electrode and the acid in which it is immersed is zero, then the electromotive force of the

cell is a measure of the difference in the potential between the platinum electrode immersed in the mixture of oxidizing agent and its reduction products and the solution. The reaction involved in the cell may be represented

$$\text{Oxidizing agent} + H_2 + H_2O \rightleftarrows \text{Reduction products} + 2\,H_3O^+$$

If the mixture of oxidizing agent and reduction products in the cell is a strong oxidizing agent, this electrode is positive. For example, with chlorine (1 At.) and chloride ion (1-*M*), the chlorine-chloride electrode is the positive electrode and the hydrogen electrode is the negative. The electromotive force of the cell is 1.35 V. If the electrode is a strong reducing agent, zinc for example, which is immersed in a 1-*M* solution of zinc ions, the hydrogen electrode is the positive electrode of the cell whose electromotive force is 0.76 V. The cell may be represented Zn | 1-*M* Zn^{++} || 1-*M* H_3O^+ | H_2(Pt). The standard electrode potential, therefore, of the chlorine-chloride electrode is + 1.36 *V* and that of the zinc-zinc ion electrode is −0.76 *V*. By making a large number of cells, all of which have a standard hydrogen electrode, the standard electrode potentials of many oxidizing and reducing agents have been determined. A negative value of the standard electrode potential indicates that the system consisting of an oxidizing agent and its reduction products is a better reducing agent than the mixture of hydrogen and hydronium ions. A positive value indicates that the mixture of hydrogen and hydronium ions is the better reducing agent. The better reducing agent is, of course, the poorer oxidizing agent. The greater the negative value of the standard electrode potential, the stronger the reducing agent. Conversely, the greater the positive value, the stronger the oxidizing agent.

A method of calculating equilibrium constants from the standard electrode potentials is given on page 123. A table of standard electrode or oxidation-reduction potentials is included in the Appendix.

COMPLEX IONS

A complex ion is formed by the union of a simple ion with a neutral molecule or with a second ion.

$$Cd^{++} + 4\,NH_3 \rightleftarrows Cd(NH_3)_4^{++}$$
$$Zn^{++} + 4\,NH_3 \rightleftarrows Zn(NH_3)_4^{++}$$
$$Cd^{++} + 4\,CN^- \rightleftarrows Cd(CN)_4^{=}$$
$$Ag^+ + S_2O_3^{=} \rightleftarrows Ag(S_2O_3)^- \text{ or } Ag(S_2O_3)_2^{\equiv}$$
$$Ag^+ + 2\,Cl^-\ \text{xs} \rightleftarrows AgCl_2^-$$
$$Sn^{++++} + 6\,Cl^-\ \text{xs} \rightleftarrows SnCl_6^{=}$$
$$Hg^{++} + 4\,Cl^-\ \text{xs} \rightleftarrows HgCl_4^{=}$$

These reactions are reversible, but when equilibrium has been established, the concentration of metallic ions in the solution has been very markedly decreased. The application of the law of mass action to a typical reaction involving the formation of a complex ion

$$Ag^+ + 2\ NH_3 \rightleftarrows Ag(NH_2)_3^+$$

gives the expression

$$\frac{C_{Ag^+} \times C^2_{NH_3}}{C_{Ag(NH_3)_2^+}} = K_{eq} = K_{instability} \tag{31}$$

This constant is known as the instability constant. The instability constants of some complex ions are given in Appendix III. The smaller the value of the constant, and consequently the greater the stability of the complex ion, the larger is the concentration of the undissociated complex ion. The expression for the instability constant of the silver-diammine ion shows that the concentration of the silver ion is inversely proportional to the square of the concentration of the ammonia present. It should be possible, then, to reduce the concentration of silver ions in a solution of silver nitrate by the addition of ammonia to such an extent that no precipitation of silver chloride will result on the addition of chloride ions; i.e., $C_{Ag^+} \times C_{Cl^-} < SP_{AgCl}$. If bromide ions are added to a portion of such a solution containing the silver-diammine ion, some precipitation of silver bromide will take place, since the solubility product of silver bromide is about three-thousandths that of silver chloride. The addition of iodide ions to the second portion of the solution brings about the nearly complete removal of silver ions as silver iodide, for the solubility product of silver iodide is approximately one millionth of the value of the solubility product of silver chloride. The value of the solubility products of the silver halides are given in the Appendix.

It is not surprising that silver chloride is soluble in ammonia, for the silver ions from the silver chloride are converted into silver ammine ions $Ag(NH_3)_2^+$. Since C_{Ag^+} from the silver-diammine ion $\times C_{Cl^-} < SP_{AgCl}$, the solution becomes unsaturated and more silver chloride dissolves. On the addition of an excess of ammonia the process continues until all of the solid silver chloride is dissolved. The concentration of ammonia must be greater to dissolve silver bromide, for the concentration of silver ion from the silver bromide is only somewhat larger than the concentration of silver ion which can be present in a solution of concentrated ammonia. The concentration of the silver ion, then, need be lowered only slightly before

it is equal to the concentration of the silver ion present in a solution of ammonia of the same concentration. Hence, silver bromide is but slightly soluble in dilute ammonia and sparingly soluble in the concentrated reagent. Silver iodide does not dissolve in dilute ammonia, but is very slightly soluble in the concentrated reagent. The concentration of the silver ions in a saturated solution of silver iodide is less than the concentration of the silver ions which may be present in a concentrated solution of ammonia. The problem is complicated by the fact that silver iodide forms an insoluble compound ($2\ AgI \cdot NH_3$) when treated with the concentrated ammonia.

Only cadmium sulfide will precipitate from a solution containing cadmium and cupric ions to which an excess of potassium cyanide has been added. The metallic ions become parts of the complex cadmium-cyanide ($Cd(CN)_4^{=}$) and cupro-cyanide ($Cu(CN)_2^{-}$) ions. The cupric copper has been reduced to the cuprous state by the cyanide ion. However, no cuprous sulfide will be formed since $C^2_{Cu^+}$ from the cupro-cyanide ion $\times\ C_{S^=} < SP_{Cu_2S}$ but cadmium sulfide will precipitate because $C_{Cd^{++}}$ from $Cd(CN)_4^{=} \times C_{S^=} > SP_{CdS}$. The difference in the stability of these complex ions, then, makes it possible to test for cadmium in the presence of copper. Some other complex cyanide ions are:

$Fe(CN)_6^{\equiv}$ $Fe(CN)_6^{=}$ $Co(CN)_6^{=}$ and $Ag(CN)_2^{-}$

The stability of these ions is so great that their solutions fail to give ordinary tests for the metallic ions.

Many of the metallic ions react with fluoride, chloride, bromide or iodine ions to form soluble complex ions such as $HgCl_4^{=}$, $SnCl_4^{=}$, $AgCl_2^{-}$, $SnCl_6^{=}$, $PtCl_6^{=}$, etc. The formation of the complex silver chloride ion is of some importance in the precipitation of the chlorides in Group I. If the concentration of chloride ion present in a solution is greater than 2-N, a considerable quantity of silver ion will escape precipitation as the chloride and thus traces of silver may be overlooked. This will cause trouble in the analysis of Group II.

Many organic substances such as tartrates, glycerine and oxalates react with metallic ions to form complex ions which are so stable that the metallic ions cannot be detected by the usual tests. For example, ferric hydroxide will not precipitate from a solution of a ferric salt to which an excess of glycerine has been added. It is essential, then, that organic matter be removed before the cation analysis is started.

Calculations Involving Instability Constants. If the value of the instability constant of a complex ion and the molarity of a solution are known, the concentration of the metallic ions in the solution can be calculated. Assume the molarity of a solution of silver-diammine chloride is 0.01. Except for the dissociation of the complex ion, the concentration of silver-diammine ion is 0.01, since the salt is assumed to be completely ionized.

Let x = the concentration of the silver ion, then
$2x$ = the concentration of ammonia, and
$0.01 - x \fallingdotseq$ the concentration of the undissociated complex ion.

$$\underset{0.01}{Ag(NH_3)_2Cl} \rightarrow \underset{0.01}{Ag(NH_3)_2^+} + Cl^-$$

$$\underset{0.01 - x}{Ag(NH_3)_2^+} \leftrightarrows \underset{x}{Ag^+} + \underset{2x}{2\,NH_3}$$

Substituting these values, the expression for the instability constant, equation 31, becomes

$$K_{inst} = 6.0 \times 10^{-8} = \frac{C_{Ag^+} \times C^2_{NH_3}}{C_{Ag(NH_3)_2^+}} = \frac{x \times (2x)^2}{0.01 - x}$$

$$\text{and} \quad x = 5.3 \times 10^{-4}$$

If an excess of ammonia is added, the concentration of the complex ion will increase and that of the silver ion will decrease, thus keeping the ratio constant.

Constitution of Complex Ions. Complex ions are formed by the union of a simple ion with one or more molecules or other ions. An ion serves as a nucleus to which the other groups become attached. The coordination number, or the number of groups associated with the ion serving as a nucleus, depends a great deal on the position of the element in the Periodic Table or, more strictly speaking, upon its ionic radius. Thus, four groups are usually associated with the elements in the first three periods; and six, although occasionally eight, with those in the other periods. In aqueous solutions water molecules become attached to the ion. Since the ordinary valences of the elements in the groups are satisfied, what are the forces which bind the groups in the complex ion together? Werner, whose work in this field is classical and after whom this type of compound was

named, recognized two kinds of valence: *principal valence*, which corresponds to ordinary valence; and *auxiliary valence*. The latter are valences which are exerted in addition to the usual valence. Groups held by the auxiliary or residual valences are thought to be in an inner sphere since they do not ionize appreciably. Groups held by principal valences may be in either the inner sphere, in which case they do not ionize, or in the outer sphere where they ionize in the usual way.

An explanation of the structure of these compounds in terms of the modern ideas of valence has been offered by Sidgwick. The ions or molecules found in the complex have a pair of electrons which may be used to form a covalent link. Thus, ammonia has the following structure $H:\underset{\cdot\cdot}{\overset{H}{\underset{\cdot\cdot}{N}}}:H$; a chloride ion, $(:\underset{\cdot\cdot}{Cl}:)^-$; and water $H:\underset{\cdot\cdot}{O}:H$.

According to this the silver-diammine ion would be represented as $(H_3N:Ag:NH_3)^+$, the cupric-tetrammine ion as $(H_3N:\underset{\cdot\cdot}{\overset{NH_3}{\underset{NH_3}{Cu}}}:NH_3)^{++}$, and the hydronium ion as $(H:\underset{\cdot\cdot}{\overset{H}{O}}:H)^+$. A covalence in which both electrons are supplied by a single atom or ion is called a *coordinate covalence*. For example, $:NH_3$ furnishes both electrons when ammonia combines with a proton to form the ammonium ion. Other examples are the formation of complex ions by the reaction of chlo-

Table V. Formulas of Complex Ions

Complex Ion	Metallic Ions
$[M'X_2]^-$	Ag, Hg, Cu
$[M''X_4]^=$	Pb, Cu, Cd, Hg, Zn, Sn, Co, Ni
$[M''X_6]^=$	Fe
$[M'''X_6]^=$	Sb, As, Fe, Mn, Co
$[M''''X_6]^-$	Mn, Sn
$[M'''''X_6]^-$	As, Sb

rides, cyanides, thiocyanates and hydroxides with an excess of the anion. The formulas of the complex ions usually assumed to be formed are given in Table V. In the table the valence of the metallic coordinating ion (M) is shown by the number of marks above and

to its right. The valence of the complex ion is indicated in the usual way.

A mechanism for the formation of a coordinate covalence bond has been suggested. It is well known that the centers of the positive and negative charges on molecules which form coordination compounds do not coincide. Such molecules are dipoles, the strength of which is determined by the charge and the distance between the centers of the charges. If two dipoles or an ion and a dipole come in

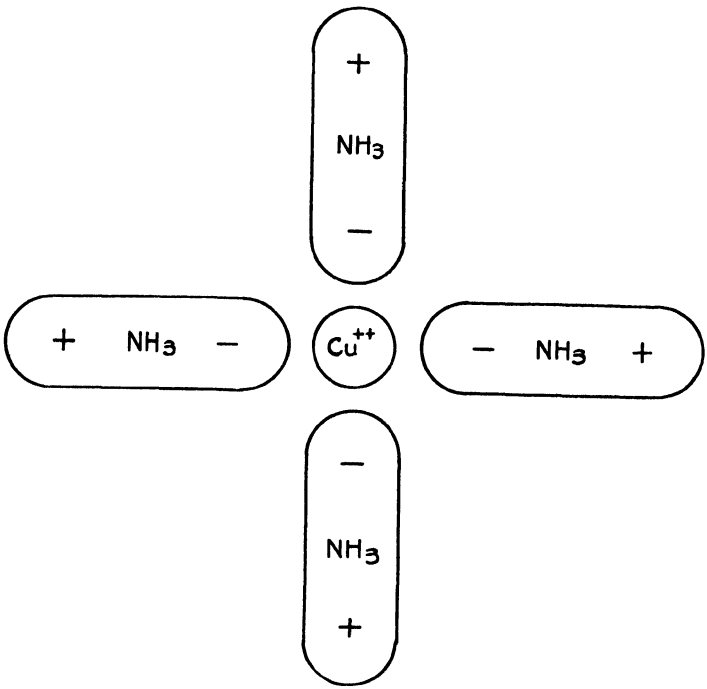


Fig. 3.

the vicinity of one another, and if the attraction is sufficiently great, the groups come close enough together so that a pair of electrons becomes associated with both groups, thus forming a coordinate covalence. Should a dipole or ion approach a group which is not a permanent dipole, there may be a distortion of the particle so that the centers of positive and negative charges no longer coincide—that is, the particle temporarily becomes a dipole and acts similarly to a permanent dipole.

The structure of the cupric-ammine ion is diagrammatically represented in Figure 3. The negative part of the dipole ammonia is attracted by the positive metallic ion. When the ammonia molecules come sufficiently close to the ion, the pair of electrons available on the nitrogen atom become associated with both the metallic ion and the nitrogen thus forming a coordinate bond, or covalence, as it is sometimes called. Water is also a dipole and acts similarly to ammonia.

Nomenclature of Coordination (Werner) Compounds. Just as in writing the formula of a simple compound, the formula of the cation of a Werner compound, now usually called a coordination compound, precedes that of the anion. In the formula of a complex cation or anion, the coordinating positive ion is followed by those of the acid radicals and these in turn by the formulas of the molecules. The formulas of the groups in the complex ion are enclosed in brackets, for example:

$$[Co(NO_3)_2(NH_3)_4]^+ \quad \text{and} \quad [Cr(CNS)_4(NH_3)_2]^-$$

When naming a coordination compound, the name of the cation always precedes that of the anion. The name of an acid radical in a complex ion always ends in *o*. For example, the names of the chloride and sulfate groups are chloro and sulfato respectively. Water in a complex ion is called aquo although the ending *o* is usually reserved for acid radicals. Some writers designate the ammonia in a complex ion as ammino instead of ammine although the latter name is preferred. When giving the name of a complex cation or anion the names of the acid radicals are followed by those of molecules and finally by the name of the coordinating positive ion. An appropriate prefix, *di*, *tri*, etc., precedes the name of each group when more than one is present in the complex. Hyphens are not necessary between the names of the groups. According to the Werner system, the valence of the coordinating ion is indicated by the endings *a*, *o*, *i*, and *e'* on the name of the coordinating positive ion. These endings designate *uni*, *di*, *tri*, and *tetra* valent coordinating positive ions. The name of the complex cation having the formula $[CrCl(NH_3)_5]^{++}$ is the chloropentamminechromi ion.

The names of complex anions always end in *ate*. In the Werner system of nomenclature this suffix is attached to the name of the coordinating positive ion whose valence has been indicated by the endings *a*, *o*, *i*, and *e'*. For example, the name of the compound whose formula is $[Cr(SCN)_4(NH_3)_2]^-$ is the tetrathiocyanatodiamminechromiate ion. The name of the compound, $[Co(NO_3)_2(NH_3)_4]_2$

$(Cr(CNS)_4(NH_3)_2]$, is dinitratotetramminecobalti tetrathiocyanatodiamminechromiate.

Recently the Werner system of naming coordination compounds has been modified. One major change is the method of designating the oxidation state of a coordinating ion. Instead of using the endings *a*, *o*, *i* and *e*,' the appropriate Roman numeral in parentheses is placed after the name of the coordinating ion. According to this system the names of the ions $[CrCl(NH_3)_5]^{++}$ and $[Cr(SCN)_4(NH_3)_2]^-$ are chloropentamminechromium (III) and tetrathiocyanatodiamminechromate (III), respectively. The name of the compound whose formula is $[CrCl(NH_3)_5]\ [Cr(SCN)_4(NH_3)_2]_2$ is chloropentamminechromium (III) tetrathiocyanatodiamminechromate (III).

If the compound is not an electrolyte, the names and order of the groups is the same as the complex cations and anions, but the coordinating ion has the name of the metal. For example, the name of the compound whose formula is $[CrCl_3(NH_3)_3]$ is trichlorotriamminechromium according to the Werner system and trichlorotriamminechromium (III) according to the more modern system. Rules for naming more complicated compounds can be found in more advanced books.*

These rules are illustrated for mono-, bi- and trivalent coordinating groups.

Compounds with Complex Cations

	Werner Nomenclature	*Modern Nomenclature*
$[CoCl(NH_3)_5]Cl_2$	Chloropentammine cobalti chloride	Chloropentammine cobalt (III) chloride
$[Ag(NH_3)_2]Cl$	Diammine-argenta chloride	Diamminesilver (I) chloride
$[Cu(H_2O)_5]SO_4$	Pentaaquocupro sulfate	Copper (II) sulfate pentahydrate or pentaquocopper II sulfate
$[Cr(NH_3)_6](NO_3)_3$	Hexamminechromi nitrate	Hexamminechromium (III) nitrate

Compounds with Complex Anions

$Na[AgCl_2]$	Sodium dichloroargentaate	Sodium dichloroargentate (I)
$(NH_4)_3[ZnCl_5]$	Ammonium pentachlorozincoate	Ammonium pentachlorozincate (II)
$K_3[Fe(CN)_6]$	Potassium hexacyanoferriate	Potassium hexacyanoferrate (III)

* For further information consult the references given in the footnote on page 39 and Fernelius: Chem. and Eng. News *267*:520–23, 1948.

Compounds with Complex Cations and Anions

	Werner Nomenclature	*Modern Nomenclature*
$[CoCl(NH_3)_5]_3[Cr(C_2O_4)_3]_2$	Chloropentammine-cobalti trioxalato-chromiate	Chloropentammine-cobalt (III) trioxalato-chromate (III)
$[PtCl(NH_3)_5]_2[PtCl_4]_3$	Chloropentammine-platine' tetrachloro-platoate	Chloropentammine-platinum (IV) tetra-chloroplatinate (II)

Non-ionizing Molecules

$[Co(NH_3)_3Cl_3]$	Trichlorotriammine cobalt	Trichlorotriammine cobalt (III)
$[Pt(NH_3)_2Cl_4]$	Tetrachlorodiammine platinum	Tetrachlorodiammine platinum (IV)

Some of the ammines are very stable and can be crystallized from concentrated hydrochloric acid. However, the compounds used in effecting separations in qualitative analysis react readily with acids to give the simple hydrated ion.

Hydrates are also a type of Werner compound. However, in writing the formula of a hydrate the water of hydration usually is not associated with the metallic ion but is written after the formula of the simple compound; for example, $CuSO_4 \cdot 5\,H_2O$. Even though crystalline hydrates of some salts cannot be prepared, in solution the ions are undoubtedly closely associated with water molecules numerically equal to the coordination number of the ion.

THE COLLOIDAL STATE

Some substances do not precipitate even though more than sufficient solute is present to make a saturated solution. Such a condition is caused by the formation of a super-saturated solution or by the formation of a colloidal suspension. An example of the former is the non-precipitation of magnesium ammonium phosphate until nuclei are present upon which the magnesium ammonium phosphate can deposit. Dust particles, a small crystal of the crystalline material, or fine particles of glass, formed when the inside of the container is scratched with a stirring rod, are nuclei upon which the solute in excess of that needed to make a saturated solution can deposit.

When hydrogen sulfide is passed into an ammoniacal solution of a nickel salt, a brown solution is formed which will pass unchanged through a filter paper or other filtering medium. Similarly, if hydrogen sulfide is passed into an aqueous solution of arsenious oxide, the clear solution turns yellow and becomes

opalescent, but no precipitate forms. The addition of a small specimen of the nickel sulfide to the first solution or arsenious sulfide to the second solution fails to start precipitation of the difficultly soluble sulfide, hence the solution is not supersaturated. Solutions which contain more solute than is necessary to saturate the solution and which are not supersaturated are colloidal and are frequently called *sols*. No particles can be detected when these solutions are examined with the eye. However, the ultramicroscope or the recently developed electron microscope show that there are minute particles of these sulfides suspended in the liquid. These particles are somewhat larger than molecules but they are not large enough to settle to the bottom of the container. If the suspended particles are small droplets of a liquid, the liquid mixture is an emulsion.

Preparation of Colloidal Suspensions

Colloidal particles can be prepared by the condensation of small particles—usually of molecular size—or by the dispersion of larger particles. Some examples of colloidal suspensions prepared by the first method are colloidal solutions of the metals. These can be prepared by the reduction of a suitable compound dissolved in an appropriate solvent. Many other colloidal suspensions can be prepared by oxidizing suitable compounds. A suspension of colloidal sulfur, for example, can be prepared by the oxidation of an aqueous solution of hydrogen sulfide.

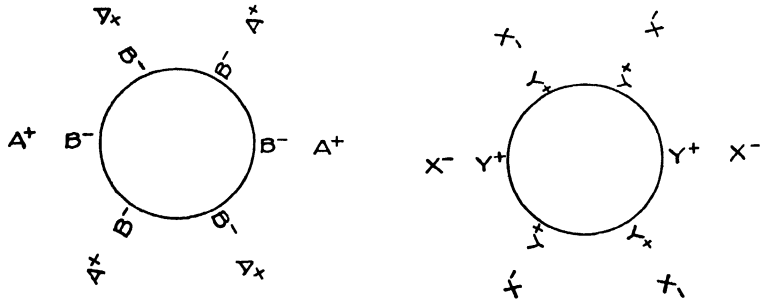
Colloid mills are frequently used to break up larger particles until they are of colloidal size. These mills are also used to break up droplets of a second immiscible liquid to form a more or less stable emulsion.

Properties of Colloids

When colloidal suspensions are viewed through the ultramicroscope, the particles are found to be in constant zig-zag motion. The motion of the particles is known as the *Brownian movement*. The movement of the particles is explained by the kinetic theory. If a suspended particle is bombarded on all sides by the molecules of the liquid in which the colloid is suspended, no appreciable movement of the particle takes place. However, if the particle is so small that the impacts on one side are not counterbalanced by the impacts on the other side, the particle will move. The smaller the particle the less is the probability that the impacts will counterbalance one another. The particle appears to move

in a jagged line, but its path does not lie in a single plane. The diameters of particles which show the Brownian movement vary between 1 and 100 millimicrons; that is, 10^{-6} and 10^{-4} mm. It is because of the Brownian movement that colloidal particles do not settle to the bottom of the container. Particles which have the Brownian movement will pass through the holes in ordinary filter paper or other commonly used filtering mediums. They will be retained, however, on an ultrafilter made of parchment, collodion or other suitable material.

If a colloidal suspension is placed in a vessel fitted with two electrodes which are connected to a suitable source of an electric current, the finely divided colloidal particles usually migrate toward one of the electrodes. This indicates that the particles are



a. Negatively Charged Particle

b. Positively Charged Particle

Fig. 4.

electrically charged. Those positively charged move toward the negative electrode, while those negatively charged move toward the positive electrode. The stability of many colloidal suspensions is due to the repulsion between the particles carrying like electrical charges. These charges prevent particles from coming close enough together to coalesce and form larger aggregates. A colloidal particle tends to adsorb on or attach to its surface the ions of which it is composed. If the cation is adsorbed, then the colloidal particles will move toward the negative electrode. If the anion is adsorbed, then the particle will migrate toward the positive electrode. A diagrammatic sketch to show both kinds of colloidal particles is given in Figure 4. The ions A^+ and X^- are in the liquid surrounding the particle and are at a somewhat greater distance from B^- and Y^+ than are these groups in the

compounds *AB* and *XY*. Other colloidal particles are stabilized by being surrounded by protective films of glue, gelatin, or some other similar substance. These films act like the charges in preventing the coalescence of the small particles.

Colloidal suspensions stabilized by adsorbed ions may be precipitated by adding an electrolyte. The ability of an electrolyte to precipitate a negative colloid depends largely on the valence of the cation. The larger the positive valence of a cation, the smaller is the quantity of the electrolyte required. Similarly, the larger the negative valence of an anion the smaller is the amount required to precipitate a positive colloid. The ability of potassium, calcium and ferric ions to break down negative colloids increases in the order given, and the ability of nitrate, sulfate, ferricyanide and ferrocyanide ions to precipitate positive colloids increases in the order given. In Table VI a number of substances which form colloidal suspensions are listed. Colloidal particles stabilized by glue, gelatin or similar substances are not precipitated by the addition of electrolytes. The stabilizing substances are usually destroyed by oxidation.

Table VI. Some Colloidal Suspensions

Positively Charged	Negatively Charged
Ferric hydroxide	Arsenious sulfide
Chromic hydroxide	Nickel sulfide
Aluminum hydroxide	Silicic acid
Cadmium hydroxide	Stannic acid
	Gold, silver and platinum
	Sulfur

In qualitative analysis care should be taken to avoid the formation of colloidal suspensions rather than to rely on breaking down the colloid by a suitable regent. Many precipitates become colloidal when they are washed with distilled water. Wash precipitates which have this tendency with a solution of an indifferent electrolyte, ammonium nitrate for example, or water containing a small amount of the precipitating agent. The sulfides of Group II, for example, should be washed with a saturated solution of hydrogen sulfide. Nickel sulfide frequently forms a brown colloidal solution. Since the colloidal particles have adsorbed sulfide ions, they are charged negatively. In some cases the addition of a weak acid is sufficient to neutralize the negative

charge on the colloid. In other cases, a higher concentration of hydronium ion is required and a strong acid must be added. In extreme cases, it may be necessary to add a salt of a di- or trivalent metal to precipitate the colloid. After separating the colloid, the cation added may be removed by appropriate reagents.

EXERCISES

1. Define: oxidation, reducing agent, electron.
2. Distinguish between valence number and valence.
3. Show that the reducing agent is oxidized in an oxidation-reduction reaction.
4. Give several illustrations to show how oxidation-reduction reaction may be used to cause a change in an ionic equilibrium.
5. Account for the fact that cupric sulfide is almost insoluble in concentrated hydrochloric acid but readily dissolves in this acid after concentrated nitric acid has been added.
6. Assuming that hydrogen peroxide is represented by the structural formula $H + - O - + O - + H$, show that the loss or gain of electrons will be two when it acts as a reducing or oxidizing agent.
7. What is the principle used in balancing oxidation-reduction equations?
8. Make a brief outline showing the steps involved in balancing an oxidation-reduction equation.
9. What are the products of the following when they act as oxidizing or reducing agents?

   a. MnO_4^- in acid solution.
   b. $Cr_2O_7^=$ in acid solution.
   c. MnO_4^- in neutral or alkaline solution.
   d. I^-
   e. Br^-
   f. H_2SO_4 conc.
   g. NO_3^- dil. and conc. H_3O^+
   h. Fe^{+++}
   i. H_2S
   j. HNO_2

10. Make a list of common oxidizing agents and their reduction products.
11. Make a list of common reducing agents and their oxidation products.
12. Balance the following equations:

   a. $H_2S + NO_3^- + \text{conc. } H_3O^+ \leftrightarrows H_2O + S + NO_2$
   b. $CoS + NO_3^- + \text{conc. } H_3O^+ \leftrightarrows S + Co^{++} + H_2O + NO_2$
   c. $O_2^= + CrO_2^- + H_2O \leftrightarrows CrO_4^= + OH^-$
   d. $S_2O_8^= + Br^- + H_3O^+ \leftrightarrows HSO_4^- + Br_2 + H_2O$
   e. $MnO_4^= + Cl_2 \leftrightarrows MnO_4^- + Cl^-$
   f. $ClO_3^- + HNO_2 + H_2O \leftrightarrows Cl^- + NO_3^- + H_3O^+$
   g. $Cr_2O_7^= + H_2S + H_3O^+ \leftrightarrows S + Cr^{+++} + H_2O$
   h. $NO_3^- + \text{conc. } H_3O^+ + AsS_4^= \leftrightarrows NO + H_3AsO_4^- + HSO_4^- + H_2O$

13. Complete and balance the following:

   a. $SO_2 + Cr_2O_7^= + H_3O^+ \leftrightarrows$
   b. $Bi_2S_3 + NO_3^- + H_3O^+ \text{ dil.} \leftrightarrows$
   c. $Bi(OH)_3 + HSnO_2^- \leftrightarrows$
   d. $Fe^{++} + NO_3^- + H_3O^+ \text{ dil.} \leftrightarrows$
   e. $Sb^{+++} + Al + H_3O^+ \leftrightarrows$
   f. $HOCl + H_3O^+ + I^- \leftrightarrows$
   g. $I^- + AsO_4^= + H_3O^+ \leftrightarrows$
   h. $Sn^{++} + HgCl_2 \leftrightarrows$

14. What is a complex ion?

15. Derive the expression for the instability constant of the cuprocyanide ion starting with the law of mass action.
16. How may the stability of a complex ion be increased?
17. The value of instability constant for the silver-diammine ion is 6.0×10^{-8} and that for the silver-cyanide ion is 3.8×10^{-17}. Chloride ion is added to 10 ml. of each of the two solutions containing 0.01 of a formula weight of the complex ion until precipitation occurs in one of the solutions. In which solution will the precipitation occur? Give adequate reasons for your answer.
18. Account for the fact that ZnS can be precipitated from the complex $Zn(NH_3)_4^{++}$ by hydrogen sulfide.
19. From the expression for the instability of the cupric-tetrammine ion, deduce the effect of increasing the concentration of ammonia, and of the addition of an acid.
20. Account for the solubility of silver chloride in ammonia and the slight solubility of silver iodide in the same reagent.
21. The instability constant for the silver-diammine ion is 6.0×10^{-8} while that for the complex silver-cyanide ion is 3.8×10^{-19}. Given two solutions which contain the same concentration of these complex ions, in which will there be the greater concentration of silver ion?
22. Point out complications which may arise from the presence of complex ions.
23. Account for the non-precipitation of cuprous sulfide and the precipitation of cadmium sulfide from a solution containing the complex cupro-cyanide and cadmium-cyanide ions.
24. Account for the difference in the action of silver chloride and silver bromide toward ammonia.
25. A solution contains the soluble complex silver chloride ion ($AgCl_2^-$). How can the silver be precipitated as the chloride?
26. Calculate the concentration of cupric ion in a 0.1-*M* solution of cupric-tetrammine chloride. The instability constant of the complex ion is 4.6×10^{-14}. Assume 100% ionization of the salt into cupric-tetrammine and chloride ions. *Ans.* 4.5×10^{-4}.
27. What will be the concentration of the cupric ion if the concentration of ammonia is increased to 1.0 in Exercise 26?
28. How did Werner account for the formation of complex ions?
29. Differentiate between a coordinate covalence and a covalence.
30. What is meant by the coordination number of an ion?
31. State the rules for naming compounds containing complex ions.
32. Name: $[CoBr(NH_3)_5]Br_2$; $[Cr(NH_3)_3Br_3]$; $[Co(NH_3)_6]I_3$ and $[Cr(NH_3)_3(H_2O)Cl_2]Cl$.
33. Give the formulas of: hexamminenickelochloride; bromochlorotetrammine-cobaltinitrate; potassium hexacyanoferrate; bromochlorodiaquodiammine-cobalt (III) nitrate.
34. How will each compound in Exercises 32 and 33 ionize in aqueous solutions?
35. According to Sidgwick how are the coordinated groups attached to the central ion?
36. Draw conclusions concerning the colloidal state as a factor in qualitative analysis.
37. Name several ways of breaking down a colloidal suspension.
38. How many grams of silver iodide will dissolve in a liter of 0.1-*M* sodium cyanide?

39. Derive the expressions for the equilibrium constants for the reactions in acid solutions between
    1. Ferricyanide ions and sulfide ions.
    2. Ferric ions and iodide ions.
    3. Ferric ions and bromide ions.
    4. Nitrous acid and iodide ions.
    5. Bromate ions and manganous ions.
    6. Fluoride ions and permanganate ions.
    7. Mercuric ions and copper.
    8. Stannous ions + chlorine.

CHAPTER V

Hydrogen Sulfide as a Precipitating Agent and the Solution of Sulfides

THE SOLUBILITY products of the sulfides of Group II are smaller than those of Group III. With the same concentration of the ions of these groups it should be possible to precipitate the sulfides of Group II without precipitating those of Group III, if the concentration of the sulfide ion is properly adjusted. Since the solution is saturated with hydrogen sulfide in bringing about the precipitation, it is convenient to use the constant of hydrogen sulfide to determine the conditions for the proper concentration of the sulfide ions. The value of the constant can be calculated from the ionization constants, page 48, because it is known that a saturated solution of hydrogen sulfide at 25° and 760 mm. is practically 0.1-*M*. Since hydrogen sulfide is a weak acid and the concentration of the un-ionized substance is nearly 0.1, equation 16 may be written

$$C^2_{H_3O^+} \times C_{S^=} = 1.2 \times 10^{-22} \times 0.1 = 1.2 \times 10^{-23} \qquad (32)$$

This expression shows that the concentration of sulfide ion is inversely proportional to the square of the concentration of the hydronium ion. Therefore, the concentration of the hydronium ion must be adjusted if a separation of the two groups is to be effected. The problem involved is to bring about the complete precipitation of the sulfide of Group II having the largest solubility product without precipitating the sulfide of Group III which has the smallest solubility product. We must, then, calculate the concentration of hydronium ions which will permit a sulfide ion concentration sufficient to precipitate cadmium sulfide but which is not large enough to precipitate any zinc sulfide. Assume that not more than 3.14 mg. of zinc will be present in 1 ml. of the solution which is to be saturated with hydrogen sulfide to precipitate the sulfides of Group II. The concentration of zinc ion in this solution is 0.048 if the zinc

salt is ionized completely. If the apparent degree of ionization is 0.7, the concentration of zinc ion is 0.034. The activity of the zinc ion should be used in making this calculation. However, since the calculation of activities of ions has not yet been considered in detail, the apparent degree of ionization of the salt is used to obtain a reasonably accurate value of the concentration of the sulfide ion. The solubility product of zinc sulfide, $C_{Zn^{++}} \times C_{S^{-}}$, is 4.5×10^{-24}. The maximum concentration of sulfide ion which can be present in the solution without the formation of a precipitate is given as

$$C_{S^{-}} = \frac{SP_{ZnS}}{C_{Zn^{++}}} = \frac{4.5 \times 10^{-24}}{0.034} = 1.32 \times 10^{-22}$$

The $C_{H_3O^+}$ which must be present to have this concentration of sulfide ion is calculated by substituting this value in the expression for the constant for hydrogen sulfide.

$$C^2_{H_3O^+} = \frac{K_{H_2S}}{C_{S^{-}}} = \frac{1.2 \times 10^{-23}}{1.3 \times 10^{-22}} = 0.09 \qquad (33)$$

$$C_{H_3O^+} = 0.3$$

If a solution having an effective concentration of zinc ion of 0.034 and a concentration of hydronium ion of 0.3 is saturated with hydrogen sulfide, no precipitate of zinc sulfide will be formed. Since zinc sulfide has the lowest solubility product of Group III, the solubility product of none of the sulfides of this group will be exceeded, and no sulfide of Group III will be precipitated. To determine whether a concentration of sulfide ion of 1.32×10^{-22} is large enough to precipitate quantitatively the sulfide of Group II having the largest value of the solubility product—namely cadmium sulfide whose value is 1.4×10^{-28}, we make the following calculation:

$$C_{Cd^{++}} = \frac{SP_{CdS}}{C_{S^{-}}} = \frac{1.4 \times 10^{-28}}{1.3 \times 10^{-22}} = 1.07 \times 10^{-6}$$

There remain 120×10^{-6} g. ($1.07 \times 10^{-6} \times 112.4$ g.) of cadmium ions in a liter of the solution from which cadmium sulfide has been precipitated. In one milliliter of solution there are 1.2×10^{-7} g. or 1.2×10^{-4} mg. of cadmium ions. A second method of calculating the concentration of cadmium ion which is not precipitated when a 0.3-*N* solution of hydrochloric acid containing cadmium ions is saturated with hydrogen sulfide is to use the equilibrium constant of the reaction

$$Cd^{++} + H_2S + 2\,H_2O(+H_3O^+) \rightleftarrows CdS + 2\,H_3O^+$$

Parentheses around the hydronium ion on the left hand side of the equation indicates that the ion is present but that it is not necessary to balance the equation. The expression for the constant is

$$K = \frac{C^2_{H_3O^+} \times C_{CdS}}{C_{Cd^{++}} \times C_{H_2S} \times C^2_{H_2O}} \tag{34}$$

Since the concentration of a solid is constant and the concentration of water is known, equation 34 may be written

$$K_{eq} = \frac{C^2_{H_3O^+}}{C_{Cd^{++}} \times C_{H_2S}} \tag{35}$$

where

$$K_{eq} = \frac{K \times C^2_{H_2O}}{C_{CdS}}$$

The value of the equilibrium constant K_{eq} may be calculated by multiplying equation 35 by C_{S^-}/C_{S^-}

$$K_{eq} = \frac{C^2_{H_3O^+} \times C_{S^-}}{C_{Cd^{++}} \times C_{S^-} \times C_{H_2S}} = \frac{K_{1\ H_2S}}{SP_{CdS}}$$
$$= \frac{1.2 \times 10^{-22}}{1.4 \times 10^{-28}} = 0.85 \times 10^6 \tag{36}$$

By substituting the value for the concentration of hydrogen sulfide in a saturated solution at 25° and 760 mm. (0.1) and the other appropriate values in equation 35 we have

$$\frac{0.3^2}{C_{Cd^{++}} \times 0.1} = 0.85 \times 10^6 \tag{37}$$

Solving equation 37 for the concentration of the cadmium ion, we have

$$C_{Cd^{++}} = \frac{0.09}{0.1 \times 0.85 \times 10^6} = 1.06 \times 10^{-6}$$

This method of calculation is useful in many cases. Thus, by adjusting the concentration of hydronium ion in a milliliter of a solution containing 3.14 mg. of zinc ions and cadmium ions to 0.3-*M*, no zinc sulfide or other sulfides of Group III will be precipitated, and only 0.00012 mg. of cadmium ion will remain in the solution. If the concentration of hydronium ion is greater than 0.3-*M*, the concentration of sulfide ion will be too small to precipi-

tate traces of cadmium ion which may be present. On the other hand, if the concentration of hydronium ions is less than 0.3-*M*, some zinc sulfide may precipitate with the sulfides of Group II.

To be sure that the concentration of the hydronium ion in the solution to be treated with hydrogen sulfide is correct, prepare the solution as directed at the beginning of Procedure II. After the precipitation of the sulfides the concentration of the hydronium ion in the solution may be checked by testing the solution with methyl violet after separating the precipitate from the solution.

Precipitation of the Sulfides of Group III. Since a high concentration of sulfide ion is required to precipitate the sulfides of Group III, the concentration of hydronium ions must be low. The concentration of hydronium ions can be lowered by adding a base (*B*) which reacts with the hydrogen sulfide to form an acid (*A*) according to the equation

$$H_2S + B \rightleftarrows S^{=} + A$$

The stronger the base which is added and the greater its concentration, the greater will be the concentration of sulfide ion.

Ammonia is the base generally used to regulate the concentration of the hydronium ion. For the reaction we may write

$$H_2S + 2\,NH_3 \rightleftarrows S^{=} + 2\,NH_4^+$$

and the expression for the constant for the reaction is

$$\frac{C^2_{NH_4^+} \times C_{S^=}}{C^2_{NH_3} \times C_{H_2S}} = K$$

Since the solution is saturated with hydrogen sulfide, the concentration of hydrogen sulfide is constant and

$$\frac{C^2_{NH_4^+} \times C_{S^=}}{C^2_{NH_3}} = K_{eq} \tag{38}$$

Equation 38 may be written

$$C_{S^=} = \frac{C^2_{NH_3}}{C_{NH_4^+}} \times K_{eq}$$

If the concentration of ammonium ion is small compared to that of ammonia, the concentration of sulfide ion is determined

largely by the square of the concentration of ammonia in the solution. If the concentration of ammonium ion is appreciable, the concentration of the sulfide ion is fixed by the square of the ratio of the concentration of ammonia to the concentration of ammonium ion. The addition of ammonia serves not only to increase the concentration of sulfide ion to insure the practically complete precipitation of the sulfides of cobalt, nickel, zinc, manganese and iron, but also to precipitate the hydroxides of chromium and aluminum. The necessity of adding ammonium chloride to the ammoniacal solution to prevent the precipitation of magnesium hydroxide with Group III is discussed on page 226.

SOLUTION OF SULFIDES IN ACIDS

The solubility of sulfides varies considerably. Some are soluble in 1-*N* hydrochloric acid. Others require a more concentrated acid, and still others are practically insoluble in concentrated hydrochloric acid, but will dissolve in a mixture of hydrochloric and nitric acids. An explanation of the difference in the solubility of the sulfides in the different concentrations of acid is given by the rule for the solution of a slightly soluble substance. If the product of the $C_{M^{++}} \times C_{S^{-}}$ is numerically less than the solubility product of the metallic sulfide, MS, the solution will be unsaturated, and more of the sulfide will dissolve. The product $C_{M^{++}} \times C_{S^{-}}$ may fall below the value of the solubility product of the metallic sulfide if either or both of the concentrations of the metallic or sulfide ions is decreased. Since, usually, sulfides are dissolved by reducing the concentration of the sulfide ion, this case will be considered first. The concentration of the sulfide ion can be reduced by the addition of a strong acid if the $C_{S^{-}}$ from the metallic sulfide is greater than the $C_{S^{-}}$ which can be present in a solution of hydrogen sulfide containing the same $C_{H_3O^+}$. The concentration of the sulfide ion present in the solution of hydrogen sulfide is determined by the relation

$$C_{S^{-}} = \frac{1.2 \times 10^{-23}}{C^2_{H_3O^+}}$$

If the metallic sulfide is somewhat soluble, the concentration of sulfide ion is appreciable and only a small concentration of hydronium ion need be present to make the product $C_{S^{-}}$ from the metallic sulfide and $C^2_{H_3O^+}$ from the acid greater than the K_{H_2S}. A reduction of the value of the product is brought about by the formation of molecular hydrogen sulfide, some of which escapes from the solution if it is saturated. The decrease in the $C_{S^{-}}$ causes

the product $C_{M^{++}} \times C_{S^{-}}$ to become less than the solubility product of MS and some of the solid dissolves. If the concentration of the hydronium ion is maintained, all of the suspended sulfide will dissolve. Thus, if the value of the solubility product is relatively large, that of MnS for example, only a small quantity of acid is necessary to reduce the concentration of sulfide ion to less than that demanded by the equation

$$C_{Mn^{++}} \times C_{S^{-}} = 5.6 \times 10^{-16}$$

The product of the concentrations of these ions is less than 5.6×10^{-16} and the solution is unsaturated. Since the solution is unsaturated, more of the sulfide dissolves. Hydronium ions continue to react with the sulfide ions and the process proceeds until all of the sulfide dissolves or until equilibrium is established. In the case of the very insoluble sulfides (silver and copper, for example) the concentration of sulfide ions in a saturated solution of the salt is almost equal to the concentration of sulfide ion which can be present in the concentrated acid. Hence, there can be practically no removal of sulfide ions and no further solution of the sulfide on adding even concentrated hydrochloric acid. Dilute nitric and sulfuric acids act similarly to hydrochloric acid if they are not concentrated enough to oxidize the sulfide ion. No appreciable oxidation of the sulfide ion by 0.3-*N* nitric acid or 18-*N* sulfuric acid takes place.

The decrease in the concentration of the sulfide ion caused by the addition of concentrated hydrochloric acid to a suspension of a very insoluble sulfide is not sufficient to increase appreciably the solubility of the sulfide. However, the concentration of sulfide ions present can be reduced by the addition of an oxidizing agent, such as concentrated nitric acid or potassium chlorate, to the acid suspension of the metallic sulfide, thus oxidizing the sulfide ion to free sulfur. The product of the concentration of the M^{++} and that of the S^{-} becomes less than the solubility product of MS and more of the sulfide dissolves until the product of the ions is again equal to the solubility product. If an excess of the oxidizing agent is added, the sulfide ions will be oxidized, chiefly to sulfur, and the sulfide will be dissolved completely.

The solution of metallic sulfides also may be brought about by the removal of the metallic ion, thus making the product $C_{M^{++}} \times C_{S^{-}}$ less than the solubility product of MS. This is followed by the solution of more of the solid. The process continues until equilibrium is established, or until all of the solid dissolves. The metallic ion may be removed by becoming a part of a little

ionized compound, a part of a stable complex ion or by being oxidized or reduced.

The non-precipitation of the sulfides of cobalt and nickel in the presence of 0.3-*N* hydrochloric acid and their failure to dissolve in rather concentrated hydrochloric acid seem to be inconsistent. Their failure to precipitate in the slightly acid solution when treated with hydrogen sulfide indicates that the $C_{S^=}$ is so small that the solubility product of the sulfides is not exceeded, but the difficulty in dissolving the sulfides after they have been precipitated from an alkaline solution is rather good evidence for small values of the solubility products. This inconsistency may be explained by the fact that these sulfides exist in a number of modifications. The sulfide which precipitates has a relatively high value for the solubility product, but is not stable and changes to a form not soluble in more concentrated hydrochloric acid. This second modification also changes to a third whose solubility product is but little greater than those of the sulfides of the ions of Group II. It is the high value of the solubility product of the modification that first forms which determines that a high concentration of sulfide ion is necessary for the solubility product to be exceeded. On account of the low value of the solubility product of the third modification, an appreciable concentration of sulfide ion cannot be removed by treating the sulfide with rather concentrated hydrochloric acid. Since the product $C_{M^{++}} \times C_{S^=}$ is not appreciably less than the value of the solubility product, very little of the solid dissolves.

The occasional large solubility of the freshly precipitated sulfides of the cobalt and nickel may be caused by the abnormal slowness of the change from the more soluble to the less soluble modifications.

Solution of Sulfides in Soluble Sulfides

Some of the common metallic sulfides react with sulfide ions to form complex sulfide ions. The reaction may be represented by the general equation

$$MS + S^= \rightleftarrows MS_2^=$$

The formation of the complex metallic sulfide ions is analogous to the formation of the complex metallic cyanide ions by the reaction of insoluble cyanides with an excess of cyanide ion. In Group II the sulfides of lead, bismuth, copper and cadmium do not react with sulfide ions in a solution of sodium hydrogen

sulfide to form complex sulfide ions. The sulfides of both tri- and pentavalent arsenic and antimony as well as stannic sulfide react with the sulfide ion in cold or warm solutions of sodium sulfide, sodium hydrogen sulfide, or ammonium sulfide, forming complex sulfide ions. Stannous sulfide scarcely dissolves in these reagents even when the mixture is warmed. However, if a little polysulfide ion, $S_2^=$ for example, is present stannous sulfide is oxidized to stannic sulfide and the complex stannic sulfide ion is formed. Mercuric sulfide, when treated with cold sodium hydrogen sulfide or with hot or cold ammonium sulfide, does not form a complex mercuric sulfide ion. Mercuric sulfide reacts with sodium sulfide or with sodium hydrogen sulfide if the mixture is digested. The reaction with hot sodium hydrogen sulfide is undoubtedly accounted for by the increase in the concentration of sulfide ions because of the decomposition of the hydrogen sulfide ion to sulfide ions according to the equation

$$2\,HS^- \rightleftarrows H_2S + S^=$$

In the procedures used, a small amount of sodium hydroxide is added to the sodium hydrogen sulfide to increase the concentration of sulfide ion. The concentration of sulfide ion is 1×10^{-3} in a 0.1-*M* solution of sodium sulfide, 1.1×10^{-6} in a 0.1-*M* solution of sodium hydrogen sulfide and 1.8×10^{-7} in a 0.1-*M* solution of ammonium sulfide. Since the sulfides of arsenic, antimony and stannic tin are changed to complex sulfide ions by the small concentration of sulfide ion in sodium hydrogen sulfide or ammonium sulfide, the value of the equilibrium constant for the reaction of these metallic sulfides and sulfide ions $S^= + MS \rightleftarrows MS_2^=$ must be quite large. On the other hand, the equilibrium constant for the reaction between stannous sulfide or mercuric sulfide and sulfide ions must be small.

EXERCISES

1. State clearly the problem involved in separating the ions of Groups II and III by the use of hydrogen sulfide.
2. Calculate the concentration of sulfide ion in 0.3-*N* hydrochloric acid which has been saturated with hydrogen sulfide. The constant of hydrogen sulfide is 1.2×10^{-23}. *Ans.* 1.33×10^{-22}.
3. The solubility products of manganese and cadmium sulfides are 5.6×10^{-16} and 1.4×10^{-28} respectively. If 50 ml. of a solution containing 15 mg. manganese and cadmium ions having a concentration of hydronium ions equal to 0.1 is saturated with hydrogen sulfide, will any precipitation take place?
4. Using the solubility product concept, explain why the acidity of a solution should not be above 0.3-*N* when Group II is to be precipitated

5. Using the solubility product concept, explain why the concentration of hydronium ion must not fall below 0.3-*N* when the sulfides of Group II are being precipitated.
6. Account for the fact that the precipitation of cobalt sulfide is prevented by the presence of 0.3-*N* hydrochloric acid, but that cobalt sulfide is nearly insoluble in concentrated hydrochloric acid (12-*N*).
7. What is the concentration of sulfide ions in 0.3-*N* nitric acid which has been saturated with hydrogen sulfide? (Note: Practically no oxidation of the hydrogen sulfide takes place at this concentration.)
8. Hydrogen sulfide is passed into an acidified solution of silver nitrate until no further precipitation occurs. The concentration of hydronium ions is 0.3-*N* when precipitation stops. The solubility product of silver sulfide is 1×10^{-51}. What concentration of silver ions remains in the solution? How many milligrams of silver ions will be left in a liter of the solution?
   Ans. (*a*) 2.73×10^{-15}, (*b*) 2.95×10^{-10} mg.
9. A solution of zinc chloride in which the concentration of hydronium ion is 0.1 is saturated with hydrogen sulfide. What concentration of zinc ion remains in the solution? Calculate the number of grams of zinc ion in 100 ml. of the solution. The constant of hydrogen sulfide is 1.2×10^{-23} and the solubility product of zinc sulfide is 4.5×10^{-24}.
10. A liter of a solution contains 0.1 mole of ferrous ion and 0.1 mole of zinc ion. What concentration of hydronium ions should be present so that no ferrous sulfide will precipitate when saturated with hydrogen sulfide? The solubility product of ferrous sulfide is 1.0×10^{-19} and that of zinc sulfide is 4.5×10^{-24}. What concentration of zinc ion will be left in the solution?
    Ans. (*a*) 3.5×10^{-3}; (*b*) 4.5×10^{-6}.
11. A strong acid is added to a suspension of manganese sulfide. When equilibrium is established there is 0.0001 g. of manganous ion in a liter of the solution. What is the molecular concentration of the hydronium ion? The solubility product of manganous sulfide is 5.6×10^{-16}.
12. If the concentration of hydronium ion in a solution from which the lead ion is to be precipitated by H_2S is 0.5-*N*, how many grams of lead ion will remain in 100 ml. of the solution? The constant of H_2S is 1.2×10^{-23}. That of PbS is 1.0×10^{-29}. *Ans.* 4.4×10^{-6} g.
13. Calculate the actual number of sulfide ions in a liter of a saturated solution of mercuric sulfide if its solubility product is 3×10^{-53}. Avogadro's number is 6.1×10^{23}.
14. Calculate the number of grams of sulfide ion in 100 ml. of a saturated solution of hydrogen sulfide which contains 25 ml. of hydrochloric acid (sp. gr. 1.2 containing 39% by weight of HCl). *Ans.* 3.8×10^{-24} g.
15. By means of the solubility product concept, account for the solubility of manganous sulfide in 1-*N* hydrochloric acid.
16. Using the solubility product concept, account for the insolubility of cupric sulfide in 1-*N* hydrochloric acid.
17. Using the solubility product concept, account for the non-precipitation of nickel sulfide from a solution having a concentration of hydronium ions of 0.3-*N* and its insolubility in a solution having a concentration of hydronium ions of 0.3-*N*.
18. Using the solubility product concept, account for the fact that silver sulfide is practically insoluble in dilute hydrochloric acid but is soluble in a mixture of nitric and hydrochloric acids.

19. Show that the concentration of sulfide ion in a solution of hydrogen sulfide is almost numerically equal to the second ionization constant of hydrogen sulfide.
20. In the precipitation of Group II with hydrogen sulfide at room temperature the solution contains 10 ml. of concentrated hydrochloric acid in each 100 ml. of the solution. The solubility product of lead sulfide is 1.0×10^{-29}. Calculate the number of grams of lead chloride which escape precipitation per liter of solution. Concentrated hydrochloric has a sp. gr. of 1.2 and contains 39% of hydrogen chloride. The constant of hydrogen sulfide is 1.2×10^{-23}.
21. Set up the expression for the equilibrium constant of the reaction which takes place in each of the following systems. Then evaluate the constant and make the necessary calculations
    a. Calculate the minimum concentration of hydronium ion which will prevent the precipitation of zinc sulfide from a solution whose effective concentration of zinc ion is 0.034 which has been saturated with hydrogen sulfide.
    b. Calculate the concentration of copper ions remaining in a solution when to a liter of a 0.1-*M* solution of copper chloride is added 0.3 moles of hydrogen chloride gas and the solution is then saturated with hydrogen sulfide.
    c. What concentration of hydronium ion would have to be present to dissolve 0.001 formula weight of manganese sulfide which is added to a liter of the acid?

CHAPTER VI

Hydrolysis and Amphiprotic Substances

A REACTION between an ion and a solvent, which involves the transfer of protons, is called *solvolysis.*

HYDROLYSIS

Hydrolysis is a special case of solvolysis in which the solvent is water. The present discussion is limited to the transfer of protons between water and the ions present in the aqueous solution of a salt.

The aqueous solution of a few salts are neutral but by far the great majority are somewhat acid or alkaline. To discuss adequately the reasons for the acid or alkaline reaction of solutions of salts as well as the extent of hydrolysis, it is convenient to divide salts into two general classes depending on whether or not the cation can lose protons. Each of the general classes is subdivided into three subdivisions. The classification into subgroups is determined by the strength of the anion as an acid or a base in the Brønsted sense.

I. Salts whose cations are aprotic; that is, the cation can neither lose nor gain protons.
   Sodium and potassium salts are examples.
   a. The anion is a very weak base; that is, it has no tendency to react with a proton. Sodium chloride is an example of this type. Neither hydronium nor hydroxide ions are removed as a part of a little ionized substance. There is no hydrolysis and the concentration of hydronium and hydroxide ions is essentially that in water.

$$\begin{array}{l} NaCl \rightarrow Na^+ + Cl^- \\ 2\,H_2O \leftrightarrows OH^- + H_3O^+ \\ \qquad\quad \uparrow \qquad\quad \uparrow \\ \qquad NaOH \qquad HCl + H_2O \end{array}$$

b. The anion is a strong base; that is, it reacts with a proton to form a weak acid. Potassium acetate is an example of a salt of this type. Since the acetate ion is a strong base (page 54), un-ionized acetic acid will be formed.

$$\begin{array}{l} KOAc \rightarrow K^+ + OAc^- \\ 2\,H_2O \leftrightarrows OH^- + H_3O^+ \\ \qquad\quad \uparrow \qquad\quad \uparrow\downarrow \\ \qquad KOH \qquad HOAc + H_2O \end{array}$$

Since the potassium ion does not enter into the reaction, the equation may be written

$$OAc^- + H_2O \rightleftarrows HOAc + OH^-$$

Acetic acid is only 1.34% ionized in a dilute solution (0.1-*N*), consequently, the concentration of hydroxide ion is greater than that in water and the solution is alkaline. The concentration of the hydronium ion is even less than would be expected from the low degree of ionization of the acid because of the repression of its ionization by the effect of the common acetate ion from the potassium acetate. Equilibrium will be established when the concentration of the hydroxide ions increases to such an extent that the constant of water is satisfied. The extent of hydrolysis will be calculated later.

c. The anion is amphiprotic; that is, it can either lose or gain protons. This type includes the so-called "acid" or hydrogen salts of the polyprotic acids, the alkali hydrogen salts of carbonic and phosphoric acids. Let us consider a solution of sodium hydrogen carbonate. Since the hydrogen carbonate ion is amphiprotic, it may either lose or gain protons. Some hydrogen carbonate ions may lose protons to water forming the carbonate ion, while others gain protons forming carbonic acid.

$$\begin{array}{l} HCO_3^- + H_2O \leftrightarrows CO_3^{=} + H_3O^+ \\ H_2O + HCO_3^- \leftrightarrows OH^- + H_2CO_3 \\ H_3O^+ + OH^- \rightleftarrows 2\,H_2O \end{array}$$

Since the carbonate ion is a strong base and has a great tendency to combine with protons, the first reaction cannot take place to any appreciable extent. The hydrogen carbonate ion acts as a base in the second equation. However, since a strong base—hydroxide ion—is one of the products,

the reaction cannot take place to any great extent. Equilibrium will be established when the constant of water and the ionization constants of carbonic acid are satisfied. The system is rather complicated and one cannot predict by an inspection of the equations whether a solution of sodium hydrogen carbonate will react acidic or alkaline. Calculations show that the solution should be slightly alkaline and this is confirmed by experiment.

II. The cation can lose protons; that is, it is a cation acid. Cations which may lose protons are of two types—ammonium ions $NH_4^+ \leftrightharpoons NH_3 + H^+$ and hydrated cations $M(H_2O)_x^{y+}$ in which the acid properties of water have been increased by the positive ion to which they are attached, for example,

$$Al(H_2O)_6^{+++} \leftrightharpoons Al(OH)_3(H_2O)_3 + 3\ H^+$$
$$3\ H^+ + 3\ H_2O \rightleftarrows 3\ H_3O^+$$

The number of molecules of water attached to an ion is usually assumed to be four or six.

a. The anion is a weak base. Ammonium chloride and cupric chloride are examples of this type.

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$
$$NH_4^+ + H_2O \leftrightharpoons NH_3 + H_3O^+$$

Equilibrium will be established when but little ammonia is formed since ammonia is a stronger base than water. A solution of ammonium chloride will react acid since only a very small fraction of the ammonia formed reacts with water forming ammonium and hydroxide ions.

The reaction of water with salts of weak alkalies and strong acids also falls in this subdivision. In a solution of cupric chloride, for example, the following equilibria are present:

$$CuCl_2 \rightarrow Cu^{++} + 2\ Cl^-$$
$$Cu^{++} + 4\ H_2O \rightleftarrows Cu(H_2O)_4^{++}$$
$$Cu(H_2O)_4^{++} + 2\ H_2O \leftrightharpoons Cu(H_2O)_2(OH)_2 + 2\ H_3O^+$$

The number of molecules of water attached to ions varies from one to six and can be deduced from the table on page 82. Since cupric hydroxide is little ionized, the solution contains an excess of hydronium ions and is acidic. The intermediate, $Cu(H_2O)_3(OH)^+$, is probably formed and loses a proton to form the hydrated cupric hydroxide, but is not considered in this discussion.

b. The anion is a strong base. Ammonium cyanide is an example of a salt of this type. The equilibria involved are

$$\begin{aligned} NH_4CN &\rightarrow NH_4^+ + CN^- \\ NH_4^+ + H_2O &\leftrightharpoons NH_3 + H_3O^+ \\ CN^- + H_2O &\rightleftarrows OH^- + HCN \\ H_3O^+ + OH^- &\rightleftarrows 2\,H_2O \end{aligned}$$

Since the ammonium ion is a much weaker acid than the cyanide ion is a base, the solution is alkaline.

c. The anion is amphiprotic. Ferrous hydrogen carbonate is an example of this type. The equilibria involved are

$$\begin{aligned} Fe(HCO_3)_2 + 4\,H_2O &\rightarrow Fe(H_2O)_4^{++} + 2\,HCO_3^- \\ Fe(H_2O)_4^{++} + 2\,HCO_3^- &\rightleftarrows Fe(H_2O)_2(OH)_2 + 2\,H_2CO_3 \\ HCO_3^- + H_2O &\leftrightharpoons H_3O^+ + CO_3^= \end{aligned}$$

Since carbonic acid is more highly ionized than ferrous hydroxide, the solution is acidic.

Calculation of the Degree of Hydrolysis of a Solution of Potassium Acetate. The reaction between potassium acetate and water is given by the ionic equation

$$OAc^- + H_2O \leftrightharpoons OH^- + HOAc$$

The expression for the constant is

$$\frac{C_{OH^-} \times C_{HOAc}}{C_{OAc^-} \times C_{H_2O}} = K \tag{39}$$

Since the C_{H_2O} is a constant (55.6),

$$\frac{C_{OH^-} \times C_{HOAc}}{C_{OAc^-}} = K \times C_{H_2O} = K_{eq} = K_{hydrolysis} \tag{40}$$

If the fraction is multiplied by $\frac{C_{H_3O^+}}{C_{H_3O^+}}$ the terms rearranged, and the values of the constants substituted, the expression for the hydrolysis constant (equation 40) becomes

$$\begin{aligned} C_{H_3O^+} \times C_{OH^-} \times \frac{C_{HOAc}}{C_{H_3O^+} \times C_{OAc^-}} &= K_w \times \frac{1}{K_{i_{HOAc}}} \\ &= \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = K_{hydrolysis} \end{aligned} \tag{41}$$

The degree of hydrolysis of a 0.1-*M* solution of potassium acetate may be calculated by letting

α = fraction hydrolyzed, and
$1 - \alpha$ = fraction not hydrolyzed.

Then $0.1(1 - \alpha) = C_{OAc^-}$

and $0.1\,\alpha = C_{HOAc} = C_{OH^-}$

$$\underset{0.1(1-\alpha)}{OAc^-} + H_2O \rightleftarrows \underset{0.1\,\alpha}{HOAc} + \underset{0.1\,\alpha}{OH^-}$$

By substituting these values in equation 40 we have

$$\frac{C_{OH^-} \times C_{HOAc}}{C_{OAc^-}} = \frac{0.1\,\alpha \times 0.1\,\alpha}{0.1 - 0.1\,\alpha} = 5.6 \times 10^{-10} = K_{\text{hydrolysis}}$$

and dividing by 0.1 the above expression becomes

$$\frac{0.1\,\alpha^2}{1 - \alpha} = 5.6 \times 10^{-10}$$

Since α is small, $1 - \alpha$ will not differ appreciably from 1 and

$$0.1\,\alpha^2 = 5.6 \times 10^{-10}$$
$$\alpha = 7.5 \times 10^{-5}$$

The concentration of hydronium ions in the solution can be calculated by substituting the value of the C_{OH^-}($0.1\,\alpha$ or $0.1 \times 7.5 \times 10^{-5}$) in the expression for the constant of water

$$C_{H_3O^+} \times 7.5 \times 10^{-6} = 10^{-14}$$
$$C_{H_3O^+} = \frac{10^{-14}}{7.5 \times 10^{-6}} = 1.33 \times 10^{-9}$$

By a similar process of reasoning the hydrolysis constants and the concentration of the hydronium ions in solutions of other salts may be calculated. A number of typical calculations are given on pages 127–33. The necessity of taking into account the hydrolysis of the anion of weak acids in calculating the solubility of slightly soluble sulfides is shown on page 134. Since salts formed by neutralizing a weak acid or base are usually not neutral, a method of expressing the concentration of the hydronium ion is desirable. A method suggested by Sorenson, and now universally used, will now be discussed.

The pH Method of Expressing the Concentration of Hydronium Ions. The concentration of hydronium ions is frequently expressed as the pH. The pH is defined as the negative logarithm of the molecular concentration of hydronium ions. Thus, if the concentration of hydronium ions is 10^{-2}, the negative logarithm, or pH, is 2. This relationship is expressed by the equation $pH = -\log C_{H_3O^+} = \log 1/C_{H_3O^+}$. Since a liter of the solution contains 10^{-2} gram formula weights of hydronium ion, the volume containing a gram formula weight is 10^2 liters. The pH, then, is the logarithm of the volume of the solution which contains a gram formula weight of hydronium ions. The greater the concentration of hydronium ions, the smaller will be the volume of solution which will contain a gram formula weight of hydronium ions and consequently the smaller the pH. The concentration of hydronium ions in pure water is 10^{-7} and the pH of water is 7.

A solution whose pH is less than 7 is acidic while one having a numerical value greater than 7 is alkaline. Since the pH is an exponent of ten, a change in the pH of 1 designates a tenfold change in the concentration of the hydronium ion. A pH of 2.1 means that the concentration of the hydronium ion is $\frac{1}{10^{2.1}}$ or $10^{-2.1}$. Ordinarily fractional exponents are not used. The change of $\frac{1}{10^{2.1}}$ to a decimal is accomplished as follows:

$$\frac{1}{10^{2.1}} = \frac{1}{10^2 \times 10^{0.1}} = \frac{1}{100 \times 1.26} = \frac{1}{126} = 0.0079$$

The number having a logarithm of 0.1 is 1.26. A pH of 2.1 corresponds to a

$$C_{H_3O^+} = \frac{1}{10^{2.1}} = \frac{1}{126} = 0.0079$$

A second method of expressing the concentration of the hydronium ion as a decimal is to evaluate the exponential quantity $10^{-2.1}$ as follows:

$$10^{-2.1} = 10^{-3} \times 10^{0.9} = 10^{-3} \times 7.9 = 0.0079$$

Thus a change in the pH from 2 to 2.1 decreases the $C_{H_3O^+}$ from 0.01 to 0.0079—a change of 21%. Small changes in the pH, then, denote relatively large changes in the concentration of hydronium ion. The concentration of hydronium ion calculated by any method may be expressed as its pH.

Buffer Solutions. If to a liter of 0.1-*N* sodium chloride and to a liter of 0.1-*N* ammonium acetate a milliliter of 0.1-*N* hydrochloric acid is added, one might expect the concentration of hydronium ion to change from 10^{-7}, the concentration in dilute solutions of neutral salts, to 10^{-4}, the concentration of hydronium ion in a 0.0001-*N* solution of hydrochloric acid. The expected increase in the concentration takes place in the solution of sodium chloride to which hydrochloric acid was added. However, the concentration of hydronium ions in the solution of ammonium acetate is essentially the same before and after the addition of the acid. A solution to which small amounts of an acid or a base may be added without causing an appreciable change in the concentration of the hydronium ion is a buffer solution. If a solution contains both a weak acid and one

Table VII. Concentration of Hydronium Ion after Adding NaOH or HCl to 1 L. Water and to 1 L. of 0.1-M HOAc Containing 0.1-Mole NaOAc

Moles	Water		0.1-*M* HOAc + 0.1-*Mole* NaOAc	
	NaOH	HCl	NaOH	HCl
Electrolyte Added				
0.0000	1×10^{-7}	1×10^{-7}	1.81×10^{-5}	1.81×10^{-5}
.0001	1×10^{-10}	1×10^{-4}	1.8×10^{-5}	1.82×10^{-5}
.001	1×10^{-11}	1×10^{-3}	1.8×10^{-5}	1.85×10^{-5}
.01	1×10^{-12}	1×10^{-2}	1.5×10^{-5}	2.2×10^{-5}

of its soluble salts, the addition of small amounts of a strong acid or base will not cause an appreciable change in the concentration of hydronium ions. The concentration of the hydronium ion after adding various amounts of hydrogen chloride and of sodium hydroxide to a liter of 0.1-*N* acetic acid in which a mole of sodium acetate is dissolved, is given in Table VII. The concentration of the hydronium ion present when the acid or base is added to water is also given. Note that the ratio of the final concentration of hydronium ion to the initial concentration is 10^{-5} when the acid or base is added to water, but is nearly 1 when these electrolytes are added to the buffer solution.

There is no appreciable change in the concentration of hydronium ion in the buffer solution, acetic acid-sodium acetate, because on the addition of an acid, hydronium ions react with acetate ions

to form weak acetic acid. Since the per cent of ionization of acetic acid changes but little with a slight change in the concentration, the concentration of hydronium ions will change but slightly. When a small amount of an active base is added to the mixture, there is only a slight change in the concentration of hydronium ion. As the hydronium ions react with hydroxide ions forming water, more acetic acid ionizes. Since the concentration of acetic acid is little changed, the per cent of ionization and concentration of hydronium ion are nearly constant.

Other electrolytes which act as buffers are sodium hydrogen carbonate, sodium hydrogen and sodium dihydrogen phosphate. Their action with hydronium and hydroxide ions is shown by the following equations:

$$HCO_3^- + H_2O \rightleftarrows H_3O^+ + CO_3^=$$
$$HCO_3^- + OH^- \rightleftarrows H_2O + CO_3^=$$
$$HCO_3^- + H_3O^+ \rightleftarrows 2\,H_2O + CO_2$$
$$HPO_4^= + H_2O \rightleftarrows H_3O^+ + PO_4^{\equiv}$$
$$HPO_4^= + OH^- \rightleftarrows H_2O + PO_4^{\equiv}$$
$$HPO_4^= + H_3O^+ \rightleftarrows H_2O + H_2PO_4^-$$
$$H_2PO_4^- + H_2O \rightleftarrows H_3O^+ + HPO_4^=$$
$$H_2PO_4^- + OH^- \rightleftarrows H_2O + HPO_4^=$$
$$H_2PO_4^- + H_3O^+ \leftrightarrows H_2O + H_3PO_4$$

AMPHIPROTIC (AMPHOTERIC) SUBSTANCES

The hydroxides of many metals react with hydronium ions, forming the metallic ion and water. Some metallic hydroxides also react with bases, forming water and an acid radical which contains the metallic ion. The reactions with acids and bases formerly were explained by the ionization of the hydroxides to give hydronium and hydroxide ions. It was thought that aluminum hydroxide, which is typical of these hydroxides, ionized according to the equation

$$H_3O^+ + AlO_2^- \rightleftarrows Al(OH)_3 \leftrightarrows Al^{+++} + 3\,OH^-$$

Such hydroxides were said to be amphoteric. Since aluminum hydroxide ionized to give hydronium and hydroxide ions, it acted as an acid or base, respectively, when it was treated with a strong base or acid. The reactions are shown by the following equations:

$$Al(OH)_3 \leftrightarrows H_3O^+ + AlO_2^-$$
$$NaOH \rightarrow OH^- + Na^+$$
$$\downarrow\uparrow$$
$$2\,H_2O$$

$$Al(OH)_3 \leftrightarrows Al^{+++} + 3\,OH^-$$
$$3\,HCl + 3\,H_2O \rightarrow 3\,Cl^- + 3\,H_3O^+$$
$$\downarrow\uparrow$$
$$6\,H_2O$$

Since the reaction of these hydroxides with strong bases or acids is due to the loss and gain of protons respectively, it is appropriate that the adjective amphiprotic—signifying loss or gain of protons—be used instead of amphoteric.

Recently, Brønsted suggested a mechanism to account for these facts based on coordination or Werner chemistry. The tendency of water molecules in complex ions to lose protons and to form hydroxo-compounds is well known. For example, the ionization constant of the reaction

$$[Co(NH_3)_5H_2O]^{+++} + H_2O \leftrightarrows [Co(NH_3)_5OH]^{++} + H_3O^+$$

is 2.0×10^{-6}. The aquo-pentammine cobaltic ion is nearly as strong an acid as acetic acid.

There is a great deal of evidence that cations are hydrated and that the hydrated ion is a complex ion of the type described by Werner. The number of molecules of water and non-ionizable groups associated with the coordinating cation always tends to be equal to the coordination number (page 81). The positively charged cation tends to attract the electrons further away from the hydrogen nuclei, thus loosening the strength of the tie between the oxygen and hydrogen. A proton dissociates from a coordinated water molecule and reacts with water, forming a hydronium ion. Further ionization of protons from other molecules of water coordinated with the cation takes place with greater difficulty, possibly because the attraction of the electrons toward the coordinating cation is offset by the repulsion of the electrons by the negative charge on the complex ion. Thus, the ionization of hydrated aluminum hydroxide $\left[Al \begin{matrix}(OH)_3 \\ (H_2O)_3\end{matrix} \right]$ takes place fairly readily and is represented by the equation

$$Al \begin{matrix}(OH)_3 \\ (H_2O)_3\end{matrix} + H_2O \leftrightarrows \left[Al \begin{matrix}(OH)_4 \\ (H_2O)_2\end{matrix} \right]^- + H_3O^+$$

The further loss of protons to form $\left[Al \begin{matrix}(OH)_5 \\ (H_2O)\end{matrix} \right]^-$ according to the equation

$$\left[Al \begin{matrix}(OH)_4 \\ (H_2O)_2\end{matrix} \right]^- + H_2O \rightleftarrows \left[Al \begin{matrix}(OH)_5 \\ (H_2O)\end{matrix} \right]^- + H_3O^+$$

is negligible under ordinary conditions. The addition of a high concentration of a strong base, hydroxide ions for example, to a suspen-

sion of aluminum hydroxide causes the removal of hydronium ions by forming water and the solution contains the hydrated aluminate ion $\left[\mathrm{Al}\begin{matrix}(\mathrm{OH})_4\\(\mathrm{H_2O})_2\end{matrix} \right]^-$. The complex ion $\left[\mathrm{Al}\begin{matrix}(\mathrm{OH})_4\\(\mathrm{H_2O})_2\end{matrix} \right]^-$ may be regarded as $(\mathrm{AlO_2 \cdot 2\ H_2O})^-$.

When aluminum hydroxide acts as a base the reaction is

$$\mathrm{Al}\begin{matrix}(\mathrm{H_2O})_3\\(\mathrm{OH})_3\end{matrix} + 3\ \mathrm{H_3O^+} \rightleftarrows \mathrm{Al(H_2O)_6^{+++}} + 3\ \mathrm{H_2O}$$

The reaction of an amphiprotic hydroxide with hydronium and hydroxide ions is shown by the equation

$$[\mathrm{Al(H_2O)_6}]^{+++} \underset{\mathrm{H_3O^+}}{\overset{\mathrm{OH^-}}{\rightleftarrows}} \mathrm{Al}\begin{matrix}(\mathrm{OH})_3\\(\mathrm{H_2O})_3\end{matrix} \underset{\mathrm{H_3O^+}}{\overset{\mathrm{OH^-}}{\rightleftarrows}} \left[\mathrm{Al}\begin{matrix}(\mathrm{OH})_4\\(\mathrm{H_2O})_2\end{matrix} \right]^-$$

A sufficiently high concentration of hydronium or hydroxide ions will dissolve aluminum hydroxide. Nitric, sulfuric and hydrochloric acids will dissolve aluminum hydroxide while the hydroxide is only slightly soluble in weak acids, such as carbonic or hydrocyanic acids. Similarly, aluminum hydroxide is soluble in sodium or potassium hydroxide but is only slightly soluble in weak alkalies, such as ammonia.

Since the hydrogen carbonate and carbonate ions are strong bases, one would expect these ions to remove protons from the hydrated aluminum ion to form aluminum hydroxide. This is actually the case. The equations for the reactions are

$$\mathrm{Al(H_2O)_6^{+++}} + 3\ \mathrm{HCO_3^-} \rightleftarrows \mathrm{Al}\begin{matrix}(\mathrm{OH})_3\\(\mathrm{H_2O})_3\end{matrix} + 3\ \mathrm{H_2CO_3}$$

$$\mathrm{Al(H_2O)_6^{+++}} + 3\ \mathrm{CO_3^=} \rightleftarrows \mathrm{Al}\begin{matrix}(\mathrm{OH})_3\\(\mathrm{H_2O})_3\end{matrix} + 3\ \mathrm{HCO_3^-}$$

However, the carbonate ion is a much weaker base than the hydroxide ion and only a small amount of aluminate ion forms even when an excess of carbonate ion is added. Since the hydrogen carbonate ion is a still weaker base than the carbonate ion, no aluminate will be formed when aluminum hydroxide is treated with an excess of the hydrogen carbonate ion.

Similarly ammonia is a base and precipitates the hydroxide

$$Al(H_2O)_6^{+++} + 3\ NH_3 \rightleftarrows Al\begin{matrix}(OH)_3\\(H_2O)_3\end{matrix} + 3\ NH_4^+$$

Since ammonia is a weaker base than the hydroxide ion, only a small amount of aluminate ion is formed. Other hydroxides which behave similarly to aluminum hydroxide are those of chromium, zinc, tin, lead, antimony and arsenic.

The precipitation of other insoluble weak hydroxides can be explained in an analogous way. For example, when a base is added to a solution containing ferric ions, the reaction, which formerly was assumed to be a double decomposition, probably takes place according to the equations

$$Fe(H_2O)_6^{+++} + 3\ H_2O \leftrightharpoons Fe\begin{matrix}(H_2O)_3\\(OH)_3\end{matrix} + 3\ H_3O^+ \qquad \text{and}$$

$$3\ H_3O^+ + 3\ OH^- \rightleftarrows 6\ H_2O \qquad \text{or}$$

$$Fe(H_2O)_6^{+++} + 3\ OH^- \rightleftarrows Fe\begin{matrix}(H_2O)_3\\(OH)_3\end{matrix} + 3\ H_2O$$

EXERCISES

1. What is an amphiprotic hydroxide?
2. Show how the amphiprotic nature of chromium and aluminum is utilized in their separation from ferric and manganous ions in the analysis of Group III.
3. In what part of the Periodic Table are the amphiprotic elements found?
4. Account for the insolubility of aluminum hydroxide in ammonia and its solubility in sodium hydroxide.
5. An element, M, forms an acidic, a basic and an amphiprotic oxide. They have the following formulas: MO, M_2O_3 and MO_3. Which oxide will be basic, which amphiprotic and which acidic? Give reasons for your answer.
6. Cite examples to show that the higher the positive valence of an element, the more pronounced are its non-metallic properties.
7. Write equations to show the reaction of lead nitrate with an excess of sodium hydroxide.
8. Calculate the number of milliliters of 2-*N* sodium hydroxide necessary to prepare a solution of sodium hydrogen stannite ($NaHSnO_2$) from 5 ml. of a 0.2-*M* solution of stannous chloride which contains 0.2 ml. of 12-*M* hydrochloric acid. *Ans.* 2.7 ml.
9. State a number of instances in which the amphiprotic nature of an ion is used in qualitative analysis.

10. If only sodium hydroxide, ammonia, and nitric acid are available, devise procedures to effect the separation of the following ions:
    a. Zinc ions and silver ions
    b. Aluminum ions and ferric ions
    c. Ferrous ions, aluminum ions and bismuth ions
    d. Stannous ions and nickel ions
11. Account for the reaction of aqueous solutions of the following substances toward litmus and write ionic equations to show the equilibria involved.
    a. cupric nitrate
    b. ammonium chloride
    c. manganese sulfate
    d. magnesium acetate
    e. ammonium carbonate
    f. potassium chloride
12. Account for the difference in alkalinity of a 0.1-*M* solution of sodium carbonate and a 0.1-*M* solution of ammonium carbonate.
13. A high concentration of carbonate ion is wanted. Which should be used—a solution of sodium or ammonium carbonate?
14. How may the hydrolysis of a salt be prevented?
15. Write ionic equations to show the action of solutions of the various types of salts toward litmus.
16. The constant of water is 10^{-14}. What is the per cent of ionization of water? Assume that the density is 1. *Ans.* 1.8×10^{-7}.
17. In what type of compound will hydrolysis be complete? Illustrate, and give reasons for your answer.
18. Derive the hydrolysis constants of sodium acetate, cupric chloride, ammonium chloride, and ammonium acetate.
19. What is the pH of 0.01-*N* sodium hydroxide? *Ans.* pH 12.
20. What is the pH of 0.01-*N* hydrochloric acid?
21. What is the pH of 0.025-*N* potassium hydroxide? *Ans.* pH 12.4.
22. What is the pH of 0.015-*N* nitric acid?
23. Account for the amphiprotic properties of aluminum hydroxide in terms of recent theories of acids and bases.
24. Write equations to show the equilibria between zinc hydroxide and sodium hydroxide, ammonia and hydrochloric acid.
25. Show that the concentration of hydronium ions in a solution of sodium bicarbonate is numerically equal to the square root of the product of the primary and secondary ionization constants of carbonic acid.
26. The pH of a solution is 3.2. What is the concentration (1) of the hydronium ions? (2) Of the hydroxide ions?
27. The pH of a solution is 8.1. What is the concentration (1) of the hydronium ions? (2) Of the hydroxide ions?
28. Set up the expression for the equilibrium constant of the reaction which takes place in each of the following systems. Then evaluate the constant and make the necessary calculations.
    a. Calculate the concentration of hydroxide ion in a 2-*M* solution of calcium acetate.
    b. Calculate the concentration of sulfide ion in a 1-*M* solution of sodium sulfide.
    c. What is the percentage of 0.1-*N* ammonium cyanide that reacts with water?
    d. Calculate the concentration of hydroxide ion in a 0.1-*M* solution of sodium bicarbonate.
    e. Calculate the concentration of undissociated acetic acid in 2-*N* calcium acetate.

f. Calculate the concentration of hydronium ion in a solution made by mixing equal volumes of 2-*M* hydrochloric acid and 2-*M* ammonia.

g. How many formula weights of potassium hydroxide must be added to a liter of a suspension of aluminum hydroxide to dissolve 0.001 mole of aluminum hydroxide?

h. How many moles of zinc hydroxide will dissolve in a liter of 0.1-*N* sodium hydroxide?

i. Aluminum hydroxide is added to a liter of sodium hydroxide until 0.001 mole has dissolved when equilibrium has been established. What is the concentration of hydroxide ion in the solution?

j. If an excess of aluminum hydroxide is suspended in a liter of 0.01-*N* acetic acid, what will be the concentration of hydronium ions when equilibrium is established?

CHAPTER VII

The Activity Concept

THE LAW OF mass action has been applied to dilute solutions of weak electrolytes and to saturated solutions of slightly soluble substances in the absence of foreign salts with fairly satisfactory results. However, the simple law is inadequate if a highly ionized substance is present. For example, the concentration of hydronium and hydroxide ions present in pure water at 25° is 10^{-7}, but the concentration at the same temperature is 1.12×10^{-7} in a 0.01-*M* solution of sodium chloride. The concentrations of the hydronium and hydroxide ions increase as the concentration of sodium chloride increases, as can be seen from the data in Table VIII. Furthermore, the solubility of a slightly soluble salt increases

Table VIII. Changes in the Concentration of Hydronium and Hydroxide Ions in Water at 25° with Increasing Molarity of Sodium Chloride

Molarity	$C_{H_3O^+}$ and $C_{OH^-} \times 10^{-7}$
0.0001	1.02
0.001	1.05
0.005	1.09
0.01	1.12

as the concentration of a highly ionized substance present increases. Typical data are given in Table IX. Thus, the solubility of silver chloride* is 12% greater in a 0.01-*M* solution of potassium nitrate than in water. Furthermore, the solubility of a slightly soluble substance in the presence of even a small concentration of an electrolyte having an ion in common is greater than that calculated previously (page 64). The difference between the calculated solubility and the experimental values increases with the increase in the concentration of the ions present in the solution. These observations indicate that the simple application of the theory of ioniza-

* Popoff and Neuman: *Journal of Physical Chemistry 34*:1853, 1930.

tion of Arrhenius and the mass law to strong electrolytes and to slightly soluble electrolytes in the presence of other ions fails to account adequately for their behavior. Other discrepancies between the behavior predicted on the basis of the theory of Arrhenius and the law of mass action, and that observed experimentally may be cited. For example, the apparent per cent of ionization of a strong

Table IX. Solubility of Silver Chloride in Potassium Nitrate Solution

Molarity of KNO_3	Solubility in KNO_3 Solution $\times 10^5$	Solubility in KNO_3 Solution / Solubility in H_2O
0.000	1.278	
0.001	1.325	1.04
0.005	1.385	1.08
0.01	1.427	1.12

electrolyte depends on the method used to determine it as is shown in Table X. The degree of ionization should be the same. Then, too, since crystals of most electrolytes are built up of ions, not molecules, it is difficult to see why these ions would combine in water, a substance having a high dielectric constant, to form molecules of the solute. Furthermore, the ions are hydrated,

Table X. Degree of Ionization of Potassium Chloride by Different Methods

Molarity	Conductivity	E. M. F.	F. P.
0.001	0.98	0.98	0.98
0.005	0.95	0.92	0.95
0.01	0.94	0.89	
0.1	0.86	0.75	

whereby the size of the ions is increased and the attractive forces between those of opposite charge are decreased.

G. N. Lewis of the University of California, accepting the principle of complete ionization of strong electrolytes, showed that the discrepancy between the calculated and observed values even at higher concentrations and in the presence of salts are largely eliminated "if the activities of the ions" rather than their molecular

concentrations are used in the calculations. The activity (a) of an ion is its effective concentration, and is numerically equal to the product of the molecular concentration (C) and the activity coefficient (γ).

$$a = C\gamma \tag{42}$$

When activities of ions are used, the expression for the equilibrium between a weak electrolyte and its ions, $B_xC_y \leftrightarrows xB^{y+} + yC^{z-}$, is

$$K_i = \frac{(a_{By+})^z \times (a_{Cz-})^y}{a_{BxCy}}$$

Unlike the expression derived from the law of mass action, this equation holds for higher concentrations of weak electrolytes even in the presence of strong electrolytes. The equation

$$SP = (a_{M^{b+}})^c \times (a_{X^{c-}})^b$$

holds more accurately for the equilibrium between a solid solute and its ions in a saturated solution of M_cX_b than equation 21 derived on page 58.

For the equilibrium between a complex ion, $(MP_4)^+$, and the groups composing it

$$(MP_4)^+ \leftrightarrows M^+ + 4\,P$$

we have the equation

$$\frac{a_{M^+} \times a_P^4}{a_{(MP_4)^+}} = K_{\text{instability}}$$

Since the activity of an ion is the product of the molecular concentration of the ion (C) and the activity coefficient (γ), the ionization constant for acetic acid is

$$K_i = \frac{a_{H_3O^+} \times a_{OAc^-}}{a_{HOAc}} = \frac{C_{H_3O^+} \times C_{OAc^-}}{C_{HOAc}} \times \frac{\gamma_{H_3O^+} \times \gamma_{OAc^-}}{\gamma_{HOAc}}$$

in which the terms $C_{H_3O^+}$, C_{OAc^-} and C_{HOAc} denote the molecular concentrations of the substances and $\gamma_{H_3O^+}$, γ_{OAc^-} and γ_{HOAc} are the activity coefficients. Activity coefficients calculated on theoretical grounds are given in Table XI. In the table the values of activity coefficients are related to the ionic strength of solutions. The activity coefficient of a dilute solution of an electrolyte is the same in any solution of the same ionic strength. The values de-

crease with the increase in the ionic strength of the solution. The ionic strength (s) is defined as one-half of the sum of the products of the square of the valence (z_+) and the concentration (C_+) of the

Table XI. Ionic Strengths and Activity Coefficients

Ionic Strength (s)	Activity Coefficients (γ)		
	Uni-univalent (A^+B^-)	Bi-univalent ($X^{2+}B_2^-$)	Bi-bivalent ($X^{2+}Y^{2-}$)
0.0001	0.99	0.98	0.95
0.0002	0.98	0.97	0.94
0.0005	0.97	0.95	0.90
0.001	0.96	0.93	0 86
0.002	0.95	0.90	0.81
0.005	0.92	0.85	0.72
0.01	0.89	0.79	0 63
0.05	0.81	0.66	0.47
0.1	0.78	0.56	0 33
0.15	0.72	0.52	0.28
0.3	0.66	0.44	0.22
0.5	0.62	0.39	0.18
1.0	0.56	0.31	0.13
1 5	0.52	0.27	0.12
2.0	0.50	0.25	0.09
2.5	0.49	0.23	0.08
3 0	0.48	0.23	0.075

positive ion and the square of the valence (z_-) and the concentration (C_-) of the negative ion

$$s = 1/2[(z_+{}^2C_+) + (z_-{}^2C_-)]$$

The ionic strength of a solution containing a number of electrolytes is given by the expression

$$s = 1/2[(z_+{}^2C_+) + (z_{1+}{}^2C'_+) + \text{etc.} + (z_-{}^2C_-) + (z_1{}^{-2}C'_-) + \text{etc.}]$$

where z^+, z_{1+}, z_-, z_{1-} etc. are the positive and negative valences of the cations and anions respectively. The concentrations of the cations are C_+, C'_+ and those of the anions are C_-, C'_-, etc. Thus the ionic strength of a 0.01-M solution of a strong electrolyte composed of uni-univalent radicals is

$$s = 1/2[(1^2 \times .01) + (1^2 \times .01)] = 0.01$$

The molarity (M) of a solution of a strong electrolyte composed of uni-univalent groups having an ionic strength of 0.01 is

$$0.01 = 1/2[(1^2 \times M) + (1^2 \times M)]$$
$$M = 0.01$$

If a strong electrolyte is composed of bi-bivalent groups, the molarity of a solution having an ionic strength of 0.01 is

$$0.01 = 1/2[(2^2 \times M) + (2^2 \times M)]$$
$$M = 0.0025$$

The ionic strength of a solution a liter of which contains 0.2 of a mole of barium nitrate and 0.1 of a mole of hydrogen chloride is given by the equation

$$s = 1/2[(2^2 \times 0.2) + (1^2 \times 0.1) + (1^2 \times 0.4) + (1^2 \times 0.1)] = 0.7.$$

Activity coefficients can be determined experimentally from the electromotive force of suitably arranged cells and from measurements of the changes in the boiling point, freezing point, and vapor pressure of solutions. The experimentally determined values of the activity coefficients of a number of substances are given in Table XII.

Table XII. Experimental Values of Activity Coefficients (γ)

M	HCl	KCl	KNO_3	K_2SO_4	$BaCl_2$	$CuSO_4$
0.0001	0.99	0.98	0.99	0.94	0.94	0.85
0.0005	0.98	0.97	0.98	0.89	0.89	0.75
0.001	0.97	0.96	0.98	0.85	0.87	0.69
0.005	0.94	0.93	0.94	0.75	0.77	0.50
0 01	0.92	0.90	0.92	0.69	0.72	0.40
0 05	0.84	0 82	0.81	0 51	0.57	0.22

The activity coefficient of undissociated molecules is considered to be one, although according to calculations based on theoretical considerations it is somewhat less than unity. Calculated and experimentally determined values of the activity coefficients of ions of uni-univalent electrolytes agree at an ionic strength of 0.1, but differ at higher ionic strengths. Since the activity coefficient at low ionic strengths—less than 0.0001—approaches unity, the concentration and the activity of the ions are very nearly the same and concentrations are ordinarily used instead of activities. The

activity of pure liquids and solids is one. The activity of water in an aqueous solution is assumed to be one.

What is the activity of the silver and nitrate ions in a 0.0001-*M* solution of silver nitrate to which enough sodium nitrate, for example, has been added so that the ionic strength of the solution is 0.5? The activity coefficient of a uni-univalent electrolyte in a solution having an ionic strength of 0.5 is 0.62. Hence,

$$a_{Ag^+} = \gamma_{Ag^+} \times C_{Ag^+} = 0.62 \times 0.0001 = 6.2 \times 10^{-5}$$
$$a_{NO_3^-} = \gamma_{NO_3^-} \times C_{NO_3^-} = 0.62 \times 0.0001 = 6.2 \times 10^{-5}$$

What is the activity of barium and chloride ions in a 0.0001-*M* solution of barium chloride to which sufficient neutral salt, sodium nitrate for example, has been added so that the solution has an ionic strength of 0.3? The activity coefficient of a uni-bivalent electrolyte in a solution having an ionic strength of 0.3 is 0.44 and

$$a_{Ba^{++}} = C_{Ba^{++}} \times \gamma_{Ba^{++}} = 0.0001 \times 0.44 = 4.4 \times 10^{-5}$$
$$a_{Cl^-} = C_{Cl^-} \times \gamma_{Cl^-} = 2 \times 0.0001 \times 0.44 = 8.8 \times 10^{-5}$$

What is the activity of the calcium and sulfate ions in a 0.0001-*M* solution of calcium sulfate to which sufficient neutral salt has been added to make the ionic strength 0.1? The activity coefficient of a bi-bivalent electrolyte in a solution whose ionic strength is 0.1 is 0.33 and

$$a_{Ca^{++}} = C_{Ca^{++}} \times \gamma_{Ca^{++}} = 0.0001 \times 0.33 = 3.3 \times 10^{-5}$$
$$a_{SO_4^{=}} = C_{SO_4^{=}} \times \gamma_{SO_4^{=}} = 0.0001 \times 0.33 = 3.3 \times 10^{-5}$$

Activities, Ionization Constants and Solubility Products. Using the activity concept the expression for the ionization constant (K_i) of acetic acid is

$$K_i = \frac{a_{H_3O^+} \times a_{OAc^-}}{a_{HOAc}} = \frac{\gamma_{H_3O^+} \times \gamma_{OAc^-} \times C_{H_3O^+} \times C_{OAc^-}}{\gamma_{HOAc} \times C_{HOAc}} \quad (43)$$

Since $\gamma_{H_3O^+} = \gamma_{OAc^-} = \gamma$ and $\gamma_{HOAc} = 1$, equation 43 becomes

$$K_i = \frac{\gamma^2 \times C_{H_3O^+} \times C_{OAc^-}}{C_{HOAc}} \quad (44)$$

The concentration of hydronium ions in the solution equals the concentration of acetate ions and may be calculated by substituting the $C_{H_3O^+}$ for the C_{OAc^-} and rearranging equation 44

$$C_{H_3O^+} = \frac{1}{\gamma}\sqrt{K_i \times C_{HOAc}} = \frac{1}{\gamma}\sqrt{1.8 \times 10^{-5} \times C_{HOAc}} \quad (45)$$

Since γ decreases with the increase in the ionic strength, the values of $C_{H_3O^+}$ and C_{OAc^-} will increase on the addition of salts. In other words, the per cent of ionization of acetic acid, or any weak electrolyte, is increased by the presence of neutral salts.

What will be the concentration of hydronium ion in a 0.1-*N* solution of acetic acid to a liter of which 0.1 mole of solid sodium chloride has been added? Since acetic acid is a weak electrolyte, the concentration of its ions is negligible in comparison with that from the salt added and may be omitted from the calculations. The ionic strength is

$$s = 1/2[(1 \times 0.1) + (1 \times 0.1)] = 0.1$$

and the activity coefficient (Table XI) is 0.78. These values substituted in equation 45 give

$$C_{H_3O^+} = \frac{1}{0.78}\sqrt{1.8 \times 10^{-5} \times 0.1} = \frac{1.34 \times 10^{-3}}{0.78} \qquad (46)$$
$$= 1.72 \times 10^{-3}$$

In the absence of sodium chloride the concentration of hydronium ion is 1.3×10^{-3} (page 46) or only 77% of that in the solution having the higher ionic strength.

The application of the activity concept to the solubility of a slightly soluble substance A_2B in the presence of strong electrolytes leads to the expression

$$SP_{A_2B} = a_{A^+}^2 \times a_{B^-} = (\gamma_{A^+} \times C_{A^+})^2 \times (\gamma_{B^-} \times C_{B^-}) \qquad (47)$$

For silver chloride the expression for the solubility product is

$$SP_{AgCl} = a_{Ag^+} \times a_{Cl^-} = \gamma_{Ag^+} \times C_{Ag^+} \times \gamma_{Cl^-} \times C_{Cl^-} \qquad (48)$$
$$= \gamma^2 \times C_{Ag^+} \times C_{Cl^-}$$

Since γ decreases with an increase in the ionic strength, the solubility of silver chloride increases on the addition of an electrolyte. A similar conclusion must be drawn about the ionization of water since

$$K_w = a_{H_3O^+} \times a_{OH^-} = \gamma_{H_3O^+} \times C_{H_3O^+} \times \gamma_{OH^-} \times C_{OH^-} \qquad (49)$$
$$= \gamma^2 \times C_{H_3O^+} \times C_{OH^-}$$

The term γ^2 is the square of the mean activity coefficient.

Activity of Ions and the Common Ion Effect. The activity of the ions rather than their concentrations should be used in calculating

the effect of the addition of a common ion, since the ionic strength is increased by the excess of the reagent added. The expression for the $K_{i_{NH_3}}$ is

$$K_{i_{NH_3}} = \frac{a_{NH_4^+} \times a_{OH^-}}{a_{NH_3}} = \frac{\gamma^2 \times C_{NH_4^+} \times C_{OH^-}}{C_{NH_3}} \qquad (50)$$

The calculation of the C_{OH^-} after the addition of 0.01 mole of an ammonium salt to a liter of 0.01-*M* ammonia which is 4.8% ionized necessitates the calculation of the ionic strength and the activity coefficient. Since very little ammonia reacts with water to form ammonium and hydroxide ions, these ions may be neglected in calculating the ionic strength. The ionic strength, then, is

$$s = 1/2[(1^2 \times 0.01) + (1^2 \times 0.01)] = 0.01$$

The activity coefficient is 0.89 and equation 50 becomes

$$1.8 \times 10^{-5} = \frac{0.89^2 \times 0.01048 \times C_{OH^-}}{0.00952}$$

$$C_{OH^-} = \frac{0.00952 \times 1.8 \times 10^{-5}}{0.89^2 \times 0.01048} = 2.1 \times 10^{-5}$$

Similarly, the concentration of silver ion in a 0.01-*N* solution of sodium chloride saturated with silver chloride may be calculated. The solubility product of silver chloride is 1.6×10^{-10}. The concentration of ions from the silver chloride is so small that it may be neglected. The ionic strength of 0.01-*N* sodium chloride is 0.01 and the activity coefficient is 0.89.

$$SP_{AgCl} = 1.6 \times 10^{-10} = a_{Ag^+} \times a_{Cl^-} = \gamma^2 \times 0.01 \times C_{Ag^+}$$
$$= 8.89^2 \times 0.01 \times C_{Ag^+}$$

$$C_{Ag^+} = \frac{1.6 \times 10^{-10}}{0.89^2 \times 0.01} = \frac{1.6 \times 10^{-10}}{7.9 \times 10^{-3}} = 2.0 \times 10^{-8}$$

Calculation of Equilibrium Constants of Oxidation-Reduction Reactions. The standard electrode or oxidation-reduction potential (E_0) of an electrode has been discussed on page 78 and a table of values is given in the Appendix on page 324. If the ions in the electrode system are not at unit activity, the potential of the electrode (E) is related to the standard electrode potential by the equation

$$E = E_0 + \frac{0.059}{m} \log \frac{a_{ox}}{a_{red}}$$

In this equation m is the number of electrons lost or gained by an atom of the element taking part in the oxidation-reduction, and

a_{ox} and a_{red} represent the activities of the oxidizing and reducing agents respectively.

The standard electrode potential of the system

$$Cl_2 + 4\,H_2O \rightleftarrows 2\,HOCl + 2\,H_3O^+ + 2\epsilon \text{ is } 1.49 \text{ V.}$$

The electrode potential (E) is given by the expression

$$E = 1.49 + \frac{0.059}{2} \log \frac{a^2_{HOCl} \times a^2_{H_3O^+}}{a_{Cl_2}}$$

Suppose that we have a cell consisting of two platinum electrodes which are immersed in solutions of different oxidizing agents and their reduction products and that the reaction taking place in the cell is given by the generalized equation

$$ox + red' \rightleftarrows red + ox'$$

where ox and red designate the oxidizing agents and their reduction products respectively. The electromotive force of the cell is the algebraic difference of the electrode potentials E and E'. Thus

$$E - E' = \left(E_0 + \frac{0.059}{n} \log \frac{a_{ox}}{a_{red}}\right) - \left(E'_0 + \frac{0.059}{n} \log \frac{a_{ox'}}{a_{red'}}\right) \qquad (51)$$

where n represents the number of electrons lost and gained when the equation for the reaction is balanced. If the platinum electrodes are connected by a conductor, electrons will pass over the conductor until equilibrium between the substances present around the electrodes is reached. When equilibrium is established, no more electrons pass over the conductor. The electromotive force of the cell is 0 and equation 51 may be written

$$0 = E_0 + \frac{0.059}{n} \log \frac{a_{ox}}{a_{red}} - E'_0 - \frac{0.059}{n} \log \frac{a_{ox'}}{a_{red'}} \qquad (52)$$

The equilibrium constant for the reaction can be calculated by factoring and rearranging the terms of equation 52

$$E_0 - E'_0 = \frac{0.059}{n}\left(\log \frac{a_{ox'}}{a_{red'}} - \log \frac{a_{ox}}{a_{red}}\right) \qquad (53)$$

By further simplification, equation 53 becomes

$$E_0 - E'_0 = \frac{0.059}{n} \log \frac{a_{ox'}}{a_{red'}} \times \frac{a_{red}}{a_{ox}} \qquad (54)$$

Rearrangement of the terms gives

$$\log \frac{a_{ox'} \times a_{red}}{a_{red'} \times a_{ox}} = \frac{n(E_0 - E_0')}{0.059}$$

and

$$\frac{a_{ox'} \times a_{red}}{a_{red'} \times a_{ox}} = 10^{\frac{n(E_0 - E_0')}{0.059}} = K_{eq} \qquad (55)$$

The equilibrium constant, then, is ten raised to the power, $\frac{n(E_0 - E_0')}{0.059}$. Since the standard electrode potentials of a great many oxidizing and reducing agents are known, a large number of equilibrium constants can be calculated. For example, in the reaction between permanganate ions and iodide ions in an acid solution the standard electrode potential E_0 of the reaction

$$12\ H_2O + Mn^{++} \rightleftarrows MnO_4^- + 8\ H_3O^+ + 5\ \epsilon \text{ is } 1.52\ V$$

and the standard electrode potential (E_0') of the reaction

$$2\ I^- \leftrightarrows I_2 + 2\ \epsilon \text{ is } 0.53\ V$$

Adjust the amounts of oxidizing and reducing agents so that the loss and gain of electrons is 10. The balanced equation is then

$$2\ MnO_4^- + 16\ H_3O^+ + 10\ I^- \leftrightarrows 5\ I_2 + 2\ Mn^{++} + 24\ H_2O$$

and the expression for the equilibrium constant (K_{eq}) is

$$\frac{a_{I_2}^5 \times a_{Mn^{++}}^2}{a_{MnO_4^-}^2 \times a_{H_3O^+}^{16} \times a_{I^-}^{10}} = K_{eq}$$

The value of the equilibrium constant K_{eq} is calculated by substituting the appropriate values in equation 52.

$$O = E - E' = 0.53 + \frac{0.059}{10} \log \frac{a_{I_2}^5}{a_{I^-}^{10}} - 1.52 + \frac{0.059}{10} \log \frac{a_{MnO_4^-}^2 \times a_{H_3O^+}^{16}}{a_{Mn^{++}}^2}$$

Collecting the terms

$$1.52 - 0.53 = \frac{0.059}{10}\left(\log \frac{a_{I_2}^5}{a_{I^-}^{10}} - \log \frac{a_{MnO_4^-}^2 \times a_{H_3O^+}^{16}}{a_{Mn^{++}}^2} \right)$$

and simplifying, we have

$$\frac{0.99 \times 10}{0.059} = \log \frac{a_{I_2}^5 \times a_{Mn^{++}}^2}{a_{I^-}^{10} \times a_{MnO_4^-}^2 \times a_{H_3O^+}^{16}}$$

and

$$10^{\frac{9.9}{0.059}} = 10^{168} = \frac{a_{I_2}^5 \times a_{Mn^{++}}^2}{a_{I^-}^{10} \times a_{MnO_4^-}^2 \times a_{H_3O^+}^{16}}$$

Since the value of the constant is large, the value of the denominator is small compared to the numerator. When equilibrium is established, the concentrations of the permanganate and iodide ions in the solution must be small; i.e., the reaction goes practically to completion.

Thus, if standard oxidation-reduction potentials are available, the extent to which a reaction between an oxidizing and a reducing agent takes place can be calculated. The calculations enable one to predict the extent to which such reactions take place when equilibrium is finally established, but no clue is given as to the time required. Concentrations of the ions may be used instead of their activity if great accuracy is not required.

In many cases, the calculation of the equilibrium constant for an oxidation-reduction reaction will permit the evaluation of the equilibrium constant for a system which also involves the equilibrium of the ions of slightly soluble substances, complex ions, or weak electrolytes, as well as oxidation-reduction. The expression for the equilibrium constant of the system

$$3\ CuS + 2\ NO_3^- + 8\ H_3O^+ \rightleftharpoons 3\ Cu^{++} + 3\ S + 2\ NO + 12\ H_2O$$

is

$$\frac{C_{Cu^{++}}^3 \times C_{NO}^2}{C_{H_3O^+}^8 \times C_{NO_3^-}^2} = K_{eq}$$

The constant may be evaluated by multiplying the expression for the equilibrium constant by $\frac{C_{S^-}^3}{C_{S^-}^3}$ which gives

$$C_{Cu^{++}}^3 \times C_{S^-}^3 \times \frac{C_{NO}^2}{C_{NO_3^-}^2 \times C_{S^-}^3 \times C_{H_3O^+}^8} = K_{eq} = SP_{CuS}^3 \times K'_{eq},$$

when K'_{eq} is the equilibrium constant of the reaction

$$3\ S^- + 2\ NO_3^- + 8\ H_3O^+ \rightleftharpoons 2\ NO + 12\ H_2O + 3\ S$$

which is

$$\frac{C_{NO}^2}{C_S^3 \times C_{NO_3^-}^2 \times C_{H_3O^+}^8} = K'_{eq}$$

The equilibrium constant, K_{eq}, for the reaction between $S^=$ and NO_3^- in the presence of an acid can be calculated from the oxidation potentials. A table of standard oxidation-reduction potentials is given in the Appendix.

Activities of Ions and Hydrolysis Calculations. In some cases the extent of the hydrolysis of ions may be calculated just as accurately by using the concentrations as by using the activities of the ions. However, the concentration of the hydronium ions may be calculated more accurately when the activities of the ions are used instead of their concentrations.

The classification of the salts into groups and subgroups to aid in the study of hydrolysis was made on page 103. Let us calculate the degree of hydrolysis and the concentration of the hydronium ions present in each typical case.

I. The cation is aprotic, that is, it can neither lose nor gain protons. Sodium and potassium ions are typical.

a. The anion is a very weak base. There is no hydrolysis.

b. The anion is a strong base. A solution of sodium or potassium acetate is typical. The equation for the reaction is $OAc^- + H_2O \rightleftarrows HOAc + OH^-$. What is the degree of hydrolysis of a 0.1-*N* solution? The ionic strength is given by the expression

$$s = 1/2[(z_+^2 \times 0.1) + (z_-^2 \times 0.1)]$$
$$= 1/2[(1^2 \times 0.1) + (1^2 + 0.1)] = 0.1$$

The activity coefficient for an ionic strength of 0.1 is 0.78 according to Table XI on page 119

$$0.78 = \gamma_{K^+} = \gamma_{OAc^-} = \gamma_{H_3O^+}$$
$$1 = \gamma_{HOAc}$$

Let α = fraction hydrolyzed

$$0.1\,\alpha = C_{OH^-} = C_{HOAc}$$
$$1 \times 0.1\,\alpha = a_{HOAc}$$
$$0.1\,\alpha \times 0.78 = 0.078\,\alpha = a_{OH^-}$$
$$(1 - \alpha) = \text{fraction not hydrolyzed}$$
$$0.1(1 - \alpha) = C_{OAc^-}$$
$$0.78 \times 0.1(1 - \alpha) = 0.078 - 0.078\,\alpha = a_{OAc^-}$$

Summarizing

Concentration	$0.1(1-\alpha)$		$0.1\,\alpha$	$0.1\,\alpha$
Activity	$0.1(1-\alpha) \times 0.78$		$0.1\,\alpha$	$0.78 \times 0.1\,\alpha$
	OAc^-	$+ H_2O \rightleftarrows$	$HOAc$	$+ OH^-$

The expression for the hydrolysis constant is

$$\frac{a_{HOAc} \times a_{OH^-}}{a_{OAc^-}} = K_{hyd} \tag{56}$$

The constant may be evaluated by multiplying equation 56 by $\frac{a_{H_3O^+}}{a_{H_3O^+}}$ which gives

$$\frac{a_{HOAc} \times a_{OH^-} \times a_{H_3O^+}}{a_{H_3O^+} \times a_{OAc^-}} = \frac{K_w}{K_{i_{HOAc}}} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \tag{57}$$

By substituting the values of the various terms, equation 56 becomes

$$\frac{0.1\,\alpha \times 0.078\,\alpha}{0.078 - 0.078\,\alpha} = 5.6 \times 10^{-10} \tag{58}$$

Since $0.078\,\alpha$ is small in comparison with 0.078 equation 59 becomes

$$\frac{0.0078\,\alpha^2}{0.078} = 5.6 \times 10^{-10} \tag{59}$$

and

$$\alpha^2 = \frac{5.6 \times 10^{-10}}{0.0078} \times 0.078$$

$$\alpha = 7.5 \times 10^{-5}$$

Thus, the calculated value for the fraction of the acetate ions hydrolyzed is the same whether the activities of the ions or their concentrations are used. This is because the activity coefficient appears in both the numerator and the denominator of the expression. The activity of hydroxide ions is $0.078\,\alpha$ or 5.9×10^{-6}. Substitution of this value in the expression for the constant of water gives

$$a_{H_3O^+} \times 5.9 \times 10^{-6} = 10^{-14}$$

and

$$a_{H_3O^+} = \frac{10^{-14}}{5.9 \times 10^{-6}} = 1.7 \times 10^{-9}$$

Since the activity of the hydronium ion is given by the expression

$$a_{H_3O^+} = \gamma \times C_{H_3O^+}$$

and the activity coefficient (γ) is 0.78, the concentration of hydronium ions ($C_{H_3O^+}$) is

$$\frac{1.7 \times 10^{-9}}{0.78} \quad \text{or} \quad 2.2 \times 10^{-9}$$

c. The anion is amphiprotic. Sodium hydrogen carbonate is typical of this type. The equilibria involved are

$$HCO_3^- + H_2O \leftrightarrows CO_3^{=} + H_3O^+$$
$$HCO_3^- + H_2O \leftrightarrows OH^- + H_2CO_3$$
$$OH^- + H_3O^+ \rightleftarrows 2\,H_2O$$

When equilibrium has been established, if the solution is not too dilute, nearly all of the hydronium and hydroxide ions from the hydrolysis of the hydrogen carbonate ions have reacted to form water. The net result of the process is

$$\underset{B'}{HCO_3^-} + \underset{A}{HCO_3^-} \rightleftarrows \underset{A'}{H_2CO_3} + \underset{B}{CO_3^{=}}$$

and the equilibrium constant is

$$\frac{a_{H_2CO_3} \times a_{CO_3^{=}}}{a_{HCO_3^-} \times a_{HCO_3^-}} = K_{eq} \tag{60}$$

The constant may be evaluated by multiplying equation 60 by $\frac{a_{H_3O^+}}{a_{H_3O^+}}$ and arranging the terms

$$\frac{a_{H_2CO_3}}{a_{H_3O^+} \times a_{HCO_3^-}} \times \frac{a_{H_3O^+} \times a_{CO_3^{=}}}{a_{HCO_3^-}} = K_{eq} = \frac{K_2}{K_1}$$
$$= \frac{4.7 \times 10^{-11}}{4.3 \times 10^{-7}}$$
$$= 1.09 \times 10^{-4}$$

where K_1 and K_2 are the ionization constants for the primary and secondary ionization of carbonic acid.

Let us calculate the fraction of a 0.1-*N* solution of sodium bicarbonate that is hydrolyzed.

Let
$$\begin{aligned}
\alpha &= \text{the fraction hydrolyzed} \\
1 - \alpha &= \text{the fraction not hydrolyzed} \\
0.1\,\alpha &= C_{H_2CO_3} = C_{CO_3^=} \\
0.1(1 - \alpha) &= C_{HCO_3^-} \text{ after hydrolysis} \\
1 &= \gamma_{H_2CO_3} \\
0.78 &= \gamma_{CO_3^=} = \gamma_{HCO_3^-} \\
0.78 \times 0.1\,\alpha &= 0.078\,\alpha = a_{CO_3^=} \\
0.78 \times 0.1(1 - \alpha) &= 0.078 - 0.078\,\alpha \\
&= a_{HCO_3^-} \text{ after hydrolysis.}
\end{aligned}$$

Substituting these values in equation 52 we have

$$\frac{0.1\,\alpha \times 0.078\,\alpha}{(0.078 - 0.078\,\alpha)^2} = 1.09 \times 10^{-4}$$

and

$$\frac{0.0078\,\alpha^2}{(0.078 - 0.078\,\alpha)^2} = 1.09 \times 10^{-4}$$

Since $0.078\,\alpha$ is small in comparison with 0.078, it may be dropped without changing the value of the ratio appreciably, and

$$\frac{0.0078\,\alpha^2}{(0.078)^2} = \frac{0.1\,\alpha^2}{0.078} = 1.09 \times 10^{-4}$$

$$\alpha^2 = \frac{1.09 \times 10^{-4}}{0.1} \times 0.078 = 0.85 \times 10^{-4}$$

$$= 85 \times 10^{-6}$$

$$\alpha = 9.2 \times 10^{-3}$$

The activity of the hydronium ions in the solution can be calculated by making appropriate substitutions in the expression

$$\frac{a^2_{H_3O^+} \times a_{CO_3^=}}{a_{H_2CO_3}} = 2.02 \times 10^{-17}$$

Since the activities of the $CO_3^=$ and H_2CO_3 are equal, the activity of the H_3O^+ is equal to the square root of the overall ionization constant of carbonic acid and thus is independent of the concentration of the solution.

II. The cation is a cation acid, that is, it can lose protons. The ammonium ion and the hydrated cations are examples.

a. The anion is a weak base. Consider a solution of ammonium chloride. The equilibrium involved is

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$$

and the expression for the constant is

$$\frac{a_{NH_3} \times a_{H_3O^+}}{a_{NH_4^+} \times a_{H_2O}} = K \tag{61}$$

Since the activity of water is one, the above expression becomes

$$\frac{a_{NH_3} \times a_{H_3O^+}}{a_{NH_4^+}} = K_{eq} = K_{hydrolysis}$$

The expression for the hydrolysis constant is identical with the expression for the ionization constant of the ammonium ion when it acts as an acid. The value of the constant is 5.6×10^{-10} and

$$\frac{a_{NH_3} \times a_{H_3O^+}}{a_{NH_4^+}} = K_{hyd} = 5.6 \times 10^{-10} \tag{62}$$

What is the extent of hydrolysis and the concentration of the hydronium ion in a 0.1-*N* ammonium chloride solution? The ionic strength of the solution is 0.1.

Let

$$\begin{aligned}
\alpha &= \text{fraction hydrolyzed} \\
1 - \alpha &= \text{fraction not hydrolyzed} \\
0.1\,\alpha &= C_{NH_3} = C_{H_3O^+} \\
0.1(1 - \alpha) &= C_{NH_4^+} \\
0.78 &= \gamma_{NH_4^+} = \gamma_{H_3O^+} \\
0.78 \times 0.1\,\alpha &= 0.078\,\alpha = a_{H_3O^+} \\
0.78 \times 0.1(1 - \alpha) &= 0.078 - 0.078\,\alpha = a_{NH_4^+}
\end{aligned}$$

Substituting these values in equation 62 we have

$$\frac{0.1\,\alpha \times 0.078\,\alpha}{0.078 - 0.078\,\alpha} = 5.6 \times 10^{-10}$$

Since $0.078\,\alpha$ is small in comparison to 0.078, it may be dropped and

$$\begin{aligned}
\frac{0.1\,\alpha \times 0.078\,\alpha}{0.078} &= 5.6 \times 10^{-10} \\
\frac{0.0078\,\alpha^2}{0.078} &= 5.6 \times 10^{-10} \\
\alpha^2 &= 5.6 \times 10^{-9} = 56 \times 10^{-10} \\
\alpha &= 7.5 \times 10^{-5}
\end{aligned}$$

The fraction hydrolyzed is 7.5×10^{-5}. The activity of the hydronium ion is $0.078 \times 7.5 \times 10^{-5} = 5.9 \times 10^{-6}$ and the concentration of the hydronium ion is

$$\frac{0.078}{0.78} \times 7.5 \times 10^{-5} = 7.5 \times 10^{-6}$$

b. The anion is a strong base. The case of ammonium cyanide is typical. Since the ammonium ion is an acid and the cyanide ion is a strong base, both ions undergo hydrolysis. The equilibria involved are

$$\begin{aligned} NH_4^+ + H_2O &\rightleftharpoons NH_3 + H_3O^+ \\ CN^- + H_2O &\rightleftharpoons OH^- + HCN \\ H_3O^+ + OH^- &\rightleftharpoons 2\,H_2O \end{aligned}$$

If the solution is not too dilute, nearly all of the hydronium and hydroxide ions from the hydrolysis of the ammonium and cyanide ions react to form water and the net result of the process is

$$NH_4^+ + CN^- \rightleftarrows NH_3 + HCN$$

The equilibrium constant for the system is

$$\frac{a_{NH_3} \times a_{HCN}}{a_{NH_4^+} \times a_{CN^-}} = K_{eq} = K_{hydrolysis} \qquad (63)$$

The value of the constant may be evaluated by multiplying the left hand side of equation 63 by $\frac{a_{H_3O^+}}{a_{H_3O^+}}$ and by rearranging the terms

$$\frac{a_{NH_3} \times a_{H_3O^+}}{a_{NH_4^+}} \times \frac{a_{HCN}}{a_{CN^-} \times a_{H_3O^+}} = \frac{K_{acid\ NH_4^+}}{K_{iHCN}} = \frac{5.6 \times 10^{-10}}{4 \times 10^{-10}} = 1.4 \qquad (64)$$

The expression for the hydrolysis constant of ammonium cyanide, equation 63, may be changed to the more usual form by substituting $\frac{K_W}{a_{OH^-}}$ for the $a_{H_3O^+}$ in the first term of equation 64 and simplifying

$$K_{hyd} = \frac{a_{NH_3} \times K_W}{a_{NH_4^+} \times a_{OH^-}} \times \frac{a_{HCN}}{a_{CH^-} \times a_{H_3O^+}} = \frac{K_W}{K_{iNH_3} \times K_{iHCN}}$$

Let
$$\alpha = \text{fraction hydrolyzed}$$
$$1 - \alpha = \text{fraction not hydrolyzed}$$
$$0.1\,\alpha = C_{NH_3} = C_{HCN}$$
$$0.1(1 - \alpha) = C_{NH_4^+} = C_{CN^-}$$
$$0.78 = \gamma_{NH_4^+} = \gamma_{CN^-}$$
$$1 = \gamma_{HCN} = \gamma_{NH_3}$$
$$0.1\,\alpha = a_{NH_3} = a_{HCN}$$
$$0.78 \times 0.1(1 - \alpha) = 0.078(1 - \alpha) = a_{NH_4^+} = a_{CN^-}$$

Substituting appropriate values equation 63 becomes

$$\frac{0.1\,\alpha \times 0.1\,\alpha}{[0.078(1 - \alpha)]^2} = 1.4$$

and

$$\frac{0.01\,\alpha^2}{(0.078 - 0.078\,\alpha)^2} = 1.4 \qquad (65)$$

Extracting the square root of both sides of equation 65 we have

$$\frac{0.1\,\alpha}{0.078 - 0.078\,\alpha} = 1.19$$

and

$$0.1\,\alpha = 1.19(0.078 - 0.078\,\alpha) = 0.093 - 0.093\,\alpha$$
$$0.1\,\alpha + 0.093\,\alpha = 0.093$$
$$0.193\,\alpha = 0.093$$
$$\alpha = 0.48$$

The per cent of hydrolysis is $(0.48 \times 100) = 48$.

The concentration of hydronium ion can be calculated from the acid ionization constant of the ammonium ion

$$\frac{a_{NH_3} \times a_{H_3O^+}}{a_{NH_4^+}} = 5.5 \times 10^{-10} \qquad (66)$$

The activity of the ammonia is $0.1\,\alpha = 0.1 \times 0.48 = 0.048$ and that of the ammonium ion is $0.078 \times 0.52 = 0.041$, hence equation 66 becomes

$$\frac{0.048 \times a_{H_3O^+}}{0.041} = 5.5 \times 10^{-10}$$

and

$$a_{H_3O^+} = \frac{5.5 \times 10^{-10} \times 0.041}{0.048} = 4.66 \times 10^{-10}$$

The concentration of the hydronium ion is

$$C_{H_3O^+} = \frac{4.66 \times 10^{-10}}{0.78} = 6 \times 10^{-10}$$

c. The anion is amphiprotic. The calculations are complicated and will not be discussed.

Solubility of Slightly Soluble Salts from the Solubility Product Considering the Hydrolysis of the Anion. The solubility of slightly soluble salts of weak acids, the sulfides for example, calculated from the solubility products will be considerably in error unless the hydrolysis of the anion is taken into account. The solubility product of cadmium sulfide is 1.4×10^{-28}. The concentration and the activity of the ions are practically the same at this low ionic strength. If the hydrolysis of the sulfide ion is not taken into consideration, the molar solubility of cadmium sulfide is $\sqrt{1.4 \times 10^{-28}}$ or 1.2×10^{-14}. The hydrolysis of the sulfide ion is shown by the equation

$$S^= + H_2O \rightleftarrows HS^- + OH^- \tag{67}$$

The hydrolysis of the hydrosulfide ion

$$HS^- + H_2O \rightleftarrows H_2S + OH^- \tag{68}$$

will be neglected since the order of magnitude of the final value will not be affected greatly and the calculations can be simplified. The constant for the hydrolysis of the sulfide ion is

$$K_h = \frac{C_{HS^-} \times C_{OH^-}}{C_{S^=}} = \frac{C_{HS^-} \times C_{OH^-} \times C_{H_3O^+}}{C_{S^=} \times C_{H_3O^+}}$$
$$= \frac{K_W}{K_{2^\circ H_2S}} = \frac{10^{-14}}{1 \times 10^{-15}} = 10 \tag{69}$$

Since the solubility of the sulfide is small, the concentration of hydroxide ion is not greatly different from that in water (10^{-7}) and equation 69 becomes

$$K_h = 10 = \frac{C_{HS^-} \times 10^{-7}}{C_{S^=}} \tag{70}$$

or

$$C_{S^=} = \frac{C_{HS^-} \times 10^{-7}}{10} = C_{HS^-} \times 10^{-8} \tag{71}$$

Substituting the value of the concentration of the sulfide ion from equation 71 in the equation for the solubility product of cadmium sulfide, the expression for the solubility product of cadmium sulfide becomes

$$C_{Cd^{++}} \times C_{S^{=}} = C_{Cd^{++}} \times C_{HS^{-}} \times 10^{-8} = 1.4 \times 10^{-28} \quad (72)$$

From the equation

$$Cd^{++} + S^{=} + H_2O \rightleftarrows Cd^{++} + HS^{-} + OH^{-}$$
$$C_{Cd^{++}} = C_{HS^{-}}$$

and substituting the $C_{Cd^{++}}$ for the $C_{HS^{-}}$, equation 72 becomes

$$C_{Cd^{++}} \times 10^{-8} = 1.4 \times 10^{-28}$$

then

$$C^2_{Cd^{++}} \times \frac{1.4 \times 10^{-28}}{1 \times 10^{-8}} = 1.4 \times 10^{-20}$$

and

$$C_{Cd^{++}} = 1.2 \times 10^{-10} = \text{molar solubility}_{CdS}$$

The solubility of cadmium sulfide, ignoring the hydrolysis as calculated from the solubility product, is 1.2×10^{-14}. If the hydrolysis of the sulfide ion is taken into account, the solubility is 1.2×10^{-10} or ten thousand times greater. The divergent values of the solubilities of many insoluble substances given in the literature may be attributed in part to the failure to take into account the hydrolysis of the anion. A second reason for the widely different values is the failure to use carbon dioxide free water in making the determinations. The solubility of the salt is thus actually being determined in a slightly acid rather than a neutral solvent.

EXERCISES

For the activity coefficients of ions see page 119. For the values of constants not given see Table of Equilibrium Constants in the Appendix.

1. Why are the activities of ions used instead of their concentrations?
2. What is the activity coefficient, and upon what does it depend? What is the ionic strength and how is it calculated?
3. Calculate the normality and the molarity of solutions of the following salts which have an ionic strength of 0.01. Assume 100% ionization and no hydrolysis.

Sodium sulfate	Aluminum chloride
Potassium nitrate	Zinc sulfate
Barium chloride	Ferrous ammonium sulfate

4. Calculate the ionic strength of 0.001-*N* solution of each of the following. Assume 100% ionization and no hydrolysis.

Ammonium chloride	Magnesium nitrate
Calcium sulfate	Ferric sulfate
Potassium sulfate	Sodium hydroxide

5. Show that the ionic strength of an electrolyte composed of (*a*) uni-univalent groups is the same as the molarity, (*b*) bi-bivalent groups is four times the molarity and (*c*) uni-bivalent groups is three times the molarity.
6. Under what conditions are the concentrations and activities of ions the same?
7. Calculate the concentration of hydronium and hydroxide ions in a 0.002-*M* solution of potassium nitrate. The constant of water is 10^{-14}.
Ans. 1.06×10^{-7}.
8. Calculate the concentration of hydroxide ion in 0.1-*N* ammonia to a liter of which has been added 0.2 of a mole of potassium chloride. The K_i of ammonia is 1.8×10^{-5}.
9. Calculate the concentration of hydroxide ion in 0.01-*N* ammonia to a liter of which 0.3 of a mole of ammonium sulfate has been added.
Ans. 8.8×10^{-7}.
10. Calculate the concentration of hydronium ion in 0.005-*M* acetic acid to a liter of which has been added 0.02 of a mole of solid ammonium acetate.
11. Calculate the concentration of hydroxide ion in 0.002-*N* acetic acid to a liter of which 0.001 mole of ammonium sulfate has been added.
Ans. 5.62×10^{-11}.
12. Calculate the concentration of hydronium and hydroxide ions in 0.001-*M* sodium sulfate.
13. Calculate the activity coefficient of the hydronium and hydroxide ions in a 0.005-*N* solution of sodium chloride. The concentration of hydroxide and hydronium ions is 1.09×10^{-7} and the constant of water is 1×10^{-14}.
Ans. 0.92.
14. What is the solubility of silver chloride in 0.1-*N* potassium nitrate?
15. What is the solubility of barium sulfate in 0.01-*N* potassium nitrate?
Ans. 1.58×10^{-5}.
16. What is the solubility of silver chromate in 0.005-*N* ammonium sulfate?
17. Calculate the concentration of hydronium ion in 0.1-*M* ammonia to a liter of which 0.1 of a mole of ammonium chloride has been added. The K_i of ammonia is 1.8×10^{-5}. *Ans.* 3.4×10^{-14}.
18. Calculate the concentration of the hydronium ion in a liter of a solution containing 0.1 mole hydrocyanic acid and 0.1 of a mole of potassium chloride. The ionization constant of hydrocyanic acid is 4×10^{-10}. What is the pH of the solution?
19. Calculate the solubility of calcium oxalate in 0.0025-*M* magnesium chloride. The constant for calcium oxalate is 2.3×10^{-9}. *Ans.* 6.0×10^{-5}.
20. Calculate the degree of hydrolysis of 0.1 ammonium nitrate.
21. Calculate the molar solubility of cupric sulfide. Take into account the hydrolysis of the sulfide ion to the hydrogen sulfide ion. The $SP_{CuS} = 4 \times 10^{-38}$, and the secondary ionization constant of hydrogen sulfide is 1×10^{-15}. *Ans.* 2×10^{-15}.
22. Calculate the pH of 0.1-*N* acetic acid containing 0.1 of a mole of potassium acetate per liter. The ionization constant of acetic acid is 1.8×10^{-5}.
23. Calculate the pH of 0.05-*N* ammonia which contains 0.2 of a mole of ammonium chloride per liter. The ionization constant of ammonia is 1.8×10^{-5}. *Ans.* 8.70.

PART II

EXPERIMENTAL

THE CATIONS

CHAPTER VIII

General Laboratory Directions

APPARATUS and its care and use are outlined below:

a. Keep all apparatus clean both when in use and when in the desk.

b. Make a wash bottle of 250 ml. capacity according to Figure 5, page 140.

c. Prepare a set of six stirring rods. Round the ends of three of the glass rods in the flame of a Bunsen burner. Heat the other three rods and draw out one end of each to a diameter of approximately 2 mm.

d. Seal a piece of platinum wire in a piece of glass tubing—see Figure 12, page 155.

e. Obtain the special equipment listed on page 336.

f. Fill the reagent bottles in your desk and fit them with rubber stoppers containing medicine droppers if dropping bottles are not available.

g. Keep the top of your desk clean.

h. Carry out all tests in small centrifuge tubes (3 or 5 ml.) or in test tubes (13 × 100 mm.) unless otherwise directed.

i. To clean glass or porcelain apparatus, use a test tube brush and gritty soap. Then wash it thoroughly with tap water, and finally remove the small amount of tap water left after draining the apparatus by rinsing twice with distilled water, using approximately 5–10% of the volume of the apparatus each time.

Notebook. Provide a notebook in which to record the results of the preliminary experiments or tests which you perform. Record all observations, tests, etc., as soon as you have completed them. Write equations in your notebook to show the behavior of each ion in a group with the reagents with which it comes into contact. This notebook is a good place to outline briefly the properties of the ions.

Chemicals. The substances used in the course are found in racks marked Reagents and Test Solutions.

a. Reagents. The solids and solutions needed to carry out the preliminary experiments and analyses of knowns and unknowns are in small bottles in the racks marked "Reagents." The concen-

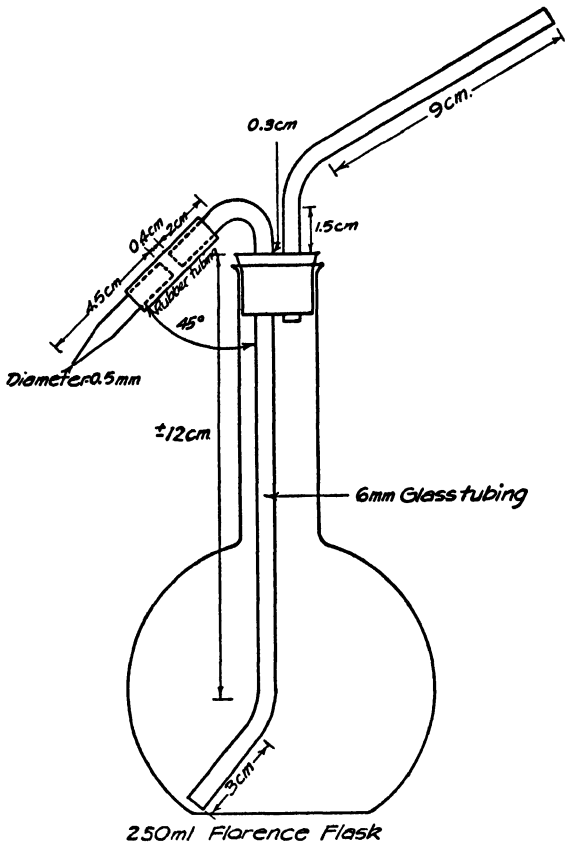


Fig. 5.

trations of the solutions are given on pages 330 to 335. Unless otherwise specified, dilute reagents are to be used. Do not use solids unless specifically directed to do so. Be very careful not to contaminate the solutions by interchanging the droppers or by permitting the end of a dropper to touch other surfaces. If you contaminate a

reagent, empty the bottle, rinse both the dropper and bottle thoroughly with tap and then distilled water. Have the bottle refilled at the stockroom. Before returning a dropper to a reagent bottle, empty the contents of the dropper into the bottle and let the bulb resume its normal shape before replacing it.

b. Test Solutions. The concentration of the ions in the test solutions is the same as that in the known and unknown solutions—5 mg. per ml. or 1 mg. per 4 drops. Use 4 drops of the test solutions to which 5 drops of distilled water have been added to carry out the preliminary experiments, so that the same amount of precipitate will be obtained as when analyzing a known or an unknown. These solutions are also useful for determining the quantity of precipitate which should be obtained when 1 mg. of the ion is present. Final tests which are less definite than those given by 4 drops of the test solution indicate traces of an ion. Ions should be reported as being present as traces or as absent depending on the conclusiveness of the tests.

Preliminary Experiments. Carry out the preliminary experiments assigned by your instructor. Carefully observe what happens and then write equations to show the reactions which take place. Connect the experiment with the theory presented in the lectures. Whether you carry out all of the preliminary experiments or not you are held responsible for the equations which show the reactions involved. Record all observations at the time they are made but do not give a detailed description of the experiment. Answer all questions and write equations for all reactions.

Known Solutions. After a student has performed the preliminary experiments assigned, recorded the observations and the proper conclusions in his notebook, and worked out the equations for the reactions in the experiments whether assigned or not, he should bring his notebook to his instructor to be corrected. If satisfactory, the instructor will quiz the student on the general principles involved in the analysis of the group, and if the questions are answered satisfactorily, the instructor will initial the blank showing that the student is entitled to receive a sample which contains all of the ions of the group. Use 4 drops of the solution to which 5 drops of distilled water have been added and carefully analyze the solution.

Note the quantity of precipitate obtained in each test. The

concentration of the ions in this solution is the same as that in the unknown. Record each step in the analysis as you proceed. Note the colors of the solutions and precipitates.

Unknown Solutions. When the analysis of the known solution has been successfully carried out, go to your instructor for a detailed quiz on the analysis of the group. The quiz will include questions on the reactions involved, colors of ions, solutions, precipitates and the theory. If the questions have been answered satisfactorily, the instructor will initial the blank showing that the student is entitled to a sample of the unknown which may contain any or all of the ions of the group or groups studied. Carefully analyze 4 drops of the solutions to which 5 drops of distilled water have been added for the ions which may be present. Unless otherwise stated by your instructor, the concentration of the ions in an unknown is the same as that in the known. If only a trace of an ion is found, indicate this on the report blank. The valences of the ions present must be given correctly and all spaces on the blank must be filled in before handing it in to be corrected. Duplicate samples will be given only in very exceptional cases.

Record of Laboratory Work. Each test, the result and conclusions drawn should be recorded as soon as it has been performed. To aid students to develop a system of recording data, a part of the record of the analysis of a general unknown is reproduced (page 143).

Calculation of the Volume of Precipitating Agents. In simple combination reactions one equivalent of an anion reacts with one equivalent of a cation. To calculate the volume of the precipitating agent required, it is necessary to determine the number of equivalents of the ion or ions to be precipitated and the number of equivalents per milliliter of the ion used as the precipitating agent. Assume that a sample contains 1 mg. of silver ions and 0.5 mg. of mercurous ions and that 2-*N* hydrochloric acid is to be used as the precipitating agent. There is $\frac{0.00100}{107.9}$, $(0.0000093 = 9.3 \times 10^{-6})$, of an equivalent of silver ion and $\frac{0.0005000}{200.6}$, $(0.0000025 = 2.5 \times 10^{-6})$, of an equivalent of mercurous ion in the solution, making a total of 0.0000118 or 1.18×10^{-5} of an equivalent of cation to be precipitated. Since a milliliter of 2-*N* hydrochloric acid contains 0.002 of

	Substance	Reagent	Result	Conclusion
1	Unknown which may contain Groups I–V		Colorless solution	Probable absence Co^{++}, Ni^{++}, Cr^{+++}, Cu^{++}, Fe^{+++}
2	"	Flame test	Yellow, bright red and green flame	Probable presence Na^{+}, Sr^{++}, and Ba^{++}
3	"	Flame test through chrome alum filter	Violet flame	K^{+} present
4	"	NaOH xs	Red litmus → blue	NH_4^{+} present
5	"	HCl	No ppt.	No Ag^{+} and Hg_2^{++}
6	Solution 5	0.3-*N* HCl and H_2S	No ppt.	No Group II
7	Solution 6	Boil		Removes H_2S
8	Solution 7	NH_3 xs	White ppt.	Al^{+++} indicated, Fe^{+++}, and Cr^{+++} absent
9	Mixture 8	H_2S	Increase in amount of white ppt.	Zn^{++} indicated. Ni^{++}, Co^{++}, Mn^{++}, Fe^{++} absent
10	Ppt. 9	1-*N* HCl	Ppt. dissolved	No CoS and NiS
11		Etc.		
12	Filtrate 9	Evaporate and ignite		Removes NH_4 compounds
13	Residue 13	H_2O, NH_4Cl, NH_3 and $(NH_4)_2CO_3$	White ppt.	Some carbonate of Group IV
	Etc.			

The unknown contains the following ions: K^{+}, NH_4^{+}, etc.. . . . . .
. . . . . .
Traces . . . . . None. . . . . .

If this record is written on the left hand page, the equations for the reactions can be written on the right hand page.

an equivalent of chloride ion, the volume of acid required will be $\frac{0.0000118}{0.00200} = 0.0059$ ml. Since 20 drops from a medicine dropper have a total volume of 1 ml., the number of drops of reagent to be added is 0.0059×20 or 0.12. One drop of the reagent contains sufficient chloride ion to precipitate the silver and mercurous ions present and provides an excess of chloride ion to reduce the solubility of the slightly soluble chlorides.

Since the weights of the ions in a solution of a sample to be analyzed are usually not known, an accurate calculation of the amount of precipitating agent cannot be made. The maximum amount required may be calculated, however, if the weight of the sample used or the maximum quantities of the ion which may be present is known. It is necessary only to assume that the total number of milligrams to be precipitated is that of the ion having the smallest equivalent weight. For example, assume that the maximum amount of an ion in the sample is 1 mg. and that lead, silver and mercurous ions may be present. The equivalent weights of these ions are 103.6, 107.9 and 200.6 respectively. The maximum number of equivalents that can be present is $\frac{0.0030}{103.6}$. If 2-*N* hydrochloric acid is to be used as the precipitating agent the maximum volume required is $\frac{0.00300}{103.6 \times 0.002} = 0.0145$ ml. or $0.0145 \times 20 = 0.29$ of a drop.

Precipitation. Calculate the maximum amount of the precipitating agent (precipitant) required and add it slowly while vigorously stirring the solution which is being tested. The slow addition of the precipitating agent, preferably from a medicine dropper, tends to promote the formation of large particles, thus making the separation of the precipitate from the solution easier. The formation of large particles is also favored by warming the solution. A slight excess of the precipitating agent is added to reduce the solubility of the precipitate by the common ion effect. Separation of the precipitate should not be started until the particles have become large enough to settle to the bottom of the container. A small amount of precipitate in a liquid may be detected by imparting a circular motion to the liquid and carefully examining for the movement of particles.

An appropriate background and suitable light are necessary if a very small amount of precipitate is present.

Precipitation with Hydrogen Sulfide. Since hydrogen sulfide has been proved by the U.S. Bureau of Mines to be as poisonous as prussic (hydrocyanic) acid, care must be exercised in its use. If hydrogen sulfide is bubbled through a solution, the greater part escapes into the air and is wasted, and in a poorly ventilated room may accumulate to such an extent as to be dangerous. To avoid waste and danger, a pressure container must always be used. For small volumes (2 drops—2 ml.) use a small test tube or centrifuge tube. For larger volumes use an Erlenmeyer or Florence flask fitted with a one hole rubber stopper through which a glass tube with fire

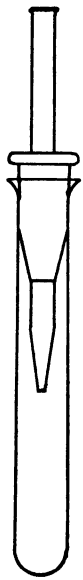


Fig. 6.

polished ends has been inserted. Take care when pushing the tube through the stopper! Wet both the tube and the stopper. The end of the tube should be somewhat above the surface of the solution. If a centrifuge test tube is used, the top part of the bulb from a medicine dropper makes an excellent stopper. Make a small hole in the rubber bulb and carefully push a glass tube through it (Fig. 6). By means of a rubber tube attach the container to the source of the hydrogen sulfide. Allow the hydrogen sulfide to enter and remove the stopper for a moment to displace the air. Replace the stopper and agitate the contents of the container. Take care to prevent the

liquid from being shaken into the rubber tubing, otherwise contamination of the solutions will take place.

A Kipp generator or an improvised individual generator* can be used for preparing hydrogen sulfide if a central supply from tanks or a large generator is not available. The gas can also be prepared by heating equal parts of sulfur and rosin or a mixture of asbestos shreds (5 g.), paraffin (25 g.), and sulfur (15 g.). A mixture of substances which gives off hydrogen sulfide when warmed is sold in glass cartridges under the name of Aitch-tu-ess.†

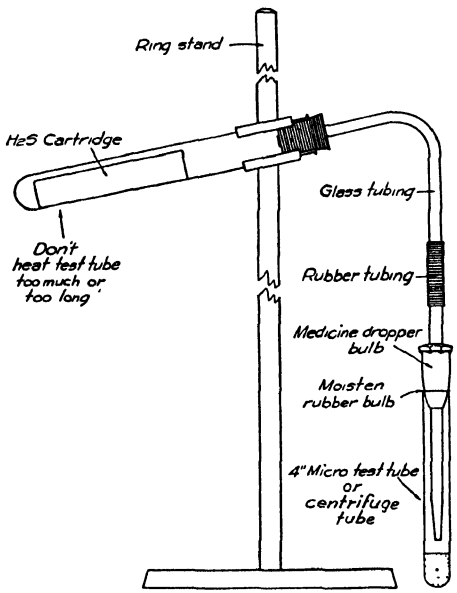


Fig. 7.

A convenient generator for using this product is shown in Figure 7. To avoid too rapid an evolution of hydrogen sulfide, cautiously heat the mixture with a flame 1 inch high. Close the test tube containing the liquid to be treated with hydrogen sulfide with the rubber bulb from a medicine dropper fitted with a glass delivery tube (Fig. 6). Moisten the rubber bulb with water, and do not force it into the test tube. Constantly agitate the contents of the tube

* J. Chem. Educ. *11*:305–7, 1934; *13*:382, 1935; *14*:581, 1937; *16*:34, 1939; *20*:136, 1943; Proc. Iowa Acad. Sc. *44*:107–8, 1937.

† Hengar Co., Philadelphia, Pa.

being saturated with hydrogen sulfide. When the solution in the pressure tube is saturated (about a minute will be sufficient time) remove the flame from beneath the generator and replace the test tube containing the solution being analyzed by one containing distilled water. A solution of hydrogen sulfide is thus prepared for washing the sulfides of Group II and the escape of hydrogen sulfide into the air is prevented.

A small side arm test tube may be used as the container for the solution to be saturated with hydrogen sulfide instead of the ordinary small test tube. Any excess of hydrogen sulfide which is gen-



Fig. 8.

erated escapes through the tube attached to the side arm and passes into water. Be sure that the rubber tube does not extend below the surface of the water.

Separating Precipitates. 1. SEMIMICRO METHODS. Precipitates may be separated from small volumes of liquids by centrifuging or filtering.

(*a*) By centrifuging. A method of separating a precipitate from a small volume of a liquid is to use a centrifuge. By whirling the mixture at a high speed in a centrifuge the precipitate is forced to the bottom of the tube by the centrifugal force which may be two hundred times the force of gravity. Place the liquid containing the precipitate in a centrifuge tube, Figure 8, or a small test tube

(13 × 100 mm.), and balance the centrifuge by placing a second tube containing the same amount of liquid in the opposite arm of the centrifuge. Start the centrifuge and let it run two or three minutes after it develops its full speed. Then, turn off the current and when the centrifuge stops, remove the tube. Do not attempt to stop the centrifuge, for you may injure your hands or cause the precipitate to be dispersed. Incline the tube at an angle of approximately 30 degrees and remove the supernatant liquid (the solution) by slowly drawing it into a medicine dropper. Invert the tube and remove any drops adhering to the walls. Wash the precipitate by adding the wash liquid to the precipitate, breaking up the cake thoroughly with a stirring rod, and centrifuging. Remove the solution as before. Usually a precipitate should be washed at least three times. The first wash liquid should be saved and added to the first solution. As a rule, the precipitate is treated with suitable reagents while in the centrifuge tube. If the precipitate must be transferred to another container, add the reagent to be used, stir the mixture well and pour it into the other container. After the precipitate settles, use the supernatant liquid to remove any precipitate remaining in the centrifuge tube.

(*b*) By filtering. To filter small volumes (2 drops to 2 ml.) the ordinary funnel is not satisfactory. Instead use a filter tube, Figure 9.*

For the filtering medium pack glass wool (No. 790 Pyrex Brand is satisfactory) tightly in the filter tube by means of a glass rod (4 mm.) or the end of a semimicro spatula. A tightly packed layer about 0.5 cm. thick is usually adequate. To filter, assemble the apparatus as shown in Figure 9. Pour the mixture to be filtered into the filtering tube and increase the pressure on the surface of the liquid by compressing the air in the bulb of an ear syringe, the end of which has been cut off so that it projects only a short distance into the filtering tube. The finer the precipitate, the tighter the glass wool must be packed and the less must be the pressure used to force the liquid through the filter. Unless otherwise directed, a precipitate should be washed. To wash a precipitate add repeatedly 3 or 4 drops of a liquid and force it through the glass wool filter by increasing the pressure. The liquid being filtered may be kept hot by immersing the test tube in a water bath. A filter tube may be used to filter relatively large amounts of difficultly filterable precipitates if a second loosely packed plug of glass wool

* Barber, Ind. and Eng. Chem. Anal. Ed. *12*:58–60, 1940. Dimensions are given. The apparatus may be obtained from Wilkens-Anderson Co , Chicago, Ill., or Geo. T. Walker and Co., Minneapolis, Minn.

is placed over the usual plug to retain most of the precipitate. Remove the glass wool filter plug by pushing it through the larger opening of the filter tube with a piece of nichrome or chromel wire.

Aluminum ions have been found in solutions which have been filtered through a glass wool filter. To determine whether the glass wool to be used will contaminate the solution with aluminum ion, circulate dilute hydrochloric acid several times through a glass wool filter and test the solution for aluminum ions by Experiment 17*c*. If a positive test is obtained, the glass wool must be extracted several times with dilute hydrochloric acid and washed thoroughly before use.

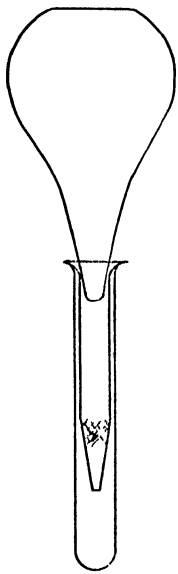


Fig. 9.

Absorbent cotton may be used as the filtering medium instead of glass wool if the precipitate is not suspended in or is not to be treated with concentrated nitric, sulfuric, or acetic acid.

If some of the precipitate remains in the tube in which the precipitation was made, add some of the separated liquid to the tube and after using a stirring rod to loosen any of the precipitate adhering to the walls, again separate the precipitate in the apparatus containing the major part of the precipitate. Repeat until all of the precipitate has been collected.

2. Ordinary Filtration. The technique of using an ordinary funnel is included since many students will take courses in which ordinary funnels are used. The usual method of filtering a solution is to fit a funnel with filter paper whose pores are as large as possible without permitting the precipitate to pass through. A paper with large pores may be used to filter gelatinous or curdy precipitates, such as ferric or aluminum hydroxides or silver chloride, whereas a very fine grained paper must be used for filtering finely divided particles of barium or strontium chromate, or barium sulfate. Prepare the filter for use by folding the paper exactly in half and then once again through the center so that the straight edges do not quite coincide. Then place it in a funnel so that the upper edge of the paper fits snugly about the wall and the paper near the apex of the cone does not quite touch the glass. Tear off the corner of the fold in contact with the glass. Now moisten the paper and replace in the funnel. If the paper has been properly fitted, no air will be drawn between the paper and the funnel, and the stem will be filled with a column of the filtrate which will tend to pull the liquid through the paper, thus increasing the rate of filtration. The paper should be as small as possible and still permit the collection and washing of the precipitate. In no case should it come closer than 5 mm. to the edge of the funnel. If a precipitate passes through the paper, the larger pores may be plugged if the cloudy filtrate is returned to the funnel several times, otherwise a filter paper having smaller pores must be used. Place the funnel in a funnel arm (Fig. 10) rather than in an iron clamp or ring to avoid contamination of the filtrate with rust.

In some cases filtration may be hastened by using suction. To support the apex of the paper, place in the apex of the funnel a basket of glass wool or a small cone of muslin or of platinum. Finely divided precipitates have a tendency to be pulled through the paper.

To prevent the solution from running down the side of the container when it is being poured into the funnel, touch a stirring rod to the lip of the beaker or other container and tip the vessel until the liquid flows down the rod onto the paper without splashing (Fig. 10). The level of the liquid in the filter should never be less than 2 to 3 mm. from the edge of the paper. Finally, wash the precipitate onto the filter by a fine stream from a wash bottle. Wash the precipitate several times, taking care that all of the precipitate and paper come in contact with each portion of the wash liquid and that each portion is allowed to drain before the next is added.

The rate of filtration is affected by the temperature of the wash liquid. The rate of flow of the liquid through a filter is more rapid the less the viscosity of the liquid. At 100° the viscosity of water is only one-sixth of that at 0° and consequently the water will filter faster at the higher temperature. *The rule is always to filter a solution as hot as conditions will allow.*

3. DECANTATION. If a precipitate settles to the bottom rapidly, with care the liquid may be poured off, or removed by a medicine dropper if the volume is small. This process is known as *decantation.* It is usually an inefficient process but is rapid and convenient to carry out. The precipitate may be washed or more soluble

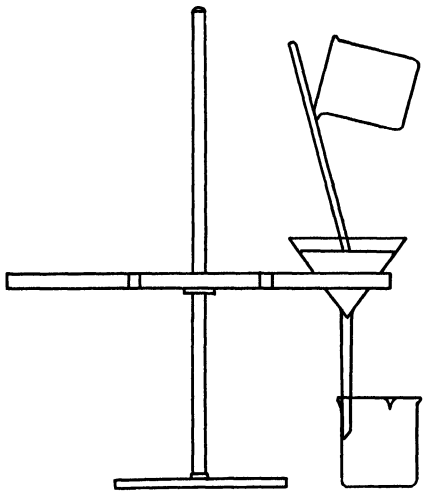


Fig. 10.

parts removed by adding more of the appropriate liquid and repeating the process.

Washing Precipitates. Wash a precipitate by adding from 2 to 5 drops of the wash liquid to the precipitate while it is in the centrifuge tube or on the filter. Let the wash liquid remain in contact with the precipitate a few moments and then separate the precipitate from the wash liquid as described previously. Let the wash liquid remain on the glass wool for a few moments and then force the liquid from the tube with a rubber bulb. Repeat several times. Usually only the first wash liquid is added to the mother liquor. The others are discarded.

Keep a small flask containing distilled water and a medicine dropper on your desk to use for washing precipitates.

If an ordinary funnel and filter paper are used, wash the precipitate with a fine stream of the wash liquid from the wash bottle, taking care that all of the precipitate and filter paper come into contact with each portion of the wash liquid. As in the previous case only the first wash liquid should be added to the filtrate.

Is it more efficient to wash a precipitate several times with small portions of a wash liquid or once or twice with larger portions? That the former is more efficient can be demonstrated mathematically.

Three quantities must be considered: the volume (r) in milliliters of the liquid remaining in contact with the precipitate, the volume (v), of water added for each washing, and the concentration (c) of the dissolved salts in the liquid. The volume of liquid remaining in the precipitate and that of the wash water is assumed to be the same for each operation. From a consideration of these factors the amount of dissolved salts remaining in contact with the precipitate after filtration will be the volume of the liquid times the concentration, or rc. The concentration of the dissolved salts in the liquid in contact with the precipitate after the first washing depends upon the volume of the water used. If v is the volume of water added, the total volume becomes $v + r$ and the new concentration (c_1) of the solution is

$$\frac{rc}{v + r} = c_1 \text{ (after the first washing)} \tag{73}$$

After the liquid (v) passes into the filtrate until the liquid in contact with the precipitate is again r, the amount of dissolved salts in the liquid (r) is given by the product rc_1. The concentration (c_2) of the salts in the solution after adding the second wash water is

$$\frac{rc_1}{v + r} = c_2 \tag{74}$$

If the value of c_1, expressed in terms of the concentration of the impurities in the original solution, equation 73, is substituted in equation 74 and the terms rearranged, the concentration in the filtrate from the second washing is obtained.

$$\frac{r\left(\frac{rc}{v + r}\right)}{v + r} = \left[\frac{r}{v + r}\right]^2 c = c_2 \quad \text{(after the second washing)}$$

If, therefore, the same volume of water is used in making each of n extractions and the amount of liquid left in contact with the precipitate after each extraction is the same, then the concentration of the dissolved salts present in the final liquid is given by the expression

$$c_n = \left[\frac{r}{v + r}\right]^n c \tag{75}$$

in which c_n is the final concentration of the dissolved salts in the liquid left in the precipitate after n washings.

Suppose, for example, that we wish to wash a precipitate with 5 ml. of water. Would it be better to make five washings using 1 ml. for each than to make one washing with the entire amount of water? Assume that $r = 0.1$ ml. and that $c = 0.01$ g./ml. The concentration of the impurities in the liquid adhering to the precipitate after adding 5 ml. of water is calculated by substituting these values in equation 75.

$$c_1 = \frac{0.1}{5 + 0.1} \times 0.01 = 0.0002 = 2 \times 10^{-4}$$

A similar calculation can be made to determine the concentration of impurities after five separate washings with 10 ml. of water.

$$c_5 = \left[\frac{0.1}{1 + 0.1}\right]^5 \times 0.01 = 0.00000006 = 6 \times 10^{-8}$$

Hence, if only the washing and solubility factors are considered, it is 3333 times as efficient to wash a precipitate five times with 1 ml. of water each time as it is to wash once with 5 ml. of water. The time required in either operation is very nearly the same.

Solution and Extraction of Precipitates. To dissolve all or a part of a precipitate, add several drops of the solvent, usually about 4, to the precipitate which is in a centrifuge tube or on a filter in a filter tube. Separate the liquid and repeat the operation several times. To avoid diluting the solution unduly, the process may be repeated several times, using the same liquid. Fresh solvent should be used for the last operation. Portions of a precipitate may be removed by the addition of an appropriate reagent instead of a pure solvent. Both of these processes are usually known as *extraction*. Frequently the efficiency of the extraction depends upon the temperature of the system, hence it is important to maintain the

appropriate temperature. If it is necessary to heat the mixture while dissolving or extracting a precipitate, place the assembled filter or centrifuge tube in a water bath maintained at a suitable temperature. A stand (Fig. 11) is convenient to hold a number of tubes in the water bath. If a stand is not available, a 50 ml. Erlenmeyer flask can be used as a water bath.

Heating the Contents of a Test Tube. To avoid the loss of the liquid contents of a test tube, use a flame 1 to 2 cm. high. Hold the tube at a 15 degree angle with the desk and heat just below the surface of the liquid. Agitate constantly while the heating continues. While

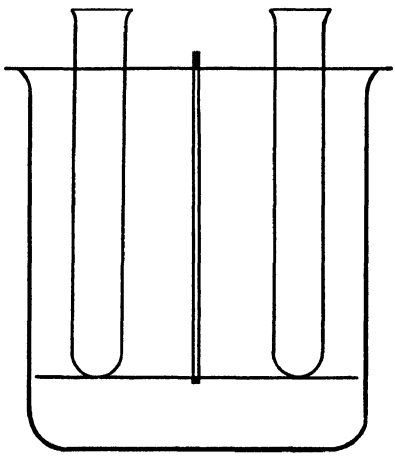


Fig. 11.

heating a liquid in a test tube, *never direct the open end toward your neighbor.*

Bead and Flame Tests. Seal a platinum wire in a piece of glass tubing, one end of which has been drawn to a capillary whose diameter is slightly larger than that of the platinum wire. Insert the glass tube in the rubber stopper and place the stopper in a test tube containing enough dilute hydrochloric acid to cover the wire. To insure a clean wire the acid must be changed frequently. Make a loop 3 mm. in diameter in the end of the wire to hold the solution to be tested in the flame or the sodium carbonate or borax used to make a bead. The assembled apparatus is shown in Figure 12. To make a flame test heat the wire until no color is imparted to the

flame. Then bring the loop into contact with the material to be tested, and heat in the flame. When testing for potassium, use a chrome alum filter to absorb the yellow flame of sodium. To prepare a bead, heat the wire and touch the material used to make the bead with the hot wire. Heat the adhering material until it fuses. Repeat until a bead of sufficient size has been made. Touch the hot bead to the material to be tested and again heat the bead until it fuses. Too much of the precipitate often gives an opaque bead and makes it difficult to determine the color. In some cases the color of the



Fig. 12.

bead is different in the reducing and oxidizing portions of the flame. For the colors of the hot and cold beads which have been heated in the oxidizing or reducing flames, see the table on page 309.

A nickel or chromel wire may be used instead of a platinum wire to make flame tests. However, these wires cannot be used to make bead tests.

Handling of Stoppers of Reagent Bottles. Stoppers of reagent bottles must not be laid on the top of a laboratory table since the stopper will become contaminated by foreign substances. The contents of the bottle will in turn become contaminated and the results

of tests may be useless. The stopper should be removed by pinching it between the index and second fingers of the right hand when the palm is upward and raising the hand. While still retaining the stopper between these fingers, hold the bottle by the thumb and fingers and pour the required amount of reagent. The stopper should then be replaced and the bottle returned to its proper place.

Disposal of Matches, Glass Wool, etc. Keep a beaker on the desk to use as a receptacle for burnt matches, glass wool, etc. Empty the beaker at the close of each laboratory period.

CHAPTER IX

Ions of Group I

PROPERTIES OF METALS AND IONS

SILVER

METAL. Silver is affected only slightly by water or strong, even fused alkalies. It reduces HNO_3 to NO, or NO_2. Hot concentrated H_2SO_4 is reduced to SO_2. Silver does not react with non-oxidizing acids.

Ion. Chloride ion precipitates white curdy AgCl which is soluble in an excess of chloride ion, forming $AgCl_2^-$. It is also soluble in ammonia, forming $Ag(NH_3)_2^+$ and in $S_2O_3^=$, forming $Ag(S_2O_3)^-$ or $Ag(S_2O_3)_2^{\equiv}$.

Strong bases precipitate Ag_2O (brown) insoluble in an excess of the strong base but soluble in ammonia, forming $Ag(NH_3)_2^+$. It is dangerous to keep solutions containing the $Ag(NH_3)_2^+$ because unstable fulminating silver forms.

Ammonia first precipitates AgOH (white) which rapidly turns brown due to its change to Ag_2O. The hydroxide, oxide and chloride are soluble in an excess of ammonia because of the formation of $Ag(NH_3)_2^+$. The less soluble AgBr and AgCNS are but slightly soluble in an excess of NH_3, while AgI is practically insoluble although it reacts to form $2\ AgI \cdot NH_3$.

Hydrogen sulfide or other soluble sulfides precipitate very slightly soluble silver sulfide (dark brown) which is insoluble in NH_3, dilute acids, soluble hydroxides, or dilute cyanides. Silver sulfide dissolves in concentrated solutions of soluble cyanides or in oxidizing agents such as hot nitric acid.

Silver halides are converted to the sulfides by the addition of a soluble sulfide. They are reduced to free silver by adding a metal more active than hydrogen, zinc for example, to an acid suspension of the halide. The solubilities of some of the common salts are given in the following table. The compounds are white unless otherwise stated.

Table XIII. Solubility of Silver Salts (25°)

Salt	Solubility g./100 g. H_2O	Salt	Solubility g./100 g. H_2O
Acetate	1.04	Fluoride	172
Arsenate (brown)	3.85×10^{-4}	Iodate	4.0×10^{-3}
Arsenite	1.15×10^{-3}	Iodide (yellow)	3×10^{-7} (30°)
Borate	0.905	Nitrate	222
Bromate	0.196	Nitrite	0.340
Bromide (light yellow)	8.4×10^{-6}	Oxide (brown)	2.48×10^{-3}
Carbonate (yellow)	3.2×10^{-3}	Oxalate	3.78×10^{-3}
Chloride	1.5×10^{-4}	Phosphate (yellow)	6.8×10^{-4}
Chromate (crimson)	3.6×10^{-3} (30°)	Sulfate	0.796
Cyanide	2.2×10^{-5}	Sulfide (brown)	1.4×10^{-51}
Ferricyanide (orange)	6.6×10^{-5}	Sulfite less than	5.0×10^{-3}
		Thiocyanate	2.5×10^{-5}

MERCURY

Metal. Mercury is below hydrogen in the electromotive force series and consequently does not react with non-oxidizing acids. With dilute nitric acid mercurous nitrate is formed, but with an excess of hot concentrated nitric acid the product is mercuric nitrate.

$$6\ Hg + 8\ H_3O^+ + 2\ NO_3^- \rightleftarrows 3\ Hg_2^{++} + 2\ NO + 12\ H_2O$$
$$Hg + 2\ NO_3^- + 4\ H_3O^+ \text{ conc.} \rightleftarrows Hg^{++} + 2\ NO_2 + 6\ H_2O$$

Mercurous nitrate hydrolyzes to form a basic salt $Hg_2(OH)NO_3$. The hydrolysis may be prevented by the addition of a small amount of nitric acid. On standing, however, the mercurous salt is oxidized. Hot concentrated H_2SO_4 reacts with mercury to give Hg_2SO_4 in the presence of an excess of mercury or $HgSO_4$ if the acid is in excess.

Mercurous Ion. Soluble chlorides precipitate mercurous chloride.

$$Hg_2^{++} + 2\ Cl^- \rightleftarrows Hg_2Cl_2$$

Hydrogen sulfide precipitates a black mixture of mercuric sulfide and mercury.

Strong alkalies give a black precipitate of Hg_2O. The reaction with ammonia depends on the anion associated with the Hg_2^{++}.

$$2\ Hg_2^{++} + NO_3^- + 4\ NH_3 \rightleftarrows 2\ Hg + Hg{=}N{-}HgNO_3 + 3\ NH_4^+$$
$$2\ Hg_2Cl_2 + 4\ NH_3\ xH_2O \rightleftarrows 2\ Hg + Hg{-}N{=}HgCl \cdot xH_2O + 3\ NH_4^+ + 3\ Cl^-$$

The addition of a reducing agent, $SnCl_2$ or $SnCl_4^=$ for example, produces free mercury and Sn^{+4} or $SnCl_6^=$

$$Hg_2^{++} + Sn^{++} \rightleftarrows 2\,Hg + Sn^{++++}$$

or

$$Hg_2^{++} + SnCl_4^{=} + 2\,Cl^- \rightleftarrows 2\,Hg + SnCl_6^{=}$$

Oxidizing agents change mercurous salts into mercuric compounds.

Mercuric Ion. Mercuric nitrate, sulfate and chloride are soluble. The latter is slightly ionized. The iodide is red and soluble in an excess of iodide ions.

$$Hg^{++} + 2\,I^- \rightleftarrows HgI_2$$
$$HgI_2 + 2\,I^- \rightleftarrows HgI_4^{=}$$

Sodium or potassium hydroxides precipitate reddish brown basic salts which change to the yellow oxide on the addition of more hydroxide.

Ammonia reacts with the chloride and nitrate according to the equations:

$$HgCl_2 + 2\,NH_3 \rightleftarrows Hg\begin{matrix}Cl\\NH_2\end{matrix}\text{ (white)} + NH_4^+ + Cl^-$$

$$2\,Hg^{++} + NO_3^- + 4\,NH_3 + H_2O \rightleftarrows H_2NHg\text{–}O\text{–}HgNO_3 + 3\,NH_4^+$$

Hydrogen sulfide when passed into a solution of mercuric chloride forms $HgCl_2 \cdot 2\,HgS$, a white precipitate, which when treated with more of the reagent becomes successively yellow, red, orange, brown and black. The change in color is accompanied by an increase in the ratio of $HgS \cdot HgCl_2$. The black modification changes to the more stable red form when ground in a mortar or when heated with dilute solutions of the alkali or ammonium sulfides. Mercuric sulfide is soluble in sodium sulfide

$$HgS + S^= \rightleftarrows HgS_2^=$$

from which it is precipitated by the addition of an excess of a dilute acid.

$$HgS_2^= + 2\,H_3O^+ \rightleftarrows HgS + H_2S + 2\,H_2O$$

The sulfide is somewhat soluble in hot concentrated hydrochloric acid but is reprecipitated when the solution is saturated with hydrogen sulfide. The sulfide, because of its very low solubility, is attacked only by very strong oxidizing agents.

$$3\,HgS + 2\,NO_3^- + 8\,H_3O^+ + 6\,Cl^- \rightleftarrows 3\,HgCl_2 + 2\,NO + 3\,S + 12\,H_2O$$

Reducing agents reduce mercuric compounds to the mercurous condition and finally to free mercury. Since copper is more active than mercury, mercury is displaced when a drop of a solution containing either a mercurous or mercuric compound is placed on bright copper. When gently polished, the surface assumes the characteristic silvery appearance of an amalgam.

LEAD

Metal. Lead is acted upon by all acids to some extent. The action usually ceases when a film of insoluble salt covers the surface. Lead is dissolved completely by hot hydrochloric and sulfuric acids since their lead salts are soluble in the hot acids, thereby exposing a fresh surface of the metal to the action of the acid.

$$PbCl_2 + 2\ Cl^- \text{ conc.} \rightleftarrows PbCl_4^=$$
$$PbSO_4 + H_2SO_4 \rightleftarrows Pb^{++} + 2\ HSO_4^-$$

With concentrated H_2SO_4 the reaction is

$$Pb + 3\ H_2SO_4 \text{ conc.} \rightleftarrows Pb^{++} + 2\ HSO_4^- + SO_2 + 2\ H_2O.$$

Ion. Soluble chlorides precipitate lead chloride from cold not too dilute solutions of lead salts.

$$Pb^{++} + 2\ Cl^- \rightleftarrows PbCl_2$$

The solubility of lead chloride increases greatly with the temperature. About 3.4 g. are soluble in 100 ml. of boiling water. The chloride is also soluble in an excess of soluble chlorides because of the formation of the $PbCl_4^=$. Soluble bromides and iodides precipitate $PbBr_2$ and PbI_2, soluble in an excess of the reagent, forming complex ions of the type $PbX_4^=$. Soluble chromates precipitate $PbCrO_4$ from HOAc or very dilute HNO_3 solutions of lead salts. Lead chromate is soluble in NaOH, forming $HPbO_2^-$ or $HPb(OH)_4^-$.

Soluble sulfates precipitate lead sulfate. The sulfate is somewhat soluble in strong acids due to the formation of the hydrogen sulfate ion. It is also soluble in acetic acid or soluble acetates because of the formation of slightly ionized lead acetate.

$$PbSO_4 + 2\ OAc^- \rightleftarrows Pb(OAc)_2 + SO_4^=$$

Hydrogen sulfide or other soluble sulfides precipitate lead sulfide (black) from slightly acid solutions. The sulfide is soluble in oxidizing agents. Sulfur is the chief oxidation product but if an active

oxidizing agent is used, some HSO_4^- is formed, especially if the mixture is boiled.

$$3\ PbS + 2\ NO_3^- + 8\ H_3O^+ \rightleftarrows 3\ Pb^{++} + 3\ S + 2\ NO + 12\ H_2O$$

$$3\ PbS + 8\ NO_3^- + 11\ H_3O^+ \rightleftarrows 3\ Pb^{++} + 8\ NO + 3\ HSO_4^- + 15\ H_2O$$

Nitric oxide is a product since the HNO_3 added is diluted by the solution in which the PbS is suspended.

Sodium or potassium hydroxide precipitates the hydroxide (white) which is soluble in an excess of the reagent forming a plumbite.

$$Pb(OH)_2(H_2O)_2 + OH^- \rightleftarrows H_2O + H[Pb(OH)_4]^- \text{ or } [HPbO_2 \cdot 2\ H_2O]^-$$

Ammonia precipitates white basic salts which are insoluble in an excess of the reagent.

REACTIONS OF THE IONS*

Silver Ion, Ag^+

Experiment 1. (*a*) To 4 drops of a solution of silver nitrate add an excess of sodium hydroxide. Does the precipitate dissolve? Has silver oxide any acid properties? The oxide is soluble in an acid, in potassium cyanide and in sodium thiosulfate. Give reasons.

(*b*) From a medicine dropper add, drop by drop, 1-*N* ammonia to 4 drops of a 0.1-*N* silver nitrate solution until no further precipitation takes place, and then add just enough more of the ammonia to give a clear solution. Note the volume of ammonia used. Stir the mixture vigorously during the addition of the ammonia. Explain fully why silver oxide dissolves in ammonia, while it fails to do so in sodium hydroxide. From the amounts of ammonia and silver nitrate used, calculate the formula of the silver-ammine ion.

(*c*) Put into each of three test tubes 1 drop of a 0.1-*N* silver nitrate solution. To one add a sodium chloride solution; to another, a potassium bromide solution; and to the last, a solution of potassium iodide. Note the color of each precipitate. Slowly add an excess of ammonia to each test tube. Shake the contents of the tube after each addition of the reagent. Note the relative solubilities of the precipitates in ammonia.

(1) $Ag^+ + Cl^- \rightleftarrows$?
(2) $Ag^+ + Br^- \rightleftarrows$?
(3) $Ag^+ + I^- \rightleftarrows$?
(4) $AgCl + NH_3 \rightleftarrows$?
(5) $AgBr + NH_3 \rightleftarrows$?
(6) $AgI + NH_3 \leftrightarrows$?

(*d*) Repeat Experiment 1*c* using a solution of potassium cyanide instead of ammonia. Note any difference in results. Explain these differences on the basis

* Test solutions are to be used in the preliminary tests. The concentration of the ions in the test solutions is 5 mg. per ml. This is the same as the concentration of the ions in the unknowns. To have the same concentrations of ions in carrying out preliminary experiments as are used in carrying out the analysis of a known or unknown, add 5 drops of distilled water to 4 drops of the test solution.

of the instability constants of the complex ions $Ag(NH_3)_2^+$ and $Ag(CN)_2^-$. Which is the more stable complex ion? Write the equations.

(*e*) Pass hydrogen sulfide into a solution of silver nitrate. Separate the precipitate and determine whether it is soluble in nitric acid. Is it soluble in ammonia or potassium cyanide? Explain the behavior of the sulfide with each of the reagents.

(*f*) Add just enough ammonia to 4 drops of a silver nitrate solution to give a clear solution. Divide the solution into two portions. To one add an ammonium chloride solution and to the other a large excess of ammonia and then a drop of ammonium chloride. Explain the results. To the ammoniacal solution of silver nitrate from which ammonium chloride gave no precipitate add nitric acid. Explain the results.

(*g*) Gently warm a little freshly precipitated silver chloride with an excess of mercuric nitrate solution. Account for the fact that silver chloride is soluble in mercuric nitrate solution. Would the presence of mercuric nitrate interfere with the precipitation of silver chloride? Is silver chloride soluble in concentrated hydrochloric acid? Explain.

(*h*) Add to 4 drops of a solution of silver nitrate a drop of a solution of sodium dihydrogen phosphate. To another solution of the nitrate add a potassium chromate solution. Give the color of each precipitate. Explain why each precipitate is soluble both in ammonia and in nitric acid.

(1) $Ag^+ + H_2PO_4^- \rightleftarrows ? + ?$
(2) $Ag^+ + CrO_4^= \rightleftarrows ?$

(*i*) Add 2 drops of silver nitrate solution to 10 drops of mercurous nitrate. Add hydrochloric acid to the mixture until precipitation is complete. Separate the precipitate and wash it several times with 4 drops of water. Then extract the precipitate several times with 4 drops of ammonia. Acidify the combined ammoniacal extract with nitric acid. Note the amount of precipitate (if any) formed. Compare this result with that obtained by adding hydrochloric acid to 10 drops of water containing 2 drops of silver nitrate. Explain.

Mercurous Ion, Hg_2^{++}

Experiment 2. (*a*) Add to 4 drops of a solution of mercurous nitrate an excess of sodium hydroxide. Complete:

$$Hg_2^{++} + OH^- \rightleftarrows Hg_2O + ?$$

(*b*) To 4 drops of a solution of mercurous nitrate add hydrochloric acid until no further precipitation is observed. Separate the precipitate, wash it thoroughly, and extract it with ammonia. A black insoluble product consisting of free mercury and the white mercuric compound $Hg(NH_2)Cl$ results. Mercurous mercury is identified and separated from silver by this reaction. Complete:

(1) $Hg_2^{++} + Cl^- \rightleftarrows ?$
(2) $Hg_2Cl_2 + NH_3 \rightleftarrows Hg + Hg{=}N{-}HgCl + NH_4 + Cl^-$

(*c*) Treat separately 4 drops of mercurous nitrate with potassium bromide-potassium iodide and hydrogen sulfide respectively. Give the color of each precipitate. Complete:

(1) $Hg_2^{++} + Br^- \rightleftarrows ?$
(2) $Hg_2^{++} + I^- \rightleftarrows ?$
(3) $Hg_2^{++} + H_2S + H_2O \rightleftarrows HgS + Hg + ?$

Lead Ion, Pb^{++}

Experiment 3. (*a*) Precipitate lead chloride from 8 drops of lead nitrate solution by the addition of 1 drop of hydrochloric acid. Separate the precipitate from the solution and then wash it once with 10 drops of cold water. Extract it twice with 5 drops of boiling water. A total of 10 drops of water is to be used. Does the chloride dissolve? Is either silver chloride or mercurous chloride soluble in hot water? Pass hydrogen sulfide into one half of the solution from which the lead chloride was precipitated. Does a precipitate form? Treat the other half of the solution with a few drops of a potassium chromate solution. What is the precipitate? How completely does hydrochloric acid precipitate lead chloride from a lead nitrate solution? Can lead chloride be separated from a mixture of $AgCl$, Hg_2Cl_2 and $PbCl_2$ by treating the three substances with boiling water? Complete:

(1) $Pb^{++} + H_2S + H_2O \rightleftarrows ? + ?$
(2) $Pb^{++} + CrO_4^{=} \rightleftarrows ?$

(*b*) Add an excess of sodium hydroxide to a solution of a lead salt. Is lead hydroxide soluble in sodium hydroxide? Has lead hydroxide any acidic property? Is lead hydroxide soluble in ammonia? Explain. Complete:

(1) $Pb(OH)_2 + OH^- \rightleftarrows HPbO_2^- + ?$ or
$Pb(H_2O)_2(OH)_2 + OH^- \rightleftarrows [HPb(OH)_4]^- + ?$
(2) $Pb(OH)_2 + NH_3 \rightarrow ?$ or $Pb(H_2O)_2(OH)_2 + NH_3 \rightarrow ?$

(*c*) Add an excess of sodium hydroxide to a suspension of lead sulfate. Why is lead sulfate soluble in sodium hydroxide? In concentrated sulfuric acid? Why does the presence of nitric acid increase the solubility of lead sulfate? Add 3 drops of a concentrated solution of ammonium acetate and 1 drop of acetic acid to a suspension of lead sulfate. Explain why the precipitate dissolves. Complete:

(1) $Pb^{++} + SO_4^{=} \rightleftarrows ?$
(2) $PbSO_4 + H_2SO_4$ conc. $\rightleftarrows ?$
(3) $PbSO_4 + OAc^- \rightleftarrows ? + ?$

(*d*) To 4 drops of a solution of lead acetate add a drop of solution of potassium chromate. A yellow precipitate of lead chromate forms. Explain why this precipitate is formed under these conditions and why lead chromate is soluble in an excess of sodium hydroxide or an excess of nitric acid. Complete:

(1) $Pb(OAc)_2 + CrO_4^{=} \rightleftarrows ? + ?$
(2) $PbCrO_4 + OH^-$xs $\rightleftarrows ? + ?$
(3) $PbCrO_4 + H_3O^+ \rightleftarrows ? + ? + ?$

ANALYSIS

Procedure I

1. Precipitation of the Chlorides. To 4 drops of the unknown solution add 5 drops of distilled water and enough dilute hydrochloric acid to precipitate the ions of Group I. Use a centrifuge (page 147) or a filter tube assembly (page 148) to separate the

precipitate from the cold reaction mixture. Wash the precipitate four times with 4 drops of 2-*N* hydrochloric acid to dissolve any antimonyl or bismuthyl chlorides which may have precipitated. Add the wash liquid to the solution to be tested for Groups II–V. If the solution can contain only the ions of Group I, the washing of the precipitate with 2-*N* hydrochloric acid should be omitted.

Analysis of Group I—Procedure I

Original Unknown Containing Any or All of the Ions of Groups I–V (4 drops): Add 5 drops of distilled water and enough dilute HCl to precipitate completely the ions of Group I. Separate the precipitate from the cold mixture and wash the precipitate 4 times with 4 drops of 2-*N* hydrochloric acid. Add the wash liquid to the solution. If only the ions of Group I are present, omit washing with 2-*N* HCl.

<table>
<tr><td colspan="2">Precipitate: $PbCl_2$, if a large concentration was present, Hg_2Cl_2, AgCl. Extract 5 times with 4 drops of boiling water.</td><td rowspan="3">Solution: Ions of Groups II–V. Adjust the acidity and test for the ions of Groups II–V.</td></tr>
<tr><td colspan="2">Precipitate: Hg_2Cl_2, AgCl. Extract twice with 5 drops of NH_3. Separate the precipitate.</td><td>Solution: Pb^{++}. Add a drop of K_2CrO_4 to the solution. A yellow precipitate of $PbCrO_4$ proves the presence of Pb^{++}.</td></tr>
<tr><td>Precipitate: Hg, Hg–N–HgCl and Ag if a large quantity of Hg_2^{++} was present. The black precipitate is sufficient proof of the presence of Hg_2^{++}. Test for Ag by Proc. I, 5.</td><td>Solution: $Ag(NH_3)_2^+$. Acidify the solution with HNO_3. A white precipitate of AgCl proves the presence of Ag^+.</td></tr>
</table>

2. Separation and Identification of the Lead Ion. Extract (page 153) the precipitate five times with 4 drops of boiling water. Add a drop of potassium chromate to the solution. A yellow precipitate of lead chromate proves the presence of the lead ion.

3. Separation and Identification of the Silver Ion. While the precipitate which may contain silver and mercurous chlorides is in the centrifuge tube or on the filter extract it twice with 5 drops of

ammonia. Separate any residue which may remain. The solution contains the silver as the silver-diammine ion. Acidify the solution with nitric acid. A white precipitate of silver chloride proves the presence of the silver ion. If the test for the silver ion is negative and a large quantity of the mercurous ion is found subsequently, the absence of silver ion is not proved until the absence of silver in the black residue has been established.

4. Identification of the Mercurous Ion. A black residue of Hg and Hg=N–HgCl is usually sufficient proof of the presence of the mercurous ion in the sample. However, if further evidence is required, the residue may be dissolved as directed in the following paragraph. After boiling to remove the excess of the oxidizing agent, the solution may be tested for the mercurous ion by adding stannous chloride.

5. Identification of the Silver Ion in the Presence of a Large Amount of Mercurous Ion. If the silver ion was not found by Procedure I, 3, treat the black residue of Hg and Hg=N–HgCl, which may contain silver, with 3 drops of hydrochloric acid and 1 drop of bromine water. Heat the mixture in a hot water bath, separate any residue which remains and wash it several times with boiling water. Extract the residue with concentrated ammonia. Acidify the ammoniacal solution with nitric acid. A yellowish precipitate of silver bromide proves the presence of the silver ion.

Discussion of the Analysis

Precipitating Agent. The reagent used for precipitating this group is hydrochloric acid, or, to be more specific, the chloride ion. The concentration of the acid should never be great, for silver chloride is soluble in solutions containing a high concentration of chloride ion. If the unknown solution has an acidity greater than that of 0.5-*N* hydrochloric acid, ammonium chloride should be used instead of hydrochloric acid to precipitate the ions of the group.

The presence of mercuric nitrate in the solution hinders the precipitation of silver chloride since silver chloride is slightly soluble in mercuric nitrate at ordinary temperatures and more readily soluble at higher temperatures. This action seems to be due partially to the formation of slightly ionized mercuric chloride

$$2\,AgCl + Hg^{++} \rightleftarrows 2\,Ag^{+} + HgCl_2.$$

and also to the formation of a double salt. An excess of the precipitant tends to prevent the solvent action of the mercuric salt since mercuric ions are removed as part of the slightly ionized mercuric

chloride. It will not be necessary to modify the procedure for precipitating the group unless the ratio of the concentration of the silver ion to that of mercuric nitrate is quite small.

If no precipitate is obtained on adding the precipitating agent for this group, the absence of the lead ion has not been proved, for lead chloride is somewhat soluble, and if only small amounts are present will not precipitate as the chloride in Group I but it will be precipitated as lead sulfide in Group II. Its molar solubility at 18° is 0.035 and it is far more soluble in hot water. Hence, lead chloride can be separated from the chlorides of silver and mercurous mercury by extracting the precipitate with boiling water.

Lead Ion. The identification of the lead ions is discussed under Group II. In Group I the lead chloride is precipitated only if a large concentration is present. It is separated from the chloride of silver and mercurous mercury by extraction with boiling water. If the solution is allowed to cool, often characteristic crystals of lead chloride separate in the form of needles. The presence of lead ion is confirmed by adding a drop of a solution of potassium chromate.

$$Pb^{++} + CrO_4^{=} \rightleftarrows PbCrO_4$$

Mercurous Ion. After lead chloride is removed the other chlorides are treated with ammonia. Mercurous chloride gives with this reagent a black residue consisting of finely divided mercury and a mercuric compound Hg=N−HgCl. The equation

$$2\,Hg_2Cl_2 + 4\,NH_3 + xH_2O \rightleftarrows 2\,Hg + Hg{=}N{-}HgCl\cdot xH_2O + 3\,NH_4^+ + 3\,Cl^-$$

may represent the reaction. Ammonia, at the same time, dissolves silver chloride, forming the complex silver-diammine ion. The filtrate containing the silver-diammine ion will be cloudy if the lead chloride was not extracted completely from the precipitated chlorides by the boiling water.

Silver Ion. The silver ion is identified by destroying the silver-diammine ion with nitric acid, thus precipitating the silver chloride.

$$Ag(NH_3)_2^+ + 2\,H_3O^+ + Cl^- \rightleftarrows AgCl + 2\,NH_4^+ + 2\,H_2O$$

When a large quantity of mercurous chloride is present, an appreciable amount of silver may be retained by the black residue obtained by the treatment with ammonia. When only a trace of silver

chloride is present, it may not dissolve. It is possible that the silver ion is reduced to metallic silver by the free mercury.

$$2\,AgCl + 2\,Hg \rightleftarrows Hg_2Cl_2 + 2\,Ag$$

High concentrations of chloride ion react with silver chloride to form the silver chloride ion and should be avoided, if possible.

$$Cl^- + AgCl \rightleftarrows AgCl_2^-$$

EXERCISES

1. What effect will the presence of a large concentration of the chloride ion have on the analysis of Group I?
2. Why should the ions of Group I be precipitated from a cold solution?
3. Account for the formation of a white precipitate on the addition of a chloride to a solution being analyzed for Group I. The precipitate is soluble in 2-*N* hydrochloric acid.
4. How many milliliters of 2-*N* sodium hydroxide are required to react with 1 mg. of magnesium ion? *Ans.* 0.04 ml. or 0.8 drop.
5. How many milliliters of 0.1-*N* sulfuric acid will be required to neutralize 10 ml. of a 0.2-*N* base?
6. How many milliliters of 2-*N* ammonium carbonate will contain 0.003 of an equivalent of carbonate? *Ans.* 1.5 ml.
7. How many milliliters of 0.1-*N* acid are required to neutralize 15 ml. of 3-*N* base?
8. What is the most efficient method of washing a precipitate?

CHAPTER X

Ions of Group II

PROPERTIES OF METALS AND IONS

LEAD

THE PROPERTIES of lead and its ions have been discussed with the ions of Group I (page 160).

BISMUTH

Metal. Bismuth is below hydrogen in the electromotive force series, and the metal is insoluble in non-oxidizing acids. Oxidizing acids, such as concentrated H_2SO_4 or HNO_3, dissolve bismuth and are reduced to SO_2 or NO_2. The solution contains Bi^{+++}, BiO^+ or possibly BiX_4^-. Bismuthyl (BiO^+) compounds precipitate when an acid solution of a bismuth salt is diluted.

Ion. Soluble bases precipitate $Bi(OH)_3$ (white) even in the presence of ammonium salts.

Alkali hydrogen stannite reduces $Bi(OH)_3$ immediately. The product is "coal black" metallic bismuth. Hydrogen sulfide precipitates Bi_2S_3 (dark brown) which is soluble in dilute nitric acid.

Bismuth sulfide is not sufficiently acidic to react with sulfide ions even when they are present in a high concentration. Bismuth sulfate is not very soluble in concentrated H_2SO_4 but dissolves in the 10% acid used to precipitate lead sulfate.

COPPER

Metal. Copper does not react with non-oxidizing acids in the absence of oxygen, but in the presence of oxygen forms cupric ions and water. The metal is attacked by dilute or concentrated HNO_3 and by hot concentrated H_2SO_4, forming the corresponding salt.

Ions. Cuprous salts are usually white or yellow in color. They are only slightly soluble in water but are soluble in HCl, forming

$CuCl_2^-$. Cuprous compounds are oxidized to blue or green cupric compounds by moist air.

Sodium or potassium hydroxides precipitate yellow cuprous and blue cupric hydroxides from solutions of their respective salts. Cupric hydroxide is slightly soluble in an excess of the reagent, forming $Cu(OH)_4^=$ which has a deep blue color. Ammonia precipitates a blue basic cupric salt which is changed to the hydroxide on the addition of an equivalent amount of the base. Cupric hydroxide dissolves in an excess of the NH_3, forming $Cu(NH_3)_4^{++}$ (cupric-tetrammine ion) which is deep blue.

Cupric sulfide (black) forms when a soluble sulfide is added to a solution of a cupric salt.

Soluble cyanides reduce $Cu(NH_3)_4^{++}$ to $Cu(CN)_2^-$ (colorless), a complex ion which is much more stable than $Cd(CN)_4^=$.

Cupric salts impart a blue to green color to a non-luminous flame.

The ferrocyanide ion precipitates $Cu_2Fe(CN)_6$ (pink) from solutions of Cu^{++} acidified with HOAc.

CADMIUM

Metal. Cadmium dissolves slowly in dilute HCl or H_2SO_4 but dissolves readily in HNO_3, forming bivalent salts.

Ion. Soluble bases precipitate $Cd(OH)_2$ (white) which is not amphiprotic. In the presence of NH_4^+ no precipitation takes place. An excess of NH_3 dissolves the precipitate, forming $Cd(NH_3)_4^{++}$.

Sulfide ions precipitate the yellow sulfide from solutions having a $C_{H_3O^+}$ of 0.3. The sulfide is soluble in hot dilute nitric acid.

Cyanide ions precipitate $Cd(CN)_2$ (white) from solutions containing $Cd(NH_3)_4^{++}$. Cadmium cyanide is soluble in an excess of CN^-, forming $Cd(CN)_4^=$ (colorless) which is more highly dissociated than $Cu(CN)_2^-$; hence only CdS is precipitated from a solution containing both complex ions.

Ferrocyanide ions added to an HOAc solution or cadmium ions precipitate $Cd_2Fe(CN)_6$ (white). The slightly ionized cadmium chloride reacts with chloride ions to form $CdCl_4^=$.

MERCURY

The properties of mercury and its ions have been discussed on page 158.

ARSENIC

Metal. The element is dissolved by an oxidizing acid

$$As + H_3O^+ + NO_3^- \rightleftarrows NO + HAsO_2 + H_2O$$

$$As + 3\,H_3O^+ + 5\,NO_3^-\ \text{conc.} \rightleftarrows HAsO_4^= + 5\,NO_2 + 4\,H_2O$$

but does not react appreciably with non-oxidizing acids.

Ions. Hydrogen sulfide precipitates As_2S_3 (yellow) insoluble in concentrated HCl. A high $C_{H_3O^+}$ favors the precipitation of the sulfide.

Arsenious sulfide reacts with $S^=$

$$3\ S^= + As_2S_3 \rightleftarrows 2\ AsS_3^=$$

or with OH^-.

$$6\ OH^- + As_2S_3 \rightleftarrows AsS_3^= + AsO_3^= + 3\ H_2O$$

Orthoarsenites $AsO_3^=$ or $AsS_3^=$ may become meta AsO_2^- or AsS_2^- by loss of oxygen or sulfur as a part of H_2O or H_2S. The $AsO_3^=$ and $AsS_3^=$ react with H_3O^+ according to the equations

$$4\ H_3O^+ + AsO_2^- \rightleftarrows As^{+++} + 6\ H_2O$$
$$6\ H_3O^+ + 2\ AsS_3^= \rightleftarrows As_2S_3 + 3\ H_2S + 6\ H_2O$$

Arsenious sulfide is oxidized by the $S_2^=$.

$$S^= + As_2S_3 + 2\ S_2^= \rightleftarrows 2\ AsS_4^=$$

Arsenic sulfide is insoluble in concentrated HCl. It reacts with $S^=$

$$As_2S_5 + 3\ S^= \rightleftarrows 2\ AsS_4^=$$

The thioarsenate ion reacts with hydronium ions to form As_2S_5.

$$2\ AsS_4^= + 6\ H_3O^+ \rightleftarrows As_2S_5 + 3\ H_2S + 6\ H_2O$$

Arsenic sulfide is soluble in alkalies.

$$As_2S_5 + 6\ OH^- \rightleftarrows AsS_4^= + AsO_3S^= + 3\ H_2O$$

Ammonium molybdate in HNO_3 reacts with an arsenate to give a yellow precipitate of ammonium arseno-molybdate $[(NH_4)_3AsO_4 \cdot 12\ MoO_3 \cdot 5\ H_2O]$ analogous to that obtained by the reaction with a phosphate. The arseno-molybdate does not precipitate from a cold solution. The temperature must be raised to at least 60 to 70°. Arsenites do not give a precipitate with ammonium molybdate.

All arsenic compounds are reduced by $SnCl_4^=$ to As.

$$5\ SnCl_4^= + 2\ AsO_4^= + 10\ Cl^- + 16\ H_3O^+ \text{ conc.} \rightleftarrows 2\ As + 24\ H_2O + 5\ SnCl_6^=$$

The ions of Sb, Sn, Pb, Cu and Cd do not interfere. The ions of Ag, Hg and Bi are reduced to the metals.

The Marsh and Gutzeit tests are used to detect very small concentrations of arsenic. The arsenic is reduced to AsH_3 and appropriate tests are made for this gas.

ANTIMONY

Metal. Antimony is not attacked by strong non-oxidizing acids. Hot nitric acid reacts to give Sb_2O_3 or possibly Sb_4O_6.

$$2\,H_3O^+ + 2\,Sb + 2\,NO_3^- \rightleftarrows Sb_2O_3 + 2\,NO + 3\,H_2O$$

Concentrated nitric acid gives

$$2\,Sb + 10\,NO_3^- + 10\,H_3O^+ \text{ conc.} \rightleftarrows Sb_2O_5 + 10\,NO_2 + 15\,H_2O$$

If the metal is treated with concentrated HCl and if small portions of concentrated HNO_3 are added from time to time, the final product is $SbCl_6^{=}$.

$$Sb + 6\,H_3O^+ + 6\,Cl^- + 3\,NO_3^- \rightleftarrows 3\,NO_2 + SbCl_6^{=} + 9\,H_2O$$

Ions. The halides of antimony, $SbCl_3$ and $SbCl_5$, react with water or bases forming white insoluble SbOCl and SbO_2Cl. These oxy-compounds form $SbCl_4^-$, or $SbCl_6^{=}$ and $SbCl_6^-$ when treated with an excess of hydrochloric acid. The insoluble oxy-chlorides are converted to sulfides by the action of hydrogen sulfide.

The oxy-halides are soluble in an excess of a strong base, forming $Sb(OH)_4^-$ or $Sb(OH)_6^-$.

Ammonia, even in excess, precipitates SbOCl and SbO_2Cl from solution of tri- and pentavalent antimony chlorides.

Hydrogen sulfide changes neutral or slightly acid solutions or suspensions of antimony compounds to the trivalent antimony sulfide (orange). The trisulfide is soluble in dilute hydrochloric acid. It is also soluble in alkali or ammonium sulfides and hydrogen sulfides. Both sulfides are sparingly soluble in NH_3 and $(NH_4)_2CO_3$.

Metals above antimony in the electromotive force series, such as Zn, Sn, Fe and Al, reduce the ions to the free metal.

Pauling has shown recently that all of the antimonates are salts of the acid $H[Sb(OH)_6]$. Thus, the salt usually given the formula $Na_2H_2Sb_2O_7$ is really $NaSb(OH)_6$.

TIN

Metal. The metal dissolves slowly in dilute H_2SO_4 and HCl, forming Sn^{++} and probably $SnCl_4^=$. Concentrated H_2SO_4 is reduced to

SO_2 by the metal. Very dilute nitric acid dissolves it, forming Sn^{++} and NH_4^+; while concentrated HNO_3 oxidizes the tin to $SnO_2 \cdot xH_2O$. With aqua regia, $SnCl_6^=$ is formed.

Ions. Stannous salts are hydrolyzed by water, forming basic salts, $Sn\begin{matrix}OH\\Cl\end{matrix}$ for example.

Soluble hydroxides and Na_2CO_3 precipitate $Sn(OH)_2$ or basic salts. These are soluble in an excess of the reagent, forming $Sn(OH)_4^=$.

Stannous salts are oxidized to stannic compounds by oxygen.

$$2\,SnCl_4^= + 4\,Cl^- + O_2 + 4\,H_3O^+ \rightleftarrows 2\,SnCl_6^= + 6\,H_2O$$

Stannic compounds are not reduced by hydrogen sulfide but are reduced by metals higher than Sn in the electromotive force series.

From 0.3-*N* HCl containing Sn^{++} hydrogen sulfide precipitates dark brown SnS, insoluble in alkali sulfides or hydrogen sulfides. Stannous sulfide is oxidized to yellow SnS_2 by the persulfide ion, $S_2^=$. From 0.3-*N* HCl solutions of stannic salts, yellow SnS_2 is precipitated. This sulfide is soluble in alkali sulfides and hydrogen sulfides.

Mercuric chloride oxidizes $SnCl_4^=$ to $SnCl_6^=$ and is reduced to Hg_2Cl_2 or Hg.

Both stannous and stannic hydroxides are amphiprotic, and dissolve in acids and bases.

REACTIONS OF THE IONS: DIVISION A

Bismuth Ion, Bi^{+++}

Experiment 4. (*a*) Pass H_2S into 4 drops of a solution of bismuth nitrate. What is the color of the precipitate? Is the precipitate soluble in boiling, dilute nitric acid? Balance:

$$Bi_2S_3 + H_3O^+ + NO_3^- \rightleftarrows Bi^{+++} + S + NO + H_2O$$

(*b*) Add an excess of ammonia to 4 drops of bismuth nitrate solution. Is bismuth hydroxide soluble in an excess of ammonia? Divide the liquid in which the precipitate is suspended into two parts and use them in *c* and *d*.

(*c*) Dissolve one part of the precipitated bismuth hydroxide in a minimum of hydrochloric acid and add the solution to 1 ml. of water. What is the result? What does this result indicate as to the basic property of bismuth hydroxide? Is bismuth hydroxide soluble in excess of sodium hydroxide? Complete:

(1) $Bi(OH)_3 + H_3O^+ \rightleftarrows ? + ?$ or $Bi(OH)_3(H_2O)_3 + H_3O^+ \rightleftarrows ? + ?$

(2) $Bi^{+++} + H_2O + Cl^- \rightleftarrows Bi\begin{matrix}O\\Cl\end{matrix} + ?$

(*d*) Add to 3 drops of a stannous chloride solution an excess of sodium hydroxide (about 9 drops) and treat the other part of the bismuth hydroxide precipitate with the sodium hydrogen stannite solution. Balance:

$$Bi(OH)_3 + HSnO_2^- \rightleftarrows Bi + HSnO_3^- + ?$$

or

$$Bi(OH)_3(H_2O)_3 + HSn(OH)_4^- \rightleftarrows Bi + HSn(OH)_6^-$$

Copper Ion, Cu^{++}

Experiment 5. (*a*) Treat 4 drops of a cupric nitrate solution with an excess of ammonia. What is formed? Add ammonium sulfide to the solution. What is the precipitate? What is the color of the cupric-ammine ion? Balance:

(1) $Cu^{++} + NH_3 \rightleftarrows Cu(NH_3)_4^{++}$
(2) $Cu(NH_3)_4^{++} + H_2S \rightleftarrows CuS + NH_4^+ + ?$

(*b*) Add to a solution containing the cupric-ammine ion a little more than enough potassium cyanide solution to discharge the blue color. Caution! Cyanides are poisonous! Do not acidify a solution containing a cyanide. Treat the solution with ammonium sulfide. Does any precipitate form in this case? Judging from this experiment and the preceding one, which is the more stable, the cupric-ammonio ion or the cuprocyanide ion, $Cu(CN)_2^-$? Potassium cyanide precipitates cuprous cyanide from a solution of a cupric salt. Explain. Complete:

(1) $Cu(NH_3)_4^{++} + CN^-$ xs $\rightleftarrows [Cu(CN)_2]^- + (CN)_2 + ?$
(2) $Cu(CN)_2^- + S^= \rightleftarrows ?$

(*c*) To 4 drops of a dilute solution of a cupric salt acidified with acetic acid add a drop of a potassium ferrocyanide solution. The formation of a reddish-brown precipitate is a delicate test for copper. Complete:

$$Cu^{++} + Fe(CN)_6^= \rightleftarrows ?$$

Cadmium Ion, Cd^{++}

Experiment 6. (*a*) Add an excess of sodium hydroxide to 4 drops of a solution of cadmium nitrate. Is cadmium hydroxide soluble in a solution of sodium hydroxide? Balance:

(1) $Cd^{++} + OH^- \rightleftarrows ?$ or $Cd(H_2O)_4^{++} + OH^- \rightleftarrows Cd(H_2O)_2(OH)_2 + ?$
(2) $Cd(OH)_2 + OH^-$ xs $\rightleftarrows ?$

(*b*) Treat 4 drops of cadmium nitrate solution with an excess of ammonia. Does a clear solution result? Explain. Balance:

$$Cd(OH)_2 + NH_3 \rightleftarrows Cd(NH_3)_4^{++} + OH^-$$

(*c*) To ammoniacal solutions prepared by adding an excess of ammonia to 4 drops of copper nitrate and of cadmium nitrate, in separate test tubes, add potassium cyanide, a drop at a time, until the reaction is complete, and then

add 2 or 3 drops in excess. Saturate each of these solutions with hydrogen sulfide. Balance:

(1) $Cu(NH_3)_4^{++} + CN^- \rightleftarrows Cu(CN)_2^- + (CN)_2 + NH_3$
(2) $NH_3 + (CN)_2 + H_2O \rightleftarrows CN^- + CNO^- + NH_4^+$
(3) $Cd(NH_3)_4^{++} + CN^- \rightleftarrows Cd(CN)_4^- + NH_3$
(4) $Cd(CN)_4^- + H_2S \rightleftarrows CdS + CN^- + HCN$

Explain the results. Can these reactions be used to separate copper from cadmium?

REACTIONS OF THE IONS: DIVISION B

Mercuric Ion, Hg^{++}

Experiment 7. (*a*) To 4 drops of a solution of mercuric chloride add a few drops of stannous chloride. Note the color of the precipitate. Add an excess of the reagent. Account for the change in color of the precipitate. Can the mercuric ion be identified by this means? Complete:

(1) $HgCl_2 + Sn^{++} + Cl^- \rightleftarrows Hg_2Cl_2 + ?$
(2) $Hg_2Cl_2 + Sn^{++} + Cl^- \rightleftarrows Hg + ? +$

(*b*) Place a drop of solution of mercuric chloride on a bright piece of copper. Gently polish the spot and note any change in the appearance. Complete:

$$HgCl_2 + Cu \rightleftarrows ? + ?$$

This is a very characteristic and specific reaction of the ions of mercury.

(*c*) Saturate a solution of mercuric chloride with hydrogen sulfide. Note any color changes that take place during the treatment with hydrogen sulfide. Separate the precipitate and digest it with 15 drops of sodium hydrogen sulfide reagent. Does the sulfide dissolve? What is formed? Treat the solution with dilute hydrochloric acid. What is the precipitate? Dissolve the precipitate in hydrochloric acid containing a few drops of concentrated nitric acid. Boil the solution to remove all the chlorine and nitrosyl chloride (NOCl) and then add to it a solution of stannous chloride. The formation of white precipitate is a characteristic test for the mercuric ion. If an excess of stannous ion is present, the white precipitate should turn gradually to a gray one. Complete:

(1) $HgS + (HS^-) + S^= + (HS_2^-) \rightleftarrows HgS_2^=$
(2) $HgS_2^= + H_3O^+ \rightleftarrows HgS + ? + ?$
(3) $H_3O^+ + NO_3^- + HgS + Cl^- \rightleftarrows HgCl_2 + S + H_2O + NO$

(*d*) Boil a little freshly precipitated mercuric sulfide with 5 drops of concentrated hydrochloric acid. Separate any precipitate which forms, dilute the solution to five times its volume and saturate with hydrogen sulfide. Using instability constants, solubility products, etc., account for your observations. Complete:

(1) $HgS + Cl^-$ conc. $+ H_3O^+$ conc. $\rightleftarrows HgCl_4^= + H_2S + ?$
(2) $HgCl_4^= + (H_2O) \rightleftarrows HgCl_2 + Cl^-$

Arsenious Ion, As^{+++}; Arsenite Ion, $AsO_3^{=}$; Arsenate Ion, $AsO_4^{=}$

Experiment 8. (*a*) Pass hydrogen sulfide into a hydrochloric acid solution of 4 drops of arsenious acid and then into 4 drops of a water solution of the oxide. Account for the difference in behavior. Add hydrochloric acid to the water solution after saturating it with hydrogen sulfide. Is arsenious sulfide precipitated? Explain this behavior of the sulfide. Is arsenious sulfide soluble in concentrated hydrochloric acid?

(*b*) Add an excess of ammonia to 4 drops of a solution of arsenic acid. Then add 10 drops of magnesium nitrate mixture. Separate the precipitate which forms, add a drop of acetic acid to the precipitate on the filter or in the centrifuge tube, and then a drop of silver nitrate. Complete:

$$(1)\ HAsO_4^{=} + NH_3 + Mg^{++} + (NH_4^{+}) \rightleftarrows ?$$
$$(2)\ Ag^{+} + HAsO_4^{=} + OAc^{-} \rightleftarrows ? + ?$$

(*c*) Prepare a small quantity of arsenic sulfide and dissolve it in a little ammonia. Neutralize the solution with concentrated nitric acid. If a precipitate forms, dissolve it by boiling with a slight excess of concentrated nitric acid. To the clear hot solution add an excess of ammonium molybdate. Allow the mixture to stand for several minutes. The formation of a yellow precipitate is a test for an arsenate. Complete:

$$(1)\ As_2S_5 + NH_3 + H_2O \rightleftarrows NH_4^{+} + AsS_4^{=} + AsO_3S^{=}$$
$$(2)\ AsS_4^{=} + AsO_3S^{=} + H_3O^{+} + NO_3^{-} \rightleftarrows AsO_4^{=} + NO + HSO_4^{-} + H_2O$$
$$(3)\ AsO_4^{=} + H_3O^{+} + MoO_4^{=} + NH_4^{+} \rightleftarrows (NH_4)_3AsO_4 \cdot 12\,MoO_3 \cdot 5\,H_2O + ?$$

(*d*) Gutzeit Test. Place a few pieces of granulated zinc (arsenic free) in a small test tube and add 1 ml. of sulfuric acid. Loosely plug the upper part of the test tube with glass wool and moisten it with 2 drops of lead acetate. Place a piece of filter paper moistened with silver nitrate on the top of the tube for a minute. Then remove the paper and the glass wool. Add to the tube 4 drops of a solution of an arsenate. Replace the plug of glass wool and the filter paper so that the new spot will be near but not over the first. After a minute remove the paper and compare the stains. Unless the second stain is darker than the first, no arsenic is present. The first stain may be caused by arsine formed from the arsenic present in the chemicals used. The test is not satisfactory in the presence of oxidizing agents or in the presence of sulfides. Complete:

$$HAsO_4^{=} + Zn + H_3O^{+} \rightleftarrows AsH_3 + H_2O + ?$$

Antimonous Ion, Sb^{+++}; Antimonite Ion, SbO_2^{-}; Antimonate Ion, $Sb(OH)_6^{-}$

Experiment 9. (*a*) Add a drop of antimonous chloride to 10 drops of water. Recall the behavior of bismuth trichloride. Is the precipitate formed by the hydrolysis of antimonous chloride soluble in tartaric acid? What salts show a strong tendency to hydrolyze? Complete:

$$(1)\ SbCl_4^{-} + H_2O \rightleftarrows Sb\overset{Cl}{\underset{O}{}} + ? + ?$$
$$(2)\ SbOCl + H_2\,Tar \rightleftarrows (SbO)H\,Tar + ?$$

(*b*) Saturate 4 drops of a solution of antimonous chloride with hydrogen sulfide. What is formed? Note the color of the precipitate. Dissolve the precipitate in the sodium hydrogen sulfide reagent. Complete:

(1) $SbCl_4^- + H_2S + H_2O \rightleftarrows ? + ? + ?$
(2) $Sb_2S_3 + HS^- + (S^-) + HS_2^- \rightleftarrows ? + ?$

(*c*) To 4 drops of a solution of antimonous chloride add one half its volume of concentrated hydrochloric acid. Drop two or three pieces of aluminum wire or granules of magnesium into the solution and warm it. Note what occurs. Complete:

$$SbCl_4^- + Al + (H_3O^+) \rightleftarrows Sb + ? + ?$$

(*d*) Does a solution containing the antimonyl tartrate ion, upon the addition of an excess of water, behave analogously to a solution containing the antimonous ion? Saturate a solution of potassium antimonyl tartrate with hydrogen sulfide. What is the precipitate? Explain why a precipitate is not formed in the first case and why one is produced in the latter.

(*e*) Place a drop of antimonous chloride on a filter paper. Then place a drop of phosphomolybdic acid on the paper so that the edges of the drop overlap. If a blue color does not form immediately, warm the paper. Other reducing agents act similarly. Complete:

$$H_3PO_4 \cdot 12\ MoO_3 + SbCl_4^- + H_3O^+ + Cl^- \rightleftarrows H_3PO_4 \cdot 10\ MoO_3 \cdot Mo_2O_5 + SbCl_6^- + ?$$

Stannous Ion, Sn^{++}; Stannic Ion, Sn^{+4}

Experiment 10. (*a*) Treat 4 drops of a stannous chloride solution with sodium hydroxide until no further precipitation occurs. Divide the mixture into two parts and to one part add an excess of sodium hydroxide. Does the precipitate dissolve? Add hydrochloric acid to the other part. What is formed? Complete:

(1) $Sn^{++} + OH^- \rightleftarrows Sn(OH)_2$
or $Sn(H_2O)_4^{++} + OH^- \rightleftarrows Sn(H_2O)_2(OH)_2 + ?$
(2) $Sn(OH)_2 + OH^- \rightleftarrows HSnO_2 + ?$
or $Sn(H_2O)_2(OH)_2 + OH^- \rightleftarrows (Sn\overset{(H_2O)}{(OH)_3})^- + ?$
(3) $Sn(OH)_2 + H_3O^+ \rightleftarrows ? + ?$
or $Sn(H_2O)_2(OH)_2 + H_3O^+ \rightleftarrows Sn(H_2O)_4^{++} + ?$

(*b*) Saturate a slightly acid solution of 4 drops of stannous chloride with hydrogen sulfide. What is the brown precipitate? Is the precipitate soluble in concentrated hydrochloric acid? Boil some stannous sulfide for five minutes with some sodium hydrogen sulfide reagent. Does the sulfide dissolve? Is stannous sulfide soluble in sodium hydroxide? Is it soluble in yellow ammonium sulfide? Does it dissolve in colorless ammonium sulfide? Why is stannous tin oxidized before precipitating the ions of Group II as sulfides? Complete:

$$SnS_2 + HS^- + (S^= + HS_2^-) \rightleftarrows SnS_3^= + ?$$

(*c*) Add a few drops of mercuric chloride to 4 drops of a stannous chloride solution. Note the formation of a grey to white precipitate. Do these reactions give a characteristic test for the stannous ion? Complete:

(1) $Sn^{++} + HgCl_2 + Cl^- \rightleftarrows Hg_2Cl_2 + ?$
or $SnCl_4^= + HgCl_2 \rightleftarrows Hg_2Cl_2 + SnCl_6^=$
(2) $Sn^{++} + Hg_2Cl_2 + Cl^- \rightleftarrows ? + ?$
or $SnCl_4^= + Hg_2Cl_2 \rightleftarrows ? + SnCl_6^=$

(*d*) Dissolve some freshly prepared stannic sulfide in hot, concentrated hydrochloric acid and boil the solution to remove all of the hydrogen sulfide. Divide the solution into two portions. Treat one portion with a mercuric chloride solution. Does any action take place? Add to the other portion a few pieces of aluminum wire and warm the mixture. After a few minutes test the solution for stannous tin with a solution of mercuric chloride. Explain all observations. Complete:

(1) $SnS_2 + H_3O^+ + Cl^- \rightleftarrows SnCl_6^= + ? + ?$
(2) $SnCl_6^= + Al + (H_3O^+ + Cl^-) \rightleftarrows SnCl_4^= + Al^{+++} + ?$
(3) $SnCl_4^= + HgCl_2 \rightleftarrows Hg_2Cl_2 + ?$

General Reactions

Experiment 11. (*a*) Add 4 drops of solutions of cadmium nitrate and mercuric chloride to 3 drops of water and then sufficient hydrochloric acid to make the solution 1-*N*. Saturate the solution with hydrogen sulfide. Dilute the solution until it is 0.3-*N* with respect to the hydrochloric acid and again saturate the solution with hydrogen sulfide. Explain your observations in terms of solubility products. Separate the precipitate and reserve it for (*b*).

(*b*) Digest the precipitate with 15 drops of sodium hydrogen sulfide reagent. Carefully observe what takes place and explain. Which ions of Group II act like cadmium and which like mercury?

(*c*) Acidify 8 drops of a cadmium nitrate solution with 1 drop of 2.5-*N* hydrochloric acid and saturate the solution with hydrogen sulfide. To 4 drops of cadmium nitrate solution add 4 drops of concentrated hydrochloric acid and saturate with hydrogen sulfide. Dilute this solution with eight or ten times its volume of water and again treat it with hydrogen sulfide. Give the results obtained with these solutions and compare their behavior with that of a solution of a zinc salt under like conditions; of a solution of a copper salt under the same conditions. What effect has a high concentration of the hydronium ion on the equilibrium of a hydrogen sulfide solution and on the concentration of the sulfide ion? Explain all facts observed in this experiment.

(*d*) From Experiment 11c it was learned that a low concentration of hydronium ion is sufficient to prevent the precipitation of Group III but permits the complete precipitation of Group II. To determine the proper hydronium ion concentration, put into each of six test tubes or depressions of a porcelain testing tile 1 drop of methyl violet solution and proceed as follows: Treat one of the solutions of methyl violet with 1 drop of 0.5-*N* hydrochloric acid and add respectively to the other five 1 drop each of 0.4, 0.3, 0.25, 0.2 and 0.1-*N* hydrochloric acid. The blue-green tint given by the 0.3-*N* hydrochloric acid indicates the concentration of hydronium ions recommended for the precipitation of Group II.

ANALYSIS

Procedure II

1. Precipitation of the Sulfides. Add 2 drops of nitric acid to the solution from Group I or 4 drops of the unknown which has been acidified with hydrochloric acid. Evaporate the solution nearly to dryness in a test tube. Remove the tube from the flame while the residue is still moist. Heat the upper part of the tube to remove any

condensate. Moisten the residue with 1 drop of 12-*N* hydrochloric acid. Warm the tube and dilute the acid to 1-*N* by adding 10 drops of water and 1 drop of ammonium iodide. Warm the solution, and saturate it with hydrogen sulfide. When hydrogen sulfide is used as a precipitating agent, use a pressure tube (page 145). Dilute the mixture to 0.3-*N*. Heat to boiling and again saturate with hydrogen sulfide. Separate any precipitate and wash it with hydrogen sulfide water. If phosphates may be present, test the solution for phosphates by Experiment 31*c* before precipitating Group III. *Test the solution for the ions of Groups III, IV and V by Procedures III, IV and V.* If ammonium iodide is not available, a small crystal of iodine may be used or an equivalent amount of sodium or potassium iodide, provided the test for sodium or potassium ions be made on a different portion of the sample. An alternate method of adjusting the concentration of the hydronium ion is to add 2 drops of nitric acid to the sample which, if alkaline, has been acidified with hydrochloric acid. Neutralize by the careful addition of ammonia from a medicine dropper. Stir the solution after each addition of the base and test with litmus. To the neutral solution add 1 drop of 1-*N* ammonium iodide and sufficient concentrated hydrochloric acid to make the solution 1-*N*. After warming, saturate the solution with hydrogen sulfide. Use a pressure tube. Dilute to 0.3-*N* by increasing the volume three and one-third times. Heat the mixture to boiling and again saturate with hydrogen sulfide. Treat the precipitated sulfides and the solution as directed in the first method.

2. Separation of the Ions of Division A from Division B. Immerse the centrifuge tube or filtering apparatus containing the sulfides of Group II in boiling water, add 20 drops of sodium hydrogen sulfide reagent and heat 5 minutes. Separate the sulfides of Division A from the solution of the thiosalts of Division B. If a filter is used, circulate the sodium hydrogen sulfide reagent through the filter several times. Separate the residue and wash it three times with 5 drops of the sodium hydrogen sulfide reagent, twice with 5 drops of 1% sodium hydroxide, and once with water. The solution from the residue should be yellow and clear.

3. Identification of the Lead Ion. Place the centrifuge tube or the filter tube assembly containing the sulfides of Division A in the boiling water bath. Add 5 to 10 drops of dilute sulfuric acid and a drop of concentrated nitric acid to oxidize the sulfide to free sulfur. Separate the sulfur with a centrifuge or if the precipitate is on a filter blow the liquid through the filter and circulate the hot filtrate through the filter repeatedly. Boil the solution to remove the excess of nitric acid and dilute with 9 drops of water. Separate

any residue by centrifuging or by filtering the liquid through the glass wool containing the sulfur and any precipitate of lead sulfate which may be on the filter. Wash the precipitate twice with 4 drops of 2-*N* sulfuric acid. Reserve the combined solution and the first wash acid to test for bismuth, copper and cadmium. To confirm the presence of lead in the precipitate in the centrifuge tube or on the filter, add 3 drops of ammonium acetate and 1 drop of acetic acid. If the precipitate is on a filter pass the solution through the filter repeatedly. To the solution add a drop of potassium chromate. The formation of a yellow precipitate of lead chromate proves the presence of lead.

4. Identification of the Bismuth Ion. Add an excess of ammonia to the solution from the precipitate of lead sulfate. The formation of a white flocculent precipitate indicates the presence of the bismuth ion. Confirm the presence of bismuth by adding 5 drops of a freshly prepared solution of sodium hydrogen stannite to the precipitate. The immediate formation of a black substance (chiefly Bi) proves the presence of bismuth.

5. Identification of the Cupric Ion. If the solution from the precipitate of bismuth hydroxide has a deep blue color, the presence of the cupric-ammine ion is proved. If the solution is colorless, acidify 3 drops of the solution with acetic acid and add a drop of potassium ferrocyanide. A pink precipitate proves the presence of a small amount of cupric ion. The solution used for the ferrocyanide test should be discarded. A white precipitate indicates the absence of cupric ions and the probable presence of cadmium ions.

6. Identification of the Cadmium Ion. If the cupric ion is present, convert it to the cuprocyanide ion by the addition of an excess of potassium cyanide. Saturate the solution with hydrogen sulfide. The formation of a yellow precipitate of cadmium sulfide proves the presence of cadmium ions. If the cadmium sulfide is so finely divided that it forms a yellow colloidal solution, acidify the solution with acetic acid and heat in the water bath. If the cadmium sulfide does not precipitate, add a drop of hydrochloric acid and again heat.

At times a slight black precipitate is obtained when the test for the cadmium ion is made, which may mask the yellow color of cadmium sulfide. If such is the case, separate the precipitate and wash it with water to free it from potassium cyanide. Heat the precipitate from five to ten minutes with 5 drops of 1.2-*N* sulfuric acid. Separate the residue, dilute the acid solution with three times its volume of water and saturate the diluted solution with hydrogen sulfide. A yellow precipitate of cadmium sulfide proves the presence

of cadmium ion. Cadmium sulfide is the most soluble sulfide of the metals of Division A. For this reason cadmium sulfide may be dissolved in 1.2-*N* sulfuric acid, while an interfering sulfide, probably lead or bismuth, remains insoluble.

If the cupric ion was proved absent, barely acidify the solution which may contain the cadmium ion with dilute hydrochloric acid and saturate it with hydrogen sulfide. A yellow precipitate proves the presence of the cadmium ion.

7. Precipitation of the Sulfides of Division B and the Separation of Mercuric and Arsenic Sulfides from Those of Antimony and Tin. Add an excess of dilute hydrochloric acid to the solution of the thiosalts of Division B and separate the precipitate. Wash the precipitate once with water. Reject the solution and wash water. To the precipitate add 10 to 15 drops of concentrated hydrochloric acid and heat the mixture for 10 minutes in the water bath. If a filter is used and the acid goes through the glass wool filter, return it to the filter tube. Separate any residue and saturate the solution with hydrogen sulfide for one minute. Add any precipitate to the residue. The precipitate contains a little sulfur and may contain the sulfides of arsenic and mercury. Test the solution for the ions of tin and antimony.

8. Identification of the Mercuric Ion. Add 5 to 10 drops of ammonia to the precipitate and warm the mixture. Separate the residue. Test the solution for arsenic by Procedure II, 9. The residue consists of sulfur and may contain mercuric sulfide. While the residue is still in the tube dissolve the mercuric sulfide by adding 5 drops of concentrated hydrochloric acid, and one drop of concentrated nitric acid. Heat the mixture. Separate the precipitate and boil the solution to remove the excess of nitric acid and oxides of nitrogen. Place two drops on a bright penny. A gray deposit which becomes silvery when polished shows the presence of mercury. Add to the rest of the liquid a *freshly prepared solution of stannous chloride.* A white precipitate of mercurous chloride followed by a gray or black precipitate of free mercury proves the presence of mercuric ion.

9. Identification of the Arsenic Ion. Add a slight excess of concentrated nitric acid to the ammoniacal solution which may contain the sulphoxyarsenate ($AsO_3S^{\equiv}$) and thioarsenate ions. Heat the solution if it is not clear and divide it into two parts. To the first part add an excess of ammonia and 5 drops of a solution of the magnesium nitrate reagent. Scratch the inside of the test tube and allow the solution to stand at least 10 minutes if a precipitate does not form immediately. A white precipitate of magnesium ammonium arsenate indicates the presence of the arsenate ion.

Confirm by separating the precipitate and adding a drop of acetic acid and a little silver nitrate to the precipitate. The formation of a chocolate colored precipitate of silver arsenate proves the presence of the arsenate ion. To the second portion add an equal volume of a nitric acid solution of ammonium molybdate. Stand the tube in a beaker containing water at 85 to 90°. The formation of a yellow precipitate of hydrated ammonium arseno molybdate $(NH_4)_3AsO_4 \cdot 12\ MoO_3 \cdot 5\ H_2O$ proves the presence of the arsenate ion. If a white precipitate of molybdic oxide (MoO_3) forms, dissolve it in a minimum amount of concentrated ammonia and then acidify the solution with nitric acid and proceed as before.

10. Separation of Antimony and Tin Ions. Boil the solution from the precipitate, which may contain mercuric and arsenic sulfides, to remove the hydrogen sulfide. Add an equal volume of water to the solution and a piece of aluminum wire ¼ inch long. Heat the acid solution in a boiling water bath until all of the aluminum wire has dissolved. Then add 1 drop of concentrated hydrochloric acid and heat. Immediately separate any precipitate and add 4 drops of mercuric chloride to the solution.

11. Identification of Antimonous Ion. Dissolve the coal-black precipitate of antimony in a mixture of 1 drop of tartaric acid and 4 drops of nitric acid. Dilute the solution to ten times its volume and saturate it with hydrogen sulfide. An orange precipitate confirms the presence of antimonous ions.

12. Identification of Tin Ions. The formation, in the mercuric chloride solution, Procedure II, 10, of a white precipitate of mercurous chloride confirms the presence of the stannous ion.

Discussion of the Analysis

Precipitating Agent. Only a small concentration of the sulfide ion is necessary to separate the ions of Group II from those of Groups III–V because the values of the solubility products of the sulfides of Group II are much lower than those of the succeeding groups. The concentration of the sulfide ion must be regulated carefully, otherwise the sulfides of Group III having the smaller values of the solubility products will be precipitated with those of Group II. If the concentration of sulfide ion is not large enough, the more soluble sulfides of Group II—those having the larger solubility products—will not be precipitated completely. The concentration of the sulfide ion is fixed by the equation

$$C_{S^=} = \frac{K_{H_2S}}{C^2_{H_3O^+}}$$

Original Unknown (4 drops) or Solution from Group I: Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, Hg^{++}, As^{+++}, $AsO_4^{=}$, Sb^{+++}, Sb^{+5}, Sn^{+4}, Sn^{++}. Add 2 drops of HNO_3 and evaporate until a moist residue remains. Add 1 drop NH_4I and HCl conc. Dilute until 1-*N*. Warm and saturate with H_2S. Dilute to 0.3-*N*, heat to boiling and again saturate with H_2S. Separate the precipitate—wash it with H_2S water. See alternate method, page 178.

Precipitate: PbS, Bi_2S_3, CuS, CdS, HgS, As_2S_3, Sb_2S_3, SnS_2. Immerse the centrifuge tube or filter apparatus in boiling water. Add 20 drops of NaHS reagent and heat 5 minutes. Separate the precipitate and wash it three times with 5 drops of the reagent. Then wash twice with 5 drops of 1% NaOH.

Solution: Groups III–V. Boil to remove all H_2S and test for a phosphate and the remaining groups.

Precipitate: PbS, Bi_2S_3, CdS, CuS. Add 5–10 drops of dilute H_2SO_4, one drop of HNO_3 conc., heat and let stand to convert the sulfide to sulfur. Separate the residue. Heat the solution to remove HNO_3 and add 9 drops of water. Separate the precipitate.

Solution: $HgS_2^{=}$, $AsS_4^{=}$, $SbS_4^{=}$, $SnS_3^{=}$. See next page for the analysis of Division B.

Precipitate: $PbSO_4$ and S. Wash twice with 4 drops of 2-*N* H_2SO_4. Extract with a mixture of 3 drops of NH_4OAc and 1 drop of HOAc. Confirm by adding one drop of K_2CrO_4.

Solution: Bi^{+++}, Cu^{++}, Cd^{++}. Add an excess of NH_3.

Precipitate: $Bi(OH)_3$. Confirm by adding 5 drops of $NaHSn(OH)_4$ to the precipitate. The immediate formation of a black substance (chiefly Bi°) confirms the presence of Bi^{+++}.

Solution: $Cu(NH_3)_4^{++}$, $Cd(NH_3)_4^{++}$. A blue solution proves the presence of copper. If the solution is colorless acidify 3 drops with HOAc and add $K_4Fe(CN)_6$. A pink ppt. indicates a small amount of Cu^{++}. (Discard.) Convert the remainder of the $Cu(NH_3)_4^{++}$ to $Cu(CN)_2^{-}$ by adding KCN until the solution is colorless, add one drop more and saturate with H_2S or add one drop of colorless $(NH_4)_2S$.

Precipitate: CdS. If the precipitate is black, test for Cd^{++} by Procedure II, 6.

Solution: Pour into the sink and allow the water to run.

Filtrate: $HgS_2^=$, $AsS_4^{\equiv}$, $SnS_3^=$, $SbS_4^{\equiv}$. Add an excess of HCl.

Precipitate: S, HgS, As_2S_5, Sb_2S_5, SnS_2. Add 10 to 15 drops of HCl conc. Heat at 70° for 10 minutes and separate any precipitate. Saturate the solution with H_2S for one minute. Separate the precipitate and combine it with the main precipitate.

Solution: Discard.

Precipitate: S, HgS, As_2S_5. Extract twice with 5 to 10 drops of NH_3. Warm.

Solution: $SbCl_4^-$, $SnCl_6^=$. Heat until all H_2S is gone. Add an equal volume of water to the remainder of the solution and a piece of aluminum wire 1/4 inch long. Heat until the wire dissolves. Then add one drop of HCl conc. and heat. Separate immediately and add the solution to a $HgCl_2$ solution.

Precipitate: S, HgS. Dissolve the HgS by adding 5 drops of HCl conc. and one drop HNO_3 conc. Boil to remove Cl_2 and nitrogen oxides. Separate the precipitate.

Solution: $AsO_3S^{\equiv}$, $AsS_4^{\equiv}$. Carefully add a slight excess of HNO_3 conc. Heat if the solution is not clear. Divide into two parts.

To the first add an excess of NH_3 and then the $Mg(NO_3)_2$ reagent. Scratch and let stand. A white crystalline ppt. of $MgNH_4AsO_4$ indicates the presence of the arsenate ion. Confirm by separating any precipitate and adding a drop of HOAc and $AgNO_3$ to the precipitate. A chocolate ppt. of Ag_3AsO_4 proves the presence of the arsenate ion.

To the second portion add an equal volume of $(NH_4)_2MoO_4$. Let the tube stand in a beaker containing water at 85° to 90°.

A yellow precipitate of hydrated $(NH_4)_3AsO_4 \cdot 12\,MoO_3 \cdot 5\,H_2O$ proves the presence of the arsenate ions.

Precipitate: S. Discard.

Solution: $HgCl_4^=$. Place 2 drops on a bright penny. Grey stain indicates mercuric ion. To the remainder add $SnCl_2$.

Precipitate: Hg_2Cl_2, white turns gray on the further addition of $SnCl_2$ confirms the presence of Hg^{++}.

Solution: Discard.

Precipitate: Sb. Treat the black scales with a mixture of 1 drop of tartaric acid and 4 drops of HNO_3.

Solution: $(SbO)HC_4H_4O_6$. Dilute to 10 times its volume and saturate with H_2S.

Precipitate: Sb_2S_3.

Solution: Discard.

Solution: $SnCl_4^=$. This reacts with $HgCl_2$ forming Hg_2Cl_2, thus confirming the presence of Sn^{++}.

This expression shows the necessity for regulating carefully the concentration of the hydronium ion. The proper concentration of hydronium ion to permit the quantitative precipitation of the ions of Group II having the larger values of their solubility products and yet exclude the precipitation of the sulfides of Group III having the smaller values of their solubility products is given on page 94. Concentrated nitric acid is added to oxidize any arsenious arsenic to an oxidation state of five. The nitric acid also oxidizes any stannous to stannic tin, thus making it unnecessary to have polysulfide in the sodium hydrogen sulfide reagent used to separate the sulfides of Divisions A and B. The oxidation of the arsenic prevents the loss of arsenious chloride during the evaporation to dryness. Concentrated hydrochloric acid and ammonium iodide are then added and the acidity is adjusted to 1-*N*. The hot solution is saturated with hydrogen sulfide to reduce the arsenate ion to the arsenite ion. The reduction is aided by the iodide ion which is added. The concentration of hydronium ions is finally adjusted to 0.3-*N* and the solution is again thoroughly saturated with hydrogen sulfide. It is always well to saturate the solution from Group II with hydrogen sulfide to be sure that no further precipitation of the sulfides of Group II and particularly the sulfides of arsenic occur. Arsenic pentasulfide is difficult to precipitate since arsenic in its higher oxidation state has almost no metallic properties. The arsenate ion, even in the presence of a high concentration of hydrochloric acid, is in equilibrium with a negligible concentration of the arsenic ions (As^{5+}). As these ions are removed, the equilibrium

$$8\,H_3O^+ + AsO_4^{\equiv} \leftrightharpoons As^{+5} + 12\,H_2O$$

is very slowly reestablished. Furthermore, there is some evidence that sulfoxyarsenic acids (H_3AsO_3S, for example) are formed as intermediate products when a solution containing the arsenate ion is saturated with hydrogen sulfide. In hot acid solutions, especially those containing iodide ions, the arsenate ion is reduced to the arsenite ion which reacts with hydronium ions forming arsenious acid. Since arsenious acid is a weaker acid than arsenic acid, its basic properties are more pronounced, and a sufficient concentration of arsenious ions (As^{+++}) is formed to make the precipitation of arsenious sulfide reasonably rapid.

To be sure of the correct concentration of the hydronium ion in the solution to be saturated with hydrogen sulfide take care to prepare the solution as directed at the beginning of Procedure II. After the precipitation of the sulfides the solution can be checked for the proper hydronium ion concentration by the use of methyl violet (Experiment 11*d*).

When the solution is saturated with hydrogen sulfide the precipitate may be sulfur or a mixture of sulfur and the sulfides of Group II. The sulfur is produced by the reaction of hydrogen sulfide with the oxidizing ions of Groups II or III, arsenate or ferric ions, for example. The sulfur will dissolve in the solution of sodium hydrogen sulfide which is used to separate the ions of Divisions A and B. Hydrogen polysulfide ions will be formed according to the equation

$$HS^- + S \leftrightharpoons HS_2^-$$

Separations of Divisions A and B. The sulfides of arsenic, antimony and stannic tin are soluble in either sodium hydrogen sulfide or sodium sulfide. Mercuric sulfide is soluble in sodium sulfide, by prolonged boiling in a solution of the sodium hydrogen sulfide and more readily in a solution of the hydrogen sulfide containing some sulfide. The sulfides of lead, copper, cadmium, bismuth and stannous tin are insoluble in these reagents. Stannous sulfide is oxidized to stannic sulfide by a polysulfide (Na_2S_2 or $NaHS_2$). Sodium sulfide or the hydrogen sulfide can be used to separate the ions of Group II into two divisions—A and B—if the tin is oxidized to the higher valence. This is done in this scheme of analysis by adding 2 drops of dilute nitric acid. Sodium hydrogen sulfide containing a small concentration of sodium sulfide is preferred to the normal sulfide since there is less tendency for traces of bismuth and copper sulfides to dissolve and complicate the analysis of Division B. The small amount of bismuth and copper sulfides which dissolves is reprecipitated during the digestion with the reagent. If no precautions are taken to oxidize the tin to the higher valence, sodium polysulfide must be used. Polysulfides also oxidize the sulfides of arsenic and antimony having the lower valences. Even if no sulfur is added to the sodium sulfide or hydrogen sulfide solution, polysulfides form as a result of the oxidation of a portion of the sulfide by oxygen absorbed from the air.

After the sulfides of lead, bismuth, copper and cadmium have been separated, add a slight excess of dilute hydrochloric acid to the solution containing the thiosalts of mercury, arsenic, antimony and tin to precipitate the sulfides.

$$HgS_2^= + 2\,H_3O^+ \rightleftharpoons H_2S + HgS + 2\,H_2O$$

Some free sulfur is always formed when the sodium hydrogen sulfide reagent is acidified because the acid reacts with the polysulfide.

$$HS_2^- + H_3O^+ \rightleftharpoons H_2S + S + H_2O$$

The polysulfide is formed by the reaction of sulfur with the hydrogen sulfide ion. The sulfur is formed by the oxidation of some of the hydrogen sulfide ion by oxygen absorbed from the air. The color of the precipitate obtained on the addition of an excess of hydrochloric acid should be noted carefully for evidence as to the probable presence or absence of the sulfides of Division B.

Lead Ion. The sulfides of Division A are not dissolved completely by dilute non-oxidizing acids. Boiling dilute nitric acid will convert them into nitrates. Since the lead ion is to be separated from the ions of bismuth, copper and cadmium as the sulfate, the most favorable conditions for the complete precipitation of lead sulfate are:

(1) The absence of large concentrations of hydrochloric and nitric acids, since these acids increase the solubility of lead sulfate.
(2) The presence of not more than 10 per cent by volume of sulfuric acid. As the concentration of sulfuric acid becomes higher, the acid sulfate begins to form and the amount of lead ion in solution increases.

The sulfides of Division A are converted to sulfates and free sulfur by the action of boiling, dilute sulfuric acid containing a drop of concentrated nitric acid. An oxidizing acid will dissolve these sulfides while a non-oxidizing acid will not, because an oxidizing acid converts the sulfide ion to sulfur.

$$3\,S^{=} + 8\,H_3O^{+} + 2\,NO_3^{-} \rightleftarrows 3\,S + 2\,NO + 12\,HO_2$$

Consequently, the value $C_{Pb^{++}} \times C_{S^{=}}$ is no longer equal to the solubility product of lead sulfide and more of the compound dissolves. The sulfide ion is removed as fast as it forms so the process continues until no more undissolved sulfides remain.

Bismuth Ion. The bismuth ion is separated from the ions of copper and cadmium by the addition of an excess of ammonia. Cadmium and copper ions form complex ammine ions which are soluble, while the ions of bismuth are precipitated as bismuth hydroxide.

$$Bi^{+++} + 3\,NH_3 + 3\,H_2O \rightleftarrows Bi(OH)_3 + 3\,NH_4^{+}$$

or

$$Bi(H_2O)_6^{+++} + 3\,NH_3 \rightleftarrows Bi^{(OH)_3}_{(H_2O)_3} + 3\,NH_4^{+}$$

The confirmatory test for bismuth is based on the ease of reduction of bismuth hydroxide to metallic bismuth by the hydrogen stannite ion.

$$2\ Bi(OH)_3 + 3\ HSnO_2^- \rightleftarrows 2\ Bi^\circ + 3\ HSnO_3^- + 3\ H_2O$$

or

$$2\ Bi^{(OH)_3}_{(H_2O)_3} + 3\ HSn(OH)_4^- \rightleftarrows 2\ Bi^\circ + 3\ HSn(OH)_6^- + 6\ H_2O$$

Other substances which are reduced to dark colored products and which might be found in the precipitate are antimonic and antimonous acids, lead hydroxide and copper hydroxide. These compounds, however, are not reduced by short contact with cold sodium hydrogen stannite and are consequently not readily mistaken for bismuth hydroxide.

Copper Ion. The copper ion is one of the most easily detected ions in cation analysis because of the characteristic deep blue color of its complex ion—$Cu(NH_3)_4^{++}$. Even small quantities of this complex ion give a color which is easily detected. However, if very small quantities of copper may be present, the ferrocyanide test for cupric ions must not be omitted.

$$2\ Cu^{++} + Fe(CN)_6^{\blacksquare} \rightleftarrows Cu_2Fe(CN)_6$$

Cupric ferrocyanide is not formed in an ammoniacal solution since the cupric-ammine ion does not give a sufficiently high concentration of the cupric ion to exceed the solubility product of cupric ferrocyanide. A portion of the solution which may contain the cupric and cadmium ions is acidified with acetic acid to decompose the complex ions before potassium ferrocyanide is added. Cadmium ions form a white ferrocyanide but the red color of the cupric ferrocyanide is readily detected in the presence of the white cadmium ferrocyanide.

Cadmium Ion. The formation of a white gelatinous precipitate when testing for the copper ion with potassium ferrocyanide is ordinarily sufficient proof of the presence of the cadmium ion. In the presence of copper ion, however, the ferrocyanide test cannot be used to test for cadmium ions. The cupric ion is, therefore, changed to a complex ion which is more stable than the corresponding complex ion of cadmium. Cupric ions unite with cyanide ions to form an unstable cupric cyanide.

$$Cu^{++} + 2\ CN^- \rightleftarrows Cu(CN)_2$$

This compound decomposes, forming cuprous cyanide and cyanogen.

$$2\ Cu(CN)_2 \rightleftarrows 2\ CuCN + (CN)_2$$

Cuprous cyanide reacts with the excess of potassium cyanide, forming the cupro-cyanide ion.

$$CuCN + CN^- \rightleftarrows Cu(CN)_2^-$$

Cyanogen resembles the halogens and reacts with water to form hydrocyanic acid (HCN) and cyanic acid (HCNO).

$$(CN)_2 + H_2O \rightleftarrows HCN + HCNO$$

If a base is present, a solution of the salts of these acids is formed. Under the same conditions cadmium ions react with cyanide ions to form insoluble cadmium cyanide, but this compound dissolves in an excess of potassium cyanide to form the cadmium-cyanide ion.

$$Cd^{++} + 2\ CN^- \rightleftarrows Cd(CN)_2$$
$$Cd(CN)_2 + 2\ CN^- \rightleftarrows Cd(CN)_4^=$$

The cupro-cyanide ion dissociates only very slightly into cuprous ions and cyanide ions. In fact, the dissociation is so small that the $C_{Cu^+}^2 \times C_{S^=}$ is less than the solubility product of cuprous sulfide. The cadmium-cyanide ion, however, dissociates sufficiently so that the $C_{Cd^{++}} \times C_{S^=}$ is greater than the solubility product of cadmium sulfide and cadmium sulfide is precipitated.

Ions of Arsenic. The sulfides of arsenic and mercury and the free sulfur obtained from the decomposition of the polysulfide in the sodium hydrogen sulfide reagent are separated from antimonic and stannic sulfides by heating them with concentrated hydrochloric acid for 10 minutes and then saturating the mixture with hydrogen sulfide. The treatment with hydrogen sulfide should not be neglected, for a considerable amount of mercuric sulfide may dissolve in the concentrated hydrochloric acid under the conditions used, probably because of the formation of the very slightly ionized $HgCl_4^=$. The mercuric ion is separated from the arsenic ion by treatment with ammonia. Arsenic sulfide is soluble in this reagent, forming thioarsenate and sulfoxyarsenate ions, but the mercuric sulfide and sulfur are practically insoluble.

$$As_2S_5 + 6\ NH_3 + 3\ H_2O \rightleftarrows AsS_4^= + AsO_3S^= + 6\ NH_4^+$$

The thioarsenic and the sulfoxyarsenic ions are converted to the arsenate ion by treatment with nitric acid.

$$AsS_4^{\equiv} + 30\ H_3O^+ + 32\ NO_3^- \rightleftarrows H_2AsO_4^- + 4\ HSO_4^- + 42\ H_2O + 32\ NO_2$$

$$9\ H_3O^+ + 8\ NO_3^- \rightleftarrows H_2AsO_4^- + HSO_4^- + 12\ H_2O + 8\ NO_2$$

If the nitric acid is added slowly, precipitation of arsenic sulfide usually occurs and may be regarded as an indication of the presence of arsenic. However, if no precipitate forms, the absence of an arsenate is not proved.

The arsenate ion is precipitated as ammonium arseno-molybdate $(NH_4)_3AsO_4 \cdot 12\ MoO_3 \cdot 5\ H_2O$, by adding a nitric acid solution of ammonium molybdate and maintaining the temperature at 85 to 90°. If the temperature exceeds these values, the ammonium molybdate will decompose with the formation of ammonium nitrate and molybdic oxide (MoO_3), which is almost white. The arsenate may be precipitated also as magnesium ammonium arsenate from an ammoniacal solution. This method of precipitation has the advantage that silver arsenate (Ag_3AsO_4), which is chocolate colored, is formed from the white magnesium ammonium arsenate by adding a drop of acetic acid and some silver nitrate to the precipitate, thus offering an additional confirmatory test. The precipitation of magnesium ammonium arsenate requires considerable time, since supersaturated solutions of the salt are formed readily. The inside of the test tube should, therefore, be scratched with a stirring rod and the solution should be allowed to stand before concluding that the arsenate ion is not present.

Mercuric Ion. The mixture of mercuric sulfide and sulfur is treated with concentrated hydrochloric and nitric acids until the black or gray color vanishes. The mixture oxidizes the sulfide ion to sulfur and the mercuric sulfide dissolves, since $C_{Hg^{++}} \times C_{S^=}$ is less than the solubility product of mercuric sulfide. An excess of the oxidizing agent must be avoided, because in testing for the mercuric ion a reducing agent, stannous ion, is added.

$$8\ Cl^- + 2\ Hg^{++} + Sn^{++} \rightleftarrows Hg_2Cl_2 + SnCl_6^=$$

$$4\ Cl^- + Hg_2Cl_2 + Sn^{++} \rightleftarrows 2\ Hg + SnCl_6^=$$

If the solution of stannous chloride is added slowly, a white precipitate of mercurous chloride forms. This is reduced to free mercury by the addition of an excess of the reagent. Use only a freshly prepared solution of stannous chloride, since all of the stannous ion

in an old solution may have been oxidized to the stannic ion by the oxygen in the air.

The gray deposit which forms when a solution is placed on a bright piece of copper is a good test for mercury. When it is rubbed gently the deposit becomes silvery as a result of the coalescence of the finely divided droplets of mercury and the amalgamation of the copper. Silver is also displaced by copper, but the deposit is black.

Ions of Antimony. Phosphomolybdic acid ($H_3PO_4 \cdot 12\ MoO_3$) is reduced to a phosphomolybdic acid ($H_3PO_4 \cdot 10\ MoO_3 \cdot Mo_2O_5$) containing molybdenum having an oxidation state of five, by the antimonous ion. The reaction is not specific and other reducing agents including hydrogen sulfide and stannous ion cause the formation of the blue color. The reaction with antimonous ion is probably represented by the equation

$$H_3PO_4 \cdot 12\ MoO_3 + Sb^{+++} + 2\ H_3O^+ \rightleftarrows H_3PO_4 \cdot 10\ MoO_3 \cdot Mo_2O_5 + 3\ H_2O + Sb^{+5}$$

Since the tin in the solution from the mercuric and arsenic sulfides is in the stannic condition, it will not interfere with the test for antimony.

Antimony is separated from tin by precipitation as black flakes of metallic antimony from a hot solution containing hydrochloric acid. The solution should contain 50% of concentrated hydrochloric acid by volume and the aluminum should be added in the form of wire. If the stannic ion is present, metallic tin may be formed as a gray moss-like precipitate. Any tin, however, dissolves on heating the solution. A little concentrated hydrochloric acid is then added and the solution is boiled to remove any reducing substances which would interfere with the test for tin. The black scales of antimony dissolve in dilute nitric acid after the addition of a little tartaric acid forming antimonyl hydrogen tartrate, $(SbO)HC_4H_6O_4$.

$$2\ H_3O^+ + 2\ NO_3^- + 2\ Sb \rightleftarrows Sb_2O_3 + 2\ NO + 3\ H_2O$$

$$Sb_2O_3 + 2\ H_2C_4H_6O_4 \rightleftarrows 2\ (SbO)HC_4H_6O_4 + H_2O$$

The characteristic antimonous sulfide is precipitated from the solution of antimonyl hydrogen tartrate by diluting sufficiently so that the solubility product of antimonous sulfide is exceeded when hydrogen sulfide is passed into the solution. If the precipitate is dark, the separation of antimony from the other ions of Group II

is not complete. When the dark precipitate is treated with concentrated ammonia, antimonous sulfide dissolves. To precipitate antimony sulfide boil the solution to remove the ammonia and then saturate it with hydrogen sulfide.

Ions of Tin. The solution from the precipitation of antimony contains stannous tin.

$$3\ SnCl_6^{=} + 2\ Al + (H_3O^+) \rightleftarrows 3\ SnCl_4^{=} + 2\ Al^{+++} + 6\ Cl^-$$

The stannous tin is detected by adding its solution to one containing mercuric chloride.

$$SnCl_4^{=} + 2\ HgCl_2 \rightleftarrows Hg_2Cl_2 + SnCl_6^{=}$$

Since the mercuric ion is ordinarily present in excess, the reduction usually does not proceed further than the formation of the mercurous chloride. After the reduction of the antimonous ion to the metal and of tin to the stannous condition, phosphomolybdic acid may be used to test for tin. Other reducing agents if present interfere with the test.

EXERCISES

1. Why is nitric acid added to the solution to be analyzed for Group II?
2. Why is ammonium iodide added to a solution being analyzed for Group II and the solution then saturated with hydrogen sulfide at different concentrations of hydronium ion?
3. State the reason for having sodium sulfide in the sodium hydrogen sulfide reagent.
4. Account for the solubility of lead sulfate in a mixture of acetic acid and ammonium acetate.
5. Account for the non-precipitation of cadmium and cupric ions on the addition of an excess of ammonia and the precipitation of bismuth hydroxide.
6. Explain why potassium cyanide is added to a solution of cadmium and copper ions before testing for cadmium.
7. Why should bismuth be confirmed by adding sodium hydrogen stannite to the precipitate of bismuth hydroxide? Will the stannite reduce lead hydroxide?
8. Why should a test be made for copper ions even though the solution appears colorless?
9. Account for the insolubility of mercuric and arsenic sulfides in concentrated hydrochloric acid saturated with hydrogen sulfide.
10. Why are the thio salts of mercury, arsenic, antimony and tin decomposed by the addition of an acid?
11. Account for the formation of a precipitate on acidifying sodium hydrogen sulfide reagent.
12. Why must all of the oxidizing agents used in dissolving mercuric sulfide be removed before testing for mercury?

13. Account for the formation of a large amount of a light colored solid which frequently forms in solutions of ammonium molybdate.
14. Account for the change in the oxidation state of antimony when antimonic sulfide is dissolved in concentrated hydrochloric acid.
15. Upon what is the separation of antimony and tin from a strongly acid solution by the addition of aluminum wire based?
16. Why is the test for tin made immediately after the reduction of stannic chloride by aluminum wire?
17. Account for the solubility of antimony in a mixture of nitric acid and tartaric acid.
18. How will the analysis of Groups II and III be affected if the concentration of hydronium ion in the solution saturated with hydrogen sulfide is 0.1-*N*? 1-*N*?
19. Calculate the value of the equilibrium constant for the reaction between copper sulfide and nitric acid. Can the reaction take place to any appreciable extent?
20. Calculate the value of the equilibrium constant for the system

$$Cd\,S + 4\,CN^- \rightleftarrows Cd\,(CN)_4^= + S^=$$

Will the reaction take place to any appreciable degree?

CHAPTER XI

Ions of Group III

PROPERTIES OF METALS AND IONS

COBALT

METAL. The metal is attacked slowly by dilute H_2SO_4 and HCl, more rapidly by dilute HNO_3. Concentrated HNO_3 renders cobalt passive. Strong alkalies do not attack the metal.

Ion. Sodium and potassium hydroxide precipitate a blue basic salt from solutions of Co^{++}. An excess of base changes the basic salt to pink $Co(OH)_2$. Oxygen oxidizes $Co(OH)_2$ to $Co(OH)_3$.

Ammonia precipitates a blue basic salt which is soluble in an excess of reagent, forming $[Co(NH_3)_6]^{++}$. No precipitate forms if NH_4^+ is present.

Hydrogen sulfide or ammonium sulfide precipitates CoS from an alkaline solution of the complex ion. The sulfide is nearly insoluble even in concentrated HCl but is dissolved by hot oxidizing acids.

Nitrous acid oxidizes an acetic solution of Co^{++} to Co^{+++} and NO is evolved. In the presence of an excess of KNO_2, yellow potassium cobaltinitrite, $K_3Co(NO_2)_6$, precipitates.

Alpha-nitroso-beta-naphthol gives a brick-red precipitate of the cobaltic salt from an acetic acid solution. Soluble thiocyanates added to an HCl or H_2SO_4 solution give a blue color due to the $Co(CNS)_4^{=}$. The addition of acetone increases the sensitivity of the test.

Simple cobaltic salts are unstable and are not encountered in elementary courses. Many complex ions of Co^{+++} are stable.

NICKEL

Metal. The properties of the metal are essentially the same as those of cobalt.

Ion. Sodium and potassium hydroxides precipitate a green basic salt which changes to light green $Ni(OH)_2$. Ammonia in the absence of NH_4^+, partially precipitates the hydroxide. The hydroxide is soluble in an excess of the reagent, forming the bluish $Ni(NH_3)_6^{++}$. In the presence of NH_4^+ no precipitation takes place.

Hydrogen sulfide or ammonium sulfide precipitates brown NiS from alkaline solutions. The sulfide frequently forms a brown colloidal solution if a high concentration of NH_3 or $S_2^=$ is present.

Dimethylglyoxime forms a pink precipitate when added to $Ni(NH_3)_6^{++}$. The precipitate is soluble in an excess of NH_3 or HOAc.

ZINC

Metal. Pure zinc, in contrast to the commercial product, dissolves very slowly in dilute H_2SO_4 or HCl. Very dilute HNO_3 is reduced chiefly to NH_4^+, while NO or NO_2 is formed if dilute or concentrated HNO_3 is used. Strong alkalies also react with the metal, forming H_2 and $HZnO_2^-$ or $HZn(OH)_4^-$.

Ion. Strong bases precipitate $Zn(OH)_2 \cdot (H_2O)_2$ soluble in an excess, forming $HZn(OH)_4^-$ or $HZnO_2^-$. The action may be formulated

$$Zn(OH)_2 \cdot (H_2O)_2 + OH^- \rightleftarrows HZn(OH)_4^- + H_2O$$

Ammonia gives a partial precipitation of $Zn(OH)_2 \cdot (H_2O)_2$ which dissolves in an excess of the reagent, forming $Zn(NH_3)_4^{++}$. In the presence of NH_4^+ no precipitation takes place.

Hydrogen sulfide or ammonium sulfide added to alkaline solutions containing $Zn(NH_3)_4^{++}$ or $HZnO_2^-$ precipitates ZnS (white). The sulfide is also precipitated from an acetic acid solution by H_2S.

Ammonium and the alkali carbonates precipitate a basic zinc carbonate which is soluble in an excess of $(NH_4)_2CO_3$.

MANGANESE

Metal. Manganese slowly displaces H_2 from dilute HCl and H_2SO_4, forming Mn^{++}. It reduces hot concentrated H_2SO_4, forming SO_2 and Mn^{++}. Dilute HNO_3 reacts with the metal, forming NO and Mn^{++}. Concentrated HNO_3 reacts with the metal, forming NO_2 and Mn^{++}.

Ion. Strong bases precipitate $Mn(OH)_2$ (white) which is rapidly oxidized by the oxygen of the air to $MnO_2 \cdot xH_2O$ (dark brown). Ammonia partially precipitates $Mn(OH)_2$. In the presence of NH_4^+ no precipitate forms.

Soluble sulfides precipitate flesh colored MnS which is soluble in acetic acid. There is also a green modification of the sulfide, but it is encountered rarely in qualitative analysis.

Oxidizing agents such as BiO_3^-, PbO_2 or ClO_3^- added to a concentrated HNO_3 solution, change Mn^{++} to MnO_4^- or MnO_2.

$$2\ Mn^{++} + 5\ BiO_3^- + 14\ H_3O^+ \rightleftarrows 2\ MnO_4^- + 5\ Bi^{+++} + 21\ H_2O$$

$$2Mn^{++} + 5\ PbO_2 + 4\ H_3O^+ \rightleftarrows 2\ MnO_4^- + 5\ Pb^{++} + 6\ H_2O$$

$$Mn^{++} + 2\ ClO_3^- \rightleftarrows MnO_2 + 2\ ClO_2$$

Sodium peroxide added to an alkaline suspension of $Mn(OH)_2$ oxidizes the hydroxide to $MnO_2 \cdot xH_2O$. Acidified H_2O_2 reduces MnO_2 or $MnO_2 \cdot xH_2O$ to Mn^{++}, and O_2 is evolved.

A manganous salt fused in an oxidizing region with Na_2CO_3 changes to green sodium manganate, Na_2MnO_4. To insure oxidation add a small amount of an oxidizing agent such as $NaNO_3$ or $KClO_3$.

$$3\ MnCl_2 + 6\ Na_2CO_3 + 2\ KClO_3 \rightleftarrows 3\ Na_2MnO_4 + 2\ KCl + 6\ CO_2 + 6\ NaCl$$

The $MnO_4^=$ is oxidized to MnO_4^- by OCl^- which is reduced to Cl^-.

The pink permanganate ion (MnO_4^-) is a very good oxidizing agent. The reduction products depend on the acidity of the solution (page 75).

IRON

Metal. Dilute HCl and H_2SO_4 react with iron, forming H_2 and Fe^{++}. Hot concentrated sulfuric acid dissolves iron, forming SO_2 and Fe^{++}. Very dilute cold HNO_3 dissolves the metal, forming Fe^{++} and chiefly NH_4^+. Hot dilute HNO_3 forms Fe^{+++} and NO, but concentrated HNO_3 renders the metal passive and it does not dissolve.

Ions. Strong bases precipitate $Fe(OH)_2$, white if pure, from solutions of Fe^{++}; however, the precipitate is usually light green and becomes darker due to oxidation by O_2. The color finally becomes red-brown because of the formation of $Fe(OH)_3 \cdot xH_2O$. This compound is precipitated by adding a base to Fe^{+++}. An excess of base dissolves an insignificant amount of $Fe(OH)_3 \cdot xH_2O$.

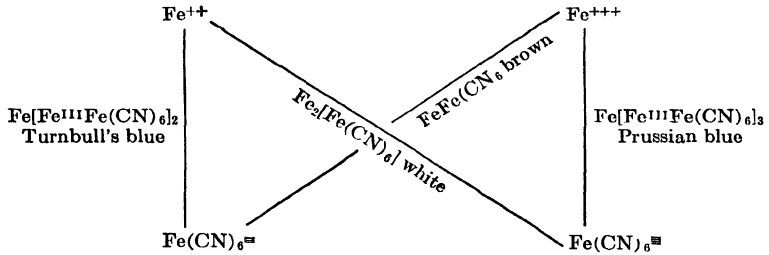
Ammonia precipitates a portion of Fe^{++} as an impure $Fe(OH)_2$ having a greenish color. No precipitate forms immediately on the addition of NH_3 to a solution of Fe^{++} containing NH_4^+. Ammonia quantitatively precipitates Fe^{+++} as $Fe(OH)_3 \cdot xH_2O$ even in the presence of NH_4^+.

Soluble carbonates precipitate Fe^{++} as $FeCO_3$ and Fe^{+++} as $Fe(OH)_3 \cdot xH_2O$.

Soluble sulfides precipitate ferrous and ferric ions as the corresponding sulfides (black). The sulfides are not precipitated by hydrogen sulfide from a slightly acidified solution. The Fe^{+++} is reduced.

$$2\,Fe^{+++} + H_2S + (H_3O^+) + 2\,H_2O \rightleftarrows 2\,Fe^{++} + S + 2\,H_3O^+$$

The reactions of an excess of Fe^{++} and Fe^{+++} with $Fe(CN)_6^{\equiv}$ and $Fe(CN)_6^{\equiv}$ are shown diagrammatically.



Recent work shows that Prussian and Turnbull's blue are salts of berlinic acid: $H[Fe^{III}Fe(CN)_6]$. Prussian blue, $Fe^{III}[Fe^{III}Fe(CN)_6]_3$, is formed by the reaction of an excess of Fe^{+++} with $Fe(CN)_6^{\equiv}$. The formula $H[Fe^{II}Fe(CN)_6]$ is also given for berlinic acid. The reaction probably takes place according to the equations

$$Fe^{+++} + Fe(CN)_6^{\equiv} \rightleftarrows [Fe^{III}Fe(CN)_6]^- \text{ (berlinate ion)}$$

The berlinate ion then reacts with ferric ions forming

$$Fe^{+++}(xs) + [Fe^{III}Fe(CN)_6]^- \rightleftarrows Fe[Fe^{III}Fe(CN)_6]_3$$

If the $C_{Fe(CN)_6^{\equiv}}$ and $C_{Fe^{+++}}$ are the same, soluble Prussian blue $K[Fe^{III}Fe(CN)_6]$ is formed according to the equation

$$K^+(\text{from } K_4Fe(CN)_6) + [FeFe(CN)_6]^-(xs) \rightleftarrows K[Fe^{III}Fe(CN)_6]_3$$

Turnbull's blue, $Fe^{++}[Fe^{III}Fe(CN)_6]_2$, is formed when an excess of Fe^{++} reacts with $Fe(CN)_6^{\equiv}$. The formation of the berlinate ion may be represented by the following equations:

$$Fe^{++} + Fe(CN)_6 \rightleftarrows Fe^{+++} + Fe(CN)_6^{\equiv}$$
$$Fe^{+++} + Fe(CN)_6^{\equiv} \rightleftarrows [Fe^{III}Fe(CN)_6]^-$$

or perhaps

$$Fe^{++} + Fe(CN)_6^{\equiv} \rightleftarrows [Fe^{II}(FeCN)_6]^-$$

followed by oxidation-reduction within the complex ion

$$[Fe^{II}Fe(CN)_6]^- \rightleftarrows [Fe^{III}Fe(CN)_6]^-$$

The reaction of berlinate ions with an excess of ferrous ions then takes place according to the equation

$$Fe^{++}(xs) + [Fe^{III}Fe(CN)_6]^- \rightleftarrows Fe[Fe^{III}Fe(CN)_6]_2$$

If the $C_{Fe^{++}}$ and $C_{Fe(CN)_6^{=}}$ are the same, the reaction is

$$K^+(\text{from } K_3Fe(CN)_6) + [Fe^{III}Fe(CN)_6]^- \rightleftarrows K[Fe^{III}Fe(CN)_6]$$

Thus the same product is obtained by mixing equimolecular quantities of Fe^{+++} and $Fe(CN)_6^{=}$ as by mixing equimolecular quantities of Fe^{++} and $Fe(CN)_6^{=}$.

The CNS^- does not react with Fe^{++} but Fe^{+++} forms red $Fe(CNS)^{++}$, $Fe(CNS)_3$ or $Fe(CNS)_6^{=}$ if an excess of the reagent is added. The complex salt $K_3[Fe(CNS)_6]$ may be extracted from water by ether. The red color may be due to $Fe(CNS)^{++}$.

Hydrofluoric acid (HF) forms a stable complex ion $FeF_6^{=}$ when added to Fe^{+++}. In concentrated HCl and HBr, Fe^{+++} probably forms the unstable complexes FeX_4^-, $\cdots$ $FeX_6^{=}$.

Concentrated solutions of acetates react with Fe^{+++} forming the red, slightly stable $Fe(OAc)_6^{=}$ which is sometimes mistaken for $Fe(CNS)_3$.

Even weak oxidizing agents oxidize Fe^{++} to Fe^{+++}. Reducing agents reduce Fe^{+++} to Fe^{++}.

ALUMINUM

Metal. Aluminum dissolves slowly in cold dilute acids but rapidly in hot acids. With hot concentrated H_2SO_4 sulfur dioxide is evolved. Concentrated nitric acid renders the metal passive. Strong alkalies react with the metal forming $Al(OH)_4^-$ or $AlO_2 \cdot 2\ H_2O$.$^-$

$$2\ Al + 2\ OH^- + 6\ H_2O \rightleftarrows 2\ Al(OH)_4^- + 3\ H_2$$

Ion. Sodium and potassium hydroxides precipitate $Al(OH)_3 \cdot xH_2O$ (white). The hydroxide dissolves in an excess of a strong base or an acid. The reaction has been discussed previously on page 112.

Ammonia precipitates aluminum hydroxide completely only in the presence of NH_4^+. The precipitate is somewhat soluble in an excess of the reagent, forming $[Al(H_2O)_2(OH)_4]^-$ or $AlO_2 \cdot 2\ H_2O^-$.

Soluble sulfides precipitate the hydroxide. The sulfide reacts with water.

$$Al_2S_3 + 6\ H_2O \rightleftarrows 2\ Al(OH)_3 + 3\ H_2S$$

Soluble phosphates precipitate $AlPO_4$ which is soluble in dilute HCl, H_2SO_4 and HNO_3 but not in HOAc.

The salts of weak acids are practically completely hydrolyzed.

When $Al(OH)_3$ is heated with a very small amount of $Co(NO_3)_2$, cobalt aluminate, $Co(AlO_2)_2$ (blue), is formed.

CHROMIUM

Metal. The metal dissolves very slowly in dilute HCl and H_2SO_4. On account of becoming passive—even in the dilute acid—it is not attacked by HNO_3. The metal is slightly attacked by alkalies at room temperature.

Ions. Chromous ion (Cr^{++}, blue) is a powerful reducing agent, and since it reacts rapidly with oxygen, is not encountered in elementary qualitative analysis. Chromic ion (Cr^{+++}) is usually green. Strong bases partially precipitate blue green hydrated hydroxide which is soluble in an excess of the base, forming CrO_2^- or $Cr(OH)_4^-$ (green), or in acids forming Cr^{+++}. The interpretation of these facts is the same as that offered for the other amphiprotic hydroxides and is discussed in detail on page 112.

Ammonia precipitates the hydroxide even in the presence of NH_4^+. The hydroxide is appreciably soluble in an excess of ammonia because of the formation of CrO_2^- and complex ammine ions. The chromium is reprecipitated as $Cr(OH)_3$ on boiling the solution. Chromic hydroxide is amphiprotic.

Alkali and ammonium carbonates precipitate the hydroxide. Ammonium sulfide also precipitates the hydroxide. The sulfide, like that of aluminum, hydrolyzes.

The chromite ($Cr(OH)_4^-$ or CrO_2^-) is oxidized to $CrO_4^=$ by peroxides and hypochlorites.

$$2\ Cr(OH)_4^- + 3\ HO_2^- \rightleftarrows 2\ CrO_4^= + 5\ H_2O + OH^-$$

$$2\ Cr(OH)_4^- + 3\ OCl^- + 2\ OH^- \rightleftarrows 2\ CrO_4^= + 3\ Cl^- + 5\ H_2O$$

If a solution containing $CrO_4^=$ is acidified, the yellow $CrO_4^=$ changes to the orange $Cr_2O_7^=$.

$$2\ CrO_4^= + 2\ H_3O^+ \rightleftarrows 3\ H_2O + Cr_2O_7^=$$

The $HCrO_4^-$ is undoubtedly formed as an intermediate step in the process. The equilibrium between $CrO_4^=$ and $Cr_2O_7^=$ is discussed on page 62.

If H_2O_2 is added to an acidified solution containing $Cr_2O_7^=$, a blue color appears momentarily in the solution. The color is due

to perchromic acid whose formula is variously given as H_7CrO_{10}, H_3CrO_8, H_2CrO_5 and $HCrO_5$. This acid is quite soluble and is more stable in ether than in water. It can be extracted from an aqueous solution by shaking with ether.

Reducing agents reduce the $Cr_2O_7^=$ to the Cr^{+++}.

REACTIONS OF THE IONS

Cobalt Ion, Co^{++}

Experiment 12. (*a*) Make a borax bead in a loop of a platinum wire. See borax bead tests, page 155. Moisten the bead with a solution of a cobalt salt and heat it strongly in an oxidizing flame. Note the color of the bead when hot and after it cools. Repeat the experiment using a mixture of cobalt and nickel nitrates. What color does the mixture impart to the bead?* Balance:

$$Na_2B_4O_7 + Co(NO_3)_2 \rightleftarrows NaNO_3 + Co(BO_2)_2 + B_2O_3$$

(*b*) Add an excess of sodium hydroxide to 4 drops of a solution of cobalt nitrate. Does the precipitate dissolve in an excess of sodium hydroxide? Is it soluble in ammonia? Note the colors of the precipitates and solutions. Complete:

(1) $Co^{++} + OH^- \rightleftarrows ?$ or $Co(H_2O)_6^{++} + OH^- \rightleftarrows Co(H_2O)_4(OH)_2 + ?$
(2) $Co(OH)_2 + OH^- \rightleftarrows ?$
(3) $Co(OH)_2 + NH_3 \rightleftarrows Co(NH_3)_6^{++} + ?$

(*c*) Acidify 4 drops of a solution of cobalt nitrate with acetic acid and add to the solution several large crystals of potassium nitrite. Warm the mixture. Balance:

$$Co^{++} + HOAc + NO_2^- \text{ xs} + K^+ \rightleftarrows K_3Co(NO_2)_6 + OAc^- + NO + ?$$

(*d*) Acidify 1 drop of a solution of cobalt nitrate with acetic acid and add 1 drop of a solution of alpha-nitroso-beta-naphthol. Boil the solution. The precipitate has the formula $(C_{10}H_6(NO)O)_3Co$.

(*e*) Vogel's test. Add 2 drops of ammonium thiocyanate to 4 drops of a solution of a cobalt salt to which a drop of hydrochloric acid has been added. If the solution does not become blue, add acetone. The test is characteristic and very sensitive for the cobaltous ion.

$$Co^{++} + CNS^- \text{ xs} \rightleftarrows Co(CNS)_4^=$$

Ferric ions interfere with the test but may be removed as a part of the complex ion, $FeF_6^{\equiv}$, by adding a drop of a soluble fluoride or by reduction to the ferrous ion with stannous chloride. The color of the solution is greenish blue instead of blue if ferric ions are removed.

Nickel Ion, Ni^{++}

Experiment 13. (*a*) Repeat Experiment 12*a* using a nickel salt instead of a cobalt salt. Balance:

$$Na_2B_4O_7 + Ni(NO_3)_2 \rightleftarrows NaNO_3 + Ni(BO_2)_2 + B_2O_3$$

* If the mixture of cobalt and nickel salts contains less than 2.5 per cent of the former, the nickel masks the blue color of the cobalt.

(*b*) Add an excess of sodium hydroxide to a solution of nickel nitrate. Does the precipitate which is formed dissolve in an excess of the hydroxide? Is nickel hydroxide soluble in ammonia? Note all colors of precipitates and solutions. Complete:

(1) $Ni^{++} + OH^- \rightleftarrows ?$ or $Ni(H_2O)_6^{++} + OH^- \rightleftarrows Ni(H_2O)_4(OH)_2 + ?$
(2) $Ni(OH)_2 + NH_3 \rightleftarrows Ni(NH_3)_6^{++} + ?$

(*c*) Add a drop of 1-*N* hydrochloric acid to 4 drops of a nickel nitrate solution and saturate it with hydrogen sulfide. See page 145 for directions for the use of hydrogen sulfide. Is a precipitate formed? Add an excess of ammonia to the acid solution and saturate it with hydrogen sulfide. Explain why a precipitate forms in this case but does not in the previous one. Separate the precipitate and wash it. Is the precipitate soluble in 1-*N* hydrochloric acid? What is peculiar about the fact that nickel sulfide is not precipitated from a dil .te acid solution, while the sulfide fails to dissolve or dissolves with extreme slowness in 1-*N* hydrochloric acid? Does cobalt sulfide show a similar behavior? Complete:

$$Ni^{++} + S^= \rightleftarrows ?$$

(*d*) Add a slight excess of ammonia to 4 drops of a solution of nickel nitrate. Then add 1 drop of a solution of dimethylglyoxime. The precipitate has the formula $(C_4H_7O_2N_2)_2Ni$. Test its solubility in acetic acid and ammonia.

Zinc Ion, Zn^{++}

Experiment 14. (*a*) Add to 4 drops of zinc nitrate a drop of a 0.1 per cent solution of cobalt nitrate and a drop of sodium carbonate solution. Evaporate the mixture to dryness and heat it until the purple color of the cobalt disappears. Cool the residue and note its color. Complete:

$$ZnO + Co(NO_3)_2 + Na_2CO_3 \rightleftarrows CoZnO_2 + CO_2 + ?$$

(*b*) Add sodium hydroxide to 4 drops of a zinc nitrate solution until zinc hydroxide precipitates. Treat one half of the mixture with an excess of sodium hydroxide, and the other half with hydrochloric acid. Interpret the results. Complete:

(1) $Zn^{++} + OH^- \rightleftarrows ?$ or $Zn(H_2O)_4^{++} + OH^- \rightleftarrows Zn(H_2O)_2(OH)_2 + ?$
(2) $Zn(OH)_2 + OH^- \rightleftarrows HZnO_3^- + ?$
or $Zn(H_2O)_2(OH)_2 + OH^- \rightleftarrows H[Zn(OH)_4]^- + ?$
(3) $Zn(OH)_2 + H_3O^+ \rightleftarrows ? + ?$
or $Zn(H_2O)_2(OH)_2 + H_3O^+ \rightleftarrows Zn(H_2O)_4^{++} + ?$

(*c*) Place 4 drops of a solution of zinc nitrate in each of two test tubes. Acidify one portion with acetic acid, the other with hydrochloric acid. Using a pressure tube, pass hydrogen sulfide into each solution. Explain your observations. What is the solubility of zinc sulfide in water? Complete:

(1) $Zn^{++} + H_3O^+ + H_2S \rightleftarrows ?$
(2) $Zn^{++} + (HOAc) + H_2S + H_2O \rightleftarrows ? + ?$

(*d*) Add 1 drop of ammonium chloride and ammonia to 4 drops of a solution of zinc nitrate. Why is zinc hydroxide not precipitated? Can this method be used to separate zinc ions from aluminum ions? Complete:

$$Zn^{++} + (NH_4^+) + NH_3 \rightleftarrows Zn(NH_3)_4^{++} + ?$$

(*e*) Treat 4 drops of a zinc nitrate solution with a drop of potassium ferrocyanide. Is the precipitate which is formed soluble in acetic acid? Complete:

(1) $Zn^{++} + Fe(CN)_6^{=} \rightleftarrows Zn_2Fe(CN)_6$
(2) $Zn_2Fe(CN)_6 + Fe(CN)_6^{=} \rightleftarrows Zn_3(Fe(CN)_6)_2^{=}$

Manganese Ion, Mn^{++}

Experiment 15. (*a*) Determine whether 1 drop each of solutions of ammonium chloride and ammonia will precipitate manganese hydroxide from 4 drops of a solution of manganous nitrate. Divide the solution into two parts. To one part add a solution of ammonium carbonate. Expose the second portion to the air. Balance:

(1) $Mn^{++} + (NH_4^+) + (NH_3) + CO_3^{=} \rightleftarrows MnCO_3$
(2) $Mn^{++} + (NH_4^+) + NH_3 + O_2 + H_2O \rightleftarrows Mn(OH)_3 + MnO(OH)_2 + NH_4^+$

(*b*) Add sodium hydroxide to 4 drops of a solution of manganous nitrate until no further precipitation occurs. Treat the mixture with a slight excess of hydrogen peroxide. Dilute the solution with an equal volume of water and boil until the excess of hydrogen peroxide is decomposed, that is, until the evolution of small bubbles ceases. Separate the precipitate and wash it with hot water. What is the precipitate? Complete:

(1) $Mn^{++} + OH^- \rightleftarrows ?$ or $Mn(H_2O)_4^{++} + OH^- \rightleftarrows Mn(H_2O)_2(OH)_2 + ?$
(2) $Mn(NO_3)_2 + Na_2CO_3 + KClO_3 \rightleftarrows KCl + NaNO_3 + Na_2MnO_4 + CO_2$

(*c*) Treat the precipitate from 15*b* with 4 drops of concentrated nitric acid (it may not dissolve completely) and add a small crystal of potassium chlorate. Boil the acid. CARE. What precipitate is formed? Balance:

$$Mn^{++} + [H_3O^+ \text{ (conc.)}] + ClO_3^- \rightleftarrows ClO_2 + MnO_2$$

(*d*) Make a sodium carbonate bead on your platinum wire, and touch the hot bead to a small piece of manganous salt or manganese dioxide. Then touch the hot bead to a crystal of potassium chlorate and heat in the oxidizing portion of the flame. Balance:

$$Mn(NO_3)_2 + Na_2CO_3 + KClO_3 \rightleftarrows KCl + NaNO_3 + Na_2MnO_4 + CO_2$$

(*e*) Saturate 4 drops of a solution of potassium permanganate acidified with sulfuric acid with hydrogen sulfide. What change occurs? Complete:

$$MnO_4^- + H_2S + H_3O^+ \rightleftarrows S + ? + ?$$

(*f*) Add 4 drops of sodium or potassium periodate to a drop of manganous nitrate to which a drop of a dilute solution of sulfuric or nitric acid has been added and heat the solution.

$$IO_4^- + Mn^{++} + H_2O + (H_3O^+) \rightleftarrows IO_3^- + MnO_4^- + ?$$

This sensitive and characteristic reaction can be used as a confirmatory test for manganese. Add 4 drops of sodium or potassium periodate to the precipitate which is in a centrifuge tube or on a filter and warm the mixture in a hot water bath. A pink solution proves the presence of manganese. If the solution is not pink add an additional 2 drops of the sodium or potassium periodate and warm the solution. Sometimes a red to brown precipitate, of the sodium or potassium

salt of $H_2Mn_2I_2O_{11}$, forms after the oxidation to the permanganate starts. The formation of the precipitate is favored if the temperature of the solution is above 40° and if the acidity is too low.

Ferrous Ion, Fe^{++}; and Ferric Ion, Fe^{+++}

Experiment 16. (*a*) Determine the action of 1 drop of pure ferrous ammonium sulfate (test solutions) with potassium ferricyanide; note the color of the precipitate. What is it? Test a second portion with ammonium thiocyanate and a third with potassium ferrocyanide. Complete:

(1) $Fe^{++} + Fe(CN)_6^{\equiv} \rightleftarrows ?$
(2) $Fe^{++} \quad SCN^- \rightleftarrows ?$
(3) $Fe^{++} + Fe(CN)_6^{\equiv} \rightleftarrows ?$

(*b*) Repeat Experiment 16*a*, but use 4 drops of ferric nitrate instead of the ferrous salt. Tabulate and compare the results. How may both ferrous and ferric ions be identified in a mixture of the two? One part of the ferric iron in 1,600,000 parts of water may be detected by the thiocyanate test. This test, however, cannot be used in the presence of a high concentration of nitric acid. Complete:

(1) $Fe^{+++} + Fe(CN)_6^{\equiv} \rightleftarrows ?$
(2) $Fe^{+++} + SCN^- \rightleftarrows ?$
(3) $Fe^{+++} + Fe(CN)_6^{\equiv} \rightleftarrows ?$

(*c*) Pass hydrogen sulfide into 4 drops of a ferric nitrate solution until no further action is observed. Note any change in the color of the solution. What is the precipitate? What change in the state of oxidation of the iron occurred? Complete:

$$Fe^{+++} + H_2S + H_2O \rightleftarrows S + ? + ?$$

(*d*) Heat 4 drops of a solution of ferrous ammonium sulfate with nitric acid. Note any change in color. Complete:

$$Fe^{++} + NO_3^- + H_3O^+ \rightleftarrows Fe^{+++} + NO + ?$$

(*e*) Add an excess of ammonia to 4 drops of a solution of ferric nitrate. Test the solubility of the precipitate in nitric acid and in sodium hydroxide. Complete:

(1) $Fe^{+++} + NH_3 + H_2O \rightleftarrows ? + ?$ or $Fe(H_2O)_6^{+++} + NH_3 \rightleftarrows Fe^{(OH)_3}_{(H_2O)_3} + ?$
(2) $Fe^{+++} + OH^- \rightleftarrows ?$ or $Fe(H_2O)_6^{+++} + OH^- \rightleftarrows Fe(H_2O)_3(OH)_3 + ?$
(3) $Fe(OH)_3 + H_3O^+ \rightleftarrows ? + ?$ or $Fe^{(OH)_3}_{(H_2O)_3} + H_3O^+ \rightleftarrows Fe(H_2O)_6^{+++} + ?$

Aluminum Ion, Al^{+++}

Experiment 17. (*a*) Add a drop of a 0.1% solution of cobalt nitrate to 4 drops of a solution of aluminum nitrate. Then add a few shreds of asbestos and an excess of ammonia. Separate the solid matter from the solution. Place the shreds with the adhering precipitate in the loop of the platinum wire. Ignite in the full Bunsen flame. Complete:

$$Al(OH)_3 + Co(NO_3)_2 \rightleftarrows Co(AlO_2)_2 + O_2 + NO_2 + ?$$

(*b*) Add sodium hydroxide, a drop at a time, to 4 drops of a solution of aluminum nitrate until a large precipitate of aluminum hydroxide is formed.

Treat one half of the mixture with an excess of sodium hydroxide. Does the precipitate dissolve? Does aluminum hydroxide, in this case, act as an acid or a base? Express the reaction by an ionic equation. To the other half of the mixture add hydrochloric acid. Does the precipitate dissolve? What property of aluminum hydroxide is shown by this treatment? Give an ionic equation to express this reaction. Does aluminum hydroxide ionize both as an acid and as a base? Illustrate by equations the effect of hydrochloric acid. Also show the effect of sodium hydroxide. Complete:

(1) $Al^{+++} + OH^- \rightleftarrows ?$ or $Al(H_2O)_6^{+++} + OH^- \rightleftarrows Al(H_2O)_3(OH)_3 + ?$

(2) $Al(OH)_3 + OH^-_{(excess)} \rightleftarrows AlO_2 + ?$
or $Al(H_2O)_3(OH)_3 + OH^- \rightleftarrows [Al(H_2O)_2(OH)_4]^- + ?$

(3) $Al(OH)_3 + H_3O^+ \rightleftarrows ? + ?$

(*c*) Add an excess of ammonia to 4 drops of aluminum nitrate. Separate the precipitate and dissolve it in 4 drops of hydrochloric acid. Add 4 drops of 2-*N* ammonium acetate and 2 drops of a 0.5% solution of aluminon, the ammonium salt of aurin tricarboxylic acid. Shake the tube. An insoluble salt (lake) of aurin tricarboxylic acid and aluminum will be formed in a few minutes. Add ammonia to the mixture until it is alkaline, and then 2 drops of ammonium carbonate. The bright red precipitate should persist. Silicic acid, and salts of bismuth, lead, antimony, stannic tin, and mercuric mercury give white precipitates. Salts of cadmium, zinc, nickel, cobalt, and manganese give no precipitate. Large amounts of the ions of the alkaline earth group give red lakes but the addition of the carbonate ion converts the alkaline earths to their carbonates, thus causing the disappearance of the red precipitate. Ferric salts give a deep violet precipitate in the acetic acid solution, which is changed to a reddish brown color by ammonia. The chromic ion gives a precipitate that is similar to that obtained with aluminum ion before neutralizing with ammonia. The precipitate disappears on the addtion of an excess of ammonia and ammonium carbonate.

(*d*) To determine the amount of aluminum ion in an acid solution which has been filtered through glass wool, circulate 10 drops of dilute hydrochloric acid through a glass wool filter. Add an excess of ammonia and note the quantity of precipitate which forms. If no precipitate forms, test the solution for a very small concentration of aluminum ion by Experiment 17*c*.

Chromic Ion, Cr^{+++}

Experiment 18. (*a*) Add 1 drop of a solution of ammonium chloride and ammonia to 4 drops of a solution of chromic nitrate. Note the color of the precipitate. Is the precipitate soluble in sodium hydroxide? In hydrochloric acid? Heat the solution of chromic hydroxide in sodium hydroxide. What is the result? Complete:

(1) $Cr^{+++} + (NH_4^+) + NH_3 + H_2O \rightleftarrows Cr(OH)_3 + NH_4^+$
or $Cr(H_2O)_6^{+++} + (NH_4^+) + NH_3 \rightleftarrows Cr^{(OH)_3}_{(H_2O)_3} + NH_4^+$

(2) $Cr(OH)_3 + NH_3 \leftrightarrows ?$

(3) $Cr(OH_3) + H_3O^+ \rightleftarrows ? + ?$

(4) $Cr(OH)_3 + OH^- \rightleftarrows CrO_2^- + ?$
or $Cr(H_2O)_3(OH)_3 + OH^- \rightleftarrows [Cr(H_2O)_2(OH)_4]^- + ?$

(*b*) Acidify 4 drops of a solution of potassium chromate with dilute hydrochloric acid, and divide the solution into three parts. Add a saturated solution

of sulfur dioxide to one sample and one of hydrogen sulfide to a second. To the third add alcohol and heat the solution. Complete:

(1) $SO_2 + Cr_2O_7^{=} + H_3O^+ \rightleftarrows HSO_4^- + Cr^{+++} + ?$
(2) $H_2S + Cr_2O_7^{=} + H_3O^+ \rightleftarrows S + Cr^{+++} + ? + ?$
(3) $C_2H_5OH + Cr_2O_7^{=} + H_3O^+ \rightleftarrows CH_3COOH + Cr^{+++} + ?$

(*c*) Add sodium hydroxide to 4 drops of a solution of chromium nitrate. Then add a slight excess of hydrogen peroxide. Add water to the mixture and boil the solution until the excess of hydrogen peroxide is decomposed. Acidify the solution with acetic acid. To the acid solution add lead acetate. What is the yellow precipitate? Complete:

(1) $Cr(OH)_3 + OH^- \rightleftarrows CrO_2^- + ?$
or $Cr(H_2O)_3(OH)_3 + OH^- \rightleftarrows [Cr(H_2O)_2(OH)_4]^- + ?$
(2) $CrO_2^- + HO_2^- \rightleftarrows CrO_4^{=} + OH^- + ?$
or $[Cr(H_2O)_2(OH)_4]^- + HO_2^- \rightleftarrows CrO_4^{=} + OH^- + ?$
(3) $CrO_4^{=} + HOAc \rightleftarrows Cr_2O_7^{=} + ?$
(4) $Cr_2O_7^{=} + H_2O + Pb(OAc)_2 \rightleftarrows PbCrO_4 + HOAc + ?$
(5) $PbCrO_4 + OH\ xs^- \rightleftarrows PbO_2^{=} + ? + ?$

General Reactions

Experiment 19. (*a*) Add hydrochloric acid to a solution containing 4 drops of zinc nitrate and 4 drops of aluminum nitrate. What group is precipitated by this reagent? Pass hydrogen sulfide into the solution. What group is precipitated? Boil, and make the solution alkaline with ammonia. What ions in Group III are precipitated by ammonia in the presence of ammonium chloride. Saturate the solution with hydrogen sulfide. What ions in Group III are precipitated by hydrogen sulfide in the presence of ammonia.

(*b*) Make a list of the ions of Group III which form complex ions with ammonia. Indicate the color of each ion.

(*c*) Make a list of the ions of Group III whose hydroxides are soluble in an excess of sodium hydroxide. Give the color and formulas of the compounds which are formed.

ANALYSIS

Procedure III

1. Precipitation of the Hydroxides and Sulfides. Use 4 drops of the unknown, or the solution from Group II, for the analysis of Group III. If phosphates are present, follow Procedure III, 11. If phosphates are absent, add one drop of ammonium chloride to prevent the precipitation of magnesium as the hydroxide, and sufficient distilled water to make the volume of the solution about 20 drops. Add ammonia until the solution is distinctly alkaline. A large excess should be avoided, since chromic hydroxide forms a soluble complex compound whose color may be pink, lavender or red. The complex compound is decomposed by boiling the solution. Note the color of the precipitate. Saturate the solution with hydrogen sulfide. When hydrogen sulfide is used as a precipitating agent,

a pressure tube must be used (page 145). After the liquid is saturated with hydrogen sulfide, warm it, and allow it to stand until the precipitate settles. Separate the precipitate using either a centrifuge, or a filter tube with two plugs of glass wool (page 148). Unless the solution is colored brown because of the presence of colloidal nickel sulfide, immediately evaporate the solution to dryness and ignite the residue to remove the ammonium salts. *Test the residue for the ions of Groups IV and V by Procedures IV and V.* If the solution is brown, boil it to precipitate the colloidal nickel sulfide. If the nickel sulfide does not precipitate, add a drop or two of acetic acid and again boil the solution. If the nickel sulfide does not precipitate, add a drop or two of hydrochloric acid and again boil the solution. Separate the precipitate and treat the solution as described previously. Add the precipitate of nickel sulfide to the precipitate of the sulfides and hydroxides of Group III or analyze it separately for the nickel ion.

2. Separation of Cobalt and Nickel Sulfides. Add 10 drops of 1-*N* hydrochloric acid to the precipitated sulfides and hydroxides which are in a centrifuge tube or on the glass wool filter. Let the acid remain in contact with the sulfides one-half minute and separate the precipitate. Wash the sulfides of cobalt and nickel five times, each time with 4 drops of the 1-*N* acid. Test the combined solutions for the other ions of Group III by Procedure III, 5. The traces which dissolve may interfere with the test for zinc unless the special procedure is followed to prevent their interference. Cobaltic hydroxide is quite dark and may be mistaken for the mixture of $MnO(OH)$ and $MnO(OH)_2$ which is precipitated by the sodium hydroxide-hydrogen peroxide reagent. It does not interfere, however, in carrying out the subsequent tests for iron or manganese. If no test for cobalt or nickel is obtained in an unknown which may contain traces, they should be tested for in the solution from the final precipitation of ferric hydroxide. Their presence is accounted for by the adsorption of cobalt and nickel ions by the hydroxides of aluminum, chromium and iron.

3. Identification of the Nickel Ion. Dissolve the sulfides of nickel and cobalt by adding 3 drops of concentrated hydrochloric acid and then one drop of concentrated nitric acid to the precipitate in the centrifuge tube or in the filter assembly immersed in boiling water. Separate any residue present and boil the solution to remove any excess of nitric acid or oxides of nitrogen which would destroy the reagents used in making the tests for the nickel and cobalt ions. Make the thoroughly stirred solution alkaline with a small excess of ammonia and divide it into two parts. Test one part for the

nickel ion by adding one drop of dimethylglyoxime. A pink precipitate whose composition is given by the formula $Ni(C_4H_7O_2N)_2$, is satisfactory proof of the presence of the nickel ion. Cobalt ions do not interfere with the test unless they are present in a large excess. If there is a large excess of the cobalt ion—a condition not ordinarily met with in an undergraduate course—treat a small part of the solution to be tested for cobalt and nickel ions with enough ammonia to make the solution strongly alkaline, and add two drops of hydrogen peroxide to oxidize the cobaltous ion to the cobaltic condition. Boil the solution until the excess of hydrogen peroxide is decomposed. Add a drop of dimethylglyoxime to the hot solution. A pink precipitate indicates the presence of the nickel ion.

4. Identification of the Cobalt Ion. Acidify the second part of the alkaline solution containing the nickel-ammine and cobalt-ammine ions with hydrochloric acid and add 2 drops of ammonium thiocyanate. If the solution is colorless, add an equal volume of acetone. A blue color proves the presence of cobalt. If the solution becomes red on the addition of the thiocyanate, ferric ions are present. Remove the ferric ions as a part of the complex ferric-fluoride ion ($FeF_6^{\equiv}$) by adding a drop of a soluble fluoride or by reducing the ferric ions by adding stannous ions. If the solution is colorless after removing the ferric ions, add acetone as before. If the solution is colored from bluish-green to green, the presence of cobalt is proved. Cobalt ions may also be identified by Experiment 12c.

5. Separation and Identification of the Zinc Ion. Boil the solution from the cobalt and nickel sulfides to remove all of the hydrogen sulfide. Then add 1 drop of concentrated nitric acid to oxidize the ferrous iron to the ferric condition and again boil the solution. Make the mixture alkaline with ammonia and add ammonium carbonate until no further precipitation occurs (about 3 drops). Heat the mixture in boiling water and separate the precipitate. Test the precipitate for manganese, aluminum and chromium by Procedure III, 6. The solution contains the complex zinc-ammine ion and traces of the cobalt-ammine and nickel-ammine ions if any of the cobalt and nickel sulfides dissolved in the 1-*N* hydrochloric acid. Make the solution acid to litmus with acetic acid and saturate it with hydrogen sulfide. Watch the solution very carefully for the immediate formation of a white precipitate of zinc sulfide. If traces of cobalt and nickel ions are present, the sulfides of these elements will also precipitate. The speed of formation of these sulfides, however, is much less than that of zinc sul-

fide; therefore there is usually but little trouble in detecting the presence of zinc in the solution. Zinc can be separated from the nickel and cobalt by extracting the dark colored precipitate with 10 drops of 0.25-*N* hydrochloric acid. Separate any residue and add a slight excess of sodium hydroxide to the solution to precipitate any cobalt or nickel ions as their hydroxides. Separate the hydroxides of nickel and cobalt and make the solution slightly acid with acetic acid. On saturating the solution with hydrogen sulfide a white precipitate which forms almost immediately and which is soluble in an excess of concentrated hydrochloric acid (5 to 10 drops) is zinc sulfide.

6. Separation of the Manganese and Ferric Ions from the Aluminum and Chromium Ions. Dissolve the precipitate which may be manganous carbonate, ferric hydroxide, aluminum hydroxide and chromic hydroxide in the least possible amount of hydrochloric acid. Make the solution distinctly alkaline with sodium hydroxide, and cool. Add hydrogen peroxide to the cool mixture containing manganous hydroxide, ferric hydroxide, aluminate ions and chromite ions until a stream of oxygen bubbles indicates that an excess of the reagent has been added. About 4 drops of hydrogen peroxide will be required. Heat the mixture to decompose the excess of hydrogen peroxide, and separate the hydrated manganese dioxide and ferric hydroxide from the aluminate and chromate ions. Manganese may be detected in this precipitate by making a carbonate bead, Experiment 15*d*. Test the solution for aluminum and chromium by Procedure III, 9.

7. Separation of the Ferric Ion from Manganese Ion. Add 5 drops of sulfuric acid to the hydrated manganese dioxide and ferric hydroxide in the centrifuge tube or on the glass wool filter. Place the centrifuge tube or the filter tube assembly in a hot water bath until no more of the precipitate dissolves and then separate the residue. Repeat twice, using 5 drops of sulfuric acid.

If manganese is present usually a portion of the hydrated dioxide does not dissolve. To precipitate the manganese which has dissolved add to the solution 2 to 3 drops of 2-*M* sodium bromate and boil the solution until no further precipitation occurs. Boil a few minutes if a precipitate does not form immediately. Separate the precipitate, using the centrifuge or filter tube containing the hydrated manganese dioxide. Confirm the presence of manganese in the precipitate by making a sodium carbonate-potassium chlorate bead, Experiment 15*d*, or by oxidizing it to the permanganate ion as directed in Experiment 15*f*. Test the solution for ferric ions by Procedure III, 8.

8. Identification of the Ferric Ion. Add ammonia to the solution which may contain the ferric ion until the solution is distinctly alkaline to litmus. About 20 drops will be required. A reddish brown, flocculent precipitate indicates the presence of the ferric ion. Carefully note the quantity of precipitate to decide whether more than a trace is present. Confirm the presence of ferric ion by Experiment 16*b*.

9. Separation of Aluminum from Chromium. Acidify the solution from Procedure III, 6, containing the aluminate and chromate ions, with dilute nitric acid. Then add ammonia until the solution is alkaline to litmus. If a white precipitate forms, it is probably aluminum hydroxide. Separate any precipitate, carefully note the quantity of precipitate and decide whether more than a trace is present. Confirm the presence of aluminum in it by the cobalt aluminate test, Experiment 17*a*, or by the aurin tricarboxylate test, Experiment 17*c*. Test the solution for chromium by Procedure III, 10.

10. Identification of the Chromate Ion. If the alkaline solution is yellow, the presence of a chromate is indicated. If the solution becomes orange when acidified with acetic acid, the presence of the chromate ion is practically certain. Test the solution which may contain the chromate ion by adding a drop of ammonium acetate, an excess of acetic acid, and a solution of lead acetate. If a white precipitate of basic lead acetate forms, add ammonium acetate and acetic acid drop by drop until the white precipitate dissolves. A yellow precipitate, $PbCrO_4$, proves the presence of the chromic ion.

11. Removal of the Phosphate Ion. METHOD A. BY MEANS OF NITRIC ACID AND TIN. If a molybdate test on the solution to be tested for the ions of Group III (for details see Experiment 31*c*, page 248) shows that a phosphate is present, evaporate the solution containing the ions of Groups III to V almost to dryness to remove the hydrogen sulfide and hydrochloric acid used to precipitate Group II. Then add 2 drops of concentrated nitric acid and again evaporate almost to dryness. The treatment with nitric acid removes the chloride ion. Be careful not to bake the residue, for the oxides of aluminum, iron and chromium are insoluble in acids after they have been heated to even a moderately high temperature. Add 5 drops of dilute nitric acid and a piece of chemically pure granulated tin. The $SnO_2 \cdot xH_2O$ which is formed adsorbs the phosphate ion. Remove any stannic ions by evaporating the solution to 0.5 ml. Then add about 1 ml. of water, boil, and separate any precipitate. Wash the precipitate several times with small amounts of water. Carry out the analysis of Groups III to V as usual.

METHOD B. BY BASIC ACETATES. Dissolve a portion of the precipitate, Procedure III, 8, of the ferric hydroxide or, in the absence of ferric hydroxide, a portion of the light colored precipitate in a little concentrated nitric acid, and add an excess of ammonium molybdate. If the presence of a phosphate is proved, dissolve the remainder of the precipitate in a minimum quantity of dilute hydrochloric acid. Add ammonia until any precipitate which forms just fails to dissolve, after shaking the mixture for 10 to 15 seconds. Add 5 drops of 2-*N* ammonium acetate. If the solution is not distinctly reddish in color, add ferric chloride dropwise until such a color is produced. Boil the mixture gently for 2 to 3 minutes, adding 6 to 10 drops of water if a large amount of precipitate separates. If the basic ferric acetate does not precipitate but remains in a colloidal condition, add 2 drops of ammonia and boil again. Separate any precipitate while hot. If the solution is allowed to cool before removing the precipitate, some ferric ion may remain in the solution. Wash the basic ferric acetate, $Fe(OH)_2OAc$, which is precipitated with several small portions of hot water, and drain the wash water thoroughly before the next portion is added. Test the solution for the ions of Groups IV and V. The carbonates of Group IV are not precipitated in the presence of a high concentration of ammonium ion. The presence of these ions may be detected by the addition of ammonium sulfate and ammonium oxalate to small portions of the solution containing the ions of Groups IV and V.

Discussion of the Analysis

Colors of Ions. With the exception of the cupric ion in Group II, the colored cations are in Group III. The chromic ion is blue green and the chromate and dichromate ions are yellow and orange respectively. The cobaltous ion is red, the nickel ion is yellow green, and the manganous ion is pink. The ferrous ion is light green. Solutions of ferric salts are amber colored. The color of the unknown solution should be noted, since much valuable information as to the presence or absence of colored ions may be obtained. It is sometimes possible to prepare a colorless solution of colored salts by using appropriate relative amounts. A greenish colored solution in which a very small amount of a precipitate is suspended, such as is sometimes obtained on passing hydrogen sulfide into the ammoniacal solution, is usually due to small amounts of ferrous sulfide. A colored solution from which the ions of Group III have been precipitated may be due to the incomplete precipitation of some of the colored ions of Group III or to a very finely divided

Original Unknown (4 drops) or Solution from Group II: Co^{++}, Ni^{++}, Zn^{++}, Mn^{++}, Fe^{++}, Al^{+++}, Cr^{+++}. Add 1 drop of NH_4Cl and distilled water until the volume is 20 drops. Make the solution distinctly alkaline to litmus with NH_3—note the color of the precipitate—and then saturate with H_2S using a pressure tube. Warm, allow the precipitate to settle and separate the precipitate, using a centrifuge (page 147) or a filter tube with two glass wool plugs (page 148).

Precipitate: CoS, NiS, ZnS, MnS, FeS, $Al(OH)_3$, $Cr(OH)_3$. Add 10 drops of 1-*N* HCl, let stand one-half minute. Wash five times with 4 drops of 1-*N* HCl.

Solution: Ions of Groups IV and V. Evaporate to dryness and ignite.

Precipitate: CoS, NiS. Place the centrifuge tube or the filter assembly in a beaker of boiling water, add 3 drops of HCl (conc.) and one drop of HNO_3 (conc.). Separate any precipitate and boil the solution to remove any oxidizing agents. Neutralize with NH_3 and divide into 2 parts: Test one part for the Ni^{++}, with dimethylglyoxime, Exp. 13*d*. Test another for Co^{++} by Vogel's test, Exp. 12*e* or by the potassium cobaltinitrite test, Exp. 12*c*.

Solution: Zn^{++}, Mn^{++}, Fe^{++}, Al^{+++}, Cr^{+++}. Boil off the H_2S. Add one drop of HNO_3 (conc.) to oxidize the Fe^{++}, boil, and make alkaline with NH_3. Add 3 drops of $(NH_4)_2CO_3$ and heat in boiling water. Separate any precipitate.

Precipitate: $MnCO_3$, $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$. Dissolve in the minimum amount of HCl (about 9 drops). Make distinctly alkaline to litmus with NaOH to convert to $Mn(OH)_2$, $Fe(OH)_3$, $Al(OH)_4^-$ and $Cr(OH)_4^-$. Add H_2O_2 (about 4 drops). Heat to decompose the excess of H_2O_2 and filter.

Solution: $Zn(NH_3)_4^{++}$. Make acid to litmus with HOAc to form Zn^{++}. Pass in H_2S. The immediate formation of a white ppt. soluble in an excess of HCl conc. indicates ZnS.

Precipitate: MnO(OH), $MnO(OH)_2$, $Fe(OH)_3$. Add 5 drops of H_2SO_4. Heat and separate any precipitate. Repeat twice. Add 2–3 drops of 2-*M* sodium bromate to the combined solutions and boil until no more precipitate forms. Filter through glass wool containing the undissolved $MnO(OH)_2$.

Solution: $Al(OH)_4^-$, $CrO_4^=$. Add a slight excess of HNO_3 to form Al^{+++} and $Cr_2O_7^=$. Then add NH_3 until alkaline to litmus. Separate any precipitate.

Precipitate: MnO_2, $MnO(OH)_2$. Confirm by the $Na_2CO_3 - KClO_3$ bead, Exp. 15*d* or by oxidation to the MnO_4^-, Exp. 15*f*.

Solution: Fe^{+++}. If phosphates may be present, see Proc. III, 11. Add NH_3 (about 2 ml.) until the solution is alkaline to litmus.

Precipitate: $Fe(OH)_3$. Note quantity of the precipitate.

Solution: This solution may contain traces of $Co(NH_3)_6^{++}$ and $Ni(NH_3)_6^{++}$ if the treatment of sulfides with 1-*N* HCl has been improperly done.

Precipitate: $Al(OH)_3$. Note the quantity of precipitate, and confirm by the cobalt aluminate test Exp. 17*a*, or the aurin tricarboxylic acid test, Exp. 17*c*.

Solution: $CrO_4^=$. Add NH_4OAc, an excess of HOAc and $Pb(OAc)_2$. A yellow precipitate is $PbCrO_4$. If a white ppt. forms, add NH_4OAc and HOAc to dissolve the basic lead salt.

colloidal precipitate of nickel sulfide. It usually may be coagulated by boiling, or if this fails, acidifying with acetic acid and then boiling.

Precipitating Agent. Reagents used in precipitating the third group are ammonium chloride, ammonia and hydrogen sulfide. A sufficient concentration of ammonium ion must be present to prevent the precipitation of magnesium hydroxide.

Ammonia in the presence of ammonium salts will not precipitate the hydroxides of bivalent ions. The non-precipitation of the bivalent ions by ammonia in the presence of a high concentration of ammonium salts is due to the reversal of the reaction

$$M(H_2O)_6^{++} + 2\,NH_3 \rightleftarrows M_{(OH)_2}^{(H_2O)_4} + 2\,NH_4^+$$

or to the action of ammonia to form complex ions

$$M(H_2O)_6^{++} + 6\,NH_3 \rightleftarrows M(NH_3)_6^{++} + 6\,H_2O$$

Manganous hydroxide is not precipitated by the mixture of ammonia and ammonium chloride. If the solution is kept in an open container, it will absorb oxygen. The manganese will be oxidized, and will precipitate as MnO(OH). The concentration of ammonium ion cannot be increased to such an extent that the hydroxides of the trivalent metals will not precipitate on the addition of ammonia to a solution containing the ions of trivalent metals. The color of the precipitate formed when ammonium chloride and ammonia are added to an unknown gives evidence of the possible presence or absence of aluminum, chromium and ferric ions.

Hydrogen sulfide in an alkaline solution precipitates all of the ions of Group III as sulfides except those of aluminum and chromium, which are precipitated as hydroxides. It is necessary to use an alkaline solution of hydrogen sulfide because the solubility products of the sulfides of Group III are too large to permit the complete precipitation of the sulfides by hydrogen sulfide from neutral or acid solutions (page 96).

$$NH_3 + H_2S \rightleftarrows HS^- + NH_4^+$$
$$NH_3 + HS^- \rightleftarrows S^= + NH_4^+$$

These equations show that the greater the concentration of ammonia, the greater will be the concentration of the sulfide ion. The use of hydrogen sulfide as a precipitating agent is discussed in Chapter V.

Removal of Hydrogen Sulfide from the Solution Containing the Ions of Groups IV and V. Hydrogen sulfide should be removed completely from the solution containing the ions of Groups IV and V, for the sulfide ion is oxidized readily to the sulfate ion and the calcium, strontium and barium ions may be precipitated as sulfates.

Since the solution from Group III contains a high concentration of ammonium ions, the precipitation of calcium and barium carbonates may be incomplete. To insure the complete precipitation of these carbonates evaporate the solution to dryness and ignite the residue to remove the ammonium salts.

Action of 1-N Hydrochloric Acid on the Sulfides and Hydroxides of Group III. One-normal hydrochloric acid will dissolve the sulfides of zinc, manganese, iron and the hydroxides of aluminum and chromium. Nickel and cobalt sulfides, however, are only slightly attacked by this reagent (page 97) if the acid is allowed to remain in contact with the solids for a short time. If the treatment is long (over 3 to 4 minutes), an appreciable amount of the sulfides of cobalt and nickel will dissolve.

Cobalt and Nickel Ions. The insolubility of the sulfides of cobalt and nickel in 1-*N* hydrochloric acid and their non-precipitation from a 0.25-*N* hydrochloric acid is explained by the existence of a number of modifications of the sulfides. The more soluble modification which forms at first changes quickly to a less soluble one. However, if these sulfides remain in contact with 1-*N* hydrochloric acid for more than a few minutes, an appreciable quantity may dissolve. This indicates that the explanation is not entirely satisfactory.

If a deep blue colored solution due to the complex cobaltous chloride ion ($CoCl_4^=$) is obtained when the sulfides of cobalt and nickel are dissolved in hydrochloric and nitric acids, the presence of cobalt is indicated. On dilution the deep blue or greenish blue color will disappear since the complex ion dissociates into cobaltous and chloride ions.

The formation of the blue or greenish blue complex cobaltous thiocyanate ion is a characteristic and sensitive test for cobalt. The addition of acetone greatly increases the intensity of the color and consequently the sensitivity of the test. Ferric ion interferes since it reacts with an excess of the thiocyanate ion, forming the red complex ferric thiocyanate ion ($Fe(CNS)_6^=$). The ferric ion may be removed by adding a soluble fluoride to form the very slightly dissociated complex ferric fluoride ion ($FeF_6^=$) or by reducing the

ferric ion to the ferrous ion by adding stannous chloride. The nickel ion does not interfere with this test for cobalt.

Another method of testing for cobalt is to oxidize the cobaltous to the cobaltic ion by a large excess of nitrous acid. The cobaltic ion thus formed reacts immediately with the excess of nitrite, forming the cobaltinitrite ion. A high concentration of potassium ion must be present to react with complex cobaltinitrite ion to form the insoluble potassium cobaltinitrite. The nickel ion is not precipitated by this reagent.

Alpha-nitroso-beta-naphthol oxidizes the cobaltous ion to the cobaltic ion. The latter then reacts with more of the reagent to form a brick red precipitate. Cupric, ferric and cobaltous ions are precipitated completely by this reagent. Silver, stannous and bismuth ions are partially precipitated. If the concentration of the nickel ion is very high, a partial precipitation of the nickel salt of alpha-nitroso-beta-naphthol will take place, especially if the acidity is too low. If a solution of the reagent is diluted, a brown precipitate of alpha-nitroso-beta-naphthol, which is not to be confused with the cobalt salt, will form.

Nickel is detected by adding dimethylglyoxime to an ammoniacal solution. The test is very sensitive unless a large excess of ammonia is present. One part of nickel in 400,000 parts of water may be detected. The cobaltous ion does not interfere unless it is present in very large excess—a condition not ordinarily met with in a beginning course. The cobaltic ion, however, does not interfere with the test for nickel ion, so hydrogen peroxide in the presence of ammonia is used to oxidize the cobaltous ion. The excess of hydrogen peroxide should be removed by boiling, and the nickel ion detected in the ordinary way. A borax bead test may be made to confirm the presence of cobalt and nickel in the precipitates. A large amount of the precipitate must be used, however, for the per cent of nickel and cobalt in the precipitate is very small.

Zinc Ion. The zinc ion forms a colorless complex ion with ammonia. The formula for the ion is $Zn(NH_3)_4^{++}$. Zinc carbonate is not precipitated by ammonium carbonate from a solution containing the complex zinc-ammine ion; therefore, the zinc ion is not precipitated along with the ions of manganese, chromium, aluminum and iron. The complex zinc-ammine ion is decomposed by the addition of a slight excess of acetic acid. When hydrogen sulfide is added to this solution zinc sulfide forms almost immediately, while cobalt and nickel sulfides form more slowly. Zinc sulfide could be precipitated from the ammoniacal solution but if traces

of manganese, iron, cobalt or nickel were present, they would precipitate at the same time and mask the color of the zinc sulfide. For this reason the solution is first acidified with acetic acid. Zinc sulfide is the only sulfide of Group III which precipitates almost immediately when an acetic acid solution is saturated with hydrogen sulfide.

Manganous Ion. Ammonium carbonate in the presence of ammonia precipitates the manganous ion as the carbonate along with the hydroxides of the trivalent ions of aluminum, iron and chromium. The manganous and ferric ions are then separated from the ions of chromium and aluminum by adding sodium hydroxide and hydrogen peroxide. The hydrogen peroxide oxidizes the manganous ion to a mixture of $MnO(OH)_2$ and $MnO(OH)$ and the chromite ion to the chromate ion. When sulfuric acid is added to a mixture of the oxides, $MnO(OH)_2$ and $MnO(OH)$, the lower oxide of manganese and possibly a portion of the hydrated manganese dioxide, react forming some manganous ion. This does not matter, since any manganous ion is precipitated as manganese dioxide by adding sodium bromate and boiling. The equation for the reaction is

$$5\,Mn^{++} + 2\,BrO_3^- + 12\,H_2O + (H_3O^+) \rightleftarrows 5\,MnO_2 + Br_2 + 8\,H_3O^+$$

Soon after the addition of the sodium bromate, if manganous ions are present, the solution becomes pink due to oxidation of some of the manganous ions to permanganate ions. When the solution is boiled, the unchanged manganous ions reduce the permanganate according to the equation

$$2\,MnO_4^- + 3\,Mn^{++} + 6\,H_2O + (H_3O^+) \rightleftarrows 5\,MnO_2 + 4\,H_3O^+$$

Both manganese dioxide and hydrated manganese dioxide are reduced to the manganous ion by sulfuric acid containing a drop or two of hydrogen peroxide. The green compound of manganese formed in the potassium chlorate-sodium carbonate bead is sodium manganate (Na_2MnO_4).

Ferrous and Ferric Ions. The iron present in an unknown which has been tested for Group II is always in the ferrous condition, for the ferric ion is reduced by an acid solution of hydrogen sulfide. After the separation of the sulfides of cobalt and nickel from the other ions of Group III, it is necessary to oxidize the ferrous to the ferric ion before ferric hydroxide will precipitate with the hydroxides of chromium and aluminum. This is accomplished by adding

a few drops of concentrated nitric acid to the hydrochloric acid solution and boiling. Since the final precipitation of ferric ion is made by adding ammonia to a nitric acid solution, sufficient ammonia must be added to make the solution alkaline before drawing any conclusions as to the presence or absence of the ferric ion. Since compounds of iron are present in nearly all reagents, it is essential to compare the quantity of hydroxide which is precipitated with the amount formed when the known for Group III was analyzed. Small quantities of iron give the same test as large amounts; therefore, the quantity of the precipitate must be noted to distinguish between a trace or a relatively large quantity.

Aluminum Ion. Aluminum, like iron, is present in almost all reagents as an impurity, hence there is the same necessity for noting the quantity of the precipitate of the hydroxide as was pointed out for iron. The precipitate which is thought to be aluminum hydroxide should always be tested to prove the presence of aluminum, for silica from the ammonia is often mistaken for aluminum hydroxide. There are two confirmatory tests for the aluminum ion—the cobalt aluminate test and the aurin tricarboxylate test. Either or both of these tests should be used. The only way to tell whether the aluminum is present as a trace or not is by the amount of precipitate of the aluminum hydroxide that is obtained.

Chromic Ion. The chromic ion is converted to the chromate ion and is precipitated as lead chromate in the presence of acetic acid and sodium acetate. To avoid reducing the chromate ion, all of the hydrogen peroxide must be decomposed before the solution is acidified for the test for the chromate ion. The color of the solution from the aluminum hydroxide should be noted, for the chromate ion has a characteristic yellow color.

The Phosphate Complication in Cation Analysis. If the phosphate ion is present, the trivalent ions of Group III will precipitate as their normal phosphates when the solution is alkaline. If there is an excess of the phosphate ion, the bivalent ions of Groups III and IV will precipitate as the simple normal phosphates except in the case of manganous, zinc and magnesium ions which precipitate as $MnNH_4PO_4$, $ZnNH_4PO_4$ and $MgNH_4PO_4$. If a very large amount of the phosphate ion is present, all of the ions of Group IV may precipitate with Group III, and they will not be detected unless proper precautions are taken. Two methods of avoiding the possible loss of the ions of Group IV are given.

In the first method, test for the phosphate ion after precipitating the ions of Group II. If the phosphate ion is present, remove it before precipitating the ions of Group III by adding tin to a nitric acid solution and boiling. The phosphate ion seems to be adsorbed by the metastannic acid ($SnO_2 \cdot xH_2O$) which is formed. After separating the precipitate analyze the solution for Groups III to V according to the regular procedures.

In the second method, analyze the solution from Group II for Group III in the usual way. The phosphates of the alkaline earth elements (magnesium is included in the term alkaline earths) and of the ions of Group III precipitate when the solution is alkaline. If phosphates may be present, test a portion of the red precipitate of ferric hydroxide which may also contain ferric phosphate and the phosphates of the alkaline earths, or the light colored precipitate which contains only the phosphates of the alkaline earths, for the phosphate ion. If the phosphate ion is present, dissolve the remainder of the precipitate in a minimum quantity of hydrochloric acid. Remove the phosphate ion as ferric phosphate after adjusting the concentration of the hydronium ion. The ferric phosphate is carried down with the basic ferric acetate, $Fe(OH)_2OAc$. The phosphates of the alkaline earths do not form under these conditions since their solubility products are too high. This method is said to be objectionable on account of the adsorption of the barium ion and to a lesser extent the strontium ion and their consequent loss. The details for carrying out these methods are given in Procedure III, 11.

EXERCISES

1. Explain the purpose of each reagent used in the separation of the ions of Group III from those of Groups IV and V.
2. Explain why ferrous hydroxide is not precipitated by ammonia in the presence of ammonium chloride, while ferric hydroxide is precipitated by these reagents under the same conditions.
3. Explain why manganous sulfide is not precipitated by hydrogen sulfide in the presence of hydrochloric acid but is precipitated completely by ammonium sulfide.
4. Why is sodium peroxide added to the solution containing $Fe(OH)_3$, $Mn(OH)_2$, $Cr(OH)_4^-$ and $Al(OH)_4^-$?
5. Why is cobalt sulfide soluble in a mixture of nitric and hydrochloric acids but insoluble in hydrochloric acid?
6. Why is the hydrogen sulfide removed from the solution which contains Groups IV and V?
7. How do you explain the precipitation of lead chromate from an orange solution of a dichromate?
8. Why is the ferrous ion oxidized before the zinc ion is separated from the ions of manganese, aluminum, chromium and iron?

9. Will the presence of ammonium salts affect the solubility of aluminum hydroxide in ammonia?
10. If a blue solution is obtained on dissolving the precipitate which may be the sulfides of cobalt and nickel, what ion is probably present?
11. If a pure white precipitate is obtained when ammonia is added to the solution containing the ions of Groups III to V, which ions of Group III must be absent?
12. If a pure white precipitate is obtained when ammonia is added to the solution containing the ions of Groups III to V, and the amount of the pure white precipitate is increased when hydrogen sulfide is passed into the mixture, what ions are present?
13. A solution containing the ions of Group III is colorless. What ions are probably absent?
14. A solution containing the ions of Group III is dark green. What ion is present?
15. How is the amphiprotic nature of some of the hydroxides of Group III used in the analysis of the group?
16. Cite cases to show the use of complex ions in the analysis of Group III.
17. If an insufficient concentration of ammonium salts is present when Group III is precipitated, how will the analysis of Group IV be affected?

CHAPTER XII

Ions of Group IV

PROPERTIES OF METALS AND IONS

BARIUM

METAL. Barium decomposes water with the evolution of hydrogen and the formation of the hydroxide.

Ion. The strong bases, KOH and NaOH, if free from carbonate, give no precipitate unless added to solutions containing a high $C_{Ba^{++}}$. Ammonia, free from carbonate, gives no precipitate. The alkali carbonates precipitate $BaCO_3$, a white, finely divided precipitate which becomes crystalline on standing. Scarcely any ammonium salts can be present if $(NH_4)_2CO_3$ is used as the precipitating agent since they promote the change of the $CO_3^=$ to HCO_3^-.

$$NH_4^+ + CO_3^= \rightleftarrows HCO_3^- + NH_3.$$

The hydrogen carbonates of the alkaline earths are soluble. The carbonates are soluble in acids since

$$CO_3^= + H_3O^+ \rightleftarrows HCO_3^- + H_2O$$

thereby removing the $CO_3^=$. If an excess of acid is used the HCO_3^- forms H_2O and CO_2.

Barium sulfate is precipitated by the addition of a solution of a soluble sulfate to a solution of a barium compound. Barium sulfate is nearly insoluble in dilute HCl or HNO_3. It is somewhat soluble in concentrated H_2SO_4, HCl, or HNO_3 acids since

$$SO_4^= + H_3O^+ \rightleftarrows HSO_4^- + H_2O$$

and the hydrogen sulfates are soluble.

A soluble chromate precipitates $BaCrO_4$ (yellow) from an acetic acid solution of a barium salt which contains NH_4OAc to reduce the $C_{H_3O^+}$. The $BaCrO_4$ is soluble in dilute HCl, HNO_3, and H_2SO_4 acids because of the action

$$2\,H_3O^+ + 2\,CrO_4^= \rightleftarrows Cr_2O_7^= + 3\,H_2O$$

Addition of $C_2O_4^=$ causes the precipitation of $BaC_2O_4 \cdot H_2O$, which is somewhat more soluble than $CaC_2O_4 \cdot 2\,H_2O$, in hot HOAc.

The $HPO_4^=$ precipitates $BaHPO_4$ from neutral solutions and $Ba_3(PO_4)_2$ from alkaline solutions both of which are soluble in HOAc.

Barium compounds impart a yellow-green color to the flame. The color is absorbed by a chrome alum filter.

STRONTIUM

Metal. Metallic strontium is less active than barium but more active than calcium. It decomposes water, liberating hydrogen and forming a solution of $Sr(OH)_2$.

Ion. The reactions with strong alkalies and ammonia are similar to those of barium. Because of the insolubility of strontium carbonate, a high $C_{NH_4^+}$ increases the solubility of the carbonate but little. Strontium sulfate is more soluble than barium but less than calcium sulfate. Strontium sulfate is much more soluble in high $C_{H_3O^+}$ than is $BaSO_4$. The precipitation of $SrCrO_4$ from alkaline solutions of 50% alcohol is practically complete. The precipitates obtained by adding $C_2O_4^=$ or $HPO_4^=$ are similar in appearance to those obtained by adding these ions to Ca^{++}. Both SrC_2O_4, and $SrHPO_4$ are soluble in dilute HOAc.

Strontium salts impart a crimson color to a Bunsen flame. The color is absorbed by a chrome alum filter, although a flash may be discerned when the wire is placed in the flame.

CALCIUM

Metal. The metal reacts slowly with water, forming the hydroxide and liberating hydrogen. The metal burns in nitrogen or oxygen, forming Ca_3N_2 or CaO.

Ions. Strong bases (carbonate free) precipitate calcium hydroxide from solutions containing a high concentration of calcium ion. Ammonia or ammonium sulfide gives no precipitate. Ammonium carbonate precipitates calcium carbonate from solutions which contain a small $C_{NH_4^+}$.

Soluble sulfates precipitate $CaSO_4 \cdot 2\,H_2O$ from concentrated solutions of Ca^{++}.

Chromate ion precipitates $CaCrO_4$ from solutions having a very high $C_{Ca^{++}}$.

Calcium oxalate is precipitated from alkaline or neutral solutions

by the addition of $C_2O_4^{=}$. Unlike the oxalates of barium and strontium, $CaC_2O_4 \cdot 2\,H_2O$ is insoluble in HOAc. It is readily soluble in strong acids.

From neutral solutions $HPO_4^{=}$ precipitates $CaHPO_4$ as well as $SrHPO_4$ and $BaHPO_4$. From alkaline solutions the normal phosphate is precipitated.

Calcium fluoride, sulfite and arsenate (dibasic) are insoluble in neutral or slightly alkaline solutions.

The calcium flame test is brick red and is difficult to distinguish from a strontium flame test, particularly if a low concentration of strontium is present. The color is absorbed by a chrome alum filter.

MAGNESIUM

Metal. Magnesium liberates hydrogen from dilute HCl, H_2SO_4 and also from very dilute cold HNO_3. It is quite resistant to HF.

Ions. Strong bases precipitate $Mg(OH)_2$, insoluble in an excess of the reagent. Ammonia partially precipitates $Mg(OH)_2$ but no precipitate forms if NH_4^+ is present.

Ammonium sulfide in the absence of NH_4^+ precipitates a part of the Mg^{++} as $Mg(OH)_2$. No precipitation takes place in the presence of NH_4^+ because of the decreased C_{OH^-} formed by the hydrolysis of $(NH_4)_2S$.

Sodium carbonate precipitates basic magnesium carbonate of variable composition. The normal carbonate may be precipitated by the addition of $NaHCO_3$ and boiling the solution.

Ammonium carbonate does not precipitate $MgCO_3$ if NH_4^+ is present.

Magnesium chromate is very soluble. The oxalate forms supersaturated solutions from which $MgC_2O_4 \cdot 2\,H_2O$ slowly precipitates.

The addition of the $H_2PO_4^-$ to an ammoniacal solution of Mg^{++} containing NH_4^+ causes the precipitation of crystalline $MgNH_4PO_4$. The precipitation is slow because of the tendency to form supersaturated solutions. Magnesium ammonium phosphate is soluble in acetic acid. The ions of the alkaline earths give a flocculent precipitate when treated with a phosphate.

REACTIONS OF THE IONS

Barium Ion, Ba^{++}

Experiment 20. (*a*) Determine the color which barium salts impart to a flame. (*b*) Test the solubility of freshly prepared barium chromate in acetic acid; in hydrochloric acid. Explain the difference in the behavior of the two acids. Complete:

$$BaCrO_4 + H_3O^+ \rightleftarrows Cr_2O_7^{=} + ? + ?$$

Strontium Ion, Sr^{++}

Experiment 21. (*a*) What coloration do strontium salts impart to a flame? Use a solution of the nitrate.

(*b*) Add 4 drops of a saturated solution of calcium sulfate to an equal volume of a strontium nitrate solution. Heat the mixture in the water bath. Why is a precipitate formed under these conditions? Complete:

$$Sr^{++} + SO_4^{=} \text{ (low concentration)} \rightleftarrows ?$$

(*c*) Treat separately 4 drops each of solutions of barium and strontium nitrate with 2 drops of acetic acid and 2 drops of 2-*N* ammonium acetate and heat each solution to boiling. Add to each, dropwise, a 3-*N* K_2CrO_4 solution until precipitation is complete. Which chromate precipitates? Make the strontium solution alkaline with ammonia and add to it 8 drops of 95 per cent alcohol. Can barium be separated from strontium by this procedure? How would a solution of calcium chloride behave under these conditions? Account for the difference in the behavior of the barium and strontium ions. Complete:

$$CrO_4^{=} + CH_3COOH \rightleftarrows Cr_2O_7^{=} + CH_3COO^{-} + H_2O$$
$$Cr_2O_7^{=} + NH_3 + H_2O \rightleftarrows CrO_4^{=} + NH_4^{+}$$

What is the color of the chromate ion? Of the dichromate ion?

Calcium Ion, Ca^{++}

Experiment 22. (*a*) Determine the color which calcium salts impart to a flame by heating a platinum wire which has been dipped in a calcium nitrate solution.

(*b*) Treat 4 drops of a solution of calcium nitrate with sodium hydroxide. Repeat, using ammonia instead of sodium hydroxide. Explain the difference in results. Complete:

$$(1)\quad Ca^{++} + OH^{-} \rightleftarrows ?$$
$$(2)\quad Ca^{++} + NH_3 + H_2O \rightleftarrows ?$$

(*c*) To 4 drops of a solution of calcium nitrate slowly add dilute sulfuric acid until no further precipitation results. Separate the precipitate from the solution. Dilute a part of the solution to four times its volume by the addition of 95% alcohol. Is calcium sulfate soluble in water? What is the purpose of adding the alcohol?

(*d*) Heat 4 drops of a solution of calcium nitrate and add to it 1 drop of a saturated solution of ammonium oxalate. Is the precipitate soluble in acetic acid? In hydrochloric acid? What is the least soluble salt of calcium? Calculate the solubilities of the salts from their solubility products or consult a table of exact solubilities. Complete:

$$CaC_2O_4 + H_3O^{+} \rightleftarrows Ca^{++} + ? + ?$$

Magnesium Ion, Mg^{++}

Experiment 23. (*a*) To 4 drops of water add a drop of ammonia and phenolphthalein. Note the change in color. To what is it due? Now add to the dilute solution, drop by drop, 1 or 2 drops of ammonium chloride solution. What does the gradual fading of the color indicate about the concentration of hydroxide ion? Test the solution with litmus paper. Which is the more sensitive

to the hydroxide ion—litmus or phenolphthalein? To 4 drops of a solution of magnesium nitrate add one drop of a solution of ammonium chloride, and then ammonia until the solution is distinctly alkaline. Does a precipitate form? What does this show about the concentration of the hydroxide ion? Complete:

(1) $Mg(H_2O)_6^{++} + NH_3 \rightleftarrows Mg(H_2O)_4(OH)_2 + ?$
or $Mg^{++} + NH_3 + H_2O \rightleftarrows Mg(OH)_2 + ?$

(2) $Mg(H_2O)_6^{++} + NH_4^+ + NH_3 \rightleftarrows ?$
or $Mg^{++} + NH_3 + H_2O + NH_4^+ \rightleftarrows ?$

(*b*) Add to 4 drops of magnesium nitrate solution, a drop of ammonium chloride, a drop of ammonia, and then a drop of $(NH_4)_2HPO_4$. A white crystalline precipitate, $MgNH_4PO_4$, is a test for magnesium. Test its solubility in dilute acetic acid. When the magnesium solution is very dilute, the precipitate forms slowly. Scratching the inside of the tube with a glass rod hastens precipitation. Balance:

$Mg^{++} + NH_3 + (NH_4^+) + HPO_4^= \rightleftarrows MgNH_4PO_4$
$MgNH_4PO_4 + CH_3COOH \rightleftarrows H_2PO_4^- + Mg^{++} + CH_3COO^- + NH_4^+$

(*c*) To 4 drops of a solution of magnesium nitrate add 4 drops of water. Add 1 drop of magnesium reagent (p-nitrobenzene azoresorcinol) and make the solution alkaline with sodium hydroxide. A blue precipitate indicates the presence of the magnesium ion.

General Reactions

Experiment 24. (*a*) Tabulate the values for the molar solubility of the sulfates, carbonates and oxalates of the four ions of Group IV and decide which compound of each ion serves as the best means for its detection. What other ion not in Group IV forms a difficultly soluble sulfate?

(*b*) Add a few drops of solutions of ammonium chloride, ammonia and ammonium carbonate to 4 drops of a solution of an ion of Group III—for example, manganese nitrate. What conclusion do you draw from this experiment concerning the presence of the ions of Group III when Group IV is tested for?

(*c*) Treat 4 drops of a solution of one of the ions of Group IV, for example, calcium nitrate, with a little dilute hydrochloric acid. What ions does dilute hydrochloric acid precipitate? Pass hydrogen sulfide through the acidified solution. Use a pressure tube. What ions will be precipitated by this reagent? Now add an excess of ammonia and add a few drops of a solution of ammonium sulfide or pass in hydrogen sulfide. What ions will be precipitated by this reagent?

ANALYSIS

Procedure IV

1. Precipitation of Carbonates. Evaporate the solution being tested for Group IV to dryness in a crucible and ignite the residue to remove the ammonium salts. Heat until practically no white clouds of ammonium salts form above the container. Moisten the residue with 1 drop of concentrated hydrochloric acid, add 10 drops of water and heat until the solid dissolves. Use this solution

for Groups IV and V. Add enough ammonia to make the solution alkaline and ammonium carbonate dropwise until no more precipitate forms when a drop of the reagent is added to a portion of the liquid, from which the precipitated carbonates have been separated. Heat the mixture (40° to 50°) until the precipitate assumes a crystalline appearance. When the precipitate settles to the bottom of the container, separate it from the solution. Test the precipitate for the barium ion (Procedure IV, 3). Add a drop of ammonium sulfate to the solution and note whether a small amount of a fine white precipitate forms in the course of two or three minutes. If a precipitate forms, it is barium sulfate. Then add a drop of ammonium oxalate to the solution. A white precipitate of calcium oxalate indicates calcium. Separate any precipitate and test 4 drops of the solution for sodium ions by Procedure V, 5. Test the rest of the solution for magnesium ion by Procedure IV, 2.

2. Identification of the Magnesium Ion. Concentrate the solution to be tested for the magnesium ion to about 0.5 ml. Make the solution alkaline with ammonia, and then add 3 drops of diammonium hydrogen phosphate. A crystalline precipitate shows the presence of magnesium. A flocculent precipitate would probably be aluminum phosphate. Separate the precipitate. Test the solution by Procedure V and the white precipitate for magnesium. While the precipitate is in a centrifuge tube or on the glass wool in the filter tube, treat it with 1 drop of acetic acid and 3 drops of distilled water. Magnesium ammonium phosphate dissolves while the phosphate of aluminum does not. Separate any precipitate present in the acetic acid solution. Add to the solution 1 drop of the magnesium reagent and 4 drops of sodium hydroxide to make the solution alkaline, and separate. A blue precipitate confirms the presence of magnesium.

3. Identification of the Barium Ion. Wash the ammonium carbonate precipitate (Procedure IV, 1) thoroughly with warm water, and dissolve it in from 2 to 4 drops of acetic acid. Add 2 drops of 2-*N* ammonium acetate, heat the solution to boiling, and add 2 drops of potassium chromate. Separate any precipitate and treat the solution by Procedure IV, 4. Dissolve the precipitate in a drop of hydrochloric acid and make a flame test for barium (Experiment 20*a*). Add 1 drop of sulfuric acid. A white precipitate confirms the presence of barium.

4. Identification of the Strontium Ion. Add to the solution from the barium chromate precipitate, Procedure IV, 3, enough ammonia to change the dichromate (orange) to the chromate (yellow). Add a volume of alcohol equal to that of the solution and mix thoroughly.

A fine, light yellow precipitate indicates strontium. Warm the mixture until the precipitate coagulates and separate any precipitate. Confirm the presence of strontium in the precipitate by adding 10 drops of water to the precipitate and heat in the water bath. Circulate the hot solution through the filter several times if a filter was used. Add a drop of potassium chromate and 11 drops of alcohol to the clear solution. A fine yellow precipitate which does not dissolve when the mixture is heated proves the presence of strontium. Further confirmation of the presence of strontium in the precipitate may be had by making a flame test on the solution obtained by dissolving the precipitate in 2 drops of hydrochloric acid.

5. Identification of the Calcium Ion. Heat to boiling the solution from Procedure IV, 4, and add to it a drop of a solution of ammonium oxalate. A white precipitate indicates the presence of calcium. If a precipitate does not form immediately, let the solution stand for 3 to 4 minutes in the water bath before concluding that no calcium is present. Confirm the presence of calcium by separating the calcium oxalate precipitate, dissolving it in 4 drops of hydrochloric acid and making a flame test on the solution by experiment 22*a*.

Discussion of the Analysis

With the exception of the magnesium ion, the ions of the metals of Group IV are precipitated as carbonates by ammonium carbonate in the presence of ammonium chloride and ammonia. The magnesium ion is precipitated from the solution from the carbonates by the addition of ammonium phosphate. Magnesium carbonate has a molar solubility of 3.1×10^{-3} while the most soluble of the other three carbonates is calcium carbonate whose molar solubility is 6.9×10^{-5}. The problem involved in separating the ions of calcium, strontium and barium from those of magnesium, sodium and potassium is to furnish a sufficient concentration of the carbonate ion to precipitate quantitatively the former ions and to leave the latter in solution.

Since the carbonates of sodium and potassium are quite soluble, only magnesium carbonate is likely to precipitate if the concentration of the carbonate ion becomes too great.

The concentration of the carbonate ion can be regulated by varying the concentration of the ammonium ion as is shown by the following equation:

$$CO_3^{=} + NH_4^{+} \rightleftarrows HCO_3^{-} + NH_3$$

Original Unknown 4 drops or Solution from Group III: Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, Na^{+}, K^{+}. Evaporate to dryness and ignite to remove ammonium salts. Add 1 drop of HCl conc., 10 drops of distilled water and make the solution alkaline to litmus by the addition of NH_3. Treat the solution with $(NH_4)_2CO_3$ until precipitation is complete (about 2 drops). Warm the mixture and let it stand until the precipitate settles.

Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$. Add from 2 to 4 drops of HOAc and 2 drops of NH_4OAc_4 to the precipitate. Heat the solution to boiling and add K_2CrO_4 until precipitation is complete (about 1 drop). Separate any precipitate.

Solution: Mg^{++}, NH_4^{+}, Na^{+}, K^{+} (traces of Ca^{++} and Ba^{++}). Remove traces of Ca^{++} and Ba^{++} by adding $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$. Separate the precipitate and test 4 drops for Na^{+} using uranyl zinc acetate (Exp. 26c). Test the remainder for magnesium by making alkaline with NH_3 and adding $(NH_4)_2HPO_4$, about 3 drops. Separate any precipitate.

Precipitate: $BaCrO_4$. Dissolve in 2 drops of HCl. Test with flame. Add H_2SO_4 to solution. A white precipitate shows the presence of Ba^{++}.

Solution: Ca^{++} and Sr^{++}. Add enough NH_3 to change the orange color of the dichromate to the yellow of the chromate. Then add a volume of alcohol equal to the volume of the solution and mix thoroughly. Warm. A fine yellow precipitate which persists after warming indicates Sr^{++}.

Precipitate: $SrCrO_4$. Add 10 drops of water and heat. If a filter tube was used circulate the hot filtrate through the filter several times. Add 1 drop of K_2CrO_4, 11 drops of alcohol and heat. A finely divided yellow precipitate proves the presence of Sr^{++}.

Solution: Ca^{++}. Heat to boiling. Add $(NH_4)_2C_2O_4$. A white precipitate indicates Ca^{++}. Allow the solution to stand if a precipitate does not form immediately. A white precipitate proves the presence of Ca^{++}.

Precipitate: $MgNH_4PO_4$. This precipitate should be crystalline. Add 1 drop of HOAc, 3 drops of water to the precipitate and separate. To the solution add a drop of the magnesium reagent, an excess of sodium hydroxide and filter. A blue precipitate confirms the presence of Mg^{++}.

Solution: NH_4^{+}, Na^{+} and K^{+}. Save this solution and test it by Proc. V. Remove the ammonium salts before testing for K^{+}.

In this reaction the carbonate ion is a base and the ammonium ion is an acid. Since the carbonate ion is quite a strong base, the carbonate ion is largely changed to hydrogen carbonate ion in the presence of a moderate concentration of ammonium ion. The greater the concentration of ammonium ion, or any acid, the smaller will be the concentration of the carbonate ion and the greater will be the concentration of the hydrogen carbonate ion. In fact, if the concentration of the ammonium ion or any other acid is too large, the concentration of the carbonate ion will be so low that the carbonates of calcium, strontium and barium will not precipitate when the carbonate ion is added to the solution.

The addition of a base will cause the formation of more carbonate ions. The base reacts with the hydrogen carbonate ions.

$$HCO_3^- + OH^- \rightleftarrows CO_3^= + H_2O$$
$$HCO_3^- + NH_3 \rightleftarrows CO_3^= + NH_4^+$$

In fact, the addition of a large excess of ammonia or other base may increase the concentration of carbonate ion to such an extent that magnesium carbonate will precipitate in spite of its relatively high molar solubility.

If the concentration of the ammonia is too large, then the partial precipitation of magnesium hydroxide will take place.

$$Mg(H_2O)_6^{++} + 2\ NH_3 \rightleftarrows Mg^{(OH)_2}_{(H_2O)_4} + 2\ NH_4^+$$

However, the precipitation of magnesium hydroxide will not take place if a suitable concentration of ammonium ions is present. Ordinarily the magnesium ion and magnesium hydroxide are written Mg^{++} and $Mg(OH)_2$, respectively, although both are undoubtedly hydrated.

It is clear, then, that enough ammonia must be added to the solution to insure a sufficient concentration of carbonate ions to precipitate completely the carbonates of calcium, strontium and barium. However, an excess must be avoided to prevent the partial precipitation of magnesium hydroxide. In practice it is customary to regulate the concentration of carbonate ion by adding both ammonia and ammonium chloride.

Since the freshly precipitated carbonates of calcium, strontium and barium are apt to be colloidal, the mixture should be warmed to 40° to 50° and then set aside until the precipitate coagulates before attempting to separate the precipitate. Do not boil the mixture, for the ammonium carbonate will decompose into ammonia, carbon dioxide and water.

Flame Tests. Since flame tests are easily made, the solution which may contain the ions of Group IV should be tested in this way. The yellowish green color which volatile barium compounds impart to the non-luminous flame of the Bunsen burner is quite characteristic. The only other fairly common substances which give a green colored flame are cupric compounds and boric acid. Strontium compounds give a bright red flame test which is not confused with that of other substances. The brick-red colored flame given by calcium compounds may be mistaken for that caused by strontium compounds so that the conclusions drawn from the test should be compared carefully with other evidence. It should be noted that only volatile compounds of these elements color the flame. Magnesium compounds do not color the flame.

Barium Ion. The barium ion is precipitated as the chromate by potassium chromate from a solution which contains ammonium acetate and a low concentration of acetic acid. The concentration of the hydronium ion is reduced by the addition of the ammonium acetate. The solution has the color of the dichromate ion although the chromate ion is present in a higher concentration. When dilute hydrochloric or nitric acid is added to solid barium chromate, the chromate ion is converted to the dichromate ion and the barium chromate dissolves. The solution thus obtained should be used for making a confirmatory test for barium. For the action of acids on slightly soluble chromates see page 62.

Strontium Ion. The strontium ion is precipitated as the chromate from an alcohol solution (50%) having a high concentration of chromate ion. A high concentration of chromate ion is obtained by adding enough ammonia to make the solution alkaline, thus changing the dichromate ion to the chromate ion.

$$Cr_2O_7^{=} + H_2O + 2\,NH_3 \rightleftarrows 2\,CrO_4 + 2\,NH_4^{+}$$

The solubility of the strontium chromate is reduced by adding an equal volume of alcohol. Strontium chromate is insoluble in the hot alcohol solution. A precipitate which dissolves completely when the mixture is warmed is not strontium chromate.

Calcium Ion. The calcium ion is precipitated as calcium oxalate after removing the strontium ions.

Magnesium Ion. The magnesium ammonium phosphate test for the magnesium ion is a difficult one for the beginning student in

qualitative analysis. To be sure of the absence of the magnesium ion the solution must be allowed to stand. Traces of barium, strontium or calcium ions must be absent, for these ions form the normal phosphates when treated with an alkaline solution of a soluble phosphate, and this precipitate may be confused with magnesium ammonium phosphate. An organic reagent (p-nitrobenzene azoresorcinol) is used to confirm the presence of magnesium ions in the precipitate. A precipitate is obtained with 1/500,000 g. of magnesium ion, provided ammonium salts are not present.

EXERCISES

1. What change occurs in the color of an acetic acid solution containing methyl orange when ammonium acetate is added? Explain.
2. What will be the effect on the hydroxide-ion concentration of adding ammonium chloride to a solution of ammonia?
3. Write equations for the equilibria involved when solid ammonium carbonate is dissolved in water.
4. Using the equations in 3, what ion should be removed to increase the concentration of the hydrogen carbonate ion?
5. From the equations in 3, determine what ion should be removed to increase the concentration of the carbonate ion?
6. If ammonia is added to a solution of magnesium chloride, a partial precipitation of magnesium hydroxide occurs. However, if an ammonium salt is added before adding the ammonia, no precipitation of the hydroxide occurs. Explain.
7. Ammonium carbonate causes the formation of a precipitate when added to a solution of magnesium chloride. If, however, ammonium chloride is added no precipitation occurs. Explain.
8. Explain why barium chromate is precipitated from a solution of potassium dichromate containing acetic acid and ammonium acetate.
9. Explain why only the barium ion is precipitated as the chromate in an acetic acid solution containing ammonium acetate, barium chloride and strontium chloride, while both the barium and strontium ions are precipitated as chromates from an alkaline solution containing barium and strontium ions.
10. Why does sodium carbonate precipitate calcium ions as the carbonate from a solution containing high concentrations of ammonium salts whereas ammonium carbonate fails to cause complete precipitation?
11. Why does magnesium ammonium phosphate dissolve in acetic acid?
12. Why is the presence of ammonia necessary for the quantitative precipitation of magnesium ammonium phosphate?
13. What is the function of the ammonium chloride in the reagent used to precipitate magnesium ammonium phosphate?
14. Explain how a change in the concentration of the hydronium ion changes the concentration of chromate and dichromate ions in a solution of a chromate.

CHAPTER XIII

Ions of Group V

PROPERTIES OF METALS AND IONS

POTASSIUM

METAL. Potassium is the most active of the metals commonly studied in elementary texts. It decomposes water with the evolution of sufficient heat to ignite the hydrogen evolved. On evaporating the solution, potassium hydroxide is obtained.

Ion. The common salts are soluble. Identification is usually made by precipitating yellow potassium sodium cobaltinitrite, $K_2NaCo(NO_2)_6$, from an acetic acid solution. The corresponding ammonium salt is also insoluble and has the same color as the potassium salt; hence it is necessary to remove all ammonium ions before testing for potassium ions. The $K_2NaCo(NO_2)_6$ reacts with strong acids forming Co^{++}, Na^+, K^+ and NO_3^-. Potassium is sometimes precipitated as $KClO_4$ since the sodium and ammonium salts are soluble. However, $KClO_4$ is much more soluble than $K_2NaCo(NO_2)_6$ unless alcohol is added. Potassium compounds impart a violet color to a non-luminous flame. The yellow color of the compounds of sodium, the red of the calcium and the strontium and the green of the barium obscure the violet flame caused by those of potassium. A saturated solution of chrome alum, however, absorbs the interfering colors and transmits the violet, thus making it possible to detect potassium compounds in the presence of the interfering ions.

SODIUM

Metal. Sodium reacts vigorously with water forming sodium and hydroxide ions and liberating hydrogen. The metal reacts with oxygen to form Na_2O_2.

Ion. The common salts are soluble. Usually the ion is precipitated as the antimonate $NaSb(OH)_6$ sometimes written

$Na_2H_2Sb_2O_7$ or the uranyl acetate, $(UO_2)_3NaZn(OAc)_9 \cdot 6\ H_2O$. The test involving the formation of sodium zinc uranyl acetate is the more satisfactory, but must be carried out precisely as described. All sodium salts impart a yellow color to a flame.

AMMONIUM

Ammonium is not a metal although an amalgam can be prepared by electrolyzing an ammonium salt using a mercury cathode. The amalgam reacts with water, forming hydrogen and ammonia.

Ion. Common ammonium salts are soluble. Those formed by the action of ammonia and a non-oxidizing acid (HX) decompose when heated according to the equation

$$NH_4X \rightleftarrows NH_3 + HX$$

If HX is volatile, the ammonia and the acid recombine when cooled. If the acid is an oxidizing agent such as nitric, nitrous or dichromic acids, oxidation and reduction take place.

$$NH_4NO_3 \rightleftarrows N_2O + 2\ H_2O$$
$$NH_4NO_2 \rightleftarrows N_2 + 2\ H_2O$$
$$(NH_4)_2Cr_2O_7 \rightleftarrows N_2 + Cr_2O_3 + 4\ H_2O$$

Strong bases react with ammonium salts, forming NH_3 and H_2O.

REACTIONS OF THE IONS

Potassium Ion, K^+

Experiment 25. (*a*) Clean a platinum wire until it gives no color to a non-luminous flame and then dip the end of the wire in a solution of potassium nitrate. Examine the flame with the naked eye and then through a piece of thick cobalt glass. Repeat the experiment with a mixture of the nitrates of potassium and sodium. Can both metals be identified in this way? Better results are obtained by using a chrome alum filter. This is made by placing a saturated solution of chrome alum in a 60 ml. bottle. The bottle should have flat sides which are about an inch apart. Make tests using this filter and note the color of the flame.

(*b*) Heat separately in a small beaker or test tube 4 drops of test solutions of the hydroxides of potassium and sodium. Test the vapor above each solution with moist litmus paper. Give results.

(*c*) Treat 4 drops of a potassium nitrate solution, made acid with acetic acid, with 1 drop of a sodium cobaltinitrite, $Na_3Co(NO_2)_6$, solution. Repeat, using 5 drops of sodium cobaltinitrite. What is the effect of adding the larger quantity of the reagent? Do ammonium salts give precipitates similar to those of potassium? Potassium sodium cobaltinitrite is soluble to the extent of 1 g. in 11,000 ml. of water at 15°. Balance:

$$K^+ + Na^+ + Co(NO_2)_6^{=} \rightleftarrows K_2NaCo(NO_2)_6$$

Sodium Ion, Na^+

Experiment 26. (*a*) What flame test is given by sodium salts? Make the test with a solution of sodium nitrate and then with a more dilute one. Do the intensity and duration of the coloration indicate the amount of sodium present? Note the color of the light of a sodium flame reflected from an orange object. A satisfactory orange reflector is made by placing a layer (3 mm.) of finely divided potassium dichromate in the bottom of a small vial or test tube and holding it in place by a plug of glass wool. The bottom should be held close to the flame, and the light reflected from this surface should be observed. This is a delicate test for sodium.

(*b*) Place in a test tube 4 drops of sodium nitrate. Add 1 drop of potassium hydroxide and 8 drops of some potassium antimonate, $KSb(OH)_6$, and allow the mixture to stand for an hour or more. Precipitation may be hastened by scratching with a stirring rod the inside of the tube just below the surface of the liquid. Complete:

$$Sb(OH)_6^- + Na^+ \rightleftarrows NaSb(OH)_6$$

(*c*) Neutralize or slightly acidify 4 drops of a solution of a sodium salt with acetic acid. Add 1 drop of the slightly acid solution to 5 drops of the uranyl-zinc acetate reagent. Shake the solution and allow it to stand for 5 minutes. A yellow crystalline precipitate, $ZnNa(UO_2)_3(OAc)_9 \cdot 6\ H_2O$, shows the presence of sodium ions. Complete:

$$(UO_2)^{++} + Zn^{++} + Na^+ (+ HOAc) + OAc^- \rightleftarrows NaZn(UO_2)_3(OAc)_9$$

Ammonium Ion, NH_4^+

Experiment 27. (*a*) Do ammonium salts give a characteristic flame test?

(*b*) Test the vapor from ammonia with moist red litmus paper. Interpret the result. Write an equation to show all of the equilibria.

(*c*) In a small Erlenmeyer flask (25 ml.) fitted with a stopper into which a wire or pin bent at right angles or into a loop has been inserted, place 1 ml. of sodium hydroxide. Hang a piece of moist red litmus paper folded to make an inverted V on the wire or pin. Warm to about 40°, and if the litmus paper is unchanged showing the absence of ammonium compounds, cool the flask to room temperature and add 4 drops of a solution of an ammonium salt. Gently warm the solution to approximately 40° (do not boil) and note any change in the color of the litmus paper. Explain the results in terms of chemical equilibria. Complete:

$$NH_4^+ + OH^- \rightleftarrows H_2O + NH_3 \text{ dis.} \rightleftarrows ?$$

(*d*) Repeat Experiment 27*c*, using a small piece of filter paper moistened with a mercurous nitrate solution instead of moist litmus paper. Balance:

$$Hg_2^{++} + NO_3^- + NH_3 \rightleftarrows Hg + Hg_2(N)NO_3 + NH_4^+$$

General Reactions

Experiment 28. (*a*) Treat separately in the apparatus used in Experiment 27*c*, 4 drops of solutions of the hydroxides of potassium, sodium and ammonia. Warm the solutions to about 40°. To avoid spattering do not boil them. Give results.

(*b*) Heat separately to dull redness in a porcelain crucible one small crystal of the sulfates of potassium, sodium and ammonium. Can this method be employed for separating ammonium salts from those of sodium and potassium?

(*c*) Mix 4 drops each of solutions of the nitrates of ammonium, sodium and potassium. Treat 4 drops of this mixture with 1 drop of dilute hydrochloric acid. Do you observe any change? Pass hydrogen sulfide into the acidulated solution. Be sure to use a pressure tube or flask. Does any precipitate form? Heat the solution to drive off the hydrogen sulfide and make it alkaline with ammonia. Again pass in hydrogen sulfide. Do you note the formation of a precipitate? (If the solution darkens the presence of a trace of iron is indicated. Separate any precipitate which may form.) To the clear solution add ammonium carbonate. Is any change observed? Also, determine whether or not a precipitate is formed upon the addition of diammonium phosphate to the solution. Can the reagents employed in these tests be used to determine the presence or absence of the ions in Groups I, II, III or IV?

ANALYSIS

Procedure V

1. Identification of the Ammonium Ion. Treat 4 drops of the solution of the unknown to which no ammonium compound has been added with an excess of sodium hydroxide according to Experiment 27*c*.

2. Preparation of the Solution for the Analysis of Sodium and Potassium Ions. In a crucible, evaporate to dryness the solution from Group IV or 4 drops of the original solution of the unknown if the ions of Groups I–IV are known to be absent. Place the crucible on a clay triangle and heat it until white fumes of ammonium salts are no longer evolved. Cool, add 1 drop of hydrochloric acid and 10 drops of water. Warm to dissolve the residue.

3. Flame Tests for Sodium and Potassium Ions. Make a flame test for potassium according to Experiment 25*a*, and for sodium by Experiment 26*a*.

4. Potassium Ion. To remove any traces of ammonium ion, add 5 drops of a concentrated solution of sodium nitrite and boil the solution. Then acidify with acetic acid, add 2 drops of concentrated sodium nitrite and 4 drops of 1-*N* cobalt nitrate or sodium cobaltinitrite. Warm the mixture. A yellow crystalline precipitate, $K_2NaCo(NO_2)_6$, indicates potassium.

5. Sodium Ion. Slightly acidify with acetic acid, 4 drops of the solution from the carbonate precipitate, Procedure IV, 1. Test for the sodium ion by adding a drop of the acidified solution to 5 drops of the zinc-uranyl acetate reagent, $ZnH(UO_2)_3(OAc)_9$. Shake the solution and allow it to stand 5 minutes. A pale yellow crystalline precipitate, $ZnNa(UO_2)_3(OAc)_9 \cdot 6\,H_2O$ indicates the presence of sodium. This test must be made before a phosphate is added.

Original Unknown, 4 drops, or Solution from Group IV: NH_4^+, K^+, and Na^+. Evaporate to dryness in a crucible. Place the crucible on triangle and heat until all ammonium salts are expelled. Cool, add 1 drop of hydrochloric acid and 10 drops of water. Warm.

Flame Tests. Test the solution for potassium and sodium by Experiments 25*a* and 26*a*

Potassium Ion. Test the solution for potassium ions by Procedure V, 4.

Sodium Ion. Test 4 drops of the solution from the carbonate precipitate, Procedure IV, 1, for sodium ions by Procedure V, 5.

Ammonium Ion. Test 4 drops of the original solution for the ammonium ion by Experiment 27*c*. Discard the solution.

Discussion of the Analysis

In its properties the ammonium ion closely resembles the potassium ion. For this reason ammonium salts must be removed before testing for the potassium ion with sodium cobaltinitrite or any other precipitating agent. When other groups are present, some of them are separated from others by the addition of ammonium salts. Hence, in any analysis of the cations, the test for the *ammonium ion must be made on the original solution.*

Solid ammonium salts present in an unknown containing Group V are more easily decomposed and volatilized than the corresponding salts of sodium and potassium. This makes it possible to remove interfering ammonium salts by ignition. After evaporating the solution from the $MgNH_4PO_4$ precipitate of Group IV, heat the residue to dull redness, but not hotter, otherwise some sodium and potassium compounds may also be volatilized.

Test for Ammonium Salts. According to the procedure the ammonium ion is identified by treating a portion of the original solution with sodium hydroxide. The ammonium ion, acting as an acid, loses a proton to a hydroxide ion, since this ion is a stronger base than ammonia.

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

Solutions of ammonia contain a low concentration of hydroxide ions. Sodium hydroxide is completely ionized in a solution of the same normality. Thus, the high concentration of the hydroxide ion from the excess of sodium hydroxide decreases the solubility of ammonia gas. In a warm solution the gas escapes and the forward reaction is favored.

$$NH_4^+ + OH^- \rightleftarrows H_2O + NH_3 \text{ (dissolved)} \rightleftarrows NH_3 \text{ (gas)}$$

The absence of ammonia in the sodium hydroxide must be established since the reagent is frequently contaminated with ammonia.

When the ions of metals having insoluble hydroxides are present, a precipitate will form upon the addition of sodium hydroxide, thereby removing some of the hydroxide ions. In addition many unknowns contain acids which must be neutralized before the ammonia is liberated. An excess of sodium hydroxide must be added before concluding that the ammonium ion is absent.

Flame Tests. The flame tests for potassium and sodium are reliable when properly carried out. The intensity and duration of the flame colorations should be compared carefully with the coloration given by solutions of known concentration. For the identification of potassium, the chrome alum filter is preferred to the cobalt glass. Each absorbs the rays of yellow light but permits rays of purple light to pass through it. The chrome alum filter makes it possible to test for potassium in the presence of calcium, strontium, barium and copper ions. In the presence of these ions the use of cobalt glass is unsatisfactory because it is not specific enough in its absorption. An orange object appears yellow when illuminated by a yellow flame. Thus, if an orange object, held close to the flame, appears yellow in the light from a Bunsen burner in which a platinum wire is being heated, sodium compounds are present.

Tests for the Potassium Ion. Sodium cobaltinitrite is given preference over other precipitating agents for potassium ions because dipotassium sodium cobaltinitrite is one of the least soluble salts of the element. Furthermore, moderate concentrations of the ions of the alkaline-earth metals do not interfere with this test. Since ammonium salts give a similar precipitate, they must be removed. This is accomplished by digesting with sodium nitrite.

$$NH_4^+ + NO_2^- \rightleftarrows N_2 + H_2O$$

It is preferable to add acetic acid, cobalt nitrate and an excess of sodium nitrite as described in Procedure V, 4 to precipitate dipotassium sodium cobaltinitrite than to add a solution of sodium cobaltinitrite, since any ammonium ions not removed by evaporating the solution and igniting the residue are destroyed by the nitrite ions. Other reagents for precipitating potassium are sodium perchlorate ($NaClO_4$), sodium hydrogen tartrate, picric acid and chloroplatinic acid.

Test for Sodium. Zinc hydrogen uranyl acetate, $ZnH(UO_2)_3(OAc)_9$, precipitates zinc sodium uranyl acetate, $ZnNa(UO_2)_3(OAc)_9$, from a solution containing a low concentration of acetic acid. Calcium, strontium, barium, magnesium, potassium and ammonium salts do not interfere with this test unless the concentration of the cation is above 5 mg. in a final volume of 1 ml. However, phosphates and arsenates will cause the formation of a white gelatinous precipitate which does not resemble that obtained with sodium ions. The test for sodium ions should be made before a phosphate is added to precipitate magnesium ions. The phosphate ion interferes by precipitating zinc phosphate, hence the test must be made before a phosphate is added to test for magnesium. It is essential that the proper volumes are used in making the test.

EXERCISES

1. How many milliliters of 2-*N* sodium hydroxide are required to react with 1 mg. of ammonium ion? *Ans* 0.028 ml. or 0.56 drop.
2. How many milliliters of 0.1-*N* sulfuric acid will be required to neutralize 10 ml. of a 0.3-*N* base?
3. How many milliliters of 2-*N* ammonium carbonate will contain 0.006 of an equivalent of carbonate? *Ans.* 3 ml.
4. How many milliliters of 3-*N* potassium chromate must be added to precipitate 15 mg. of barium ion?
5. How many milliliters of 0.1-*N* acid are required to neutralize 15 ml. of 0.3-*N* base? *Ans.* 45 ml.
6. How many milliliters of 2-*N* sodium hydroxide will be required to precipitate completely the iron in 10 ml. of a solution containing 1 mole of ferric chloride ($FeCl_3$) per liter?
7. If all the ammonium salts are not driven off after the removal of the magnesium ion, how will the analysis of sodium and potassium be affected?
8. Why should the solution used in testing for the sodium ion with potassium pyroantimonate be made slightly alkaline?
9. A yellow precipitate is obtained when sodium cobaltinitrite is added to a solution prepared for the analysis of sodium and potassium, but no flame test for potassium can be obtained with the solution prepared by dissolving the precipitate in hydrochloric acid. Explain this inconsistency.
10. How may supersaturated solutions be changed to saturated solutions?
11. Write equations to show the action of ammonium salts toward heat.
12. State the general rule for the solubility of sodium and potassium salts.
13. Why is the test for the ammonium ion made on the original solution?
14. Write equations to show the effect of igniting ammonium chloride, ammonium nitrate, ammonium nitrite.
15. If the stannous ion is present in a solution being analyzed for Groups I to V, what ions cannot be present?
16. A solution contains the sulfate ion. What ions are absent?
17. A solution contains the chloride ion. What ions are absent?
18. No precipitate formed on adding an excess of sodium hydroxide to a solution being analyzed for Groups I to V. What ions are absent?

19. A solution being analyzed for Groups I to V is colorless. What ions are probably absent?
20. Some precipitate was formed on adding ammonia to a solution being analyzed for Groups I to V. No precipitate was formed when an ammonium salt was added and then ammonia. What ions are absent?
21. Draw diagrams to show the analysis of Groups I to V.
22. Write equations to show the action of each ion toward each reagent with which it is treated during the analysis.

THE ANIONS

CHAPTER XIV

General Discussion

THE ANIONS which are included in the system of analysis are given in the following list.

Anions

Arsenate	Ferricyanide	Perchlorate
Borate	Ferrocyanide	Phosphate
Bromate	Fluoride	Sulfate
Bromide	Hypochlorite	Sulfide
Carbonate	Iodate	Sulfite
Chlorate	Iodide	Thiocyanate
Chloride	Nitrate	Thiosulfate
Chromate	Nitrite	
Cyanide		

In the procedures for the detection of the anions as many ions as possible have been separated into groups based on the solubilities of their calcium, barium, cadmium and silver salts, as follows:

Group I. Ions whose calcium salts are insoluble in neutral solutions.
Group II. Ions whose calcium salts are soluble but whose barium salts are insoluble in neutral solutions containing 20% of acetone by volume.
Group III. Ions whose calcium and barium salts are soluble but whose cadmium salts are insoluble in neutral solutions.
Group IV. Ions whose calcium, barium and cadmium salts are soluble but whose silver salts are insoluble in solutions slightly acid with nitric acid.
Group V. Ions whose salts are practically all soluble.

Since some of the ions form difficultly soluble salts with more than one of the group reagents, these ions may be found in more than one group. For this reason the separation of the anions into

* The procedures for the analysis of anions is based on the work of Sneed and Duschak, J. Chem. Ed. *8*:1177–86; 1386–95, 1931, and were adapted to semimicro analysis by Heisig and A. Lerner.

Division into Groups

Neutral Solution Containing All Anions. Add $Ca(CH_3CO_2)_2$.

Group I	Group II	Group III	Group IV	Group V
Precipitate: $CaCO_3$ (0.1)* CaF_2 (0.1) $CaHPO_4$ (0.04) $CaSO_3$ (0.8) $CaHAsO_4$ $[Ca_2Fe(CN)_6]$ (17.5) $[Ca(IO_3)_2]$ (12.5)	*Precipitate:* $SrSO_4$ (0.02) $SrSO_2$ (0.2) $[SrCrO_4]$	*Precipitate* $BaCrO_4$ (0.05) $Ba(IO_3)_2$ (0.4) $[Ba(BrO_3)_2]$ (4.5) $[Ba_2Fe(CN)_6]$ (3.0) $[BaS_2O_3]$ (4.5)	*Precipitate* $Cd_2Fe(CN)_6$ (0.05) $Cd_3(Fe(CN)_6)_2$ (0.05) CdS (0.03) $[Cd(CN)_2]$ (5.0) $[Cd(BO_2)_2]$	*Precipitate:* $Ni(CN)_2$ (0.2)	*Precipitate:* AgCl, AgBr, AgI, AgCNS, $Ag_2S_2O_3 \rightarrow Ag_2S$ (0.05 for each ion)
See Table VIII	*Solution* Add $Ba(CH_3CO_2)_2$ and acetone.				
	See Table IX	*Solution:* Add $Cd(CH_3CO_2)_2$.			
		See Table X	*Solution* Add $Ni(NO_3)_2$.		
			Solution Add $AgNO_3$ and HNO_3.		
			See Table XI	*Solution:* ClO_3^-, (0.1) ClO_4^-, (0.1) BrO_3^-, (0.1) IO_3^-, (0.1) NO_3^-, (0.1) NO_2^-, (0.1) BO_2^-, (0.05) †	
				See Table XII	

* These numbers designate the minimum number of milligrams of the anion which must be present in 1 ml.

† The hypochlorite ion is not shown in this diagram, but is identified in Group V.

groups is not quite so definite and clean cut as that of the cations. In the outline for division into groups, formulas enclosed in brackets indicate precipitates which are formed only in solutions containing high concentrations of the anions concerned. This table shows that when the maximum concentration of the anions present is 1 mg. per milliliter, there are only two ions which are precipitated in more than one group. Discussions of the individual cases are included in the procedures for the respective groups.

Since the separation into groups depends on the precipitation of substances insoluble in water but in many cases soluble in acids, it is essential that the solution at the beginning of the analysis be slightly alkaline. If the solution is acid, it should be neutralized by adding a very slight excess of ammonia. If a large excess of base is present in the original solution (for example when sodium carbonate or sodium hydroxide has been used to prepare a solution of an insoluble substance), it should be nearly neutralized with acetic acid, leaving the solution slightly alkaline.

In precipitating the first three groups the acetates of calcium, barium and cadmium are used as precipitating agents for two reasons:

1. The acetate ion does not interfere with any of the succeeding separations, since it does not form precipitates with any of the ions used as reagents, nor does it oxidize or reduce any of them.

2. Solutions of the acetates of calcium, barium and cadmium are neutral or slightly alkaline due to hydrolysis; while the corresponding salts of the strong acids, such as nitrates, are slightly acid. Since the group separations depend on the insolubility of the salts in neutral solutions, the acidity produced by hydrolysis in solutions of salts other than acetates may be sufficient to prevent complete precipitation.

GENERAL DIRECTIONS

In carrying out the analysis results will be much more satisfactory if the following directions and precautions are observed:

1. Each student should make a wash bottle according to the sketch on page 140. The wash bottle should be kept filled with distilled water to rinse equipment after it has been washed thoroughly with tap water. All apparatus must be kept scrupulously clean.

2. To wash precipitates each student should have on the desk a 25 ml. flask containing cold distilled water and a medicine dropper. A similarly fitted flask should be kept on a wire gauze above

a small flame to furnish hot distilled water for washing precipitates. Read the sections on the separation, solution and extraction of precipitates and the heating of the contents of a test tube on pages 153–154.

3. Place a beaker on the desk to use as a receptacle for burnt matches, glass wool, etc. Empty the beaker at the close of each laboratory period.

4. Carry out the preliminary experiments with the same concentration of anions used for the analysis (1 mg. of the anion—4 drops of test solution to which 5 drops of distilled water have been added).

5. To have 1 mg. of each anion in the sample used for the analysis, use 4 drops of the known or unknown. To this sample add 5 drops of distilled water. If the solution is acidic add ammonia until it is slightly alkaline. If the solution is alkaline add a slight excess of acetic acid and again make it alkaline by adding ammonia.

6. Always test the sample for oxidizing and reducing anions. Frequently, much valuable information can be obtained from these tests.

(*a*) *Detection of Oxidizing Anions.* The oxidizing anions, with the exception of the arsenites and perchlorates, change a colorless solution of manganous chloride in concentrated hydrochloric acid to a brown or black solution of manganic chloride ($MnCl_3$). To detect the presence of oxidizing agents in the absence of reducing agents, add 8 drops of a saturated solution of manganous chloride in concentrated hydrochloric acid (12-*N*) to 2 drops of a solution of an unknown which has been prepared for the analysis of anions and heat. A positive test proves the presence of oxidizing agents such as chromate, dichromate, ferricyanide, chlorate, bromate, iodate, hypochlorite, nitrate, and nitrite ions. A negative test, however, does not prove the absence of oxidizing anions.

(*b*) *Detection of Reducing Anions.* The formation of a blue precipitate of ferrous ferricyanide or ferric ferrocyanide by the reduction of either the ferric or ferricyanide ion is the basis for a test for reducing anions. The ferricyanide ion is reduced more readily than the ferric ion except by reducing agents which react with hydrochloric acid forming sulfur dioxide. The ferric ion is more rapidly reduced than the ferricyanide ion by such anions.

To a solution of ferric ferricyanide (brown) made by mixing 1 drop of a recently prepared solution of 0.5-*N* potassium ferricyanide, 1 drop of a 1-*N* solution of ferric nitrate and 1 drop of 5-*N* hydrochloric acid add 1 drop of a neutral solution of an unknown. Let the mixture stand for 2 to 3 minutes. A blue precipitate

or blue coloration proves the presence of a reducing agent. If a thiocyanate reacts with the ferric ions and makes it impossible to determine whether or not a precipitate is present, separate the solution with a centrifuge or filter tube.

About 0.001 mg. of a reducing anion may be detected by this procedure thus assuring the absence of reducing anions if a negative test is obtained. The test gives the desired information even in the presence of oxidizing anions unless the oxidizing agents are so powerful (permanganates, chromates and hypochlorites for, example) that the reducing agents are destroyed before they can react.

7. Always determine whether any anions are present which form insoluble silver salts. Note the character and the color of the precipitate which forms and whether it is soluble wholly or in part in nitric acid, for this information frequently enables one to establish the presence or absence of many anions. The test is made by adding dropwise to 4 drops of the neutral unknown solution, 2 drops of silver nitrate. If a precipitate forms, it may be any of the following silver salts: acetate if present in high concentration, arsenate, borate if present in high concentration, bromate, bromide, carbonate, chloride, chromate, cyanide, ferro- and ferricyanide, iodate, phosphate, sulfide, sulfite if present in high concentration, and thiocyanate. The colors of these salts are found on page 158. Without separating the precipitate, add a drop of nitric acid and then a second drop. Make a list of the silver salts previously listed which are soluble in nitric acid.

8. Calculate the maximum volume of precipitating agent required if all of the ions which may react are present and then add 10% excess. For the method of calculation see page 142.

9. Keep the solution cool and slightly alkaline until Group IV is precipitated.

10. Precipitates must always be washed thoroughly. Usually this can be accomplished by four or five washings of 3 to 4 drops of the wash liquid. To make the process as efficient as possible direct the drops around the top of the tube and break up the precipitate. Allow the liquid to remain in contact with the precipitate for a few moments and then remove all of the liquid from the tube before adding more of the wash liquid. Remember that several washings with successive small amounts of the wash liquid are much more efficient than fewer washings with larger amounts (page 151). To keep the volume of the solution as small as possible add only one or two washings to the solution. Reject the rest.

11. Keep the volume of the solution as small as possible by

adding the smallest volume of precipitating agent that will percipitate the ions completely. In precipitating each group add the precipitating agent dropwise, agitating the mixture and allowing it to settle between additions, until no further precipitation takes place. After separating the precipitate add a drop of the reagent to the solution to make certain that the precipitation has been complete. To remove any precipitate adhering to the walls of a container, return the solution and again separate the precipitate.

12. If the precipitate is finely divided and has a tendency to run through the glass wool filter used in a filter tube, repeatedly circulate it through the glass wool until the filtrate is clear. If the suspended material cannot be removed in this way, pack the glass wool filter tighter and again pass the liquid through the filter. Use only enough pressure to force the liquid through the glass wool. The finer the precipitate, the less should be the pressure.

13. To extract a solute from a small volume of a solution, shake the solution with several drops of the immiscible liquid. Then, using a medicine dropper of appropriate length, transfer the aqueous solution to a second test tube. Repeat these operations until the solute is removed from the aqueous solution. A second method of separating two immiscible liquids is to pour the mixture quickly from one test tube to another until only a small amount of liquid is left in the test tube. If the operation has been carried out properly, the lighter solution remains in the test tube. With a little practice two immiscible liquids can be separated by carrying out this process several times.

14. The cations of the heavier metals should not be present in the solution to be analyzed for anions. Precipitate the cations as hydroxides or carbonates by adding 3-*N* sodium carbonate and digesting the mixture 20 minutes at the temperature of boiling water. Use the solution for the analysis of the anions and the precipitate for the analysis of cations. Directions are given on page 315.

CHAPTER XV

Anions of Group I

PROPERTIES OF ACIDS AND IONS

CARBONATE

ACID. Carbon dioxide combines to a small extent with water, forming H_2CO_3, a weak, diprotic (dibasic) acid.

Ions. Two series of salts are formed, the normal carbonates and the hydrogen carbonates. All normal carbonates except those of the alkalies and ammonium are insoluble. The hydrogen carbonates are usually more soluble than the carbonates.

Acids react with either the normal carbonate or the hydrogen carbonate ion forming CO_2 and H_2O.

The alkaline earth metals precipitate the normal carbonate from alkaline or even neutral solutions.

Phenolphthalein turns pink in solutions containing $CO_3^=$ but is colorless in solutions containing the HCO_3^-.

Silver nitrate precipitates Ag_2CO_3 (yellow) from solutions containing either $CO_3^=$ or HCO_3^-.

The $CO_3^=$ and HCO_3^- are neither oxidizing nor reducing agents.

SULFITE

Acid. Sulfurous acid is a weak, diprotic (dibasic) acid. It is unstable, decomposing into SO_2 and H_2O.

Ions. With the exception of the Na and K salts, the normal sulfites are slightly soluble. The hydrogen sulfites are soluble.

Sulfites and hydrogen sulfites decompose when treated with HCl or H_2SO_4, forming SO_2 and H_2O.

Ions of the alkaline earths precipitate normal sulfites. The calcium salt is the most soluble of the sulfites of the alkaline earths.

Sulfurous acid is a reducing agent and is usually oxidized to $SO_4^=$. Dilute acid solutions of MnO_4^- oxidize the HSO_3^- to $H_2S_2O_6$ (dithionic acid). This acid, like all of the acids containing sulfur,

is oxidized to the $SO_4^=$ by an excess of oxidizing agents, such as iodine, bromine, chlorine, chlorates, bromates or chromates. Since the halogens are oxidizing agents, the reduction products of the oxy-halogen ions cannot be a halogen unless an excess of the oxidizing agent is present. The reduction of Fe^{+++} by HSO_3^- is more rapid than the reduction of $Fe(CN)_6^=$, hence Turnbull's blue, $Fe^{II}[Fe^{III}[Fe(CN)_6]]_2$ is formed by the action of HSO_3^- with $Fe[Fe(CN)_6]$.

Sulfur dioxide oxidizes HS^- to S.

$$HSO_3^- + 2\,HS^- + 3\,H_3O^+ \rightleftarrows 3\,S + 6\,H_2O$$

It also changes $SnCl_4^=$ to SnS_2 and $SnCl_6^=$, a second case in which sulfur dioxide, or possibly more correctly the HSO_3^-, acts as an oxidizing agent.

$$6\,SnCl_4^= + 10\,H_3O^+ + 2\,HSO_3^- + 6\,Cl^- \rightleftarrows SnS_2 + 5\,SnCl_6^= + 16\,H_2O$$

If the $C_{H_3O^+}$ is high, the products are $SnCl_6^=$ and H_2S.

FLUORIDE

Acid. Hydrofluoric acid, the aqueous solution of hydrogen fluoride, is a weak acid. The molecular weight of hydrogen fluoride above 90° corresponds to the formula HF. At low temperatures the formula is H_6F_6. The simplest formula for the acid will be used. The existence of HF_2^- is probably explained by the coordination of an F^- with the hydrogen in an HF molecule. A constant boiling solution contains 35.4% of HF.

Ions. The fluorides of Ag, Hg, Na, K and NH_4 are soluble and those of Cu, Pb and Fe^{+++} are slightly soluble. The alkaline earths precipitate insoluble fluorides, BaF_2 being the most soluble and CaF_2 the least.

Concentrated H_2SO_4 liberates HF from fluorides. The HF may be detected by the etching of glass or by the formation of $Si(OH)_4$ in a drop of water. The equation for the reaction is

$$3\,SiF_4 + 6\,H_2O \rightleftarrows Si(OH)_4 + 2\,HSiF_6^- + 2\,H_3O^+.$$

The F^- cannot be oxidized to F_2 by ordinary chemical means.

PHOSPHATE

Acids. There are at least three common phosphoric acids: H_3PO_4 (ortho), HPO_3 (meta) and $H_4P_2O_7$ (pyro). These differ in the hydra-

tion of the acid anhydride. The ortho acid is a distinctly weaker acid than HCl, in fact 1-*M* H_3PO_4 has about the same $C_{H_3O^+}$ as 0.1-*M* HCl. The meta acid is really $(HPO_3)_x$ where x has values starting with 2. Only the orthophosphate ions are included in the procedure.

Ions. The alkaline earths precipitate mono-hydrogen phosphates from neutral or slightly alkaline solutions.

Yellow Ag_3PO_4 is precipitated from neutral solutions by the addition of Ag^+.

An excess of a HNO_3 solution of $(NH_4)_2MoO_4$ precipitates yellow $(NH_4)_3PO_4 \cdot 12\ MoO_3 \cdot 5\ H_2O$ from cold or warm solutions. Other formulas, such as $(NH_4)_3H_4[P(Mo_2O_7)_6]$ aq., have been suggested for this salt. Arsenates form a precipitate which has a similar formula and color, but precipitation does not start until the temperature is about 90°.

The $PO_4^{\equiv}$ interferes with the analysis of cations. Its removal is discussed on pages 208 and 215.

Solutions of tribasic salts (M_3PO_4) are alkaline toward phenolphthalein, those of the dibasic salts (M_2HPO_4) are neutral toward phenolphthalein, while the solutions of the monobasic salts (MH_2PO_4) are slightly acid toward methyl orange. Heat changes solid monobasic orthophosphates to PO_3^-, and the dibasic phosphates to the $P_2O_7^{\equiv}$. An orthophosphate can be distinguished from the meta- and pyrophosphates by its silver salt (Ag_3PO_4) which is yellow while $Ag_4P_2O_7$ and $Ag(PO_3)$ are white. The $P_2O_7^{\equiv}$ or $H_2P_2O_7^{=}$ precipitates $Zn_2P_2O_7$ (white) whereas the PO_3^- does not give a precipitate. Luteo cobaltic chloride gives a brownish yellow precipitate, $Co(NH_3)_6(PO_3)_3$, when added to PO_3^- in the presence of dilute acetic acid. No precipitate is formed on adding PO_3^- to fairly concentrated solutions of $ZnSO_4$ whereas $PO_4^{\equiv}$ and $P_2O_7^{\equiv}$ give white precipitates.

ARSENATE

Acids. Arsenic pentoxide reacts with water to form three acids: H_3AsO_4, $HAsO_3$ and $H_4As_2O_7$—ortho-, meta- and pyro-arsenic acids. Ortho-arsenic acid is one of the stronger weak acids. Its strength as an acid is about the same as that of orthophosphoric acid.

Ions. The ions of the alkaline earths precipitate monohydrogen arsenates from neutral or slightly alkaline solutions. The normal arsenates are precipitated from an alkaline solution. Both the

monohydrogen and the normal arsenates are soluble in mineral acids, forming $H_2AsO_4^-$.

Hydrogen sulfide precipitates a mixture of As_2S_3 and As_2S_5 from strongly acid solutions containing the ions of H_3AsO_4. The precipitation is slow.

$$H_3AsO_4 + H_2S \rightleftarrows H_3AsO_3S + H_2O$$
$$H_3AsO_3S \rightleftarrows HAsO_2 + H_2O + S$$
$$2\,HAsO_2 + 3\,H_2S \rightleftarrows As_2S_3 + 4\,H_2O$$

Chocolate colored silver arsenate (Ag_3AsO_4), soluble in mineral acids and NH_3, precipitates on the addition of $AgNO_3$ to a neutral or slightly acid solution (HOAc) of an arsenate.

Iodides reduce strongly acid solutions of arsenates to arsenious acid.

$$H_3AsO_4 + 2\,I^- + 2\,H_3O^+ \rightleftarrows H_3AsO_3 + I_2 + 3\,H_2O$$

Magnesium ammonium arsenate precipitates when a solution of a magnesium salt containing NH_3 and NH_4^+ is added to an arsenate.

$$AsO_4^{\equiv} + NH_4^+ + Mg^{++} \rightleftarrows MgNH_4AsO_4$$

For more of the chemistry of arsenic see page 169.

REACTIONS OF THE IONS

Carbonate Ions, $CO_3^=$

Experiment 29. (*a*) Add a saturated solution of carbon dioxide or pass a stream of carbon dioxide into 4 drops of a clear solution of limewater until precipitation is complete, and then continue the treatment for several minutes. Explain the results. Complete:

$$CO_2 + Ca^{++} + OH^- \rightleftarrows ? + ?$$
$$CaCO_3 + CO_2 + H_2O \rightleftarrows Ca^{++} + ?$$

(*b*) Add a saturated solution of carbon dioxide or pass carbon dioxide into a barium hydroxide solution. What is the precipitate? Sulfur dioxide and carbon dioxide are the only two gases which give white precipitates with barium hydroxide. If the two gases are present together (sulfur dioxide can be recognized by its smell), the sulfur dioxide must be removed before testing for carbon dioxide.

(*c*) Fit a small test tube with a stopper containing a glass tube 4 cm. long (Fig. 13) constricted at the center. Cut a groove in the stopper so that the pressure on the inside of the test tube does not vary from that of the atmosphere. Place a drop of freshly prepared, clear solution of barium hydroxide in the constricted part of the tube. Place 4 drops of a solution of sodium carbonate in the test tube. Quickly add 4 drops of acetic acid and reassemble the apparatus. Put the test tube in a hot water bath maintained at 70° to 80°. What is

the white precipitate which forms in the surface of the solution below the constriction? Complete:

$$Ba^{++} + CO_3^{=} \rightleftarrows ?$$

Repeat using 4 drops of a sulfite instead of a carbonate. Complete:

$$Ba^{++} + SO_3^{=} \rightleftarrows ?$$

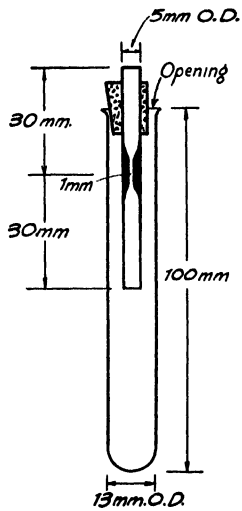


Fig. 13.

Sulfite Ion, $SO_3^{=}$

Experiment 30. (*a*) Add a saturated solution of sulfur dioxide to an acidified solution of potassium chromate. What is the result? Repeat, using a solution of potassium permanganate. Prove that the stannous ion is oxidized to the stannic ion. Complete:

(1) $Cr_2O_7^{=} + SO_2 + H_3O^+ \rightleftarrows Cr^{+++} + HSO_4^- + ?$
(2) $MnO_4^- + SO_2 + H_2O + H_3O^+ \rightleftarrows Mn^{++} + HSO_4^-$
(3) $SnCl_4^{=} + SO_2 + H_3O^+ + Cl^- \rightleftarrows SnS_2 + SnCl_6^{=} + ?$

(*b*) Treat a dilute ferric nitrate solution with a solution of sulfur dioxide. Note the change in color of the solution. Add a solution of sulfur dioxide to 4 drops of a solution of barium hydroxide. Is the precipitate soluble in an excess of the gas? In dilute hydrochloric acid? Balance:

(1) $Fe^{+++} + SO_2 + H_2O \rightleftarrows Fe_2(SO_3)_3 + ?$
(2) $Fe_2(SO_3)_3 \rightleftarrows SO_3^{=} + S_2O_6^{=} + Fe^{++}$

(*c*) Add 1 drop of 0.5-*N* potassium ferricyanide to a mixture of 1 drop of ferric nitrate and 1 drop of 5-*N* hydrochloric acid. To the brown solution of

ferric ferricyanide, add 1 drop of a solution of sulfur dioxide. What is a common name of the precipitate? Balance:

$$FeFe(CN)_6 + SO_3^{=} + (H_3O^+) + H_2O \rightleftarrows Fe^{II}[Fe^{III}Fe(CN)_6]_2 + HSO_4^- + Fe(CN)_6^{=} + H_3O^+$$

(*d*) Add enough of a clear solution of barium hydroxide to fill the constricted part of the tube used in Experiment 29*c*. Then add enough of an acidified solution of ferric ferricyanide (see Experiment 30*c*) to form a film in the lower end of the tube. Place 4 drops of a solution of sodium sulfite in the test tube, add 4 drops of acetic acid and quickly assemble the apparatus. Place the test tube in the water bath maintained at 70° to 80°. Note whether there is any change in the color of the solution and whether any precipitate forms in the barium hydroxide in the constructed part of the tube. Repeat but omit the addition of the sulfite ion to the test tube. Balance:

$$FeFe(CN)_6 + SO_3^{=} + (H_3O^+) + H_2O \rightleftarrows Fe^{II}[Fe^{III}Fe(CN)_6]_2 + HSO_4^- + Fe(CN)_6^{=} + H_3O^+$$

(*e*) Add 4 drops of a solution of sodium sulfite to 4 drops of a solution of lead acetate. Heat the mixture. Is there any change? Repeat, using sodium thiosulfate instead of the sulfite. Note the difference and explain. Do these reactions distinguish a sulfite from a thiosulfate? Complete:

$$PbS_2O_3 + H_2O \rightleftarrows PbS + HSO_4^- + ?$$

(*f*) To 4 drops of a solution of sulfur dioxide add a slight excess of bromine water. Add to the solution 1 drop of hydrochloric acid and then 2 drops of a barium chloride solution. Explain the resutls. Complete:

$$Br_2 + SO_2 + H_2O \rightleftarrows HSO_4^- + ? + ?$$

(*g*) To a solution containing 4 drops of sodium sulfite and 4 drops of sodium thiosulfate add a solution of strontium acetate. Allow the mixture to settle, separate the precipitate and wash it. Test the precipitate for a sulfite and the solution for a thiosulfate (see Experiment 41*c*). This method may be used to identify the sulfite ion in the presence of a thiosulfate.

Phosphate Ion, $PO_4^{\equiv}$

Experiment 31. (*a*) Test with litmus paper, phenolphthalein and methyl orange, solutions of mono-, di-, and trisodium hydrogen orthophosphates, respectively, and give results. Judging from the behavior of the solutions, what is the relative tendency of the three hydrogens in phosphoric acid to ionize?

(*b*) Treat 4 drops of a solution of sodium phosphate with 4 drops of magnesium nitrate mixture. To 4 drops of a solution of disodium hydrogen phosphate add silver nitrate. Give the color of the precipitate. Complete:

(1) $HPO_4^{=} + Mg^{++} + (NH_4^+) + NH_3 \rightleftarrows MgNH_4PO_4$

(2) $HPO_4^{=} + Ag^+ \rightleftarrows ?$

(*c*) To 4 drops of a solution of sodium phosphate add 10 drops of ammonium molybdate (nitric acid solution). Warm the mixture and note the formation of a canary-yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12\ MoO_3 \cdot 5\ H_2O$. Separate the precipitate, wash it, and dissolve it in a little

ammonia. Add magnesia mixture to the ammoniacal solution. What is the precipitate? Complete:

(1) $HPO_4^{=} + MoO_4^{=} + H_3O^+ + NH_4^+ \rightleftarrows (NH_4)_3PO_4 \cdot 12\,MoO_3 \cdot 5\,H_2O + ?$
(2) $(NH_4)_3PO_4 \cdot 12\,MoO_3 \cdot 5\,H_2O + NH_3 + H_2O \rightleftarrows PO_4^{=} + MoO_4^{=} + NH_4^+$

(*d*) Add a drop of a solution of sodium trimetaphosphate to 4 drops of a solution of calcium nitrate. Then add an excess of the solution of the sodium trimetaphosphate. Account for your observation. Balance:

(1) $Ca^{++} + (PO_3)_3^{3-} \rightleftarrows Ca_3[(PO_3)_3]_2$
(2) $Ca_3[(PO_3)_3]_2 + (PO_3)_3^{3-} \rightleftarrows [Ca(PO_3)_3]^-$

Arsenate Ion, $AsO_4^{=}$

Experiment 32. (*a*) To 4 drops of a solution of sodium arsenate add 10 drops of ammonium molybdate. Divide the solution into two parts. Heat one in the

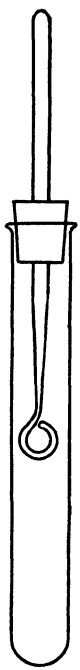


Fig. 14.

water bath and let the other stand at room temperature. Note any differences in the color of the two solutions. Compare the result with that obtained in Experiment 31*c*. Complete:

$MoO_4^{=} + HAsO_4^{=} + NH_4^+ + H_3O^+ \rightleftarrows (NH_4)_3AsO_4 \cdot 12\,MoO_3 \cdot 5\,H_2O + ?$

(*b*) Add a drop of silver nitrate to 4 drops of a solution of sodium arsenate. Silver arsenate can be detected in a mixture of silver arsenate and phosphate if the ratio of arsenate to phosphate is greater than one to four. Complete:

(1) $HAsO_4^- + Ag^+ \rightleftarrows ?$
(2) $HPO_4^- + Ag^+ \rightleftarrows ?$

Fluoride Ion, F^-

Experiment 33. (*a*) Add 2 drops of silver nitrate to 4 drops of a solution of ammonium fluoride.

(*b*) Add several drops of calcium acetate to 4 drops of a solution of a fluoride. Is the precipitate soluble in acetic acid? Hydrochloric acid? Nitric acid? What other salt of calcium behaves towards acids in the same manner?

(*c*) Moisten glass wool with 4 drops of a solution of sodium fluoride. Dry the glass wool by heating it over the flame of a Bunsen burner. Place the glass wool in a dry test tube fitted with a rubber stopper containing a glass rod 6 cm. long, one end of which is drawn out and bent into a ring having a diameter of 3 mm. (Fig. 14). Break up the glass wool with a stirring rod or spatula. Dip the glass rod in water so that a film of water stretches over the ring. Then add 6 drops of concentrated sulfuric acid to the glass wool, and assemble the apparatus. A distinct white precipitate, H_4SiO_4, which collects on the glass shows the presence of a fluoride. Complete:

(1) $SiO_2 + HF \rightleftarrows SiF_4 + ?$
(2) $SiF_4 + H_2O \rightleftarrows H_4SiO_4 + HSiF_6^- + ?$
(3) $H_4SiO_4 \rightleftarrows SiO_2 + ?$

ANALYSIS

Procedure VI

1. Precipitation of the Calcium Salts. To 4 drops of the sample which may contain any or all of the anions of Groups I to V, add 5 drops of distilled water and then make the solution slightly alkaline as described in paragraph 5, page 240. Then add 2-*N* calcium acetate until the precipitation is complete. A maximum of 3 drops is necessary. Stir the mixture well and allow it to settle. Separate the precipitate with a centrifuge (page 147) or with a filter tube fitted with a plug of glass wool (page 148) and wash the precipitate thoroughly four times with 4 drops of hot water. Add the first wash liquid to the solution from the calcium salts.

*2. Identification of the Carbonate Ion.** Dry the precipitate of the calcium salts, which are in a centrifuge tube or on a glass wool filter, above a small flame of a Bunsen burner. Fit the centrifuge tube containing the calcium salts or a small test tube into which the glass wool plug containing the calcium salts has been placed,

* If sodium carbonate has been used to prepare the solution, test for the carbonate on a portion of the original sample (solid or liquid) in the same manner.

with a glass tube constricted near the center (Fig. 13). The tube must be very clean. Add enough of a clear solution of barium hydroxide to the top of the tube to fill the constricted part of the tube (1 drop). Then add enough of a freshly prepared acidified solution of ferric ferricyanide (Experiment 30c) to form a film in the lower end of the tube. With a clean piece of filter paper remove any liquid on the outside of the tube. The solution of ferric ferricyanide must be brown, not green. Moisten the precipitate of the ions of Group I with 6 drops of acetic acid. Reassemble the apparatus and place the tube for 2 minutes in the hot water bath kept between 70° to 80°. A white precipitate of barium carbonate in the lower meniscus of the solution in the constricted part of the tube shows the presence of a carbonate.

3. Identification of the Sulfite Ion. The immediate formation of a blue precipitate or a blue color in the solution containing the ferricyanide shows the presence of a sulfite.

4. Identification of a Fluoride. Separate any insoluble matter that is in the tube used in making the tests for the carbonate and sulfite ions by a centrifuge or by a filter using the glass wool used previously to separate the calcium salts of the anions of Group I from the solution containing the ions of Groups II to V and to make the tests for the carbonate and sulfite ions. Take care not to contaminate or to lose the adhering precipitate or liquid. Wash the residue twice with 3 drops of distilled water.

Use the clear solution and wash water to test for the arsenate and phosphate ions according to Procedure VI, 5 and 6. Heat the centrifuge tube containing the precipitate of calcium fluoride and possibly calcium phosphate and arsenate to which has been added powdered silicon dioxide or glass wool above a low flame of a Bunsen burner for 10 minutes to remove all moisture. Heat the entire tube to prevent the condensation of any liquid on the walls. If a filter was used to separate the precipitate, carefully remove the glass wool filter and dry it by heating it in a crucible over a low flame from a Bunsen burner for 10 minutes. Then place the dry glass wool in a small test tube. Fit the centrifuge or test tube containing the precipitate with a rubber stopper containing a glass rod 6 cm. long, one end of which is drawn out and bent into a ring having a diameter of 3 mm. (Fig. 14). Break up the glass wool with a stirring rod or spatula. Dip the glass rod in water so that a film stretches over the ring. Then add 6 drops of concentrated sulfuric acid, assemble the apparatus, and warm it to about 50°. A distinct white precipitate, H_4SiO_4, which collects on the glass ring shows the presence of a fluoride. Reserve the contents of the tube to test for a phosphate

Analysis of Group I—Procedure VI

Slightly Alkaline Solution Containing All Anions. Add $Ca(CH_3COO)_2$—maximum 3 drops. Separate the precipitate with a centrifuge (page 147) or a filter tube containing a glass wool plug (page 148).

Precipitate: $CaCO_3$, $CaSO_3$, CaF_2, $CaHAsO_4$, $CaHPO_4$. Dry, add CH_3COOH, place in a water bath at 80° and pass the gases through $FeFe(CN)_6$ into a $Ba(OH)_2$ solution.

$Ba(OH)_2$ solution. White precipitate, $BaCO_3$, shows *Carbonate.*	*$FeFe(CN)_6$ solution.* Blue precipitate or solution $Fe^{II}[Fe^{III}Fe(CN)_6]_2$ shows *Sulfite.*	*Mixture in test tube.* Separate any residue.				
		Residue: CaF_2 and possibly $CaHAsO_4$ and $CaHPO_4$. Dry, heat the precipitate and glass wool with H_2SO_4 conc. Hold H_2O in vapor.		*Solution:* $H_2AsO_4^-$ and $H_2PO_4^-$: Add H_2SO_4, Zn and $AgNO_3$ paper.		
		Drop of H_2O. White precipitate, H_4SiO_4, shows *Fluoride.*	*Mixture in test tube.* Test for a phosphate and an arsenate only if a negative test is obtained in the solution.	*$AgNO_3$ paper.* Dark stain shows *Arsenate.*	*Mixture in tube.* Separate the precipitate.	
					Precipitate: Discard.	*Solution:* Add 10 drops of ammonium molybdate. Yellow precipitate shows *Phosphate.*

and an arsenate, should the tests for these ions on the solution from the precipitate of calcium fluoride prove negative.

5. Identification of the Arsenate Ion. Place a few pieces of granulated arsenic free zinc in a test tube. Then add 1 ml. of sulfuric acid and a drop of copper sulfate. Loosely plug the upper part of the test tube with glass wool and moisten it with 2 drops of lead acetate. Place a piece of filter paper moistened with silver nitrate on top of the tube. After two minutes remove the filter paper and note the color and intensity of the spot which forms. Then remove the glass wool and add the solution from the calcium fluoride (Procedure VI, 4) to the test tube. Quickly replace the glass wool plug and the filter paper moistened with silver nitrate so that a new spot forms near but not over the first one. Remove the filter paper after two minutes, unless the rate of evolution of hydrogen has decreased, and compare the two spots. A spot darker than the first having a silvery sheen shows the presence of an arsenate.

6. Identification of a Phosphate. Separate any precipitate in the tube used to test for an arsenate (Procedure VI, 5). Add 10 drops of ammonium molybdate, warm to 30°, and let the solution stand for a few minutes. A bright yellow precipitate shows the presence of a phosphate.

If the tests for the arsenate and phosphate ions (Procedure VI, 5, 6) are negative, tests for these ions may be made on the solution from the test for the fluoride ion (Procedure VI, 4). This should not be necessary unless very small amounts of these ions may be present.

Discussion of the Analysis

In a neutral solution calcium acetate precipitates the carbonate, phosphate and fluoride ions almost completely as $CaCO_3$, $CaHPO_4$ and CaF_2. If the solution is alkaline, the phosphate precipitate is probably $Ca_3(PO_4)_2$. Calcium arsenate does not precipitate unless the solution is alkaline. Since the solubility of calcium sulfite is about 0.8 mg. per milliliter of water, the sulfite ion will not precipitate in this group unless the concentration is very high. If a test for a sulfite is obtained in this group, it should also be found in the analysis of Group II. If very high concentrations of the ferrocyanide and iodate ions are present, a part will precipitate on the addition of calcium acetate; but sufficient amounts will always remain in solution so that tests for these ions will be obtained in their respective groups.

Freshly precipitated calcium fluoride is slimy and difficult to filter. Filtration may be facilitated by adding a drop of a sodium

carbonate solution. If sodium carbonate is added, the test for a carbonate must be made on a portion of the original unknown. Usually the addition of sodium carbonate can be avoided if the glass wool filter is tightly packed and the solution is filtered slowly. This difficulty does not arise if a centrifuge is used.

Dry the group precipitate before treating it with acetic acid, because freshly precipitated calcium fluoride is somewhat soluble in acetic acid.

Carbonate Ion. Calcium carbonate reacts with warm acetic acid to give carbon dioxide which precipitates barium carbonate from a solution of barium hydroxide. Any sulfur dioxide present must be removed by passing the gas through an oxidizing solution of ferric ferricyanide. It must be remembered that on heating the solution, the air already in the system will be driven over and may contain enough carbon dioxide to give a precipitate in the barium hydroxide solution in the constriction. For this reason as small an apparatus as possible should be used. If a small precipitate is obtained, a blank should be run using the same apparatus and the same volume of solution without any carbonate.

Sulfite Ion. Calcium sulfite reacts with an excess of acetic acid to form sulfurous acid, which on heating breaks down completely into sulfur dioxide and water. The sulfur dioxide passes through the solution of ferric ferricyanide and is oxidized to sulfuric acid, and the ferric ferricyanide is changed to Turnbull's blue. It is very essential that the tube be clean, for impurities, even a thin film of one of the blue ferri- or ferrocyanides, will cause the decomposition of the ferric ferricyanide in the absence of a sulfite. However, the solution will be green and not blue.

Phosphate Ion. Dried calcium phosphate is soluble in acetic acid. However, in the presence of the fluoride ion a double salt of calcium fluoride and calcium phosphate may form which is insoluble in acetic acid. In this case some of the phosphate ion may be present in the residue containing the calcium fluoride and the test must be made on the mixture left from the fluoride test. The test for the phosphate depends on the formation of a yellow precipitate having the formula $(NH_4)_3PO_4 \cdot 12\,MoO_3 \cdot 5\,H_2O$, on the addition of a large excess of ammonium molybdate to the solution just acid with nitric acid. The arsenate ion, if present in high enough concentration, gives a similar precipitate and, therefore, must be removed before the test for a phosphate can be carried out. If a cation

analysis has been made, the presence or absence of the phosphate ion will already have been determined and this test may be omitted.

Arsenate. The arsenate ion behaves quite similarly to the phosphate ion. However, calcium arsenate does not precipitate when calcium acetate is added to an arsenate unless the solution is alkaline. Moreover, ammonium-arsenomolybdate does not usually precipitate unless the temperature is raised to approximately 60° to 70°. The test used for arsenic, the Gutzeit test, is exceedingly sensitive. The equation for the reaction between arsine, silver and nitrate ions to give the black product may be represented by the equation

$$AsH_3 + 6\,Ag^+ + 6\,NO_3^- + 9\,H_2O \rightarrow 6\,Ag + H_3AsO_3 + 6\,H_3O^+ + 6\,NO_3^-$$

The ions of antimony, sulfites and sulfides interfere with the test, but these ions are not present when the test is made. It is not necessary that all of the arsenic be removed from the solution before testing for a phosphate, for any arsenic will be present as an arsenite. A precipitate does not form when ammonium molybdate is added to a solution of an arsenite.

Fluoride Ion. Dried calcium fluoride is almost insoluble in acetic acid but reacts with hot concentrated sulfuric acid, liberating hydrogen fluoride. The hydrogen fluoride reacts with the glass wool to form silicon tetrafluoride which, when warmed, is driven off as a gas. On coming in contact with a drop of water, the silicon tetrafluoride forms a white precipitate of orthosilicic acid (H_4SiO_4), leaving fluosilicic acid in the solution. It is absolutely necessary to have the test tube and all materials dry, for if any water is present the silicon tetrafluoride will be decomposed before it comes into contact with the film of water at the end of the glass rod.

EXERCISES

1. Calculate the volume of 2-*N* calcium acetate required to precipitate the ions of Group I if 1 mg. of each ion is present. *Ans.* 0.08 ml.—1.6 drops.
2. Calculate the volume of calcium acetate required to precipitate the ions of Group I in a solution containing 1 mg. of each of the following: fluoride ions, chromate ions, carbonate ions and nitrate ions.
3. Calculate the volume of 0.1-*M* potassium permanganate required to react with the sulfur dioxide from 1 mg. of sulfite ion. *Ans.* 0.05 ml.—1 drop.
4. What is the normality of a base if 10 ml. react with 20 ml. of a 1-*N* acid?

5. If 10 ml. of a 0.1-*N* acid reacts with 40 ml. of a solution of sodium hydroxide, how many grams of sodium hydroxide are in the sample used?
   Ans. 0.04 g.
6. What is a light colored precipitate that forms while making a phosphate or arsenate test? What should be done to remedy the condition?
7. Why is the precipitate of the calcium salts of the ions of Group I dried before treatment with acetic acid?
8. What is the condition for the formation of hydrogen salts?
9. If one equivalent of an acid is added to a mole of calcium carbonate, what will be the products?
10. If hydrogen salts are heated, what reaction takes place?
11. If silver nitrate is added to a solution containing the ions of Group I, will any precipitation take place?
12. Classify the ions of Group I according to their ability to act as oxidizing or reducing agents.
13. Define: oxidation, reduction, oxidizing agent, electron.

CHAPTER XVI

Anions of Group II

PROPERTIES OF ACIDS AND IONS

SULFATE

ACID. The concentration of HSO_4^- in concentrated and dilute H_2SO_4 is high. Very little of the HSO_4^- ionizes to give $SO_4^=$ and H_3O^+. Concentrated H_2SO_4 is an oxidizing agent and is reduced to SO_2 or by strong reducing agents, such as I^- or some of the active metals, to H_2S. It also forms stable hydrates. The dilute acid is a non-oxidizing acid. Concentrated H_2SO_4 reacts with solid chlorates forming ClO_2 which explodes when warmed.

$$2\ H_2SO_4\ \text{conc.} + 3\ KClO_3 \rightleftarrows 2\ ClO_2 + 2\ KHSO_4 + KClO_4 + H_2O$$

Ion. The sulfate ion is precipitated by Pb^{++}, Ba^{++}, Sr^{++} and Ca^{++} as the sulfate. Calcium sulfate is by far the most soluble sulfate of those named and barium sulfate the least soluble. With the exception of $BaSO_4$, these sulfates are somewhat soluble in the presence of H_3O^+ because of the conversion of $SO_4^=$ to HSO_4^-. The increase in the solubility of barium sulfate is negligible at low concentrations of H_3O^+.

CHROMATE—DICHROMATE

Acid. The equilibria which exist in a solution of a soluble chromate to which an acid has been added have been considered on page 62.

Ions. The chromates of Ba, Mn, Bi, Ag, Hg(ous) and Pb are insoluble. Those of Sr and Hg(ic) are slightly soluble. All are soluble in strong acids.

The chromate ion is a poor oxidizing agent in alkaline solutions. The dichromate ion in acid solutions, however, is a strong oxidizing agent. It is reduced to Cr^{+++} by H_2S, H_2SO_3, $S_2O_3^=$, $Fe(CN)_6^{\equiv}$, CNS^-, I^- and Br^-.

The chromate ion is precipitated by Ba^{++}, Pb^{++} and Ag^{+} from slightly acid solutions. These chromates are soluble in dilute nitric acid.

The reaction of hydrogen peroxide with a slightly acid solution of $Cr_2O_7^{=}$ to form the unstable blue chromic acid (page 198) can be used as a test for either the $CrO_4^{=}$ or $O_2^{=}$.

IODATE

Acid. Iodic acid, unlike the other halogenate acids, is a white, crystalline solid. If dehydrated at 110°, I_2O_5 is the product.

Ion. The iodates are less soluble than the corresponding chlorates or bromates. Lead iodate is even less soluble than silver or barium iodate. These salts are all white.

The IO_3^- in an acid solution is a less powerful oxidizing agent than the BrO_3^-. It oxidizes As^{+++}, Sb^{+++}, Sn^{++}, Cu_2^{++}, Fe^{++}, $Fe(CN)_6^{\equiv}$, HNO_2, H_2S, $S_2O_3^{=}$, $SO_3^{=}$, Br^- and I^-. The reduction product is I^- if an excess of reducing agent is added, or I_2 if an excess of IO_3^- is used. In concentrated HCl I_2 is oxidized and forms ICl.

$$6\ H_3O^+ + 5\ Cl^- + IO_3^- + 2\ I_2 \rightleftarrows 5\ ICl + 9\ H_2O$$

When solid alkali iodates are heated, O_2 is evolved and an iodide is formed.

SULFITE, FERROCYANIDE, THIOSULFATE AND BROMATE

The properties and reactions of the *sulfite* ion have been considered previously on pages 243 and 247. Those of the *ferrocyanide* ion are considered on pages 270 and 271. The properties and reactions of the *thiosulfate* ion are taken up on pages 276 and 280 while those of the *bromate* ion are on pages 293 and 295.

REACTIONS OF THE IONS

Iodate Ion, IO_3^-

Experiment 34. (*a*) Add three drops of chlorine water to 4 drops of a solution of an iodide. Account for the change of color. Complete:

$$I^- + Cl_2 \rightleftarrows Cl^- + ?$$

Then add an excess of chlorine water to the solution. Complete:

$$I^- + Cl_2\ xs + H_2O \rightleftarrows IO_3^- + ? + ?$$

(*b*) Try the action of the following reducing reagents on 4 drops of iodic acid acidified with a drop of a strong acid: hydrogen sulfide, sulfur dioxide, arsenious

acid, sodium thiosulfate, ferrous ammonium sulfate and potassium ferrocyanide acidified with sulfuric acid. Which of these reducing agents, in excess, will reduce the iodate ion to the iodide ion and which will reduce the iodate ion to iodine only? Complete:

(1) $H_3O^+ + IO_3^- + H_2S \rightleftarrows I_2 + S + ?$
(2) $I_2 + H_2O \rightleftarrows I^- + ? + ?$
(3) $IO_3^- + H_3O^+ + S_2O_3^= \rightleftarrows I_2 + HSO_4^- + ?$
(4) $IO_3^- + SO_2 + H_2O \rightleftarrows H_3O^+ + I^- + HSO_4^-$
(5) Fe^{++} xs $+ H_3O^+ + IO_3^- \rightleftarrows Fe^{+++} + ? + ?$

(*c*) Acidify with acetic acid a solution containing 4 drops of potassium iodate and potassium iodide. Shake the mixture with carbon tetrachloride. What is the result? This reaction serves to identify iodates in the presence of iodides, except when other ions (for example OCl^-, ClO_3^-, NO_3^-, NO_2^- and $Cr_2O_7^=$) which oxidize the iodide ion to free iodine, are present. Balance:

$$H_3O^+ + IO_3^- + I^- \rightleftarrows I_2 + H_2O$$

(*d*) Add silver nitrate to 4 drops of potassium iodate to which 4 drops of potassium iodide have been added. Decant the liquid from the precipitate and extract the precipitate twice with ammonia. Decant the ammoniacal liquid from the residue and acidify the alkaline solution with sulfuric acid. Separate the precipitate which forms and heat it with an excess of a solution of sulfur dioxide. Is the residue soluble in ammonia? What is its color? What is it? 1 ml. of 1-*N* ammonia at 25° dissolves only 0.006 milligram of silver iodide. Balance:

$$AgIO_3 + NH_3 \rightleftarrows Ag(NH_3)_2^+ + IO_3^-$$

(*e*) Add a drop of sulfuric acid to 4 drops of a solution of potassium iodate. Then add 2 drops of starch emulsion and cover the mixture with a few drops of 0.04-*N* sodium thiosulfate. What causes the blue color? What other ions act similarly? Complete:

$$IO_3^- + H_3O^+ + S_2O_3^= \rightleftarrows I_2 + HSO_4^- + ?$$

Sulfate Ion, $SO_4^=$

Experiment 35. (*a*) Contrast the properties of dilute and concentrated sulfuric acid. What two classes of salts does it give? Arrange the sulfates in the order of their decrease in solubility.

(*b*) Add a drop of hydrochloric acid to 4 drops of sodium sulfate. Heat the solution to boiling and add 2 drops of barium chloride. The precipitate ($BaSO_4$) is insoluble in dilute acids. Complete:

$$Ba^{++} + SO_4^= + H_3O^+ \rightleftarrows ?$$

(*c*) Digest barium sulfate for five minutes with 10 drops of 3-*N* sodium carbonate. Add water to keep the volume constant. Separate the solid matter and test its solubility in hydrochloric acid. Is it completely or only partly soluble? Test the solution for barium. Test the sodium carbonate solution from the first separation for sulfate. Explain.

(*d*) Mix 0.05 g. of barium sulfate with 4 times its volume of a mixture of anhydrous sodium and potassium carbonates. Strongly ignite the mixture in a bead on a platinum wire until it fuses. Cool and digest the melt with boiling

water until the fused material disintegrates. Separate the precipitate and test the solution for a sulfate. What is the residue? Complete:

$$BaSO_4 + CO_3^{=} \rightleftarrows BaCO_3 + ?$$

(*e*) Mix 0.05 g. of barium sulfate with an equal amount of sodium carbonate and the same quantity of powdered charcoal. Moisten the mixture and place it in a cavity on a piece of charcoal. Heat in the reducing flame of a blowpipe. Remove the residue and place it on a bright silver coin. Moisten the fused mass with water and crush it with a stirring rod. Add a drop of hydrochloric acid and note the odor; also examine the coin. Is it discolored? Explain. Could this test be carried out with barium sulfate? Balance:

$$BaSO_4 + Na_2CO_3 + C \rightleftarrows Na_2S + BaCO_3 + CO$$
$$Na_2S + H_3O^+ \rightleftarrows H_2S + H_2O + Na^+$$

Chromate Ion, $CrO_4^{=}$

Experiment 36. (*a*) Add a drop of sodium hydroxide to 4 drops of a solution of potassium dichromate. Account for the color change. Add a drop of dilute nitric acid to 4 drops of potassium chromate. Account for the color change. Complete:

(1) $Cr_2O_7^{=} + OH^- \rightleftarrows H_2O + ?$
(2) $CrO_4^{=} + H_3O^+ \rightleftarrows H_2O + ?$

(*b*) Acidify 10 drops of water containing 4 drops of potassium dichromate with sulfuric acid. To the solution add 5 drops of ether and shake the mixture; then add a drop or two of hydrogen peroxide and shake. The ether extracts the blue unstable perchromic acid from the water. How could this test be applied to the detection of chromium in a lower state of oxidation? An excess of either dichromate or hydrogen peroxide renders the test less delicate and may destroy the blue color entirely. Balance:

$$Cr_2O_7^{=} + H_3O^+ + H_2O_2 \rightleftarrows H_7CrO_{10} + H_2O$$

(*c*) Add sulfurous acid to 4 drops of an acidified solution of potassium dichromate. What change in color is noted? Boil off the excess sulfur dioxide, make the solution just alkaline with ammonia, and boil it for one minute. What is precipitated? Complete:

$$Cr_2O_7^{=} + H_3O^+ + SO_2 \rightleftarrows Cr^{+++} + HSO_4^{=} + ?$$

ANALYSIS

Procedure VII

1. Precipitation of the Strontium Salts. To the solution from Group I add 2-*N* strontium acetate until no more precipitate forms (maximum 2 drops) and let stand for at least ten minutes. Separate the precipitate by centrifuging or by filtering the mixture through a double plug of glass wool. Heat the tube which contains the precipitate in the water bath while washing the precipitate six times with 3 drops of boiling water. Discard the wash liquid after testing for a chromate with lead acetate.

2. Identification of the Sulfate Ion. Cool and add 5 drops of hydrochloric acid. If a precipitate remains, the presence of a sulfate is proved. If the test for a sulfate is inconclusive, add a drop of barium chloride to the solution. A white precipitate of barium sulfate proves the presence of a sulfate.

3. Identification of the Sulfite Ion. Test the solution used to establish the presence or absence of the sulfate ion, for a reducing anion. If a reducing anion is present, it is a sulfite.

4. Precipitation of the Barium Salts. To the solution from which the strontium salts were precipitated, add 2-*N* barium acetate until no more precipitate forms (maximum 2 drops). Add a volume of acetone equal to one-fourth the volume of the solution, agitate the mixture thoroughly, and allow it to stand for ten minutes. Separate the precipitate and wash it with cold water containing a little barium acetate and 20% acetone by volume. Test the solution for the ions of Groups III to V and the precipitate for a chromate and iodate by Procedure VII, 5 and 6 unless a ferrocyanide, bromate or thiosulfate may be present. If the latter ions may be present, add 3 drops of water and one of barium acetate to the precipitate and heat the mixture for a minute or two. Separate any residue and wash it several times with 3 drops of hot water containing a drop of barium acetate. The residue contains all of the chromate ion and most of the iodate ions. The solution may contain some iodate, and if this ion was not found in the precipitate, test it for an iodate. The solution may also contain some bromate, thiosulfate and ferrocyanide, but only if a high concentration of these ions were present.

5. Identification of the Chromate Ion. The original precipitate from Procedure VII, 4 or the residue remaining after boiling the barium precipitate with barium acetate, may contain only the iodate and chromate ions. Dissolve the precipitate in a little hydrochloric acid and add sulfurous acid to the solution until it smells strongly of sulfur dioxide.* Boil to remove the excess of sulfur dioxide, and reject the residue of barium sulfate. A color change in the solution from orange to green is usually a sufficient indication of the presence of the chromate ion. Make the solution *just* alkaline with ammonia and *heat* for one or two minutes. A greenish blue precipitate of chromic hydroxide confirms the presence of the chromate ion. A special test for a chromate may be made on a portion of the original unknown by Experiment 36*b*, unless interfering ions are present.

* If sulfurous acid is not available, sodium acid sulfite may be used but two or three drops of hydrochloric acid must be added before the sulfur dioxide can be boiled off completely.

Solution from Group I. Add $Sr(CH_3COO)_2$ and let stand 10 minutes to insure complete precipitation. Separate the precipitate by a centrifuge or filter apparatus, using a double plug of glass wool.

Precipitate: $SrSO_4$, $SrSO_3$, ($SrCrO_4$). Wash 6 times with 3 drop portions of boiling water.

Precipitate: $SrSO_4$, $SrSO_3$. Cool, add H_2O, HCl and separate any precipitate.

Precipitate: $SrSO_4$, white shows *Sulfate.*

Solution: Add $BaCl_2$. A white precipitate of $BaSO_4$ shows *Sulfate.* Test this solution for the presence of a reducing anion. A positive test shows *Sulfite.*

Solution: $CrO_4^=$. Identify by the color or by the addition of CH_3COOH and $Pb(CH_3COO)_2$. A yellow precipitate shows *Chromate.*

Solution: $CrO_4^=$, IO_3^-, $[BrO_3^-$, $Fe(CN)_6^{\equiv}$, $S_2O_3^=]$, and ions of Groups III–V. Add $Ba(CH_3COO)_2$ and acetone.

Precipitate: $BaCrO_4$, $Ba(IO_3)_2$,* $[Ba(BrO_3)_2$, $Ba_2Fe(CN)_6$, $BaS_2O_3]$. Heat with H_2O and $Ba(CH_3COO)_2$.

Precipitate: $BaCrO_4$, $Ba(IO_3)_2$. Add HCl.

Solution: IO_3^- and $Cr_2O_7^=$. Add SO_2. A green color shows $CrO_4^=$. Boil off SO_2 and add NH_3.

Precipitate: $Cr(OH)_3$ confirms *Chromate.*

Solution: Add HNO_2, $Fe(NO_3)_3$, CCl_4. Violet color in CCl_4, I_2. Shows *Iodate.*

Solution: $IO_3^-[Fe(CN)_6^{\equiv}$, $S_2O_3^=$, $BrO_3^-]$. To 2 drops add $AgNO_3$ to test for $S_2O_3^=$. To the remainder add CH_3COOH and $Cd(CH_3COO)_2$.

Precipitate: $Cd_2Fe(CN)_6$. Add HCl and $FeCl_3$. Blue ppt. shows *Ferrocyanide.*

Solution: $IO_3^-[S_2O_3^=$, $BrO_3^-]$. Add SO_2, HNO_3, $Fe(NO_3)_3$ and CCl_4.

CCl_4 Layer: Violet color, I_2, shows *Iodate.*

Water Layer: $[Br^-]$. Boil. Add HNO_3, $KMnO_4$ and CCl_4. Yellow color in CCl_4, Br_2, shows *Bromate.*

* Test this precipitate for a chromate and an iodate unless more than 3 mg. of ferrocyanide or 4.5 mg. of thiosulfate and bromate ion can be present in 1 ml.

6. Identification of the Iodate Ion. To test for an iodate, separate the precipitate of chromium hydroxide obtained in Procedure VII, 5. Acidify the cooled solution with nitric acid, add 5 drops of carbon tetrachloride and then 1-*N* ferric nitrate until the water layer is colored yellow. Shake the mixture well. A violet color in the carbon tetrachloride layer indicates the presence of an iodate. Let the mixture stand at least 3 minutes before concluding that an iodate is absent for the reaction is slow. The presence of an iodide from an iodate also may be established by oxidizing it to iodine with nitrous acid as described in Experiment 45*e*. If a pink or brown solution makes it difficult to determine the color of the carbon tetrachloride, separate the two layers.

7. Tests for the Thiosulfate and Ferrocyanide Ions. Unless it is known that more than 4.5 mg. of the thiosulfate or 3 mg. of the ferrocyanide ions cannot be present per milliliter, tests for these ions should not be omitted. To test for a thiosulfate, add silver nitrate to 2 drops of the solution from Procedure VII, 4. A white precipitate which changes to brown or buff indicates the presence of a thiosulfate. To test for a ferrocyanide, acidify the main part of the solution with acetic acid and add a drop of cadmium acetate. If a white precipitate of cadmium ferrocyanide forms, add cadmium acetate until the ferrocyanide is all precipitated. Separate, and wash the precipitate. Confirm the presence of the ferrocyanide ion in the precipitate by adding a drop of hydrochloric acid and of ferric chloride. A dark blue precipitate (see Procedure VIII, 4, Analysis of Group III) confirms the presence of a ferrocyanide.

8. Tests for the Bromate Ion. If the bromate ion may be present, add sulfurous acid to the solution from Procedure VII, 7 or Procedure VII, 4, if a ferrocyanide is absent, until the solution smells strongly of sulfur dioxide. Then boil the solution until it no longer smells of sulfur dioxide and separate any barium sulfate. Add 2 drops of nitric acid, 5 drops of carbon tetrachloride and 1-*N* ferric nitrate until all of the iodide has been oxidized. Remove the iodine by extracting the solution repeatedly with carbon tetrachloride or by heating and test the solution for a bromide if more than 4.5 mg. of the bromate ion could be present. To the well-cooled solution add 5 drops of carbon tetrachloride, 2 drops of nitric acid, and then a potassium permanganate solution until the water layer is purple. Shake the mixture well. A yellow to orange color in the carbon tetrachloride indicates the presence of a bromate.

Discussion of the Analysis

The sulfite and sulfate ions are precipitated with strontium acetate to prevent the precipitation of the sulfite ion as its barium

salt along with barium iodate and chromate later in the procedure. The precipitation of the sulfite with these ions must be avoided since the sulfite would be oxidized to a sulfate when the mixture is acidified with hydrochloric acid. Thus, a test for the sulfate ion would be obtained even though it was not present in the original sample. It is necessary to loosen the upper plug of the glass wool, if a filter tube is used, and to wash thoroughly the precipitate which may contain the strontium sulfite with many small portions of hot water to dissolve any strontium chromate which is co-precipitated.

If all of the strontium precipitate dissolves in the hydrochloric acid, the absence of the sulfate ion is not proved unless a precipitate fails to form on adding barium chloride. Strontium sulfate is appreciably soluble in hydrochloric acid.

In a neutral solution the sulfite, sulfate and chromate ions are precipitated almost completely as insoluble barium salts by the addition of barium acetate. The precipitation of barium iodate is less complete under these conditions, and barium bromate is not precipitated at all unless a high concentration of bromate ion is present. The solubility of these two salts is greatly reduced by the addition of acetone. In a neutral solution containing an excess of barium acetate and 20% acetone by volume, barium iodate is precipitated almost completely. The precipitation of barium bromate is still far from complete, but sufficient bromate ion is removed so that no precipitate of silver bromate is obtained in Group IV, thus insuring the separation of bromide and bromate. It is important to add an excess of barium acetate before the acetone is added, otherwise the precipitation of barium iodate and barium bromate is not satisfactory.

Ferrocyanide, bromate and thiosulfate ions will not precipitate in Group II unless more than 3 mg. of the first and 4.5 mg. of the last two ions are present in a milliliter of the solution. The directions for the detection of these ions and the removal of the ferrocyanide ion are given so that a procedure will be available should higher concentrations be present. If these ions are found in Group II, they need not be identified later in the analysis.

Sulfite Ion. Strontium sulfite is readily soluble in hydrochloric acid. If an excess of hydrochloric acid is added and the mixture is heated, sulfur dioxide escapes from the solution. However, there is little or no loss of sulfur dioxide if the solution is not heated and if a large excess of acid is avoided. The reduction of ferric ferricyanide by sulfur dioxide is a sensitive but not specific test, satisfactory here since no other reducing ion can be present in the precipitate.

Strontium sulfate and strontium sulfite form very fine precipitates which often pass through the filter. Usually this can be prevented by tightly packing the glass wool and by filtering very slowly.

Sulfate Ion. The solubility product of strontium sulfate is relatively large and strontium sulfate dissolves when hydrochloric acid is added. The increased solubility is due to the reaction of sulfate ions with hydronium ions to form hydrogen sulfate ions.

$$SrSO_4 + H_3O^+ \rightleftarrows HSO_4^- + H_2O + Sr^{++}$$

Because the solubility product of barium sulfate is much smaller than that of strontium sulfate, barium sulfate precipitates when barium chloride is added to the solution.

Chromate Ion. If the concentrations of ferrocyanide, bromate and thiosulfate ions are so low that the solubility of the barium salts is not exceeded, the precipitate obtained on adding barium acetate should be tested for the chromate and iodate ions. However, if any or all of the ferrocyanide, bromate and thiosulfate ions may be precipitated, the barium precipitate should be boiled in a dilute solution of barium acetate. All of the barium ferrocyanide, thiosulfate and bromate will dissolve as well as some of the barium iodate.

Barium chromate dissolves in hydrochloric acid because of the change of the chromate ion to the dichromate ion. When sulfur dioxide is passed into the acid solution, the dichromate ion is reduced to the chromic ion, and the color changes from orange to green. If a very slight excess of ammonia is added to the solution and the mixture boiled, chromium hydroxide is precipitated as a bluish or brownish green gelatinous precipitate. If too large an excess of ammonia is added, the solution becomes violet because of the formation of a complex ion, and no hydroxide precipitates. On boiling, however, the complex ion is decomposed and the hydroxide precipitates. If the test is unsatisfactory, the chromate ion may be identified by the formation of the characteristic blue color of perchromic acid (H_7CrO_{10}) on treatment with sulfuric acid and hydrogen peroxide. If a cation analysis has been made, the chromate will have already been found as the chromic ion in Group III, Procedure III.

Iodate Ion. The test for the iodate ion in the presence of a bromate depends on its reduction to an iodide by sulfurous acid, and its

oxidation to free iodine by a mild oxidizing agent, such as nitrous acid or ferric nitrate in dilute nitric acid. The bromate is reduced to a bromide by sulfurous acid, but the bromide is not oxidized under the same conditions as the iodide. If a thiosulfate and a ferrocyanide are present, they must be separated from the chromate and iodate to prevent their oxidation to a sulfate and a ferricyanide. Barium iodate is somewhat soluble in the dilute solution of barium acetate used to dissolve barium ferrocyanide, barium thiosulfate and barium bromate. If a positive test for an iodate is not obtained on the residue left after boiling the precipitate, test the solution for an iodate.

Only 4 to 6 drops of carbon tetrachloride should be used to extract the iodine from the aqueous solution. If a large volume of the solvent is used, the concentration of the iodine will be low and it will be difficult to detect the violet color. To remove the iodine liberated by the oxidation of the iodide it is better to make a number of extractions with small volumes of the immiscible liquid rather than to make a single extraction with a larger volume. That such is the case can be demonstrated in the following way:

For any two immiscible solvents in which each of the dissolved substances has the same molecular weight, the ratio of the concentrations of the solute in the two solvents at a given temperature is a constant. In accordance with this generalization, known as the *law of distribution or partition*, we have

$$\frac{\text{Concentration of solute in one solvent}}{\text{Concentration of solute in other solvent}} = \frac{C_1}{C_2} = \text{a constant}$$

After making one extraction of an aqueous solution of iodine with carbon tetrachloride, the concentration of the iodine in the carbon tetrachloride (C_1) divided by the concentration of the iodine in water (C_2) has a value of 85

$$\frac{\text{Concentration of } I_2 \text{ in } CCl_4}{\text{Concentration of } I_2 \text{ in } H_2O} = \frac{C_1}{C_2} = \text{constant} = 85$$

Most of the iodine is removed from the water because the iodine is more soluble in carbon tetrachloride than in water. The solute is not always more soluble in the organic liquid than in water; for example, succinic acid can be extracted from ether by means of water. In this case

$$\frac{\text{Concentration of succinic acid in water}}{\text{Concentration of succinic acid in ether}} = 5.2 \text{ at } 15°$$

The usefulness of these ratios will be seen from the example which follows. Since the molecular weight of the solute considered is the same in both liquids, the ratio C_1/C_2 is a number, and therefore the ratios of the concentrations expressed in any units will have the same value as the ratio of the molecular concentrations. The same units must be used to express the concentrations in both the numerator and denominator. In the example given, the concentrations will be expressed as the number of grams of solute per milliliter of solution.

Extraction of Iodine from Water by Carbon Tetrachloride. The solubility of iodine in water at 18° is 2.765×10^{-4} g. per milliliter of water. If a milliliter of the saturated aqueous solution is shaken with 1 ml. of carbon tetrachloride, the amount of iodine removed from the water may be calculated in the following way:

Let x = number of grams of I_2 removed by 1 ml. of CCl_4. Then

$2.765 \times 10^{-4} - x$ = number of grams left in the H_2O

$\frac{x}{1}$ = concentration of I_2 in the CCl_4 layer = C_1

$\frac{2.765 \times 10^{-4} - x}{1}$ = concentration of I_2 left in the H_2O layer = C_2

By substituting these values, the equation, $\frac{C_1}{C_2} = 85$, becomes

$$\frac{\frac{x}{1}}{\frac{2.765 \times 10^{-4} - x}{1}} = 85, \quad \text{and} \quad x = 85(2.765 \times 10^{-4} - x)$$

Solving, $x = 2.735 \times 10^{-4}$ = the amount of iodine extracted.

Only 2.765×10^{-4} g. $- 2.735 \times 10^{-4}$ g. $= 0.03 \times 10^{-4}$ g. $= 3 \times 10^{-6}$ g. of iodine remain in the aqueous solution after the one extraction. This amount is very small but still less would remain in the water were we to make two extractions using 0.5 ml. of the carbon tetrachloride for each extraction, as the following calculations show:

For the first extraction

$$\frac{\frac{x}{0.5}}{\frac{2.765 \times 10^{-4} - x}{1}} = 85, \quad x = 2.7 \times 10^{-4}$$

This leaves 2.765×10^{-4} g. $- 2.7 \times 10^{-4} = 0.065 \times 10^{-4}$ g. $= 6.5 \times 10^{-6}$ g. of iodine in the water. Then for the second extraction

$$\frac{\frac{x}{0.5}}{\frac{0.065 \times 10^{-4} - x}{1}} = 85, \quad \text{and} \quad x = 0.0635 \times 10^{-4} \text{ g.}$$

The two extractions leave only 0.065×10^{-4} g. $- 0.0635 \times 10^{-4}$ g. $= 0.0015 \times 10^{-4} = 1.5 \times 10^{-7}$ g. in the aqueous solution instead of 3×10^{-6} g. left after a single extraction using 1 ml. of the carbon tetrachloride. It is more efficient to make two extractions using 0.5 ml. of the solvent than to make a single extraction with 1 ml.

Ferrocyanide Ion. No test will be obtained for the ferrocyanide ion unless more than 3 mg. of the ion was present in 1 ml. of the solution from which Group II was precipitated. The formation of ferric ferrocyanide on the addition of the ferric ion to an acid solution of a ferrocyanide is an excellent test for the ion. If a positive test for the ion is obtained in this group, no test need be made for the ion in Group III.

Bromate Ion. The bromate ion, like the iodate, is reduced by sulfur dioxide to the corresponding halide. A bromide, unlike an iodide, is not oxidized by the ferric ion in a dilute nitric acid solution, but is oxidized by the permanganate or persulfate ions in an acid solution. Since an iodide will also be oxidized by the stronger oxidizing agent, the iodide must be removed before testing for a bromide.

Thiosulfate Ion. On adding an excess of silver ion to a neutral solution of a thiosulfate, white unstable silver thiosulfate is precipitated. Silver thiosulfate decomposes almost immediately, going through a series of color changes to form dark brown silver sulfide. If the brown silver sulfide is mixed with a white precipitate, the final color of the mixture may be buff. Usually the change in color can be detected easily. The brown color of silver oxide precipitated by the addition of silver salt to an alkaline solution should not be confused with that of silver sulfide.

EXERCISES

1. Why is strontium acetate used to separate the sulfite and sulfate ions from the other ions of Group II? (Suggestion: Consider the oxidizing and reducing properties of the ions, especially in acid solution.)

2. If the precipitate which may be the sulfate and sulfite of strontium dissolves completely on the addition of an acid, why is barium chloride added before concluding that the sulfate ion is absent?
3. Why is acetone added to the solution to which barium acetate has been added to separate the remaining ions of Group II from those of Groups III–V?
4. If the sulfite ion is not found in Group I, but is found in Group II, should it be reported as a trace or full amount?
5. Account for the fact that chlorine and no iodine is formed by the action of an iodate with hydrochloric acid (conc.).
6. A solution may contain either a sulfite or a thiosulfate. The only change on acidifying the solution is the formation of sulfur dioxide. What ion was present?
7. A yellow solution being analyzed for Group II, becomes orange on being acidified and green on saturating with sulfur dioxide. What ion is indicated?
8. Silver nitrate is added to a portion of a solution being analyzed for Group II. A red precipitate is formed. What ion is indicated?
9. A test for a reducing agent is obtained when a portion of a solution which may contain only the ions of Group II is analyzed. What ion is indicated?
10. A test for an oxidizing agent is obtained on testing a solution being analyzed for Group II. If the solution is colorless, what ion is indicated?
11. State the law of partition, or distribution, as it is sometimes called.
12. Can the iodine in a chloroform solution be extracted by shaking with water? Is the process an efficient one?
13. A solution of 2 mg. of iodine dissolved in 1 ml. of water is shaken with 0.2 ml. of carbon tetrachloride. If the distribution constant of iodine between water and carbon tetrachloride is 0.0118, how many milligrams of iodine will remain in the aqueous solution? *Ans.* 0.11 mg.
14. Calculate which would be the more effective way of removing the iodine from 10 ml. of a saturated aqueous solution, (*a*) one extraction with 10 ml. of chloroform or (*b*) two extractions using 5 ml. of chloroform each time. The distribution constant of iodine between water and chloroform is 0.131.
Ans. The fractions left in the water are: (*a*) 0.11; (*b*) 0.21; 0.04.

W. D. LEAVITT

CHAPTER XVII

Anions of Group III

PROPERTIES OF ACIDS AND IONS

FERROCYANIDE

ACID. The anhydrous acid ($H_4Fe(CN)_6$) is a stable, white, crystalline solid which decomposes carbonates. When acid solutions of $Fe(CN)_6^{=}$ are boiled, HCN is evolved.

Ion. The ferrocyanide ion is yellow. The normal ferrocyanides of the alkalies and alkaline earths are soluble in water. The mixed salts, $K_2SrFe(CN)_6$, $K_2BaFe(CN)_6$ and others composed of an alkali and a heavy metal, are only slightly soluble. The reactions with Fe^{++} and Fe^{+++} are given on page 196.

The $Fe(CN)_6^{=}$ in acid solutions is oxidized to $Fe(CN)_6^{=}$ by $O_2^{=}$, $Cr_2O_7^{-}$, H_2O_2, MnO_4^{-}, HNO_2, HNO_3, Cl_2, ClO_3^{-}, etc. Alkaline solutions of the ion are oxidized to $Fe(CN)_6^{=}$ by OCl^{-}.

FERRICYANIDE

Acid. Ferricyanic acid, $H_3Fe(CN)_6$, is a non-volatile crystalline solid. Solutions containing the $Fe(CN)_6^{=}$ are affected by light and, unless freshly prepared, contain $Fe(CN)_6^{-}$. Hydrogen cyanide is evolved on boiling acid solutions of $Fe(CN)_6^{=}$.

Ion. The ferricyanide ion is reddish-brown. All salts are insoluble except those of the alkali, alkaline earths and iron (ic). Ferric ferricyanide is brown and is used as a test for reducing anions.

Cadmium and silver ions precipitate $Cd_3[Fe(CN)_6]_2$ (orange) and $Ag_3[Fe(CN)_6]$ (orange), respectively. Both salts are soluble in NH_3 as a result of the change of the metallic ions to complex ammonio anions. The reactions with Fe^{+++} and Fe^{++} are given on page 196.

In cold alkaline solutions, the $Fe(CN)_6^{=}$ is reduced to $Fe(CN)_6^{-}$ by CN^{-}, $S^{=}$, I^{-}, $SO_3^{=}$, etc. It is also reduced to $Fe(CN)_6^{-}$ by I^{-}, H_2SO_3, H_2S in acid solutions.

SULFIDE

Acid. Hydrogen sulfide is a weak, diprotic acid. A saturated solution at ordinary temperature and pressure is about 0.1-*M*. The gas is about as poisonous as HCN and care should be exercised in its use.

Ion. Nearly all metallic ions are precipitated from neutral solutions by hydrogen sulfide. The ions not precipitated as sulfides are those of Al, Cr, Mg, Ca, Sr, Ba, Na, K and NH_4. The sulfides of As, Sn(ic), Hg and Sb are soluble in NaHS, Na_2S and NaOH. Those of As, Sn(ic) and Sb dissolve in $(NH_4)_2S$. Stannous sulfide is insoluble in NaHS or $(NH_4)_2S$ but is oxidized by HS_2^-, or $S_2^=$ to SnS_2 which is soluble. The theory of precipitation and solution of sulfides is discussed on page 93.

Acid solutions of H_2S are oxidized chiefly to S although some $SO_4^=$ may be formed. The MnO_4^-, $Cr_2O_7^=$, Fe^{+++}, IO_3^-, BrO_3^- and NO_2^- are reduced in acid solutions by H_2S.

Solutions of the alkali sulfides usually contain some polysulfides, $S_2^=$ for example. Polysulfide ions are formed by action of S on $S^=$. The polysulfides are oxidizing agents and oxidize SnS, As_2S_3 and Sb_2S_3 to sulfides or thio-acids containing the metal at a higher oxidation state. The solutions of the alkali sulfides usually contain some $SO_3^=$, $S_2^=$ and $S_2O_3^=$.

REACTIONS OF THE IONS

Ferrocyanide Ion, $Fe(CN)_6^=$

Experiment 37. (*a*) Add a drop of silver nitrate to 4 drops of a solution of potassium ferrocyanide. Complete:

$$Ag^+ + Fe(CN)_6^= \rightleftarrows ?$$

Test the solubility of the precipitate in 3-*N* ammonia and in 3-*N* nitric acid. Complete:

(1) $Ag_4Fe(CN)_6 + NH_3 \leftrightarrows ?$
(2) $Ag_4Fe(CN)_6 + H_3O^+ \leftrightarrows ?$

(*b*) Add to 1 ml. of water a drop of ferric chloride and treat one-half of the dilute solution with a drop of potassium ferrocyanide solution. To the other half of the solution add a drop of potassium ferricyanide. Give results. Balance:

(1) $Fe^{+++} + Fe(CN)_6^= \rightleftarrows Fe[Fe^{III}Fe(CN)_6]_3$
(2) $Fe^{+++} + Fe(CN)_6^= \rightleftarrows FeFe(CN)_6$

(*c*) Add a drop of cadmium acetate to 4 drops of solutions of potassium ferrocyanide and ferricyanide in separate test tubes. Give the color of each

precipitate. Separate the precipitates and test their solubilities in 3-*N* hydrochloric acid; in 3-*N* ammonia. Complete:

(1) $Fe(CN)_6^{=} + Cd^{++} \rightleftarrows ?$
(2) $Fe(CN)_6^{=} + Cd^{++} \rightleftarrows ?$
(3) $Cd_3(Fe(CN)_6)_2 + NH_3 \rightleftarrows Cd(NH_3)_4^{++} + ?$
(4) $Cd_3(Fe(CN)_6)_2 + H_3O^+ \leftrightharpoons ?$
(5) $Cd_2Fe(CN)_6 + NH_3 \leftrightharpoons ?$
(6) $Cd_2Fe(CN)_6 + (H_3O^+) \rightleftarrows H_2Fe(CN)_6^{=} + ?$

(*d*) Add a drop of chlorine water to 4 drops of a solution of potassium ferrocyanide. Then add a drop of a solution of silver nitrate. Complete:

(1) $Fe(CN)_6^{=} + Cl_2 \rightleftarrows Cl^- + ?$
(2) $Fe(CN)_6^{=} + Ag^+ \rightleftarrows ?$

Ferricyanide Ion, $Fe(CN)_6^{\equiv}$

Experiment 38. (*a*) Add a few drops of silver nitrate to 4 drops of a solution of potassium ferricyanide. Complete:

$$Ag^+ + Fe(CN)_6^{\equiv} \rightleftarrows ?$$

Test the solubility of the precipitate in 3-*N* ammonia and in 3-*N* nitric acid. Complete:

(1) $Ag_3Fe(CN)_6 + NH_3 \rightleftarrows Fe(CN)_6^{\equiv} + ?$
(2) $Ag_3Fe(CN)_6 + (H_3O^+) \leftrightharpoons ?$

(*b*) Add a drop of a solution of ferrous ammonium sulfate to 4 drops of potassium ferrocyanide and to 4 drops of potassium ferricyanide. Compare the results with those obtained in Experiment 37*b*. How may ferrocyanide and ferricyanide ions be distinguished? Complete:

(1) $Fe^{++} + Fe(CN)_6^{\equiv} \rightleftarrows ?$
(2) $Fe^{++} + Fe(CN)_6^{=} \rightleftarrows ?$

(*c*) Add an excess of sodium sulfite to 4 drops of a solution of potassium ferricyanide to which a drop of sodium hydroxide has been added. What causes the change in color?

$$Fe(CN)_6^{=} + SO_3^{=} + OH^- \rightleftarrows SO_4^{=} + ? + ?$$

Repeat using an acidified solution of potassium ferricyanide. Complete:

$$Fe(CN)_6^{=} + H_2SO_3 + H_2O \rightleftarrows HSO_4^- + H_3O^+ + ?$$

Sulfide Ion, $S^=$

Experiment 39. (*a*) Add a little sulfur to 4 drops of ammonium sulfide (colorless). Account for the change in color. To the resulting solution add an excess of hydrochloric acid. Complete:

(1) $S^= + S \rightleftarrows ?$
(2) $S^= + H_3O^+ \rightleftarrows ? + ?$
(3) $S_2^= + H_3O^+ \rightleftarrows S + ? + ?$

(*b*) Warm separately the freshly precipitated sulfides of ferrous iron, cadmium, stannous tin, arsenic (ic) and mercury from 4 drops of the appropriate

test solutions with 4 drops of both dilute and concentrated hydrochloric acid. Test the vapor given off with a strip of filter paper moistened with lead acetate. Complete:

(1) $FeS + H_3O^+$ conc. $\rightleftarrows$? + ? + ?
(2) $CdS + H_3O^+$ conc. $\rightleftarrows$? + ? + ?
(3) $SnS + H_3O^+$ conc. $\rightleftarrows$? + ? + ?
(4) $As_2S_5 + H_3O^+$ conc. $\rightleftarrows$?
(5) $HgS + H_3O^+$ conc. $+ Cl^-$ conc. $\rightleftarrows HgCl_4^- +$? + ?

Write the equations for the reactions with dilute acids.

(*c*) Heat a sulfide with concentrated sulfuric acid; with concentrated nitric acid; with aqua regia. Note whether hydrogen sulfide is evolved in each case. Write equations. Complete:

(1) $S^= + H_2SO_4$ conc. $\rightleftarrows S +$? + ?
(2) $H_2S + H_2SO_4$ conc. $\rightleftarrows H_2O + S + SO_2$
(3) $H_3O^+ + NO_3^-$ conc. $+ S^= \rightleftarrows S +$? + ?
(4) $H_3O^+ + NO_3^-$ conc. $+ S^= + Cl^-$ conc. $\rightleftarrows S + NOCl +$?

(*d*) Pass hydrogen sulfide into ammonia and add to the solution one drop of a 20 per cent solution of sodium nitroferricyanide. Note the color. The color is destroyed by sodium hydroxide. The alkali sulfides give this color reaction.

(*e*) Some sulfides are oxidized to the oxide or sulfate. Fuse mercuric sulfide with sodium carbonate in the oxidizing flame in the loop of a platinum wire. Cool and treat the residue with hydrochloric acid. Is hydrogen sulfide evolved? Complete:

$$HgS + O_2 \rightleftarrows ? + ?$$

Under what condition does a sulfate give a sulfide upon fusion? A sulfide a sulfate? Place a mixture of sodium carbonate and mercuric sulfide in a hard glass test tube and cover the mixture with anhydrous sodium carbonate. Treat the product with hydrochloric acid. Is hydrogen sulfide evolved?

ANALYSIS

Procedure VIII

1. Precipitation of the Cadmium Salts. To the solution from Group II, Procedure VII, 4, add a slight excess of 2-*N* cadmium acetate. Separate the mixture and wash the precipitate with hot water.

2. Identification of the Ferricyanide Ion. Extract the precipitate while it is in the centrifuge tube or on the glass wool filter 4 times with 5 drops of 3-*N* ammonia and wash it with water twice. The ammoniacal solution contains most of the ferricyanide but may contain some ferrocyanide ion. Acidify the solution with hydrochloric acid and add a drop of ferric chloride. If a dark blue precipitate forms (showing the presence of a ferrocyanide), separate it, and to the clear solution add a drop of freshly prepared ferrous ammonium sulfate. A dark blue precipitate shows the presence of a ferricyanide.

Analysis of Group III—Procedure VIII

Solution from Group II. Add $Cd(CH_3COO)_2$.

Precipitate: CdS, $Cd_2Fe(CN)_6$, $Cd_3(Fe(CN)_6)_2$, $[Cd(BO_2)_2]$. Treat with 3-*N* NH_3.

Residue: CdS, $Cd_2Fe(CN)_6$. Add 3-*N* HCl, warm, hold $Pb(CH_3CO_2)_2$ paper in vapor.		*Solution:* $Fe(CN)_6^{=}$, $(Fe(CN)_6^{=})$. Add HCl, $FeCl_3$, separate any precipitate and discard it. Add $Fe(NH_4)_2(SO_4)_2$ to the solution. Dark blue precipitate shows *Ferricyanide.*
$Pb(CH_3COO)_2$ Paper. Brown or black color, PbS, shows *Sulfide.*	*Solution:* $Fe(CN)_6^{=}$. Add $FeCl_3$. Dark blue color shows *Ferrocyanide.*	

3. Identification of the Sulfide Ion. To the residue insoluble in 3-*N* ammonia, add 3-*N* hydrochloric acid and cover the tube with a strip of filter paper moistened with lead acetate solution. Warm the mixture. A brown or black coloration of the lead acetate paper, caused by the formation of lead sulfide, indicates the presence of a sulfide.

4. Identification of the Ferrocyanide Ion. To the contents of the tube, Procedure VIII, 3, add ferric chloride, if a test for ferrocyanide was not obtained in Procedure VII, 7, or in the test for ferricyanide in Procedure VIII, 2. A dark blue precipitate shows the presence of a ferrocyanide.

Discussion of the Analysis

The precipitation of the sulfide, ferrocyanide and ferricyanide ions by cadmium acetate in a neutral solution is almost complete. Cadmium cyanide may precipitate if a high concentration of the cyanide ion is present, but it will dissolve almost completely in the 3-*N* ammonia and will not interfere with the analysis of the group. A sufficient amount always remains in the solution to give a precipitate with the nickel nitrate used in the next group. Silver ferrocyanide and ferricyanide are white and orange, respectively. The latter is soluble in 3-*N* ammonia while the former is nearly insoluble.

Ferricyanide Ion. Cadmium ferricyanide dissolves in 3-*N* ammonia, but cadmium ferrocyanide is very slightly soluble in ammonia of the same concentration. The separation is not complete, a little ferrocyanide being dissolved with the ferricyanide. However, the small amount of ferrocyanide should be removed by treating the acidified solution with ferric chloride to precipitate Prussian blue, $Fe[Fe^{III}Fe(CN)_6]_3$, before testing for a ferricyanide by the

addition of ferrous ion. The ferrous ion reacts with the ferricyanide ion to form a dark blue precipitate of Turnbull's blue, whose formula is $Fe[Fe^{III}Fe(CN)_6]_2$.

Ferrocyanide Ion. If only a trace of ferrocyanide is present, all of it may dissolve in 3-*N* ammonia with the ferricyanide. If a larger amount is present, the greater part of it will remain undissolved and will be found in the hydrochloric acid solution after the removal of the sulfide. The test for the ferrocyanide ion depends on the formation of the dark blue precipitate, Prussian blue, $Fe[Fe^{III}Fe(CN)_6]_3$, on the addition of ferric chloride to the acidified solution.

Sulfide Ion. Cadmium sulfide, unlike most cadmium salts, is almost insoluble in 3-*N* ammonia. It dissolves, however, on warming with 3-*N* hydrochloric acid with the evolution of hydrogen sulfide. The hydrogen sulfide, coming in contact with a filter paper moistened with lead acetate, forms lead sulfide which is brown or black.

EXERCISES

1. Account for the solubility of silver chloride in a solution of ammonia and the nearly complete insolubility of silver iodide in a portion of the same reagent.
2. Account for the solubility of silver ferricyanide in 3-*N* ammonia and the nearly complete insolubility of silver ferrocyanide in the same reagent.
3. Why is ferrous ammonium sulfate used rather than ferrous sulfate?
4. Account for the solubility of cadmium sulfide in 3-*N* hydrochloric acid and its insolubility in the 0.3-*N* acid.
5. Why does ferrous ferrocyanide invariably have a bluish tinge unless special precautions are taken in its preparation?
6. A blue precipitate was obtained when ferric chloride was added to a solution being tested for Group III. What ion is indicated?
7. A white precipitate forms when silver nitrate was added to a solution being tested for Group III. What ions cannot be present?
8. A student analyzing a solution for Group III found it to be basic and without neutralizing added cadmium acetate. A white precipitate was formed which failed to give a test for any of the ions of Group III. Explain.
9. If the sulfide ion is present in a solution being tested for Groups I to III, what anions cannot be present?
10. How many milliliters of 2-*N* cadmium acetate will be required to precipitate 1 mg. of each of the following ions: sulfide, ferricyanide and ferrocyanide? *Ans.* 0.048 ml. or 0.96 drop.

CHAPTER XVIII

Anions of Group IV

PROPERTIES OF ACIDS AND IONS

CYANIDE

Acid. Hydrogen cyanide is a liquid which boils at 26.5°. It is very poisonous and the pure acid as well as its salts must be handled with care. In aqueous solution it is ionized only slightly.

Ions. Only the cyanides of the alkali and alkaline earth metals and $Hg(CN)_2$ are soluble. Solutions of the cyanides of the alkali and alkaline earth metals are alkaline because the cyanide ion is a strong base and reacts with water.

$$CN^- + H_2O \rightleftarrows HCN + OH^-$$

The insoluble cyanides dissolve in an excess of CN^-, forming complex ions whose composition depends somewhat on the concentrations.

$$AgCN + CN^- \rightleftarrows Ag(CN)_2^-$$
$$Cd(CN)_2 + 2\,CN^- \rightleftarrows Cd(CN)_4^=$$

The CN^- is a mild reducing agent; Cu^{++} salts are reduced to Cu^+ (page 169). It reduces $S_2^=$, forming CNS^- and $S^=$.

$$S_2^= + CN^- \rightleftarrows CNS^- + S^=$$

The CN^- is changed to CNO^- (cyanate ion) by alkaline MnO_4^-.

THIOSULFATE

Acid. Thiosulfuric acid is unstable and cannot be isolated. When a thiosulfate is treated with H_3O^+, the chief reaction is

$$S_2O_3^= + 2\,H_3O^+ \rightleftarrows SO_2 + S + 3\,H_2O$$

Ion. With the exception of the thiosulfates of Ba, Pb and Ag, most thiosulfates are soluble in water. The thiosulfates of the less

active metals are not stable but react with water to give the sulfide of the metal and HSO_4^-.

$$Ag_2S_2O_3 + 2\,H_2O \rightleftarrows Ag_2S + H_3O^+ + HSO_4^-$$

The decomposition of the silver salts is fairly rapid even at room temperature, although the temperature must be raised to decompose the others. The changes of color from white through yellow, orange, to dark brown, make the identification of $Ag_2S_2O_3$ rather certain.

An excess of the $S_2O_3^=$ reacts with the insoluble thiosulfates, forming soluble complex ions, for example:

$$Ag_2S_2O_3 + S_2O_3^= \rightleftarrows 2\,Ag(S_2O_3)^-$$
$$Ag_2S_2O_3 + 3\,S_2O_3^= \rightleftarrows 2\,Ag(S_2O_3)_2^=$$

The complex ions do not decompose at room temperature.

The $S_2O_3^=$ is a reducing agent and is oxidized to the $SO_4^=$ by strong oxidizing agents such as MnO_4^-, $Cr_2O_7^=$, Cl_2, Br_2, OCl^- etc. Iodine, however, oxidizes it quantitatively to $S_4O_6^=$ (tetrathionate ion). The $S_4O_6^=$ is oxidized to the $SO_4^=$ by strong oxidizing agents such as OBr^-, OCl^-, etc.

THIOCYANATE

Acid. Anhydrous HCNS is an unstable, colorless liquid. In an aqueous solution the HCNS is ionized completely.

Ion. With the exception of the thiocyanates of Ag^+, Hg^{++}, Pb^{++} and Cu^+ (all white), thiocyanates are soluble. The insoluble thiocyanates are soluble in an excess of CNS^-, forming complex ions. The solubility of AgCNS in NH_3 is about the same as that of AgBr.

Ferric ion forms $Fe(CNS)_3$ (red) which reacts with an excess of CNS^- forming $Fe(CNS)_6^=$ (red).

Acid solutions of CNS^- are oxidized to HSO_4^- and HCN by NO_3^-, Br_2, HOBr, H_3AsO_4, $Cr_2O_7^=$, MnO_4^-, HOCl, $S_2O_8^=$, H_2O_2, etc. In alkaline solutions CNS^- is oxidized to CNO^- and $SO_4^=$ by OCl^-, MnO_4^- and PbO_2. Dilute HNO_3 or Cl_2 frequently reacts with hot solutions of CNS^-, forming $C_3N_3S_3H$ (perthiocyanogen) the color of which may be yellow, red or blue.

The CNS^- is decomposed by Zn or Al + OH^-, or H_3O^+. Among the products are NH_3 (NH_4^+ in acid solutions) and $S^=$ or H_2S.

CHLORIDE

Acid. Hydrogen chloride is very soluble in water forming hydrochloric acid, a strong non-oxidizing acid. A solution containing 20.2% of hydrogen chloride forms a constant boiling mixture. Chlorine reacts reversibly with water, forming hypochlorous acid (HOCl), hydronium and chloride ions.

Ion. The Cl^- precipitates AgCl (white) insoluble in HNO_3 but soluble in NH_3, forming $Ag(NH_3)_2^+$; in Cl^-, forming $AgCl_2^-$; in an excess of CN^-, forming $Ag(CN)_2^-$ and in an excess of $S_2O_3^=$, forming $Ag(S_2O_3)^-$ or $Ag(S_2O_3)_2^=$. Silver chloride is converted to Ag_2S by digestion with $S^=$ and is reduced to Ag by Zn and H_3O^+.

The Cl^- is a poor reducing agent; however, in the presence of a high $C_{H_3O^+}$ it will reduce powerful oxidizing agents, such as MnO_4^-, $Cr_2O_7^=$, MnO_2, etc., forming Cl_2 which is a slightly weaker oxidizing agent than those just named.

BROMIDE

Acid. Hydrogen bromide is very soluble in water, forming a strong acid which is a reducing agent. Bromine reacts reversibly with H_2O to form hypobromous acid, hydronium and bromide ions.

Like the other hydrogen halides, hydrogen bromide forms a constant boiling mixture with water which contains 47% of HBr.

Ion. The Br^- precipitates AgBr (yellow) insoluble in HNO_3 and slightly soluble in NH_3. The AgBr is soluble in excess CN^- and also $S_2O_3^=$. It is changed to Ag_2S by digestion with soluble sulfides and is reduced to Ag by Zn and H_3O^+. With the exception of Hg_2Br_2 (yellow), AgBr (yellow), and $PbBr_2$ (white), the bromides are soluble in water.

Oxidizing agents such as MnO_4^-, $Cr_2O_7^=$, MnO_2 and $S_2O_8^=$ oxidize Br^- in the presence of H_3O^+ to Br_2. Concentrated H_2SO_4 is reduced to SO_2 and Br_2 is liberated. Nitrous acid, Fe^{+++} and H_2O_2 do not oxidize the Br^-. Chlorine oxidizes Br^- to Br_2. If an excess of Cl_2 is added, BrCl is formed.

IODIDE

Acid. Hydrogen iodide is very soluble in water forming a strong acid which is a strong reducing agent. The constant boiling mixture contains 57% of HI. Iodine reacts reversibly with H_2O to form hypoiodous acid, hydronium and iodide ions.

Ion. The I^- precipitates AgI (yellow) which is insoluble in HNO_3 and in NH_3, although it becomes white in concentrated NH_3, possibly because of the formation of $2\ AgI \cdot NH_3$. Silver iodide is soluble in an excess of CN^- or $S_2O_3^=$ forming $Ag(CN)_2^-$ and $Ag(S_2O_3)^-$ or $Ag(S_2O_3)_2^=$. Soluble sulfides change AgI to Ag_2S. Mercurous ion precipitates Hg_2I_2 (yellow to green) and mercuric ion precipitates HgI_2 (yellow, turning red). An excess of I^- dissolves HgI_2, forming $HgI_4^=$. Lead ion precipitates PbI_2 (yellow) also soluble in excess of I^-, forming $PbI_4^=$. Antimonous ion precipitates SbI_3 (yellow), Bi^{+++} precipitates BiI_3 (brown) soluble in an excess of I^-, forming BiI_4^-.

Ferric and cupric ions in dilute acid solutions are stronger oxidizing agents than I_2, so both oxidize I^-. The I^- is also oxidized by $AsO_4^=$, MnO_4^-, HNO_2, $Cr_2O_7^=$, H_2O_2, etc., in dilute acid solutions. Chlorine and bromine oxidize the I^- to I_2. An excess of Cl_2 oxidizes I^- to IO_3^-.

REACTIONS OF THE IONS

Cyanide Ion, CN^-

Experiment 40. (*a*) Add a solution of sodium cyanide to 1 drop of a solution of silver nitrate until a precipitate is formed. Then add an excess of sodium cyanide. Does the precipitate dissolve? If no precipitate is formed when silver nitrate is added to a solution, is the absence of a cyanide proved? Complete:

(1) $Ag^+ + CN^- \rightleftarrows\ ?$
(2) $Ag^+ + CN^-$ xs $\rightleftarrows\ ?$

(*b*) Determine the solubility of silver iodide and silver sulfide formed from 4 drops of a solution of potassium iodide and sodium sulfide in an excess of potassium cyanide. Complete:

(1) $AgI + CN^-$ xs $\rightleftarrows Ag(CN)_2^- +$
(2) $Ag_2S + CN^-$ xs $\rightleftarrows\ ? + ?$

(*c*) Treat a solution of mercuric cyanide with hydrochloric acid; with sulfuric acid. Is hydrocyanic acid liberated? Saturate a mercuric cyanide solution with hydrogen sulfide. What is the result? Explain the peculiar behavior of mercuric cyanide toward hydrochloric and sulfuric acids.

(*d*) Add 2 drops of ferrous ammonium sulfate to 2 drops of sodium cyanide. Make the solution alkaline with sodium hydroxide; add a few drops of ferric nitrate and heat the mixture. Acidify it with hydrochloric acid and note the formation of a blue precipitate. What is it? Is this a characteristic test for a cyanide? Would mercuric cyanide give this test? What modification of the test is necessary in order to identify the cyanide group in mercuric cyanide? Complete:

(1) $Fe^{++} + OH^- \rightleftarrows Fe(OH)_2$
(2) $Fe(OH)_2 + CN^- \rightleftarrows Fe(CN)_2 + ?$
(3) $Fe(CN)_2 + CN^- \rightleftarrows Fe(CN)_6^=$
(4) $Fe(CN)_6^= + Fe^{+++} \rightleftarrows Fe[Fe^{III}Fe(CN)_6]_3$

(*e*) To 4 drops of sodium cyanide add 3 drops of ammonium polysulfide. Evaporate the mixture *just to dryness* on a water bath. Dissolve the residue in water; acidify the solution with hydrochloric acid and add a drop or two of ferric nitrate. Give explanations. Balance:

$$S_2^- + CN^- \rightleftarrows CNS^- + S^-$$

(*f*) Treat 4 drops of a solution of sodium cyanide with a nickel nitrate solution. Test the solubility of the precipitate in ammonia and in an excess of potassium cyanide. Complete:

(1) $Ni^{++} + CN^- \rightleftarrows ?$
(2) $Ni(CN)_2 + CN^- \rightleftarrows ?$

Thiosulfate Ion, $S_2O_3^-$

Experiment 41. (*a*) Add hydrochloric acid to 4 drops of a solution of sodium thiosulfate. Compare the action with that given by a sulfite when treated with hydrochloric acid. Complete:

(1) $S_2O_3^- + H_3O^+ \rightleftarrows SO_2 + ? + ?$
(2) $SO_3^- + H_3O^+ \rightleftarrows SO_2 + ?$

(*b*) Add sodium thiosulfate to 2 drops of lead acetate until no further precipitate occurs. Boil the mixture. What is the black precipitate? Does the sulfite of lead behave in this manner? Balance:

(1) $S_2O_3^- + Pb(CH_3COO)_2 \rightleftarrows PbS_2O_3 + CH_3COO^-$
(2) $PbS_2O_3 + S_2O_3^- \rightleftarrows Pb(S_2O_3)_3^=$
(3) $Pb(S_2O_3)_3^= \rightleftarrows S_2O_3^- + SO_4^- + SO_2 + S + PbS$

(*c*) Add sodium thiosulfate to 2 drops of a solution of silver nitrate. What changes are observed? Complete:

(1) $S_2O_3^- + Ag^+ \rightleftarrows Ag_2S_2O_3$
(2) $Ag_2S_2O_3 + H_2O \rightleftarrows Ag_2S + HSO_4^- + ?$

(*d*) Mix 4 drops of each solution: sodium sulfate, sodium sulfite and sodium thiosulfate. Add an excess of barium chloride to the solution, and then just enough hydrochloric acid to dissolve all of the precipitate except the barium sulfate. Separate the precipitate which forms and treat the solution with an aqueous solution of iodine (as long as it is decolorized) to oxidize the sulfite to the sulfate and to change the thiosulfate to the tetrathionate ion, $S_4O_6^-$. Add more barium chloride, if necessary, to precipitate all of the sulfate. Again separate any precipitate which forms, treat the solution with bromine water and note the formation of a white precipitate of barium sulfate. The bromine water oxidizes the tetrathionate to a sulfate. Can the presence of the sulfate, sulfite and thiosulfate ions be determined in a mixture of the three by this means? Complete:

(1) $H_2O + SO_3^- + I_2 \rightleftarrows HSO_4^- + ? + ?$
(2) $S_2O_3^- + I_2 \rightleftarrows S_4O_6^- + ?$
(3) $S_4O_6^- + Br_2 + H_2O \rightleftarrows H_3O^+ + HSO_4^- + ?$

Thiocyanate Ion, CNS⁻

Experiment 42. (*a*) Add 4 drops of a solution of ferric nitrate to 1 drop of potassium thiocyanate. Then shake the solution with ether. Complete:

$$Fe^{+++}\ xs + CNS^- \rightleftarrows ?$$

Then add a drop of a solution of ferric nitrate to 4 drops of potassium thiocyanate and shake the solution with ether. Account for the difference. Complete:

$$Fe^{+++} + CNS^-\ xs \rightleftarrows ?$$

(*b*) Add a drop of ferric nitrate to 4 drops of a solution of potassium thiocyanate acidified with a drop of hydrochloric acid. The red color which results is discharged by mercuric chloride, stannous chloride or a soluble fluoride. Complete:

(1) $Fe^{+++} + CNS^- \rightleftarrows ?$
(2) $Fe(CNS)_3 + HgCl_2 \rightleftarrows Hg(CNS)_2 + ? + ?$
(3) $Fe(CNS)_3 + Sn^{++} \rightleftarrows Fe^{++} + ? + ?$
(4) $Fe(CNS)_3 + F^- \rightleftarrows FeF_6^{---} + ?$

(*c*) Heat a little precipitated silver thiocyanate for three minutes with 3 drops of concentrated sulfuric acid. Repeat, using concentrated nitric acid instead of sulfuric acid. Is the thiocyanate decomposed in each instance? What effect would these reagents have on silver chloride under similar conditions? Balance:

$$AgCNS + H_2SO_4 + H_2O \rightleftarrows SO_4^{--} + NH_4^+ + COS + Ag^+$$

Chloride Ion, Cl⁻

Experiment 43. (*a*) Add 1 drop of concentrated hydrochloric acid to 1 drop of a solution of sodium chlorate. Complete:

$$H_3O^+\ conc. + Cl^- + ClO_3^- \rightleftarrows Cl_2 + ?$$

(*b*) Acidify 4 drops of a solution of sodium chloride with nitric acid and add silver nitrate to the solution. Add to the precipitate an excess of ammonia. Give the result. What other silver salts are white and insoluble in dilute nitric acid? When is this test conclusive for a chloride? What colored silver salts which are insoluble in nitric acid are likely to mask the white color of silver chloride? The chloride ion is identified after the removal of other ions which interfere with the test.

Bromide Ion, Br⁻

Experiment 44. (*a*) Add bromine water to 4 drops of an acidified solution of ferrous ammonium sulfate and then an excess of ammonia. Complete:

(1) $Fe^{++} + (H_3O^+) + Br_2 \rightleftarrows Br^- + ?$
(2) $Fe^{+++} + NH_3 + H_2O \rightleftarrows ? + ?$

(*b*) Add a drop of silver nitrate to 4 drops of a solution of potassium bromide acidified with nitric acid. What is the color of the precipitate? Is silver bromide as soluble in ammonia as silver chloride?

(*c*) Add a drop of chlorine water to 4 drops of a solution of potassium bro-

mide. Extract the solution with carbon tetrachloride. When is this a specific test for a bromide? Complete:

$$Cl_2 + Br^- \rightleftarrows ? + ?$$

(*d*) To 4 drops of a solution of potassium bromide and 4 drops of sodium chloride, add 4 drops of carbon tetrachloride and 5 drops of sulfuric acid. Treat the mixture with potassium permanganate, drop by drop, until a slight pink color remains after the mixture is shaken vigorously. Extract the water solution two times with carbon tetrachloride. Test the aqueous solution for a chloride. Complete:

$$MnO_4^- + Br^- + H_3O^+ \rightleftarrows Mn^{++} + Br_2 + ?$$

(*e*) Mix 4 drops of a potassium bromide solution with an equal volume of sodium chloride solution. Add 5 drops of nitric acid and an equal volume of water. Add a few crystals of potassium persulfate and heat the solution. Continue the addition of the persulfate and the heating until all the bromine is expelled and the solution remains colorless upon the addition of persulfate. Heat the colorless solution for two minutes and test it for a chloride. In the presence of acetic acid, persulfates do not oxidize the bromide ion to bromine but oxidize the iodide ion to iodine. Complete:

$$S_2O_8^= + H_3O^+ + Br^- \rightleftarrows HSO_4^- + Br_2 + ?$$

Iodide Ion, I^-

Experiment 45. (*a*) Add a solution of silver nitrate to 4 drops of a solution of potassium iodide. Let the precipitate settle and pour off the liquid. Add concentrated ammonia to the precipitate. Complete:

(1) $I^- + Ag^+ \rightleftarrows ?$
(2) $AgI + NH_3$ conc. $\rightleftarrows ?$

(*b*) Add a solution of mercuric chloride to 4 drops of a solution of potassium iodide acidified with nitric acid. What is the color of the precipitate? Is mercuric iodide soluble in an excess of potassium iodide? Complete:

(1) $I^- + Hg^{++} \rightleftarrows ?$
(2) $HgI_2 + I^-$ xs $\rightleftarrows ?$

(*c*) Add chlorine water to 4 drops of a solution of potassium iodide. Extract the solution with carbon tetrachloride. What is the color of the carbon tetrachloride layer? Is this a specific test for an iodide? Complete:

$$Cl_2 + I^- \rightleftarrows ? + ?$$

(*d*) Acidify a solution of 4 drops of sodium chloride and 4 drops of potassium iodide with nitric acid and add 3 drops of ammonium acetate, 1 drop of acetic acid and 4 drops of carbon tetrachloride. Treat the solution with potassium permanganate, drop by drop, until the pink color remains after the mixture is shaken vigorously. (See Experiment 44*d*.) Extract the water solution two times with carbon tetrachloride and test it for a chloride.

(*e*) Acidify 4 drops of a solution of potassium iodide with acetic acid and

add a drop of 5-*N* sodium nitrite and 4 drops of carbon tetrachloride. Will a bromide and an iodide act similarly? Complete:

$$I^- + HOAc + HNO_2 \rightleftarrows I_2 + NO + ? + ?$$

(*f*) Repeat Experiment 44*e*, using potassium iodide instead of potassium bromide. Write equations.

(*g*) Devise a method for the detection of the components of a mixture containing a chloride, a bromide and an iodide; this may be accomplished by removing the iodide by Experiment 45*d*, the bromide by Experiment 44*d*, and testing the remaining solution for a chloride with silver nitrate. The separation can also be effected by carrying out Experiment 45*e*, using acetic acid and Experiment 44*e*, as directed.

(*h*) To a solution containing 4 drops of each of the halogen salts in a test tube, add 1 drop of nitric acid and 4 or 5 drops of carbon tetrachloride, and then ferric nitrate solution until the water layer is yellow. Shake the mixture to extract the iodine. Reject the carbon tetrachloride layer, transfer the water layer to another test tube and boil for a minute to expel the iodine. Cool the solution and make certain that the iodine has been removed completely by shaking again after the addition of a drop of ferric nitrate and carbon tetrachloride. When the iodide ion has been removed, add 2 drops of nitric acid and 4 drops of carbon tetrachloride to the cool solution and then potassium permanganate drop by drop until the water layer is purple. Shake the mixture to extract the bromine. Reject the layer of carbon tetrachloride and boil the water layer to expel bromine. Reduce excess permanganate with the smallest possible amount of hydrogen peroxide. Separate any precipitate and to the solution add nitric acid and silver nitrate. A white precipitate is silver chloride.

(*i*) Another method of removing a bromide and an iodide consists in boiling a mixture of the two with a crystal of potassium dichromate. This liberates and expels iodine. Now add 3 drops of dilute sulfuric acid (consisting of equal volumes of water and concentrated sulfuric acid) to the solution, and boil to remove bromine. If a chloride is present in the mixture, it will not be affected and can be tested for after the removal of bromine and iodine. Complete:

(1) $I^- + Cr_2O_7^= + H_2O \rightleftarrows Cr(OH)_3 + ? + ?$
(2) $Cr_2O_7^= + Br^- + H_3O^+ \rightleftarrows Br_2 + ? + ?$

ANALYSIS

Procedure IX

1. Precipitation of Nickel Cyanide and Identification of the Cyanide Ion. To the solution from Group III add 2-*N* nickel nitrate solution until no more precipitate forms, then a drop more. Agitate the mixture frequently for at least 10 minutes and then separate any precipitate. Wash the precipitate thoroughly. Reject all but the first washing to avoid diluting the solution excessively. To the precipitate add 4 drops of ammonia and 2 or 3 drops of ammonium polysulfide (yellow ammonium sulfide). Heat, and if a filter was used, circulate the liquid through the glass wool filter repeatedly until the colloidal suspension of nickel sulfide is separated and the

filtrate is clear. Add an excess of hydrochloric acid to the clear solution. Heat until all of the hydrogen sulfide is removed. Separate any precipitate of sulfur which forms and to the clear solution add 1 or 2 drops of ferric chloride. The red color of ferric thiocyanate shows the presence of a cyanide.

2. Identification of the Thiocyanate Ion. Acidify 2 drops of the solution from the nickel cyanide precipitate with concentrated hydrochloric acid and add a drop of ferric chloride. A deep red color indicates the presence of a thiocyanate. If the color is brown rather than red, it may be caused by iodine. In this case add 4 drops of carbon tetrachloride and shake the mixture. If the carbon tetrachloride is pink or purple, iodine is present. Remove the iodine by extracting the solution with fresh portions of carbon tetrachloride. Add more ferric chloride if the water layer becomes colorless. If the water layer is still colored red, the presence of a thiocyanate is confirmed.

3. Precipitation and Solution of the Silver Salts. Identification of the Thiosulfate Ion. To the remainder of the solution from Procedure IX, 1, add an excess of a silver nitrate and acidify the solution with nitric acid. A light precipitate turning yellow, then brown or black, indicates the presence of a thiosulfate. This color change, caused by the decomposition of silver thiosulfate, is a sufficient test for the thiosulfate ion. If a large amount of white or light colored precipitate (silver thiocyanate or halide) is present, the change in color will be less pronounced—from nearly white to cream or light buff. If the precipitation with silver nitrate does not give an indication of the presence of the thiosulfate ion and the thiocyanate ion is not present, treat a separate portion of the unknown solution as follows:

If a sulfide is present, add an excess of cadmium acetate to the neutral solution. If a sulfite is present, add an excess of barium acetate. Separate the precipitated cadmium sulfide and barium sulfite. Acidify the solution with hydrochloric acid and add a drop of a solution of iodine and of barium chloride to oxidize and precipitate any traces of sulfide or sulfite which may not have been removed. If a precipitate forms, separate it and to the clear solution add a drop of a saturated solution of bromine water to oxidize the tetrathionate ion ($S_4O_6^-$) to a sulfate. A white precipitate of barium sulfate indicates the presence of a thiosulfate.

4. Solution of the Silver Salts. Separate the precipitate of the silver salts, Procedure IX, 3, add 10 drops of nitric acid and heat in the water bath. Circulate the acid through the precipitate and separate the precipitate from the hot mixture. Wash it well with hot water

Solution from Group III. Add $Ni(NO_3)_2$.

<table>
<tr><td colspan="2">Precipitate: $Ni(CN)_2$. Add NH_3 and $(NH_4)_2S_x$.</td><td colspan="5">Solution: Cl^-, Br^-, I^-, CNS^-, $S_2O_3^=$ etc. Divide into two portions.</td></tr>
<tr><td>Precipitate: NiS. Reject.</td><td>Solution: Add HCl and $FeCl_3$. Red color, $Fe(CNS)_3$, shows Cyanide.</td><td>Small portion (2 drops): Add HCl conc. and $FeCl_3$. Red color, $Fe(CNS)_3$, shows Thiocyanate.</td><td colspan="4">Large portion: Add 1-N $AgNO_3$, and HNO_3 in the order given. Light precipitate turning dark shows Thiosulfate. Yellow precipitate shows Bromide or Iodide. White precipitate shows Chloride or Thiocyanate. Heat and while hot separate any precipitate. Extract the precipitate with 10 drops of HNO_3 and wash with H_2O.</td></tr>
<tr><td colspan="3"></td><td colspan="3">Precipitate: AgCl, AgBr, AgI, AgCNS and Ag_2S (from $Ag_2S_2O_3$). Add NH_3 and a slight excess of colorless* $(NH_4)_2S$.</td><td rowspan="4">Solution and extract: Use to test for Bromate and Iodate if Bromide or Iodide was found.</td></tr>
<tr><td colspan="3"></td><td>Residue: Ag_2S. Reject.</td><td colspan="2">Solution:† CNS^-, Cl^-, Br^- and I^-. Boil to remove $(NH_4)_2S$. Add HNO_3, $Fe(NO_3)_3$ and CCl_4 or CH_3COOH, $NaNO_2$ and CCl_4.</td></tr>
<tr><td colspan="3"></td><td colspan="2"></td><td>CCl_4 layer: Violet color shows Iodide.</td><td>Water Layer: Boil. Add HNO_3, $KMnO_4$, and CCl_4.</td></tr>
<tr><td colspan="3"></td><td colspan="3"></td><td>CCl_4 Layer: Yellow or orange color shows Bromide.</td><td>Water layer: Boil. Add chloride free H_2O_2 or SO_2 and $AgNO_3$. White precipitate shows Chloride.</td></tr>
</table>

* If sodium sulfide is used instead of ammonium sulfide, acidify the solution with acetic acid, boil, and remove any sulfur which forms before testing for an iodide.

† The following procedure is satisfactory only in the absence of a thiocyanate. If a thiocyanate is present test the solution by Procedure IX, 6.

and remove as much of the wash liquid as possible. Reserve the solution to test for a bromate and iodate if these ions were not found in Group II and if a bromide and iodide are present. The solution also may be tested for perchlorate and borate ions.

To the precipitate add 5 drops of concentrated ammonia and 4 drops of freshly prepared colorless ammonium sulfide. Digest the mixture in the water bath at the temperature of boiling water for a few minutes. This is important since the reaction between the silver halides and sulfide ions takes place quite slowly. Separate the precipitate and if a filter was used, circulate the hot solution through the filter five times. To the solution add a drop of the colorless ammonium sulfide. If more silver sulfide precipitates, add colorless ammonium sulfide dropwise until no further precipitate forms. Separate the precipitate from the mixture. Discard the silver sulfide and evaporate the solution to a small volume (10 drops or less) to decompose all of the ammonium sulfide. Separate any sulfur which precipitates during the evaporation and test the solution for the halides.

5. Identification of the Halides in the Absence of the Thiocyanate Ion.

(A) IDENTIFICATION OF THE IODIDE ION. Pour the cooled solution containing the halides into a test tube, add one drop of nitric acid and 5 drops of carbon tetrachloride, then ferric nitrate until the solution is distinctly yellow. Shake the mixture well. A violet color in the carbon tetrachloride indicates the presence of an iodide. Let the mixture stand at least 3 minutes before concluding that an iodide is absent, for the reaction is slow. The presence of the iodide ion may be established by oxidizing the iodide ion to iodine with nitrous acid as described in Experiment 45*e*.

(B) IDENTIFICATION OF THE BROMIDE ION. If an iodide is present, heat the solution until the iodine is expelled. Add more ferric nitrate, if necessary, to insure the complete oxidation of the iodide. Cool the solution, add 5 drops of carbon tetrachloride and shake the mixture. If iodine is still present, repeat the heating process. When all the iodine has been removed, add to the solution 2 drops of nitric acid, then a potassium permanganate solution drop by drop until the water layer remains pink. Extract the solution with carbon tetrachloride as before. A yellow or orange coloration in the carbon tetrachloride indicates the presence of a bromide. If the color of the carbon tetrachloride is doubtful, remove the water layer with a medicine dropper.

(C) IDENTIFICATION OF THE CHLORIDE ION. Reject the carbon tetrachloride layer and transfer the water layer to a test tube. If a

bromide is present, heat the solution for 5 minutes, adding more permanganate if the pink color disappears. Add a drop of chloride free hydrogen peroxide or sulfurous acid to reduce the excess of permanganate, boil off the excess of the reducing agent, separate any precipitate and add silver nitrate. A white curdy precipitate indicates the presence of a chloride.

6. Identification of the Halides in the Presence of Thiocyanates.

METHOD A

(A) IDENTIFICATION OF THE IODIDE ION. To the neutral solution add in the order named 5 drops of carbon tetrachloride and a small crystal of potassium persulfate ($K_2S_2O_8$), about one-half the size of a small pea, and shake. A violet color indicates the iodide ion. Shake thoroughly to remove as much of the iodine from the aqueous solution as possible. Remove the carbon tetrachloride and destroy the remainder of the iodide and thiocyanate ions, if present, by neutralizing the solution with 3-*N* sodium carbonate, adding an additional milliliter of sodium carbonate and evaporating to dryness in a crucible. Determine the completeness of the removal of the iodide ion by dissolving the residue in 1 ml. of water, adding 4 drops of carbon tetrachloride, acidifying with dilute nitric acid and adding a crystal of potassium persulfate, about one-half the size of a small pea. Warm gently until the potassium persulfate decomposes. Unless a very large amount of iodide was present, the solution will become colorless. If iodine is liberated, repeat the addition of a few crystals of potassium persulfate and the extraction until the carbon tetrachloride is no longer colored. This last step will be necessary only if a very large concentration of iodide ions was present in the original solution.

(B) IDENTIFICATION OF THE BROMIDE ION. When a test for an iodide is no longer obtained, add 5 drops of carbon tetrachloride and 4 drops of concentrated nitric acid to the cool, iodide free solution. Shake the mixture about a minute to allow the orange color of the oxidation products of the thiocyanate to disappear. If the bromide ion is present, a yellowish color due to bromine will remain. Determine the color of the carbon tetrachloride solution against a white background by daylight if possible. If a very small amount of bromide ion is present, it may be necessary to run a blank and compare the color of the carbon tetrachloride used to make the extractions.

(C) REMOVAL OF THE BROMIDE ION AND THE IDENTIFICATION OF THE CHLORIDE ION. Remove the bromide ion, if present, before testing for the chloride ion by adding a slight excess of potassium

permanganate and boiling one minute. Remove sulfate ion formed by the decomposition of potassium persulfate by the addition of a slight excess of barium nitrate; otherwise a turbidity due to silver sulfate may form and be mistaken for a small amount of silver chloride. Separate any precipitate and add silver nitrate. A white curdy precipitate proves the presence of the chloride ion.

METHOD B

(A) IDENTIFICATION OF THE IODIDE ION. Test for the iodide ion as directed in Experiment 45*e*. If an iodide is present, add a slight excess of sodium nitrite to oxidize the iodide to iodine and heat the solution to decompose the excess nitrous acid which may be present.

(B) IDENTIFICATION OF THE BROMIDE ION. Neutralize the solution used to test for the iodide with 3-*N* sodium carbonate and add an additional milliliter. Evaporate the mixture to a dryness in a crucible. Cool and add 5 drops of carbon tetrachloride, a few drops of water and 4 drops of concentrated nitric acid. Shake the mixture about a minute to allow the colored oxidation products of the thiocyanate to decompose. If the carbon tetrachloride layer becomes colorless, add a solution of potassium permanganate until the solution is pink as in Procedure IX, 5. If the color of the carbon tetrachloride is doubtful, remove the solution with a dropper and again note the color of the carbon tetrachloride. A brown or yellow color in the carbon tetrachloride indicates the presence of the bromide ion.

(C) IDENTIFICATION OF THE CHLORIDE ION. Completely oxidize the bromide ion to bromine by adding an excess of potassium permanganate. Remove the bromine by repeatedly extracting with carbon tetrachloride or by heating. Reduce the excess of permanganate ion by adding a drop of chloride free hydrogen peroxide or sulfurous acid. Separate any precipitate and add an excess of silver nitrate. A white curdy precipitate proves the presence of the chloride ion.

Discussion of the Analysis

Cyanide Ion. Nickel nitrate is used to precipitate the cyanide ion. Nickel cyanide precipitates slowly, and the precipitation is not complete unless an excess of the nickel ion is present, the solution agitated and allowed to stand for several minutes. Sometimes the addition of a drop of ammonia hastens the coagulation of the precipitate. Since nickel cyanide is soluble in an excess of an alkali cyanide because of the formation of a complex ion, it is essential to add an excess of nickel nitrate to insure the complete precipita-

tion of the cyanide ion. It is likewise important to wash the nickel cyanide precipitate well, especially if a thiocyanate is present, since any thiocyanate present in the nickel precipitate will give a red color with ferric chloride and thus be mistaken for a cyanide. In a neutral solution any precipitate formed on the addition of nickel nitrate should be the cyanide, but if the solution is alkaline, the hydroxide or a basic salt of nickel may be precipitated. The confirmatory test should not be omitted.

Thiocyanate Ion. The thiocyanate ion is detected in a small portion of the solution by the formation of the characteristic deep red of ferric thiocyanate on the addition of ferric chloride. The brown color of iodine should not be mistaken for the red color. After repeated extraction of the solution with carbon tetrachloride, however, not enough iodine will remain to interfere with the test. If the solution is not sufficiently acid, red basic ferric acetate—$Fe(OAc)(OH)_2$—may form in sufficient concentration to be mistaken for ferric thiocyanate. The test for a thiocyanate ion is made at this point because, if present, it must be destroyed before the tests are made for the halides. If not destroyed, the thiocyanate ion interferes with the test for the bromide ion, and in the presence of a high concentration of a thiocyanate a small amount of a bromide ion cannot be detected.

Thiosulfate Ion. In a neutral solution the halides, the thiocyanate and the thiosulfate are precipitated completely by silver nitrate. Silver thiosulfate almost immediately decomposes, going through several color changes and finally forming silver sulfide and hydrogen sulfate ions. This is a sensitive and specific test for the thiosulfate ion unless a large white or light colored precipitate of the thiocyanate or halides obscures the color change. In this case make a special test as directed.

The mixture is acidified with nitric acid and boiled to dissolve any silver bromate which might have precipitated from the neutral solution and to prevent the precipitation of silver acetate. It is important to separate the precipitate while hot, since silver bromate may precipitate on cooling.

Halides. The iodide ion is the only one of the halides oxidized to the free halogen by the ferric ion in a dilute solution of nitric acid. The characteristic purple color of the solution of free iodine in carbon tetrachloride is a sensitive and specific test for an iodide.

On boiling the acid solution containing an excess of ferric nitrate the iodide ion is oxidized and the iodine is expelled completely.

On treating the nitric acid solution with potassium permanganate, the bromide ion is oxidized to free bromine, which on extraction with carbon tetrachloride gives a characteristic yellow or orange color, depending on the concentration. If the pink color of the excess of permanganate ion or the brown color of manganese dioxide makes it difficult to determine the color of the carbon tetrachloride, use a medicine dropper to remove the colored aqueous solution. On boiling a solution containing an excess of permanganate all of the bromide is oxidized and expelled, while the chloride ion is not appreciably oxidized if the concentration of hydronium ion is low. Because thiocyanates interfere with this test for bromide, the procedure must be modified to insure its destruction before testing for a bromide.

When the iodide and bromide ions have been removed, the formation of a white precipitate on adding silver nitrate is a specific test for a chloride. Since chlorides are common impurities in chemical reagents, a small precipitate cannot be taken as proof of the presence of a chloride in the original unknown. If a small amount of precipitate is obtained, a blank test for a chloride should be made on all of the reagents used up to this point in the analysis.

If a thiocyanate is present, a bromide cannot be identified by the procedure just discussed. It is possible, however, to destroy nearly all of the thiocyanate by evaporating an alkaline solution to dryness after the removal of any iodide. Then, after adding carbon tetrachloride and acidifying to prove the complete removal of the iodide, identify the bromide by the addition of concentrated nitric acid. Any thiocyanate remaining is destroyed and the bromide is oxidized to bromine which is dissolved in the carbon tetrachloride present. The carbon tetrachloride will become orange even in the absence of a bromide, possibly because of the formation of perthiocyanic acid ($H_2C_2N_2S_3$). However, any color caused by these decomposition products disappears within a minute when the mixture is agitated.

EXERCISES

1. Account for the use of ammonium polysulfide in testing for the cyanide ion.
2. Account for the addition of silver nitrate and nitric acid in the above order when precipitating the ions of Group IV.
3. Using the solubility product principle, show that the concentration of iodide ion is proportional to the square root of the concentration of sulfide ion on digesting silver iodide with ammonium sulfide.
4. On adding a few drops of a solution of silver nitrate or nickel nitrate to a

solution of a soluble cyanide a precipitate forms which immediately dissolves. Explain.

5. Account for the fact that if a few drops of silver nitrate are added to several milliliters of sodium thiosulfate a white precipitate is formed which dissolves, while if a few drops of the thiosulfate are added to a solution of silver nitrate, a white precipitate forms which passes through a series of color changes.
6. Why is a small volume of carbon tetrachloride used to extract the iodine in making the test for an iodide?
7. An acetic acid solution of a permanganate oxidizes an iodide but not a bromide to the free halogen. A nitric acid solution will oxidize a bromide to bromine. Will an iodide be oxidized by a nitric acid solution of a permanganate? Explain.
8. Account for the oxidation state of sulfur in sodium tetrathionate.
9. Give in diagram form a method of detecting a sulfite, sulfate and a thiosulfate in a mixture.
10. Differentiate between the oxidation state and the average net oxidation state.

CHAPTER XIX

Anions of Group V

PROPERTIES OF ACIDS AND IONS

HYPOCHLORITE

ACID. Hypochlorous acid is a weak oxidizing acid. Aqueous solutions decompose in sunlight.

$$5\,HOCl + 5\,H_2O \rightleftarrows 5\,H_3O^+ + 4\,Cl^- + ClO_3^- + O_2$$

Alkali hypochlorites are fairly stable in alkaline solutions but decompose into Cl^- and ClO_3^- when heated.

Ion. The OCl^- oxidizes Mn^{++} to $MnO_2 \cdot H_2O$, $MnO_4^=$ to MnO_4^-, Pb^{++} to PbO_2, Br^- to BrO_3, I^- to IO_3^-, $S^=$, $S_2O_3^=$ and $SO_3^=$ to $SO_4^=$, Fe^{++}, Sn^{++}, etc., to the higher oxidation state. Hypochlorous acid is reduced to Cl^- by H_2O_2, HNO_2, $S_2O_3^=$, $Pb(OAc)_2$, Fe^{++}, Sn^{++}, etc.

The OCl^- changes rapidly in the presence of Ag^+ into ClO_3^- and AgCl.

CHLORATE

Acid. Chloric acid is an unstable, strong oxidizing acid. When concentrated above 40%, it decomposes giving ClO_4^-, ClO_2 and Cl^-.

$$4\,HClO_3 \rightleftarrows 3\,HClO_4 + HCl$$
$$2\,HClO_3 \rightleftarrows 2\,HCl + 3\,O_2$$
$$4\,HClO_3 \rightleftarrows 4\,ClO_2 + O_2 + 2\,H_2O$$

Chlorine dioxide formed from $KClO_3$ in the presence of concentrated H_2SO_4 explodes when warmed.

Ions. An acidified solution of ClO_3^- is an excellent oxidizing agent. It is reduced to Cl^- by $Fe(CN)_6^=$, $O_2^=$, HNO_2, Br^-, H_2SO_3, $S_2O_3^=$ and Fe^{++}. It is reduced to ClO_2 by Mn^{++} in concentrated HNO_3.

BROMATE

Acid. The free acid has not been isolated. A 50% solution can be obtained by evaporating a dilute solution under reduced pressure.

Ion. The bromates of the common metals are soluble except those of Ag, Ba and Pb. Other metals form insoluble basic bromates.

The BrO_3^- in an acid solution is a powerful oxidizing agent. It is usually reduced to Br^-. If an excess of the reducing agent is not used, i.e., if an excess of BrO_3^- is present, the reduction product is Br_2. Even Mn^{++} and Cr^{+++} are oxidized to MnO_2 and $Cr_2O_7^=$ by BrO_3^- in moderately concentrated acid solutions. The BrO_3^- in acid solution oxidizes Cl^- to Cl_2, Br^- to Br_2 and I^- to I_2. With an excess of BrO_3^-, I_2 is oxidized to IO_3^-.

If a bromate of an alkali metal is heated, oxygen is evolved and a bromide is formed. In some cases, $Co(BrO_3)_2$ and $Zn(BrO_3)_2$ for example, the residue is an oxide and O_2 and Br_2 are evolved.

IODATE

The properties and reactions of the iodate ion have been considered on page 258.

PERCHLORATE

Acid. Pure perchloric acid is an unstable acid. The 70% acid is stable at 60°. The hot concentrated acid reacts explosively with many organic compounds. Iodine reacts with the acid forming free Cl_2 and HIO_4.

Ion. The perchlorates are all soluble in water. Potassium perchlorate is one of the less soluble perchlorates and is particularly insoluble in alcohol containing a small amount of the free acid.

Solutions of H_2S, HNO_2, Fe^{++}, H_2SO_3, $S_2O_3^=$, HI, HBr and all other common reducing agents are not oxidized by the ClO_4^-.

Solid perchlorates when heated decompose, giving O_2 and a chloride.

BORATE

Acid. Boric acid, H_3BO_3, is a very weak acid. The formulas of the borates indicate the existence of a number of complex acids whose structures are not well known. Nearly all of the borates are

salts of HBO_2. Borax, however, is a salt of $H_2B_4O_7$. In aqueous solutions, salts of this acid are hydrolyzed.

$$B_4O_7^{=} + 3\,H_2O \rightleftarrows 2\,H_3BO_3 + 2\,BO_2^-$$

Further hydrolysis of the BO_2^- occurs at still greater dilution.

$$BO_2^- + H_2O \rightleftarrows HBO_2 + OH^-$$

Ions. The solubility of the Ca, Ba and Cd salts depends a great deal on the $C_{H_3O^+}$.

Turmeric paper moistened with an acidified solution of a borate and dried turns red and becomes an evanescent greenish-blue when moistened with dilute NaOH or NH_3. This test cannot be used if strong oxidizing agents are present because they destroy the turmeric.

Only volatile compounds of boron such as BF_3, H_3BO_3, $B(OCH_3)_3$, etc., impart the characteristic green color to a flame.

NITRITE

Acid. Nitrous acid is a weak acid. It oxidizes I^- to I_2, Fe^{++} to Fe^{+++} and is reduced to NO. When nitrous acid oxidizes NH_4^+ the nitrogen in the oxidizing and reducing agent each supply one atom of the N_2 formed. Oxidizing agents such as MnO_4^-, ClO_3^-, BrO_3^-, etc., oxidize HNO_2 to NO_3^-.

Ion. Silver ions precipitate $AgNO_2$ (white) from concentrated solutions of NO_2^-. The precipitate is soluble in HNO_3. The NO_2^- is oxidized by oxidizing agents to NO_3^- in neutral or alkaline solutions.

NITRATE

Acid. Nitric acid is a strong oxidizing acid. When concentrated HNO_3 is boiled, it decomposes into NO_2, O_2 and H_2O.

Ions. All nitrates are soluble, although a few insoluble basic nitrates are known. Antimony and arsenic do not form nitrates. Stannic nitrate hydrolyzes and $SnO_2 \cdot xH_2O$ is formed.

The usual rule that very dilute cold HNO_3 is reduced to NH_4^+, dilute HNO_3 to NO, and concentrated HNO_3 to NO_2 means that these products usually predominate at these concentrations and not that they are the sole products.

Both nitrates and nitrites react with Fe^{++} in concentrated H_2SO_4

to give $Fe \cdot NO^{++}$ (brown). Ions which form colored compounds interfere with the test. Interfering ions are discussed on page 300.

The NO_3^- is reduced to NH_3 by Al or Zn in an alkaline solution. Ammonia is formed also by the action of Al or Zn on other ions containing nitrogen.

REACTIONS OF THE IONS OF GROUP V

Hypochlorite Ion, OCl^-

Experiment 46. (*a*) Treat a little bleaching powder with dilute hydrochloric acid. What is the formula of bleaching powder? Of calcium hypochlorite? Treat a little with dilute hydrochloric acid. Complete:

(1) $CaCl(OCl) + H_3O^+ \rightleftarrows Cl_2 + ? + ?$
(2) $Ca(OCl)_2 + H_3O^+ \rightleftarrows HOCl + ? + ?$

(*b*) Carefully acidify 4 drops of a solution of sodium hypochlorite with acetic acid. Add to the clear solution (separate any precipitate which may form) 3 drops of lead acetate, and heat the mixture to boiling. Give the color of the precipitate. What is it? This is a characteristic and specific test for a hypochlorite. Balance:

$$Pb(CH_3COO)_2 + HOCl + H_2O \rightleftarrows PbO_2 + H_3O^+ + CH_3COOH + Cl^-$$

Chlorate Ion, ClO_3^-

Experiment 47. (*a*) Add a drop of a solution of sodium nitrite to 4 drops of a solution of sodium chlorate containing 2 drops of nitric acid. Then add silver nitrate. Complete:

$$ClO_3^- + HNO_2 + H_2O \rightleftarrows NO_3^- + ? + ?$$

(*b*) Warm a *small* crystal of potassium chlorate with concentrated sulfuric acid. (CARE!!) What explosive substance is formed? A chlorate when ignited leaves a chloride as a residue. Hydrochloric acid decomposes chlorates with the evolution of chlorine and chlorine dioxide. Balance:

$$KClO_3 + H_2SO_4 \text{ conc.} \rightleftarrows HSO_4^- + ClO_4^- + ClO_2 + K^+ + H_2O$$

(*c*) Using 4 drops of a test solution of a chlorate for each test, determine whether chlorates are reduced to chlorides by zinc in acid solutions; by aluminum and sodium hydroxide; by a solution of sulfur dioxide. Complete:

(1) $ClO_3^- + Zn + H_3O^+ \rightleftarrows Zn^{++} + Cl^- + ?$
(2) $ClO_3^- + Al + OH^- + H_2O \rightleftarrows Cl^- + ?$
(3) $ClO_3^- + SO_2 + H_2O \rightleftarrows H_3O^+ + HSO_4^- + Cl^-$

Bromate Ion, BrO_3^-

Experiment 48. (*a*) Add 4 drops of concentrated hydrochloric acid to an equal volume of potassium bromate. Complete:

$$H_3O^+ \text{ conc.} + Cl^- + BrO_3^- \rightleftarrows Cl_2 + Br_2 + ?$$

(*b*) Unless an excess of reducing agent is added, bromic acid is reduced to bromine by oxalic acid, hydrobromic acid, nitrous acid, sulfur dioxide (sulfurous acid) and a number of other reducing agents. It is reduced to a bromide by phosphorous acid, arsenious acid, or sulfur. Write the equations for these reactions.

(*c*) Treat 4 drops of a solution of potassium bromide with cold dilute sulfuric acid. Is any change noted? Acidify 4 drops of potassium bromate with cold dilute sulfuric acid. Is there any evidence of a chemical change? Does the solution remain colorless? Now mix the two solutions. Give the result and explain. Extract the mixture with carbon tetrachloride. Under what conditions would this test give conclusive evidence of the presence of a bromate? Complete:

$$BrO_3^- + H_3O^+ + Br^- \rightleftarrows Br_2 + ?$$

(*d*) Make 4 drops of a solution of potassium bromate just acid to litmus with sulfuric acid and treat the solution with 4 drops of manganous sulfate. Boil the mixture. What is the precipitate? Iodates and chlorates do not show a similar behavior. Balance:

$$Mn^{++} + BrO_3^- + (H_3O^+) + H_2O \rightleftarrows MnO_2 + H_3O^+ + Br^-$$

(*e*) Add barium acetate to 4 drops of a neutral solution of potassium bromate. Then add acetone to the mixture. Note the difference in the amount of precipitate formed. Test the solubility of the precipitate in boiling water.

Perchlorate Ion, ClO_4^-

Experiment 49. (*a*) Determine whether sodium perchlorate (4 drops) acidified with nitric acid is reduced by: nitrous acid, ferrous ion, hydrogen peroxide.

(*b*) Add a solution of sulfurous acid to an acidified solution of 4 drops of sodium perchlorate. Test the solution for a chloride. Is the perchlorate reduced? Chlorates or hypochlorites are reduced by sulfurous acid and may be removed as silver chloride.

(*c*) Boil a solution containing 4 drops each of sodium hypochlorite, chlorate and perchlorate with concentrated hydrochloric acid. Add a slight excess of silver nitrate to the solution. Separate any precipitate which forms and evaporate the solution to dryness. Fuse the residue with a mixture of sodium and potassium carbonates in the loop of a platinum wire. Dissolve the fused mass in water and test the solution for a chloride with silver nitrate. Explain. Complete:

(1) $HOCl + H_3O^+ + Cl^- \rightleftarrows Cl_2 + ?$
(2) $ClO_3^- + H_3O^+ + Cl^- \rightleftarrows Cl_2 + ?$ (principal reaction)
(3) $ClO_3^- + H_3O^+ + Cl^- \rightleftarrows H_2O + Cl_2 + ClO_2$
(4) $KClO_4 + (Na_2CO_3) \rightleftarrows KCl + ?$

Metaborate Ion, BO_2^-; Tetraborate Ion, $B_4O_7^=$

Experiment 50. (*a*) Add a little borax ($Na_2B_4O_7$) to 1 ml. of dilute sulfuric acid. Boil the mixture. Balance:

$$B_4O_7^= + H_3O^+ + H_2O \rightleftarrows H_3BO_3$$

(*b*) Add, drop by drop, hydrochloric acid to 4 drops of a solution of sodium tetraborate (borax) until it is just acid to litmus. Moisten a slip of turmeric paper with the solution and dry it on a water bath. The reddish brown color of the paper becomes more pronounced as the strip becomes dry. The color be-

comes blue to black on moistening the test paper with 1% sodium hydroxide. It is better to carry out the test by placing a drop of an extract of turmeric in a crucible, adding the acidified borax solution, evaporating *just to dryness*, cooling and moistening with ammonia. The color will change to an evanescent blue.

(*c*) Mix 0.05 g. of powdered borax ($Na_2B_4O_7$) with an equal weight of calcium fluoride and four times its weight of sodium acid sulfate. Add to the mixture enough water to make a paste. Collect some of the material in a loop of a platinum wire and heat it in the edge of a nonluminous flame. What causes the green color? Complete:

$$Na_2B_4O_7 + CaF_2 + NaHSO_4 \rightleftarrows BF_3 + CaSO_4 + Na_2SO_4 + ?$$

(*d*) Introduce into a 25 ml. conical flask 4 drops of sodium tetraborate, 1 ml. of concentrated sulfuric acid and 1 ml. of methyl alcohol. Fit the flask with a one-hole stopper carrying a 3 cm. straight glass tube. Heat the mixture and ignite the alcohol vapor as it issues from the jet. Keep the alcohol boiling rather vigorously and note the green coloration of the flame. Balance:

$$B_4O_7^{=} + H_2SO_4 \text{ conc.} + CH_3OH \rightleftarrows B(OCH_3)_3 + HSO_4^- + H_2SO_4 \cdot H_2O$$

(*e*) Make a flame test using a solution of borax, and a second, using a solution of boric acid. Account for the difference in the color of the flame.

Nitrite Ion, NO_2^-

Experiment 51. (*a*) Add hydrochloric acid to 4 drops of a solution of sodium nitrite. What is the gas which forms? Complete:

(1) $NO_2^- + H_3O^+ \rightleftarrows ? + ?$
(2) $HNO_2 + H_2O \rightleftarrows NO + ? + ?$

(*b*) Acidify 4 drops of a solution of sodium nitrite with acetic acid and add to it 2 drops of a solution of ferrous sulfate. What is the color of the mixture? Boil it and note the change. Does a nitrate give this reaction in the presence of acetic acid? Complete:

(1) $Fe^{++} + HOAc + HNO_2 \rightleftarrows Fe^{+++} + NO + OAc^- + ?$
(2) $Fe^{++} + NO \rightleftarrows (Fe \cdot NO)^{++}$

(*c*) Acidify 4 drops of a solution of sodium nitrite with acetic acid and add to the solution a drop of potassium iodide. Shake the mixture with 5 drops of carbon tetrachloride. Explain the results. Do nitrates give a similar test? Does nitric acid? Complete:

$$HNO_2 + CH_3COOH + I^- \rightleftarrows NO + I_2 + CH_3COO^- + ?$$

(*d*) To 4 drops of a solution of potassium permanganate acidified with sulfuric acid add sodium nitrite, drop by drop, until the color of the permanganate is discharged. Write the equation. Complete:

$$HNO_2 + MnO_4^- + H_3O^+ \rightleftarrows NO_3^- + ? + ?$$

(*e*) To 4 drops of a solution of urea in hydrochloric acid, add 4 drops of a solution of sodium nitrite and warm the solution. The immediate evolution of gas (carbon dioxide and nitrogen) is a specific test for a nitrite. The reaction is

$$(NH_2)_2CO + 2\,HNO_2 \rightleftarrows CO_2 + 3\,H_2O + 2\,N_2$$

(*f*) Boil a solution containing 4 drops of sodium nitrite and 0.1 g. of ammonium sulfate until every trace of nitrite is destroyed. Test small portions of the solution at five-minute intervals for the nitrite ion. How much time is required for the complete decomposition? Give the results and explain. Balance:

$$NO_2^- + NH_4^+ \rightleftarrows N_2 + ?$$

(*g*) Add 4 drops of a solution of sodium nitrite acidified with acetic acid to a solution of mercurous ion. The mercurous ion is reduced to free mercury. Balance:

$$Hg_2^{++} + HNO_2 + H_2O \rightleftarrows 2\,Hg + H_3O^+ + NO_3^-$$

Nitrate Ion, NO_3^-

Experiment 52. (*a*) Heat a small crystal of cupric nitrate in a small Pyrex test tube. Complete:

$$Cu(NO_3)_2 \rightleftarrows NO_2 + ? + ?$$

Do all nitrates decompose in this way?

(*b*) Heat a small crystal of sodium nitrate and a piece of copper turnings or foil with 6 drops of concentrated sulfuric acid. Give the result and explain. Complete:

$$Cu + NaNO_3 + H_2SO_4 \text{ conc.} \rightleftarrows ? + ? + ? + H_2SO_4 \cdot H_2O$$

(*c*) Place 20 drops of concentrated sulfuric acid in a test tube. Then saturate 5 drops of water with ferrous ammonium sulfate. Thoroughly cool the solution, and add to it a drop or two of sodium nitrate. Carefully pour the solution into the tube of sulfuric acid, so that the two fluids do not mix. A purple color, which afterwards turns brown, is produced at the junction of the two liquids. Balance:

$$Fe^{++} + H_2SO_4 + NO_3^- \rightleftarrows Fe^{+++} + H_2SO_4 \cdot H_2O + HSO_4^- + (Fe \cdot NO)^{++}$$

(*d*) Nitrites interfere with the test for a nitrate. A method for destroying a nitrite is to neutralize the solution and heat it with a solution of ammonium sulfate until a portion no longer gives a test for the nitrite ion when tested by Experiment 51*b*. Then test the solution for a nitrate by Experiment 52*c*.

(*e*) Place a solution (free from cyanides and ammonium salts) to be tested for a nitrate in a test tube. Then add a piece of aluminum wire and some sodium hydroxide. Put a loose plug of glass wool in the upper part of the test tube. Place a moist piece of red litmus paper on the top of the plug and loosely close the tube with a cork. Warm the solution. Examine the litmus paper and explain. Balance:

$$NO_2^- + Al + OH^- + H_2O \rightleftarrows NH_3 + (Al(OH)_4(H_2O)_2)^-$$

ANALYSIS

Procedure X

1. Identification of the Hypochlorite Ion. Remove any anions whose lead salts are insoluble from 4 drops of the original solution of the unknown. Precipitate the chromate, iodate and sulfate ions from a neutral solution by barium acetate and the ferro- and

ferricyanide ions by cadmium acetate. Then test the solution for the hypochlorite ion, making the solution just acid with acetic acid and adding an excess of lead acetate solution. Heat the solution to boiling and allow it to stand for 5 minutes. The appearance of a brown precipitate, PbO_2, is a specific test for a hypochlorite.

Analysis of Group V—Procedure X

Unknown solution: Test 4 drops for OCl^- with CH_3COOH and $Pb(CH_3COO)_2$. A brown precipitate, PbO_2, shows *Hypochlorite.* If OCl^- is present, add to another portion NaOH and H_2O_2; neutralize, and add a slight excess of $AgNO_3$. Then make the solution distinctly acid with HNO_3, heat to boiling and separate any precipitate while hot. (In absence of OCl^- omit NaOH and H_2O_2.)

Precipitate: Insoluble silver salts, including most of the $AgBrO_3$ and $AgIO_3$. Discard after extracting repeatedly with 10 drops of hot HNO_3. Add the HNO_3 extract to the solution.	*Solution and acid extract:* ClO_3^-, BrO_3^-, IO_3^-, ClO_4^-, etc. Heat to boiling, add 1 drop of $AgNO_3$. If a precipitate forms, separate it from the hot solution. Add SO_2, heat to boiling, add $AgNO_3$ to precipitate the halides and separate any precipitate.	
	Precipitate: Ag halides. Test as in Proc. IX. AgCl shows *Chlorate.* AgBr shows *Bromate.* AgI shows *Iodate.*	*Solution:* ClO_4^-, etc. Evaporate, fuse with $Na_2CO_3-K_2CO_3$. Dissolve, add HNO_3 and $AgNO_3$. White precipitate, AgCl, shows *Perchlorate.*

2. Identification of the Chlorate, Bromate and Iodate Ions. If a hypochlorite is present, to 4 drops of the original unknown add 2 drops of 2-*N* sodium hydroxide and a drop of 3% hydrogen peroxide to reduce the hypochlorite to a chloride. Just neutralize with nitric acid the solution from which the hypochlorite was removed or in the absence of a hypochlorite, 4 drops of the original solution and add a slight excess of silver nitrate to remove all of the anions which form insoluble silver salts. Make the mixture distinctly acid with nitric acid, and heat to boiling. Separate any precipitate in the hot solution. To the centrifuge or filter tube assembly containing the insoluble silver salts add 10 drops of dilute nitric acid and heat in the water bath. If the acid goes through the filter, circulate the filtrate through the precipitate several times. Reject the precipitate. Add the nitric acid extract to the first solution containing the rest of the chlorate, bromate, iodate and perchlorate ions. Heat the solution to boiling and add a drop of silver nitrate to make sure that the precipitation of the halides is complete. Then add sulfurous acid until the solution smells strongly of sulfur dioxide. The sulfur dioxide reduces the chlorate, bromate and iodate

ions to the respective halides. Heat the mixture until it no longer smells of sulfur dioxide. If a precipitate forms add more silver nitrate until the precipitation is complete. Separate the precipitate from the hot mixture and wash the precipitated silver halides. Reserve the solution for the identification of the perchlorate ion and analyze the precipitate for halides as directed for the silver precipitate in Group IV, Procedure IX, 4 and 5. A test for a chloride here indicates the presence of a chlorate; a bromide indicates a bromate; and an iodide an iodate. Do not omit the tests for an iodate and a bromate unless these ions were found in Group II, Procedure VII. A small amount of an iodate and a somewhat larger amount of a bromate may be missed completely in the analysis of that group, because the barium salts are somewhat soluble even in the presence of acetone. If tests for these ions were obtained in Group II, they need not be tested for again, but after the reduction with sulfurous acid, the bromide and iodide must be oxidized and removed before precipitating silver chloride in the test for a chlorate. If a bromide or iodide was present, a hypochlorite cannot be present in the original solution and the solution from Group IV may be used to test for the halogenates. The test for a chlorate, however, must always be made on a portion of the original unknown as directed.

3. Identification of the Perchlorate Ion. Add to the solution from Procedure X, 2 a little more silver nitrate to insure the complete removal of the halides and separate any precipitate that forms. Transfer the solution to a porcelain crucible and evaporate it carefully to dryness. To the dry residue add a mixture of equal parts of sodium and potassium carbonates (chloride free). Mix thoroughly and fuse in the loop of a platinum wire. Cool the melt and dissolve it in hot water. Make the solution acid with nitric acid and heat it to expel the carbon dioxide. If the bead does not dissolve completely, separate any residue and add silver nitrate to the solution. A white precipitate of silver chloride shows the presence of a perchlorate. If no precipitate formed in the solution, treat the residue with dilute ammonia. Separate any precipitate in the mixture, acidify the solution and add a drop of silver nitrate. A white precipitate of silver chloride indicates a perchlorate.

4. Identification of the Nitrate and Nitrite Ions. In the absence of a nitrite, test a portion of the original unknown for the nitrate ion by the tests given in Experiment 52*c* or *e*. Other ions besides the nitrite which interfere with the tests in Experiment 52*c* are the bromide, iodide, bromate, iodate, thiocyanate, ferrocyanide and ferricyanide ions. Remove the interfering halides, oxyhalogen

salts, chromate and the thiocyanate by adding silver sulfate or silver acetate. Then add sodium chloride to precipitate the excess silver ion. Precipitate the ferro- and ferricyanide by adding cadmium acetate. Ammonium salts interfere with the test described in Experiment 52*e* and must be removed by making the solution alkaline with sodium hydroxide and boiling before reducing the nitrate ion to ammonia. Other ions which contain nitrogen also interfere and must be removed by the addition of suitable reagents.

The nitrite ion gives the same tests as a nitrate, and must be tested for and removed before analyzing the solution for a nitrate. Test a portion of the original unknown for a nitrite by Experiment 51*b* or *e*. The chlorate, bromate, iodate, iodide, ferricyanide and thiocyanate ions interfere with the test for a nitrite given in Experiment 51*b*. The carbonate ion interferes with the urea test for the nitrite ion described in Experiment 51*e* and must be removed by acidifying the solution with hydrochloric acid before adding the urea solution, otherwise an evolution of carbon dioxide from a carbonate might be mistaken for the test for a nitrite.

To remove a nitrite from the solution to be tested for a nitrate, add a few small crystals of solid ammonium sulfate to the neutral solution or 5 drops of a solution of urea in hydrochloric acid and heat the solution until the nitrite is decomposed. This process will take from 1/4 to 1/2 hour. Occasionally test a small amount of the solution for the nitrite ion. When the nitrite ion has been removed, cool the solution and test for a nitrate.

5. Identification of the Metaborate or Tetraborate Ion. Make a portion of the unknown solution slightly alkaline with sodium hydroxide and evaporate it almost to dryness in a crucible. Pyrex containers cannot be used since they are attacked by the hot alkali and the solution will give a test for a borate. Test the residue for a borate by Experiment 50*b* or by adding 10 drops of concentrated sulfuric acid and transferring the mixture to a test tube (13 × 100 mm.) fitted with a two-hole rubber stopper into which two bent glass tubes have been inserted. One tube reaches almost to the bottom of the test tube. The second tube ends just below the stopper and its other end is drawn into a capillary 3 cm. long and with a bore not greater than 0.5 mm. Attach a trap, consisting of another test tube with a two-hole stopper and two bent glass tubes, one acting as a mouth piece. Allow the sulfuric acid solution to cool, add 5 ml. of methyl alcohol, and assemble the apparatus as shown in Figure 15. Blow through the warm solution and direct the exit vapors from the capillary into a small nonluminous Bunsen flame. A very small amount of a borate will give a green color to

the flame. The long capillary prevents the flame from traveling back into the test tube and also concentrates the flame coloration to a small area and makes the test more sensitive. It is important to insert a trap between the mouth and the test tube containing the solution being tested. This prevents the solution from getting into the mouth in case the capillary becomes plugged.

If a chlorate is present, destroy it before testing for a borate, because of the explosive nature of mixtures of alcohol, sulfuric

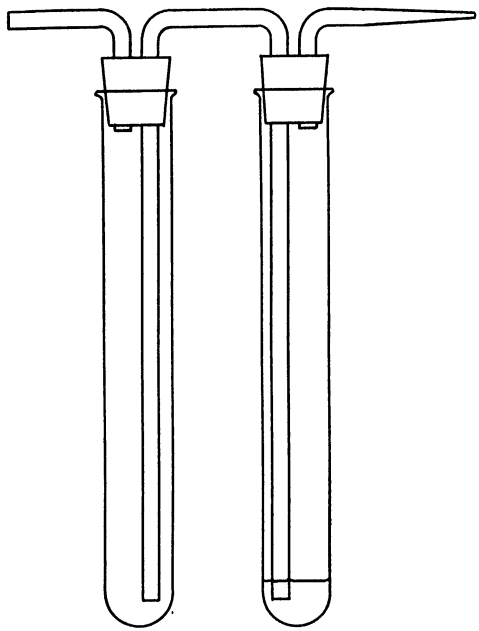


Fig. 15.

acid and chlorates. To effect this, add sulfurous acid to the neutral solution until the solution smells of sulfur dioxide. Make the solution slightly alkaline with sodium hydroxide, evaporate it almost to dryness and test it for a borate as directed. The chlorate is reduced to a chloride, which does not interfere with the test. Chromates, iodides and nitrites interfere and should be removed or destroyed.

Turmeric extract can be used to test for a borate. Place two drops of the barely acid solution of the unknown or the solution

being analyzed for Group V in a crucible. Add two drops of an extract of turmeric and carefully evaporate the mixture just to dryness. Do not heat the residue above 100°. Cool and add a drop of ammonia. A distinct blue color that fades shows the presence of a borate. Be sure to cool the residue to room temperature before adding the ammonia.

Discussion of the Analysis

Hypochlorite Ion. In a hot solution, neutral or slightly acid with acetic acid, lead acetate is oxidized to lead dioxide by the hypochlorite ion. The test is specific and very sensitive. If a hypochlorite is present, reducing agents must be absent. The converse is also true.

Chlorate, Bromate and Iodate Ions. The hypochlorite ion, if present, is easily reduced by hydrogen peroxide in a cold alkaline solution containing sodium hydroxide, while the other oxyhalogen ions are not affected. After the solution is acidified with nitric acid, the chloride formed together with any ions present which form insoluble silver salts is precipitated by adding silver nitrate. The hypochlorite must be reduced before the silver nitrate is added, for silver hypochlorite decomposes spontaneously into the chloride and the chlorate, and thus a test for a chlorate would be obtained when only a hypochlorite was originally present.

The chlorate, bromate and iodate ions are reduced by sulfur dioxide to their respective halides. The solution must be boiled to drive off the sulfur dioxide, for otherwise the precipitate of silver sulfite first formed may be mistaken for silver chloride. The separation and identification of the halides is carried out as in Group IV.

Perchlorate Ion. The perchlorate ion is not reduced by sulfur dioxide and is in the solution from the silver halides obtained by the reduction and precipitation of the other oxyhalogen ions. On fusing the residue (left from the evaporation of the solution) with sodium and potassium carbonates, the perchlorate decomposes. A chloride and free oxygen form. After dissolving the melt in water, destroying the carbonate by acidifying the solution with nitric acid and boiling off the carbon dioxide, the chloride is precipitated by adding silver nitrate. A residue insoluble in dilute nitric acid, left after extracting the melt, may contain silver chloride. If the solution fails to give a test for a chloride, test the residue for silver chloride by treating it with ammonia and then acidifying the

resulting solution with nitric acid. If silver chloride is present, it is dissolved by the ammonia and is reprecipitated by the addition of an excess of nitric acid.

A small precipitate of silver chloride obtained in the test for the chlorate and perchlorate ion may be due to impurities in the reagents. A blank test for chlorides should, therefore, be made on the reagents used for both of these tests.

Nitrate and Nitrite Ions. Both nitrite and nitrate ions are reduced to nitric oxide by a mixture of ferrous sulfate and sulfuric acid. The nitric oxide combines with some of the excess ferrous sulfate to form the brown ion $Fe \cdot NO^{++}$. Only the nitrite ion is reduced by ferrous sulfate in the presence of acetic acid. Both ions are reduced to ammonia by warming with metallic aluminum and sodium hydroxide. Other ions containing nitrogen interfere with this test.

The removal of the nitrite ion before testing for the nitrate is accomplished by boiling the neutral solution with an excess of an ammonium salt. Free nitrogen and water are formed. Urea reacts with nitrous acid forming carbon dioxide and nitrogen and may be used to destroy the nitrite ion. The nitrate ion is not affected.

Metaborate and Tetraborate Ions. When a borate is heated with concentrated sulfuric acid and methyl alcohol the volatile methyl ester of boric acid, $B(OCH_3)_3$, is formed which burns with a green flame. Copper and barium salts, which give a green color to a flame, do not interfere with the test described in Procedure X, 5, since only the volatile components of the solution are carried into the flame. The turmeric test is sensitive. Strong oxidizing agents interfere with the test since they oxidize the turmeric.

EXERCISES

1. Should silver nitrate be added to a solution containing a hypochlorite which is to be tested for the other ions of Group V?
2. If the hypochlorite ion is present, what anions cannot be present?
3. Is the name lead peroxide applied correctly to PbO_2?
4. Why is silver nitrate added to the solution being analyzed for the iodate, bromate, chlorate and perchlorate before reducing these ions?
5. Explain how a nitrite interferes with the test for a nitrate. Give equations to show how it may be removed.
6. Why must ammonium salts be removed before testing for a nitrate or nitrite with aluminum and sodium hydroxide?
7. What ions interfere with the test for a borate?
8. How will a bromide interfere with the test for bromate?

9. Make a list of the anions which are oxidizing agents and list their reduction products.
10. Make a list of anions which are reducing agents and list their oxidation products.
11. If a sample is highly acid, what anions cannot be present in an appreciable concentration?
12. A solution contains a nitrite and is acid; what anions cannot be present?
13. A solution contains a chromate and is acid; what anions cannot be present?
14. A solution contains silver ions; what anions are probably absent?
15. A solution contains a sulfate ion; what cations are absent?
16. A solution contains the hypochlorite ion; what cations cannot be present?
17. A solution is slightly acid and contains the sulfide ion; what cations are absent?

CHAPTER XX

Complete Analysis

SYSTEMATIC ANALYSIS OF A SOLID OR LIQUID SAMPLE

THE SYSTEMATIC ANALYSIS of a solid or liquid sample involves the following steps:

1. Preliminary examination.
2. Preparation of solutions for the analysis of anions and cations.
3. Analysis of the solution prepared for cation analysis.
4. Elimination of anions from a knowledge of the behavior of the sample toward the reagents used in preparing the solution and the results of the tests for oxidizing and reducing anions and the solubilities of the silver salts.
5. Analysis of the solution prepared for anion analysis.
6. Tests of the reasonableness of the results of the analysis.
7. Determination of the probable substances used to prepare the material analyzed.

Much information can be obtained by carrying out the preliminary examination outlined on page 307ff. Frequently, if a sample has not been prepared in the laboratory, some of the constituents can be deduced if the source of the material is known. The use made of the material, too, often gives a clue as to its probable composition. These facts and deductions often aid the analyst to devise a method of preparing a solution of a solid sample. In general, samples to be analyzed are metallic or non-metallic. This classification is convenient for the discussion of the preparation of a sample for analysis.

Sampling. If the material to be analyzed is a solution or a homogeneous solid, it is relatively easy to obtain a sample portion whose composition is the same as that of the large aggregate. If the mass is not homogeneous, however, the process may be difficult and

time consuming; for no matter how carefully the analysis of a small sample of the material is carried out, the results are of little value unless the sample has the same composition as the source. The general procedure in obtaining a representative sample which may weigh as much as 11 or 12 kilograms is to select large and small pieces of the components of the mixture in the same proportion in which they occur in the "pile" and then, after reducing the size of the pieces, to discard three-quarters. Reduce the size of the pieces in the one-quarter kept and again retain a quarter. Continue this until a relatively few grams of a very finely divided sample are obtained. Use this material for the analysis.

Size of the Sample. The sample usually given beginning students should contain approximately 1 mg. of each cation and anion. Since about 50% of a solid is anion, and since in general there are about 5 anions and 5 cations in a sample, 15 mg. of material is sufficient to carry out the analysis. It is convenient to prepare 2 ml. of a solution containing 0.15 g. of the solid and to use 4 drops of this solution for the analysis. If the sample is a liquid, evaporate a known volume to dryness in a weighed crucible and determine the weight of the residue. For the analysis use a volume of the liquid that contains 15 mg. of solid.

PRELIMINARY EXAMINATION

A. Physical Properties
   - Hardness
   - Color
   - Density
   - Form
   - Homogeneity
     - Separation using a magnet, sieve, etc.

B. Chemical Properties
   1. Heat in closed tube
      - Unchanged
        - No organic matter
        - No hydrates
        - No readily fusible substances
        - No volatile matter
      - Changes color without melting
        - Copper and cobalt salts darken

Zinc and lead oxides are yellow when hot, white when cold

Bismuth oxide and salts, orange to reddish brown hot, pale yellow when cold

Cadmium hydroxide and salts are brown when hot or cold

Stannic oxide brown when hot and yellow when cold

Melts without giving off water

Oxygen is given off. Halogenates, peroxides or nitrates may be present

Water condenses

Test the water with litmus. Hydrates, ammonium salts, hydrogen salts, hydrogen carbonates and unstable hydroxides may be present

Gas is evolved

Odorless and supports combustion. Indicates oxygen from peroxides, per-salts, oxides of some metals, halogenates or nitrates of alkali metals

Odorless and inactive. May be carbon dioxide

Odorous, not colored. Sulfur dioxide, hydrogen sulfide, ammonia

Odorous colored. Nitrogen dioxide from a nitrate, nitrite or halogen

Sublimate is formed

Yellow. Sulfur, arsenious sulfide

Black, non-metallic. Indicates mercuric sulfide

Violet vapor. Iodine

Black to gray, metallic. Indicates mercury

White. Ammonium salts, mercurous or mercuric salts or arsenious oxide

Gray. Arsenic

2. Test the sample or its aqueous solution with litmus.

3. Heat on charcoal in flame of the blowpipe.

Decrepitation. Crystals without water of crystallization

Deflagrates. Nitrates, halogenates, or other oxidizing agents

Fuses, absorbed by the charcoal. Salts of alkalies and some salts of alkaline earths

Forms crust on the charcoal

Lead oxide, yellow while hot, pale yellow when cold

Bismuth oxide, orange yellow while hot, lemon yellow when cold
Zinc oxide, yellow while hot, white when cold
Cadmium oxide, red brown while hot
Arsenic oxides, white, faint blue colored flame
Antimony oxide, white, pale green flame
Tin oxide, pale yellow while hot, white when cold

4. Heat on charcoal after moistening with cobalt nitrate.
The residue is colored—
Zinc oxide, yellowish green
Stannous oxide, bluish green
Antimonic oxide, dirty dark green
Aluminum oxide, silicon dioxide, or phosphates, blue
Magnesium oxide, flesh color
Barium oxide, brick red

5. Warm with concentrated sulfuric acid—CARE!
Gas
Colorless
Does not fume. Carbon dioxide, sulfur dioxide, hydrogen sulfide, hydrocyanic acid
Fumes. Hydrogen chloride
Colored
Does not fume. Nitrogen dioxide
Fumes. Hydrobromic acid and bromine, hydriodic acid and iodine, chromyl chloride (CrO_2Cl_2)

6. Colors imparted to a Bunsen flame

Color	*Indicates Volatile Compounds of—*
Yellow	Sodium
Violet	Potassium—visible through a chrome alum filter
Crimson	Strontium or lithium
Brick red	Calcium
Yellowish green	Barium, molybdenum, boric acid
Emerald green	Copper

7. Bead tests

Color of Bead	*Borax*		*Microcosmic Salt*	
	Oxidizing flame	Reducing flame	Oxidizing flame	Reducing flame
Colorless	SiO_2 (no skeleton), Hg, Pb, Bi, Sb, Cd, Zn, Sn	SiO_2 (no skeleton), alkaline earths, Mn, Cu	SiO_2 (with skeleton), alkaline earths	SiO_2 (with skeleton), alkaline earths, Mn, Cu

Color of Bead	Borax		Microcosmic Salt	
	Oxidizing flame	Reducing flame	Oxidizing flame	Reducing flame
Gray		Ag, Pb, Bi, Sb, Cd, Zn, Ni		Ag, Pb, Bi, Sb, Cd, Zn, Ni
Yellow or Brown	Fe h,* Ag h, Ni (c brown)		Fe h-c, Ag h, Ni (c brown)	Fe h
Green	Cr c, Cu h	Fe h-c, Cr h	Cr c, Cu h	Cr c
Blue	Co h-c, Cu c	Co h-c	Co h-c, Cu c	Co h-c
Violet	Mn h-c, Ni (with cobalt)		Mn h-c	
Red	Fe h	Cu + trace of Sn	Fe h	Cu + trace of Sn

Sodium carbonate, chlorate bead—opaque green bead—Mn.

ANALYSIS OF A METALLIC SUBSTANCE

Action of Metals with Non-oxidizing Acids. The metals above hydrogen in the electromotive force series displace hydrogen from hydrochloric acid and dilute sulfuric acid. In general the reaction is slower the lower the position of the metal in the series. These acids react with the metals below hydrogen in the series in the presence of oxygen. Water is formed and hydrogen is not displaced.

$$2\ Cu + O_2 + 4\ H_3O^+ + 2\ Cl^- \rightleftarrows 2\ Cu^{++} + 2\ Cl^- + 6\ H_2O$$

The hydrides of antimony, arsenic, sulfur and phosphorus are formed if the free elements or their compounds are present when these acids react with a metal above hydrogen. These elements may thus escape detection if a non-oxidizing acid is used to effect the solution of the metallic unknown—unless the gases evolved are passed through a suitable solution to absorb the hydrides. Another objection to the use of these acids is that some of the metals form insoluble salts. Silver, mercurous and lead chlorides and the sulfates of barium, strontium, calcium and lead are insoluble. Silver chloride is appreciably soluble in a solution containing an excess of hydrochloric acid or the chlorides of the soluble metals, due to the formation of $AgCl_2^-$. The solubility of silver chloride increases with the concentration of the chloride ion and is quite pronounced when the concentration of the chloride ion is greater than two. Lead chloride is quite soluble in hot water; hence, if a hot solution is clear and white crystals form on cooling, the presence of lead may be suspected.

The sulfates of the alkaline earths are quite inert and are difficult to get into solution; hence, their formation is to be avoided. Lead

*h = hot, c = cold.

sulfate dissolves in a mixture of acetic acid and a soluble alkali or ammonium acetate.

Action of Metals with Oxidizing Acids. The common oxidizing acids used in preparing a solution of a metallic unknown are concentrated sulfuric acid and dilute or concentrated nitric acids. Hydrogen is not liberated when these acids react with metals. These acids react with all of the common metals except gold and platinum. The reactions are typical oxidation-reduction reactions. The reduction products are determined in part by the concentration of the acids and the reactivity of the metals. It may be necessary to heat the mixture of the metal and acid to the boiling point to increase the speed of the reaction. Usually sulfur dioxide is the chief reduction product of concentrated sulfuric acid. Hydrogen sulfide is the chief product if the metal is zinc. Nitrogen dioxide is the chief reduction product when concentrated nitric acid is used. Nitric oxide is the chief product if dilute nitric acid is the oxidizing agent but ammonium nitrate and possibly other nitrogen compounds may be formed simultaneously. The formation of the latter is favored, the lower the temperatures at which the reaction takes place and the more dilute the acid. The hydrides of arsenic, antimony, phosphorus and sulfur are oxidized by these oxidizing acids.

The insolubility of some of the sulfates and the disagreeable character of the sulfur trioxide fumes given off from the hot mixture makes the use of concentrated sulfuric acid objectionable. The use of nitric acid, either dilute or concentrated, results in the formation of metastannic acid or hydrated stannic oxide, as some prefer to call the compound. This compound is usually insoluble in acids but is soluble in the sodium hydrogen sulfide reagent used in separating divisions A and B of Group II. The oxides of antimony which form by the action of antimony and oxidizing acids are also insoluble but dissolve in the sodium hydrogen sulfide reagent forming the thioantimonate ion. Many metals, notably iron, nickel, chromium and aluminum, become passive in concentrated nitric acid and are not dissolved by this reagent even after long continued heating.

A mixture of nitric and hydrochloric acids is sometimes used to dissolve a sample of a metal. A mixture of these acids reacts with all of the common metals forming chlorides if an excess of hydrochloric acid is present. The insolubility of some metallic chlorides is an objection to the use of the mixture of these acids. In many cases, however, it is possible to obtain a solution of a sample containing antimony and tin by the continuous addition of small

amounts of concentrated nitric acid to the boiling mixture of the metal in concentrated hydrochloric acid. Any antimony or tin in the sample is converted to complex chlorides.

Preparation of a Solution of a Metallic Substance for Analysis. Place a small amount of the finely divided sample in each of seven test tubes and determine their behavior with each of the following reagents; dilute and concentrated hydrochloric, sulfuric, nitric and a mixture of nitric and hydrochloric acids. If the reaction is slow, heat the mixture. Note carefully the results of these experiments so that the larger portion of the sample can be treated with the most effective reagent. It is better to use a reagent which dissolves the sample completely than to devise a method of dissolving a precipitate which has formed.

If a white solid forms when hydrochloric acid is used to dissolve the sample, the presence of Group I is indicated. However, many chlorides are not soluble in concentrated hydrochloric acid, but dissolve when the solution is diluted. If a white precipitate forms when water is added to the concentrated hydrochloric acid solution, antimonyl or bismuthyl chloride may be present. A white solid which forms when concentrated nitric acid is used to dissolve the sample may be metastannic acid (hydrated stannic oxide) or the oxides of antimony. A white gelatinous precipitate formed when dissolving an iron alloy is frequently silicon dioxide. Much of the silicon may form orthosilicic acid and be present as a colloid. Break down the colloidal suspension by adding hydrochloric acid or nitric acid and evaporating the solution to dryness on a steam bath or by evaporating to dryness and heating for 20 minutes at 120°. Moisten the residue with concentrated hydrochloric acid, warm and add water.

When the best reagent to dissolve the metallic unknown has been determined, weigh accurately about 0.1 g. of the material on a balance and treat it with about 1.5 ml. of the reagent. Heat, if necessary, to complete the reaction. Analyze for Groups I–V a volume of the solution which corresponds to 7 mg. of the metallic sample.

Frequently a solution of the sample can be prepared by gently heating about 0.1 g. of the metal or alloy, preferably in the form of shavings or filings, with 2 ml. of approximately 8-*N* nitric acid. Determine the exact weight of the sample used on a balance. If the sample dissolves, test a portion of the solution which corresponds to 7 mg. of the sample for the ions of Groups I–V. If a white precipitate forms, shake the mixture thoroughly and place a vol-

ume corresponding to 7 mg. of the sample in another test tube. Add concentrated hydrochloric acid to the small portion and heat. If the solution becomes clear, analyze it for the ions of Groups I–V by Procedures I–V. If the precipitate remains, separate the precipitate in another portion of the thoroughly mixed solution corresponding to 7 mg. of the sample. Analyze the solution for Groups I–V by Procedures I–V. Treat the precipitate with the sodium hydrogen sulfide reagent as described in Proc. II, 2. Analyze the residue for the ions of division A and the solution for the ions of division B of Group II.

The formation of a large amount of sulfur by the reaction between hydrogen sulfide and ferric ions can be avoided by reducing the ferric ions to ferrous ions prior to precipitating the sulfides of Group II. An alternate method of removing ferric ions is to add an excess of concentrated hydrochloric acid and to extract ferric chloride by shaking the solution with ethyl or isopropyl ether.

ANALYSIS OF NON-METALLIC SAMPLES

Organic material, if present, must be removed since it may react with many of the ions forming non-ionizing compounds or it may cause the premature or tardy precipitation of some of the ions. Some organic matter may be removed by extraction with a suitable solvent, such as ether, carbon tetrachloride, etc., or by oxidation usually with hot concentrated nitric, or sulfuric acids or a mixture of these acids. The former is preferred unless efficient hoods are available, since sulfur trioxide fumes are very objectionable in the laboratory. Do not use sulfuric acid if ions are present which form insoluble sulfates. Concentrated nitric acid changes the ions of tin and antimony, especially in the absence of chlorides, to oxides which are not very soluble. Many silicates are not attacked by treatment with these acids. A great many anions will be destroyed or removed by this treatment. If concentrated acids are used to prepare the solution the mixture should be diluted before concluding that an insoluble substance has been formed. Sodium chloride, for example, is insoluble in concentrated hydrochloric acid but is soluble in the dilute acid.

Removal of Organic Matter. (A) BY EXTRACTION. Shake an appropriate amount of the solid or liquid sample with 0.5 ml. portions of the solvent which preliminary tests on small quantities have shown will dissolve the organic matter. Carbon tetrachloride, ether or carbon disulfide are used frequently for this purpose. Repeat

until all of the organic matter has been removed. Then proceed with the analysis in the usual way if the sample is a liquid or with the preparation of a solution if the sample is a solid.

(B) BY OXIDATION. Add 0.5 ml. of concentrated nitric or sulfuric acid to 0.1 g. of the solid sample or a volume of liquid in which 0.1 g. of solute is dissolved. Cautiously raise the temperature. Place the container in a hood and evaporate the solution just to dryness. Repeat the treatment with acid until the organic material has been removed. Since nitric acid reacts with many organic substances to form explosive compounds, determine the behavior of a small portion of the sample toward the acid before using large quantities. If sulfuric acid is used and carbon forms, add cautiously small amounts of concentrated nitric acid to the cold mixture and then heat to oxidize the carbon. Finally add a suitable volume of water and use the solution for the analysis. If the residue does not dissolve, treat the insoluble material by one of the methods given on page 316.

Preparation of a Solution of a Solid for Analysis. Determine the best solvent by treating small samples of the finely pulverized material with:

1. Water
2. Nitric acid, dilute and concentrated
3. Hydrochloric acid, dilute and concentrated
4. Mixtures of concentrated and dilute hydrochloric and nitric acids

in the order mentioned. If but little action is noted, heat the mixture. If preliminary tests show that the sample does not dissolve completely in any of the reagents, treat the large sample with those found to be most effective and allow the reagent to remain in contact with the sample as long as action takes place. Then decant the solvent and add another reagent to the residue. The partial solutions obtained in this way may be kept separate and treated as different unknowns or they may be mixed. Nitric acid is preferable to hydrochloric acid since all nitrates are soluble and many of them are less volatile than the corresponding chlorides.

If the sample is entirely soluble in water or acids, or if the sample is a solution, neutralize the solution or solutions containing a total of 0.15 g. of the solid with sodium hydroxide or ammonia if the solution is acid and acetic acid if it is basic. To a drop of the neutral or slightly alkaline solution add several drops of 3-*N* sodium carbonate and heat. If a precipitate does not form, only

compounds of the alkali metals, ammonium, copper and small concentrations of metals whose hydroxides are amphiprotic are present. Analyze a fresh portion of the neutral solution containing 7 mg. of solid material for cations and a second portion containing the same amount of solid matter for anions. If a precipitate forms on the addition of the sodium carbonate, add to the solution containing 0.15 g. of the solid matter, 2 ml. of 3-*N* sodium carbonate and digest the mixture for 20 minutes at the temperature of boiling water. Test the vapor above the mixture for ammonia formed by the action of the ammonium ion with the carbonate ion. Separate any precipitate. Neutralize the solution with acetic acid to remove the carbonate ion. Make the solution slightly alkaline with ammonia, dilute to 15 ml. and analyze 4 drops of the slightly alkaline solution for anions by Procedures VI to X. Dissolve the precipitate containing the cations in a minimum amount of the acid shown to be satisfactory by trials on small portions of the precipitate. Dilute the solution to 1.5 ml. and analyze 4 drops of the solution for the cations according to Procedures I to V.

If the sample cannot be dissolved completely by treating it with acids, the residue may be changed more or less to substances soluble in acids by digesting it in a solution of sodium carbonate, by treating it with hydrofluoric acid (the latter reagent is especially applicable if the material is a silicate), or by fusing it with potassium acid sulfate. Sometimes it is well to use special methods such as the reduction of silver halides with zinc and sulfuric acid, conversion of stannic oxide to the thiostannate by boiling with sodium hydrogen sulfide, reduction of barium sulfate with charcoal, etc., to assist in the preparation of a solution of a difficultly soluble substance.

A solution of a water insoluble unknown, such as is usually given to students, can be prepared by digesting 0.15 g. of the solid material with 2 ml. of 3-*N* sodium carbonate for 20 minutes at the temperature of boiling water. Test the vapor above the mixture for ammonia formed by the action of the ammonium ion with the carbonate ion. If necessary add water to maintain the volume of the mixture constant. Separate any precipitate. Neutralize the solution with acetic acid to remove the carbonate ion. Make the solution alkaline with ammonia and analyze 4 drops of the neutral solution for anions by Procedures VI to X. Dissolve the precipitate in a minimum amount of the acid shown to be satisfactory by trials on small portions of the precipitate. Dilute the solution to 2 ml. and use 4 drops of this solution to analyze for the cations by Procedures I to V. Only very insoluble sub-

stances, such as some phosphates, fluorides, sulfides, silicates and salts of silver, are not changed to hydroxides or carbonates by the digestion with sodium carbonate. Small amounts of the elements whose hydroxides are amphiprotic and copper found in the solution from the digestion with sodium carbonate will not interfere with the analysis for the anions, and a sufficient amount of these ions will be in the precipitate for their detection. Tests for sodium ions, carbonate ions and for anions which decompose at the higher temperature or which are oxidized or reduced during the digestion must be made on the water or acid extracts of the sample. Irrespective of the method used to obtain a solution of the sample for analysis, the acidity of the portions used for the analysis of cations and anions must be regulated carefully according to directions given previously. The solutions prepared for the analysis of anions should always be tested for the presence of oxidizing and reducing agents as described on page 240.

METHOD OF CHANGING VERY INSOLUBLE SUBSTANCES INTO MORE SOLUBLE ONES

1. Fusion with a Mixture of Sodium and Potassium Carbonates. By increasing the concentration of carbonate and the temperature it is possible to change some of the very insoluble silicates, etc. into sodium silicate and metallic carbonates within a reasonable time. Thoroughly mix the sample (0.1 to 0.2 g.) with six times its weight of a 50 per cent mixture of anhydrous sodium and potassium carbonates. Put the mixture in a nickel crucible. Place the crucible on a clay triangle and heat to a dull red color until no bubbles are given off from the fused mass. Then pick up the crucible with crucible tongs and rotate it so that the mass solidifies on the side of the crucible, leaving but a thin layer on the bottom. When the crucible is cool, fill it one-third full of water and warm it gently until the cake loosens. Then transfer the contents of the crucible to an evaporating dish. Cautiously add 1.5 to 2.0 ml. of concentrated hydrochloric acid and after breaking up the lumps evaporate, preferably on a water bath, and heat at 100° for an hour. Add 6 drops of concentrated hydrochloric acid to dissolve any basic salts and then 5.0 ml. of water. Warm until the salts are dissolved, separate the silica, and analyze suitable volumes of the solution for anions and cations. The solution prepared in this way is contaminated with nickel from the crucible.

If a small sample (15 to 20 mg.) is used, the fusion may be carried out in the loop on the end of a platinum wire. Use proportionate

amounts of regents to separate the silica and to prepare a solution for analysis.

2. Treatment with Hydrofluoric Acid. Most silicates are decomposed by treatment with hydrofluoric acid. Sulfuric acid is generally added to convert the residue to sulfates. Since glass is attacked by hydrofluoric acid, carry out the reaction in lead or magnesium vessels. Hydrogen fluoride is very poisonous and the dish must be kept under a hood.

3. Fusion with Potassium Hydrogen Sulfate. Many insoluble substances can be converted to soluble sulfates by fusing with potassium hydrogen sulfate. Carry out the action in porcelain or glass vessels. Mix from five to six times the weight of potassium hydrogen sulfate with the sample and increase the temperature gradually until the sample disintegrates. Then cool and add water to dissolve the cake.

4. Special Cases. Insoluble silver compounds may be reduced to silver and the anion put into solution by treatment with sulfuric acid and finely divided zinc. Stannic oxides may be converted to the thiostannate ion by digesting with the sodium hydrogen sulfide reagent or by fusing with a mixture of sodium carbonate and sulfur. Insoluble sulfates may be reduced to sulfides by heating with charcoal.

Rules of Solubility. It is impossible to give rules for the solubility of salts to which there are no exceptions; however, the following generalizations are useful:

The salts of the common strong acids are soluble except the sulfates of lead, strontium and barium. The sulfates of calcium, mercury and silver are sparingly soluble. Chlorides, bromides, iodides, and oxides of silver, mercurous mercury and lead are insoluble. The halides of lead are soluble in hot water.

The salts of common weak acids are insoluble except the acetates.

The hydroxides of sodium, potassium, barium, strontium and calcium are soluble.

The salts of sodium, potassium and ammonium are soluble.

The following compounds are almost insoluble in water but dissolve readily in dilute nitric or hydrochloric acids: basic salts of antimony, bismuth, tin, arsenates, arsenites, borates, carbonates, phosphates and peroxides. The following are almost insoluble in acids: silicon dioxide, stannic oxides, calcined chromium, aluminum, ferric and magnesium oxides, chromic chloride (calcined) and many ferro- and ferricyanides.

Colors of Inorganic Compounds. The following generalization will be of aid in remembering the colors of the common compounds met with in qualitative analysis.

The common compounds of the metals are white or faintly colored with the following exceptions:

Compounds of copper are blue to green, those of nickel are green; cobalt, red; manganese, pink; chromium, dark green; iron, yellow to red; and the bromide, iodide and carbonate of silver are yellow.

The sulfides which are insoluble in water or which do not react with water are colored except that of zinc which is white. The sulfides of silver, lead, copper, bismuth, mercury, tin (ous), nickel, cobalt, iron, are brown or black. Those of cadmium, arsenic, tin (ic) are yellow. Manganous sulfide is pink and the antimony sulfides are orange.

Compounds containing colored anions. Some colored anions are: chromate, yellow; dichromate, orange; cobalt chloride, blue; chromite, green; ferric thiocyanate, red; ferricyanide, brown; ferrocyanide, yellow; manganite, green; and permanganate, pink.

The iodides of lead, silver, tin (ous and ic) are yellow. Mercuric and antimonous iodide are yellow or red. Bismuth iodide is brown.

Appendix

I. REFERENCE BOOKS

Qualitative Analysis:

1. Analytical Chemistry Vol. I Qualitative Analysis—Treadwell and Hall
2. Qualitative Chemical Analysis—Prescott and Johnson, revised by MacAlpine and Soule
3. Qualitative Chemical Analysis—A. A. Noyes and Swift
4. Elements of Qualitative Analysis—Vol. I Theoretical; Vol. II Laboratory Directions—Stieglitz
5. A System of Qualitative Analysis for Rare Elements—Noyes and Bray
6. Qualitative Analysis—Böttger
7. Qualitative Analysis—Engelder
8. Introduction to Semimicro Qualitative Chemical Analysis—Curtman
9. Semimicro Qualitative Analysis—Cornog
10. Introduction to Theoretical Chemistry—Meldrum and Gucker
11. Microchemical Laboratory Manual—Emich and Schneider
12. Microtechnique of Inorganic Qualitative Analysis—Benedette-Pichler and Spikes
13. Theoretical Qualitative Analysis—Reedy
14. Qualitative Analysis and Chemical Equilibrium—Hogness and Johnson
15. Semimicro Qualitative Analysis—Engelder, Dunkelberger and Schiller
16. Introductory Qualitative Analysis—Vosburgh
17. Semimicro Qualitative Analysis—Middleton and Willard
18. A System of Chemical Analysis—Swift
19. Fundamentals of Semimicro Qualitative Analysis—Kelsey and Dietrich

General Inorganic Chemistry:

1. A Comprehensive Treatise on Inorganic and Theoretical Chemistry—(16 volumes) Mellor
2. Handbuch der Anorganischen Chemie—Gmelin
3. Handbuch der Anorganischen Chemie—Abegg
4. Textbook of Inorganic Chemistry—Friend
5. Anorganische Chemie—Ephraim (There is also an English Edition.)
6. Modern Aspects of Inorganic Chemistry—Emeleus and Anderson

Textbooks on Inorganic Chemistry:

1. General College Chemistry—Richardson and Scarlett
2. Textbook of Chemistry—Elder, Scott and Kanda
3. General Chemistry—Linus Pauling

4. An Introduction to General Chemistry—Foster and Alyea
5. General Chemistry—Deming
6. General Chemistry—Babor and Lehrman
7. Principles of Chemistry—Hildebrand
8. Reference Book of Inorganic Chemistry—Latimer and Hildebrand
9. General Inorganic Chemistry—Sneed and Maynard
10. Mellor's Modern Inorganic Chemistry—Parkes and Mellor
11. Essentials of General Chemistry—Hopkins and Bailar

Handbooks:

1. Handbook of Chemistry and Physics—Hodgman
2. Handbook of Chemistry—Lange
3. Solubilities of Inorganic and Organic Compounds, Vol. I–II—Seidell
4. A Dictionary of Chemical Solubilities—Comey, Hahn
5. International Critical Tables
6. Physikalisch Chemische Tabellen, Vol. I–II—Landolt, Bernstein

Dictionaries:

1. German-English Dictionary for Chemists—Patterson
2. French-English Dictionary for Chemists—Patterson

II. DEGREE OF IONIZATION IN 0.1-N SOLUTIONS (ACCORDING TO ARRHENIUS)

Acids

Permanganic	0.93†	Phosphoric	.27*
Hydriodic	.93	Hydrofluoric	.085
Hydrobromic	.93	Nitrous	.065
Perchloric	.88†	Acetic	.013
Hydrochloric	.92	Carbonic	.0017*
Nitric	.92	Hydrosulfuric	.0007*
Sulfuric	.61	Hypochlorous	.0002
Oxalic	.50*	Boric	.0001*
Sulfurous	.33*	Hydrocyanic	.0001

Bases

Potassium Hydroxide	0.91	Calcium Hydroxide	0.90
Sodium Hydroxide	.91	Barium Hydroxide	.77
Strontium Hydroxide	.93	Ammonia	.013

Salts

Type R^+Y^- (NaCl)	0.86
Type $R^{++}Y_2^-$ ($CaCl_2$)	.72
Type $R^{++}Y^=$ ($BaSO_4$)	.45
Type $R_2^+Y^=$ (Na_2SO_4)	.72

* Primary ionization.
† In $N/2$ solutions.

III. EQUILIBRIUM CONSTANTS (25°C.)

A very complete table of equilibrium constants is found in "Oxidation Potentials" by Latimer (Prentice-Hall Inc., New York City, 1938). The following are reproduced by the courtesy of the author and publishers. The compounds are arranged alphabetically according to the name of the main element.

Formula	$K_{instability}$	$K_{ionisation}$	S.P.
$Al(OH)_3$			1.9×10^{-33}
$Al(H_2O)_6^{+++}+H_2O \rightleftarrows H_3O^+ + [Al(OH)(H_2O)_5]^{++}$		1.4×10^{-5}	
$Al(OH)_3(H_2O)_3+H_2O \rightleftarrows H_3O^+ + [Al(OH)_4(H_2O)_2]^-$			4×10^{-13}
$HAsO_2$		6×10^{-10}	
H_3AsO_4		4.8×10^{-3} (primary)	
$BaCO_3$			4.9×10^{-9}
$BaC_2O_4\cdot 2\,H_2O$			1.1×10^{-7}
$BaSO_4$			9.9×10^{-11}
$BaCrO_4$			2×10^{-10}
BaF_2			1.7×10^{-6}
$Ba(BrO_3)_2\cdot H_2O$			5.5×10^{-6}
$Ba(IO_3)_2\cdot H_2O$			1.3×10^{-9}
$BiOCl$			7×10^{-9}
Bi_2S_3			1.6×10^{-72}
H_3BO_3		5.8×10^{-10} (primary)	
$4\,H_3BO_3+H_2O \rightleftarrows H_3O^+ + HB_4O_7^- + 5\,H_2O$		9.7×10^{-8}	
$Br_2+2\,H_2O \rightleftarrows HOBr+H_3O^+ + Br^-$		5.8×10^{-9}	
$HBrO$		2×10^{-9}	
$Cd(OH)_2$			1.2×10^{-14}
$Cd(NH_3)_4^{++}$	2.5×10^{-7}		
CdS			1.4×10^{-28}
$Cd(CN)_4^=$	1.4×10^{-17}		
$CdCO_3$			2.5×10^{-14}
$CaCO_3$			4.8×10^{-9}
$CaSO_4\cdot 2\,H_2O$			2.4×10^{-5}
$CaC_2O_4\cdot 2\,H_2O$			2.3×10^{-9}
$Ca(IO_3)_2\cdot 6\,H_2O$			1.9×10^{-6}
CaF_2			3.9×10^{-11}
H_2CO_3		4.3×10^{-7} (primary)	
HCO_3^-		4.7×10^{-11}	
$HC_2H_3O_2$		1.8×10^{-5}	
$H_2C_2O_4$		5.9×10^{-2} (primary)	
$HC_2O_4^-$		6.4×10^{-5}	
HCN		4×10^{-10}	
$HClO$		5.6×10^{-8}	
$Cr(OH)_3$ (base)			6.7×10^{-31}
$Cr(OH)_3(H_2O)_3+H_2O \rightleftarrows H_3O^+ + [Cr(OH)_4(H_2O)_2]^-$			9×10^{-17}
$Co(OH)_2$			2×10^{-16}
$Co(NH_3)_6^{++}$	1.25×10^{-5}		

Formula	$K_{instability}$	$K_{ionization}$	S.P.
CoS (alpha)			7×10^{-23}
CoS (beta)			1.9×10^{-27}
$CoCO_3$			1×10^{-12}
$NaK_2Co(NO_2)_6\cdot H_2O$			ca 2.2×10^{-11}
$Cu(CN)_2^-$	1×10^{-16}		
Cu_2S			2.5×10^{-50}
$Cu(OH)_2$			5.6×10^{-20}
CuS			4×10^{-38}
$Cu(NH_3)_4^{++}$	4.6×10^{-14}		
HF		7.2×10^{-4}	
$F^-+HF\rightleftarrows HF_2^-$			5.5
HOI		ca 1×10^{-11}	
$Fe(OH)_2$			1.7×10^{-15}
FeS			1×10^{-19}
$Fe(CN)_6^{4-}$	ca 10^{-37}		
$Fe(OH)_3$			4×10^{-38}
$Fe(H_2O)_6^{+++}+H_2O\rightleftarrows$ $[Fe(OH)(H_2O)_5]^{++}+H_3O^+$		6×10^{-3}	
$Fe(CNS)_3$			2.6×10^{-6}
$Fe(CNS)_6^{\equiv}$	3.1×10^{-4}		
Fe_2S_3			10^{-88}
$Fe(CN)_6^{\equiv}$	ca 10^{-44}		
$Pb(OH)_2$ (base)			2.8×10^{-16}
$Pb(OH)_2(H_2O)_2+H_2O\rightleftarrows$ $[Pb(OH)_3(H_2O)]^-+H_3O^+$			2.1×10^{-16}
$PbCl_2$			1.7×10^{-5}
PbI_2			8.7×10^{-9}
PbS			1×10^{-29}
$PbCrO_4$			1.8×10^{-14}
$Pb(IO_3)_2$			3.2×10^{-13}
$PbSO_4$			1.8×10^{-8}
$Pb_3(PO_4)_2$			3×10^{-44}
$Mg(OH)_2$			5.5×10^{-12}
$MgCO_3\cdot 3\ H_2O$			ca $1\ \times10^{-5}$
$Mg(NH_4)PO_4$			2.5×10^{-13}
MgF_2			6.4×10^{-9}
MgC_2O_4			8.6×10^{-5}
$Mn(OH)_2$			7.1×10^{-15}
$MnCO_3$			8.8×10^{-11}
MnS			5.6×10^{-16}
Hg_2Cl_2			1.1×10^{-18}
HgS			3×10^{-53}
$HgCl_4^=$	1.1×10^{-16}		
$Ni(OH)_2$			1.6×10^{-14}
$Ni(NH_3)_6^{++}$	2.1×10^{-8}		
$Ni(CN)_4^=$	ca 1×10^{-22}		
$NiCO_3$			1.4×10^{-7}
NiS (alpha)			3×10^{-20}
NiS (beta)			1×10^{-24}
NiS (gamma)			2×10^{-28}

Formula	$K_{instability}$	$K_{ionization}$	S.P.
HNO_2		4.5×10^{-4}	
$NH_3+H_2O\leftrightarrows NH_4^+ + OH^-$		1.8×10^{-5}	
H_2O			1×10^{-14}
$OH^- + H_2O \rightleftarrows O^= + H_3O^+$		10^{-36}	
H_2O_2		2.4×10^{-12} (primary)	
H_3PO_4		7.5×10^{-3} (primary)	
$H_2PO_4^-$		6.2×10^{-8}	
$HPO_4^=$		1×10^{-12}	
AgCl			1.7×10^{-10}
AgBr			3.3×10^{-13}
AgI			8.5×10^{-17}
AgCN			7×10^{-15}
AgCNS			1×10^{-12}
$Ag(CN)_2^-$	3.8×10^{-19}		
$Ag(NH_3)_2^+$	6×10^{-8}		
$Ag(S_2O_3)_2^=$	4.2×10^{-14}		
Ag_2S			1×10^{-51}
$AgBrO_3$			5.2×10^{-5}
$AgIO_3$			5.3×10^{-8}
Ag_2CO_3			8.2×10^{-12}
$Ag_2C_2O_4$			1.1×10^{-11}
Ag_2CrO_4			1.1×10^{-12}
$Ag_4Fe(CN)_6$			1.6×10^{-41}
Ag_2SO_4			1.2×10^{-5}
Ag_2MnO_4			3.1×10^{-11}
$AgC_2H_3O_2$			1.9×10^{-3}
$SrCrO_4$			3.6×10^{-5}
SrF_2			3×10^{-9}
$SrCO_3$			9.4×10^{-10}
$SrSO_4$			2.8×10^{-7}
$SrC_2O_4\cdot H_2O$			5.6×10^{-8}
H_2S		1.2×10^{-7} (primary)	
HS^-		1×10^{-15}	
H_2SO_3		1.2×10^{-2} (primary)	
HSO_3^-		1×10^{-7}	
HSO_4^-		1.2×10^{-2}	
$Sn(OH)_2$			5×10^{-26}
$Sn(OH)_2(H_2O)_2+H_2O\rightleftarrows$ $[Sn(OH)_3(H_2O)]^- + H_3O^+$			6×10^{-18}
SnS			8×10^{-29}
$Sn(OH)_4$			ca 1×10^{-56}
$Zn(H_2O)_6^{++} + H_2O\leftrightarrows$ $[Zn(OH)(H_2O)_5]^+ + H_3O^+$		2.45×10^{-10}	
$Zn(OH)_2$			4.5×10^{-17}
$Zn(OH)_2(H_2O)_4 + 2\ H_2O\leftrightarrows$ $[Zn(OH)_4(H_2O)_2]^= + 2\ H_3O^+$			1×10^{-29}
$ZnCO_3$			6×10^{-11}
ZnS			4.5×10^{-24}
$Zn(CN)_4^=$	2×10^{-17}		
$Zn(NH_3)_4^{++}$	9.8×10^{-10}		

IV. OXIDATION-REDUCTION POTENTIALS—ACID SOLUTIONS*

Half Cell	E_0
$Li \rightleftarrows Li^+ + \epsilon$	− 3.02
$K \leftrightarrows K^+ + \epsilon$	− 2.922
$Ba \leftrightarrows Ba^{++} + 2\epsilon$	− 2.90
$Sr \leftrightarrows Sr^{++} + 2\epsilon$	− 2.89
$Ca \leftrightarrows Ca^{++} + 2\epsilon$	− 2.87
$Na \leftrightarrows Na^+ + \epsilon$	− 2.712
$Mg \leftrightarrows Mg^{++} + 2\epsilon$	− 2.34
$H^- \leftrightarrows 1/2\ H_2 + \epsilon$	− 2.23
$Al \leftrightarrows Al^{+++} + 3\epsilon$	− 1.67
$Mn \leftrightarrows Mn^{++} + 2\epsilon$	− 1.05
$Zn \leftrightarrows Zn^{++} + 2\epsilon$	− 0.7620
$Cr \leftrightarrows Cr^{+++} + 3\epsilon$	− 0.71
$Fe \leftrightarrows Fe^{++} + 2\epsilon$	− 0.440
$Cr^{++} \leftrightarrows Cr^{+++} + \epsilon$	− 0.41
$Cd \leftrightarrows Cd^{++} + 2\epsilon$	− 0.4020
$Co \leftrightarrows Co^{++} + 2\epsilon$	− 0.277
$Ni \leftrightarrows Ni^{++} + 2\epsilon$	− 0 250
$3\ H_2O + H_3PO_3 \leftrightarrows H_3PO_4 + 2\ H_3O^+ + 2\epsilon$	− 0.20
$Sn \leftrightarrows Sn^{++} + 2\epsilon$	− 0.136
$Pb \leftrightarrows Pb^{++} + 2\epsilon$	− 0.126
$Fe \leftrightarrows Fe^{+++} + 3\epsilon$	− 0.036
$2\ H_2O + H_2 \leftrightarrows 2\ H_3O^+ + 2\epsilon$	0.000
$H_2S + 2\ H_2O \leftrightarrows S + 2\ H_3O^+ + 2\epsilon$	+ 0.141
$Sn^{++} \leftrightarrows Sn^{++++} + 2\epsilon$	+ 0.15
$Cu^+ \leftrightarrows Cu^{++} + \epsilon$	+ 0.167
$2\ S_2O_3^{--} \leftrightarrows S_4O_6^{--} + 2\epsilon$	+ 0.17
$4\ H_2O + H_2SO_3 \leftrightarrows HSO_4^- + 3\ H_3O^+ + 2\epsilon$	+ 0.20
$HCN + H_2O \leftrightarrows 1/2\ C_2N_2(g) + H_3O^+ + \epsilon$	+ 0.33
$Cu \leftrightarrows Cu^{++} + 2\epsilon$	+ 0.3448
$Fe(CN)_6^{4-} \leftrightarrows Fe(CN)_6^{3-} + \epsilon$	+ 0.36
$7\ H_2O + S \leftrightarrows H_2SO_3 + 4\ H_3O^+ + 4\epsilon$	+ 0.45
$S^= \rightleftarrows S + 2\epsilon$	+ 0.51
$Cu \leftrightarrows Cu^+ + \epsilon$	+ 0.522
$2\ I^- \leftrightarrows I_2 + 2\epsilon$	+ 0.5345
$4\ H_2O + HAsO_2 \leftrightarrows H_3AsO_4 + 2\ H_3O^+ + 2\epsilon$	+ 0.559
$CuCl \leftrightarrows Cu^{++} + Cl^- + \epsilon$	+ 0.566
$9\ H_2O + 2\ SbO^+ \leftrightarrows Sb_2O_5 + 6\ H_3O^+ + 4\epsilon$	+ 0.64
$2\ H_2O + H_2O_2 \leftrightarrows O_2 + 2\ H_3O^+ + 2\epsilon$	+ 0.682
$Fe^{++} \leftrightarrows Fe^{+++} + \epsilon$	+ 0.771
$2\ Hg \leftrightarrows Hg_2^{++} + 2\epsilon$	+ 0.7986
$Ag \leftrightarrows Ag^+ + \epsilon$	+ 0.7995
$6\ H_2O + N_2O_4 \leftrightarrows 2\ NO_3^- + 4\ H_3O^+ + 2\epsilon$	+ 0.81
$Hg \leftrightarrows Hg^{++} + 2\epsilon$	+ 0.854
$Hg_2^{++} \leftrightarrows 2\ Hg^{++} + 2\epsilon$	+ 0.910
$HNO_2 + 4\ H_2O \leftrightarrows NO_3^- + 3\ H_3O^+ + 2\epsilon$	+ 0.94
$6\ H_2O + NO \leftrightarrows NO_3^- + 4\ H_3O^+ + 3\epsilon$	+ 0.96

* Tables IV and V are taken with the permission of the author and publishers from a very complete table of Oxidation-Reduction Potentials found in "Oxidation Potentials" by Latimer (Prentice-Hall, Inc., New York City, 1938).

Half Cell	E_0
$NO + 2\ H_2O \leftrightarrows HNO_2 + 2\ H_3O^+ + \epsilon$	+ 0.99
$2\ H_2O + I^- \leftrightarrows HIO + H_3O^+ + 2\ \epsilon$	+ 0.99
$Cl^- + Cu \leftrightarrows CuCl + \epsilon$	+ 0.124
$2\ Br^- \leftrightarrows Br_2(liq.) + 2\ \epsilon$	+ 1.0652
$9\ H_2O + I^- \leftrightarrows IO_3^- + 6\ H_3O^+ + 6\ \epsilon$	+ 1.085
$2\ Br^- \leftrightarrows Br_2(aq) + 2\ \epsilon$	+ 1.087
$1/2\ I_2 + 9\ H_2O \leftrightarrows IO_3^- + 6\ H_3O^+ + 5\ \epsilon$	+ 1.195
$6\ H_2O + Mn^{++} \leftrightarrows MnO_2 + 4\ H_3O^+ + 2\ \epsilon$	+ 1.28
$2\ H_2O + Br^- \leftrightarrows HBrO + H_3O^+ + 2\ \epsilon$	+ 1.33
$1/2\ Cl_2 + 12\ H_2O \leftrightarrows 8\ H_3O^+ + ClO_4^- + 7\ \epsilon$	+ 1.34
$Cl^- \leftrightarrows 1/2\ Cl_2 + \epsilon$	+ 1.3583
$21\ H_2O + 2\ Cr^{+++} \leftrightarrows Cr_2O_7^{--} + 14\ H_3O^+ + 6\ \epsilon$	+ 1.36
$9\ H_2O + Br^- \leftrightarrows BrO_3^- + 6\ H_3O^+ + 6\ \epsilon$	+ 1.44
$1/2\ I^2 + 2\ H_2O \leftrightarrows HIO + H_3O^+ + \epsilon$	+ 1.45
$9\ H_2O + Cl^- \leftrightarrows ClO_3^- + 6\ H_3O^+ + 6\ \epsilon$	+ 1.45
$1/2\ Cl_2 + 9\ H_2O \leftrightarrows 6\ H_3O^+ + ClO_3^- + 5\ \epsilon$	+ 1.47
$2\ H_2O + Cl^- \leftrightarrows HClO + H_3O^+ + 2\ \epsilon$	+ 1.49
$1/2\ Br_2 + 9\ H_2O \leftrightarrows BrO_3^- + 6\ H_3O^+ + 5\ \epsilon$	+ 1.52
$12\ H_2O + Mn^{++} \leftrightarrows MnO_4^- + 8\ H_3O^+ + 5\ \epsilon$	+ 1.52
$1/2\ Br_2 + 2\ H_2O \leftrightarrows HBrO + H_3O^+ + \epsilon$	+ 1 59
$1/2\ Cl_2 + 2\ H_2O \leftrightarrows H_3O^+ + HClO + \epsilon$	+ 1.63
$6\ H_2O + MnO_2 \leftrightarrows MnO_4^- + 4\ H_3O^+ + 3\ \epsilon$	+ 1.67
$Pb^{++} \leftrightarrows Pb^{+4} + 2\ \epsilon$	+ 1.69
$4\ H_2O \leftrightarrows H_2O_2 + 2\ H_3O^+ + 2\ \epsilon$	+ 1.77
$2\ F^- \leftrightarrows F_2 + 2\ \epsilon$	+ 2.85
$2\ HF + 2\ H_2O \leftrightarrows F_2 + 2\ H_3O^+ + 2\ \epsilon$	+ 3.03

V. OXIDATION-REDUCTION POTENTIALS—BASIC SOLUTIONS

Half Cell	E_0
$4\ OH^- + Al \leftrightarrows H_2AlO_3^- + H_2O + 3\ \epsilon$	− 2.35
$3\ OH^- + Cr \leftrightarrows Cr(OH)_3 + 3\ \epsilon$	− 1.3
$4\ OH^- + Zn \leftrightarrows ZnO_2^{--} + 2\ H_2O + 2\ \epsilon$	− 1.216
$4\ OH^- + Cr \leftrightarrows CrO_2^- + 2\ H_2O + 3\ \epsilon$	− 1.2
$H_2O + 3\ OH^- + HSnO_2^- \leftrightarrows Sn(OH)_6^{--} + 2\ \epsilon$	− 0 96
$4\ CN^- + Cd \leftrightarrows Cd(CN)_4^{--} + 2\ \epsilon$	− 0.90
$4\ OH^- + N_2O_4 \leftrightarrows 2\ NO_3^- + 2\ H_2O + 2\ \epsilon$	− 0.85
$H_2 + 2\ OH^- \leftrightarrows 2\ H_2O + 2\ \epsilon$	− 0.828
$3\ OH^- + Sn \leftrightarrows HSnO_2^- + H_2O + 2\ \epsilon$	− 0.79
$4\ OH^- + AsO_2^- \leftrightarrows AsO_4^{---} + 2\ H_2O + 2\ \epsilon$	− 0.71
$OH^- + Fe(OH)_2 \leftrightarrows Fe(OH)_3 + \epsilon$	− 0.56
$3\ OH^- + Pb \leftrightarrows HPbO_2^- + H_2O + 2\ \epsilon$	− 0.54
$S^{--} \leftrightarrows S + 2\ \epsilon$	− 0.508
$5\ OH^- + Cr(OH)_3 \leftrightarrows CrO_4^{--} + 4\ H_2O + 3\ \epsilon$	− 0.12
$2\ OH^- + NO_2^- \leftrightarrows NO_3^- + H_2O + 2\ \epsilon$	+ 0.01
$2\ OH^- + I^- \leftrightarrows IO^- + H_2O + 2\ \epsilon$	+ 0.49
$MnO_4^{--} \leftrightarrows MnO_4^- + \epsilon$	+ 0.54
$4\ OH^- + MnO_2 \leftrightarrows MnO_4^- + 2\ H_2O + 3\ \epsilon$	+ 0 57
$2\ OH^- + Br^- \leftrightarrows BrO^- + H_2O + 2\ \epsilon$	+ 0.76
$2\ OH^- + Cl^- \leftrightarrows ClO^- + H_2O + 2\ \epsilon$	+ 0.94

VI. SOME MATHEMATICAL OPERATIONS USED IN QUALITATIVE ANALYSIS

Significant Figures. It is customary in recording data to use one more figure than is known to be correct. If this convention is followed, the recorded figures are said to be significant. Thus, if the weight of an object is given as 3500 g. the last figure is doubtful and there are four significant figures. If the weight is 3.0194 g. the last figure is doubtful and there are five significant figures. There are also five significant figures in the quantities 0.13193 g. and 0.15480 g. However there are only two significant figures if the weight of an object is 0.013 g., because zeros preceding numbers in a decimal fraction whose value is less than one are not significant figures.

In multiplication, division, addition or subtraction retain in the quantities involved and in the final result only as many significant figures as are present in the quantity which has the smallest number of significant figures. When figures are dropped, increase the preceding figure one unit if the figure dropped is five or greater.

The table of four-place logarithms on page 337 or a slide rule is adequate to make the calculations involved in the problems.

Exponents. An exponent is a number or letter placed to the right and somewhat above a quantity to denote the number of times the quantity is to be taken as a factor. Thus 2^3 means that 2 is to be used as a factor 3 times, i.e. $2 \times 2 \times 2$. This may be written in the general form $a^m = a \cdot a \cdot a$ (to m factors). Fractional exponents are used in the place of the radical sign. Instead of $\sqrt[3]{4}$ we may write $4^{\frac{1}{3}}$, or instead of $\sqrt[3]{4}$, $4^{\frac{1}{3}}$ and since 4 is 2^2 the latter expression becomes $2^{\frac{2}{3}}$. The last quantity may also be written $2^{0.67}$ since 2/3 is 0.67. These facts may be stated in the general form:

$$\sqrt[n]{a^m} = a^{\frac{m}{n}}$$

A fractional exponent, then, denotes that the quantity is to be raised to the power designated by the number in the numerator and that the root designated by the number in the denominator is to be extracted.

Negative exponents are used to denote the reciprocal of the positive root of the number. Thus 4^{-2} may be written $1/4^2$ or in general $a^{-p} = 1/a^p$.

It is customary to write very small or very large numbers as a product of a relatively small number and ten raised to an appropriate power. Thus 1,250,000 may be written 1.25×10^6 and 0.0000004 may be written 4×10^{-7}. If the exponent is a positive integer the number of digits in the quantity is one greater than the exponent of ten. The number of places in the decimal is the same as the negative integral exponent.

Multiplication of Exponential Quantities. Since $a^3 \times a^2$ means $a \times a \times a \times a \times a$, it follows that the product is a^{3+2} or a^5. This may be written in the general form: $a^m \times a^n = a^{m+n}$. Thus $3 \times 10^{-3} \times 4 \times 10^6 = 12 \times 10^{-3+6} = 12 \times 10^3$.

Division of Exponential Quantities. Since $a^3 \div a^2$ means $\frac{a \times a \times a}{a \times a}$ which equals a, we may write the general expression:

$$a^m \div a^n = a^{m-n}$$

Thus $3 \times 10^{-3} \div 4 \times 10^6 = 0.75 \times 10^{-3-6} = 0.75 \times 10^{-9} = 7.5 \times 10^{-10}$.

The Power of an Exponential Quantity. Since $(a^m)^n$ may be written $a^m \times a^n \ldots$ (to n factors), $(a^m)^n = a^{mn}$. Thus $(10^{-4})^2$ may be written $10^{-4} \times 10^{-4} = 10^{-4+(-4)} = 10^{-4\times 2} = 10^{-8}$.

Addition or Subtraction of Exponential Numbers. Since quantities must be expressed in the same units to permit their addition or subtraction, it is necessary for the power of 10 to be the same before these numbers can be added or subtracted. Thus 2×10^2 cannot be subtracted directly from or added to 6×10^3. The quantities must be changed to numbers involving the same power of 10. This is accomplished by multiplying one of the quantities by 1 thus $2 \times 10^2 = \frac{10}{10} \times 2 \times 10^2 = \frac{2}{10} \times 10^2 \times 10 = 0.2 \times 10^3$. The difference between 6×10^3 and 2×10^2 is that between 6×10^3 and $0.2 \times 10^3 = 5.8 \times 10^3$.

Logarithms. Common logarithms are the powers to which ten must be raised to equal a desired number. Thus, 10 must be raised to the 0.3010 power to be equal to 2. Tables have been constructed which give the power to which 10 must be raised to equal any number. These are known as logarithm tables, one of which is found on page 337. To multiply two numbers it is necessary to find and add their logarithms. To divide two numbers subtract their logarithms. To extract a root or raise to a higher power, divide the logarithm of the number by the root or multiply by the power. The numbers given in the table are the logarithms of quantities ranging from 0 to 100 inclusive. To determine the logarithm of a number greater than nine, factor the number into two terms one of which is a power of ten. For instance, 12 is 10×1.2, and the logarithm of 12 is the logarithm of 10 + the logarithm of 1.2 or 1 + 0.0792 which is 1.0792. Likewise 120 is $10^2 \times 1.2$ and the logarithm of 120 is therefore 2 + 0.0792 = 2.0792. The part of the logarithm preceding the decimal is the characteristic and that following, the mantissa. The logarithm of 0.012 is the same as that of 1.2/1000 and is − 3 + 0.792 or − 3.0792.

If the logarithm of a number is known, the number can be determined by the use of a logarithm table in the following way: Suppose the logarithm of x is 0.3010. Inspection of the table shows that 0.3010 corresponds to 2, hence x has the value of 2. Had the logarithm been 3.3010, it should be regarded as the sum of two logarithms 3 and 0.3010. The numbers to which these logarithms correspond must be multiplied. Ten raised to the third power is 1000 and ten raised to 0.3010 power is 2 according to the table of logarithms. Hence 3.3010 is the logarithm of 2×1000 or 2000. The logarithm − 2.3010 is composed of − 2 and 0.3010. Ten raised to the minus second power is 1/100 hence − 2.3010 is the logarithm of $2 \times 1/100$ or 0.02. In general it may be said that the characteristic of the logarithm of a number greater than 1 is one less than the number of digits preceding the decimal point and the characteristic of a number less than 1 is one more than the number of ciphers immediately following the decimal point and is negative.

Quadratic Equations. Quadratic equations may be solved by adding the same number to both sides of the equation to complete the square. Thus $x^2 + 2x = 0$ may be solved by adding 1 to both sides of the equation to give $x^2 + 2x + 1 = 1$. Extracting the square root, $x + 1 = \pm 1$ and $x = 0$ or -2. The proper root must then be chosen.

More complicated quadratic equations of the general type

$$ax^2 + bx + c = 0$$

may be solved for x by the use of the formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

The value of x in the equation $2x^2 + 3x - 14 = 0$ may be determined since a is 2, b, 3 and c is -14 and

$$x = \frac{-3 \pm \sqrt{3^2 - 4 \times 2 \times (-14)}}{2 \times 2} = \frac{-3 \pm \sqrt{121}}{4} = \frac{3 \pm 11}{4} = \frac{8}{4}$$

or

$$-\frac{14}{4} = 2 \text{ or } -3.5$$

if x is the concentration of an ion, the negative root can be discarded since the concentration of an ion cannot be less than 0.

Frequently a quadratic equation can be avoided without an appreciable sacrifice in the accuracy of the calculations by dropping an unknown when it is added to or subtracted from a number which is large in comparison. Thus in the equation,

$$(0.0002 + y)y = 1.7 \times 10^{-10}$$

if y is small, y in the term $(0.0002 + y)$ may be dropped without appreciably affecting its value. The equation becomes

$$0.0002\,y = 1.7 \times 10^{-10}$$
$$\text{and } y = 8.5 \times 10^{-7}$$

The value of y obtained by solving the quadratic equation is also 8.5×10^{-7}.

A second method of solving the equation is to drop the square of any terms which are small; for if a term is less than one its square is still smaller. If the equation just considered is simplified

$$0.0002\,y + y^2 = 1.7 \times 10^{-10}$$

and y^2 is dropped,

$$y = 8.5 \times 10^{-7}$$

Thus a careful estimate of the value of the terms may enable approximations to be made with little or no sacrifice of accuracy in the result.

VII. REAGENTS

To carry out the preliminary experiments and the analysis of cations and anions all of the solids and solutions listed are required. For the analysis of cations, only those checked in column R are needed; for the analysis of anions, those in R′. If the preliminary experiments for cations and anions are carried out, the solids and solutions checked in columns P and P′ are required in addition to those needed to carry out the analysis. The liquid reagents and test solutions should be placed in one-half or one ounce dropping bottles. The normalities of the solutions are calculated from reactions in which the ions do not change valence.

In addition to these reagents the student should have individual sets of the common acids and bases in dropping bottles.

Ammonia		5-*N*
Hydrochloric Acid, conc.		12-*N*
Hydrochloric Acid, dil.		5-*N*
Nitric Acid, conc.		14-*N*
Nitric Acid, dil.		5-*N*
Sulfuric Acid, conc.		36-*N*
Sulfuric Acid, dil.		5-*N*
Sodium Hydroxide	(8%)	2-*N*

Solids

	Cation		*Anion*	
	P	R	P′	R′
Aluminum wire 20 gauge (1/4″ pieces)		x		x
Ammonium sulfate				x
Asbestos shreds		x		
Barium sulfate			x	
Bleaching powder			x	
Borax		x	x	
Calcium fluoride			x	
Charcoal			x	
Copper foil			x	
Cupric nitrate			x	
Litmus paper (neutral)		x		x
Potassium hydrogen sulfate				x
Potassium chlorate	x		x	
Potassium carbonate—sodium carbonate 50% mixture				x
Potassium dichromate		x		
Potassium nitrite		x		
Potassium persulfate				x
Sodium carbonate (anhydrous)		x	x	
Sodium sulfate			x	
Tin (granulated)		x		
Turmeric paper			x	
Zinc (30 mesh arsenic free)	x			x

Solutions

		Grams of Solute per Liter of Solution	*Cation* P	R	*Anion* P′	R′
Acetic acid	6-*N*	360 ml.		x		x
Acetone				x		x
Aluminon (NH_4 salt of aurin tricarboxylic acid)	0.5%*	5.0		x		
Ammonia (conc.)	15-*N*	154.0				x
Ammonium acetate	2-*N*			x		
Ammonium carbonate (H_2O)	*N**			x		
Ammonium chloride	4-*N*	214.0		x		
Ammonium fluoride	*N*	37	x		x	
Ammonium iodide	*N*	145.0		x		
Ammonium molybdate (acid)	0.76-*N**			x		x
Ammonium oxalate saturated (H_2O)	±0.7-*N*	±50.0		x		
Ammonium monohydrogen phosphate	*N*	44.0		x		
Ammonium phosphomolybdate	5%	5.0	x			
Ammonium sulfate	*N*	66.1		x		
Ammonium sulfide (colorless)	±3-*N**			x		x
Ammonium polysulfide (yellow)	±3-*N**			x		x
Ammonium thiocyanate	*N*	76.0		x		
Barium acetate (H_2O)	2-*N*	273.4				x
Barium chloride (2 H_2O)	0.1-*N*	12.2				x
Barium hydroxide saturated	±0.2-*N*	±42.0				x
Barium nitrate	0.5-*N*	65.4				x
Boric acid	*N*	20.6			x	
Bromine water saturated		±50.0 ml.		x		x
Cadmium acetate (2 H_2O)	2-*N*	266.5				x
Calcium acetate (H_2O)	2-*N*	176.2				x
Calcium hydroxide saturated	(±0.04-*N*)	±10.0			x	
Calcium nitrate. *Use test solution*					x	
Calcium sulfate (2 H_2O) saturated	(±0.12-*N*)	±10.0	x			
Carbonic acid saturated					x	
Carbon tetrachloride						x
Chlorine water saturated					x	
Cobalt nitrate (6 H_2O)	*N*	145.6		x		
Cobalt nitrate (6 H_2O)	0.1% (±0.007-*N*)	1.0		x		
Dimethylglyoxime	*			x		
Ethyl alcohol (denatured)	95%			x		x
Ethyl ether					x	
Ferric chloride (6 H_2O)	*N*	90.1				x
Ferric nitrate (9 H_2O)	*N*	134.7				x
Ferrous ammonium sulfate (6 H_2O)	*N*	196.1†				x
Ferrous sulfate	*N**					x

* See list of special reagents, page 332.

† Add 7 ml. of sulfuric acid conc.

Solutions—Continued

		Grams of Solute per Liter of Solution	*Cation*		*Anion*	
			P	R	P′	R′
Hydrogen peroxide (Cl^- free)	3%*					x
Hydrogen peroxide	3%			x		x
Iodine water saturated		0.4				x
Lead acetate (3 H_2O)	*N*	189.7‡		x		x
Magnesium nitrate reagent	*N**			x	x	
Magnesium reagent	*			x		
Manganous chloride (4 H_2O) in hydrochloric acid conc. saturated						x
Manganous sulfate (4 H_2O)	*N*	112.0			x	
Mercuric chloride	0.1-*N*	13.6		x	x	
Mercuric cyanide	0.1-*N*	12.6	x			
Mercurous nitrate (H_2O)	0.2-*N*	56.1§	x		x	
Methyl alcohol (wood)						x
Methyl orange		1			x	
Methyl violet	0.1%	1		x		
Nickel nitrate (6 H_2O)	2-*N*	290.8				x
α-nitroso-β-naphthol	*			x		
Phenolphthalein 5 g. in 1 liter of 50% alcohol			x			
Phosphomolybdic acid	5%	50.0	x			
Potassium antimonate saturated	*		x			
Potassium antimonyl tartrate ($\frac{1}{2}$ H_2O)	0.2-*N*	22.3	x			
Potassium bromide	*N*	119.0	x			
Potassium chromate	3-*N*	291.3		x	x	
Potassium cyanide	*N*	65.1		x	x	
Potassium dichromate	0.1-*N*	14.7			x	
Potassium ferricyanide	0.5-*N*	54.9	x			x
Potassium ferrocyanide (3 H_2O)	0.5-*N*	52.8		x	x	
Potassium hydroxide	2-*N*	112.2	x			
Potassium iodide	0.1-*N*	16.6	x			
Potassium permanganate	0.1-*N*	15.8	x			x
Potassium sulfate	*N*	87.1		x		
Silver nitrate	0.2-*N*	34.0		x		x
Silver nitrate	*N*	169.9				x
Silver sulfate saturated	±0.05-*N*	±10				x
Sodium bromate	2-*M*	302.0		x		
Sodium carbonate	3-*N*	159.0				x
Sodium cobaltinitrite	0.3-*N**		x			
Sodium chloride	*N*	58.5				x

‡ Add 3.5 ml. of glacial acetic acid to prevent hydrolysis.

§ Add the salt to 150 ml. of 5-*N* nitric acid and dilute to 1 liter. Also add a few drops of mercury.

Solutions—Continued

		Grams of Solute per Liter of Solution	*Cation* P	R	*Anion* P′	R′
Sodium hydrogen sulfide reagent	3-*N**			x		
Sodium hypochlorite	5% (0.67-*M*)*				x	
Sodium metaphosphate (hexa)	*N*	102.0			x	
Sodium nitrite conc.	5-*N*	345.0		x		
Sodium nitroferricyanide	10%	100.0			x	
Sodium periodate	0.8-*M**			x		
Sodium dihydrogen phosphate (H_2O)	0.5-*N*	23.0			x	
Sodium hydrogen phosphate (12 H_2O)	0.5-*N*	59.7			x	
Stannous chloride (2 H_2O)	0.5-*N**			x		
Starch emulsion	*					x
Strontium acetate ($\frac{1}{2}$ H_2O)	2-*N*	214 .7				x
Sulfurous acid (freshly prepared)	saturated					x
Tartaric acid (H_2O)	*N*	84.0		x		
Turmeric extract	*					x
Uranyl zinc acetate reagent	*			x		
Urea-solution in 5-*N* hydrochloric acid	*					x

Special Reagents

Aluminon. Dissolve 5 g. of the ammonium salt of aurin tricarboxylic acid in a liter of water.

Ammonium carbonate. Dissolve 48 g. of freshly powdered ammonium carbonate in a liter of 1-*N* ammonia.

Ammonium molybdate (acid). Dissolve 150 g. of ammonium molybdate in 1000 ml. of water and add the solution to 1000 ml. of 6-*N* nitric acid in which 300 g. of ammonium nitrate are dissolved.

Ammonium sulfide (colorless). Saturate with hydrogen sulfide 700 ml. of a well-cooled solution containing 100 ml. of 15-*N* ammonia. The solution will increase in weight approximately 25 g. Then add 100 ml. of 15-*N* ammonia and water until the volume is 1000 ml.

Ammonium polysulfide. (Yellow ammonium sulfide.) Add 12 g. of flowers of sulfur to 1000 ml. of 3-*N* colorless ammonium sulfide. Shake well and after allowing the mixture to stand overnight, filter off the undissolved sulfur.

Dimethylglyoxime. Dissolve 12 g. of the reagent in 1000 ml. of 95% alcohol.

Ferrous sulfate. Dissolve 139 g. of the heptahydrate of ferrous sulfate in water containing 50 ml. of 5-*N* sulfuric acid and dilute to 1000 ml.

Hydrogen peroxide (chloride free). Add several crystals of silver nitrate and filter after allowing the mixture to stand over night.

Magnesium nitrate reagent. Dissolve 240 g. of ammonium nitrate and 130 g. of magnesium nitrate hexahydrate in water. Add 15 ml. of concentrated ammonia and dilute to 1000 ml.

Magnesium reagent. Dissolve 1.2 g. of p-nitrobenzene azoresorcinol in 240 ml. of 0.25-*N* sodium hydroxide.

α-Nitroso-β-naphthol. Add about 18 g. of α-nitroso-β-naphthol to 1000 ml. of 50% acetic acid. Let stand and carefully decant the solution from the undissolved solid.

Potassium antimonate. Carefully add 22 g. of the solid reagent to 1000 ml. of boiling water. Boil 2 minutes, cool and then add 35 ml. of 6-*N* potassium hydroxide. Let stand 12 hours and filter.

Sodium cobaltinitrite. To 230 g. of sodium nitrite dissolved in 50 ml. of water add 30 g. of cobalt nitrate hexahydrate and then 198 ml. of 5-*N* acetic acid. Dilute to 1000 ml. and let stand overnight and filter or decant.

Sodium hydrogen sulfide reagent. Saturate a liter of 3-*N* sodium hydroxide with hydrogen sulfide. The weight will increase about 102 g. To the solution add 3.5 g. of sodium hydroxide. Sodium sulfide instead of sodium hydroxide can be used to prepare the hydrogen sulfide. Pass hydrogen sulfide into a liter of 3-*N* sodium sulfide until the weight increases approximately 51 g. and add 3.5 g. of sodium hydroxide.

Sodium hypochlorite. Pass chlorine into 1000 ml. of a solution containing 72 g. of sodium hydroxide until the weight increases 47.7 g.

Sodium periodate. Dissolve 17.5 g. of sodium periodate ($NaIO_4$) in 100 ml. of 5-*N* sulfuric acid.

Stannous chloride. Dissolve 56.4 g. of stannous chloride (2 H_2O) in 85 ml. of concentrated hydrochloric acid (12-*N*). If the solution is turbid let it stand until clear (usually overnight) and then dilute to 1000 ml. Add a few pieces of metallic tin.

Starch. Add a paste made by mixing 5 g. of soluble starch and 5 ml. of water to 2000 ml. of boiling water. When cool add a few drops of toluene.

Turmeric extract. Digest 4 g. of powdered turmeric four times with 20 ml. of cold distilled water. Dry the residue at a temperature not exceeding 100°, digest with 100 ml. of 95% alcohol for several days and filter.

Uranyl zinc acetate reagent. Add 10 g. of uranyl acetate, 30 g. of zinc acetate (2 H_2O), 9 ml. of 6-*N* acetic acid to 55 ml. of water. Heat until dissolved and dilute to 100 ml. Allow to stand 24 hours and filter.

Urea solution. Dissolve 25 g. of urea in 100 ml. of 5-*N* hydrochloric acid.

VIII. PREPARATION OF SOLUTIONS

Preparation of Stock Solutions Containing 50 mg. of Cations per Milliliter. To prepare stock solutions of cations to use in making up test solutions, knowns or unknowns, pulverize the weight of salt given in the last column and add enough hot water (or acid when so stated in the footnote) to make the volume one liter when cool.

Preparation of Test Solutions Containing 5 mg. of Cation per Milliliter. To prepare test solutions mix 10 ml. of the stock solution (20 ml. of $AsCl_3$) with sufficient water, unless otherwise specified, to make 100 ml. of solution.

Preparation of Knowns and Unknowns Containing 5 mg. of Cation per Milliliter. Mix 10 ml. of the stock solutions (20 ml of $AsCl_3$) containing the cations wanted in the unknown or known and dilute the solution to 100 ml. Give each student about 1 ml. of the solution.

Stock Solutions of Cations

Ion	*Formula*	*Formula of Salt*	*Grams per Liter of Solution*
Aluminum	Al^{+++}	$Al(NO_3)_3 \cdot 9\ H_2O$	695
Ammonium	NH_4^+	NH_4NO_3	222
Antimony	Sb^{+++}	$SbCl_3$	95 (*a*)
Arsenic	$AsO_4^{\equiv}$	As_2O_5	78
		$Na_2HAsO_4 \cdot 7\ H_2O$	20.8
Arsenious	As^{+++}	As_2O_3	33 (*b*)
Barium	Ba^{++}	$BaCl_2 \cdot 2\ H_2O$	89
Bismuth	Bi^{+++}	$Bi(NO_3)_3 \cdot 5\ H_2O$	115 (*c*)
Cadmium	Cd^{++}	$Cd(NO_3)_2 \cdot 4\ H_2O$	138
Calcium	Ca^{++}	$Ca(NO_3)_2 \cdot 4\ H_2O$	295
Chromium	Cr^{+++}	$Cr(NO_3)_3$	230
Cobaltous	Co^{++}	$Co(NO_3)_2 \cdot 6\ H_2O$	247
Cupric	Cu^{++}	$Cu(NO_3)_2 \cdot 3\ H_2O$	190
Ferric	Fe^{+++}	$Fe(NO_3)_3 \cdot 9\ H_2O$	362
Ferrous	Fe^{++}	$Fe(NH_4)_2(SO_4)_2 \cdot 6\ H_2O$	352
Lead	Pb^{++}	$Pb(NO_3)_2$	80
Magnesium	Mg^{++}	$Mg(NO_3)_2 \cdot 6\ H_2O$	528
Manganous	Mn^{++}	$Mn(NO_3)_2 \cdot 6\ H_2O$	262
Mercuric	Hg^{++}	$HgCl_2$	68
Mercurous	Hg^+	$Hg_2(NO_3)_2 \cdot 2\ H_2O$	70 (*d*)
Nickel	Ni^{++}	$Ni(NO_3)_2 \cdot 6\ H_2O$	248
Potassium	K^+	KNO_3	130
Silver	Ag^+	$AgNO_3$	80
Sodium	Na^+	$NaNO_3$	185
Stannic	Sn^{+4}	$SnCl_4 \cdot 3\ H_2O$	133 (*e*)
Stannous	Sn^{++}	$SnCl_2 \cdot 2\ H_2O$	95 (*f*)
Strontium	Sr^{++}	$Sr(NO_3)_2$	120
Zinc	Zn^{++}	$Zn(NO_3)_2$	145

(*a*) Dissolve in 6-*N* HCl, and in making the test-solution, dilute with 2-*N* HCl.

(*b*) Digest with 500 ml. of 12-*N* HCl, then add 500 ml. of water, yielding the stock solution of $AsCl_3$, containing 25 mg. of As per ml.

(*c*) Dissolve in 3-*N* HNO_3.

(*d*) Dissolve in 0.6-*N* HNO_3.

(*e*) Dissolve in 6-*N* HCl.

(*f*) Dissolve in 500 ml. of concentrated HCl (12-*N*). Let stand until the solution is clear and dilute to 1000 ml. with water. Add a piece of metallic tin.

Preparation of Stock Solutions Containing 50 mg. of Anion per Milliliter. To prepare stock solutions of anions for preparing test solutions, knowns or unknowns, dissolve the weight of pulverized salt given in the last column in sufficient water to make a liter of solution.

Preparation of Test Solutions Containing 5 mg. of Anion per Milliliter. To prepare test solutions mix 10 ml. of the stock solution with sufficient water to make 100 ml. of solution.

Preparations of Knowns, and Unknowns Containing 5 mg. of Anion per Milliliter. Mix 10 ml. of the stock solutions containing the anions wanted and dilute the solution to 100 ml. Give each student about 1 ml. of the solution.

Stock Solutions of Anions

Ion	*Formula*	*Formula of Salt*	*Grams per Liter of Solution*
Arsenate	$AsO_4^{\equiv}$	$Na_2HAsO_4 \cdot 7\ H_2O$	112.0
Borate	BO_2^-	$Na_2B_4O_7 \cdot 10\ H_2O$	111.0
Bromate	BrO_3^-	$KBrO_3$	65.2
Bromide	Br^-	KBr	74.5
Carbonate	$CO_3^{=}$	Na_2CO_3 anhyd.	88.5
Chlorate	ClO_3^-	$NaClO_3$	63.7
Chloride	Cl^-	NaCl	82.3
Chromate	$CrO_4^{=}$	K_2CrO_4	86.6
Cyanide	CN^-	NaCN	94.3
Ferricyanide	$Fe(CN)_6^{\equiv}$	$K_3Fe(CN)_6$	77.6
Ferrocyanide	$Fe(CN)_6^{\equiv}$	$K_4Fe(CN)_6 \cdot 3\ H_2O$	99.6
Fluoride	F^-	NaF	110.0
Hypochlorite	OCl^-		103.0 (*a*)
Iodate	IO_3^-	KIO_3	61.2
Iodide	I^-	KI	64.9
Nitrate	NO_3^-	$NaNO_3$	68.5
Nitrite	NO_2^-	$NaNO_2$	75.0
Perchlorate	ClO_4^-	$NaClO_4$	61.7
Phosphate	$PO_4^{\equiv}$	$Na_3PO_4 \cdot 12\ H_2O$	200.0
Sulfate	$SO_4^{=}$	$Na_2SO_4 \cdot 10\ H_2O$	167.5
Sulfide	$S^{=}$	$Na_2S \cdot 9\ H_2O$	376.0
Sulfite	$SO_3^{=}$	$Na_2SO_3 \cdot 7\ H_2O$	157.6 (*b*)
Thiocyanate	CNS^-	KCNS	83.6
Thiosulfate	$S_2O_3^{=}$	$Na_2S_2O_3 \cdot 5\ H_2O$	111.0

(*a*) To prepare a test solution containing 5 mg. of hypochlorite ion per milliliter, dilute 14.5 ml. of a 5% solution of sodium hypochlorite to 100 ml.

(*b*) Stabilize by adding 0.5 ml. allyl alcohol to 100 ml.

IX. EQUIPMENT

The following equipment is needed to carry out the preliminary experiments and the procedures. Apparatus marked with an asterisk is not ordinarily furnished beginning students. It should be obtained from the stockroom.

Returnable:

1	250 ml. beaker
1	150 ml. beaker
1*	20 ml. beaker
1	250 ml. Florence flask
1	5 ml. graduate
1*	filter tube
10*	13 × 100 ml. test tubes or centrifuge tubes—3 or 5 ml.
2*	25 ml. Erlenmeyer flasks
1*	wire to remove glass wool from the filter tube (5″ of No. 18 chromel or nichrome)
1*	semimicro spatula (monel metal).† A 5 mm. glass rod can be used instead
1*	semimicro test tube rack
1*	metal rack for a water bath
1	wing top
1	Bunsen burner
1	ring stand and 4″ ring or
1	tripod
1	crucible
1	set reagent bottles
2*	ointment jars—1 oz. (containers for glass wool and cotton)
1	test tube holder
1	chrome alum filter. See Experiment 25*a*.

Non-returnable:

1 piece	glass tubing	1	towel
1	test tube brush	1	sponge
1	file	*	glass wool
1	pipestem triangle	*	absorbent cotton
2 ft.	burner tubing	1 piece	glass rod (5 mm.)
1	wire gauze	*	unknown blanks
1 ft.*	3/16″ gum rubber tubing	2 in.	platinum, nickel or chromel wire No. 27 B&S
12*	medicine droppers		
1*	ear syringe		

† Monel metal spatula No. 7027, Wilkens-Anderson Co., Chicago, Illinois, is satisfactory.

Common Logarithms

N	0	1	2	3	4	5	6	7	8	9
0	.	0000	3010	4771	6021	6990	7782	8451	9031	9542
1	0000	0414	0792	1139	1461	1761	2041	2304	2553	2788
2	3010	3222	3424	3617	3802	3979	4150	4314	4472	4624
3	4771	4914	5051	5185	5315	5441	5563	5682	5798	5911
4	6021	6128	6232	6335	6435	6532	6628	6721	6812	6902
5	6990	7076	7160	7243	7324	7404	7482	7559	7634	7709
6	7782	7853	7924	7993	8062	8129	8195	8261	8325	8388
7	8451	8513	8573	8633	8692	8751	8808	8865	8921	8976
8	9031	9085	9138	9191	9243	9294	9345	9395	9445	9494
9	9542	9590	9638	9685	9731	9777	9823	9868	9912	9956
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067
N	0	1	2	3	4	5	6	7	8	9

Common Logarithms

N	0	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996
100	0000	0004	0009	0013	0017	0022	0026	0030	0035	0039
N	0	1	2	3	4	5	6	7	8	9

Index of Subjects

Acetate(s) buffers, 109
  hydrolysis, 104, 106, 127
  ionization acetic acid, 46
  lead, solubility of, 163
Acetic acid activities and K_i, 121
    ionization, 46
      constant, 46, 121
      degree of, 46, 51
Acids, Brønsted concept, 33, 36, 53
  cation, 34, 103, 105
  characteristics, 23, 25, 34
  definition, 25, 33
  diprotic, 34
  ionization, 30, 36, 45
    constants, 46, 53, 121
  monoprotic, 34, 46
  ortho, meta, and pyro, 244, 245
  oxidizing, and sulfides, 98
  pH, 108
  polyprotic, 34, 47
  reaction with metals, 310, 311
  strength, 35, 36, 53
  strong, 34, 36, 48
  sulfides, 96
  weak, 36, 46
Actinides, 28
  chemical behavior, 28
  electron arrangements, 28
Actinium, 28
  electron arrangement, 28
Activity coefficients, 32, 118
    ionic strength, 119
    table of calculated values, 119
      of experimental values, 120
  concept, 116
    common ion effect, 122
    hydrolysis of salts, 127
    ions, 33, 56, 118
    oxidation, 123
  molecules, 120
Adsorption, 66
  of cobalt and nickel ions by hydroxides, 205
Aich-tu-ess, 461
Alkali earth metals (Group IV, cations), 218
  metals (Group V, cations), 229
Alkaline, 25
Alloys, analysis, 310, 312
  sampling, 306
  solution, 310, 312
Aluminate, cobalt, 208, 215
  formation, 198, 208
Aluminon. See *Aurin tricarboxylate.*
Aluminum, 197
  bases and colloidal, 112
  colloidal, 87
  hydroxide, acids and, 111
    amphiprotic nature, 34, 110, 197
  ion, analysis, 208
      discussion, 215
    cation acid, 34, 105
    hydrolysis, 34, 105
    properties, 197
    reactions, 202
  passivity, 197, 311
  phosphate, 198, 223
  sulfide, 197
Ammines, metallic, 82
Ammonia, base, 49, 96
  complex ions, 78, 83
  equilibrium with water, 49, 233
  ionization constant, 49
  K base, 49
  precipitating agent, 93
  reactions with arsenic sulfide, 188
  silver halides, solubility, 79
Ammonium amalgam, 230
  carbonate hydrolysis, 226
    precipitation of carbonates, 226
    reaction with metallic ions, 226
  chloride decomposition, 230
    effect on ammonia, 50
    hydrolysis, 105
  cobaltinitrite, 229
  cyanide, hydrolysis, 132

Ammonium hydroxide. See *Ammonia.*
ion, acid, 50
analysis, 232
discussion, 233
hydrolysis of, 130
ionization constant, 50
properties, 230
reactions, 231
molybdate decomposition to MoO_3, 181, 189
reagent for arsenate, 170, 180
for phosphates, 248
oxalate, 227
phosphomolybdate solubility in ammonia, 248
test for phosphates, 248
sulfide, precipitating agent, 96
solvent for Group II B, 99
Amphiprotic hydroxides, 110, 112
action with acids, 112
with bases, 112
ionization, 111
older views, 110
substances, anions, 104, 106, 110, 129
Amphoteric. See *Amphiprotic.*
Analysis, alloys and metals, 310
non-metals, 313
preliminary examination, 307
preparation of metal, 312
of solid, 313
of solution for anions, 238, 314, 315
for cations, 141, 314, 315
removal of organic matter, 313
systematic, 306
Analytical operations: bead tests, 154
centrifuge, use of, 147
decantation, 151
extraction, 153
filter tubes, 148
filtration, 148, 150
flame tests, 154, 309
handling precipitates, 153
heating solutions, 154
precipitation, 145
with H_2S, 145
separation of precipitates, 147
stoppers of bottles, 155
washing precipitates, 151
Anion, acids, 35, 104
analysis, 237
Anion, analysis, classification of ions, 15, 237, 238
general directions, 239
discussion, 237
Group I, 243
Group II, 257
Group III, 270
Group IV, 276
Group V, 292
group reagents, 15, 237
reagents, 329
sample, 240
sensitivity of, 238
test solutions, 335
tests for oxidizing and reducing, 240
unknowns, solutions for, 335
bases, 34, 103
definition, 24
interference, in Group III, 208, 215
Anode, 24
Antimonate ion, 171
Antimonic oxide, 171, 309, 311
solubility in acids, 311
in NaHS reagent, 311
Antimonous oxide, 171
sulfide, 171
Antimony chloride, 171
with chloride ion, 171
with water, 171
complex ions, 171
ions, 171
analysis, 181
discussion, 190
properties, 171
reactions, 175
metal, 171
oxides, solubility, 311
oxychloride, 164
solution in acids, 190, 311
sulfides, 171
precipitation, 171, 181
reaction with polysulfide ion, 185
solubility in acids, 171
in soluble sulfides, 185
Antimonyl chloride, 164, 171
tartrate, 190
Apparatus, list of, 336
semimicro, 139
Approximations, 52, 68, 328
Aprotic ions, 103, 127

Arrhenius, assumptions, 25
objections to, 32
Arrows, 34, 38, 46
Arsenate, action with ammonium molybdate, 170, 189, 255
with calcium acetate, 254
with hydrogen sulfide, 170
with iodide, 178, 246
with magnesium nitrate reagent, 180, 189, 246
analysis, anion, 253
cation, 180
discussion, 188, 255
Gutzeit test, 171, 175, 253
properties, 169, 245
reactions, 175, 249
Arsenic, 169
acid, 245
reaction with hydrogen sulfide, 170, 188, 246
with iodide ion, 246
with magnesium ions, 246
complex ions, 82
Gutzeit test, 171, 175, 253
ions, 170
Marsh test, 171
sulfide, action with sulfides and polysulfides, 170
precipitation, 170
reaction with ammonia, 188
solution of, 170
Arsenite ion, analysis, 180
discussion, 188
properties, 170
reactions, 175
thioarsenites, 169
Atomic number, 26
structure, 26
definition, 26
weights, back cover
Atoms, architecture, 26
composition, 26
isotopes, 26
Aurin tricarboxylate, reaction with metallic ions, 203
test for aluminum, 203, 208, 215

Babor, periodic table, front cover
Balancing equations
ionic, 37
non-ionic, 73
Balancing equations, oxidation-reduction, 37, 73
Barium, 218
acetate, precipitating agent, 238, 239, 261
carbonate precipitation, 218, 226
solution, 218
chromate precipitation, 227
solubility in acids, 62
hydroxide solubility, 218
test for carbon dioxide, 254
ion analysis, 223
discussion, 227
flame test, 219, 227
properties, 218
reactions, 220
sulfate change to carbonate, 315
precipitation of, 218
reduction with carbon, 260, 317
solubility, 218
Bases, Brønsted concept, 34, 53
characteristics, 23, 25, 34
definition, 25, 34, 35
ionization, 36, 46, 49
constant, 49, 53
polyprotic, 34
strength, 35, 36
strong, 36
weak, table, 54
Basic solutions, 25
Bath, hot water, 154
Battery cells, 77
Bead tests, borax, 154, 309
care of platinum wire, 155
microcosmic salt, 154, 309
sodium carbonate, 154, 310
Berlinic acid, 196
Bicarbonate ion. See *Hydrogen carbonate ion.*
Bismuth, 168
chloride, hydrolysis, 164, 312
complex ions of, 168
hydroxide, 186
precipitation, 186
reaction with stannite ion, 187
ion, 172
analysis, 179
discussion, 186
properties, 168
reactions, 172
oxychloride, 164, 312

Bismuth sulfide, precipitation and solution of, 168, 179
solubility in hydrogen sulfide, 185
Bismuthate ion as oxidizing agent, 195
Bismuthyl ion, 168
Blow pipe tests, charcoal, 308
with cobalt nitrate, 309
Bodenstein, 44
Boiling point, 22
electrolytes, 25
elevation, 22
formula and molecular weight from, 22
Bond. See *Valence.*
Borate ion, analysis, 301
discussion, 304
properties, 294
reactions, 296
turmeric test, 302
Borax beads, 154, 309
Boric acid, 293
Bromate ion analysis, 263, 299
discussion, 268, 303
of large amounts, 263
properties, 293
reactions, 295
Bromic acid, 293
Bromide ion analysis, 286
discussion, 290
in presence of thiocyanate, 289, 290
properties, 278
reactions, 281
Brønsted amphiprotism, 111
concept of acids and bases, 33
ionization constants and, 54
Brown ring test, 298
for nitrates, 290, 300
interfering ions, 300
Brownian movement, 87
Buffer solutions, 109
constant pH and, 109
constituents of, 110
Bulb, pressure, 148

Cadmium, 169
acetate, precipitating agent, 237, 273
complex ion, 169
cyanide, complex ion of, 80, 187
Cadmium ferricyanide solubility in ammonia, 270
ion, 169
analysis, 179
discussion, 187
properties, 169
reactions, 173
sulfide, 179
colloidal, precipitation of, 179
hydrolysis, 134
precipitation, 80, 94, 179
solution of, 275
Calcium, 219
acetate, precipitating agent, 250, 253
carbonate, common ion, effect on, 64
precipitation, 60, 226
solution, 60
hydroxide, precipitation by strong bases, 219
ions, analysis, 224
discussion, 227
flame test, 220, 227
properties, 219
reactions, 221
oxalate, 219
Calculation(s): common ion and degree of ionization, 50
solubility, 63, 65
degree of hydrolysis, 106, 127
equilibrium constant, 67ff.
and electrode potentials, 128
extraction of solutes, 267
hydrolysis and solubilities, 134
instability constants, 81
involving activities: common ion effect, 122
degree of hydrolysis, 127
equilibrium constants from electrode potentials, 123
hydronium ion in acetic acid solutions of salts, 122
hydroxide ion in ammonia solutions, 123
solutions of salts, 103
ionic strength, 119
ionization constant, 121
molarity from ionic strength, 120
solubility products, 121
ionization constant, 46, 121

Calculation(s): molar solubility, 63, 123
pH, 108
solubility product, 62, 121
volume of precipitating agent, 142
washing of precipitates, 152, 241
Carbon dioxide
detection, 246
in sulfur dioxide, 247
reaction with water, 243
Carbonate ion analysis, 250
discussion, 254
base, 35, 61, 224
properties, 243
reactions, 246
Carbonic acid, 243
Cathode, 24
Cation, acid, 34, 105, 111
analysis classification, 14
general directions, 139
Group I, 157
Group II, 168
Group III, 193
phosphate complication, 208, 215
Group IV, 218
Group V, 229
preparation of a solution for, 141, 312
reagents for, 329
removal, 242
of organic material, 313
test solutions, 141, 333
unknown solutions, 142, 333
base, 34
colors, 209, 279, 318
definition, 24
Cell, calculation of E.M.F., 78
oxidation-reduction, 77
Centrifuge, 147
Charges of ions, 26
Chemical equilibrium, 42
activities and, 118
characteristics, 42
constants, 46
effect of concentration, 43
ionic, 45
law of, 44
Chlorate ion, analysis, 299
discussion, 303
properties, 292
reactions, 295
Chloric acid, 292
Chloride ion analysis, 286, 288
discussion, 290
presence of thiocyanate, 286, 288
properties, 278
reactions, 281
reaction with Group I cations, 163
Chlorostannate ion, 80, 172
Chlorostannite ion, 80, 172
Chromate ion analysis, 261
discussion, 265
equilibrium with dichromate, 62
properties, 257
reactions, 260
reduction products, 257
solution in acids, 62
Chromic acid (dichromic acid), 62
hydroxide, amphiprotic nature, 198
complex ion formation, 204
precipitation of, 198
ion analysis, 208
discussion, 215
properties, 198
reactions, 203
Chromite ion, 198
oxidation to chromate, 198
Chromium, 198
passivity, 198
Cleaning apparatus, 139
Cobalt, 193
aluminate, 198
passivity, 193
precipitation of sulfides, 96, 212
solubility of sulfides, 99, 193, 212
sulfide modifications, 99, 212
precipitation of, 99, 204, 212
solution of, 95, 205
zincate, 200
Cobaltic complex ions, 84
Cobaltous ion analysis, 205, 206
discussion, 212
bead test, 199
properties, 193
reactions, 199
Vogel's test, 199, 212
Colloid(s), 86
Brownian movement, 87
charge, 88, 89
nickel sulfide, 86, 212
precipitation, 89
preparation, 87

Colloid(s), prevention of formation of, 89
properties, 87
protective, 89
size, 88
suspensions, preparation, 87
Colloidal state, 86
effect of electrolytes on, 89
prevention of, 89
washing of precipitates and, 89
Colors of cations, 209, 279
in flame, 309
inorganic substances. 318
Common ion effect, 50, 63
activities, 122
apparent exceptions, 65
buffer solution, 109
calculation, 50 ff., 63
repression of ionization, 50
solubility, 63
Complex ions, 78
anions 78
cadmium cyanide, 80
cations, 78
constitution, 78, 81
coordinate covalence, 31, 82
cupric tetrammine, 83
cuprocyanide, 80
cyanides, 80
formulas, 82
halides, 79
instability constant, 79
ionization, 79
of aquo compounds, 111
of hydrated ions, 111
metallic formulas, 79
nomenclature, 84
organic, 80
silver diammine, 79
chloride, 78
stability, sulfides, 100
use in analysis, 86
valence, 82
zinc, 213
Concentration(s), 19
molal, 21
molar 21
molecular, 21
normal, 20
per cent, 21
reagents, 328
speed of reactions, 143
Concentration(s), test solutions, 141
unknowns, 142
versus activities, 66
Constants: activity coefficients, 119, 120
electrode potentials, 324
equilibrium, 43, 321
hydrogen sulfide, 93
hydrolysis, 128
instability. 79, 81, 321
ionization, 46, 53, 321
reaction, 67 ff.
solubility product, 58, 321
tables of, 321, 324
water, 50, 59, 62
Coordinate compounds, 82
nomenclature, 84
valence, 29, 83
covalence, 31, 82
Coordination number, 81
theory, 81
Copper, 168
Coprecipitation, 66
Cotton, filtering medium, 149
Covalence, coordination, 31, 82
normal, 29
Covalent compounds, 30, 31
Cube roots, calculation, 326
Cubes, calculation, 326
Cupric ion, analysis, 179
discussion 187
complex, 82, 169
flame test, 304, 309
properties, 168
reactions, 173
tetrammine, 82, 83, 168
sulfide solubility in hydrogen sulfides, 185
Cuprous ion, 168
complex, 80, 169, 188
sulfide, 80
Cyanate ion. 276
Cyanide ion analysis, 283
discussion, 288
complexes, 80
properties, 276
reactions 279
Cyanogen, 188

Debye-Hückel theory, 32
Decantation, 151

Degree of ionization, 320
acid, bases, salts, 46, 47, 49, 50
by different methods, 117
common ion effect and, 50
complex ions, 111
dilution and, 47
modern ideas, 32
table of apparent, 320
weak electrolytes, 49
Depression of the freezing point, 22
Dichromate ion, 257. See also *Chromate ion*
Dichromic acid, 62
Dielectric constant, 117
Dimethylglyoxime nickel test, 205, 213
Dipoles, permanent and temporary, 83
Diprotic acids and bases, 34
Distribution law, 266
Divisions A and B, separation, 185
ammonium sulfides, 100
sodium hydrogen sulfide reagent, 100, 185
sulfide, 100, 185
Double arrows, 38

Effect, solute on solvent, 21
Electric current, 23
Electrode, hydrogen, 77
potential, 78, 124, 324
calculation of E. M. F. of cells, 78
of equilibrium constants, 123
tables of, 324
Electrolysis, 23
Electrolytes, characteristics, 23, 24
classes, 23, 25
ionization, 32
solid, 33
solution, 33
strong, 32, 36
weak, 32, 36
Electromotive force of cells, 78
Electron, arrangement in atoms, 26
differentiating, 27
electrolysis and, 24
energy levels, 27
mass, 26
sharing, 30
transfer, 29
valence, 26
Electronic structure, ammonia, 82
ammines, 82, 83
carbon tetrachloride, 29
hydrates, 86
lithium, 26
rare gases, 27
water, 82
Electro-valency, 29
Elements, atomic weights of, back cover
periodic arrangement, back cover
Equations, hydrolysis, 103
ionic, 37
test for, 37
neutralization, 45
oxidation-reduction, 73
prediction of products, 75
quadratic, 327
Equilibrium, 42
chemical, 42
concentration and, 43
constants, 43, 321
acetic acid, 46
ammonia, 49
derivation of, 43, 44
hydrogen iodide, 45
instability, 79, 81, 321
ionization, 46, 321
oxidation-reduction reactions, 76, 123
reactions, derivation, 43, 67
evaluation of constant, 67
extent of reaction, 67, 68, 76
solubility product, 321
table, 321
time to reach equilibrium and, 44
dilution and, 47
factors influencing, 42
ionic, 45
kinetic explanation, 42
law of mass action and, 43
oxidation-reduction, 76
time to reach, 44
Equipment in desk, 336
Equivalent weights, 20
compounds, 20
ions, 20
metals, 20
oxidizing and reducing agents, 20
radicals, 20

Exercises, anions, Group I, 255
Group II, 268
Group III, 275
Group IV, 290
Group V, 304
cations, Group I, 167
Group II, 191
Group III, 216
Group IV, 228
Group V, 235
theory, activity concept, 135
chemical equilibrium, 56
hydrolysis and amphiprotic substances, 113
law of mass action, 56, 69
oxidation-reduction, complex ions, and colloidal condition, 90
precipitation and solution of sulfides, 100
solution and ionization, 39
Exponents, 326
change of fractional to integers, 108
logarithms, 327
Extraction, 242
precipitates, 125, 153
solutions, 215, 239, 243, 266

Ferric acetate basic, 209, 216
ferricyanide, 196
test for oxidizing and reducing anions, 240
ion, analysis, 207, 208
discussion, 214
interference with Vogel's test, 212
properties, 195
reactions, 202
Ferricyanide ion, analysis, 273
discussion, 274
properties, 270
reactions, 272
Ferrocyanide ion, analysis, 273
discussion, 268, 275
of large amounts, 263
properties, 270
reactions, 271
test for ferric ion, 195
Ferrous ion, analysis, 207, 208
discussion, 214
properties, 195
reactions, 202

Filter tube, 148
media, 149
Filtration, 148, 150
cotton, 148
glass wool, 149
preparation of filter paper, 150
small quantities, 148
suction, 150
Flame tests, 154, 309
colors, 227, 234, 309
use of platinum wire, 155
Fluoride ion, analysis, 251
discussion, 255
properties, 244
reactions, 250
Fluosilicates, 244
Formula weights, 19
acids, bases and salts, 19
definition, 19
deviation from expected values, 22
freezing and boiling point data, 22
ions, 19
undissociated molecules, 19
Freezing point, lowering of, 21, 22, 32
Fusion, potassium hydrogen sulfate, 317
sodium carbonate, 316

General directions, anions, 237
cations, 139
reactions of cations in
Group I, 161
Group II, 177
Group III, 204
Group IV, 222
Group V, 231
Glass wool, 148
Grading unknowns, 8
Gram formula weight, 19
molecular weight, 19
Groups, classification, 14, 237
anions, Group I, 157
Group II, 257
Group III, 270
Group IV, 276
Group V, 293
cations, 14
Group I, 157
Group II, 168

Groups, cations, Group III, 204
Group IV, 218
Group V, 229
Guldberg, 43
Gutzeit test for arsenic, 171

HALIDES in complex ions, 80, 279
Handbooks, 320
Heating of sample on charcoal, 308
with cobalt nitrate, 309
in closed tube, 307
in test tube, 154
with sulfuric acid, 309
Hexacyanoferriate, 85
ferroate, 85
Hexathiocyanoferriate, 85
Hot water bath, 154
Hydrate, valence in, 82
Hydrated ions, 30, 31, 33
Hydriodic acid, 278
Hydrobromic acid, 278
Hydrochloric acid, 278
Hydrocyanic acid, 276
Hydrofluoric acid, 244, 317
Hydrogen, 26
carbonate ion, amphiprotic properties of, 104
hydrolysis of, 104, 129
strength as a base, 54
electrode, 77
ion, 31. See also *Hydronium ion.*
peroxide, oxidation products of, 75
reduction products of, 75
test for chromate, 198, 258
sulfide, complex ions, reactions with, 80
constant of, 93
effect of hydronium ions, 94, 95
generator, 146
ionization, 48
constants, primary, 48
secondary, 49
precipitating agent, 93, 145, 178, 181, 204, 211
pressure tube, 145
reaction with ammonia, 96
reducing agent, 75
sources, 146
Hydrolysis, activities, 127
amphiprotic ions, 104, 106
anion acids, 104, 106
Hydrolysis, calculation, 106
cation acids, 105
classification, 103, 127
constant, 106
degree of, 107
equations, 103 ff.
ions, 103
problems involving activities, 127
solubility of precipitates, 61, 134
Hydronium ion, 31, 82
acetic acid-acetate solutions, 51
buffer solutions, 109
concentration, 52, 108, 121
hydration, 31
methyl violet test, 177, 184
precipitation of Group I, 163, 165
of Group II, 94, 177, 181
of Group III, 96, 204, 211
of Group IV, 222, 224
relation to concentration of hydroxide ion, 50, 59
separation of Groups II and III, 93, 96
solution of sulfides, 97
Hydrosulfuric acid. See *Hydrogen sulfide.*
Hydroxide ion, ammonia solutions and, 49
concentration and hydronium ions, 59
reaction with amphiprotic anions and cations, 112
with cations, 112
Hydroxides, adsorption of cobalt and nickel ions, 205
amphiprotic, 111
mechanism of the precipitation of, 113
precipitation with ammonia, 35, 113
with strong bases, 112
solution of, 112, 212
strong and weak, 36, 49
Hydroxy-, 39
Hypobromous acid, 279
Hypochlorite ion, analysis, 298
discussion, 303
properties, 292
reactions, 295
Hypochlorous acid, 278, 292
Hypoiodous acid, 278

INERT gases, electron structure, 27
Inorganic substances, colors, 318
Insoluble residue treatment, 316
  substances, change to more soluble, 316
    preparation of a solution for analysis, anions, 242, 312 ff.
      cations, 242, 312 ff.
Instability constants, 79, 321
    concentration of ions from, 81
Interfering ions, ammonium test, 233
    bismuth test, 187
    borate test, 294, 302
    bromide test, 287, 290
    cadmium test, 179
    carbonate test, 246, 254
    cobalt test, 206
    halogenate test, 299, 303
    hypochlorite test, 298
    magnesium test, 223, 228
    nickel, 206
    nitrate test, 298, 304
    nitrite test, 298, 304
    phosphate complication, Group III, 208, 215
    potassium, 234
    sodium, 235
    zinc test, 206, 214
Iodate ion, analysis, 263, 299
      discussion, 265, 303
    properties, 258
    reactions, 258
Iodic acid, 258
Iodide, colors, 279
  complex ions of, 279
  ion, analysis, 286, 287
      discussion, 290
    presence of thiocyanate, 286, 287
    properties, 278
    reactions, 282
    reduction, of arsenate, 178, 246
Iodine, distribution between solvents, 267
  extraction, 267
Ion, activity, 32
  charge, 24
  complex, 78
  definition, 24
  electrolysis, 23
  formula weight, 19
  hydration of, 33
Ion, migration during electrolysis, 24
  molecular concentration, 21
  product constant. See *Solubility products.*
Ionic compounds, 29
    apparent ionization of, 32
    bonds or valences, 29
  equations, 37
    oxidation-reduction, 38, 74, 76
  equilibrium, 45
  strength, 119
    calculation, 119
    molarity from, 120
Ionization, 19, 25
  acids, bases, salts, 23, 36, 49, 50, 54
  bases, 23, 36, 49
  common ion, 50
  complete, 33, 35
  constants, 46, 49, 53, 55, 59, 121, 321
  degree of, 25, 320
  dilution, 47
  modern ideas of, 32, 35
  polybasic acids, 47, 54
  polyprotic acids, 47, 54
  primary, 47
  qualitative analysis and, 36
  salts, 23, 29, 50
  secondary, 47
  theories
    Arrhenius, 25, 32
    Debye-Hückel, 32, 35
    modern theory, 32, 35
    water in salt solutions, 116
Ionogen. See *Electrolytes.*
Iron, 195. See also *Ferrous ion* and *Ferric ion.*
  passivity, 199
Isotopes, 26

KINETIC theory, equilibrium, 42
Known solutions, comparative tests, 141
    preparation, 333, 335

LABORATORY, directions, 139, 238
  equipment, 336
  records, 142
  technique, 144 ff.

Lanthanides, 28
chemical behavior, 28
electron arrangement, 28
Laws, chemical equilibrium, 44
distribution, 266
Le Chatelier's, 51
mass action, 43, 48
molecular concentration, 43
partition, 266
Lead, 160
acetate, ionization, 50
chloride, solubility in hot water, 160, 166
chromate, solubility in hydroxides, 160
ion, 160
analysis, 163
discussion, 166
properties, 160
reactions, 163
sulfate, solubility in acetate-acetic acid, 160
in strong hydroxides, 163
Le Chatelier's Law, 51
Lewis, G. N., 117
Liquids, transfer, 150
Lithium, isotopes, 26
structure, 26
Logarithms, change fractional exponents to integers, 108
characteristic, 327
table, 337, 338
use, 326

MAGNESIUM, 220
ammonium arsenate, 189, 246
phosphate, 220
solubility in acetic acid, 223
non-precipitation in presence of ammonium ion, 220, 224
carbonate, 220, 226
hydroxide, molar solubility, 63
non-precipitation in presence of ammonium ion, 226
solubility in acids, 62
product, 62
ion analysis, 223
discussion, 227
properties, 220
reactions, 221
reagent, 228
Manganate ion, 195
Manganese, 194
dioxide hydrated, 195, 214
Manganous ion, analysis, 207
discussion, 214
bead test, 201
properties, 194
reactions, 201
Marsh test for arsenic, 171
Mass action, law of, 43
applications, 67
limitations, 48, 55
mathematical expression, 44, 46
other systems, 67
salt effect, 55, 118
saturated solutions, 58
number, 26
Mathematical operations, 326
Mechanism of hydrolysis, 103, 111
of oxidation-reduction, 76
of precipitation of hydroxides, 113
Mercuric ion, 159
analysis, 180
discussion, 189
properties, 159
reactions, 174
Mercurous ion, analysis, 163
discussion, 166
properties, 159
reactions, 162
Mercury, 158
Metaarsenate, 245
Metaborate, 293
Metallic ammine complexes, 78, 81
Metals, analysis, 310
ease of deposition, 24
non-oxidizing acids, 310
oxidizing acids, 311
passivity, 311
reaction with strong hydroxides, 194, 197
Metastannic acid, 172, 288, 312
Methyl orange, 51
violet, 96, 177, 184
Microcosmic salt beads, 309
Molal solutions, 21
molality, 21
Molar solubility, calculation of, 63
definition, 63
hydrolysis and, 134
salt effect, 116
solutions, 21

Molar solutions, problems, 39
Molarity, 21
Mole, 19
Molecular concentration, law of, 43
  weights, 22
Molybdic oxide, 181, 189

Neutralization, equation for, 45
Neutron, 26
Nickel, 193
  dimethylglyoxime, 213
  ion, analysis, 205
    discussion, 212
    bead test, 199
    properties, 195
    reactions, 199
  modifications of the sulfide, 99
  nitrate as precipitating agent, 283, 288
  passivity, 193
  solubility sulfides, 97
  sulfide, 89
    colloidal, 89, 205, 210
    modifications, 99
    precipitation of, 96, 204
      of colloidal, 89, 205
    solution of, 97, 205
Nitrate ion, analysis, 300
    discussion, 304
    properties, 294
    reactions, 298
Nitric acid, 294
    reduction, 294
Nitrite ion, analysis, 300
    discussion, 304
    properties, 294
    reactions, 297
Nitrous acid, 294
Nomenclature, complex compounds, 84
    ions, 84
  modern, 38
Non-electrolytes, boiling and freezing points, 21
  characteristics, 21
  molecular weights, 22
Normal solutions, 20
    problems, 39
Normality, 20
Notebook, 142
Nucleus of an atom, 26

Occlusion, 66
Organic matter, complex ions from 80
    interference in analysis, 37, 80
    removal, 313
    test for, 307
Ortho-, 38
Oxidation and reduction, 72
    balancing equations, 38, 73
    battery cells, 77
    calculation of equilibrium constants, 76
    electrolysis and, 24
    equilibrium constants for, 76
    general equation for, 75
    ionic equations, 74
    potentials, 78, 124, 324, 325
    prediction of products, 75
    table of potentials, 324, 325
  potentials, table of, 324
  state, 31, 72
    calculation, 72
Oxides, colors of, 308
Oxidizing agent, 72
    reduction products, 75
    relative strengths, 78
    test for, 240
Oxonium ion. See *Hydronium ion.*
Oxy-, 39

Partition law, 266
Passivity of metals, 311
    aluminum, 197
    chromium, 198
    cobalt, 193
    iron, 195
    nickel, 193
Per cent solutions, volume-volume, 21
    weight-volume, 21
    weight-weight, 21
Perchlorates, analysis, 300
    discussion, 303
  properties, 293
  reactions, 296
Perchloric acid, 293
Perchromic acid, 258
Periodic tables, back cover
    discussion of, 26
    electron arrangements, 26

Permanganate ion, reaction with bisulfite ion, 243
with bromide ion, 286
thiocyanate interference, 286, 290
with hydrogen sulfide, 271
with reducing agents, 75
with sulfurous acid, 243
Persulfate oxidation of halides, 287
Persulfide ion, action with cyanide ion, 276
with hydronium ion, 180, 185
with oxidizing agent, 100, 185, 271, 283,
pH, 108
Phenolphthalein, 243, 245
Phosphate complication, in Group III, 208, 215
ions, analysis, 253
discussion, 254
interference Group III, 215
properties, 244
reactions, 248
Phosphomolybdic acid, 190
test for antimony, 190
Phosphoric acids, 244
Phosphorus pentachloride dissociation, 42
Physical examination of an unknown, 307
Platinum wire, bead tests, 154, 309
care of, 155
flame tests, 155, 309
substitute for, 126
Polyprotic acids, 47
Polysulfide. See *Persulfide ion.*
Postprecipitation, 66
zinc sulfide, 66
Potassium, 229
ion, analysis, 232
discussion, 234
flame test, 230, 234
properties, 229
reactions, 230
Potentials, calculation of oxidation-reduction, 124
equilibrium constants, 123
oxidation-reduction, 77
single electrode, 78
standard electrode, 77
table of oxidation-reduction, 324, 325
Precipitates, colors, 318
handling, 148, 153
separation from mother liquor, 147
solution, 61
washing, 151, 241
Precipitating agent, calculation of volume, 142
rate of addition, 144
anions, 14, 237
Group I, 250, 253
Group II, 257, 263
Group III, 273, 274
Group IV, 283, 288
cations, 14
Group I, 163, 165
Group II, 177, 181
Group III, 204, 211
Group IV, 222, 224
Group V, 233
Precipitation of difficultly soluble substances, 59, 144
of carbonates, 60, 222, 224
of chlorides, 163, 165
of chromates, 61, 227
of hydroxides, 211
of sulfides, 93, 96, 145
rule for, 59
technique, 144
Preliminary examination of an unknown, 307
experiments, 141
Pressure tube, 145
Primary ionization constants of diprotic acids, 48
of hydrogen sulfide, 48
Problems. See *Calculations.*
Products, oxidation-reduction, 75
Proton, 26, 31
Prussian blue, 196, 275
Pyro-, 38
arsenate, 245
phosphate, 244

Quadratic equations, solving of, 52, 327
Qualitative analysis, definition, 13

Rare earth elements, 28
electron arrangements, 28

Reactions, conditions for completion of, 45
reversible, 38, 42
speed, 43
Reagents, 140, 328
bottles, 155
desk, 329
list, 329
solid, 329
solutions, 330
special, 332
Reducing agent, 92
oxidation products, 75
relative strength, 78
test, 240
Reduction, 72
potentials, 324, 325
products, 75
Reference books, 319
Report blanks, 143
Reversible reactions, 38, 42
Review questions. See *Exercises.*
Rules for balancing oxidation-reduction equations, 73
for colors of inorganic compounds, 318
for precipitation, 59
for predicting products of oxidation-reduction, 75
for solubility of salts, 317
for solution of difficultly soluble substances, 61

Salts, 25
characteristics, 21, 23
classification, 103
definition, 25
effect, 55, 117
ionization of water, 59, 116
silver chloride, 117
hydrolysis, 103
ionization, 50
weak, 50
Samples, anions, 240
knowns, 240
preliminary experiments, 240
size, 307
unknowns, 240
cations, knowns, 141
preliminary experiments, 141
unknowns, 142
Sampling, 306
Saturated solution, 59
Secondary ionization constants of diprotic acids, 48
of hydrogen sulfide, 48
Sensitivity of tests for anions, 238
Separating precipitates by centrifuge, 147
by filter tube, 148
by ordinary filtration, 150
Shells, electron, 27
Sidgwick, valence in complex ions, 82
Significant figures, 326
Silicic acid, microcosmic bead test, 309
removal, 312
Silver, 157
chromate, common ion, 65
molar solubility, 63
precipitation, 61
solubility, 157
diammine ion, 79, 157
bromide ion and, 79
instability constant, 79
iodide ion and, 80
valence, 79
halides, activities, 123
action with ammonia and sulfides, 284
common ion, 64
complex ions, 80, 278
reduction with zinc, 157, 317
solubility in ammonia, 79, 157
in chlorides, 79
in soluble cyanides, 157
ion, 157
analysis, 163
discussion, 166
properties, 157
reactions, 161
nitrate as precipitating agent, 284, 289
preliminary test, 241
phosphates, colors, 245
salts, colors, and solubility, 158, 241
thiosulfate, complex, 277
decomposition, 277
Single electrode potentials, 78, 324, 325
Sodium, 229
carbonate, fusion with, 316

Sodium hydrogen sulfide reagent, 100
ion, analysis, 223, 232
discussion, 235
flame test, 231, 234
properties, 229
reactions, 231
peroxide, 229
zinc uranyl acetate, 232, 235
Solid reagents, 329
solutions, 66
unknowns, 306, 310, 313
Solubility, 19
amphiprotic hydroxides in acids and bases, 111
barium chromate in acids, 62
calculation from solubility products, 63
carbonates in acids, 61
hydroxides in acids, 212
products, 56, 321
activities of ions, 122
calculation, 62, 63
common ion effect, 63
derivation, 58
hydrolysis and calculated solubilities, 134
of the anion and, 134
limitations, 58, 65
precipitation and, 59
solution and, 60
table, 321
rules, 318
salts, 318
silver halides in ammonia, 80
salts, 80
sulfides, 90, 97, 134
Solute and properties of the solvent, 21
Solution, 19
alkaline, 25
buffer, 105
known, 141
mechanism, 33
of precipitates by formation of complex anions, 61
cations, 61
hydroxides, 61
weak acids, 61
bases, 61
by oxidation and reduction of anions or cations, 61
of solid electrolyte, 33
Solution of soluble electrolytes, 33
of some difficultly soluble substances, 61, 316
barium chromate, 62
calcium carbonate, 60
hydroxides, 60
sulfides, 97, 99
of sulfides in acids, 97
in soluble sulfides, 99
preparation of anion analysis, 242
of cation analysis, metals, 312
non-metals, 315
removal of organic matter, 313
solid, 314, 315
reagents, 330
saturated, 59
supersaturated, 59
test, 141
unknown, 141
unsaturated, 59
Solvents, choice of metallic, 312
of non-metallic, 313
Solvolysis, 103
Special reagents, 332
Speed of a reaction, effect of concentration, 43
of temperature, 43
Stability of complex ions, 79
Standard electrodes, 77
potentials, tables of, 324, 325
use in calculating equilibrium constants, 123
Stannic acid, 172
ion analysis, 181
discussion, 191
oxide, solution of, 317
properties, 172
reactions, 176
sulfide, 172
Stannite ion, reaction with bismuth hydroxide, 187
Stannous ion, analysis, 181
discussion, 191
properties, 172
reactions, 176
sulfide, 172
State, colloidal, 86
Stirring rods, 139
Stock solutions, anion knowns and unknowns, 334

Stock solutions, cation knowns and unknowns, 333
Stoppers of bottle, 155
Strength of acids and bases, 54
Strontium, 219
  acetate as precipitating agent, 263
  ion, analysis, 223
    discussion, 227
    flame test, 219, 229
    properties, 219
    reactions, 221
Structure of atoms, 26, front cover
Sublimates colors, 308
Succinic acid and the law of distribution, 266
Sulfate ion, analysis, 261
    discussion, 265
    properties, 257
    reactions, 259
Sulfide, complex ions, 99
  ion, analysis, 271
    discussion, 275
    change with hydronium, 93
    concentration of base, 96
    properties, 271
    reactions, 272
  precipitation, 93
    Group II, 94, 177, 181
    Group III, 96, 98, 204, 211
  solution in non-oxidizing acids, 97, 212
    in oxidizing acids, 98
    in soluble sulfides, 99
Sulfite ion, analysis, 251, 261
    discussion, 254, 264
    properties, 243
    reactions, 247
Sulfur dioxide, detection, 247
    in mixture of carbon dioxide, 251
    reaction with water, 243
Sulfuric acid, 257
    preliminary test, heat with, 309
Sulfurous acid, equilibrium with water, 243
    reducing agent, 75, 243
Supersaturated solution, 59
    zinc sulfide, 66
Suspensions, 87
Sutherland, 32
Systematic analysis, 306

TABLES:
  activity coefficients, calculated, 119
    experimental, 120
  anions, 239
    classification, 14
      Group I, 252
      Group II, 262
      Group III, 274
      Group IV, 285
      Group V, 299
    division into groups, 237
  atomic weights, back cover
  cations, classification, 14
      Group I, 164
      Group II, 182, 183
      Group III, 210
      Group IV, 225
      Group V, 233
  charges on colloids, 88
  colors, solubility of silver salts, 158
  complex ions, substances with, 95
  degree of ionization (Arrhenius) by different methods, 117
  electron distribution in rare gases, 27
  hydronium ion in weak acid salt mixtures, 109
  ionic strength and activity coefficients, 119
  ions of water, change in concentration, 116
  logarithms, 337, 338
  mass law and equilibria in solutions, 46
  oxidation-reduction potentials, 324, 325
  oxidizing and reducing agents, 75
  periodic tables, back cover
  silver chloride solubility in potassium nitrate, 117
  single electrode potentials, 324, 325
  solubility of silver salts, 158
  standard oxidation and reduction potentials, 324, 325
  substances with complex ions, 85
  test solutions, 333, 334
  weak acids according to strength, 54
Tartaric acid, reaction with antimonous oxide, 190
Technique, bead tests, 154
  centrifuge, 147

Technique, extraction, 153, 242, 266
filtration, 148, 150
flame tests, 154
heating test tubes, 154
hydrogen sulfide, use of, 145
insoluble substances solution of, 153, 314, 316
precipitates, handling of, 148, 149
precipitation, 144
solution preparation of, 314, 316
stoppers, handling of, 155
washing precipitates, 151
Test solutions, 141
anions, 334
cations, 333
tubes, heating, 154
Tests, bead, 154, 309
comparison, 141
dry, 307
flame, 154, 234, 309
preliminary, 307
Tetraborate ion. See *Borate ion.*
Theories, activity concept, 116
Arrhenius, 25, 32
Bohr, 26
Brønsted, 33
modern, of ionization, 32, 35
oxidation and reduction, reactions, 77
Thiocyanate ion, analysis, 284
discussion, 289
complications in halide test, 286, 287, 290
properties, 277
reactions, 281
Thiocyanic acid, 277
Thiosulfate ion, analysis, 284
discussion, 261, 289
of large concentrations, 263
decomposition of silver salt, 277
properties, 276
reactions, 280
special test for in presence of sulfites and sulfates, 284
Thiosulfuric acid, 276
decomposition, 276
Tin, 171
ion. See *Stannous ion* and *Stannic ion.*
sulfides, solubility in soluble sulfides, 99, 185
Transfer of liquids, 151
Transfer of precipitates, 153
Transition elements, 27
Trimetaphosphate, 38
Turmeric test for a borate, 294, 302
Turnbull's blue, 196

Units of concentration, molar, 21
molarity, 21
molecular, 21
normal, 20
normality, 20
Unknowns, grading of, 8
notebook records, 142
report blanks, 143
solutions, 142
for preparing anions, 334
cations, 333
systematic analysis of, 306
volume for analysis, 142, 240
Unsaturated solutions, 59
Uranyl zinc acetate, 231, 235

Valence, 29, 72
apparent, 31, 72
auxiliary, 82
complex ions, 82
covalence, 29
coordinate, 31, 82
electrovalence, 28
ion dipole, 83
number. See *Oxidation state.*
polar, 29
principal, 82
types, 28
variable, 29
Werner's theory of, 81
Vogel's test, 199, 212
Volume precipitating agent, 142

Waage, 43
Wash bottle, 140
Washing of precipitates, 151
method, 151, 241
temperature of wash liquid, 151
theory, 152
Water, amphiprotic nature, 34
acid, 34, 104
base, 34, 104
ionizing medium, 53

Water bath, 154
constant of, 50, 59
ionization constant of, 59
salt effect, 116
Werner compounds, 84
amphiprotic substances, 111
complex ions, 78
hydrates, 86
nomenclature, 84
valence types, 82

Zinc, 194
hydroxide, amphiprotic nature, 194, 200
Zinc hydroxide, reaction with acids, 200
with ammonia, 194
with bases, 194, 200
ions, analysis, 206
discussion, 213
properties, 194
reactions, 200
sulfide, precipitation, 93, 204, 206
supersaturation, 66
uranyl acetate, sodium salt, 231, 235
Zincate, cobalt, 200

W. D. LEAVITT

International Atomic Weights 1947

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	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.54	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.066
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

Other elements have been identified whose atomic weights have not yet been fixed: technetium, Tc. (43); promethium, Pm. (61); astatine, At. (85); francium, Fr. (87); neptunium, Np. (93); plutonium, Pu. (94); americium, Am. (95); and curium, Cm. (96).

Periodic Table of the Elements

