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Quantitative Analysis

Willis Conway Pierce

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Third Edition

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THIRD EDITION

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Preface

TO THE THIRD EDITION

In the period since publication of the second edition the authors have made many changes in the presentation of material to classes and in the analytical procedures. The purpose of this revision is to incorporate in the text the features which we have found helpful to students. Essentially the book is the same in general arrangement and in the relation of theory to laboratory work. It is, however, almost completely rewritten.

Changes include the following: The questions and problems are mostly rewritten and almost doubled in number so that the teacher may have more selection in his assignments. Answer sheets are available from the publisher, on order of the instructor. In weighing, emphasis is placed on use of chain balances and single-swing rest points. The authors find that much time is saved by these changes. We recommend that, before the student is permitted to use these methods, he be required first to master the use of the rider balance, with multiple-swing rest points. Electrochemical conventions have been changed to conform to those used in most texts of Physical Chemistry. The chapter on theoretical aspects of precipitation has been expanded into three chapters, but they are so arranged that the more difficult topics may be omitted from the first course if desired. The material on complex equilibria, formerly in Appendix III, has been expanded and made into a chapter of the text. The chapter on colorimetry has been omitted, since this subject is usually treated in advanced courses on instrumental analysis. The chapter on electrometric titrations is retained because it is closely related to the theoretical discussion of oxidation–reduction equilibria.

Numerous laboratory exercises have been added, and some have been deleted. Emphasis is placed on commercially available analyzed samples although some synthetic solutions, such as those of iron and copper, have been retained as exercises. As in the previous edition, use of carbonate-free base is strongly recommended. We have found student results much better with this than with base which contains carbonate. The carbonate determination has been modified by substitution of methyl red–bromcresol green mixed indicator for modified methyl orange. Arsenious oxide is recommended as primary standard for permanganate; our expe-

rience has been that student results are considerably better with this standard than with sodium oxalate.

Emphasis is placed on use of labor-saving devices, such as the Selas filtering crucible and muffle furnaces for ignition.

We wish to thank the teachers and students who have made many helpful suggestions and have pointed out mistakes and ambiguous statements. It is hoped that errors in the present edition will be called to our attention.

Grateful acknowledgment is made to Professor Willard R. Line of the University of Rochester, for his review of the manuscript and his many helpful comments; to Professor George Schaeffer of the University of Chicago, for many specific suggestions; to Dr. G. A. Perley for helpful comments on the glass electrode section; to Dr. G. E. F. Lundell and Dr. J. I. Hoffman for permission to use the table of acid-base indicators from *Outlines of Methods of Chemical Analysis;* and to Professor G. Frederick Smith and the editor of *Industrial and Engineering Chemistry* for permission to reproduce the titration curves of Figure 34.

Willis Conway Pierce
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Claremont, Calif.
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March 1948

Preface

TO THE FIRST EDITION

Numerous objectives are sought in teaching quantitative analysis. Aside from becoming familiar with the more common analytical procedures and their applications, the student should also develop a certain degree of technical skill. Moreover, he should understand the theoretical principles on which the analytical methods are based and should be able to perform with facility the stoichiometric calculations involved in an analysis. Finally, the well-trained analyst should have a knowledge of the precision and accuracy to be expected of each determination, and he should be aware of the errors which may be encountered. The authors have attempted to correlate these various objectives in the development of this book, and to emphasize all aspects of the subject in connection with each determination. At the same time an effort has been made to keep the presentation as simple as possible.

The book is designed for use in a first-year course in quantitative analysis, and it contains all the material usually treated in a year's work. In the arrangement, however, the needs of the one-semester course have been kept in mind, and the material which is not treated in the first semester's work has been segregated in separate chapters. A logical and continuous development has been sought to facilitate the presentation in the beginning course. Each topic is introduced by a brief description of the methods to be used and a simplified explanation of the theory involved. This is followed by a presentation of the stoichiometry of the method and, finally, by the laboratory procedures. Advanced theory, when given, follows the laboratory procedures.

The book is divided into sections, in order to permit flexibility in teaching. Part I deals with fundamentals, the preparation of equipment, and the use of the analytical balance. After this section is completed, the teacher may proceed either with volumetric analysis, in Part II, or with gravimetric analysis, in Part III. Each of these sections is independent of the other, and may be studied as a unit.

Throughout the book, the procedures are set apart from the discussion of methods and of theory. Each procedure is followed by a section of explanatory notes which serves both to clarify the correlation of theory

and practice and to emphasize the need for special precautions. It is expected that the student will carefully study the procedure and notes before beginning an experiment. During the analysis he then needs to follow only the procedure, which is stated concisely and without embellishment. Details of laboratory technique are repeatedly stressed in the explanatory notes, even at the risk of tiresome repetition, since it is the experience of most teachers that these details cannot be overemphasized. A list of general errors is given in the preliminary discussion of each type of analysis, and, in addition, each procedure is followed by a list of the specific errors that may be encountered.

A detailed discussion is given for each type of stoichiometric calculation used in analysis. This discussion is illustrated by complete solutions for typical problems, and, in addition, there are provided numerous problems for home work. Many of these problems illustrate laboratory methods which space limitations have prevented including in the textual material. In connection with the problems for home work a large number of review questions are also given. Most of the questions are designed to emphasize and illustrate points which are treated in the text, but some of them require independent thinking or consultation of more advanced works. Answers have been provided for a portion of the problems, in order to enable the student to assure himself that he is using correct methods of attack, but they are not given for all problems since this may easily lead to the practice of working for an answer.

In the stoichiometry of volumetric analysis, the concept of the milliequivalent is widely used, in consistency with the use of the milliliter as the laboratory unit of volume. In the experience of the authors, the use of the milliequivalent instead of the equivalent facilitates the ability of the average student to grasp the intricacies of stoichiometric calculations.

In the chapters devoted to an advanced treatment of theory a mature level is adopted. There is assumed a thorough knowledge of chemical equilibrium, such as is usually treated in qualitative analysis. Elementary physical chemistry is freely introduced in the section on the theory of oxidation–reduction processes. Much of the theoretical material is developed by the problem method of presentation. Each new point is illustrated by the complete solution of a typical problem, and, in addition, there are given numerous problems for home work.

A chapter in the first section of the book is devoted to a discussion of precision, errors, and significant figures. The authors feel that these concepts should be introduced early in the course, and that they should be constantly emphasized in connection with all laboratory work. Throughout the earlier determinations the student is encouraged to examine the probable sources of error and to determine for himself the accuracy which

may be expected from his results. In addition he is taught to examine his results from the viewpoint of precision.

The section on analysis of a limestone rock gives, in addition to procedures for a proximate analysis, other methods of general applicability in mineral analysis. Sufficient detail is provided to enable the student to analyze most of the simpler silicate or carbonate rocks.

The last section of the book deals with specialized methods of analysis and with the use of chemical literature. Obviously, an introductory textbook cannot describe many special methods of analysis. In addition to conventional exercises in electrodeposition, the authors have selected for discussion colorimetric methods and potentiometric titrations. These are included because of their growing importance in biological analyses and are illustrated with procedures which may be included in a first course if desired. It is felt that the section on the use of chemical literature is an important item in training analytical chemists, since the student, at the conclusion of a year's work, should be able to locate and use any method which is published. The authors recommend and use the widespread practice of assigning to each student one analysis for which the original literature must be consulted.

Sections on mathematical operations and on hydrolysis are given in the Appendix. The former is included for the benefit of those students who are inadequately prepared; the latter section is offered as an advanced treatment of complex equilibria for the benefit of superior students.

The selection of student exercises for an elementary textbook is a difficult task because of the great divergence among the practices of various teachers. Therefore every general method is illustrated by procedures for several different analyses. This permits each teacher to choose the preferred type of unknown sample. The authors strongly recommend the use of synthetic solutions as unknown samples for the earlier volumetric analyses, because this type of unknown permits the teacher to give each student an individual sample of accurately known analysis. An objection to this practice is that it does not provide training in the technique of bringing samples into solution, but this training is acquired later in connection with more difficult analyses. In every place that directions are given for the analysis of a prepared solution directions are also given for the analysis of a commercial product or ore.

The authors favor the widely used procedure of teaching volumetric analysis first, because this permits the student to become acquainted with the analytical balance by means of the relatively inexact weighings necessary for calibration of volumetric apparatus, and because most of the technique of volumetric analysis is more readily acquired than the

exacting technique of gravimetric analysis. If this plan is followed students may be assigned the material of Chapters I, II, III, V, VI, VII in order. If it is desired to begin with gravimetric analysis, the material of Chapters I, II, III, XV, XVI, XVII constitutes a logical sequence.

The writers desire to acknowledge their indebtedness to Professors W. A. Noyes, Jr., T. F. Young, and W. E. Vaughan for many features of the course on which much of the book is based. Many useful problems and laboratory hints were furnished by Professors P. C. Gaines, L. O. Hill, and O. E. Sheppard. To the various students who assisted in the preparation of the manuscript and in testing procedures, the authors give their thanks, in particular, to Messrs. A. A. Danish, N. H. Koenig, A. H. Jaffey, D. P. MacMillan, and W. W. Marshall. Professor G. Frederick Smith has kindly read the completed manuscript and has given many valuable criticisms. The standard reference works and textbooks in the field have been freely consulted. Particular acknowledgment should be made to *Applied Inorganic Analysis*, by Hillebrand and Lundell, and to the various works of I. M. Kolthoff and his collaborators.

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Chicago, Illinois
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CHAPTER

1

Introduction

To the Student

Following a year or more of work in chemistry you are now beginning a new subject, quantitative analysis. Before starting this it is helpful to know what the course will cover, the objectives to be sought, the importance of the subject, and its relation to other fields of chemistry. In qualitative analysis methods have been studied for identifying the ions in a solution. Quantitative analysis is, as the name implies, the determination of the amounts or percentages of one or more constituents of a sample.

There are a variety of methods for determining the amount of a constituent in a sample. The most common are known as gravimetric and volumetric methods. Gravimetric analysis is based upon isolating and weighing the desired constituent as a chemical substance of known purity. The isolation of the constituent may be done by precipitation, just as in qualitative analyses. For example, the amount of chloride ion in a sample may be determined by treating a solution of the sample with silver nitrate, thus precipitating silver chloride which is collected on a filter, dried, and weighed. In a volumetric analysis the amount of the sought constituent in the sample is determined by means of the volume of a reagent solution that is required to react with the sample. For example, the quantity of acetic acid in a vinegar sample can be determined from the volume of a sodium hydroxide solution of known strength that is required to react with the sample. Neutralization titrations of this type have doubtless been done in your general chemistry course. In addition to gravimetric and volumetric methods there are numerous other types of quantitative analyses. Important among these are many instrumental methods which are widely used in industry.

In general, it is necessary to know the qualitative composition of a sample before a quantitative analysis can be made. For example, if

you are seeking to determine the amount of chloride in a sample, you should know that it contains no other ions that will give a precipitate with silver nitrate. Usually, however, it is not necessary to carry out a complete qualitative analysis before making the quantitative determination. The origin of the sample often gives the desired information. A sample of vinegar, for example, will not contain acids other than acetic, or a sample of table salt halogens other than chlorine.

Several objectives should be kept in mind for this course.

1. You should master the use of tools which are required in analysis, particularly the analytical balance and the burets, pipets, and so on, which are required for the accurate measurements of volume. You have used these tools in previous work but usually not with the highest accuracy. In this course you should learn how to obtain from these basic tools all the sensitivity and accuracy they are capable of giving. Further you should learn of the limitations of balances, burets, and the like, so that you may know what accuracy to expect from their use. Perhaps a fourth of your laboratory time will be devoted to use of the basic tools.

2. You should learn to do accurate and careful work. This requires not only practice but also an understanding of the factors which may affect the accuracy of analyses.

The analyst must work to a precision of $\frac{1}{1000}$, that is, make measurements which are reproducible to within an error of measurement equal to $\frac{1}{1000}$ of the total magnitude being measured. A common weight of sample is 0.2 g; $\frac{1}{1000}$ of this is 0.0002 g or 0.2 mg. You will have to learn to weigh a sample so carefully that the error in the determination of the weight does not exceed 0.2 mg. A common volume is 30 ml; reasoning similar to the foregoing shows that the error in the measurement of volume cannot exceed 0.03 ml if the desired precision is to be achieved.

3. You should, by practice, become familiar with the more common analytical methods. This you will do by successfully analyzing unknown samples, selected to illustrate various types of determinations. A list of the required determinations will be given to the class early in the course.

4. An understanding of the basic principles involved in the analytical methods is essential. You do not need to be a trained chemist to do good analytical work. Indeed, in many commercial laboratories the routine analyses are performed by non-technical personnel who are taught to do a particular type of work. Such personnel may equal or surpass the trained chemist in speed and accuracy so long as routine procedures can be applied, even though they have no understanding of the basic principles involved. But, if new methods are to be developed

or trouble occurs because of variations in the samples, the routine analyst soon becomes lost. Even in such a simple matter as the selection of an indicator for acid–base titrations a knowledge of the basic theory is essential. The competent analyst, as distinguished from the technician, is one who knows and can apply theory to his practical problems.

5. You must understand and be able to apply all types of computations employed in analytical work. It is truly surprising to find how many students report incorrect values for analyses because of faulty computations. It is quite probable that an error of this type will be made at least once by three fourths of the students in your class.

6. You should learn to keep permanent, legible, and intelligible records of your work. Many suggestions will be made throughout this book concerning methods for tabulation of data and recording of results.

7. You should develop speed in laboratory work. This comes, not from manual dexterity as from an often repeated operation, but from an understanding of and careful planning for your work. The fastest worker may be one who does each operation slowly but who makes no mistakes and who plans his work so as to avoid waste of time. Careless work will almost inevitably lead to loss of time because repetition may be required. The work of the course is designed to be done in the scheduled laboratory hours, but, if time is wasted or repeat analyses are required, it will be necessary to spend extra time in order to complete the required work.

A good principle to follow is to study and outline each procedure carefully before coming to the laboratory to begin work on it.

8. You should at all times be clean and neat in the laboratory. This applies not only to the desk and equipment, but to the notebook as well. It is possible to turn out good analyses from a dirty and disarranged desk, but such a coincidence is highly improbable.

9. Finally, a well-trained analyst should know how to use the literature when new and unusual problems are encountered. This requires an acquaintance with the standard reference books plus a knowledge of how to find information in the periodicals. Early in the course you should become acquainted with the available reference works in your library.

The objective of the course is not primarily the training of personnel to fill positions in commercial analytical laboratories. In fact, probably only a small percentage of those in your class will become professional analysts. This course is important because every chemist, regardless of his field, constantly applies the techniques and principles he learned in quantitative analysis. Every research problem and all of chemical industry depends upon chemical analyses. Every chemist must know

not only how to perform conventional analyses but also how to develop new methods to fit particular needs. Whatever his field of work, every chemist is to some extent an analytical chemist, whether he be an engineer, plant superintendent, purchasing agent, or executive. All of these must on occasion initiate chemical analyses and base decisions upon the results of analyses.

The premedical student too should have a thorough understanding of analytical methods and their limitations. Modern clinical practice is to a high degree based upon laboratory findings, and the doctor should know the techniques and principles upon which these analyses are based.

PART ONE

Fundamentals

CHAPTER

2

General Directions

EQUIPMENT

The equipment used in a quantitative analysis course is of three kinds: (1) the desk outfit, which is assigned to the student at the beginning of the course and may be returned at its close; (2) special equipment, which is constructed by each student; (3) general equipment, such as the balance, trip scale, steam bath, drying oven, and hot plate, which must be jointly used by several students. Before the work of the course can be started it is necessary to prepare the equipment needed. Instructions for the use of the various items are given in later sections.

Desk Outfit

Returnable Apparatus. The assigned desk is equipped with apparatus which must be returned in good condition at the end of the course; it should be carefully inspected before it is accepted, and each item should be checked against the list supplied by the instructor. Note in particular that the glassware is not cracked, that buret and pipet tips are not chipped, that the buret stopcock fits well, and that the crucibles are in good condition. Make a list of any apparatus missing or defective, and present this to the instructor for his approval.

Special Equipment

The apparatus provided includes non-returnable items that will be needed in preparation of special equipment. The instructor will specify that certain of the following items be constructed for later use:

Wash Bottles. Construct from flat-bottomed boiling flasks (Florence flasks), preferably with ring necks, two wash bottles as shown in Fig. 1. Either 1000- or 500-ml flasks may be used, as provided in the equipment. One bottle is for ordinary washing with cold water and the other is for hot water and special solutions. The fittings are made from glass tubing of proper size to fit the holes in the rubber stoppers. Bends can only be properly made by use of a wing tip on the burner so that the tubing is heated over a distance of 4–6 cm. While heating,

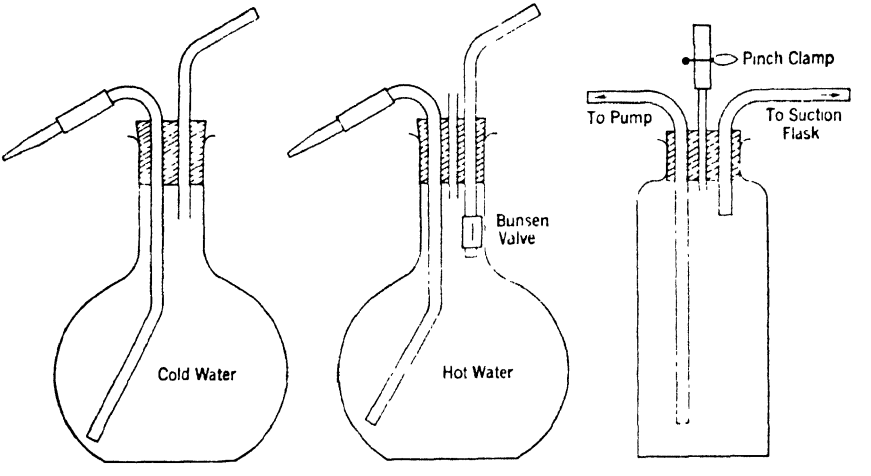

FIG. 1. Wash bottles and safety bottle.

constantly rotate the tubing, but take care not to twist it as it becomes soft. After it is soft, remove the tubing from the flame, and quickly bend it to the desired angle (if a tube is bent to a more acute angle than is desired, it is not easy to rebend, and the piece should be discarded). Place the bent tube on a wire screen, and allow it to cool. Cut the two ends to the desired length, and fire-polish the ends by heating with constant rotation in the flame from a burner (without wing tip). This is to remove sharp edges that will cut stoppers or rubber tubing.

The delivery tip is constructed as follows: Hold a short length of tubing in the blue flame from an ordinary burner (without wing tip) so that about 2 cm at the center is heated. Rotate constantly, and, when the tubing is soft, push the ends gently so as to form a slight bulge as shown in Fig. 2*a*. Now with constant rotation heat the bulge until it collapses as shown in Fig. 2*b*. Remove from the flame, and while still red hot draw out the tubing, slowly at first and then more rapidly as it cools. When it is cold, cut the tip to the proper length, fire-polish until the orifice is about 1 mm in diameter, and set aside to cool. Fire-polish

the other end after cutting to the proper length. This procedure produces a thick-walled tip that is not so fragile as is obtained when the tubing is not first thickened at the heated portion. This tip is attached by a 5-cm length of flexible rubber tubing. The ends of the glass pieces should be pushed together. The flexibility of the rubber will permit free motion of the tip. The entire fitting should be so compactly made that the tip may be manipulated by the forefinger as the bottle is held in the hand. The rubber stopper should fit the neck of the flask tightly when it is inserted not more than halfway into the flask. Before assembly the stopper should be cleaned by boiling in dilute sodium hydroxide solution.

The hot water wash bottle is provided with a pressure-regulating tube in order to prevent a rush of steam into the mouth at the cessation of

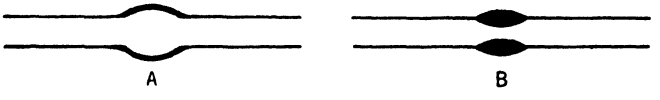

FIG. 2. Construction of wash-bottle tip.

blowing. This is a short glass tube, open at both ends, which projects through the stopper. When the bottle is in use this tube is closed by placing the thumb over the upper end; removal of the thumb instantly reduces the pressure within the bottle. If three-hole rubber stoppers are not provided, it will be necessary to drill a hole for the pressure tube. This is done by means of a sharp cork borer which is lubricated by dipping it into dilute sodium hydroxide. The hot-water wash bottle may (optionally) be provided with a Bunsen valve, which serves to keep steam from escaping through the mouthpiece as the contents of the bottle are heated. This valve is made from a 5-cm length of flexible rubber tubing, which is attached to the inner end of the mouthpiece. The lower end of the tubing is closed with a length of glass rod. A longitudinal cut in the rubber tubing acts as the valve and permits blowing into the bottle, but, when pressure is applied in the opposite direction, the edges of the cut are forced together and seal the opening. The neck of the hot-water bottle should be wrapped with asbestos paper or cord. The paper is best applied wet and allowed to dry overnight; there is sufficient adhesive material in the paper to make it cling tightly.

Safety Bottle. In all suction filtrations a safety bottle should be inserted between the water aspirator pump and the suction flask, since a change in water pressure may cause water to back up through the pump and contaminate the filtrate. The safety bottle is also used, as shown on page 75, as protection when cleaning solution is drawn by

suction into burets or pipets. Construct the safety bottle as shown in Fig. 1. The three-hole stopper carries the two glass tubes that serve as inlet and outlet and a short length of glass tubing that connects to a rubber tube that is closed with a pinch clamp. This serves as a convenient method for breaking the vacuum when apparatus is attached to the suction pump.

Stirring Rods. Cut six or eight stirring rods from solid glass rod, and fire-polish the ends. Lengths should be made for use with the 250-,

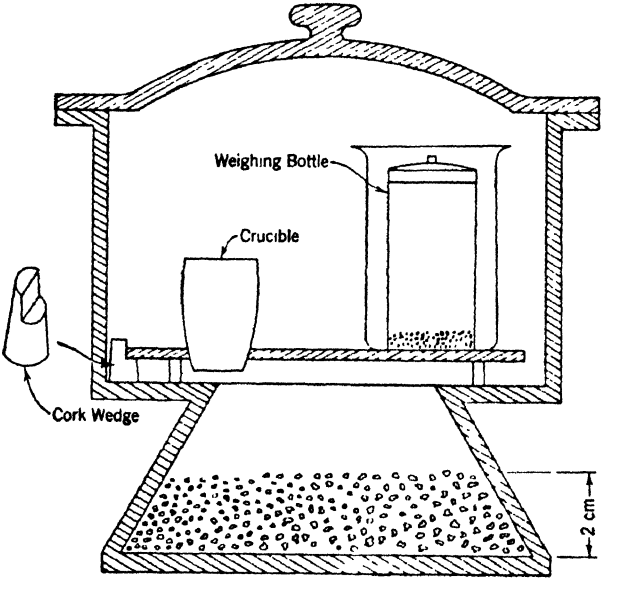

FIG. 3. Desiccator.

400-, and 600-ml beakers provided in the outfit. The rod should, when resting in the beaker, project 5–7 cm beyond the lip. Two of the rods should be fitted with rubber tips, closed at one end (policemen). These are used in the operation of filtration to remove precipitates which adhere to the walls of beakers.

Desiccator. Clean and dry the desiccator (Fig. 3), and fill the lower portion to a depth of 1–2 cm with the desiccant provided. If the plate does not fit securely, fasten it in position with three pieces of cork cut as shown in Fig. 3 and wedged in at the sides of the plate. Grease the ground glass rim lightly with petrolatum (not stopcock grease), set the cover on, and move it around until the greased joint is transparent; a minimum of grease should be used.

The desiccator is a container used to preserve samples, ignited crucibles, and the like, in an atmosphere of low constant humidity. It may

be of any form and size; the only requirement is that it be tight. The most widely used style is a two-piece glass vessel as shown in Fig. 3. Recently several forms of metal desiccators have been marketed. In some of these the cover fits by a ground joint, as in the glass desiccators; in others the cover is a cap similar to that of an ordinary metal can. Metal desiccators have the advantage of low cost, low breakage, and rapid heat interchange with the surrounding air. The only disadvantage is that most desiccants cannot be placed directly in the chamber, because of reaction with the metal; usually it is advisable to place the desiccant in an evaporating dish which rests on the bottom of the desiccator.

A desiccator is most efficient when the volume of air contained is kept small. When the cover is removed, for insertion of a sample, much of the air in the chamber is replaced by air of higher humidity from the room. Air circulation in the closed vessel is so slow that considerable time is required to establish equilibrium again, and a sample may absorb an appreciable amount of water from the moist air. Once a sample has been dried in a desiccator, it is desirable that the cover not be lifted frequently.

Care must be exercised in the handling of a desiccator. Ignited crucibles should be placed in the chamber only after they have partially cooled for 60 seconds after the removal of the flame. At the end of the cooling period the cover should be removed gradually by sliding to one side to prevent a sudden inrush of air. A partial vacuum exists in the chamber because of the escape of some air expanded by the heat from the hot objects when they were first placed in the chamber.

Desiccants. The desiccants most commonly used in the analytical laboratory are anhydrous calcium chloride and concentrated sulfuric acid, not because they are best but because of their ready availability. In fact, these are two of the poorer desiccants. Calcium chloride does not remove water at all completely, but produces a low enough humidity for student needs. Concentrated sulfuric acid is a fairly good desiccant, but it has the disadvantage that the liquid may be splashed onto the bottom of objects in the desiccator. If it is used, the bottom of the chamber should be filled with glass beads and the acid level kept below the level of the beads. Barium oxide is superior to calcium chloride, but it is not readily available in suitable form. Phosphorus pentoxide is a very good drying agent but expensive and difficult to handle. When the surface of the solid becomes moist, the powdered particles coalesce, and a film of phosphoric acid forms on the surface to give a hard glassy layer that prevents air coming into contact with the unused oxide below the surface. The newly developed desiccants barium perchlorate

(dessichlora), magnesium perchlorate (anhydrone), and calcium sulfate (drierite), are superior to those previously listed and are today available through all supply houses. All these have high drying efficiency [1] and are easily handled.

CLEANLINESS

The importance of cleanliness in the laboratory cannot be overemphasized. Good analyses cannot be performed with dirty equipment. Furthermore, a dirty or a disarranged desk is usually an indication of a poor or careless technician. The desk and the reagent bottles must be kept clean at all times. All equipment not in use must be kept within the locker, clean and neatly arranged, with the exception of the desiccator and the burets, which are allowed to remain upon the desk top to avoid the danger of breakage entailed by frequent change of location. At the conclusion of each working period, the desk top must be sponged off and dried with a towel. Reagent bottles must be washed frequently. Spilled chemicals must be washed up immediately.

Volumetric glassware is best cleaned by sulfuric acid–dichromate cleaning solution, as described on page 74. All other glassware is cleaned with soap and water (preferably hot) or with a soapless detergent, with the aid of a brush. After the apparatus is washed completely free of soap or detergent and rinsed with distilled water from a wash bottle (*never at the distilled-water tap*), it is wiped dry on the outside and is then allowed to drain by being inverted on a towel or placed on a drain board. Use of cleaning solution for general cleaning is not only dangerous, because of the powerful oxidizing properties of the mixture, but also inefficient.

REAGENTS

Chemicals are manufactured and sold in degrees of purity ranging from that of commercial grade to the best reagent grade. The well-trained analyst should know when it is advisable to use chemicals of low purity and when it is necessary to employ the purest grade obtainable. Moreover, he should know, in each analysis, which of the impurities in the chemicals used may affect his results, and by what tests he can assure himself of the absence of these impurities. In those operations in which the presence of impurities cannot cause harm, the cheapest grades of chemicals can be employed. For example, cleaning solution is prepared, not from pure sodium dichromate and sulfuric acid, but from commercial grades of these substances.

Reagents are classed as follows:

[1] See J. H. Bower, *J. Research Natl. Bur. Standards*, **12**, 241 (1934).

Commercial grade (*Com.*). This grade is not purified by the special processes necessary for the elimination of traces of other substances. It is seldom employed in the laboratory for the preparation of analytical reagents.

USP grade. This designation indicates that the standards set up in the *United States Pharmacopœia* are followed. For some uses, USP chemicals are sufficiently pure reagents.

C. P. and analyzed grades. The term C. P. (chemically pure) is somewhat elastic in meaning; there is no general list of specifications to define the term. Because of this, various manufacturers prepare "analyzed" chemicals for use as reagents. Each package of analyzed chemicals has a label giving the manufacturer's limits of certain impurities. Such an analysis does not imply that the composition of the chemical is definitely that of the formula. For example, reagent-grade sodium carbonate may contain a certain amount of sodium bicarbonate, but nevertheless be of high purity. Certain chemicals are packaged with a label which gives the "assay," or percentage of the major constituent. Such a label is valuable to the analyst, since he is often interested in the percentage purity rather than the limits of impurities.

The American Chemical Society Committee on Analytical Reagents has established standards for certain reagents (see following references). Many chemicals are now prepared to meet these specifications; they are labeled "Conforms to ACS Specifications."

It is never wise to rely upon the label of a bottle as a guarantee of the purity of a chemical. Mistakes may occur, not only in testing, but also in packaging and in handling after the bottle has been opened. Whenever the presence of an impurity in the reagent may lead to trouble, a test should be made. The usual method is to run a blank determination, as described on page 90.

In the laboratory, care must be taken to prevent contamination of reagents. No chemical should be returned to a stock bottle. All bottles should be closed except when in use. Liquid reagents should be *poured* from the bottle after first washing the lip while the bottle is stoppered; under no circumstances should a pipet be inserted into a reagent bottle. Particular care should be taken to avoid contamination of reagent bottle stoppers. When liquid is being poured from a bottle the stopper should never be placed on the desk or shelf; most chemists hold the stopper between two fingers of the right hand so that the plug projects from the back of the hand.

The most common impurity in solid reagents is moisture, which is more or less firmly held by all solids. Very often the adsorption of water causes no difficulty, but, if the weight of a chemical must be ac-

curately known, the chemical must be dried. Directions are given whenever drying is necessary.

Certain reagents are provided as concentrated solutions. Since these solutions are frequently used for the preparation of dilute solutions, the analyst should know their approximate strength. This is given, for the more common reagents, in Table 1.

Dilute solutions of these reagents are prepared, when needed, by adding the concentrated solutions to water. The concentrations of dilute solutions are usually from 3 to 6 molar; usually the value of the concentration is specified as the molarity (or normality) or as the degree of dilution, which is indicated by the ratio of the volume of concentrated

TABLE 1

STRENGTH OF LABORATORY REAGENTS

Reagent	*Density (g/ml)*	*Per Cent by Weight*	*Approximate Molarity*
HCl	1.18	36	12
HNO_3	1.42	72	16
H_2SO_4	1.83	95	18
$HC_2H_3O_2$ (glacial)	1.057	99.5	17
NH_4OH	0.90	28 (NH_3)	15

solution to that of water. For example, 1:4 hydrochloric acid indicates a solution prepared by adding 1 volume of concentrated acid to 4 volumes of water.

Distilled water is used for the preparation of all solutions employed in quantitative analysis. Even this water, as it comes from the tap, is not pure but is contaminated by dissolved gases and by material dissolved from the container in which it has been stored. Ammonia and carbon dioxide are always present, together with oxygen and other gases. The dissolved gases may be removed by boiling the water for a short time and cooling it in a stoppered container. Frequently distilled water is found to be contaminated by non-volatile impurities which have been carried over by the steam, in the form of a spray. Occasionally a still may froth, while in operation, and badly contaminate the distillate. When a fresh supply of distilled water is obtained, a test should be made for chloride or sulfate ion. If these are absent, the water may be assumed to be reasonably pure.

When water of the highest purity is required, distilled water is redistilled from an alkaline permanganate solution, in silica or block tin apparatus. (The permanganate solution oxidizes nitrogenous matter present.) Redistilled water prepared in this manner is known as *conductivity water.*

The storage vessel employed may have a marked effect on the purity of water or of reagents. Soda-glass or soft-glass vessels are much more readily attacked by reagents than the borosilicate glasses, such as Pyrex. When reagents are to be stored for long periods of time it is desirable to use some type of resistance-glass vessel. Alkaline solutions, in particular, quickly attack glassware. Portions of the glass dissolve, and other more resistant portions flake off the walls to form a suspension. Because of this action it is nearly always necessary to filter ammonium hydroxide solutions before use.

REFERENCES

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J. ROSIN, *Reagent Chemicals and Standards*, 2d Ed., Van Nostrand, 1946.

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RECORDS

One of the important details of all chemical work is the keeping of complete and legible records of experiments. Quantitative analysis provides especially valuable training in keeping records, because the work of the course is of such a nature that all data can be concisely and completely summarized in a notebook. The following suggestions for keeping the notebook should be carefully studied. They are illustrated later by sample notebook pages.

Suggestions for Keeping Notebook

1. Use only bound notebooks, of the size specified by the instructor. Reserve the first page for an index, and number all subsequent pages. Many instructors prefer that the student use two notebooks, one of which is small and is for non-permanent data such as balance swings. It can be used to jot down data as they are taken; these data are later transferred to the main book. When this is done, each page of the non-permanent data book should show the page number of the other book to which data have been transferred.

2. Record all data in a notebook as taken. Never use loose paper. Loss of data taken on loose paper has caused many students loss of valuable time.

3. Make no erasures. If a value is to be invalidated, draw a line through it but in such a way that it is still legible. State in the notebook why data are discarded.

4. Head each page with the date and title of the analysis.

5. Strive for clarity so that any other chemist would be able to interpret your figures. Before starting an experiment it is advisable to think over the data needed and construct a table in which data and computations can be neatly arranged.

WORK OF THE COURSE

A list of the determinations to be made will be furnished Each is to be made in duplicate or triplicate; that is, two or three portions of sample are analyzed with concordant results. The result of the analysis is reported on a card as specified. Sample cards are shown later. The report is graded according to the accuracy and precision of the results. If it is not accepted, a new sample must be analyzed.

Suggestions for Work

At best, many hours must be spent in the work of a course in quantitative analysis. Many students, through inefficient planning of their work, require far more time than necessary and have difficulty in completing the laboratory work. Adherence to a few simple rules may prevent much of this loss of time:

1. Study the procedure and notes before beginning an experiment. Know the reason for each operation. Such study should be done outside of laboratory hours. The notes contain many hints and explanations; they are an integral part of the procedure.

2. Prepare a written outline of the procedure, and work from this rather than from the book.

3. *Do not attempt short cuts.* The procedures are based on proved methods.

4. Obtain the necessary chemicals before starting an analysis.

5. Utilize the waiting time occasioned by the cooling of crucibles, evaporations, ignitions, digestions, and the like, by working on other experiments. Lengthy delays caused by slow evaporations can often be eliminated by so planning that these can be carried out on the steam bath while other work is in progress.

6. Keep all containers for each individual sample carefully marked, to avoid mixing or interchanging solutions at some stage of the analysis. A great deal of time can be lost by carelessness. Beakers and flasks may

be identified by gummed labels or by writing with a pencil on the etched circle provided for that purpose. Porcelain crucibles can be marked by writing on the unglazed bottoms with a dilute solution of an iron or cobalt salt and heating until the salt is well dried. Marking solutions for use on glazed surfaces are described in all the handbooks of chemistry.[2] Crucibles can also be identified by notching the rim with a file.

[2] Every student specializing in chemistry should own and frequently use a handbook. Several excellent books of this type are available. Among other useful tables they contain lists of inorganic and organic compounds and their physical properties, tables of specific gravity and composition, mathematical formulas, lists of spectral and X-ray lines, and photographic formulas.

CHAPTER

3

The Analytical Balance and Its Use

Accurate weighing of small samples is prerequisite to every analysis. Consequently the first assignment in this course is to learn how to weigh accurately and rapidly and to gain an appreciation of the principles involved in the use of a balance.

Mass and Weight. Mass and weight, although often used interchangeably, differ in meaning. The *mass* of an object is the amount of matter in the object, as referred to a standard mass of platinum–iridium alloy which is preserved at the International Bureau of Weights and Measures, near Paris. Many duplicates of this standard are in existence. The unit of mass is the gram (g), which is $\frac{1}{1000}$ of the mass of the standard; the mass of the standard, 1000 g, is known as a kilogram (kg). It was originally intended that the kilogram be the mass of 1000 cc of water, at the temperature of greatest density, 3.98°C, but because of an error in measurement this objective was not realized; it is now known that the volume of a kilogram of water at 3.98°C is 1000.028 cc. Other weight units are the centigram (cg) or 0.01 g, and the milligram (mg), or 0.001 g.

The *weight* of an object is the force exerted on that object because of gravitational attraction between the body and the earth. The weight is expressed in force units (dynes). Since the force of gravity varies with geographical location and with the elevation above sea level, the weight of an object is a variable, whereas the mass is invariant. The term *weight* is, however, often used instead of the term *mass*; the expression "weight of 1 g" is commonly used, and is correct if properly interpreted to mean "a mass whose weight is that of a 1-g mass." This usage has developed because of the method followed in determining the mass of an object, which is commonly done by comparing the weight of the object with the weight of a known mass.

value. In using a balance so graduated, care must be taken to have the rider on the beam at all times.

The entire working mechanism is enclosed within a glass case, in order to protect it from air currents while in operation and from dust. The front glass section of the case is suspended by a sash arrangement which permits it to be raised, thereby giving access to the pans for inserting objects or weights. The bottom of the case rests upon leveling screws.

2. Chain Balances. The chain-type balance is like the rider balance except that the rider is replaced by a metal chain one end of which is suspended from the right-hand side of the beam and the other end from a movable carrier so that the effective portion of the weight carried from the beam can be varied. One type of chain assembly is shown in Fig. 5.

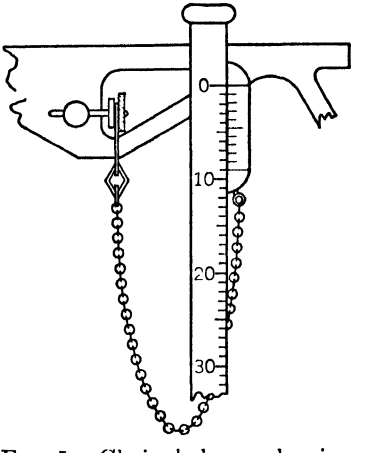


FIG. 5. Chain balance showing scale and vernier.

The advantages of the chain balance are that the chain can cover a larger range of weights than a rider and it can be adjusted more rapidly. In older models the chain range was 0–50 mg, but in recent models it is customary to provide a chain to cover the range 0–100 mg.

The chain is moved by means of a knurled wheel at the right-hand side of the case. The position is read by a graduated scale and vernier, mounted inside the case. One type of scale is shown in Fig. 5.

Weighings can be made several times as rapidly on a modern chain balance as on a rider-type balance. Consequently, the rider balance is today almost obsolete in industrial laboratories. Unfortunately, however, the chain balance is inherently less accurate than the rider balance. A chain will usually show some deviation from the nominal value as the scale is traversed, as shown in Table 5. It is not surprising that such errors accompany the use of the chain weight, in view of the mechanical features of the chain; rather it is surprising that chains can be made as accurate as they are. In most analytical work a variation of 0.2 to 0.4 mg in weight can be tolerated, to gain the added speed of the chain. However, it should be kept in mind that errors of this magnitude may occur, and a rider balance should be used in the weighings that demand high accuracy or else the chain should be calibrated.

3. Notched-beam Balances. Many modern chain balances are equipped with a rider to give weights of 0.1 to 1.0 g in 0.1-g intervals. The rider is a dumbbell-shaped bar which rests in notches cut on the top side of the beam. Its use eliminates the changing of all fractional weights and speeds up the weighing operation correspondingly.

4. Keyboard Balance. The accuracy of the rider and the speed of the chain balance are combined in the keyboard balance. Fractional weights down to 10 mg are added by depressing keys mounted on the front of the balance case. As a key is depressed, it permits a metal stirrup of the designated weight to rest on a notched arm attached to the beam. Below 10 mg the weight is obtained from a rider of conventional type.

5. Damped Balance. Dampers of various types are used to suppress the swings and to facilitate weighing. The damper is a device attached to the beam so as to offer an opposing force to motion of the beam. Usually it is a sheet of aluminum moving between poles of a magnet or a metal disk mounted as a loosely fitting piston in a cylinder. In either case the effect is to damp the swings of the beam about the rest position. Rather, when the beam is released, it moves over to the rest position and in a short time stops. The use of dampers is advantageous when highest precision is not sought, but in weighings to 0.1 mg it is usually faster to use an undamped balance with the single-swing method.

6. Microbalance. Special balances sensitive to $\frac{1}{1000}$ mg or 1 microgram are known as microbalances. They are similar in construction to the rider balances previously described but are more sensitive because of use of lighter parts and more precise workmanship. Scale readings are made by a magnifying glass mounted permanently in the case. Such balances are never used for loads greater than 10–25 g.

SENSITIVITY OF BALANCE

Balances vary in the effect produced by a small weight inequality on one side of the beam. They are rated in terms of this effect. In general, the term *sensitivity* is used to describe balance response, but the term is rather loosely used. In this text we shall define sensitivity as the change in rest point of the pointer produced by a weight of 1 mg. This requires definition of the method used to determine the rest point and is described in the following paragraphs. In another usage the sensitivity (sometimes called sensibility) denotes the smallest weight difference which can be detected with accuracy. This usage is generally more convenient for rating balances, since no reference is made to the

method for determining the rest point. Thus analytical balances are rated as having sensitivities of $\frac{1}{10}$ or $\frac{1}{20}$ mg, and a microbalance may have a sensitivity of $\frac{1}{1000}$ mg.

THE OPERATIONS OF WEIGHING[1]

Weighing an object consists, as stated previously, in determining the mass of known weights necessary to counterpoise or balance the object. The condition of equality is recognized by the motion of the pointer; if the equilibrium position of the loaded balance coincides with that of the empty balance, the masses on the two sides are equal, provided that the two arms of the beam are of equal length.

When the beam and pans are released, the beam starts to swing with a period, depending on the characteristics of the particular balance. The midpoint of this swing is the point at which the beam would be at rest; however, instead of waiting for the beam to come to rest, we *calculate* the equilibrium point from the amplitudes of successive swings of the pointer. This method is not only more rapid than waiting for the beam to come to rest but also more accurate because, if the beam were allowed to swing until it came to rest, the position of rest would be influenced by vibration, friction, and other external forces.

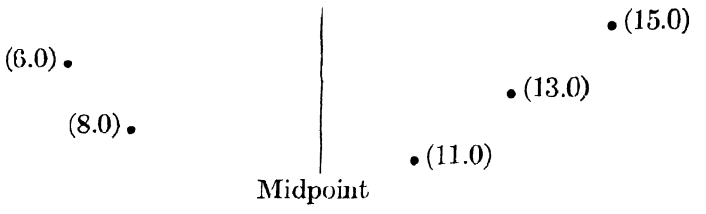
For the purpose of accurately observing the swings of the balance, the scale S is marked with equally spaced divisions. These are conveniently read[2] by denoting the center mark as 10 and calling the left-hand mark 0. In reading the position of the pointer the nearest 0.1 division is estimated.

Because of frictional and air resistance, the swings of a balance pointer are damped; that is, they are of constantly decreasing amplitude. Suppose, for example, that in a given case the equilibrium position is at 10.0 on the scale. When the beam is put into motion, the following consecutive swings are noted (trace these swings on the scale of Fig. 4; the damp-

[1] In modern analytical work the multiple-swing method of determining rest points is not usually used because of its slowness. But in the most exacting determinations this is the preferred method. Microbalances are always used with multiple swings. It is recommended that students first learn this method, regardless of what method is used later.

[2] Many chemists prefer to number the center of the scale zero and to call readings to the right and left respectively plus and minus. Thus a reading which according to the convention of this book is 8.0 would become in the other system −2.0 and a reading of 12.0 would become +2.0. The plus-and-minus system has an advantage in that the operator need observe only the number of divisions from the center mark. This system is preferred in weighing by the single-swing method since usually all rest points are to the left of the center mark.

ing is exaggerated, for purpose of illustration):



It is obvious, from a consideration of these swings, that the equilibrium position is not halfway between any two consecutive swings, such as 15.0 and 6.0 or 6.0 and 13.0. The rest point is, however, halfway between the midpoint of two swings to one side, such as 15.0 and 13.0, and a corresponding single swing to the other side, such as 6.0. That is,

$$\text{Rest point} = \frac{\frac{15.0 + 13.0}{2} + 6.0}{2} = 10.0$$

or

$$\text{Rest point} = \frac{\frac{15.0 + 13.0 + 11.0}{3} + \frac{6.0 + 8.0}{2}}{2} = 10.0$$

From the foregoing, the following rule may be formulated: *To find a rest point, observe an odd number of consecutive swings to one side and an even number to the other side. Take the average of the swings to each side. (Either three or five swings may be used.) Add the two averages and divide by two.*

In weighing, the following steps are necessary:

1. Determine the rest point of the unloaded balance.

2. Place an object on one pan, and determine the weight needed to make the rest point of the loaded balance coincide with that of the unloaded balance.

Since weights must be determined to the nearest 0.0001 g or approximately to the nearest 1/300,000 oz, it would prove a tedious procedure to continue the addition of weights, by trial and error, until the two rest points are brought into exact coincidence. It is a much simpler procedure to add weights until the rest point is near that of the unloaded balance, and, by then determining the effect of 1 mg on the rest-point position, to calculate by interpolation the exact weight that would be needed to bring the rest point to the true zero. This method is known as *weighing by sensitivity;* the displacement of the rest point caused by

1 mg is known as the *sensitivity* of the balance. Step 2 consists of three parts:

(*a*) Determine, by trial, the approximate weight of the object.

(*b*) Determine the sensitivity of the balance.

(*c*) Calculate the exact weight of the object.

These steps will be followed in the directions for weighing.

Procedure. Determination of Rest Point of Empty Balance (Zero Point). Identify the controls, and carefully operate each. Determine, by the attached spirit level or plumb bob, whether the balance is level. Carefully lower the beam by turning the beam-control knob counterclockwise. Push the pan arrest control in, and start the balance swinging (note 1) by gently fanning an air current onto one pan (note 2). Close the balance case, and observe the swings, estimating each point to the nearest 0.1 division (note 3); record each swing immediately. When three or five consecutive swings have been recorded, release the pan arrest, raise the beam arrest, and calculate the zero point as follows:

Scale readings	5.1	14.8
		14.6
Average	5.1	14.7

$$\text{Zero point} \qquad \frac{5.1 + 14.7}{2} = 9.9$$

Release the beam and pan arrests, and repeat the observations. The two rest points should agree within 0.1–0.2 unit. Should the rest point not fall between 8 and 12, consult the instructor (note 4).

Notes. 1. The amplitude of the swing should be 3–5 divisions to each side of the center mark. Take care that the rider is not so placed that it can touch the swinging beam.

2. Alternative methods of inducing swinging are: (*a*) One pan is lightly touched with a stiff hair, waxed to a match stick or to the handle of the brush that is kept in the set of weights. (*b*) With the pan arrests locked in the down position the beam is gently lowered onto its knife edge. Lin [3] advocates this method and presents data showing that student results are more reproducible with this method than when the beam is set in motion by fanning or touching one pan.

3. Care must be taken to avoid parallax (see page 78) in observing the swings. The head should be held steady, in a position directly before the scale, for the entire set of readings.

4. The position of the rest point may be adjusted by screws *HH*, on the ends of the beam. Such adjustment should be made only by the instructor.

Procedure. Determination of Approximate Weight of Object. Be sure that the beam and pan arrests are raised. Carefully place the

[3] I. Lin, *J. Chem. Education*, **16**, 340 (1939).

object on the center of the left-hand (note 1) pan. Place a weight (note 2) of the estimated amount on the right-hand pan, and partially lower the beam arrest. A large inequality in weight will be shown by a displacement of the pointer to one side. If no inequality is noted, momentarily release the pan arrests, and note the direction of swing. Raise the beam arrest, and add or subtract weights as indicated by the direction of the swing. Continue in this manner until it is necessary to employ fractional weights. Add fractional weights until the addition of a weight having the magnitude of the rider is sufficient to *overbalance* the object, then remove this weight, and use the rider to obtain a weight within 1 to 2 mg of the true weight. This point is recognized when the pointer no longer passes either end of the scale when swinging a distance of 5–6 scale divisions.

Notes. 1. The object is always placed on the left-hand pan and should be placed near the center of the pan to prevent lateral motion.

2. Place the larger weights near the center of the pan, and arrange smaller weights to both sides, so that the pan will hang in a level position.

Procedure. Determination of Sensitivity. When the object is approximately balanced by weights, determine the rest point, as in the determination of the zero point. Move the rider to a position 1 mg *heavier* if the weights are too light (note 1), or to 1 mg *lighter* if the weights are too heavy, and determine the new rest point (note 2). The numerical difference in the two rest points is the sensitivity, expressed in scale divisions per milligram.

Notes. 1. In determining the sensitivity it is desirable but not essential to choose two rest points such that one lies on either side of the zero point.

2. The rider may be moved any known amount and the sensitivity calculated by dividing the rest-point displacement by the weight difference.

Calculation of Exact Weight. Select the weight at which the rest point is nearest the true zero, and, by subtraction, determine the number of scale divisions by which the rest point for this weight deviates from the true zero. Convert the number of scale divisions into weight units by dividing by the sensitivity. To obtain the exact weight add this value to or subtract it from the approximate weight, depending on whether the approximate weight is less or greater than the exact weight.

The use of the method of sensitivity may be illustrated by a numerical example:

Weight on pan	17.360 g	17.360
Weight on rider	0.003 g	0.004
Rest point	11.0	8.5
True zero	9.9	

Calculation: The weight 17.363 g is too light by 11.0–9.9 or 1.1 scale division. Since a weight of 1 mg (if the rider is changed from 3 to 4) causes a change in rest point of 2.5 divisions (from 11.0 to 8.5), a deviation of 1.1 scale divisions corresponds to a weight of 1.1/2.5 or 0.4 mg (0.0004 g), and the true weight is obtained by adding 17.363 + 0.0004 = 17.3634 g. Note that the computation is not carried beyond the fourth decimal place. Why?

Completion of Weighing. Record (note) the weights and swings, as shown in Table 2. Release the pan arrest, and lock the beam. Remove the object and the weights, checking each weight against the notebook record as it is removed from the balance case. Remove the rider from the beam, by means of the rider carrier, and push the rider carrier into the balance case until the rider hangs above the center of the beam. Close the balance case.

Note. After more experience is gained, the weights should not be individually recorded as shown in Table 2. The experienced analyst does not record either the individual weights or the balance swings, but only the final result.

Weighing by Method of First Swing. In all but the most exacting work one can take as the rest point the first swing of the pointer, provided that the pan arrests are well adjusted and do not impart an erratic swing to the beam when they are released. The writers have used this method with several classes and find that it gives a large saving in the time required for a weighing. Another advantage is that swinging starts when the pans are released, without fanning, and that the balance case is kept closed.

To use this method the beam-adjustment weights *IIII* are so set that, when the pan arrests are gently released, the beam will swing to the left about 5 divisions. The end point of this first swing is taken as the zero point of the empty balance. The sensitivity is the change caused in the first-swing rest point by a weight of 1 mg. It should be at least 3–4 full divisions since the reproducibility of the swing determination is usually about 0.3 division.

It is essential that the pans hang vertically without swinging laterally, if a reproducible first swing is to be obtained. Before taking the swing the pan arrests should be manipulated to stop all lateral swinging of the pans.

Procedure. Weighing with Notched-beam Chain Balance. Set the rider at zero. In this type balance the rider must at all times be on the beam since the notched positions for the rider start at the left-hand end of the beam rather than at the center. Adjust the chain position so that the first swing is about 5 divisions to the left. Adjust the vernier, by its auxiliary knob, to make the chain scale reading exactly 0.00. The balance is now ready for operation.

TABLE 2

DATA FOR A TYPICAL WEIGHING

Notebook Page

Determination of true zero:

Scale readings	5.1	13.7
	5.3	13.5
	5.5	
Average	5.3	13.6

True zero $= \frac{5.3 + 13.6}{2} = 9.4$

Weighing:

Weight on pan	
	20
	10
	10
	2
	1
	0.500
	0.200
	0.050
	0.020
	0.010
	43.780

	Swings with rider at 3 mg		Swings with rider at 4 mg	
	7.6	13.5	3.6	12.5
	7.8	13.3	3.8	12.3
		13.1		12.1
Average	7.7	13.3	3.7	12.3

Rest point $= \frac{7.7 + 13.3}{2} = 10.5$ $\quad \frac{3.7 + 12.3}{2} = 8.0$

Sensitivity = 2.5 units per mg
Scale difference with weight 43.783 = 1.1 division = 1.1/2.5 = 0.4 mg
True weight = 43.783 + 0.0004 = 43.7834 g

To make a weighing proceed just as in the use of a rider balance until the weight inequality is within 1 g. Close the balance case, and make adjustments to the nearest 0.1 g with the rider. Finally, adjust the chain until the first swing point is within 5 divisions of the zero swing point as previously determined. Compute mentally the weight change needed to bring the first swing to the zero point. Move the chain the

computed amount, and again determine the swing. It should now agree with the zero point. If not, make the necessary small chain adjustment.

Example: With weight of 17.364 g the swing is −7.0. The zero point is −5.0. The previously determined sensitivity at this load is 6.0 divisions per milligram. Therefore the weight is too heavy by 2.0 divisions or 2.0/6.0 = 0.3 mg. Subtraction of this from the weight on the pans gives 17.3637 g as the exact weight.

Care of the Balance

The balance is a delicate precision instrument which will not function properly if abused. Each student is individually responsible for knowledge of and adherence to the following rules on the use and care of the balance.

1. Be sure that the beam is locked before changing a weight, whenever the inequality of mass on the two pans exceeds 1 g. The pan arrest will usually support a load of 1 g or less.

2. Always release the beam gently. Avoid a sudden jar which might damage the knife edge.

3. Always close the balance case before observing swings. Air currents must be avoided.

4. Do not overload the balance. Most student-type balances are designed for loads of 200 g on each pan.

5. Never weigh any chemical or moist object directly on the balance pan.

6. Never place a hot object on the balance pan. If an object is warm, its weight will be too light because of convection currents set up by the rise of heated air.

7. Handle the weights with forceps. Never use the fingers. Do not use the ivory-tipped weight forceps for any other purpose than to handle weights.

8. Objects to be weighed should be handled with tongs or forceps whenever the shape of the object permits. Round objects, such as weighing bottles, may be handled by the fingers, but care must be taken to prevent weight changes because of moisture from the hand. Dry the hand just before lifting an object to the balance pan. Do not hold any object longer than necessary.

9. Remove all objects, and close the balance case on completion of a weighing.

10. Clean up any material spilled on the pan or within the balance case.

11. Always support the rider on its carrier hook at the completion of a weighing. Suspend the rider directly above the center of the beam so

that it cannot interfere with free swinging of the beam. If a chain balance is used, set the chain at zero.

12. Do not monopolize the balance. Respect the rights of others.

13. If the balance is out of order, report the fact immediately.

LABORATORY EXERCISES

The following should be completed and the notebook should be submitted to the instructor for approval before new assignments are started.

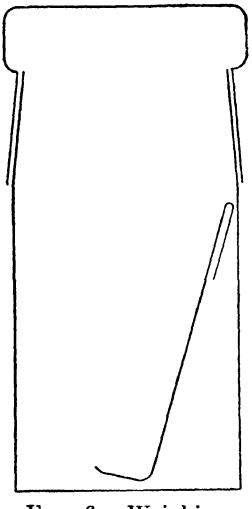


FIG. 6. Weighing bottle with spoon.

1. Practice obtaining a reproducible rest point by the method of multiple or single swings, as specified by the instructor.

2. Determine the sensitivity of the balance for loads of 0, 10, 20, and 50 g. Place weights of proper denomination on the pans so that they are approximately balanced. Determine by the proper method the rest point. Add 1 mg by the rider or chain, and again determine the rest point. Construct a graph in the notebook showing sensitivity on the y-axis as a function of load on the x-axis. This graph will be useful in making mental computations of the adjustment needed at any weight to bring the rest point into coincidence with the zero point.

3. If you are using a rider balance, test the rider. Place the rider on the 5- or 10-mg division and a corresponding weight on the left-hand pan, and then see whether the rest point coincides with the zero point. If the rider is grossly in error, notify the instructor. A difference of 0.1 to 0.2 mg in the weight of the rider and the comparison weight can be neglected.

4. Weigh separately a crucible and cover, and then reweigh the two together. The results should agree within about 0.0003 g. Record in notebook.

5. Equip a weighing bottle with a spoon, as shown in Fig. 6 (see page 34 for directions for making the spoon). Place about 1 g of some dry chemical, such as sodium chloride (the chemical will be provided on the side shelf), in the bottle, and weigh accurately. Also weigh accurately a small empty beaker. Transfer a spoonful of the salt from the weighing bottle to the beaker, taking care to avoid loss. Reweigh the bottle, and compute the exact weight of the sample withdrawn. Now

reweigh the beaker, and compute the weight of sample in it. The results of the two weights of sample should agree within 0.0003 g or better. Record in the notebook.

ERRORS IN WEIGHING

The most common weighing errors outside of personal errors in misreading turning points of the pointer or miscounting the weights are due to inaccuracies in the values of the weights; these may be eliminated by calibration, as described in a later section. Other errors are:

1. The two arms of the beam may not be of the same length.
2. Moisture may condense on an object and change its weight.
3. If the temperature of the object is not that of the surroundings, the weight will be affected.
4. Electrification of glass vessels will cause induced charges in adjacent metal parts, and the balance will be caused to swing in an erratic manner.
5. The balance may not give reproducible swings.
6. Buoyancy due to air may affect the apparent weight.

The effects of these errors and methods for their avoidance are discussed in the following paragraphs.

Inequality of Balance Arms. Most analytical balances are so accurately made that error due to inequality of arms does not exceed one part in several thousand, and this error will not affect ordinary analytical results. Further, since most analyses involve a ratio of weights, a small inequality of the balance arms will not affect the results at all; all weighings made on a particular balance will be in error by a constant factor.

Any error due to balance-arm inequality may be eliminated by (1) weighing by substitution or (2) double weighing.

Weighing by substitution. Place the object on the left pan, and counterpoise it by a suitable *tare* on the other pan. Copper shot placed in a beaker or crude weights may be used as a tare. Observe the rest point after the tare is added. Remove the object, and add weights to the left-hand pan until the rest point coincides with the one originally obtained. Since the object and weights have been placed on the same pan of the balance, their masses have been directly compared without any assumptions being made regarding the lengths of the lever arms.

Double weighing. Weigh the object as usual, then interchange the weights and object, and reweigh. The arithmetic mean in the two weights is very near to the true weight.

Let W_1 = weight when object of mass M is on the left pan
W_2 = weight when object is on the right pan
L_1 = length of the right-hand arm of balance
L_2 = length of the left-hand arm of balance
$ML_2 = W_1L_1$ and $ML_1 = W_2L_2$ (from first and second weighings)

Multiplying the equations by one another and solving for M gives

$$M^2 = W_1W_2 \quad \text{or, approximately,} \quad M = \frac{W_1 + W_2}{2}$$

Moisture. Condensation of water vapor on dry samples or precipitates may cause a weight gain of as much as several milligrams if the sample is exposed to air. Consequently, it is standard practice to weigh all samples in a stoppered bottle. Usually ignited precipitates are weighed in a covered crucible; if the weighing is made rapidly, moisture pickup will not cause appreciable error. In the most exact work it is advisable to weigh crucibles with ignited precipitates inside stoppered bottles, similar to the weighing bottles used for samples. This is not required in student work.

Glass containers may adsorb appreciable amounts of water vapor if the surface area is large. Whenever it is necessary to use containers, such as U-tubes or adsorption vessels, the weighings should be made with a *counterpoise*. This is a glass vessel similar to the one which contains the sample but lighter in weight. The counterpoise is placed on the right-hand pan for all weighings. If the amount of moisture adsorbed by the counterpoise is about the same as that of the sample container, the error due to adsorption of water is made negligibly small. To insure that counterpoise and sample vessel have the same moisture content and to avoid electrification of the glass, both are wiped with a damp cloth and placed within the balance case 10–15 minutes before the weighing is done. An adsorption tube weighed on successive days without a counterpoise showed changes of several milligrams, but, when a counterpoise was used, the variations were reduced to a few tenths of a milligram.

Temperature. It is absolutely essential that the object to be weighed be at room temperature. Frequently a student is tempted to weigh an ignited crucible while it is still warm, to save time of waiting. Invariably such weighings are too light, because convection currents set up in the balance case tend to push up on the left-hand pan and retard the swings of the balance.

Electrification. When glass vessels are wiped with a dry cloth, they acquire a charge of static electricity. This may cause the swings

of a balance to behave in a very erratic manner, since, as the beam moves, the charge on the object induces charges in other parts of the balance. Some time may be required to dissipate a static charge on a glass surface. When large glass vessels are to be weighed, they should first be wiped with a damp cloth, which will aid in dissipating charges, and then allowed to stand until most of the surface moisture is evaporated and equilibrium is attained with atmospheric humidity. Normally no special precautions are taken for weighing bottles which are of small area except that they are not rubbed or wiped prior to weighing.

Defective Balances. Occasionally it is found that a student balance will no longer give reproducible readings. The only solution for this is a thorough overhauling by a skilled repair man. A variety of defects may affect the accuracy and sensitivity of balances. Most common is a shifting of the knife edges so that they do not rest in identically the same positions each time the beam is lowered.

The student should know the following simple tests to apply to balances prior to use:

1. Determine the reproducibility of the zero point. A number of consecutive determinations should be made of the zero point, with the beam raised and lowered before each observation. If the knife edges are loose, this will show up, because they will not return to the same position each time the beam is lowered, and consequently the effective lengths of the beam arms will not remain constant.

2. Determine the sensitivity at no load and at 50 g load.

In these tests the zero point should be reproducible to 0.2 division for multiple swings and to 0.5 division for single swings. The sensitivity should be at least 2 divisions per milligram if the multiple-swing method is used and 4–5 divisions per milligram for single swings. The sensitivity at 50 g should not be decreased by more than 20 per cent from the sensitivity at no load. When these conditions are met, the balance should give readings which are reproducible to 0.1 or 0.2 mg.

Occasionally it is found that a balance suddenly tends to show a creeping rest point. Usually this is due to uneven warming and expansion of the beam, by exposure to sunlight. It is essential to protect the beam from sunlight at all times. A north exposure room is preferred for a balance room. Radiators should not be located too near the balances.

Buoyancy. When an object is weighed in air, the apparent weight is affected by the amount of air displaced. Although this effect is not of appreciable magnitude in most student work, it should be thoroughly understood, and a buoyancy correction should be applied in the rare cases where needed.

According to the Archimedes principle, a body surrounded by a fluid is buoyed up by an amount equal to the weight of fluid displaced. A pound of brass will displace about 2 oz of water when immersed. Consequently, if a pound of brass is weighed under water, the apparent weight will be only 14 oz.

Air is a fluid of low density. Under average conditions of temperature, pressure, and humidity a liter of air weighs about 1.2 g. Therefore an object whose volume is 1 l. will be buoyed up by air to the extent of 1.2 g, or the apparent weight of such an object is too light by 1.2 g.

In a weighing both the object and the weights are displacing air, and there is a buoyant effect on both sides of the beam. The effect of this

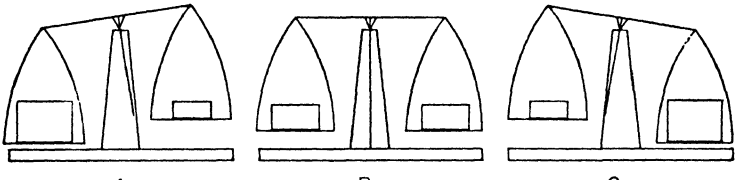


FIG. 7. Effect of buoyancy in weighing.

on the weighing depends on the relative volumes of the object and the weights. We may consider the three cases illustrated in Fig. 7. In *A* the object has a smaller density than the weights, and consequently it occupies a larger volume. If the object and weights are exactly balanced in air and the air is then pumped out of the balance case, the object will then appear to be heavier, for the left-hand pan will sink as the buoyant effect of the air is removed. To restore the condition of balance, weights must be added to the right-hand pan. Thus the true weight (weight in vacuo) is greater than the apparent weight (weight in air). In *B* the object and weights are of equal density and occupy the same volume. Removing the air does not affect the equilibrium, or the weight in vacuo is the same as the weight in air. In *C* the density of the object is greater than that of the weights. The weight in vacuo is less than the weight in air.

The relations discussed in the preceding paragraph may be put in the form of an equation:

$$W_v = W_a + \text{buoyancy on object} - \text{buoyancy on weights}$$

or

$$W_v = W_a + \frac{W_a}{D_o} \times \text{density of air} - \frac{W_a}{D_w} \times \text{density of air}$$

where W_a = weight in air (the apparent weight)
W_v = weight in vacuo (the true weight)
D_o = density of object
D_w = density of weights, or approximately 8

Since the density of air at average temperature, pressure, and humidity is about 0.0012 g per milliliter, we have

$$W_v = W_a + \frac{W_a}{D_o} \times 0.0012 - \frac{W_a}{8} \times 0.0012$$

Simplifying, we have

$$W_v = W_a \left[1 + \left(\frac{1}{D_o} - \frac{1}{8} \right) 0.0012 \right]$$

This equation [4] may be used to compute the weight in vacuo from the weight in air or the reverse, depending on what data are given.

To illustrate the use of the buoyancy correction we may consider a practical application. It is found that a 100-ml pipet delivers a volume of water which weighs 99.60 g in air. The weight in vacuo must be computed, since the density of water is given in tables on the basis of weights in vacuo. Substitution of the weight in air into the preceding equation gives a value of 99.71 g for the weight in vacuo. Handbook tables give a density of 0.9959 for water at the temperature of the experiment, 21°C. Division of the weight of water by its density gives a volume of 99.71/0.9959 = 100.12 ml.

It is not usually necessary to apply a buoyancy correction for the weighings performed in an analysis. Ordinarily the sample or precipitate weighs in the neighborhood of 0.2 to 0.5 g, and the density is of the order of 2 to 4. Therefore the volume of air displaced by the solid is not over 0.1–0.2 ml, and its weight is not over 0.1–0.2 mg, which can be neglected. Further, every analysis involves the ratio in two weights. If each of these weights is in error by about the same amount, the effect of buoyancy is canceled. The buoyancy correction is applied only when large volumes are weighed, as in calibration of glass apparatus by measuring the volume of water delivered or contained.

WEIGHING OF SAMPLES AND PRECIPITATES

Weighing Bottles. Samples for analysis are almost universally weighed in weighing bottles, except when an exact sample is to be taken as described below. Weighing bottles are small glass bottles having flat

[4] It is obvious that the equation is not strictly rigorous since we have computed the volume by the ratio W_a/D_o rather than the ratio W_v/D_o. The difference between the two volumes so computed is so small that the approximation introduces no error in the buoyancy correction.

ends with straight sides, and ground-glass stoppers. In the past the stopper was ground to fit the inside wall of the bottle. This construction has the disadvantage that particles of powdered sample may become attached to the stopper and be lost when the stopper is removed. Recently there have been marketed weighing bottles whose stoppers fit on the outside wall of the bottle, as illustrated in Fig. 6.

Samples for analysis are placed in weighing bottles after they have been properly prepared, by grinding, drying, and so on, and kept in a desiccator until needed. In weighing a sample, the bottle, with contained material, is first weighed. Approximately the desired amount of material is removed and quantitatively transferred to a suitable container. The bottle with the remaining material is then reweighed. If no material has been lost, the weight of sample taken is the difference in the two weights. This procedure has the advantage that the material is not exposed to the air while the weighings are made, thereby eliminating the possibility of absorbing moisture or carbon dioxide from the air.

In weighing by difference it is not necessary to determine the zero point of the empty balance; the second weighing is made to the same rest point as the first. It is obvious that this procedure can introduce no error, provided the zero point remains the same in the two weighings. Any error introduced into the single weighing is canceled in taking the difference.

Portions of sample may be removed from the bottle by pouring, but much time is saved by construction of a spoon that will remove portions of 0.10–0.15 g. This spoon is kept in the bottle for all weighings. It is conveniently constructed from a 1-by-3-cm sheet of aluminum or nickel. The bowl is formed by placing the sheet on a block of soft wood, holding a small steel ball at the proper place, and striking the ball a sharp blow with a hammer. After the bowl is formed, the sheet is trimmed and the handle bent to the proper angle, as shown in Fig. 6.

Exact Samples. It often happens that the accuracy of an analysis does not justify weighing samples with an accuracy greater than 0.0005 g. If many samples are to be weighed with this accuracy, time is saved by weighing out samples of a given weight, such as 0.5000 or 1.000 g. A container, usually built in the form of a grocer's scoop, is placed on the balance pan and accurately weighed. Additional weights totaling the desired amount of sample are then added to the right-hand pan, and sample is added to the left-hand pan until the two are in balance. The sample is slowly poured onto the scoop until a slight excess is added, and then the proper amount is withdrawn, by means of a small spatula. Further additions, if necessary, are made from the spatula. A pair of exactly balanced (tared) watch glasses is sometimes used. A damped balance is useful in this operation.

Liquid Samples. A clean dry weighing bottle is accurately weighed, then approximately the desired amount of liquid is introduced, from a graduated pipet, and the bottle is stoppered and reweighed. The sample is then transferred to the desired container according to the directions given on page 86. If a liquid sample is large, it may be necessary to make a correction for the buoyancy of the air, as explained previously.

Precipitates. The final precipitates obtained in gravimetric analyses are weighed after drying or ignition. Frequently these precipitates will readily take up carbon dioxide or water vapor from the air. The crucibles containing the precipitates should be weighed with the cover on. In extreme cases, where the absorption from air is very rapid, the weighing must be very quickly done as follows: After the first heating, an approximate weight is determined. After subsequent heatings, the approximate weight is placed on the balance pan before the crucible is removed from the desiccator. After the crucible is in the balance case, it is only necessary to observe the rest point, and from this and the predetermined sensitivity of the balance the exact weight is calculated. Although all weighings in crucibles are made by difference, a considerable time interval may elapse between the weighing of the empty crucible and the weighing of the sample; it is therefore necessary to determine the zero point of the balance before each weighing.

THEORY OF BALANCE SENSITIVITY

The factors in the construction of a balance which influence its sensitivity can readily be understood by the application of the principles of simple levers. When a lever is in a position of equilibrium, the force moments which tend to cause clockwise rotation must equal those which tend to produce rotation in a counterclockwise direction. It may be recalled from elementary physics that "force moment" is defined as the product of the force (mass × acceleration of gravity g) and the lever arm (the perpendicular distance from the fulcrum to the vertical line passing through the point of application of the force).

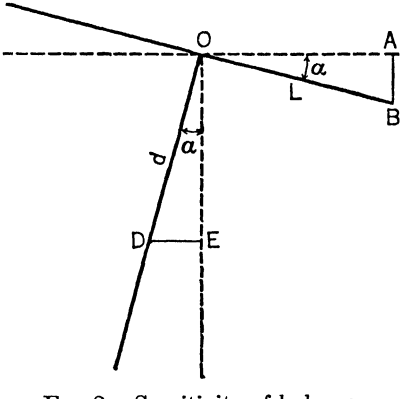


FIG. 8. Sensitivity of balance.

In Fig. 8 the dotted lines represent the equilibrium position of the unloaded balance. The solid lines indicate the condition of equilibrium attained after a small weight m

has been added to the right-hand pan. In this position the force producing clockwise rotation is caused by the attraction of gravity for the mass m. The counterclockwise rotation is produced by the gravitational attraction for the mass of the beam M, which acts through its center of gravity D, located d cm below the knife edge.

Application of the force moment principle gives

$$Mg\overline{DE} = mg\overline{OA}$$

By simple trigonometry,

$$\overline{DE} = \overline{OD} \sin \angle DOE$$

$$\overline{OA} = \overline{OB} \cos \angle AOB$$

Since their respective sides are mutually perpendicular to each other, the angles DOE and AOB are equal and are designated as α in the following. Further, it can be seen from the figure that $\overline{OD}$ is the distance d and $\overline{OB}$ is the length L of the balance arm. The use of these substitutions reduces the first equation to

$$Mgd \sin \alpha = mgL \cos \alpha$$

or

$$\frac{\sin \alpha}{\cos \alpha} = \tan \alpha = \frac{mL}{Md}$$

For small angles the tangent is directly proportional to the angle itself. Thus, the final relationship between the displacement or sensitivity of the balance and the weight causing the displacement is

$$\alpha = \frac{mL}{Md}$$

The displacement caused by unit weight has previously been designated as the sensitivity. From the foregoing equation it may be seen that the sensitivity increases with length of the beam but decreases with increase in the mass of the beam–pan system and with increase in the distance from the fulcrum to the center of gravity. This distance may be varied somewhat at will, for there is on the pointer a bob whose position is adjustable. If the bob, shown as X in Fig. 4, is raised, the sensitivity is increased, but the *period* of the balance is correspondingly increased. Increase in length of the beam also increases the period.

In the previous discussion it is assumed that the beam is rigid and that the knife edges are in a plane. As the load is increased, the sensi-

tivity may decrease very rapidly because of a bending of the beam, which brings the pan knife edges below the plane of the beam knife edge. High-quality balances show less variation of sensitivity with load than cheaper ones, because of better construction which minimizes the amount of distortion of the beam. Some balances even show increased sensitivity with load. This is achieved by constructing the balance so that the pan knife edges are slightly above the plane of the beam knife edge. As load is applied, the distortion of the beam brings the three knife edges into the same plane.

WEIGHTS

Analytical Weights. Weights are provided [5] in sets usually containing the units 50, 20, 10, 10′, 5, 2, 2′, 1 and the fractionals 0.5, 0.2, 0.1, 0.1′, 0.05, 0.02, 0.01, 0.01′, 0.005, 0.002, 0.002′, 0.001 g. When duplicate values of the same denomination are provided one of them should be marked by a punched dot. The larger weights are usually of brass and are protected from corrosion by a lacquer coat or by gold, chromium, or platinum plating. The fractional weights are of platinum or aluminum. The rider is commonly made of aluminum.

The National Bureau of Standards [6] has formulated a classification of and lists of tolerances for each type of scientific weight. The classes are designated as M, S, and S-2. Class M weights are for use as primary laboratory reference standards, against which other weights may be checked. They are of one-piece construction. Class S weights are for use in most of the accurate weighings of scientific laboratories. They may be of two-piece construction, with a screw knob, so that exact adjustment of mass may be made by placing small pieces of metal within the cavity beneath the knob. Aluminum may be used for the fractionals below 50 mg. Class S-2 weights are for common routine laboratory use and are adequate for student requirements. All the fractionals may be of aluminum. The allowable tolerances are five times those permitted for class S weights. The allowable tolerances for all three classes are shown in Table 3.

Riders. Each balance is designed for a rider of a particular weight and cannot be used with riders of other denominations. The mass of

[5] Weight sets are now available with the denominations 50, 30, 20, 10, 5, 3, 2, 1 g, and corresponding fractionals. They have the advantage that there are no duplicate weights in the set.

[6] See *Bur. Standards Circ.* 3, "The Design and Tests of Standards and Mass," 3d ed., 1916.

TABLE 3

BUREAU OF STANDARDS TOLERANCES FOR ANALYTICAL WEIGHTS

Denomination	M	S	S-2
100 g	0.5 mg	0.5 mg	2.5 mg
50	0.3	0.3	1.5
20	0.2	0.2	1.0
10	0.15	0.15	0.75
5	0.15	0.15	0.75
2	0.10	0.10	0.50
1	0.10	0.10	0.50
500 mg	0.05	0 05	0.25
200	0.05	0.05	0.25
100	0.05	0.05	0.25
50	0.03	0.03	0.15
20	0.03	0.03	0.15
10	0.02	0.02	0.10
5	0.02	0.02	0.10
2	0.01	0.01	0.05
1	0.01	0.01	0.05

the rider is the mass indicated by the graduation mark directly above the pan knife edge. The most common sizes are 5 and 10 mg, although both 6- and 12-mg riders are frequently used. Since riders of these sizes are so similar in appearance, it is necessary to test the mass of a rider, as described on page 28, before it is installed. In the calibration of weights the rider is not calibrated, since the correction to be used would vary with the position on the beam. It is tested against a calibrated weight. If it is too light, it must be discarded. Heavy riders can be adjusted to the proper weight by successively filing off small portions until the true mass is reached.

Calibration of Weights

Since the weight of an object is determined from the sum of the masses of small weights which just balance the object, it is essential in exact work that the masses of the individual weights be accurately known. Therefore every chemist should calibrate his weights before using them and should recheck his calibration at least once a year to detect any changes in mass which may occur because of corrosion. In general, calibration is not required of students in the first semester's work because it is very time-consuming for an inexperienced worker. Before the advanced work of the second semester is begun, the weights should be calibrated, and the weight corrections should be used at all times. After one semester of experience a student should be able to calibrate

his weights in a single laboratory period, if the single-swing method of weighing is used.

Weights may be calibrated on either a relative or an absolute basis. In relative calibration some one of the weights is selected as standard, and corrections are determined to make the masses of all other weights agree with that of the selected standard. That is, the correction for the 5-g weight is the value to make its mass exactly half that of the 10-g weight. In absolute calibration a weight of known mass is provided as the standard, and correction values are determined to make all weights agree with the standard one. Absolute calibration is not necessary in most work; it is sufficient to have the various weights of a set agree with one another even though the absolute values may all be in error. The reason for this is that all analyses involve the ratio in the weight of the initial sample and some product from that sample. If all weighings are in error by the same fraction, the effect of the error is canceled in taking the ratio.

Method for Calibration. A modification of the T. W. Richards[7] method is used for the relative calibration. To eliminate the effect of inequality of balance arms the method of substitution is employed. Weights from another set, which need not be calibrated, are used as tares. All the fractional weights, when taken together, should constitute a gram. Since the 1- and 2-mg weights are never used, it is convenient to add an extra 10-mg weight from another set to supplement the other small weights. The borrowed 10-mg weight is used as a preliminary standard. It is denoted in the tabulation as $\overline{0.01}$. The comparison begins with this weight and proceeds upwards.[8]

Procedure. Place the $\overline{0.01}$ weight on the left pan; counterpoise with the rider, chain, or a suitable weight; and observe the rest point. This does not need to agree with the zero point. Replace the $\overline{0.01}$ weight with a 10-mg weight from the set, and determine the new rest point. Record the data as in Table 4. From the sensitivity and the difference in the two rest points, compute the difference in weights between $\overline{0.01}$ and the 10-mg weight. In the data of Table 4, 0.01 is 0.6 mg heavier than $\overline{0.01}$. Its relative value is then 0.0106 g, if a value of 0.0100 g is assumed for the preliminary standard. In the same manner obtain a relative value for 0.01′.

Place 0.01 and 0.01′ on the left pan, and counterpoise by a suitable weight on the right (the chain may be used). Obtain the rest point.

[7] T. W. Richards, *J. Am. Chem. Soc.*, **22**, 144 (1900).

[8] If the balance has a 5- or 6-mg rider the borrowed weight is 5 mg; it is then used as the preliminary standard.

Replace 0.01 and 0.01′ by 0.02, and obtain the new rest point (see comparison 3 of Table 4). In the data of Table 4, 0.02 is 0.6 mg lighter than 0.01 + 0.01′, whose combined relative values are 0.0211 g. Therefore the relative value for 0.02 is 0.0205 g.

Proceed in this manner with all the comparisons indicated in Table 4 (data for comparisons 5–13 are omitted from the table). In comparison 15 a Bureau of Standards calibrated weight is introduced to give the basis for an absolute calibration. This step is omitted if the calibrated weight is not available.

The relative values of column *B* in Table 4 are the values of all weights in terms of the preliminary standard, the borrowed 0.01 weight. It may be noted that these values differ widely from the nominal values for the various weights. The reason is that any error in the value of the preliminary standard is greatly magnified in the comparisons; for example, the 10-g weight is 1000 times the mass of a 0.01-g weight. It is better therefore to take one of the larger weights as the final standard. In Table 4 the Bureau of Standards 10-g weight is taken as the reference.[9] If a certified weight is not used, one of the 10-g weights of the set is taken as the reference. In Table 4 the preliminary value for the reference weight is 10.1844 g. Aliquot values are computed from this for all the other weights of the set, based on ratios of their nominal values. For example, the aliquot value for the 1-g weight is one tenth of 10.1844 g, or 1.0184 g; the aliquot value of the 20-g weight is twice 10.1844 g, or 20.3688 g.

After the ideal values are computed, the correction value for each weight is determined from the relation:

$$\text{Correction} = \text{relative value} - \text{aliquot value}$$

For the 20-g weight the correction is 20.3670 − 20.3688, or −0.0018 g (−1.8 mg). When computed in this manner, the correction has the proper sign, and in the use of the weights it is to be added algebraically to their nominal values. That is, the nominal value plus the correction gives the true value. The 20-g weight has a nominal value of twice that of the 10-g weight. Adding −1.8 mg gives its true value of 19.9982 with reference to the 10-g weight as standard. The correction is negative because the weight does not weigh so much as its nominal value.

After the corrections are computed, prepare a card showing the corrections in milligrams for each weight of the set. Keep this card with

[9] If there is a correction to the face value of the reference weight, it may be taken into account by the method of Blade. See *Ind. Eng. Chem., Anal. Ed.*, **11**, 499 (1939).

TABLE 4

DATA FOR CALIBRATION OF WEIGHTS *

(Notebook Page)

Weights Compared *A* = standard *B* = weight of unknown value	*Rest Point*	*Sensitivity*	*Difference*	*Relative Value* *A*	 *B*	*Aliquot Part of 10-g Wt*	*Correction in mg*
1. *A.* $\overline{0.01}$	−5.0	6.0		0.0100			
B. 0.01	−1.5	6.0	+0.0006		0.0106	0.0102	+0.4
2. *A.* $\overline{0.01}$	−5.0	6.0		0.0100			
B. 0.01′	−2.0	6.0	+0.0005		0.0105	0.0102	+0.3
3. *A.* 0.01, 0.01′	−4.0	6.0		0.0211			
B. 0.02	−7.6	6.0	−0.0006		0.0205	0.0204	+0.1
4. *A.* 0.02, $\overline{0.01}$, 0.01, 0.01′	−3.0	6.0		0.0516			
B. 0.05	−7.2	6.0	−0.0007		0.0509	0.0509	0.0
. . .							
14. *A.* 5, 2, 2′, 1	−2.0	6.0		10.1834			
B. 10′	+1.0	6.0	+0.0005		10.1839	10.1844	−0.5
15. *A.* 10′	−3.0	6.0		10.1839			
B. 10 (Bur. Stand.)	0.0	6.0	+0.0005		10.1844	10.1844	Standard
16. *A.* 10, 10′	−3.0	5.5		20.3683			
B. 20	−10.0	5.5	−0.0013		20.3670	20.3688	−1.8
17. *A.* 20, 10, 10′, etc. . . .	−5.0	5.0		50.9187			
B. 50	+5.0	5.0	+0.0020		50.9207	50.9220	−1.3

* Rest points were determined by the single-swing method—the + and − signs refer to scale positions measured from the center mark.

the weights, for ready use.[10] If any weight has an abnormally large correction, report it to the instructor. If possible such weights should be replaced.

Calibration of Chain. Determine the zero point of the balance. Compare the chain with calibrated weights, at 10-mg intervals from 10 mg to the full value of the chain, by placing the weight on the left-hand pan and setting the chain to bring the rest point into coincidence with the zero point. The correction for each weight is given by the relation:

$$\text{Chain correction} = \text{correct weight} - \text{scale reading}$$

For each setting of the chain the correction is added to the scale reading to give the true weight.

Typical data for a chain calibration are given in Table 5. These data were obtained with a new balance, using weights which had been calibrated with reference to a Bureau of Standards 10-g weight. They

[10] Instead of adding up the corrections for all the individual pieces used in each weighing, it is convenient to prepare a table such as the following from which the *total* corrections for the fractional and the unit weights can be read directly. To employ such a table, it is necessary to use the *fewest* possible number of weights and always to use an *unprimed* weight instead of a primed one. Three lines of the table have been filled in in terms of the weights described in Table 4. The following additional corrections have been assumed: 100 mg, 0.1 mg; 1 g, −0.1 mg; 2 g, 1.4 mg; 2′ g, −1.1 mg; 5 g, —1.2 mg.

TABLE OF WEIGHT CORRECTIONS IN MILLIGRAMS

Amounts to be Added Algebraically to Face Values of Weights on Pan

Fractional Weights

Milligrams	0	10	20	30	40	50	60	70	80	90
0	..	0.4	0.1	0.5	0.8	0.0	0.4	0.1	0.5	0.8
100	0.1	0.5	0.2	0.6	0.9	0.1	0.5	0.2	0.6	0.9
200										
.										
.										
.										
900										

Unit Weights

Grams	0	1	2	3	4	5	6	7	8	9
0	..	−0.1	1.4	1.3	0.3	−1.2	−1.3	0.2	0.1	−0.9
10										
.										
.										
.										
50										

show the need for calibration of chains if precise weighings are to be made.

Construct a graph showing the correction value of the chain at the experimental points, and connect the points by straight lines. Correction values for any chain reading can then be determined by reference to this graph.

TABLE 5

CALIBRATION OF CHAIN

Weights on Left Pan	*Correction for Weights*	*True Weight*	*Scale Reading*	*Correction for Chain*
10 mg	+0.1	10.1	10.0	+0.1
20	−0.2	19.8	19.7	+0.1
20 + 10	−0.1	29.9	29.7	+0.2
20 + 10 + 10	−0.1	39.9	39.7	+0.2
50	0.0	50.0	49.8	+0.2
50 + 10	+0.1	60.1	59.8	+0.3
50 + 20	−0.2	69.8	69.6	+0.2
50 + 20 + 10	−0.1	79.9	79.6	+0.3
50 + 20 + 10 + 10	−0.1	89.9	89.6	+0.3
100	0.0	100.0	99.6	+0.4

Calibration of Notch-beam Rider. Determine the zero point of the balance. Place a calibrated 0.1-g weight on the left-hand pan, and set the rider at the 0.1-g mark. Determine the rest point. From the deviation between zero and rest points and the sensitivity of the balance, compute the weight difference between rider and weight. From the corrected value of the weight and the weight difference, compute the effective weight of the rider. The correction is given by the relation,

$$\text{Rider correction} = \text{true weight} - \text{nominal value}$$

Determine in similar manner the corrections for other settings of the rider. The correction values are to be added to nominal values of the rider at the various settings to give the true weight. It is generally found that the correction values do not exceed 0.1 mg at any setting and that they can be neglected in any but the most exact work.

QUESTIONS

1. Explain the functions of each of the following parts of the balance illustrated in Fig. 4: (*a*) *K*, (*b*) *BC*, (*c*) *PC*, (*d*) *F*, (*e*) *RC*.

2. Why are computations of rest points from swing data not carried beyond the nearest $\frac{1}{10}$ division?

3. How much should a rider weigh to be used on each of the following balances:

(*a*) The zero mark is over the central knife edge, and the 6 mark is over the knife edge which supports the pan.

(*b*) The zero mark is over the central knife edge, and the beam is graduated to 12, but the 10 mark is over the knife edge which supports the pan.

(*c*) The zero mark is over the knife edge which supports the left pan, and the 10 mark is over the knife edge for the right pan.

4. In which of the following cases is it satisfactory to assume that 10 is the zero point of the balance rather than to determine the rest point from swing data:

(*a*) An object is to be weighed to the closest 2 mg.

(*b*) A series of samples is to be weighed to the closest 0.1 mg by successive removals from a weighing bottle.

(*c*) The weight of a precipitate is to be determined to the closest 0.1 mg by the difference in weights of an empty crucible and filled with the precipitate; at least 6 hours elapse between the weighings.

(*d*) The weight of a piece of metal for a density determination is to be found to the closest 0.1 mg.

5. What is the *sensitivity* of a balance? What is the advantage of weighing by sensitivity rather than by adjustment of the rider until a point of balance is obtained?

6. Describe a procedure for determining the sensitivity curve of a balance. What should be the general shape of this curve?

7. If the method of swings is used, why is it desirable that the sensitivity of the balance be at least 2 divisions per milligram?

8. If the method of first deflection is used, why is it desirable that the sensitivity of the balance be around 6 divisions per milligram?

9. What effect does raising the bob on a balance pointer have on the sensitivity? on the period?

10. How does the mass of the balance system affect the sensitivity of the balance? How is this reflected in the construction of the balance?

11 What is the effect on the sensitivity of a balance of:

(*a*) Lowering the bob on the pointer.

(*b*) Increasing the total load.

(*c*) Changing the adjustment of one of the screws on the end of the beam.

12. What maximum load should be placed on each pan of the analytical balance? What harm will be caused if the balance is greatly overloaded?

13. What injury might be done to a balance if an object is placed on the pan while the beam is unlocked?

14. Why is it permitted to leave the beam arrest lowered while changing fractional weights?

15. Describe the method of weighing by substitution. When should this method be used? What other method of weighing can also be used in such circumstances?

16. Criticize and correct the statement, "The weight in vacuo of an object is always greater than the weight in air."

17. If the density of a metal referred to conditions in vacuo is the same as in air, what can be concluded about the density of the metal and the density of the weights used in the experiment?

18. What effects will be noticed in weighing a glass vessel if the surface is electrified? How may these effects be avoided?

19. Explain the following swing readings obtained when a sample of an anhydrous material was weighed on a watch glass.

8.0	13.4
8.3	13.5
	13.6

20. A large bulb used to weigh gases had a weight of 35.5063 g at one time and 10 hours later weighed 35.5092. Offer a possible explanation, and suggest a method of avoiding the discrepancy.

21. Why is it necessary to apply the buoyancy correction in the calibration of volumetric apparatus, for volumes of 10–250 ml? Why is it usually not necessary to apply the buoyancy correction in the weighing of sample for analysis and in the weighing of precipitates obtained in analysis?

22. Describe a proper technique for weighing each of the following:

(*a*) A piece of platinum foil.

(*b*) Solid $BaSO_4$ which is non-hygroscopic.

(*c*) Solid $Na_2CO_3 \cdot 10H_2O$ which is highly efflorescent.

(*d*) A sample of vinegar.

(*e*) An absorption tube for CO_2 which is filled with about 100 ml strong KOH solution.

23. Why is relative calibration of weights satisfactory for most analytical purposes?

24. In the calibration of weights why are the values redistributed in terms of one of the larger weights?

25. Why are not buoyancy corrections made during calibration of weights?

26. The correction for a 2-g weight is minus. Is this weight heavier or lighter than its nominal (face) value in relation to the 10-g weight which was selected as a standard for the calibration?

27. In which of the following cases would an absolute rather than a relative calibration of weights be necessary:

(*a*) In a large industrial laboratory where the samples and precipitates are weighed by different operators using various sets of weights.

(*b*) In a gravimetric analysis where the sample and precipitate are weighed with the same set of weights but on different balances.

(*c*) In a volumetric analysis in which a solid primary standard is used, and the sample is a weighed portion of a liquid.

(*d*) As in (*c*), but where the sample is a measured volume of liquid.

(*e*) In a calibration of volumetric glassware wherein weighings are being made to the closest 0.5 mg.

PROBLEMS

In the following problems which involve the computation of weight from swing or deflection data it is assumed that the object is on the left pan and the rider on the right half of the beam unless otherwise specified.

1. In your locality what is the actual weight in dynes of a 1.0000-g mass?

2. The rest point with the rider at 4 is 10.5 and at 3 is 7.0. Is the rider on the right or left half of the beam?

3. Find the weight of an object to the closest 0.1 mg from the following data:
   Swings of the unloaded balance: 8.3, 11.4, 8.5
   Weights on the pan: 10 g, 5 g, 2 g, 1 g, 500 mg, 50 mg, 20 mg, 5 mg
   Swings with the rider at 1 mg: 14.0, 10.3, 13.8
   Swings with the rider at 2 mg: 8.9, 11.8, 9.1

4. Determine the weight of an object to the closest 0.1 mg from the following:

Swings of the empty balance:	7.1	14.6
	7.3	14.4
	7.5	

Rest point with 13.73 g on the pan and the rider at 8 is 8.5; with the rider at 7 the rest point is 11.1.

5. Determine the mass of an object to the closest 0.1 mg from the following:

Zero point of the balance	10.5
Rest point for 22.513 g	10.0
Rest point for 22.5135 g	8.5

List the weights on the pan, and assume that the balance has a 10-mg rider.

6. The swings of an empty balance are: 8.3, 13.1, 8.6. The rest point with a mass of 16.56 g on the pan and the rider at 6 is 13.0; with the rider at 7 the rest point is 11.2. Where would the rider have to be placed to make the rest point and zero point coincide?

7. The swings of an empty balance are: 5.8, 14.1, 6.1, 13.8, 6.3. The object is placed on the right pan, and the weights on the left pan amount to 12.51 g. The following rest-point data are obtained with the rider on the right half of the beam:

Rider at 3 rest point is	6.8
Rider at 2 rest point is	9.0

What is the weight of the object to the closest 0.1 mg?

8. The following data were obtained with the object on the left pan and the rider on the left half of the beam:

Zero point	9.7
Mass on right pan	24.83 g
Rest point with rider at 4	9.1
Rest point with rider at 5	11.4

What is the mass of the object to the closest 0.1 mg?

9. The zero point of a balance is +4.1 when the single-deflection method is used. With a load of 12.48 g and the rider at 4 the deflection is −1.5. If the sensitivity is 6.5 divisions per milligram, where should the rider be set?

10. The first deflection of a balance with a 100-mg chain is −4.5; from the following deflections calculate where the chain should be set to complete the weighing.

With 27.343 g the deflection is +5.0.
With 27.344 g the deflection is −2.5.

11. In a series of weighings by difference the zero point of the balance is assumed to be 10.0. Actually the zero point as determined by swings is 8.8; the sensitivity at this load is 1.9 divisions per milligram. What error is made in each individual weighing? What error is made in the weight of the sample?

12. A balance has graduations on the beam from zero at the center to 10 over the right knife edge. By mistake a 5-mg rider is used on this balance, and the weight is recorded as 17.7134 g. What is the correct weight of the object?

13. Could weighings accurate to 0.1 mg be made on a balance whose sensitivity is 0.7 divisions per milligram, if rest-point data are reproducible to 0.1 division?

14. If the left-hand arm of a balance is 15.02 cm in length and the right-hand arm is 15.00 cm, what will be the apparent weight of a 20.0000-g object?

15. A sample of platinum (density = 21.45 g/ml) weighs 63.5781 g in air with brass weights (density = 8 g/ml). Compute the weight in vacuo.

16. A sample of aluminum (density = 2.7 g/ml) has a weight in vacuo of 21.5068 g. What would the sample weigh in air if gold weights (density = 19.3 g/ml) are used? Repeat the calculation using brass weights.

17. What is the value of a buoyancy factor for converting weights of mercury (density = 13.5 g/ml) determined in air with brass weights to weights in vacuo?

18. 500.0 mg of NaCl is weighed in air with brass weights. What absolute error is made in the total weight of the sample if buoyancy is neglected? Is this error detectable on the ordinary analytical balance? (Density of NaCl = 2.2 g/ml.)

19. The density of water in vacuo at 21°C is 0.99802 g per milliliter. What is the weight in air with brass weights of 50.00 ml of water?

20. A 0.5000-g sample of density 4.5 g per milliliter yields a precipitate of silver chloride (density = 5.6 g/ml) which weighs 1.3950 g. Compute the weight in vacuo of the sample and of the precipitate. Compute the ratio of the uncorrected and corrected weights of sample and precipitate. According to your results, is it necessary to apply buoyancy corrections to these data? Brass weights are used.

21. An object weighed in air with brass weights had a mass of 30.0075 g; when weighed under water at 23°C the mass was 25.8753 g. What is the density in vacuo of the substance? What would the substance weigh if it were immersed in alcohol? (Density = 0.90 g/ml.)

22. Two weights, one of aluminum (density = 2.7 g/ml) and one of copper (density = 8.92 g/ml), are each adjusted to 10.0000 g in vacuo. The aluminum weight is placed on the left-hand pan of a balance and the copper one on the right. If the zero point of the balance is 10.3 and the sensitivity is 4.5 division per milligram, where must the rider be set to make the rest point and zero point coincide? The balance beam is graduated to 10 mg on both sides of the central knife edge.

23. On the basis of the 10-mg weight the preliminary values of the 2-g and 10-g weights are 1.9962 and 10.0152 g, respectively. What is the final correction for the 2-g weight in terms of the 10-g weight? Is the 2-g weight lighter or heavier than it should be?

CHAPTER

4

Precision, Errors, and Significant Figures

One of the most important objectives of a first course in quantitative analysis is to gain an understanding of the accuracy which may be expected from a chemical analysis and a knowledge of the proper use of numbers for expressing the result of an analysis. The experimental measurement of a physical property is affected both by errors inherent in the instruments and methods used and by errors introduced by the experimenter himself. This may be illustrated by a hypothetical experiment. Suppose that a number of people are asked to determine individually the volume of a room, each one using the same meter stick for the measurements. The results obtained will not be identical. There will be individual variations, due to errors in taking successive intervals with the measuring rod. There will be an error common to all determinations, due to the fact that the meter stick is not exactly 1000 mm in length. Finally, there may be errors in the methods used for expressing the results of the measurements. The agreement among the various determinations is called the *precision* of the results. The agreement of the average result found and the true result is the *accuracy* of the determination. In this experiment we may find excellent precision, if the work is carefully done, but poor accuracy, if the meter stick is itself very inaccurate. The experimenter should seek high precision in his work, since precision is a measure of the care with which the work is done. But at all times it should be kept in mind that high precision does not necessarily indicate high accuracy.

In the following sections the factors which affect the precision and accuracy of analyses are discussed. The applications of this material to quantitative determinations will not be fully understood at this time, but the principles presented should be kept in mind and applied throughout the work of the course.

ERRORS

The errors which may affect both the precision and the accuracy of analyses may be grouped into two classes: indeterminate, accidental, or random errors; and determinate, consistent, or systematic errors.

Indeterminate. Errors which arise from unknown causes and which do not affect each determination in the same manner are known as indeterminate errors. Most of these are caused by variations in the personal factor; that is, the analyst does not perform every determination in exactly the same manner. In the hypothetical measurement just

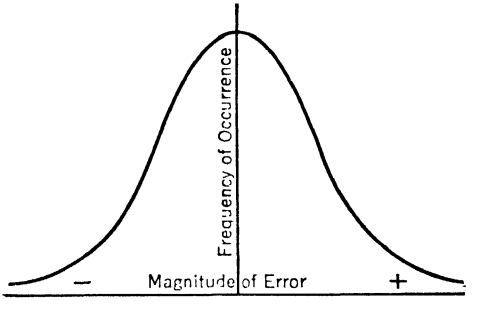


FIG. 9. The error curve.

cited, the failure to make consecutive placements of the measuring rod at exactly the same point is an indeterminate error. Common indeterminate errors in the laboratory are variations in judgment in the point of color change of an indicator, small losses of material in transfer or from leaky burets, variations in the temperature of solutions from one experiment to another, mistakes in observations of balance rest points, individual variations among the several weights, variation in moisture content of the container used for weighing, and so on. In general, the more careless or inexperienced the experimenter, the greater is the magnitude of the indeterminate errors. Lack of precision is chiefly due to indeterminate errors.

If a sufficiently large number of observations is taken, the occurrence and magnitude of the indeterminate errors may be expressed by the laws of probability. The frequency of occurrence y of an error of magnitude x is given by the relation,

$$y = ke^{-h^2x^2}$$

where k and h are constants, and e is the base of the system of natural logarithms. When y is plotted as a function of x, a curve of the shape shown in Fig. 9 results. From this curve there may be deduced:

1. The errors of most frequent occurrence are those of small magnitude. In our hypothetical measurement no one is likely to make an error of several centimeters in a dimension, but an error of 1–2 mm is very probable.

2. Large errors seldom occur. An error of 1 m in the measurement of the room is very unlikely.

3. Positive and negative errors are equally probable. This is another method of saying that the arithmetic mean of a series of results represents the most probable value. If we take the average results from the measurement of the room, we have the value which is most reliable.

Determinate. Determinate errors are those that may affect every observation of a series in the same manner. An error in the length of the meter stick used for our hypothetical measurements would constitute a determinate error common to all experiments. Determinate errors do not, therefore, affect the precision of a series of measurements, and in consequence their presence may be totally unsuspected.

In analytical chemistry determinate errors may arise from many sources. Throughout the work of the course attention will be called to possible sources of error and to methods for their avoidance. In general, the most frequent sources are (1) inexact methods, (2) impure chemicals, and (3) inaccurate equipment. The general methods used for minimization of errors are (1) calibration of apparatus, (2) blank determinations, (3) performing the analysis by several different methods, and (4) running a control, that is, analyzing a substance whose composition is known.

Calibration of apparatus is, as the name implies, a testing of the accuracy of the equipment. Apparatus for measuring volumes should, in particular, be calibrated.

Blank determinations are analyses performed without the presence of the sought constituent. For example, in the determination of the amount of acid present, the sample is titrated with a solution of standard base until an indicator shows a color change. In the blank determination, an indicator is added to distilled water, and base is added until a color change is observed. The amount of base required is known as the blank. This amount is subtracted from the total amount used in titration of the sample.

When highest accuracy is sought the analyst should employ several different methods. Hydrochloric acid solutions, for example, may be standardized by comparison with various pure substances. If several of the available substances are employed, it may be found that the results are in agreement for two or three methods, but that another method gives quite a different result. This indicates the probability that the result not in agreement with the others is subject to a determinate error.

In certain types of volumetric analyses the analyst may reduce the magnitude of determinate errors by a method of cancellation. The solution for the analysis of samples may be standardized by comparison with a sample similar to those later to be analyzed, but of known composition. Any determinate errors inherent in the methods will thereby occur both in the standardization and in the analysis and will be canceled.

EVALUATION OF PRECISION

If each member of a series of observations has the same reliability, that is, if there is no reason to assume that one observation is more correct than another, the arithmetic mean or average of the results is the most probable value of the correct result. The precision of any result is measured by its deviation from the average result, and the average precision is measured by the average deviation of the single results from the mean. In discussing the precision of results and the deviation of individual results from the mean, it is convenient to express all values in parts per thousand, in order that they may be on a directly comparable basis. If, for example, two results, 5311 and 5321, are obtained, the deviation between the two is 10 units. In another observation the results, 531 and 521, are obtained, giving likewise a deviation of 10 units. In the first set of measurements, the agreement is much better than in the second, as may be seen by expressing the results in parts per 1000. In the first set the agreement is $\frac{10}{5311}$, or roughly $\frac{10}{5000}$, which is $\frac{2}{1000}$; in the second the agreement is $\frac{10}{500}$ or $\frac{20}{1000}$.

The average deviation of the individual results in a series of measurements is obtained as follows:

1. Compute the arithmetic mean.
2. Compute the numerical deviation of each result from the mean, without regard to algebraic sign.
3. Average the deviations of the individual results.
4. Express the result in parts per 1000.

The computation of the average deviation may be illustrated by a numerical example:

	Values Found	*Deviations*
	0.0519	0.00015
	0.0521	0.00005
	0.0522	0.00015
	0 0520	0 00005
Average	0 05205	0.00010

Average deviation = 0.00010 part in 0.05205 or 10 parts in 5205
= 2/1000

The following methods are routinely employed to increase the precision of analyses:

1. Measurements of weights and volumes are so arranged that a precision of at least $\frac{1}{1000}$ may be attained. For example, the precision in weighing out a sample by difference is 0.0001 g, for each of the two weighings and the weight of sample should be 0.2000 g, in order that an error of 0.0002 g may not be greater than $\frac{1}{1000}$. Likewise, in the measurement of volume from a buret it is advisable to employ volumes of 40–50 ml in order that errors in reading the buret and in locating the end point may not exceed $\frac{1}{1000}$. If the total volume used is only 10 ml, an error of 0.01 ml amounts to $\frac{1}{1000}$, whereas with a volume of 40 ml the permitted error is 0.04 ml.

2. Several determinations are made and the average taken as the most probable result. It may be shown by the method of least squares that the arithmetic average of n equally reliable results is $\sqrt{n}$ times as reliable as a single result. That is, the average of four determinations is twice as reliable as a single result, and the average of nine determinations is three times as reliable as a single result. From this it may be seen that it is advantageous to employ two to four determinations, but that beyond this point the gain in precision is not justified by the increased labor involved.

Rejection of an Observation

It frequently happens that in a series of observations one or more results deviate widely from the average value whereas the other results are in close agreement with the average. When this occurs, the question may arise as to rejection of the disagreeing results. This question is difficult to answer. Theoretically, no result may be rejected, since the presence of a result which does not agree with the others indicates faulty technique and tends to throw doubt on the entire series of determinations. It is preferable to discard the entire series of results, seek for the source of error, and repeat the determinations after elimination of the source of error. It is understood, of course, that every result in which a known error has occurred is immediately rejected; the present discussion relates to results which have been obtained by careful work and in which the experimenter is not conscious of any error. In practice, it is permissible to discard *one* value of a series of determinations, provided that the following criteria are applied:

1. There should be at least four independent determinations.

2. The average should be determined without including the doubtful result.

3. The deviation of all results from the average is computed, and the deviation of the doubtful result is compared with the deviations of other results. If the deviation of a single result is greater than four times the average deviation of the remaining results, the single result may be discarded.

According to the theory of probability, the chances are 993 per 1000 that the rejection of a result is justified when the afore-mentioned criteria are applied.

The rejection of an observation may be illustrated by an example:

In a series of determinations the values 0.1031, 0.1033, 0.1035, and 0.1042 are obtained. May any result be rejected?

Solution:

	Results	*Deviations*
	0.1031	0.0002
	0.1033	0.0000
	0.1035	0.0002
	(0.1042)	(0.0009)
Average	0.1033	0.00013

$$\text{Average deviation} = \frac{0.00013}{0.1033} \text{ or } 1.3 \text{ parts/1000}$$

The suspected result, 0.1042, is not included in the average. Its deviation from the average is $\frac{9}{1000}$ or greater than $4 \times \frac{1.3}{1000}$. The result may therefore be rejected.

If two or more results deviate widely from the average, it is not valid to reject any result, because such an occurrence indicates careless or faulty technique. It often occurs that a student, in a series of five values, may have two values which agree closely and three other values which agree closely, but with a wide divergence between the two sets of values. Neither set may be considered reliable; the entire series of determinations should be repeated.

SIGNIFICANT FIGURES

When the measurement of a physical property is expressed by a number, care must be taken that the number contain only the digits necessary for the precision of the experiment. The digits in a number which are needed to express the precision of the measurement from which the number was derived are known as *significant figures.* In the hypothetical measurement cited previously, let us assume that the room was found to be a cube measuring 4001 mm on an edge. The precision of the meas-

urement was 1 mm, that is, the average deviation was of that amount. Computation of the volume gives 64,048,012,001 cu mm. This number contains too many significant figures and must be rounded off to express a precision of 1 part in 4000. Therefore the volume is expressed as 6405×10^7 or 6.405×10^{10} cu mm.

The number *zero* is a significant figure except when it is the first figure in a number. That is, the number 1250 contains *four* significant figures, the number 0.00125 contains only *three*, and the number 0.001250 contains *four*. Final zeros are often carelessly used For example, it may be stated that a certain geological formation is 40,000,000 years old. Strictly interpreted this figure indicates that the age is known to a precision of 1 year. Preferable usage is to say that the age is 40 million years. Even in the measurements of the laboratory we occasionally find loose usage of final zeros and of other significant figures.

In derived values which are the basis for further calculations, it is often desirable to retain one digit in excess of the significant figures. Such a retained non-significant figure is denoted by a subscript position. For example, in the number 0.987_3 it is implied that the number 3 is of doubtful significance.

The criterion for the selection of a proper number of significant figures is not the number of significant figures in the data, but the precision expressed in the data. For example, the data in an analysis may contain a weight measurement of 0.1023 g. Here there are four significant figures, but the precision implied is only 1 part per 1000. If these data lead to a percentage calculation of 90.82, the result should be rounded off to 90.8, although this number contains only three significant figures. The number 90.82 implies a precision of 1 part in 9000.

The American Standards Association [1] has issued a tentative report proposing a standard practice of rounding off decimal values (or integers) in retaining the proper number of significant figures. Three general cases are considered:

(*a*) When the figure next beyond the last one to be retained is less than 5 the last figure should be retained unchanged. For example, 1.2342 is rounded to 1.234.

(*b*) When the figure next beyond the last one to be retained is greater than 5 the last figure is increased by 1. For example, 1.6789 becomes 1.679.

(*c*) When the figure next beyond the last one to be retained is 5 and there are only zeros beyond this figure 5, the figure in the last place should be increased by 1 if odd or left unchanged if even; that is, the

[1] *Rev. Sci. Instruments*, **9**, 397 (1938).

last figure is even. For example, 1.350 and 1.35 become 1.4 if only one decimal place is to be retained. Under similar circumstances 1.450 or 1.45 becomes 1.4. When the figure next beyond the last one to be retained is 5 and it is followed by any other figures the last figure to be retained is increased by 1 regardless of whether it is even or odd. For example, 1.4501 becomes 1.5 if rounded to one decimal place.

When several numbers are combined, the result must contain the proper number of significant figures. Convenient rules for achieving this objective are:

1. In addition or subtraction, there should be in each number only as many figures to the right of the decimal point as there are in the number which contains the fewest of such figures. For example, the addition

$$\begin{array}{r} 203.1 \\ 7.21 \\ 0.3734 \\ \hline \end{array}$$

should be written

$$\begin{array}{r} 203.1 \\ 7.2 \\ 0.4 \\ \hline \end{array}$$

2. In multiplication or division retain in each factor sufficient digits to express the precision of the least accurately known quantity. For example, in the operation,

$$203.1 \times 7.21 \times 0.04144$$

all figures are left unchanged. The least accurately known number is 7.21, which indicates an accuracy of $\frac{1}{721}$. Dropping a digit from 203.1 would leave a figure which indicates a precision of $\frac{1}{203}$, while dropping a digit from 0.04144 would leave indication of a precision of $\frac{1}{414}$. In consequence of the previous rule, the number obtained by mathematical operations should contain the same number of significant figures as the least accurate term involved in the operations. Thus, the product of this multiplication is written 60.7 rather than as 60.6827, which is obtained from the calculation.

In every operation of an analysis, one should keep in mind the degree of precision and the number of significant figures needed. Only an inexperienced chemist will waste time by overly exact work. For example, a buret is calibrated by weighing the amount of water delivered. The buret readings are good only to the nearest 0.01 ml. Consequently, it is a waste of time to weigh the water to the fourth decimal place. Yet, every class has some students who will do this if not corrected. Like-

wise, in weighing out samples of about 1 g it is not necessary to determine the fourth decimal place in the weight accurately if the sample is to be used for an analysis whose over-all precision is of the order of 1 part per 1000. It is sufficient to weigh the sample only to the nearest milligram.

In computing the results of an analysis, one should also keep in mind the degree of precision commensurate with the analytical procedures used. The answer should not carry decimal figures far beyond the limits of precision in the laboratory work. If duplicate results for a sample give percentages of 15.46 and 15.68, it is misleading to report the average as 15.57, the arithmetical mean of the two figures. Obviously the precision is not better than 0.2 per cent, and it is sufficient to give the answer as 15.6.

A slide rule may be used for computation when the precision need not exceed 2–3 parts per 1000. If higher precision is required, one should use five-place log tables.

QUESTIONS

1. Which of the following can be concluded from the fact that three results of an analysis check closely: (*a*) indeterminate errors have been minimized, (*b*) the average result is accurate, (*c*) the reagents used were absolutely pure, (*d*) determinate errors have been minimized, (*e*) a blank determination is unnecessary.

2. Which of the following errors may have occurred in an analysis which has good precision but poor accuracy:

Mechanical loss of solution during titration.
Use of uncalibrated weights.
An error in recording the weight of one sample.
Use of the wrong indicator for the titration.

3. Criticize and correct the following statements:

(*a*) "A series of results cannot have high precision without also having high accuracy."

(*b*) "To express a precision in a measurement of one part in a thousand always requires the use of four significant figures."

4. List the methods used to minimize determinate errors.

5. Why is it desirable to use samples which weigh at least 0.2000 g and to use volumes of at least 40.00 ml in titration?

6. A surveyor measures a distance of 10 miles by means of a steel tape, 100 ft in length. List the most probable determinate and indeterminate errors that may affect his measurement. Would the effect of temperature on the length of the tape be classed as a determinate or indeterminate error?

7. Would you consider all the zeros significant figures in each of the following statements? Rewrite each with the proper number of significant figures.

The population of a city is 100,000.
A factory sold for $100,000.
The average life of a car is 100,000 miles.
The age of a geological specimen is 40,000,000 years.

8. List the most important determinate and indeterminate errors in the determination of the weight of a sample with the analytical balance.

PROBLEMS

1. By how many parts per thousand do the following pairs of results deviate from each other:

(*a*) 9.5 and 9.7.
(*b*) 0.507 and 0.512.
(*c*) 40.06 and 40.10.
(*d*) 0.09719 and 0.09717.

2. On a Bureau of Standards sample which contains 24.79 per cent sulfur a student reports:

24.65, 24.78, 24.55.

What are the precision and accuracy of these results expressed in parts per thousand?

3. The following student results were obtained for the purity of a sample of sodium carbonate which assayed 99.85 per cent pure:

99.65, 99.71, 99.58.

(*a*) What is the average deviation of these results in parts per thousand?
(*b*) What is the accuracy of these results?
(*c*) Are determinate errors an important factor in this analysis?

4. An analyst obtained the following results for the standardization of a HCl solution:

0.1135, 0.1134, 0.1136, 0.1144, 0.1132.

(*a*) Which result is he justified in discarding?
(*b*) In terms of the average deviation, what is the precision of the remaining results?
(*c*) What can be said about the accuracy of the results?

5. By use of the atomic weight table determine the percentage of chlorine in KCl to the proper number of significant figures.

6. In terms of the result of Problem 5 express the precision and accuracy of the following results for the analysis of a very pure sample of KCl:

46.82, 47.03, 46.98.

7. From the following results for the percentage of iron in a sample of pure FeO:

76.95, 77.02, 76.90, 77.25.

(*a*) May any of the experimental results be discarded?
(*b*) Express the precision and accuracy of the results in terms of the conclusion drawn in (*a*).
(*c*) What can be said about the presence of determinate and indeterminate errors in these results?

8. The following results were obtained for the normality of a sodium thiosulfate solution:

0.0986, 0.0988, 0.0989, 0.0981.

(*a*) What should be reported as the best experimental value of the normality of the solution?

(*b*) In terms of the average deviation, what is the precision of the results?

(*c*) The "average deviation of the mean" is defined as the average deviation of the individual results divided by the $\sqrt{n}$ where n is the number of individual results included in the average. Compute the average deviation of the best mean value for the normality of the thiosulfate solution, and express the normality as the average value $\pm$ the average deviation of the mean.

9. How carefully should a 5-g sample be weighed to achieve a precision of: (*a*) 1 per cent, (*b*) 0.5 per cent, (*c*) 0.1 per cent?

10. To what precision in parts per thousand are the following values of the fundamental physical constants, as quoted by Birge, known:

(*a*) Charge of an electron 1.6022×10^{-19} coulomb?

(*b*) Volume at STP of a gram-mole 22.4203×10^{3} cm^3?

(*c*) Melting point of ice 273.16°K?

(*d*) Speed of light 2.99776×10^{10} cm seconds^{-1}?

11. Faraday's constant is usually used in elementary courses as 96,500 coulombs per gram equivalent weight. If this constant is known to a precision of 1/10,000, express it to the proper number of significant figures.

12. How many significant figures are in each of the following numbers: (*a*) 410, (*b*) 410.0, (*c*) 0.041, (*d*) 0.04100, (*e*) 0.41×10^{-8}?

13. The weight of a 10-g sample is known to 1/100,000. How carefully was the sample weighed?

14. If a microburet can be read to the nearest 0.001 ml, what total volume should be withdrawn from the buret so that the volume will be known to a precision of 2/1000?

15. If the convention of significant figures is properly used, what is the smallest graduation interval on a thermometer for which a reading of 96.54°C is recorded?

16. Express to the proper number of significant figures:

(*a*) The density of an object whose volume is 13.25 ml and which weighs 62.5013 g.

(*b*) The percentage of silica in a mineral which weighs 1.0065 g and which yields a precipitate of SiO_2 which weighs 0.0142 g.

(*c*) The result of an analysis which calculates to 0.00296457 and which involves in the calculation a weight of sample of 0.9572 ± 0.0002 g and a volume of standard solution of 56.13 ± 0.08 ml.

17. By use of a table of atomic weights express the molecular weights of the following compounds to the proper number of significant figures: (*a*) HCl, (*b*) Au_2O_3, (*c*) $Eu(NO_3)_3$.

18. Express the following measurements with the proper number of significant figures to indicate the highest accuracy obtainable with the instrument used:

(*a*) 5 g measured on a laboratory trip scale.

(*b*) 30 g measured on a balance sensitive to 10 mg.

(*c*) 10 mg weighed on an analytical balance.

(*d*) 10 mg weighed on a microbalance sensitive to 10^{-6} g.

(*e*) 9 ml measured in a 100-ml graduated cylinder.

(*f*) 9 ml measured in a 10-ml graduated cylinder.

(*g*) 9 ml measured from a 50-ml buret.

19. What accuracy, in parts per thousand, is implied in each of the instruments listed in Problem 18?

20. The factor for the conversion of U. S. gallons into liters is 3.78533.

(*a*) Express 0.55 gallons as liters.

(*b*) Express 11.99 ml as gallons.

21. A sample of an alloy is to be analyzed for silver by electrodeposition. If the sample is approximately 20 per cent Ag, what size sample should be taken for analysis so that the error in determining the weight of the deposited silver does not exceed $\frac{1}{1000}$, provided a balance sensitive to 0.1 mg is used?

22. Copper is to be determined by electrodeposition of the metal from a solution which is approximately 0.5 per cent Cu. If the error in determining the weight of the deposited copper is not to exceed $\frac{1}{100}$ and a balance which is sensitive to 0.05 mg is to be used, what size sample should be taken for analysis? How precisely should the sample be weighed?

23. Express the results of the following calculations to the proper number of significant figures:

(*a*) $1.060 + 0.05974 - 0.0013$.

(*b*) $14.356 + 0.015 + 12.6$.

(*c*) $101.65 + 1.283 - (3 \times 10^{-5})$.

(*d*) $2.5 \times 101{,}562$.

(*e*) $15.75 \times (300 \times 10^{4}) \times 0.000035$.

(*f*) $\dfrac{29.74 \times 400}{0.080}$.

(*g*) $\dfrac{12.3456 \times 2.0}{0.002}$.

CHAPTER

5

Preparation of the Sample for Analysis

Before any quantitative analysis can be made, it is necessary (1) to procure a test sample that will represent the average composition of the material to be analyzed, and (2) to prepare a solution of the test sample. In courses in quantitative analysis, these operations often seem inconsequential because the student is given a small homogeneous well-ground sample whose analysis is known, and he is provided with explicit directions for bringing this sample into solution. In professional analyses, however, it is often more difficult to prepare a suitable solution than it is to perform the actual analysis. The material of this chapter is designed to acquaint the student with the problems involved in the preparation of a sample for analysis and with the general methods for the solution of these problems. For more detailed information reference books [1] should be consulted.

SAMPLING

Few of the natural or commercial products for which analyses are required are homogeneous in nature. A shipment of ore, for example, will show large variations in composition, even though it is all taken from the same deposit. Even alloys, such as brass or steel, are inhomogeneous within a single piece, owing to segregations that occur during the solidification of the liquid material. Since, in general, the portion used for the analysis does not weigh more than a gram, it is obviously of par-

[1] See in particular W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, Wiley, 1929; N. H. Furman, *Scott's Standard Methods of Chemical Analysis*, Van Nostrand, 1939; and H. H. Willard and Harvey Diehl, *Advanced Quantitative Analysis*, Van Nostrand, 1944.

amount importance to exercise great care in the selection of this portion so that it shall represent the composition of the whole material. An excellent analysis is completely invalidated by poor sampling.

The method of sampling is first to select a *gross* sample, which, though itself inhomogeneous, will represent the average composition of the whole and by systematic mixing and reduction in size of the gross sample to obtain a small homogeneous portion that has the same composition as the entire material.

The size of the gross sample depends on the size of the individual particles of material. If the particles are large or show wide variation in size, as in a carload of coal, the gross sample is necessarily larger than for a well-ground material of uniform particle size. In general, the gross sample varies from $\frac{1}{20}$ to $\frac{1}{100}$ of the total material, but under special conditions a much smaller fraction may be used satisfactorily.

In taking the gross sample a standardized procedure is followed to insure that the sample shall represent the composition of the whole. Small portions of uniform size, known as sample units, are taken at regular intervals from the entire bulk of material. If the material is in a large bulk, as a boatload of ore, sample units are taken along lines drawn lengthwise of the bin. When the material is in small containers, a portion is taken from every nth container. The size of the sample unit, like that of the gross sample, varies with the size of particles of the material; the larger the individual particles, the larger the sample unit needed.

From the gross sample, which may weigh hundreds of pounds, there is obtained a small sample, weighing 5–10 lb, which is called the laboratory sample. The process of reducing the gross to the laboratory sample consists of systematically mixing, dividing the mixture into two parts, mixing one part, dividing, and so on. Before the first division is made, the sample is crushed to particles 1 in. or less in size, and each fraction is again crushed to smaller particle size before it is subdivided.

When the mixing is done by hand, one of the following methods is used:

1. Long Pile and Alternate Shovel Method. This method is used for large samples of 100–1000 lb. The particles should not be larger than 1 in. The sample is mixed by piling into a cone, each shovelful being deposited at the apex so that the material runs down to all sides. The material is shoveled from the cone into a long pile about the width of the shovel; each shovelful is spread along the entire length of the pile, alternate shovels being started at opposite ends. The long pile is divided into two equal portions by taking alternate shovels of material and discarding the odd ones. The portion retained is recrushed, again piled into a cone, and spread into a long pile.

2. Coning. When the size of sample is between 10 and 100 lb, the method of coning is useful. The material, crushed to a proper size in relation to the amount present, is piled into a cone. The cone is then flattened, and the flat pile is divided into four equal portions by passing a straight board through twice, so as to make two cuts at a 90° angle to one another. Alternate quarters are rejected, and the remaining two quarters are crushed to suitable particle size, repiled, and again quartered.

3. Tabling. This method is suitable for finely ground samples of weight 10 lb or less. The material is spread on a canvas cloth and mixed by drawing in turn each corner of the cloth to the diagonal corner, in such a manner as to impart a rolling motion to the particles. After being mixed in this manner, the material is spread in a flat pile and quartered. The two opposite quarters are discarded, as in the coning procedure.

4. Riffling. A sample may be mixed and divided into two portions by a machine known as a riffle, if the particles are small. In this operation the material is fed from a hopper into a row of small chutes arranged so that the even-numbered ones deliver to one side and the odd-numbered ones to the other side. This method is applicable only when there is sufficient sample to fill all the chutes.

GRINDING AND CRUSHING

It has been pointed out that thorough mixing requires that the sample be ground or crushed to particles of uniform size. Nearly always, except in the analysis of metals, the test portion must be in the form of a very fine powder. Usually, when the original material is in large lumps, the preliminary breaking down of the particles is done by means of a *jaw crusher*, in which lumps of material are squeezed between massive metal jaws. After the particle size is made small, further reduction is accomplished by grinding.

In the school laboratory, crushing is conveniently done in a hardened-steel mortar, such as shown in Fig. 10. Single lumps of the sample are placed in the cylinder and crushed by striking the plunger with a hammer. After the material is crushed in the mortar, it is ground (in small portions) in an agate mortar until no gritty particles can be detected. After grinding, the material is thoroughly mixed, by a tabling process, on a sheet of glazed paper. When large portions of material are to be ground and mixed, a *ball mill* is advantageous. The sample is placed in a closed jar with an equal volume of hard balls, and the jar is continuously rotated on its side for several hours. Rubbing of the balls with

one another and with the wall of the container serves to give very effective grinding and mixing. Care must be taken not to have too large a sample at a single charge.

Sieving is an essential part of the grinding operation. No single grinding will pulverize all the particles, but some of the harder ones become coated with powdered material and remain unchanged. These particles must be separated, by the material being passed through a sieve, and reground. Conventionally, the size of particle to which a material must be ground is designated by the *mesh* of the sieve which the material must pass, the mesh of a sieve denoting the number of wires to the linear inch. Since part of the space is occupied by the wires themselves, an n-mesh sieve has openings slightly smaller than 1 nth of an inch. The usual sample for analysis should pass a screen of 80–100 mesh or smaller.

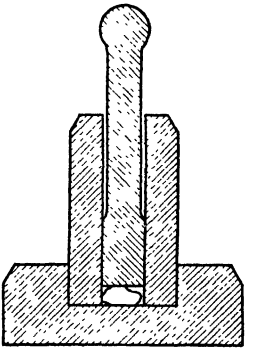


FIG. 10. Steel mortar for crushing sample.

Errors in Grinding. The process of grinding a sample may materially alter the composition. Among the changes that may occur are the following:

1. Contamination by the apparatus used for grinding or crushing. In the abrasion necessary to break up particles of the sample, there occurs to some degree an abrasion of the apparatus itself, with consequent contamination. Crushing causes less contamination than grinding, because there is less rubbing of the apparatus with particles of sample. Agate mortars are so hard that few samples will cause an abrasion sufficient to give a detectable amount of the mortar material in the sample. Porcelain mortars, such as are used in elementary chemistry courses, are not at all suitable for grinding samples for quantitative analysis. Porcelain ball mills likewise are unsuitable for quantitative samples of any but soft materials, such as crystalline salts.

2. Contamination in sieving. Sieves are usually made of brass screen, because of the resistance to corrosion. There may be enough abrasion of the brass during the operation of sieving to cause appreciable contamination. In many mineral analyses it is preferable to use silk bolting cloth for screening, rather than brass sieves, to eliminate the possibility of introducing copper, zinc, and lead into the sample.

3. Oxidation of the sample. Considerable heat is generated locally in the grinding of a mineral, and in the presence of air an appreciable amount of oxidation may occur. This is particularly noticeable with ferrous compounds, which are readily oxidized to the ferric state. At

times it may be desirable to grind samples under absolute alcohol, to prevent changes in composition.

4. Loss or gain of moisture. The moisture content of a sample may be altered in the grinding operation. A finely divided sample will absorb much more surface moisture than the same material before grinding. An opposite effect may be found in some minerals that contain combined water; the heat generated locally in grinding may expel some of this water. Hillebrand and Lundell [2] discuss both effects and cite quantitative data.

MOISTURE

In many analyses it is customary to dry the material at 105–110°C before beginning the determination, and to report the result of the analysis on a dry basis. This practice is followed because the moisture content may vary widely with differing atmospheric humidity, and analyses made under different humidity conditions may not be in agreement. Drying at 110°C does not remove all the adsorbed water, particularly in samples which contain oxides of iron or aluminum, nor does it remove all the combined water which may be present as a hydrate. For a given type of sample, however, it may be assumed that drying will give reproducible results.

In many analyses no drying at elevated temperature can be employed. For example, analyses of vegetable or animal tissue must be based on the weight of air-dried material; that is, the material is allowed to stand in air until free water has evaporated and an equilibrium is attained.

Some crystalline materials cannot be dried at 110°C without loss of combined water, and certain analyses may be based on the weight of material as dried at a definite humidity. Such drying is done by placing the sample in a desiccator with a substance of definite known vapor pressure, such as a salt hydrate. For example, borax if dried over hydrated sodium bromide will contain 10 molecules of water of crystallization, whereas if air-dried it will partially decompose to form the pentahydrate.

The determination of the moisture in a sample is a convenient preliminary exercise in quantitative technique. A mixture of barium chloride dihydrate and sodium chloride is an excellent sample. The water of hydration is completely expelled from the barium chloride on drying at a temperature of 105–110°C. The process is accelerated at higher temperatures.

Procedure. Label two weighing bottles, either with a gummed sticker or, preferably, with a glass marking ink, and dry in an electric

[2] *Applied Inorganic Analysis*, page 682.

oven at 105–130°C for a half-hour. During this period the stopper of each bottle should be placed in a slanting position in the top of the bottle, to permit escape of water vapor. Place the hot bottles in a desiccator, with the stoppers still open, and allow to cool to room temperature. When they have cooled, stopper the bottles tightly, and weigh accurately. Repeat the heating, cooling, and weighing. Successive weighings should agree within 0.3 mg.

TABLE 6

DETERMINATION OF MOISTURE

Sample Notebook Record

Sample no.	I	II
Initial weights of bottles	32.5675	34.3246
	32.5676	34.3241
		34.3240
Weight of sample	33.6684	35.2562
	32.5676	34.3240
	1.1008	0.9322
Final weights of bottles with dried sample	33.5307	35.1402
	33.5309	35.1400
Loss in weight	33.6684	35.2560
	33.5309	35.1400
	0.1375	0.1160
Per cent moisture	12.49	12.44

Obtain the sample in a stoppered weighing bottle. Transfer about 1–1.5 g of the sample to each weighing bottle, stopper, and reweigh. The difference in weight of the empty and filled bottles is the weight of sample. Place the bottles in the oven, with the stoppers open, and dry for 2 hours (or overnight). Cool in a desiccator, stopper tightly, and weigh. Heat for another 1-hour period, cool, and reweigh. The second weighing should agree with the first within 0.3 mg. If it does not, repeat the heating until constant weight is obtained. From the loss in weight, and the weight of the sample, compute the percentage of water in the sample. The duplicate determinations should agree within 0.2 per cent. Record all the data in the notebook, following the form shown in Table 6. Report the result of the analysis as directed by the instructor.

Calculations. It is often convenient to make analyses on undried portions of sample, to determine separately the moisture on another

portion, and to report the results of the analysis on a dry basis. The method may be illustrated by a sample calculation:

Problem. One portion of a sample was found to contain 5.72 per cent moisture. Analysis of another portion gave 14.56 per cent copper, on a wet basis. What is the percentage of copper, expressed on a dry basis?

Solution: Since the sample contains 5.72 per cent moisture, a 1.000-g portion will have 0.9428 g of dry material. This contains 0.1456 g of copper. Therefore the percentage of copper, on a dry basis, is

$$\frac{0.1456}{0.9428} \times 100 = 15.44\%$$

PREPARATION OF SOLUTION

No general directions can be given for bringing samples into solution; each type of material demands specific treatment. The analytic methods of frequent occurrence are given in Table 7. It may be noted that the most common methods are: (1) treatment with hydrochloric acid, (2) treatment with nitric acid, (3) fusion with sodium carbonate, and (4) fusion with potassium acid sulfate.

Hydrochloric acid is generally used when a non-oxidizing acid medium is required and nitric acid when oxidation of a metal is required. In some analyses it is advantageous to employ a mixture of nitric and hydrochloric acids (aqua regia) so that oxidation can be carried out in a hydrochloric acid medium.

TABLE 7

METHODS FREQUENTLY USED FOR BRINGING SAMPLE INTO SOLUTION

Sample	*Treatment*
Ferrous alloys	Acids
Non-ferrous alloys	HNO_3
Iron ores	HCl (fusion with $KHSO_4$)
Carbonate rocks	HCl or fusion with Na_2CO_3
Silicate rocks	Fusion with Na_2CO_3
Chromium ores	Fusion with $Na_2CO_3 + Na_2O_2$
Pyrites (FeS_2)	Fusion with $Na_2CO_3 + Na_2O_2$
SnO_2	Fusion with $Na_2CO_3 + S$

Many materials which are not soluble in acids can be brought into a soluble condition by means of reactions with fused salts. The fused salts most frequently employed, known as fluxes, are sodium carbonate and potassium acid sulfate. Sodium carbonate is the most widely used of these. Oxides of an acidic nature, such as SiO_2, are converted into soluble sodium salts by sodium carbonate fusion. In addition, many metal

salts are converted into the metal carbonates, which readily dissolve in acids. When oxidation of an acidic oxide is needed, the material may be fused with sodium carbonate plus an oxidizing agent, such as sodium peroxide. Potassium acid sulfate is an acid and is consequently used to render basic oxides soluble by conversion into the sulfates. This flux is most frequently used to bring insoluble iron oxides into solution.

QUESTIONS

1. Why is not the entire gross sample ground to the fineness of the laboratory sample?
2. Why should samples be ground in small portions when an agate mortar is used?
3. What is the advantage of crushing lumps in the steel mortar described, rather than directly in an agate mortar?
4. In the following analyses should the drying be done in air, in an oven at 110°C, or in a desiccator over a substance of very low vapor pressure:

A plant leaf.	Iodine.
An animal tissue.	An iron ore.
A commercial fertilizer.	

5. If a hydrate is to be brought to constant weight in a desiccator, what must be true about the vapor pressures of the hydrate and the desiccant?
6. What changes might occur in the mineral, hercynite, $FeO \cdot Al_2O_3$, during grinding? Name a suitable flux to bring this mineral into solution.
7. How would poor mixing of a laboratory sample be detected during the course of an analysis. Is improper mixing a determinate or indeterminate error?
8. Why is it important to record the temperature at which the sample was dried in giving the results of an analysis?
9. Why are most samples dried in an oven before the analyses are started?
10. What methods might be used to dissolve each of the following:

Arsenious oxide for arsenic analysis.
Barium sulfate for barium analysis.
Barium sulfate for sulfate analysis.
Silver iodide for silver analysis.
Metallic silver for silver analysis.
Metallic antimony for antimony analysis.
An insoluble chromium ore for chromium analysis.
A silicate rock for silica analysis.
An ignited aluminum oxide for aluminum analysis.

PROBLEMS

1. If a thorough sampling were to be made, roughly what would the gross laboratory sample from 5 tons of an ore weigh?
2. A sample of coal which weighs 2.000 g after air drying loses 0.1575 g of moisture on drying in an oven; 0.3000 g of an oven-dried sample of the same coal yields an ash residue of 0.0500 g. What is the percentage of ash in the coal on an air-dry basis?

3. A sample of iron ore contains 1.78 per cent moisture and 71.65 per cent iron on a dry basis. Compute the percentage of iron in the original material.

4. A sample of clay contains 18.3 per cent moisture and 15.8 per cent potassium on an "as-received" basis. What is the percentage of potassium on a completely dry basis? What would be the percentage of potassium if the moisture is reduced to 5.0 per cent of the "as-received" sample?

5. A sample of organic tissue showed a 2.00 per cent loss in weight on air drying and a 57.5 per cent loss of the air-dry weight on oven drying. Colorimetric analysis demonstrated the presence of 12.0 parts per million by weight of copper in the oven-dried sample. Obtain the parts per million of copper on an air-dry and "as-received" basis.

6. An oven-dried limestone sample analyzes 45.55 per cent loss in weight on ignition to red heat and 33.26 per cent CaO. What is the percentage of CaO in the ignited residue? 15.000 g of an air-dried sample of this limestone was dried in an oven at 120°C to a constant weight of 14.923 g. What would be the percentages of loss on ignition and CaO on an air-dry sample?

7. What is the smallest-size sample which contains about 2.5 per cent moisture which should be taken for analysis of moisture content to a precision of $\frac{1}{100}$ by use of an ordinary analytical balance? How carefully must this sample be weighed?

PART TWO

Volumetric Analysis

CHAPTER

6

Methods and Apparatus

Analyses which are made by means of the determination of the amount of a reagent solution required for reaction with a sample are known as *volumetric analyses*. This term is in a sense misleading, for many reactions of this type are based on the weight rather than the volume of solution required to react with the sample. For this reason, some prefer the term "titrimetric analyses" to volumetric analyses.

A great variety of determinations can be made by volumetric methods. These are generally grouped for study under the headings of neutralization, oxidation-reduction, and precipitation or complex formation reactions. Examples of all three classes are studied in this course.

Definitions. Volumetric analyses are performed by titration of a solution which contains the sample to be analyzed. *Titration* is the process of determining the volume or weight of the reagent solution just required for complete reaction with the sample. It is done by adding the solution (dropwise at the end) of reagent to the sample solution until the point is reached at which there is a sudden change in some property of the mixed solutions and at which there exists a definite relation between the number of moles of reagent used and of the sought constituent. The solution used for the titration is of known strength and is called a *standard* solution. The point at which the amount of reagent chemical added is equivalent to the substance which is being titrated is known as the *stoichiometric* point. It is recognized by a sudden change in some property of the solution, known as the *end point.* Sometimes the end point and the stoichiometric point do not coincide,

but in every titration one seeks conditions that will give an end point when the stoichiometric point is reached.

The strength of the standard solution is determined by a process of *standardization* or comparison of the solution with a known weight of a substance of known composition, which is known as a *volumetric standard.* The standard may be a reagent chemical of known purity, in which case it is known as a *primary* standard. When the standard is itself a solution that has previously been standardized by comparison with a primary standard, it is known as a *secondary standard.*

These definitions may be illustrated by familiar examples. The amount of acid in a sample of vinegar can be determined by titration of the sample with a standard sodium hydroxide solution, using phenolphthalein as indicator. The end point is reached when a permanent pink color is imparted to the phenolphthalein. In this titration, conditions are such that the end point coincides with the stoichiometric point, at which the amounts of sodium hydroxide and acetic acid are in accord with the weight relations of the chemical equation:

$$NaOH + HC_2H_3O_2 = H_2O + NaC_2H_3O_2$$

Prior to the analysis the sodium hydroxide solution is standardized by titrating a known weight of pure potassium acid phthalate, which serves as primary standard. This standardized sodium hydroxide solution may if desired be used as a secondary standard to compare with an acid solution which we wish to standardize.

Requirements for Volumetric Analyses. Before a neutralization, oxidation–reduction, or precipitation reaction can be used as the basis of a volumetric procedure it must satisfy certain requirements. These are:

1. The reagents of the standard solution and the sample must react rapidly so that each drop of solution is used up as quickly as the solutions are mixed.

2. There must be a single reaction, expressed by a chemical equation, between the reagent and sample substances. If a variety of reactions are possible, one cannot tell from the volume of reagent added just how much of the sample has entered into reaction.

3. This single reaction must go essentially to completion.

4. At or near the stoichiometric point there must be an abrupt change in some property of the solution. Usually this consists in the disappearance of some constituent ion of the sample or in a rapid rise in the concentration of a reagent ion.

5. An indicator must be available to show when the point is reached at which there is an abrupt change in some property.

To illustrate, we may compare certain reactions that can be used for volumetric analyses with some that cannot. Neutralization of strong acids by strong bases is an example of a favorable reaction. The reaction is instantaneous and is expressed by a chemical equation. At the stoichiometric point hydrogen and hydroxide ions are used up, with formation of water. Acid–base indicators show by a color change when there is an abrupt change in hydrogen-ion concentration. Precipitation of metal ions by hydrogen sulfide is an example of a reaction that cannot be utilized in volumetric procedures. The reactions are rapid and proceed to completion, but there are no indicators to show when the stoichiometric point is reached. Moreover, in some hydrogen sulfide precipitations, there may be formation of both normal and acid sulfides, so that one cannot tell from the volume of the hydrogen sulfide used the amount of metal present. A precipitation reaction which is widely used for volumetric analyses is the reaction of halide ions with silver ions. Here there is but a single reaction, and there are available indicators to show by a color change when the stoichiometric point is reached.

Advantages of Volumetric Methods. In frequency of occurrence volumetric analysis ranks far above all other types. One reason for this is the speed with which a volumetric determination can be made. After standard solutions are prepared and solutions of the sample are ready for titration, the actual determination requires but a few seconds. The accuracy and precision are at least as good as can be obtained from other methods. A gravimetric analysis, on the other hand, may require many hours' time for separating the desired constituent as a precipitate and for getting it into a form suitable for weighing. In the industrial laboratory, the majority of analyses are done either by volumetric methods or by some type of physical method which depends on measurement of a physical property of the sample.

APPARATUS

Accurate measurement of volume is essential in volumetric analysis. The instruments employed for this purpose are the buret, pipet, and volumetric flask. All these are so designed that a small change in volume will cause a large change in the level of the liquid surface. In addition to these, a Gooch crucible for suction filtration will be needed in some of the laboratory exercises of volumetric analysis.

Buret. The buret is a long glass cylinder of uniform bore. It is used for measuring the variable volumes delivered in a titration. The graduation marks indicate the volume withdrawn. Various sizes are used, the most common one being of 50-ml capacity. For this size the

graduation marks should be in 0.1-ml units; preferably the marks for the fractional values should extend halfway about the cylinder, and the integral marks should completely encircle it. (Unfortunately, this construction is not so readily available today as in the past.) The etched marks should be very narrow sharply defined lines. Delivery is made through a capillary tip whose bore should be of such size that about 100 seconds is needed for delivery of 50 ml of solution. If withdrawal is too rapid, drainage from the walls is not complete; if it is too slow, titrations are made laborious. A glass stopcock is used for controlling the rate of flow. The plug of the stopcock must be kept well greased, with stopcock grease of good grade. Vaseline is not a suitable grease.

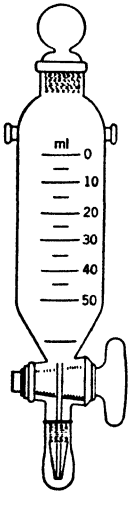


FIG. 11. Weight buret.

Weight Buret. Increased accuracy in titrations can be obtained by weighing, rather than measuring the volume of reagent required. For this purpose, a weight buret (Fig. 11) is employed. The body of a weight buret is made short, so that the entire buret can be suspended from a hook just below the pan support of the balance. The buret has a glass stopper at the top, to prevent evaporation of liquid, and a guard cap which fits over the delivery tip.

Transfer Pipet. The fixed-volume pipet is used for rapid and accurate measurement of fixed volumes of liquids. Essential features are a long delivery tip that should reach to the bottom of the volumetric flasks used, an enlarged bulb at the center to give the desired capacity, and a narrow stem. The graduation mark, which gives the level to which the pipet should be filled to deliver a given volume, is on the stem, about halfway between the bulb and the end. The tip should be tapered and ground smooth. The size of the orifice should be such that delivery is slow, to permit drainage from the walls. Minimum delivery time for a 5-ml pipet is 15 seconds; for a 50-ml pipet, 30 seconds.

The pipet is filled by placing the tip in the liquid to be used and drawing the liquid into the barrel by suction, applied with the mouth. Delivery is controlled by tightly holding the forefinger of the right hand over the stem, then slowly admitting air to permit liquid to flow from the tip.

Measuring Pipet. The measuring pipet is a straight-bore pipet, graduated along the length similarly to a buret. Usually only small sizes, ranging from 1 to 10 ml, are employed. They are for the delivery of known variable volumes and are not generally used for titrations. Delivery is controlled in the same manner as for fixed-volume pipets.

Volumetric Flask. The volumetric flask is a thin-walled flat-bottomed flask with a long narrow neck. It is used to dissolve solids in a known volume or to dilute solutions to an accurately known volume from which carefully measured fractions (aliquots) can be taken for analysis. The graduation mark, for the volume *contained* in the flask, is placed on the neck. The flask has a ground-glass stopper, so that it may be inverted without loss of liquid. Occasionally a flask is also graduated "to deliver," in which case the upper mark will be that for delivery. This usage is not recommended because the flask is not an accurate instrument for delivery of a definite volume; there is uncertainty as to the amount of liquid adhering to the rim.

Gooch Crucible. It is often necessary to make a filtration of a solution that cannot be allowed to come into contact with filter paper. Such filtrations are conveniently made through asbestos mats, in a Gooch crucible. The Gooch crucible is a flat-bottomed porcelain crucible, the bottom of which is perforated with a network of small holes. A suspension of asbestos fiber is poured through the crucible until there is formed a retentive mat of asbestos sufficiently fine to retain small particles. Suction is necessary in filtrations through Gooch crucibles. A commonly used assembly is shown in Fig. 12, but various other types of holders can be substituted for the style shown. The test tube below the funnel is used only when a small sample of filtrate is to be collected.

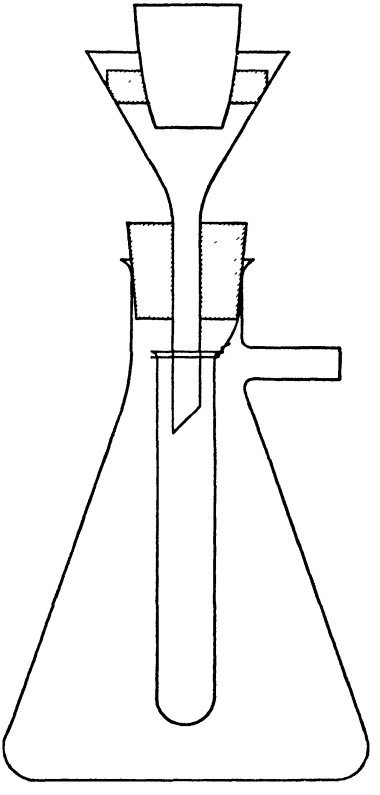


FIG. 12. Filtration through Gooch crucible. The test tube is used only for collecting samples of wash liquid. Other types of crucible holder are frequently employed.

To prepare a mat stir a small amount of acid-washed asbestos fiber into 100-ml of water to make a suspension. Arrange the crucible and holder as shown in Fig. 12. Without suction, pour a little of the suspension through the crucible. When most of the water has run through, turn on the suction, and continue to pour the suspension through until a mat 0.5 to 1 mm in thickness is formed. In filtration through the mat

the suction should be applied before any liquid is poured into the crucible.

Cleaning

All volumetric apparatus must be absolutely free of grease when used, since the least trace of grease causes aqueous solutions to adhere to the walls in drops and thereby prevents complete drainage. The most widely used cleaning agent is a solution of sodium dichromate in concentrated sulfuric acid. Because of its oxidizing power, the solution, particularly when hot, removes grease quickly and completely. Cleaning solution, as the mixture is called, is not a general solvent for cleaning all apparatus, but only for volumetric apparatus. Flasks, beakers, and similar apparatus are best cleaned with soap and water (better still are detergents such as Dreft) unless they contain organic tarry residues, in which case the oxidizing properties of cleaning solution may be useful. Other mixtures for cleaning are described in handbooks of chemistry.

Procedure. Preparation of Cleaning Solution.[1] Stir about 20 g powdered commercial sodium or potassium dichromate with just enough water to make a thick paste. Add 300 ml of commercial-grade concentrated sulfuric acid. Store in a glass-stoppered bottle. It is unnecessary to remove the residue of undissolved salt by filtration, but clear solution should be decanted from the bottle each time it is used. The solution may be repeatedly used until the reddish color of dichromate has been replaced by the green of chromic ion.

Caution: *Do not allow the solution to come into contact with the skin or clothing, for it will cause very bad burns. If any is spilled on the floor or desk, neutralize immediately with commercial-grade sodium bicarbonate, and then wash completely with water. If it is spilled on the skin, wash the skin in running water as soon as possible.*

Procedure. Cleaning Buret. Inspect the stopcock plug. If it is well greased, the plug turns easily, and the surface between the plug and barrel appears to be *transparent*. If the plug needs greasing, remove it and wipe clean; also wipe out the inside of the barrel. Both parts must be dry. Rub a thin film of grease onto the plug. A good-grade stopcock grease, *not vaseline*, must be used. Replace the plug in the barrel, and turn back and forth. If too much grease is applied, the tip will become clogged. If this happens, remove the plug, clean out the lump of grease by the method specified by the instructor, and then regrease.

Heat about 100 ml of cleaning solution in a 250-ml beaker to a temperature of 60–70°C (note 1). Use a thermometer; take care not to

[1] A large bottle is kept on the side shelf for class use. After use, return the solution to the bottle.

exceed 70°C. Clamp the buret in an inverted position, with the opening reaching nearly to the bottom of the beaker, which contains cleaning solution, as shown in Fig. 13. Attach a safety bottle to the buret tip by rubber tubing, and draw cleaning solution into the buret by suction until the level is slightly past the final graduation mark. Do not allow the solution to reach the stopcock, where it would remove the grease. Close

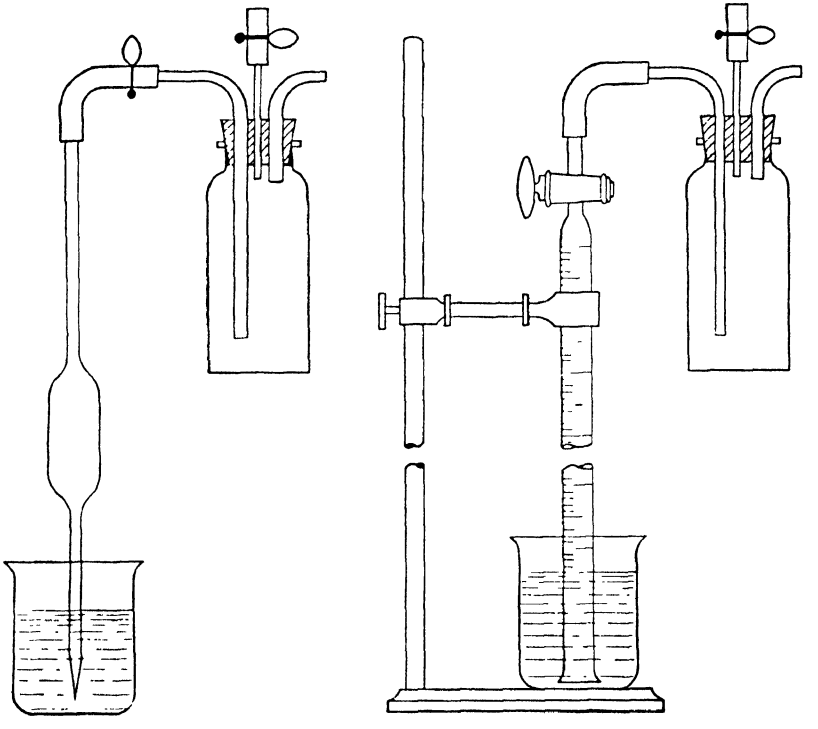


FIG. 13. Cleaning pipet and buret.

the stopcock, and allow the filled buret to stand 3–5 minutes. Open the stopcock, raise the buret above the liquid level, and allow it to drain thoroughly. Remove the beaker of cleaning solution, replace by a beaker of tap water and flush out the buret by drawing water to the 50-ml mark and allowing to drain out. Remove from the clamp; wash several times with tap water and finally with distilled water. When all trace of cleaning solution is removed clamp the buret in an upright position, fill with distilled water, wipe off the outside, open the stopcock, and allow it to drain in order to test for cleanliness. If any drops of water adhere to the inner wall, the buret must be recleaned. Fill the cleaned buret with distilled water, and leave in this condition until needed

(note 2). If the buret is left empty, it will quickly become contaminated with a film of grease.

Notes. 1. Cleaning solution may be used without warming if desired, but then the solution should stand in the buret for at least one-half hour, and preferably overnight.

2. Burets will remain clean for long periods if always stored in this way when not in use. Optionally the buret may be left empty and inverted, with the open end dipping into a beaker of water. If it is stored in this manner, less rinsing is required before the buret is ready for use, since the barrel is left in a dry condition.

Procedure. Cleaning Pipet. Clamp the pipet in a vertical position with the tip dipping into a beaker of cleaning solution, as shown in Fig. 13. Draw warm cleaning solution into the pipet until the level is within an inch of the top. *Caution. Be sure to use a safety bottle.* Close the rubber connecting tubing with a pinch clamp, and allow the solution to stand 3–5 minutes. Raise the pipet, allow to drain, wash thoroughly with tap water, and rinse with distilled water. Test for cleanliness by filling with distilled water, allowing the pipet to empty, and observing whether drops form on the side within the graduated portion. Lack of cleanliness above the volume mark does not affect the accuracy, since solution delivered from a pipet does not come in contact with this portion. Pipets must be recleaned frequently since they quickly become contaminated in use, because of organic matter deposited from the breath.

Procedure. Cleaning Flask. Pour 50–100 ml warm cleaning solution into the flask, stopper tightly, and manipulate so that all portions of the wall are repeatedly brought into contact with the solution. Continue for 3–5 minutes, then pour the cleaning solution back into its container, rinse the flask repeatedly with tap water, and finally rinse with distilled water. It is important that the neck of the flask above the graduation mark be clean because, when solutions are diluted in the flask, drops of water might adhere to an unclean wall, thus invalidating the measurement of volume contained in the flask. Small flasks may be cleaned by being filled with cleaning solution and allowed to stand overnight.

CALIBRATION

Necessity for Calibration of Volumetric Apparatus. The results of volumetric analyses are all based on accurate measurements of volumes. In precise work it is never safe to assume that the volume contained or delivered by any instrument is exactly that amount indicated by the graduation mark. All volumetric apparatus should be either purchased with a calibration certificate or calibrated by the analyst. In

addition to proving the accuracy of the apparatus the operation of calibration serves to provide the beginning student with drill in the use of volumetric apparatus before he undertakes to perform analyses with this apparatus.

Method for Calibration. Calibration is usually performed by measuring the amount of water delivered or contained by the apparatus. This measurement may be made either by weighing the water and from its density calculating the volume, or by measuring the water in an apparatus which has previously been calibrated. Water is used as calibration liquid because of its ready availability, and because it is similar in viscosity and speed of drainage to the dilute solutions ordinarily employed in volumetric analysis.

Standard Volume. The unit of volume employed in all scientific work is the *liter*, abbreviated l. The liter is defined as the volume occupied by 1 kg of water at the temperature of greatest density, 3.98°C. At the time of introduction of the metric system it was intended that the liter be 1 cubic decimeter, or 1000 cc, thereby interrelating the units of length and volume; but, because of experimental errors, this ideal was not attained, and in reality the liter is 1000.028 cc.

The liter is an inconveniently large unit for laboratory use, since most of the volumes encountered in titration are not greater than 0.05 l. Because of this, the practical unit is chosen as 0.001 l., which is known as the milliliter (ml). For all practical purposes the milliliter is identical with the cubic centimeter (cc), as the difference is only 28 parts per million, but it is preferable to follow the usage of the United States Bureau of Standards and call the volume unit a milliliter rather than a cubic centimeter.

Change of Volume with Temperature. The unit of volume is independent of temperature; if a liter container were constructed of some material which did not expand on application of heat, it would hold a liter at any temperature chosen, but the weight of material contained would change because of the variation in density with temperature. Practically, however, no such containers are available. Glass, which is used for all volumetric apparatus, does expand slightly when heated. A vessel which holds 1.0000 l. at 15°C holds a volume of 1.00025 l. at 25°C. Although small in magnitude, the change is measurable, and in precise work it is necessary to define the temperature at which apparatus is calibrated. The Bureau of Standards has chosen 20°C as the normal temperature, and apparatus calibrated by the Bureau will contain or deliver the stated volume at this temperature. In this course all apparatus will be calibrated at room temperature (20–28°C) since the variation in volume over this temperature range is slight. If de-

sired, the values obtained may be corrected to 20°C by use of the equation,

$$V_{20} = V[1 + 0.000025(20 - t)]$$

where V is the observed volume, V_{20} is the volume at 20°C, and t is the observed temperature. This correction is not necessary in student work.

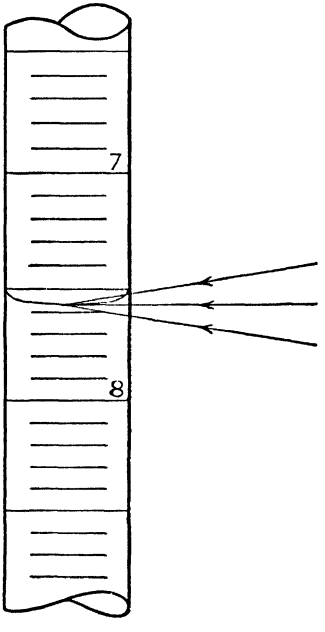


FIG. 14. Effect of parallax in reading buret.

Another effect of temperature is of importance in all volumetric work, namely, the expansion of liquids when heated. As previously noted, the change in volume of a glass vessel is only 0.25 part per 1000 for a change in temperature from 15 to 25°C. Over the same temperature interval the volume of water changes 2 parts per 1000; that is, a liter of water at 15°C will occupy a volume of 1.002 l. at 25°C. This effect is important in connection with the use of standard solutions.

Technique of Reading Volumetric Apparatus. When water is held in a glass vessel, a *meniscus*, whose radius of curvature is a function of the diameter of the column, is formed at the upper surface. With clear solutions the lowest portion of this meniscus is chosen as the point of observation, since it is the most easily reproducible point for visual measurement. Obviously it is immaterial, in a column of given constant radius, what portion of the meniscus is chosen for observation, provided the same point is used for all readings; when translucent or opaque solutions are employed, it is necessary to make the reading at the upper edge rather than at the bottom of the meniscus, since the bottom cannot be seen.

The bottom of the meniscus lies some distance behind the graduation mark on the outer surface of the container; it is necessary (to avoid errors of parallax) to hold the eye on a level with the plane of the graduation mark and the meniscus. The effect of the eye position on the reading is shown in Fig. 14. If the eye is below the meniscus, the reading is too high; that is, a graduation mark is read which lies below the true value. A similar but opposite error occurs when the eye is above the meniscus. In all readings some device must be employed to insure absence of parallax. In reading apparatus whose graduation marks extend

completely around the cylinder, such as the pipet and volumetric flask, hold the eye in such a position that the graduation on the back of the cylinder appears to merge with the line on the front. Similarly, if a buret has marks which extend halfway around the cylinder, it may be turned until the two ends of the line appear to merge as the eye is moved to a level position. Many burets have the smaller divisions marked by a short line only. In reading them some external means must be employed for avoiding parallax. A simple device is a loop of paper held about the barrel with the top edges together at the ends. This loop is moved to a position slightly below the meniscus, and the eye is brought to level by moving it until the top edge of the rear portion of the paper is just visible over the top of the front portion. With the eye in this position, the reading is made.

Procedure. Calibration of Buret.[2] See that the buret is clean, that the stopcock is well greased, and that the capillary tip permits free flow of liquid. Withdraw water (note 1) until the level is at or just below the zero mark. Wait 30 seconds for drainage (note 2), and then read the meniscus, estimating its position to the nearest 0.01 ml. Test for tightness of the stopcock by allowing the buret to stand for 5 minutes and rereading. There should be no noticeable change. During this interval weigh, to the nearest milligram (note 3), a stoppered Erlenmeyer flask of 125-ml capacity.

After tightness is assured, completely fill the buret with distilled water which is at room temperature (note 4), open the stopcock, and allow the liquid to flow rapidly until all air bubbles are expelled from the tip. Continue to withdraw liquid until the level is at or slightly below the zero mark. After allowing time for drainage, read to the nearest 0.01 ml. Touch the tip to the wall of a beaker to remove pendent drop of water. Place the weighed flask beneath the tip, and withdraw approximately 10 ml of water (note 5), taking care to avoid wetting the neck of the flask (note 6). Remove the last drop from the tip by touching it to the wall of the flask. Stopper the flask, allow time for drainage, and read the buret. Weigh the flask with water to the nearest milligram. Record the results as shown in Table 8. Refill the buret (note 7), read, withdraw approximately 20 ml into the same flask, read the buret, and reweigh the flask. Proceed in the same way with the 0–30 ml interval (note 8). After this observation empty the water from the flask, dry the neck with a towel, stopper, and reweigh before introducing the next (the 40-ml) portion of water from the buret. Again empty the flask

[2] Directions are given for calibration at 10-ml intervals for the whole range of the buret. To save time, calibration may be done only for the ranges 0–25, 0–35, 0–45 ml, which will cover the portion ordinarily used. Consult the instructor.

TABLE 8

TABULATION OF RESULTS FOR BURET CALIBRATION *

A *Initial Reading*	*B* *Final Reading*	*B − A* *Apparent Volume (ml)*	*C* *Initial Weight*	*D* *Final Weight*	*Temperature (°C)*	*D − C* *Weight in Air (g)*	*Volume*	*Correction (ml)*
0.44	10 42	9.98	43.752	53.704	26	9 952	9.99	+0.01
0.52	20.55	20.03	53.704	73.687	26	19.983	20.06	+0.03

* Assumed values are given for the 10- and 20-ml intervals.

and weigh before withdrawing the 50-ml portion. Repeat the entire series of observations in order to obtain duplicate results.

Calculate the actual volume of water delivered in each observation by multiplying the weight of water in air by the volume occupied by 1 g

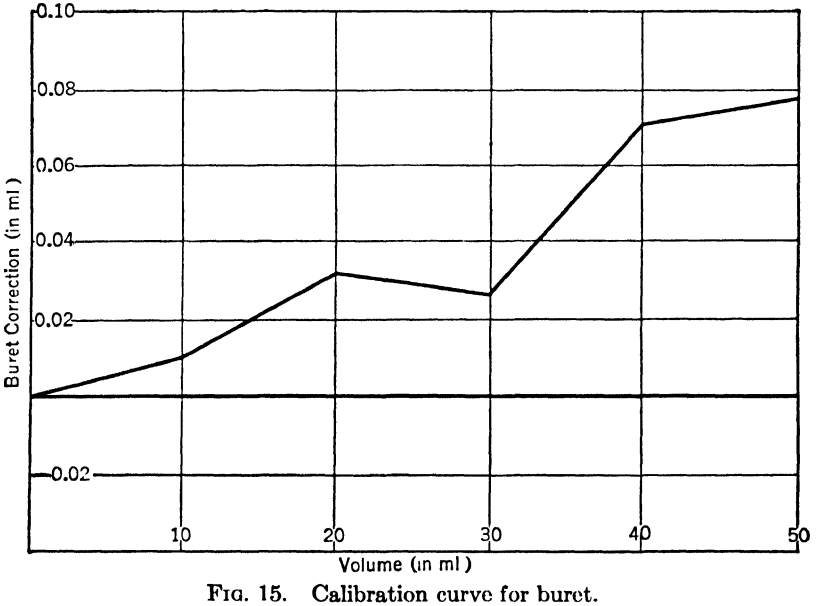


FIG. 15. Calibration curve for buret.

of water at the temperature of withdrawal (note 9). These data are given in Table 9. Subtract the apparent volume, as given by the buret readings, from the actual volume in order to obtain the buret correction

for each interval. Duplicate results should agree within 0.04 ml (note 10). If the agreement for any interval is not within this range, repeat that observation. Plot the buret corrections as shown in Fig. 15.

TABLE 9

VOLUME OCCUPIED BY 1 g OF WATER WEIGHED IN AIR WITH BRASS WEIGHTS AT VARIOUS TEMPERATURES

Temperature (°C)	*Volume* (*ml*)	*Temperature* (°C)	*Volume* (*ml*)	*Temperature* (°C)	*Volume* (*ml*)
10	1.0016	17	1.0023	24	1.0036
11	1.0017	18	1.0025	25	1.0038
12	1.0018	19	1.0026	26	1.0041
13	1.0019	20	1.0028	27	1.0043
14	1.0020	21	1.0030	28	1.0046
15	1.0021	22	1.0032	29	1.0048
16	1.0022	23	1.0034	30	1.0051

Notes. 1. The buret should, as left after cleaning, be filled with water.

2. After liquid is withdrawn from a buret, some time must be allowed for drainage. In general, 30 seconds is sufficient. The magnitude of the drainage effect may be noted by rapidly withdrawing water from a buret and then reading the position of the meniscus at 10-second intervals until the readings become constant.

3. Since the buret readings are accurate to only 0.01 ml, it is unnecessary to know the weight of water more precisely than to 0.01 g. In weighing, the nearest milligram is determined in order to insure accuracy to the nearest centigram. Weighing to the nearest milligram requires no determination of rest point. The rider is simply adjusted until nearly equal swings on each side of the central point of the scale arc obtained.

4. The temperature must be known since the density of water varies with its temperature. Only water which is at room temperature should be used. A frequent source of error in calibration is inaccuracy of the thermometer used for determining the temperature.

5. Calibration in 10-ml intervals is sufficiently accurate.

6. The portion of the flask that comes in contact with the cork should not be allowed to become wet, as the cork may absorb water, which will be lost by evaporation before the weighing.

7. In practice, a buret is so filled that the initial reading is at or near the zero mark. Calibration is consequently performed in the same manner.

8. After the addition of the 30-ml portion, the flask contains approximately 60 ml of water (10 + 20 + 30 ml). Addition of another portion might make the weight of flask plus water exceed the capacity of the balance.

9. The buoyancy correction has been used in compiling the data of Table 9. If the true density of water, as given in handbooks, is used for computing buret corrections, it is necessary to correct all observed weights for buoyancy, according to the methods on page 31.

10. Since each reading may be in error by 0.01 ml, the two readings for one calibration may be in error by 0.02 ml. Should the two readings for the duplicate

determination also be in error by 0.02 ml, but in the opposite direction, the total deviation between the results may be 0.04 ml. Any deviation of this size or greater between the two results is probably due to an accidental error, such as leakage from buret or insufficient time for drainage. Notice that nothing has been said about the possibility of an error in weighing. The reason is that the weighing is made to the nearest milligram, whereas the accuracy needed is only to the nearest 0.01 g.

Procedure. Calibration of 250-ml Volumetric Flask "To Contain." Clean the flask as directed on page 76. After thorough rinsing, clamp it in an inverted position, and allow it to remain until dry. Wipe drops of water from the rim with a clean towel. Place the dry stoppered flask on the left-hand pan of a balance whose capacity is greater than 500 g, and counterpoise the flask by pouring copper shot into a beaker placed on the right-hand pan (note 1). When the rest point is brought near the central point of the scale, note the exact position, lock the beam, remove the flask, and replace it by weights sufficient to make the rest point coincide with the one previously observed. Record the weight, and remove both weights and tare. Place a small funnel in the flask, and add distilled water, at room temperature, until the level is at the base of the neck. Remove the funnel, taking care to avoid wetting the neck above the graduation mark, and fill to the mark by adding water from a pipet. Move the eye to a position level with the graduation mark for the final addition. Should drops of water wet the neck above the mark, remove them by a piece of filter paper wrapped about a stirring rod. If too much water is added, the surplus may be removed by a pipet and the flask refilled. Stopper the flask, and reweigh by the method of substitution, as before. From the weight of water and the temperature, calculate the true volume contained by the flask. Dry the flask, and repeat the determination. Duplicate results should agree within 0.1 ml (note 2).

Notes. 1. The available large balances are not usually designed to give the accuracy of an analytical balance. Weighing by the method of substitution eliminates any error due to inequality of the balance arms.

2. This is a precision of 1/2500. Better results are readily obtainable.

Procedure. Calibration of Pipet. Clean the pipet, and rinse thoroughly. Weigh a stoppered 125-ml Erlenmeyer flask to the nearest milligram. Place the pipet tip in a beaker of distilled water which is at room temperature, and draw up liquid by suction until the level is well above the graduation mark. Quickly place the forefinger of the right hand over the upper end, while grasping the stem between the thumb and the second finger (note 1). Both the finger and the pipet should be dry. The

liquid level will be held constant as long as pressure is applied so as to prevent air leakage about the finger. Dry off surplus water on the outside with a clean towel, then place the tip against the wall of a beaker (note 2), and allow the liquid level to fall slowly by slightly releasing the pressure on the forefinger. Meanwhile, hold the pipet level with the eye and keep it in a vertical position. When the meniscus is just at the mark, apply pressure on the finger to stop the liquid flow, touch the tip to the side of the beaker to remove the pendent drop, quickly withdraw the pipet, and place the tip in the weighed flask. Allow the water to run into the flask, holding the pipet in a nearly vertical position and keeping the tip pressed against the side wall of the flask. Do not blow or shake the last portion of water from the tip. Allow to drain for 20 seconds after the flow of liquid ceases, remove the pipet, stopper the flask, and reweigh. From the weight and temperature of water, calculate the volume delivered by the pipet (note 3). Duplicate results should agree within $\frac{1}{1000}$, which, for a 10-ml pipet, is 0.01 ml. Better results are readily obtainable.

Notes. 1. In using a pipet, never grasp the bowl in the palm of the hand, for the hand will warm the instrument and its contents, thus causing a change in volume.

2. Holding the tip against a glass surface prevents the formation of drops which may adhere to the tip.

3. If it is desired to calibrate a pipet to deliver *exactly* the rated volume, first determine the volume delivered as graduated. Paste a gummed label along one side of the stem, and mark a position estimated to deliver the desired volume. Determine the volume as delivered from this mark. If it does not agree closely with the desired volume, measure the distance between the two marks, and compute by linear interpolation the exact position needed for the meniscus. Make a new mark at this point, and again test. When the exact position has been determined, cover the stem with a thin coat of paraffin, scratch a circle at the desired place, and apply a drop of hydrofluoric acid from a waxed stirring rod. Allow to stand in a hood for a time, rinse off the acid, and melt the wax by gently warming over a flame. Ask instructions before using hydrofluoric acid. It is a dangerous chemical.

Procedure. Relative Calibration of Flask and Pipet for Aliquot Portions.[3] It is often desirable to analyze a definite fraction, known as an aliquot portion, of a sample. When the available apparatus includes a 50-ml pipet and a 250-ml volumetric flask, an aliquot portion is conveniently taken by diluting the solution of the sample in the 250-ml flask and withdrawing 50-ml portions with the pipet. To do this accurately, it is necessary to calibrate the two instruments. A relative

[3] The authors recommend this calibration instead of the absolute calibrations of flask and pipet. Practically all student use of the flask and pipet is for taking aliquot portions.

calibration, as described in the following, requires less time than absolute calibration of the two separately. A further advantage of relative calibration is that the portion taken will constitute an exact $\frac{1}{5}$ fraction, whereas, if absolute calibration is employed, it is seldom that the etched volume marks are in exact 5:1 ratios. The method of relative calibration is to deliver 5 volumes of water into the flask, from the pipet, and to mark the position of the meniscus when this volume is contained in the flask.

Carefully read the instructions for use of the pipet, given in the preceding section. Good results are obtained only by rigorous adherence to the proper technique. Select a pipet and flask so that the tip of the pipet reaches to the bottom of the flask. Clean both, and dry the flask as directed on page 82. Deliver into the dry flask five 50-ml portions from the pipet. Mark the position of the meniscus by pasting a gummed label halfway about the neck. The upper edge of the label is to coincide with the meniscus. Empty and dry the flask, and repeat the determination.

It should be noted that the new mark on the flask is used only when aliquot portions are withdrawn by the pipet used for the calibration. If aliquot portions are to be withdrawn by use of a calibrated buret, the *etched mark of the flask is to be used.*

Essential Calibrations. Calibration of all the apparatus described in this section is too time-consuming for the student in a beginning course. Experience has shown that with the equipment usually available in the college laboratory it is sufficient (1) to calibrate both burets for the 0- to 25-, 35-, and 45-ml intervals and (2) to calibrate the pipet either relative to the 250-ml volumetric flask or to deliver exactly 50 ml. The relative calibration is the easier. In general, flasks are so accurate that calibration is not important, but burets and pipets must be calibrated if an accuracy of 1 part per 1000 is to be assured. Even the buret calibration may be omitted if care is taken to use the same buret for standardization and analysis of solutions, and to employ about the same volume in both operations, because the errors in volume will be largely canceled in the two titrations. If aliquot portions are to be taken by the pipet, a calibration is essential unless very high-grade instruments are used.

Tolerances for Volumetric Glassware. The National Bureau of Standards [4] has formulated a list of specifications for high-grade volumetric apparatus. The tolerances which apply to flasks, burets and transfer pipets are reproduced in Table 10.

[4] *Natl. Bur. Standards Circ.*, **9**, 1916.

TABLE 10

BUREAU OF STANDARDS TOLERANCES FOR VOLUMETRIC GLASSWARE

Capacity up to and Including	*Limit of Error*
Flasks	
25 ml	0.03 ml
50	0.05
100	0.08
200	0.10
300	0.12
500	0.15
1000	0.30
2000	0.50
Burets	
5 ml	0.01 ml
10	0.02
30	0.03
50	0.05
100	0.10
Transfer Pipets	
2 ml	0.006 ml
5	0.01
10	0.02
30	0.03
50	0.05
100	0.08

THE TECHNIQUES OF VOLUMETRIC ANALYSIS

[The material of this section is to be used in conjunction with the various exercises selected for class use and is not repeated in detail for the individual determinations.]

Certain operations occur in almost every volumetric analysis. Much of the success of the analysis will depend on the skill of the analyst in these operations; much of his skill will depend on a proper technique. The following general directions should be carefully studied and applied to the various analyses performed.

Dilution of Solutions to Volume. When only a portion of a solution is to be used in a determination, it is necessary to dilute the whole solution to a definite volume and to take a known fraction of that volume for the determination. The known fraction taken is called an

"aliquot portion." Dilution to volume is done in a volumetric flask. The portion for analysis is measured out either by a pipet or by a buret. A pipet is in general preferable, but the buret may be specified in certain determinations where the solution itself may be used for back titration (see page 90).

Procedure. Place a small funnel in the volumetric flask, and carefully pour the solution from a beaker into the funnel with a stirring rod held across the lip of the beaker. When all the solution has been transferred, wash the inside of the beaker, while still holding it in the pouring

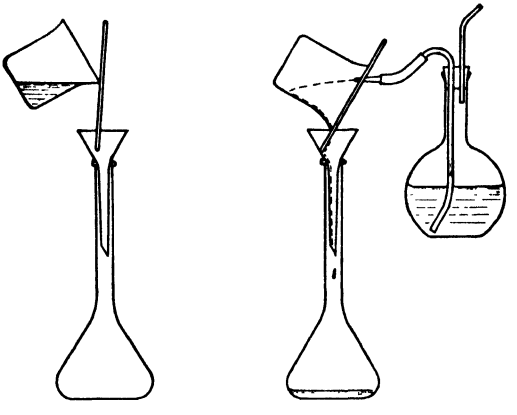


FIG. 16. Transfer of solution to volumetric flask.

position, with a stream of water from a wash bottle. The relative positions of the beaker, stirring rod, funnel, and wash bottle are shown in Fig. 16. When the entire inside wall of the beaker has been well washed, direct a stream of water onto the outside of the lip, to remove any drops that may have crept past the rim. Now rinse down the inside of the funnel, then slowly remove it from the flask, and wash the outside of the stem with a little water. The total volume of water in the flask at this point should not exceed nine tenths of its capacity. Stopper the flask, invert it while holding the stopper tightly in place, and shake. Repeat the inversion and, shaking two or three times, then add water until the level stands a few millimeters below the graduation mark. Complete the addition of water with a pipet, holding the eye level with the graduation mark and allowing water to flow in very slowly. Take care that droplets of water do not adhere to the neck above the graduation mark; this is indication of a dirty flask. When the liquid level stands just at the graduation mark, stopper the flask, invert and shake, return to an upright position, and again invert and shake. The air space will allow enough room for thorough mixing, but only when the flask is inverted.

In shaking a filled flask, rest the stopper on the left hand while holding the bulb in the right hand. Shake by a horizontal motion of the bulb.

Care must be taken that all water used for dilution is at room temperature and that the final temperature is known. When the aliquot portions are withdrawn, the solution must be at the same temperature as that at which the dilution was made.

Preparation of Known Volume of Solution from a Solid Sample. It is frequently necessary to prepare a known volume of solution from a solid sample. In the usual case the sample for student use is soluble in water. The desired weight of sample is measured out, as directed in Chapter 3, and is transferred to a small beaker. Water is added, care being taken to avoid splashing or blowing out of solid particles, and the sample is brought into solution. The resulting solution is then quantitatively transferred to the volumetric flask, as directed in the preceding section.

Transfer of Aliquot Portion by Pipet. The pipet must be clean, and all excess moisture must be shaken from the tip. Wipe the outside of the tip dry with a clean towel. Insert the pipet into the solution, and by suction with the mouth draw up enough liquid to stand at the lower end of the bulb. Quickly place the forefinger of the right hand over the stem, while holding the stem between the thumb and second finger of the right hand, and remove the pipet from the flask. Incline the pipet so that all portions of the walls of the bulb are wet by the liquid, and then discard this rinse liquid, shaking the last drop from the tip. Repeat the rinsing. The two rinsings should not require more than 10–15 ml of solution.

Insert the pipet in the liquid, letting the tip reach nearly to the bottom, and by suction draw up liquid until the level stands well above the graduation mark. Quickly place the forefinger over the stem, and withdraw the pipet from the flask. Wipe off the outside of the tip with a clean towel (or filter paper), and hold the tip back in the flask against the wall, but above the liquid level. Bring the graduation mark on the pipet level with the eye, and by slowly releasing the pressure on the forefinger allow the liquid level to fall until the meniscus stands just at the graduation mark. Stop the liquid flow at this point, quickly remove the pipet, and introduce it into the receiving vessel. Hold it in a nearly vertical position, with the tip against a wall of the vessel. Remove the forefinger, and allow the liquid to flow. Keep the pipet in position for 20 seconds after delivery, to insure thorough drainage, and then remove it from the receiving vessel without shaking or blowing the residual liquid from the tip. If several portions are desired, it is not necessary to rinse between measurements. When the transfers are completed,

rinse the pipet well with distilled water, and place in a stand to drain.

If the pipet and flask have been relatively calibrated, make certain that the solution in the flask was diluted to the proper calibration mark before taking any portion.

Transfer of Aliquot Portion by Buret. In certain titrations, it is desirable to over-run the end point and to back-titrate. When the solution of a sample may be used for back titration, it is desirable to withdraw aliquot portions from a buret, so that the total volume used will be noted after the titration is completed. No effort is then made to obtain an exact aliquot, such as $\frac{1}{5}$, but approximately 40 ml of the sample is run into a flask and is titrated by the appropriate reagent. Additional amounts of solution are added from the buret to the flask, as needed for back titration. When the end point is reached, the total volume of solution used is noted. The operations of transfer to the buret and withdrawal from the buret are described in the following sections.

Filling Buret. The cleaned buret, when not in use, is filled with distilled water. When it is ready to use, open the stopcock, and allow the water to flow into a beaker. When all the water has run out, except that standing in the tip, close the stopcock, remove the buret from its holder, and pour the desired solution directly [5] from the reagent bottle into the buret. The buret is held in the left hand, the reagent bottle in the right hand. The stopper of the bottle is held between the second and third fingers of the right hand so that the plug is kept clean. The lip of the reagent bottle must be wiped with a clean towel before any liquid is poured. Pour about 5 ml of solution into the buret, and rinse the inside walls thoroughly by holding a finger over the top and manipulating the buret so that all portions of the wall are wet by the solution. Allow the rinse liquid to run out through the tip. Repeat the rinsing three times, with 5-ml portions each time (note). Now fill the buret to a point 2–4 cm above the zero graduation mark, and replace in the stand. Open the stopcock, and allow liquid to flow through rapidly, to fill the tip completely, then nearly close the stopcock, and allow the liquid level to fall slowly until it is just at or just below the zero mark. Rinse or wipe off the tip. The buret is now ready for use. *Allow time for drainage before taking the reading.*

[5] Some burets are of such small bore that one cannot pour into them from a 1-l. bottle without spilling liquid. For such the solution is transferred by means of a small beaker or by use of a small funnel. If either method is to be used, care must be taken to avoid dilution or contamination of the solutions. Neither method should be used by students unless the instructor gives specific approval.

Note. Three rinsings with 5-ml portions will insure quantitative removal of the remaining water. If a volume of 1 ml remains in the tip (actually much less than this volume will remain), the addition and draining out of 5 ml of reagent will remove five sixths of the residual liquid, or one sixth will remain after the first rinsing. Three rinsings will reduce the amount of foreign liquid to $(\frac{1}{6})^3$ or $\frac{1}{216}$ ml.

Titration. The conditions for titration vary somewhat with the type of indicator employed to show the end point and with the type of solution undergoing reaction. In some titrations, care must be taken to add reagent just to the point of color change which shows the end point and not to over-run the end point. In others reagent A may be rapidly added until the end point is passed, and then reagent B, which will react with reagent A, is added to bring the solution back to the end-point condition. In the second case the addition of reagent after the end point is passed is known as back titration. If the indicator employed will show a sharp end point without back titration, this process is seldom used. Both cases are discussed in the following sections.

1. Deadstop end point. The measured volume of sample to be titrated should be in solution in an Erlenmeyer flask. The wide-mouth type of flask is preferable. The volume of solution depends on the particular determination. The flask should be large enough so that at the conclusion of the titration it is not more than two thirds full and so that the solution may be mixed by swirling the contents without danger of loss.

Wipe off any pendent drops from the buret tip, place the flask below the buret, and lower the buret until the tip just projects into the neck of the flask. Read the position of the meniscus, and record the value in the notebook. Add the proper amount of indicator solution to the titration vessel. The buret should be turned so that the stopcock handle is on the right-hand side, as the operator faces it. A white background should be provided, either by a white tile, or by paper or a towel placed on the table beneath the sample flask. Encircle the barrel of the buret with the left hand so that the stopcock handle can be easily manipulated by the thumb and first two fingers. Grasp the neck of the titration flask with the thumb and first two fingers of the right hand. Gently swirl the contents of the flask by imparting a rotary motion; avoid any vigorous shaking and splashing. While continuing to swirl the solution, open the stopcock and let liquid flow in rapidly from the buret. When a color change begins to appear, close the stopcock, and continue to mix the solution until the color is that of the original solution. Now add reagent from the buret more slowly, and, as the end point is approached, as shown by the slow change of color when the solution is mixed after each addition of reagent, add reagent a drop at a time. At the last, half-drop

portions may be taken by allowing a drop partly to form on the tip, then touching the tip to the wall of the flask, and allowing the excess liquid to run down the wall. The end point is reached when the addition of a half-drop or a drop will cause a permanent color change. At this point read the buret, after allowing drainage time (usually the search for the end point will automatically give sufficient time for drainage). Confirm the end point by the addition of another drop. If the first point has been prematurely taken, the addition of another drop of reagent should cause a still sharper color change.

2. Back titration. The titration is carried out just as in the previous case, except that no care is taken to avoid over-running the end point. After the end point is passed, there is added, from another buret, a solution that will react with the excess of the reagent used for the titration. The end point is successively passed, in both directions, until the addition of one drop of reagent will cause a sharp color change. At this point the buret readings are taken. The reagent for the back titration may be any substance that will react with the standard solution used for the analysis, the concentration of which is accurately known in terms of the standard solution; usually a solution of the sample to be analyzed is taken for the back titration. For example, if a solution of sodium hydroxide is to be analyzed by titration with hydrochloric acid of known strength, the base solution is put in one buret and the acid solution in another. Approximately the desired amount of the base solution is run into a flask, then acid is added in excess, and finally additional base solution is used for back titration.

Determination of Indicator Blank. In many titrations it is necessary to make a correction for the amount of reagent needed to affect the indicator. This volume of reagent is known as the *indicator blank*. It is determined as follows: To a volume of distilled water equal to the final volume of solution at the end point there are added all reagents used in an analysis except the constituent whose determination is sought. Indicator is added, and the solution is titrated with standard reagent to the same end point as that obtained in an analysis.

Precision. The student should understand the precision that may be obtained in the volumetric operations that have been described. The precision obtained in a titration is governed by the volume of solution employed. Two buret readings, each accurate to 0.01 ml, are needed. If we assume the error in location of the end point to be ± 0.05 ml (1 drop), the total variation may be $0.05 + 0.02$ (for the two buret readings). The larger the volume of reagent, the smaller the error in parts per 1000. But if a 50-ml buret is used, the volume should not exceed this amount, for otherwise it will be necessary to refill the buret, thereby

introducing additional errors. Therefore the size of sample and strength of reagent are so chosen that a titration will require about 40 ml of reagent. The total error will then amount to 0.07 in 40 ml, or 7 parts in 4000. On the average, the precision will be nearer to 1 part per 1000, because there will be some cancellation of the accidental errors. In the operations of diluting the sample to volume and taking aliquot portions, the error will in general be less than $\frac{1}{1000}$ if the pipet and flask have been calibrated and if the temperature is the same for mixing the solution in the flask and for withdrawing aliquot portions.

Precautions. The following precautions are specifically to be observed in the use of volumetric apparatus.

1. See that the apparatus is clean. If drainage is not complete, accurate measurements cannot be made.

2. Carefully rinse the buret and pipet with the solutions to be measured, to avoid dilution of the solutions.

3. *Using care in mixing solutions diluted in a volumetric flask or prepared in bottles is essential.* Failure to do this is a very common student error.

4. The temperature must be the same for the withdrawal of aliquot portions as for dilution to volume.

5. Solutions must not be allowed to stand overnight in a buret. If it is necessary to leave a solution for a period of some hours, the buret must be capped with an inverted test tube to prevent evaporation. After a buret has been standing, the tip should be flushed with fresh solution before any titration is made.

6. When not in use, the buret must be left filled with distilled water or inverted in a beaker of water. An empty buret quickly becomes dirty.

7. A sufficient and uniform drainage time must be allowed for all measurements of volume.

8. A good light and a white background are necessary for accurate titrations.

9. Use properly calibrated equipment.

10. Parallax must be avoided in reading all volumes.

OPERATIONS OF VOLUMETRIC ANALYSIS

The objective in all volumetric analyses is to determine the amount of standard solution required for reaction with a known amount of the sample to be analyzed. The general operations required are: (1) Preparation and standardization of a solution, (2) selection and preparation of the sample, and (3) titration of the sample.

Standard Solution

Concentration. No generalization can be made as to the strength desirable for standard solutions. The lower limit which can be used depends on the sensitivity of the indicator available for titrations. It is not feasible to employ solutions of such low concentration that more than 1 or 2 drops of reagent are required to affect the indicator, because any gain resulting from the use of larger volumes is offset by uncertainty as to the correct end point. Use of concentrated solutions is likewise undesirable, because large samples would be required for the analysis so that a sufficiently large volume of reagent could be used to insure the desired precision. Between the two extremes is the range of concentrations lying from 0.001 N to 1 N. More use is probably made of 0.1 N solutions than of those of any other concentration, because these solutions demand moderately small samples and are yet sufficiently concentrated to give sharp end points with the indicators ordinarily employed.

Preparation of Solution. If the reagent is a substance which can be obtained in a condition of known purity, it may be used for the direct preparation of a solution of known concentration. An accurately weighed sample is dissolved, or an accurately measured sample, if it is available as a solution, is transferred to a volumetric flask and diluted to exact volume as directed in the previous section. The strength of the resulting solution is known with the same accuracy as the strength of the reagent and the volume of the flask.

Direct preparation of a standard solution is not ordinarily feasible because the available reagents are not usually substances of known purity. It is customary, therefore, to prepare a solution of approximately the desired concentration and to standardize this solution by comparison with a reagent of known strength.

Standardization. Standardization is done by comparison of the solution with some substance of known analysis. Either a primary or a secondary standard may be used, but in general primary standards are advisable, if any are available, because every additional comparison increases the possibility of error.

A suitable substance for a primary standard must, of course, be a reagent whose *reaction with the solution to be standardized satisfies the general requirements for volumetric analysis.* Moreover, a primary standard must be a substance of *known purity and definite chemical composition,* and *it must be stable* at the temperature employed for drying. Hygroscopic substances are not desirable because of the difficulty of weighing out samples without contamination by moisture absorbed

from the air. Hydrated substances are not often employed, because it is difficult to remove surface moisture without effecting partial decomposition and thus leading to a substance of unknown purity. It is desirable that the standard have a *high equivalent weight*, in order that errors in weighing shall be reduced. Since the precision in weighing is 0.2 mg, it is necessary to employ samples weighing at least 200 mg (0.2 g) in order to attain an accuracy of $\frac{1}{1000}$. (Low equivalent weight is, however, not a serious objection, because large samples may be weighed out and dissolved, and aliquot portions of the solutions used for the standardization.) The sample must be soluble under the conditions of the analysis. Finally, it is often desirable to take as standard an analyzed sample of the constituent for whose analysis the solution is intended. Too often the end point does not exactly coincide with the stoichiometric point. If the error from this source can be made of the same magnitude in standardization as in analysis, the accuracy is increased. Because of this effect, it is desirable also that the volume of reagent be approximately the same in the titrations of standardization and of analysis.

In standardization, a weighed portion of the pure dry primary standard is dissolved and titrated with the solution to be standardized, according to the procedure necessary for the particular reaction. The weight of standard should be such that a volume of 35–45 ml of reagent is required for titration, in order to minimize the errors of reading the burets and of determining the end point. From the volume of reagent taken and the weight of standard, the concentration of the reagent is calculated.

Preservation of Standard Solutions. Standard solutions must be stored in stoppered containers, in order to prevent evaporation of water and attendant changes in concentration. Solutions for student use, which are required for only a few determinations, may be kept in small stoppered bottles. Laboratory reagents which are kept as standards for long periods of time are conveniently stored in bottles fitted with siphon delivery tubes of glass. Many standard solutions are affected by light; they must be stored in black or amber bottles.

Preparation of the Sample

General directions for the preparation of samples are given in Chapter 5. The sample prepared for a volumetric analysis is generally a solution containing an amount of the constituent to be determined that will require 35–45 ml of the standard solution for its titration.

In preparing his sample, the analyst often may choose between weighing out individual portions for each determination or weighing out a single large sample and taking aliquot portions for analysis. From the viewpoint of the proportionate error introduced in the weighing of the sample the latter procedure is preferable because of the size of sample; this reduction of error may be counterbalanced by the errors of dilution and removal of aliquot portions. It is also true that, if an error is made in recording the weight of the large sample, all the subsequent titrations are in error, even though quite satisfactory checks are obtained for the various aliquot portions. If the sample is likely to be slightly heterogeneous, the use of a large sample and aliquots is almost necessary to obtain checks. Many analysts prefer to use the method for any sample which dissolves readily and leaves no insoluble residue.

Titration of Sample

General directions for the technique of titration have been given. In the laboratory directions specific instructions for the selection of the indicator, temperature of the titration, speed of addition of reagent, exclusion of air, and so on, will be provided, and the more probable sources of error will be pointed out. The student should read the general directions on page 89 before making any titration, in order to avoid gross errors in technique.

When aliquot portions are used, instead of individual weighed samples for each titration, the method of taking the aliquot portion will be governed by the necessity for back titration. When back titration is undesirable, it is preferable to take aliquot portions by means of a pipet. When back titration is needed, and the sample solution is suitable for this purpose, the aliquot portion is more conveniently measured from a buret.

ERRORS IN VOLUMETRIC ANALYSIS

In each analysis studied, reference is made to the errors peculiar to that determination. Many of these are errors which are common to all volumetric procedures; they are of two types, determinate and indeterminate, as discussed in Chapter 4. The volumetric errors of most frequent occurrence are listed in Table 11.

Of the determinate errors, the most probable ones are associated with the concentration of the standard solution taken for the analysis. Even if this has been correctly standardized, the concentration may change before the solution is actually used for analysis. Various types of decomposition may occur, as is noted in the study of certain procedures.

TABLE 11

ERRORS OF FREQUENT OCCURRENCE IN VOLUMETRIC ANALYSIS

Determinate	*Indeterminate*
1. Calibration of apparatus.	1. Error in weighing.
2. Incorrect standardization value.	2. Loss of sample or solution.
(*a*) Purity of standard uncertain.	(*a*) Leaky buret.
(*b*) Decomposition of solution.	(*b*) Loss during transfer.
(*c*) Temperature changes.	3. Imperfect mixing of solutions.
3. Indicator errors.	4. Dilution or contamination of solutions within burets, etc.
	5. Insufficient buret drainage.
	6. Misjudged end point.

Changes in temperature may account for small but definite errors, a 5° temperature change causing a volume change of 1 part per 1000. Because of this effect, the temperature should be noted for every titration. Particular care should be taken that all dilutions to definite volume are made with water which is at room temperature and that the solution is used at the temperature at which dilution was made. The same indeterminate errors may occur in standardization as in analysis and may markedly affect the accuracy of the standardization value. Indicator errors also may be serious. This factor is discussed in each of the procedures studied. It is often very difficult to select an indicator whose end point will coincide with the stoichiometric point.

The indeterminate errors listed need little further comment, except the statement that all of them may be caused by careless work and all may be largely eliminated by careful work. In general, it may be stated that the number of transfers, dilutions, and titrations should be kept at a minimum, since every operation increases the probability of error. The greater the number of duplicate determinations made, the smaller is the average indeterminate error.

QUESTIONS

1. Aside from the fact that no indicator may be available, what objections are there to the use of the following reactions as the basis for volumetric determinations?
   (*a*) Copper + nitric acid.
   (*b*) Ethyl alcohol + acetic acid.
   (*c*) Stannous chloride + mercuric chloride.

2. Why is it necessary to calibrate volumetric glassware? Why can the calibration of a buret be omitted if the buret is to be used for both a standardization and an analysis with the same solution? In general, what is the minimum amount of calibration that will permit accurate work?

3. Why is water chosen as the calibrating liquid for most apparatus? What special precautions must be exercised if a buret which has been calibrated with water is used for measuring a viscous liquid, such as a concentrated solution?

4. What is the advantage of calibrating in intervals measured from zero rather than withdrawing successive 5- or 10-ml portions and weighing each portion?

5. Why is it unnecessary to dry the Erlenmeyer flask used for weighing water in the buret calibration? Why is it important to see that no drops of water adhere to the inside of the flask, near to the top?

6. Describe the procedure for withdrawing a measured aliquot portion by means of a pipet. What calibrations are needed if this method is followed for aliquot portions?

7. Describe the procedure for withdrawing aliquot portions by means of a buret. What calibrations are needed?

8. Two calibration marks are sometimes used for a volumetric flask, one for the absolute volume contained and the other for the volume relative to a pipet. When should the flask be filled to each mark?

9. Why should a buoyancy correction not be applied for the weight of the container for weighing water, in the buret calibration?

10. If a solution has been diluted to volume and mixed at 25°C what change will be noted if the temperature changes to 28°C? How may an accurate aliquot portion be withdrawn if the room temperature has changed after the solution has been diluted to volume?

11. In the use of a buret, what advantage is there in adjusting the volume exactly to zero before beginning a titration? What disadvantage is there in this procedure?

12. Why are burets cleaned by inverting them in cleaning solution rather than filling the upright burets with the solution?

13. Why is it desirable to have graduation marks on a buret extend at least halfway around the tube?

14. Why is ± 0.04 ml set as the outside limit within which buret calibrations must check?

15. Why are the weighings in a buret calibration made to the closest milligram rather than to the closest 0.01 or 0.0001 g?

16. Why is the calibration of the 250-ml volumetric flask not done on the analytical balance? Why is the method of weighing by substitution used?

17. A flask contains 250.1 ml of water at 21°C. If the expansion of glass is neglected, what volume will the flask contain at 30°C?

18. List the requirements for a primary standard.

19. What is meant by a "blank determination"? Should every volumetric determination be accompanied by a blank? Under what conditions may exceptions be made?

20. What are the advantages of standardizing a solution by the substance for whose analysis the solution is intended? Can this procedure always be followed? Why?

21. Why is it often desirable to weigh out a large sample and use aliquot portions for an analysis rather than to weigh out individual portions of the sample for each titration?

22. The following values were obtained in the standardization of a freshly prepared solution:

0.1037, 0.1045, 0.1053, 0.1060, 0.1065.

Would you consider the results reliable? Why? Suggest a cause for these results.

23. Might a buret be calibrated by successive additions of water from a calibrated pipet? Why? Why, then, is this procedure valid for the calibration of a flask?

24. Describe the various methods given for elimination of parallax.

25. A buret calibrator is a modified pipet which is attached to the tip of a buret so that water withdrawn from the buret is forced up into the pipet. The volume delivered by the calibrator is first determined, and then successive portions are withdrawn from the buret to fill the calibrator. For each buret interval the apparent volume withdrawn is noted. Is it necessary to know the temperature when this method is used? Why? Are the errors in buret readings cumulative or not? Is the error in knowing the volume of the calibrator cumulative or not? Explain. Must the calibrator be wet or dry at the beginning of the calibration? Explain. How might drainage errors affect the accuracy in use of a calibrator?

PROBLEMS

1. A 2000-ml volumetric flask is to be calibrated with water, and results must check within $\frac{1}{10}\frac{1}{0}\frac{1}{0}$. If the position of the meniscus can be read within ± 1 ml, how sensitive should the balance be which is used for the weighings?

2. The internal diameter of the neck of a 100-ml volumetric flask is 14 mm. The position of the meniscus can be read to within ± 0.2 mm. If the only error in the calibration is in the estimation of the meniscus position, how closely should duplicate calibrations agree?

3. A 10-ml microburet is calibrated in 0.01-ml divisions and can be read to ± 0.001 ml. If water is to be used as the calibrating liquid and the only error to be considered in setting the tolerance limit for checks is to be the meniscus reading error, how carefully should the water be weighed?

4. Repeat Problem 3 if mercury (density = 13.5 g/ml) is used as the calibrating liquid.

5. From the following data find the correction for the 0–10-ml interval of a buret:

Initial reading	0.17 ml
Final reading	10.25 ml
Weight of flask	50.632 g
Weight of flask + water	60.649 g
Temperature	24°C

6. The thermometer used in the previous calibration reads 3° too high. What is the true correction for the 0–10-ml interval? What error in parts per thousand is introduced by the temperature error?

7. At 23°C a 50-ml pipet delivers 49.754 g of water weighed in air with brass weights. What is the calibration correction for the pipet?

8. If the expansion of glass is neglected, what weight of water will the pipet deliver at 30°C?

9. Repeat Problem 8, but consider the expansion of the glass.

10. Determine the correction for a 250-ml volumetric flask from the following:

Weight of water contained	249.00 g
Temperature	25°C

11. What is the volume of this flask at 20°C?

12. An unmarked volumetric flask is to be calibrated to contain exactly 100.0 ml. The empty flask is weighed on the balance. What additional weights should

be placed on the pan for the correct amount of water weighed in air with brass weights at 20°C?

13. Repeat Problem 12, but use mercury whose density in vacuo at 20°C is 13.5461 g per milliliter.

14. A flask is to contain 200.0 ml at 20°C. It is to be calibrated with water at 25°C; if the expansion of glass is neglected, what weight of water determined in air with brass weights should be put in the flask?

15. Repeat Problem 14 considering the expansion of the glass.

16. The neck of a 250-ml volumetric flask is 18 mm in internal diameter. At 20°C the correction for the flask is −0.1 ml. If an amount of water at 20°C corresponding to a mass of 250.0 g in vacuo is placed in the flask, what is the position of the meniscus with respect to the mark?

17. Repeat Problem 16 for an amount of water corresponding to 250.0 g of water weighed in air with brass weights.

18. From the factor for 25°C in Table 9 compute the density of water in vacuo at this temperature.

19. Derive the factor similar to those of Table 9 for water at 33°C where its density in vacuo is 0.99473 g per milliliter.

20. Derive a factor similar to those of Table 9 which could be used for mercury and brass weights at 20°C. At this temperature the density of mercury in vacuo is 13.5461 g per milliliter.

21. After suitable rinsing a 50-ml pipet full of solution is withdrawn from a 250-ml volumetric flask. This aliquot portion is shown to contain 0.0502 g CaO. How many grams of CaO are present in the whole sample if the true volumes of the pipet and flask are 50.05 and 249.7 ml, respectively. How might some of the calculation of this problem been eliminated by use of different methods of calibration?

22. What is the percentage increase in volume as 1.000 l. of water at 18°C is heated to 28°C?

23. A buret calibrator (see Question 25) delivers 9.95 ml. It is attached to a buret, and the following readings are taken for successive fillings of the calibrator. Compute the correction for each interval in the buret and the total correction to be applied at volumes of 10, 20, 30, 40, 50 ml. Plot the buret corrections.

Buret readings: 0.02, 9.98, 19.93, 29.92, 39.90, 49.91.

CHAPTER

7

Neutralization I. Methods and Calculations

[The material of this chapter is to be studied concurrently with the laboratory exercises selected from Chapter 8. The general discussion given herein is separated from the laboratory exercises in order to facilitate the use of the text as a laboratory manual and to provide in one place a survey of the various applications of acidimetric methods.]

METHODS

The determinations of the amount of acid or base in a sample, by titration of the sample with a standard base or acid are known, respectively, as *acidimetry* or *alkalimetry*. These two processes are applicable to analyses of most acids and bases. In addition, many salts of weak acids may be analyzed by titration with a strong acid.

The essential reaction in all acidimetric or alkalimetric processes is the *neutralization* of hydrogen or hydroxide ion, with formation of water or of some other weak electrolyte. Neutralization reactions satisfy the requirements of volumetric determinations, since the reactions are instantaneous; they proceed practically to completion; and the completion of the reaction can be detected by available indicators.

Standard Solutions

Most of the reagents from which acid and base solutions are prepared are obtained either as concentrated solutions whose strength is not accurately known or as solids of unknown purity. Since the concentration of standard solutions must be accurately known, to within 1–3 parts per 1000, the direct preparation of a standard acid or base solution is not possible. It is customary, therefore, to prepare solutions of approximately the desired concentration and to determine the exact

strength of these solutions by standardization. It is seldom necessary to prepare solutions of exactly a given strength, but, if this is desired, it can readily be done by first preparing a solution slightly stronger than the desired concentration and then diluting it to the desired strength after its concentration is accurately known.

The concentration of a standard solution is determined by the purpose for which it is intended. Most acid or base solutions are made at concentrations of 0.1 to 1.0 normal. Stronger solutions are seldom required. If more dilute solutions are needed, they may be prepared by quantitative dilution of a more concentrated standard solution.

Either an acid or a base might serve as a permanent reference standard in a laboratory, but, because of the greater ease of preservation, an acid solution is always selected for this purpose. If one accurately standardized solution is available, it is easy to determine the strength of other acid or base solutions, by direct or indirect comparison with the standard solution.

Acids. Several factors must be considered in selecting an acid as a permanent standard:

1. The solution should be stable when it is exposed to light.
2. The solute should not be exceedingly volatile, since escape of vapor would cause the concentration to change.
3. The acid should not be a strong oxidizing agent which might, during a titration, decompose the organic substances which are used as indicators.
4. The acid should be one whose salts are soluble.
5. Strong acids are desirable, since weak acids cannot be used for the titration of solutions of weak bases. Furthermore, the choice of indicator is limited when a weak acid is employed for a titration.

Hydrochloric and sulfuric acids are the ones most often used as standard solutions. Nitric acid is seldom used for a standard solution because of its oxidizing properties and its instability when heated or exposed to light. Various organic acids are used as standards under special conditions. The best permanent standard solution is a constant-boiling hydrochloric acid solution (described in the next chapter). Such a solution can be kept almost indefinitely, because the vapor pressure of the acid and water is such that evaporation does not change the concentration. The solution is concentrated but may be used to prepare dilute solutions as needed, merely by weighing out the desired quantity and diluting to a predetermined volume.

Bases. Sodium, potassium, and barium hydroxide are the only readily available strong bases whose solubility is sufficiently great to permit their use in the preparation of standard solutions. Of these,

sodium hydroxide is most widely used. Potassium hydroxide offers no advantages, as compared with sodium hydroxide, and it is somewhat more expensive. Barium hydroxide is not sufficiently soluble to be used for solutions more concentrated than approximately 0.05 N, but it is often used for the preparation of dilute basic solutions which must be free of carbonate. Because of the insolubility of barium carbonate, a solution of barium hydroxide will show, by a precipitate, if carbon dioxide has come into contact with the solution.

Sodium hydroxide, in the solid form, is always contaminated by absorbed moisture and by sodium carbonate. In addition, there are small amounts of impurities such as sodium chloride, sulfate, and silicate. For most purposes none of the impurities except carbonate will cause any interference in the use of the reagent in standard solutions. The presence of carbonate in standard base solutions is not harmful, if the solutions are to be used for titrations of strong acids; but, when the solutions are to be used for titration of weak acids, with phenolphthalein indicator, it is expedient to remove nearly all the carbonate. This may be done in several ways, including precipitation by barium oxide or chloride. The most convenient method is to prepare a 1:1 solution of the base and to remove most of the carbonate, which is slightly soluble under these conditions, by filtration through a Gooch crucible or by decantation of clear liquid. The clear concentrated solution contains only a small amount of carbonate and may be diluted with boiled water to give a satisfactory reagent. Carbonate-free solutions must be protected from carbon dioxide of the atmosphere. The apparatus shown in Fig. 17 is simple and effective. Carbon dioxide is removed from the entering air by passage through a guard tube filled with soda lime or Ascarite.[1] A stopcock is between the absorption tube and the standard solution, to prevent diffusion of water vapor to the absorbent. In student work, the solution may be

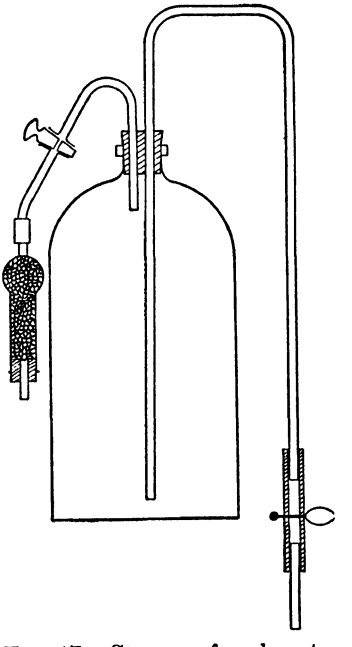


FIG. 17. Storage of carbonate-free base solution.

[1] Soda lime is a mixture of sodium hydroxide and calcium oxide. It is usually provided in the form of small pellets suitable for use in absorption tubes. Ascarite is the trade name for asbestos fibers impregnated with sodium hydroxide.

stored in a stoppered bottle and poured into the buret as needed; the amount of carbon dioxide absorbed in the limited exposure to air will not cause a noticeable error.

Standardization

A large number of substances are available for primary standards in acidimetry–alkalimetry; only a few of those more widely used are discussed here, inasmuch as these are sufficient to take care of almost any need. Since both an acid and base solution are generally prepared, it makes no difference which is compared with the primary standard when the solutions are intended for general laboratory use. The normality of the solution not compared with the primary standard can be easily determined from the *ratio* of the strengths of the acid and base solutions.

When a solution is prepared for the analysis of a particular substance, then the standard is best chosen to correspond with the conditions that will prevail in the analyses. For example, if a sodium hydroxide solution is to be used chiefly for the analysis of samples of acetic acid, it is preferable to standardize by potassium acid phthalate (a weak acid of strength comparable to that of acetic acid) rather than by constant-boiling hydrochloric acid. Similarly, an acid solution which is to be used for the analysis of carbonate samples is best standardized by sodium carbonate.

Potassium Acid Phthalate ($KHC_8H_4O_4$, mol wt 204.2). This is probably the best generally available primary standard. Assayed samples of purity 99.95 per cent or better can be obtained from the Bureau of Standards or from any chemical supply house. Advantages are a high equivalent weight, stability on drying, slight affinity for water vapor, and ready availability. The only disadvantage is that it is a weak acid, but, since base solutions are most frequently used for the analysis of weak acids, this is no handicap. Standard solutions of potassium acid phthalate may be kept for long periods of time without danger of decomposition.[2] Phenolphthalein indicator is employed with this standard, and only carbonate-free strong bases should be used. In neutralization reactions potassium acid phthalate behaves as a monobasic organic acid, comparable to acetic acid in strength.

Sodium Carbonate (Na_2CO_3, mol wt 106.0). Sodium carbonate is the best standard for acids that are to be used for titrations of samples containing carbonate. High-grade carbonate, of assay value 99.95 per cent, is available, or, if preferred, sodium bicarbonate may be purified by recrystallization and converted to carbonate by heating at 260–270°C

[2] J. I. Hoffman, *J. Research Natl. Bur. Standards*, **15**, 583 (1935).

until constant weight is obtained. If prepared sodium carbonate is used, it is advisable to heat this at 270°C to remove water completely and convert any bicarbonate present into carbonate. Care must be taken in selection of titration conditions and of the indicator.

Constant-boiling Hydrochloric Acid. Hydrochloric acid–water solutions have the property of forming a maximum boiling-point system (see textbooks of physical chemistry). At a concentration of approximately 20 per cent acid by weight, there is obtained a solution in which the ratio acid:water is not altered by continued distillation. The composition has been accurately determined as a function of the barometric pressure of the distillation. This property provides a means of readily obtaining a solution of known concentration. A solution is distilled until a constant boiling temperature is obtained. As samples of distillate are collected, the barometric pressure is observed. The concentration of the distillate is computed from the table. Solutions of the desired strength are made by accurately weighing portions of the distillate and diluting to volume in a calibrated flask.

Sulfamic Acid (HNH_2SO_3, mol wt 97.10). This monobasic acid, which is readily available in a purified solid state, has recently been recommended for use as a primary standard.[3] It is readily soluble in water, easily purified by a single recrystallization, and inexpensive. Practically all its salts are soluble. Sulfamic acid is a strong acid and can be used with either phenolphthalein or methyl orange indicator. It should be dried in air because at temperatures of 135°C or above some of the occluded water reacts with the sample, probably by hydrolysis. The only comparable standard available in solid form is potassium biiodate, which is more expensive and more difficult to purify than sulfamic acid.

Gravimetric Standardization. Hydrochloric and sulfuric acids can be, and often are, standardized by gravimetric methods, as listed in Chapter 21. For hydrochloric acid, the chloride ion is precipitated as silver chloride, which is dried and weighed. The accuracy of most other methods for standardization has been tested by comparison with the results obtained from this method. Of course, the method assumes the absence in the solution of any source of chloride ion other than the hydrochloric acid. Gravimetric standardization of sulfuric acid, by precipitation of barium sulfate, is not so satisfactory, because it is difficult, if not impossible, to obtain barium sulfate precipitates in a pure condition.

[3] M. J. Butler, G. F. Smith, and L. F. Audrieth, *Ind. Eng. Chem., Anal. Ed.*, **10**, 690 (1938).

Other Standards. Among the other standards that have been used are:

1. Benzoic acid ($HC_7H_5O_2$). This is inferior to potassium acid phthalate because it is sparingly soluble and is not so readily purified. It too is a weak acid.

2. Calcite crystals. Clear crystals of calcite are nearly pure calcium carbonate. They provide a convenient standard when highest accuracy is not required. A weighed crystal is put into a measured excess volume of acid and allowed to react. The remaining acid is determined by titration with a base that has previously been compared with the acid.

3. Oxalic acid ($H_2C_2O_4 \cdot 2H_2O$). This is open to objection because it is hydrated.

4. Borax ($Na_2B_4O_7 \cdot 10H_2O$). The recrystallized product is dried to constant weight in a desiccator kept at the desired vapor pressure of water by deliquescent sodium bromide. The titration reaction is

$$B_4O_7^{=} + 2H^{+} + H_2O \rightarrow 4HBO_2$$

Analyses

The analyses that can be made by neutralization methods may be grouped in two general classes: (1) determination of the acid or base (or anhydrides of these) in a sample by titration with a standard base or acid, and (2) determination of salts of weak acids (or bases) by titration with a standard solution of a strong acid (or base). Not all acids and bases can be satisfactorily titrated. It is shown in Chapter 9 that the titration of very weak acids or bases is not feasible because a sharp end point cannot be obtained. Failure to obtain a sharp end point is due to hydrolysis of the salt formed. For example, acetic acid, of ionization constant 10^{-5}, can be satisfactorily titrated by a standard solution of sodium hydroxide, but aqueous solutions of boric acid, of ionization constant 10^{-9}, cannot be satisfactorily titrated by sodium hydroxide solutions unless a substance is added to increase the strength of the acid. In most cases when an acid is too weak to be titrated with standard base, a salt of the acid can be titrated with standard acid. For example, carbonic acid cannot be titrated by sodium hydroxide, but sodium carbonate can be titrated by hydrochloric acid, according to the equation:

$$CO_3^{=} + 2H^{+} = H_2CO_3$$

Acid–base Indicators. In all neutralization titrations, results are dependent on the selection of the proper indicator. A comprehensive discussion of the properties of indicators and the selection of an indicator

for a titration is given in Chapter 9. Since this material may be omitted in elementary courses or be deferred until a later date, it is necessary to consider briefly the properties of indicators at this point.

The indicators used in neutralization titrations are highly colored organic compounds that have the property of changing in color when the hydrogen-ion concentration of the solution is changed over a certain range. The most widely used are phenolphthalein, methyl orange, methyl red and bromcresol green.

The hydrogen-ion concentrations at the point of color change (end point) are widely different for various indicators. Phenolphthalein is colorless in solutions in which the concentration of hydrogen ion is greater than 10^{-8} molar and pink in solutions in which the concentration of hydrogen ion is less than 10^{-10} molar. If the hydrogen-ion concentration changes from 10^{-10} to 10^{-8} molar, the phenolphthalein indicator will change from pink to colorless. If the solution assumes a hydrogen-ion concentration intermediate between these two values, the color is also intermediate between deep pink and colorless. It may be recalled that in pure water the concentration of hydrogen and of hydroxyl ion is 10^{-7} molar. Thus phenolphthalein shows a color change on the basic side of neutrality.

Methyl orange, methyl red, and bromcresol green give color changes on the acid side of neutrality, in the region of hydrogen-ion concentration 10^{-3} to 10^{-5} molar. Intermediate between phenolphthalein and these indicators there are many others, with color changes at various hydrogen-ion concentrations. A list of the more common ones is given in Table 17, page 166.

The proper indicator for a titration is one which will exhibit a color change at the hydrogen-ion concentration found at the stoichiometric point of the titration. In the titration of strong acids by strong bases, for example, hydrochloric acid by sodium hydroxide, the salt formed (sodium chloride) does not hydrolyze. Therefore the hydrogen-ion concentration at the stoichiometric point is that of pure water, or 10^{-7} molar. When a weak acid, as acetic acid, is titrated by sodium hydroxide, the salt formed will hydrolyze to give a basic reaction. It happens in this case that at the stoichiometric point the hydrogen-ion concentration is approximately 10^{-9} molar. Therefore phenolphthalein is a suitable indicator. In the titration of a weak base, as ammonium hydroxide, by a strong acid, the salt formed will hydrolyze to give an acid reaction. Methyl red happens to be the most suitable indicator. In the titration of a salt of a weak acid by a strong acid, for example, sodium carbonate by hydrochloric acid, there is formed at the stoichiometric point a solution of the weak acid (see the chemical equation on

page 104). The solution is, therefore, slightly acidic, and methyl orange is a suitable indicator.

From the foregoing it might seem that neither phenolphthalein nor methyl orange would be suitable indicators for the titration of hydrochloric acid by sodium hydroxide, since neither of the indicators shows a color change at the neutral point. It happens, however, that, at the stoichiometric point in this titration, the addition of a very small volume of reagent will greatly change the hydrogen-ion concentration. If an indicator blank is used, as described in the following paragraphs, either indicator is satisfactory.

Indicator Blank. If the indicator color change occurs exactly at the hydrogen-ion concentration found at the stoichiometric point in an analysis, it is not necessary to use an indicator blank. Since it is not always possible to select the indicator so that the end point exactly coincides with the stoichiometric point, it is advisable either to standardize the solution with an analyzed sample of the constituent which is to be determined by this solution or to use an indicator blank in both the standardization and the analysis. The first process is illustrated in the determination of carbonate by titration with hydrochloric acid. If the hydrochloric acid is standardized by pure sodium carbonate, the same indicator error will occur in both standardization and analysis, provided the concentration of carbonic acid is the same at the end point in the two processes. Therefore exact results will be obtained in the analysis.

Use of an indicator blank may be illustrated by results found for the titration of hydrochloric acid by sodium hydroxide. Duplicate titrations were made, one with methyl orange indicator and the other with phenolphthalein indicator.

I. With methyl orange, 25.00 ml of acid was titrated to the end point by 24.80 ml base. In the blank, sodium chloride was added to water, to duplicate conditions found at the stoichiometric point; indicator was added and titrated with acid. A volume of 0.20 ml was found necessary to give the end point. Subtraction of the blank from the total titration volume gives 25.00 − 0.20 ml = 24.80 ml acid. Since this required 24.80 ml of base, the acid and base solutions are of exactly the same strength.

II. With phenolphthalein, 25.00 ml of acid was titrated to the end point by 25.02 ml of base. In the blank it was found that 0.02 ml of base was needed to give the end point. Subtraction of this amount gives the net amount of base, 25.02 − 0.02 ml = 25.00 ml. Again the volume of acid and base used is found to be identical. Without use of the indicator blank a considerable error is found in comparing the two sets of titrations. The use of the uncorrected values would have indicated that

the acid is 24.80/25.00 as strong as the base in the methyl–orange titration or 25.02/25.00 stronger than the base in the phenolphthalein titration.

CALCULATIONS

Calculations of the amount of the various substances involved in a chemical reaction are known as *stoichiometric* calculations. The basis for all such calculations lies in the fact that a chemical equation is a concise statement not only of the relative number of molecules of each substance involved in the reaction but also of the relative weight of each substance. Thus the equation,

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

gives the information that 2×40 weight units of sodium hydroxide react with 98 weight units of sulfuric acid, where 40 and 98 are, respectively, the molecular weights of sodium hydroxide and sulfuric acid. It is immaterial what weight unit is chosen; the essential fact is that the relative weights are in the ratio 80:98. In chemistry the conventional weight unit is the gram.

The weight in grams numerically equal to the molecular weight of a compound is known as a *gram-molecular weight* or a *mole*. Thus 40 g of sodium hydroxide is a mole of the substance, and a mole of sulfuric acid is 98 g. It would be fully as satisfactory to define the mole in terms of any unit other than the gram (for example, the ounce), but it is convenient to use the gram.

The concept of the mole is very useful in all stoichiometric calculations, because the number of moles of each substance involved in a reaction is the number of molecules of that substance appearing in the chemical equation used to state the reaction. The above equation states that two moles of sodium hydroxide react with one mole of sulfuric acid, giving one mole of sodium sulfate and two moles of water.

In all volumetric analyses the volume and concentration of the solutions used enter into the calculations. It is necessary, therefore, to define the various methods of expressing concentration before a detailed consideration is given to the methods of calculation.

Concentration of Solutions

Physical Methods. The simplest methods for expressing the strength of a solution are in terms of the amount of solute present per unit amount of solvent or of solution. These are known as "physical methods" since they are based only on physical measurements of weight or volume, and

do not take into account the chemical reactions of the solute. The more widely used physical methods are:

1. Grams solute per liter (or 100 ml) solution.
2. Grams solute per liter (or 100 ml) solvent.
3. Grams solute per unit weight of solution. Unit weight is most often chosen as 100 g or 1000 g.
4. Grams solute per unit weight of solvent.
5. Percentage methods. The concentration of solutions is frequently stated in percentage, particularly when only an approximate value is indicated. Unless further defined, the term might mean either the weight or volume of solute per 100 g or 100 ml of solution or of solvent, but by general usage the term has come to mean the weight of solid or the volume of liquid diluted to 100 ml of solution. Thus, a 10 per cent salt solution contains 10 g salt per 100 ml of solution, and a 10 per cent alcohol solution contains 10 ml liquid alcohol per 100 ml solution. For exact expression of concentrations, the term "per cent by weight" is common. This means the grams of solute per 100 g of solution; it is a designation which is independent of the effect of temperature on volume. All handbooks give density tables for common reagents, in which the per cent by weight is expressed as a function of the density of the solution.

None of the physical methods provide any direct measure of the chemical strength of the solution. For example, a given volume of a 5 per cent by weight solution of hydrochloric acid will react with more of a base than will an equal volume of a 7 per cent by weight nitric acid solution In order to make chemical calculations involving solutions, it is first necessary to transform the concentrations into chemical units, such as the mole. It is convenient, therefore, to state the concentration in chemical units in order to eliminate the necessity for the conversion. Two chemical units are widely employed, the mole and the equivalent.

Molar Methods. A solution which contains one mole of solute per liter of solution is defined as a *molar solution.* The *molarity* of a solution denotes the number of moles of solute per liter of solution. It is designated by a numerical value[4] preceding the abbreviation "*M*." Thus, 0.1 *M* HCl is a hydrochloric acid solution which contains $\frac{1}{10}$ mole or 3.646 g of hydrogen chloride per liter. This terminology does not in any way indicate that a liter of solution is present, but merely states that the amount of hydrogen chloride is such that a liter of the solution contains $\frac{1}{10}$ mole. The total number of moles of solute in a given volume of solution is the product:

$$\text{Volume in liters} \times \text{molarity}$$

[4] Less often used is the designation $M/10$ to indicate a 0.1 *M* solution.

For example, there are, in 2 l. of 1 *M* solution, 2 moles of solute, and in 500 ml of 1 *M* solution there is $\frac{1}{2}$ mole of solute.

It follows from the definition of the mole and of molar solutions that equal volumes of equimolar solutions contain an equal number of molecules. *This statement is the basis for all calculations involving molarity and should be thoroughly understood before the reader proceeds further.* The volumes of equimolar solutions which enter into a reaction are numerically related to one another as are the respective number of molecules in the chemical equation for the reaction. Thus 2 l. of a molar solution of sodium hydroxide are needed for reaction with 1 l. of a molar solution of sulfuric acid.

The preceding definitions may be concisely summarized in the form of equations:

$$\text{Molarity} = \frac{\text{number of moles solute}}{\text{liters of solution}}$$

$$\text{Molarity} = \frac{\text{grams solute}}{\text{molecular weight}} \times \frac{1}{\text{liters of solution}}$$

$$\text{Moles of solute} = \text{molarity} \times \text{liters of solution}$$

$$\text{Grams of solute} = \text{molarity} \times \text{liters of solution} \times \text{molecular weight}$$

In many physicochemical calculations, it is convenient to employ solutions whose strengths are stated in terms of the weight of solvent rather than volume of solution. A solution which contains one mole of solute per kilogram of solvent is known as a *molal* solution. The method of expressing the concentration is not used in quantitative analysis, because in all quantitative procedures the analyst measures the volume of solution.

Equivalent Methods. The use of the mole as a concentration unit simplifies chemical calculations, as previously shown, but does not provide a basis for direct comparison of the strength of all solutions. For example, a liter of 1 *M* sodium hydroxide will neutralize a liter of 1 *M* hydrochloric acid but will neutralize only $\frac{1}{2}$ l. of 1 *M* sulfuric acid. It may be readily seen that a mole of hydrochloric acid furnishes a mole of hydrogen ion, or 1.0080 g, whereas a mole of sulfuric acid furnishes 2 moles, or 2.0160 g, of hydrogen ion. In all neutralization reactions the fundamental change is the disappearance of hydrogen or hydroxide ion from the solution, usually according to the equation,

$$H^+ + OH^- = H_2O$$

It is convenient, therefore, to choose as the unit that weight of a substance which will furnish a mole of hydrogen or hydroxide ion. The num-

ber of units of all substances involved in a reaction is thus made numerically equal. The *equivalent weight* (eq) provides such a chemical unit. The equivalent weight is defined, for neutralization reactions, as the weight in grams which will furnish or react with one gram-atomic weight of hydrogen ion. For example, an equivalent weight of hydrochloric acid is 1 mole, of sulfuric acid is $\frac{1}{2}$ mole, and of sodium hydroxide is 1 mole. The definition is further illustrated in the following list:

EQUIVALENT WEIGHTS OF SOME ACIDS AND BASES

Substance	*Weight of mole in grams*	*Equivalents per mole*	*Equivalent weight in grams*
NaOH	40.00	1	40.00
$Ca(OH)_2$	74.10	2	37.05
MgO	40.32	2	20.16
HCl	36.46	1	36.46
H_2SO_4	98.08	2	49.04
Na_2CO_3 (complete neutralization)	106.0	2	53.0
$NaHCO_3$	84.0	1	84.0
NH_4OH	35.05	1	35.05

The equivalent weight of a substance depends on the reaction involved in the titration. If H_3PO_4 is titrated with NaOH to a methyl orange end point, the reaction,

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$$

takes place, and the equivalent weight of H_3PO_4 is the same as its molecular weight, because each mole of H_3PO_4 has given up 1 mole of H^+. If phenolphthalein had been used as the indicator, the reaction involved would have been

$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O$$

For this titration the equivalent weight of H_3PO_4 is one-half its molecular weight. For most neutralization titrations the reaction is obvious and does not need to be specified to determine the equivalent weight of a substance.

Since an equivalent weight of any substance will furnish or react with a mole of hydrogen ion, the number of equivalents is numerically the same for all substances involved in a reaction. That is to say, one equivalent of any acid will neutralize one equivalent of any base, since each will furnish or react with the same amount of hydrogen ion. Because of this relation, the equivalent weight furnishes a convenient method for expressing the concentrations of solutions on a comparable basis. A

normal solution is one which contains one equivalent weight of solute per liter of solution. The normality of a solution is denoted by a numerical value followed by the symbol "*N*." Thus the expression 0.1 *N* HCl is read as one-tenth normal hydrochloric acid. Such a solution is one containing one-tenth equivalent of hydrogen chloride per liter. (Also used is the symbol $N/10$ for a 0.1 *N* solution.) This solution is likewise one-tenth molar, because the equivalent and molar weight of hydrogen chloride are the same.

The definitions may be summarized by equations, as was done for molar solutions:

$$\text{Normality} = \frac{\text{equivalents solute}}{\text{liters of solution}}$$

$$\text{Normality} = \frac{\dfrac{\text{grams solute}}{\text{molecular weight}}}{\text{hydrogen equivalents per mole}} \times \frac{1}{\text{liters of solution}}$$

Liters of solution $\times$ normality = equivalents of solute

Liters of solution $\times$ normality $\times$ equivalent weight = grams solute

There is a simple relation between the normality and the molarity of a given solution since the equivalent weight is the molecular weight divided by the number of available hydrogen ions per molecule. The number of equivalents in a mole is equal to one, two, or three; consequently the normality is always 1, 2 or 3 times the molarity—*never less than the molarity.*

Use of Milliequivalents and Millimoles. In the preceding discussion we have taken the liter as the unit of volume. Practically, in laboratory work, we generally use the milliliter as the unit of volume. Thus, the volume required in a titration is stated as 44.57 ml and not as 0.04457 l. This dual selection of units is comparable to the everyday usage in regard to currency. We select the most convenient unit for the purpose at hand. Thus, the price of a car is stated at $1200 but the cost of groceries is stated in terms of cents per pound, rather than as $0.05 per pound. In keeping with this usage, it is convenient to select as the unit of concentration the amount of solute per milliliter of solution, which is $\frac{1}{1000}$ the amount per liter of solution. We can then define a molar solution as one which contains 0.001 mole per milliliter of solution, or 1 millimole (m mol), per milliliter. Likewise a normal solution is one that contains 0.001 equivalent, or 1 milliequivalent (m e), per milliliter.

Since a mole is the molecular weight in grams, a millimole is a molecular weight in milligrams. Likewise, since an equivalent weight is the

weight in grams to furnish or to react with one gram-atom of hydrogen, a milliequivalent is the weight in milligrams necessary to furnish or to react with one milligram-atom of hydrogen. Numerically the weight of solute in grams per liter of solution is the same as the weight in milligrams per milliliter of solution. If a commodity costs \$5 per 100 pounds, it obviously costs 5 cents per pound.

The defining equations given for molar and normal solutions may be restated in terms of millimoles and milliequivalents by substitution of the prefix "milli" before each term which denotes a quantity. Thus,

Milligrams solute
= milliliters solution × normality × milliequivalent weight

In subsequent usage in this book, the choice of equivalent or milliequivalent is dictated by the unit of volume chosen. If the volume is given in liters, calculations are made on the basis of equivalents and grams. If the volume is in milliliters, the calculation uses milliequivalents and milligrams.

Titer. If a solution is to be used for analysis of a particular substance only, it is convenient to know the concentration in terms of the amount of analyzed substance that will react with one milliliter of the reagent solution. This weight is known as the *titer*. If a hydrochloric acid solution is of such strength that 1 ml reacts with 5 mg Na_2CO_3, the titer of the HCl solution is 5 mg Na_2CO_3 per milliliter. The normality is, of course, $\frac{5}{53}$ or 0.0945.

ILLUSTRATIVE PROBLEMS

General Method of Solution. The basis for the solution of all types of neutralization computations is the simple relation that the equivalents of acid are equal to the equivalents of base (which follows from the definition of equivalent). To solve any type of problem one need only to convert the given amounts into equivalents or milliequivalents, depending upon whether the volumes are in liters or milliliters; to equate the equivalents of acid and base; and to express the answer in proper units. Methods for these operations are illustrated in the following paragraphs for various typical calculations. The student should not memorize these examples but should seek to understand the reasoning of each so that he can apply the methods to similar problems.

Dimensions. The student will find that he can more readily understand stoichiometric computations if he will label from the beginning each numerical value used. These labels can be treated algebraically just as are the numbers; the result is that units are then furnished for

the numerical answer. This is not a new concept—in everyday life it is usually done. For example, if apples cost 5 cents apiece one determines the number which can be bought for $2 by the relation:

$$\text{Number of apples} = \frac{200 \text{ cents}}{\dfrac{5 \text{ cents}}{\text{apple}}}$$

$$= 40 \text{ apples}$$

A more sophisticated solution is to employ exponents for each dimension, as one does in physics problems. That is,

$$\text{Number of apples} = \frac{200 \text{ cents}}{5 \text{ cents} \cdot \text{apples}^{-1}}$$

We shall in this text use the mixed fraction form rather than the exponents, but the student should be able to use either intelligently.

The treatment of a problem involving volume and normality of a solution is exactly like the everyday apple problem. For example, the number of milliequivalents in 5 ml 2 N HCl solution is given by the relation,

$$\text{Number of milliequivalents} = 5 \text{ ml} \times \frac{2 \text{ m e}}{\text{ml}} = 10 \text{ m e}$$

The weight of HCl in 5 ml 2 N HCl is given by the relation,

$$\text{Milligrams HCl} = 10 \text{ m e} \times 36.46 \text{ mg/m e} = 364.6 \text{ mg}$$

We may now proceed to various types of problems which illustrate just about every situation that can arise in the laboratory work.

Preparation of Solutions. Most solutions are prepared by dissolving a weighed amount of solid and adding sufficient water to make the desired volume. One must determine how much solid to weigh out to prepare a given volume of solution.

Problem. How many grams of pure sodium hydroxide, mol wt 40.0, are needed for preparation of 500.0 ml 0.1000 N solution?

Solution: To illustrate the use of equivalents and milliequivalents, we shall work this problem in two ways. To use equivalents we express the volume in liters According to the definitions previously given,

$$\text{Equivalents solute} = \text{volume in liters} \times \text{normality}$$
$$= 0.5000 \text{ l.} \times 0.1000 \text{ eq/l.} = 0.0500 \text{ eq}$$

To get the weight in grams we need only multiply the equivalents by the weight of 1 eq, or

$$\text{Weight in grams} = 0.0500 \text{ eq} \times 40.0 \text{ g/eq} = 2.000 \text{ g}$$

To work the same problem in milliequivalent terminology we express the volume in milliequivalents. Then, by the previous definitions,

$$\text{Milliequivalents solute} = \text{volume in milliliters} \times \text{normality} = 500.0 \text{ ml} \times 0.1000 \text{ m e/ml} = 50.00 \text{ m e}$$

The weight in milligrams is given by the relation:

$$\text{Weight} = \text{milliequivalents} \times \text{milligrams per milliequivalent} = 50.00 \text{ m e} \times 40.0 \text{ mg/m e} = 2000 \text{ mg} = 2.000 \text{ g}$$

Note that in this problem it is equally convenient to express the volume in liters or in milliliters and therefore that either the equivalent or the milliequivalent method can be conveniently used. This is not always true. If, for example, the problem had asked for preparation of 150 l., it would lead to very large numbers if the computation were made on the milliequivalent basis. Conversely, if the volume were 15 ml, it would lead to very small numbers to work with equivalents. In every problem a choice should be made as to the most convenient unit to employ.

Problem. What is the normality of a solution prepared by dissolving 25.20 g oxalic acid ($H_2C_2O_4 \cdot 2H_2O$, mol wt 126.1) in sufficient water to give 1.200 l. of solution? What is the molarity of the solution?

Solution: First we determine the equivalents. The equivalent weight is 126.1/2 or 63.05 g, since oxalic acid has two replaceable hydrogen atoms.

Therefore,

$$\text{Number of equivalents} = \frac{25.20 \text{ g}}{63.05 \dfrac{\text{g}}{\text{eq}}} = 0.3996 \text{ eq}$$

The normality is

$$N = \frac{0.3996 \text{ eq}}{1.200 \text{ l.}} = 0.3330 \text{ eq/l.}$$

To find the molarity, we note that, since a mole furnishes two equivalents, the number of moles per liter is one-half (*never twice*) the number of equivalents. Therefore,

$$\text{Molarity} = \frac{0.3330 \dfrac{\text{eq}}{\text{l.}}}{2 \dfrac{\text{eq}}{\text{mole}}} = 0.1665 \text{ mole/l.}$$

Dilution of Solutions. A solution of known normality is frequently prepared from a more concentrated one of known strength by quantitative dilution.

Problem. What volume of 0.1500 *N* reagent is needed for the preparation of 500.0 ml 0.1000 *N* solution? (Note that in this problem it is not necessary to know what the reagent is. Since the normality is given, the computation does not in any way depend on whether the solution contains an acid, base or salt.)

Solution: We note that both the volume and normality of the final solution are given. Therefore the milliequivalents required is given by the product

$$\begin{aligned}\text{Milliequivalents required} &= 500.0 \text{ ml} \times 0.1000 \text{ m e/ml} \\ &= 50.00 \text{ m e}\end{aligned}$$

To complete the problem we need only determine what volume of 0.1500 *N* solution is needed to provide 50.00 m e:

$$\text{Volume required} = \frac{50.00 \text{ m e}}{0.1500 \dfrac{\text{m e}}{\text{ml}}} = 333.3 \text{ ml}$$

Remarks: To prepare the desired solution we may add 166.7 ml of water to 333.3 ml of the 0.1500 *N* solution, or, more accurately, place 333.3 ml of the 0.1500 *N* solution in a 500-ml volumetric flask and dilute to the mark. When solutions of a predetermined normality are required, the computation is like that of this problem. A solution is made somewhat stronger than the desired concentration and is accurately standardized. Then, by quantitative dilution, the desired strength is obtained.

Determination of Normality of Solution by Comparison with a Standard. It has previously been stated that usual practice is to prepare solutions of approximately the desired strength and then to determine the exact strength by titration against a solid primary standard. The following problems illustrate the computations needed. First we will consider a titration made just to the end point, without any back titration.

Problem. A 0.9324-g sample of pure potassium acid phthalate is dissolved and titrated with 41.73 ml of a base solution, using phenolphthalein indicator. What is the normality of the base solution? (Note that in this problem we have not stated what base is used nor what volume of water is added to the potassium acid phthalate sample. It is necessary to know neither. Any base, if strong, will neutralize the potassium acid phthalate completely. The amount of water added to the KHP does not in any way affect the titration since we add enough base to neutralize it completely. In practice we add some 50 ml of water, to dissolve the weighed sample readily, but do not measure the water.)

Solution: Here the data given are the weight of standard and its equivalent weight (look up in table on back cover of book), 204.2. We compute the millequivalents of standard by dividing the weight in milligrams by the milliequivalent weight.

$$\text{Milliequivalents} = \frac{932.4 \text{ mg}}{204.2 \text{ mg/m e}} = 4.566 \text{ m e}$$

The normality of the base is obtained by dividing the number of milliequivalents by the volume, in milliliters.

$$\text{Normality} = \frac{4.566 \text{ m e}}{41.73 \text{ ml}} = 0.1094 \frac{\text{m e}}{\text{ml}}$$

When experience has been gained with this type of problem, it should be set up so that it may be solved by a single operation with logarithms.

$$N = \frac{932.4 \text{ mg}}{204.2 \text{ mg/m e} \times 41.73 \text{ ml}} = 0.1094 \frac{\text{m e}}{\text{ml}}$$

In many titrations it is preferable to over-run the end point and then to back-titrate until the end point is just reached (see page 90). This procedure is illustrated in the following problem.

Problem. In the standardization of an acid and base solution, sodium carbonate of assay value 99.5 per cent was used. A sample weighing 0.2200 g was dissolved, 43.50 ml of acid solution was added, and 2.75 ml of base solution was required for back titration. In another titration it was found that 38.63 ml acid was needed to react with 33.27 ml of the same base. Calculate the normality of the acid and base solutions.

Solution: First we compute the milliequivalents of sodium carbonate, by dividing the weight of pure substance by the milliequivalent weight. The weight of pure substance is the gross weight times the purity factor.

$$\text{Weight sodium carbonate} = 220.0 \text{ mg} \times 0.995 = 218.9 \text{ mg}$$

$$\text{Milliequivalents sodium carbonate} = \frac{218.9 \text{ mg}}{53.00 \text{ mg/m e}} = 4.130 \text{ m e}$$

Next we compute the *net* volume of acid required to react with 4.130 m e of standard. The total volume of acid, 43.50 ml, is that required for titration of the standard and of the base consumed in the back titration. We note that the base is stronger than the acid. Therefore,

$$2.75 \times \frac{38.63}{33.27} = 3.19 \text{ ml of acid}$$

Here the ratio 38.63/33.27 is taken from the values found in a comparison titration of the acid and base.

The net volume of acid is 43.50 − 3.19 = 40.31 ml. Hence, the normality of the acid,

$$\frac{4.130 \text{ m e}}{40.31 \text{ ml}} = 0.1025 \frac{\text{m e}}{\text{ml}}$$

The normality of the base is obtained from the results of the comparison of the acid and base.

$$\text{Normality of base} = \frac{0.1025 \times 38.63}{33.27} = 0.1190$$

A very common error in this type of computation is to reverse the acid–base ratio in the last step. This can be avoided by a little thought. Since the comparison requires 38.63 ml acid for 33.27 ml base, it is obvious that the base is stronger than the acid. Therefore the normality of acid is multiplied by a ratio that is greater than unity, namely 38.63/33.27 rather than the reciprocal of this ratio.

Analysis of Samples by Titration with Standard Solutions. The whole object in the preparation of standard solutions of acids and bases is to use these solutions for analysis of samples. A weighed portion of sample is dissolved in water and titrated with standard acid or base to the proper end point. From the volume of reagent used and the weight of sample, the percentage purity of the sample is computed.

Problem. A sample of impure oxalic acid ($H_2C_2O_4 \cdot 2H_2O$, mol wt 126.1) which weighs 0.4750 g requires 35.60 ml 0.2000 *N* sodium hydroxide for its titration. Calculate the percentage of oxalic acid in the sample.

Solution:

Milliequivalents base = milliequivalents oxalic acid = 35.60 ml × 0.2000 m e/ml = 7.120 m e

Milligrams oxalic acid in sample = milliequivalents × weight of 1 m e = 7.120 m e × 126.1/2 mg/m e = 448.9 mg = 0.4489 g

$$\text{Percentage} = \frac{\text{grams oxalic acid} \times 100}{\text{weight of sample}}$$

$$= \frac{0.4489}{0.4750} \times 100 = 94.51\%$$

A sample of impure calcite ($CaCO_3$, mol wt 100.1) which weighs 0.4950 g is dissolved in 50.00 ml of standard acid, and the excess acid is titrated with standard base, 5.25 ml of base being required; 1.000 ml of acid is equivalent to 0.005300 g sodium carbonate; 1.050 ml acid = 1.000 ml base. Calculate the percentage of calcium carbonate in the sample.

Solution:

$$\text{Normality of acid} = \frac{5.300 \text{ mg/ml}}{53.00 \text{ mg/m e}} = 0.1000 \text{ m e/ml}$$

$$\text{Net volume acid required for titration of sample} = 50.00 - \left(5.25 \times \frac{1.050}{1.000}\right)$$

$$= 44.49 \text{ ml}$$

Milliequivalents acid = Milliequivalents calcium carbonate

$$44.49 \text{ ml} \times 0.1000 \frac{\text{m e}}{\text{ml}} = 4.449 \text{ m e}$$

Weight calcium carbonate = 4.449 m e × 50.05 mg/m e = 222.7 mg

$$\text{Percentage calcium carbonate in sample} = \frac{222.7 \times 100}{495.0} = 44.99$$

Preparation of Standard Solutions by Use of Constant-boiling HCl. One of the good methods for preparation of standard HCl solution is by dilution of a weighed sample of constant-boiling acid to known volume. The computations for this method introduce some variations from those previously given.

Problem. If 18.0175 g of constant-boiling HCl, prepared at a pressure of 743 mm, is diluted to exactly 1 l., what is the normality of the solution?

Solution: According to the data of Foulk and Hollingsworth, on page 131, the composition of a solution distilling at 740 mm is such that 179.766 g contain 1 mole HCl. At a pressure of 750 mm, 179.979 g of solution contain 1 mole. The amount of solution distilling at 743 mm which will contain 1 mole HCl is obtained by interpolation between the above figures. The difference in the weight of distillate needed to contain 1 mole of acid is 0.213 g distillate per 10 mm pressure. The weight of distillate at 743 mm needed for 1 mole of acid is, therefore, given by the expression

$$\text{Weight of distillate per mole HCl} = 179.766 + (\tfrac{3}{10} \times 0.213) = 179.830 \text{ g}$$

The sample, 18.0175 g, contains 18.0175/179.830 or 0.1002 mole HCl. Since the total volume of solution is 1 l., the normality is 0.1002.

Density and Composition of Aqueous Solutions. All handbooks of chemistry give numerous tables showing the per cent by weight of various solutions as a function of the density. Such tables provide a ready means of determining the strength of a solution. One merely measures the density, by means of a hydrometer or pycnometer, and by reference to the table determines the composition. He must then be able to compute from the percentage by weight the normality and molarity of the solution.

Students often confuse density and specific gravity. Density is the weight of 1 ml of a substance. Specific gravity is the relative weight as compared with an equal volume of water. If the specific gravity is given in relation to water at 4°C, then it is also the density, but, if the water temperature is not 4°C, then the specific gravity must be multiplied by the density of water at the temperature of comparison to convert to density.

Problem. Sulfuric acid of density 1.3028 g per milliliter contains 40.00 per cent H_2SO_4 by weight. Compute the normality and molarity of the solution.

Solution: Weight of 1 ml acid solution = 1302.8 mg

$$\text{Weight of acid in 1 ml} = 1302.8 \text{ mg} \times 0.4000 = 521.1 \text{ mg}$$

$$\text{Normality of acid} = \frac{521.1 \text{ mg}}{49.04 \text{ mg/m e}} = 10.63_6 \text{ m e/ml}$$

Molarity = one-half normality, since 1 mole furnished two equivalent weights. Therefore molarity = 5.31_8.

Titer and Normality. What is the normality of a hydrochloric acid solution having a sodium carbonate titer of 5.00 mg per milliliter?

Solution: According to the data 1 ml of the acid will react with 5.00 mg sodium carbonate, whose milliequivalent weight is 53.0 mg. Therefore the normality of the acid is

$$5.00 \text{ mg/ml} \div 53.0 \text{ mg/m e} = 0.0943 \text{ m e/ml}$$

Factor Weight Solutions. It is often convenient to prepare solutions of such strength that, when a predetermined weight of sample is used, the volume of the standard solution required for a titration shall represent the percentage of the constituent sought in the analysis.

Problem. What must be the normality of a sodium hydroxide solution if the volume used for the titration of a 0.5000-g sample represents the percentage of acetic acid in the sample?

Solution: According to the data 1.00 ml of the base solution is equivalent to 1.00 per cent or 5.00 mg acetic acid. Therefore the normality of the solution is

$$\frac{5.00 \text{ mg/ml}}{60.05 \text{ mg/m e}} = 0.0833 \text{ m e/ml}$$

It is sometimes convenient to weigh out exact weight samples for use with a solution of a certain normality so that a simple relation exists between the volume of solution used and the percentage of the sought constituent.

Problem. What size sample should be taken for analysis so that each milliliter of 0.1200 *N* HCl used for titration represents 0.500 per cent Na_2O in a sample of soda ash?

Solution:

$$1.000 \text{ ml acid} = 0.1200 \text{ m e} \quad \text{or} \quad 0.1200 \times \frac{61.99}{2} = 3.720 \text{ mg } Na_2O$$

This weight of Na_2O is 0.500 per cent of the sample, or the sample weighs

$$3.720 \text{ mg} \times \frac{100.0}{0.500} = 744 \text{ mg}$$

QUESTIONS

1. Which indicator, phenolphthalein or methyl orange, should be used in each of the following titrations?

HCl *vs.* NaOH
H_2SO_4 *vs.* NH_4OH
Benzoic acid *vs.* NaOH
Borax *vs.* HCl

2. A sample of 0.1000 *N* HCl of volume 25.00 ml is titrated with 0 1000 *N* NaOH (carbonate-free), and methyl red is used as the indicator. Does it require exactly 25.00 ml of base or more or less than this amount to reach the end point?

3. Why is the reaction $H^+ + OH^- = H_2O$ suitable for volumetric purposes?

4. Criticize and correct the statement, "In all acid–base titrations the *p*H of the solution at the stoichiometric point is always 7."

5. List, in order of preference, the standards which are generally available for acids and bases. Discuss the advantages and disadvantages of each.

6. If benzoic acid and potassium acid phthalate were equally suitable as a primary standard, why would it still be desirable to select the phthalate as a standard? Consider the equivalent weights in preparing your answer.

7. Why are the permanent laboratory standard solutions usually either hydrochloric or sulfuric acid?

8. Why is it desirable that sodium hydroxide solution be nearly free of carbonate?

9. Describe two methods for the preparation of carbonate-free base.

10. Define the following terms: solution, solute, concentration, equivalent weight, atomic weight, mole, molecular weight, milliequivalent, specific gravity.

11. If a buret retains 1 ml of liquid after drainage, what volume of the original liquid will be present after the buret has been rinsed three times with 5-ml portions?

12. Why is not a buoyancy correction applied to the weight of Na_2CO_3 when it is used as a primary standard?

PROBLEMS

1. Construct a table showing for HCl, NaOH, H_2SO_4, Na_2CO_3, and BaO:
   (*a*) Equivalent weight.
   (*b*) Milliequivalent weight.
   (*c*) Weight of solute in grams per liter of 0.15 *N* solution.
   (*d*) Weight of solute in milligrams per milliliter of 0.15 *N* solution.
   (*e*) Weight of solute in milligrams per milliliter of 0.15 *M* solution.

2. Use molecular weights rounded to the nearest whole number, and solve the following problems mentally to establish the fundamental concepts of stoichiometric calculations and the selection of units.
   (*a*) How many moles of NaOH are present in 1700 ml of 0.2 *M* solution?
   (*b*) How many milliequivalents of H_2SO_4 are present in 50 ml of 0.4 *N* solution?
   (*c*) How many milligrams of KOH are present in 25 ml of 0.04 *N* solution?
   (*d*) How many grams of HNO_3 are present in 1500 ml of 0.2 *M* solution?
   (*e*) 85.5 mg of $Ba(OH)_2$ is dissolved in 500 ml of solution. What is the normality of the solution?
   (*f*) How many milligrams of Na_2CO_3 will react with 50 ml of 0.2 *N* HCl?
   (*g*) How many milliliters of 0.1 *N* NaOH solution will react with 30 ml 0.15 *N* HCl solution?
   (*h*) How many milliliters of 0.025 *M* $Ba(OH)_2$ solution will react with 50 ml of 0.1 *N* H_2SO_4?
   (*i*) 25 ml 0.2 *N* KOH reacts with 50 ml of H_3PO_4 solution. What is the normality of the acid solution?
   (*j*) If the titration reaction in (*i*) is: $H_3PO_4 + 2OH^- = HPO_4^{=} + 2H_2O$, what is the molarity of the phosphoric acid solution?

3. What is the equivalent weight of:
   (*a*) Potassium tetraoxalate, $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$, if complete neutralization is assumed?
   (*b*) Sodium carbonate if it is titrated to the phenolphthalein end point with HCl?
   (*c*) Sodium tetraborate decahydrate if the titration reaction is that given on page 104.
   (*d*) $Na_3PO_4 \cdot 12H_2O$ if it is titrated with phenolphthalein as an indicator to form $HPO_4^{=}$?

4. How many grams of solute are in each of the following solutions:

Solution	*Concentration*
(*a*) 2 l. HCl	2.5 *N*
(*b*) 3 l. H_2SO_4	1.5 *N*
(*c*) 150 ml HCl	0.25 *N*
(*d*) 125 ml NaOH	1.5 *N*
(*e*) 1.5 l. Na_2CO_3	2.0 *N*

5. How may each of the following solutions be prepared:
   (*a*) 150 ml 0.1 *N* NaOH, from solid NaOH.
   (*b*) 100 ml 0.1 *N* NH_4OH, from a 1.1 *N* solution.
   (*c*) 1.5 l. 0.05 *N* $Ba(OH)_2$, from solid BaO.
   (*d*) 150 ml 0.15 *N* HCl, from a 12 *N* solution.
6. How much of substance *B* is needed to react with the given amount of *A*?

A	*B*
(*a*) 40.00 ml of 0.5000 *N* H_2SO_4	____ mg MgO
(*b*) 106.0 mg Na_2CO_3	____ ml 0.1000 *N* HCl for complete neutralization
(*c*) 30.00 ml of 0.2000 *M* H_2SO_4	____ ml 0.2000 *N* NaOH
(*d*) 25.00 ml of 0.1500 *N* KOH	____ mg benzoic acid
(*e*) 204.2 mg of potassium acid phthalate	____ ml 0.04000 *N* KOH
(*f*) 4.000 m e H_2SO_4	____ ml 0.0250 *M* $Ba(OH)_2$
(*g*) 0.5000 g 85.0% H_3PO_4 solution	____ ml 0.1200 *N* NaOH if reaction is: $H_3PO_4 + OH^- = H_2PO_4^- + H_2O$

7. What size sample (to the nearest 0.01 g) should be taken of each of the following, in order that 40.00 ml 0.2000 *N* acid or base shall be needed for the titration of the sample?
   (*a*) $KH(IO_3)_2$.
   (*b*) Na_2CO_3.
   (*c*) Sulfamic acid.
8. How many milligrams of calcite $CaCO_3$ are needed to neutralize 40.15 ml of 0.0982 *N* H_2SO_4? of 0.0982 *M* H_2SO_4?
9. What are the normality and molarity of a solution prepared by dissolving 8.050 g of $Ba(OH)_2 \cdot 8H_2O$ in 1500 ml of solution?
10. To what volume should 50.00 ml of 1.250 *N* H_2SO_4 solution be diluted to prepare a 0.8000 *N* solution?
11. 35.00 ml of a H_2SO_4 solution yields a precipitate of $BaSO_4$ which weighs 0.8000 g. What is the normality of the acid?
12. 25.00 ml of a HCl solution is required to react with 0.1854 g of pure Na_2CO_3. What is the normality of the acid? 32.16 ml of the acid reacts with 29.65 ml of NaOH. What is the normality of the NaOH?
13. From the following data compute the normality of an acid and a base:

Weight of sulfamic acid	0.3500 g
Volume of base	35.75 ml
29.17 ml acid = 31.01 ml base	

14. Find the normality of acid and base solutions from the following:

Weight of Na_2CO_3(99.5% pure)	0.2027 g
Volume of HCl	45.50 ml
Volume of NaOH (back titration)	3.57 ml
35.05 ml NaOH = 31.03 ml HCl	

15. A sample of vinegar weighs 12.00 g and requires 40.15 ml of 0.2000 *N* base for titration. Find the percentage of acetic acid in the vinegar.

16. 45.00 ml of 0.1163 *N* H_2SO_4 was added to 0.4000 g of a sample of soda ash which is 67.72 per cent Na_2CO_3. What volume of 0.1053 *N* NaOH is required for back titration?

17. A soda-lime sample is 90 per cent NaOH and 10 per cent CaO. If 3.00 g is dissolved in 250 ml, what is the total normality of the solution as a base? How many milliliters of 0.5100 *N* H_2SO_4 would be required to titrate 100 ml of the solution?

18. Compute the normality and molarity of each of the following solutions:

(*a*) HCl, of density 1.12, containing 24.0 per cent HCl by weight.

(*b*) HNO_3, of density 1.42, containing 72.0 per cent HNO_3 by weight.

(*c*) H_2SO_4, of density 1.83, containing 95 per cent H_2SO_4 by weight.

(*d*) H_2SO_4, of density 1.8022, containing 71.84 per cent SO_3 by weight.

(*e*) NH_4OH, of density 0.89, containing 30 per cent NH_3 by weight.

(*f*) NaOH, of density 1.10, containing 10 per cent NaOH by weight.

19. How many milliliters of a HNO_3 solution whose density is 1.389 g per milliliter and which contains 63.00 per cent acid by weight are required to prepare 1500 ml of a 0.3000 *N* solution?

20. A solution of sulfuric acid has a density of 1.250 g per milliliter and contains 49.00 per cent H_2SO_4 by weight.

(*a*) How many milliliters of this acid are needed to prepare 250.0 ml of 0.2000 *N* solution?

(*b*) 250.0 ml of the concentrated acid is diluted to 2.000 l. What is the normality of the diluted solution?

21. What is the normality of a sulfuric acid solution of density 1.2185 g per milliliter at 20°C? (Refer to an handbook for the necessary data to solve this problem.)

22. Express titers as follows:

(*a*) 0.1500 *N* HCl in terms of: NaOH, Na_2O, BaO, K_2CO_3.

(*b*) 0.1200 *N* NaOH in terms of: HCl, H_2SO_4, sulfamic acid, potassium acid phthalate.

For additional problems illustrating neutralization methods, see page 145.

CHAPTER

8

Neutralization II. Laboratory Exercises

INTRODUCTION

This chapter contains laboratory exercises selected to represent the acid–base determinations of most frequent occurrence. Several methods are described for standardization of the solutions. The authors recommend that students use the potassium acid phthalate method, with carbonate-free base, since this is today the generally preferred method in analytical laboratories. Moreover, by this method the titration procedure is simpler, and student results are better than those obtained with sodium carbonate standardization.

Directions are given herein only for the preparation and use of 0.1 N solutions. This choice is based chiefly on the fact that the commonly available analyzed samples used for unknowns are prepared for use with 0.1 N solutions; with stronger solutions inordinately large samples must be used, and with more dilute solutions the weights of sample are too small and the end-point difficulties too great for student use. The student should realize, however, that in later work he may need concentrations from 0.01 to 1 N, depending on the type of sample he may wish to analyze.

Directions are given for the analysis both of prepared samples of potassium acid phthalate and sodium carbonate and of acid and base solutions dispensed by the instructor. With large classes the authors have found the latter more convenient and economical, but with small classes the commercially analyzed samples are preferred. Analyzed dried-blood samples are recommended as unknowns for the Kjeldahl determination of nitrogen.

Indicators

Directions for the preparation of the more commonly used indicator solutions are given in the Appendix, on page 490. Phenolphthalein is recommended for titration of weak acids by carbonate-free base. In previous editions the authors recommended modified methyl orange for titration of carbonates, but more recently the dye, xylene cyanole FF, has not been available. Prepared solutions of the mixed indicator can be purchased, but these do not appear to be completely stable and do not give such good results as were formerly obtained with solutions mixed at the time of using. Perhaps the best generally available indicator for carbonate titrations is the mixed methyl red–bromcresol green indicator, used with boiling for removal of carbon dioxide. Methyl orange itself is good when used with 0.5 *N* solutions or stronger, but it is not recommended for student use with 0.1 *N* solutions.

PREPARATION OF ACID AND BASE SOLUTIONS

Procedure. Approximately 0.1 *N* HCl and NaOH. Carbonate-free. Directions are given for 1 l. of each solution. If larger bottles are provided for storage and if the instructor so directs, a larger volume may be prepared, by use of proportionally larger quantities.

Measure into a glass-stoppered bottle 1 l. of distilled water (notes 1, 2). With a small graduated cylinder, measure out 9 ml concentrated HCl (note 3). Pour the acid into the water, stopper the bottle, and mix well by repeated inversion and shaking. Label the bottle.

Prepare an asbestos mat in a Gooch crucible as directed on page 73 (do not use a sintered glass or porcelain filtering crucible). Wash with a little water to remove loose shreds, but do not dry the mat. Empty the suction flask, and suspend a clean dry test tube beneath the funnel, as shown in Fig. 12, page 73.

Weigh on the trip scale about 10 g reagent-grade sodium hydroxide pellets (note 4). Put in a test tube an amount of water equal to the weight (note 5) of NaOH taken, pour the pellets into the water, close the tube with a clean rubber stopper, and mix by repeated inversion (note 6) until most of the NaOH has dissolved. Cool the test tube in tap water, and filter, with suction, through the asbestos mat. Stop the suction as soon as the liquid has run through the filter. Remove and stopper the test tube which contains the filtrate. This should be clear. Pour about half the concentrated NaOH solution into a liter of distilled water free of carbon dioxide (note 2) in a stoppered bottle. *Mix well* and label.

Reserve the remainder of the saturated NaOH solution in a stoppered test tube until a comparison of the acid and base solutions has been made. It may be necessary to add more of this to the base solution (note 4) to bring it up to the same strength as the acid solution.

Notes. 1. Measure the water by a volumetric flask or large graduated cylinder. An accuracy of ±20 ml is good enough.

2. The water should be nearly free of carbon dioxide. Ordinarily laboratory distilled water is suitable for use. It may be tested if desired (ask instructor) by adding 2 drops phenolphthalein indicator to 100 ml water and titrating dropwise with 0.1 *N* NaOH solution. If more than 1 drop of NaOH is required to produce a definite pink color, the carbon dioxide should be removed. This can be done by boiling the water a short time or by aspirating CO_2-free air through the water for 15–30 minutes. The CO_2-free air may be obtained by drawing the air through a tube filled with soda-lime granules. When only a liter or two of CO_2-free water is needed, boiling is preferable, but for larger quantities the aspiration procedure is simpler.

3. Concentrated HCl of density 1.18 g per milliliter is approximately 12 *N* (see page 12). A slight excess over the calculated amount of 8.3 ml is taken since the laboratory acid is frequently slightly weaker than 12 *N*.

4. Only 4.0 g pure NaOH is needed to prepare 1 l. 0.1 *N* solution, but since the pellets contain water and sodium carbonate the purity factor is low. Also some of the NaOH is retained on the mat of the Gooch crucible. Usually about 5 g is needed to prepare a liter of 0.1 *N* solution. The directions are for preparation of twice the needed amount of the saturated NaOH solution. It is better to prepare twice the computed amount of the concentrated solution and to use only about half and hold the remainder in reserve until it is found that the base solution is of the proper strength.

5. Sodium carbonate is only slightly soluble in a 1:1 NaOH solution and is removed by filtration. An asbestos mat is necessary for this filtration since the concentrated alkali solution will destroy paper, or, if a filtering crucible is used, the mat may be ruined by the solvent action of the alkali on the fine particles.

6. Hold the test tube in a towel as a large amount of heat is developed. Hold the stopper tightly in place. Enough heat is generated to cause a little pressure in the tube, and, if care is not taken, a spray of alkali may escape, with undesirable consequences to clothing in the vicinity.

COMPARISON OF ACID AND BASE SOLUTIONS

One should be able to do the comparison, the standardization, and the analysis of an unknown in a single afternoon if samples are prepared well in advance. It is wasteful of time and solutions to fill up burets and make the comparison one day and then to wait until another period to standardize. Before starting the comparison, the student should have ready dried portions of his primary standard material and his first unknown. It is the student's responsibility to look ahead and plan his work in advance so that waste of time is avoided.

Procedure. Reread the general instructions for the operations of volumetric analysis, on pages 88 to 90. Drain the water from both burets and fill them, respectively, with the 0.1 *N* acid and base solutions, *with proper rinsing.* Do not use more than 15 ml of each solution for the rinsing. Run out liquid from each buret until the tip is filled. Rinse off surplus liquid from the tip with water from the wash bottle. Refill the buret, and lower the liquid level to or below the 0.00 mark. Remove pendent liquid drops by touching the side wall of a beaker to the tip. The burets are now ready for use. Read and record the positions of both menisci.

Run into a clean (but not necessarily dry) wide-mouth 250-ml Erlenmeyer flask between 35 and 45 ml of the acid (note). Do not read the buret accurately at this time. Touch the wall of the flask to the tip to remove pendent drops. Add 1 or 2 drops phenolphthalein indicator, and titrate with base until a faint pink color is obtained. Good lighting is essential, and the flask should be viewed against a white background. A piece of white paper or a clean towel spread on the desk will make a good background. Do not take inordinate care to stop the addition of base just at the end point. Rather, titrate rapidly and, if the end point is over-run, back-titrate by adding acid until the solution is just colorless, and then add base dropwise until a single drop imparts a pink color which pervades the entire solution when the liquid is well mixed by swirling. The color should persist at least 15 seconds. At the end of the titration, rinse off the tip of both burets with a little water. If this changes the color of the solution, add a drop of acid or base, as needed, to restore the end point. Finally, read both burets accurately. Record the data in the notebook as shown in Table 12. No indicator blank is needed for this titration. Verify this by adding a drop of phenolphthalein to 50 ml distilled water in a flask and a drop of the base solution. The intensity of color imparted should be considerably greater than the color taken as the end point of the titration.

Compute the volume of acid equivalent to 1 ml base:

$$1 \text{ ml base} = \frac{\text{volume acid (with buret corrections)}}{\text{volume base (with buret corrections)}}$$

If the ratio is less than 0.8, the base solution should be made stronger by addition of more of the 1:1 solution, and the comparison repeated. If the ratio is greater than 1.2, the base solution has been made too strong. In this case, the acid solution should be made stronger by addition of the computed amount of 12 *N* HCl.

Obtain three comparison values whose average deviation, taken as described in Chapter 4, does not exceed 1 part per 1000. When a satis-

factory comparison is obtained, proceed with standardization, following the method specified by the instructor. If this cannot be done on the same day, empty the burets, and discard the solutions taken from them. Fill the burets with distilled water, after a preliminary rinsing, and allow to stand.

Note. There is less absorption of CO_2 when acid is titrated by base than when the titration is made in the reverse direction. Explain.

TABLE 12

COMPARISON OF STRENGTH OF ACID AND BASE

Notebook Record

HCl		NaOH		$\frac{ml\ HCl\ \dagger}{ml\ NaOH}$	*Deviation*
37.92 (−0.06) *	37.86	37.07 (+0.05)	37.12		
1.10 (0.00)	1.10	0.83 (0.00)	0.83		
				1.013	0.002
	36.76		36.29		
41.10 (−0.08)	41.02	40.45 (+0.06)	40.51		
0.26 (0.00)	0.26	0.15 (0.00)	0.15		
				1.010	0.001
	40.76		40.36		
41.15 (−0.08)	41.07	40.01 (+0.06)	40.07		
0.73 (0.00)	0.73	0.17 (0.00)	0.17		
				1.011	0.000
	40.34		39.90		
41.25 (−0.08)	41.17	40.41 (+0.06)	40.47		
0.56 (0.00)	0.56	0.26 (0.00)	0.26		
				1.010	0.001
	40.61		40.21		
			Average	1.011	0.001

Average deviation $= \frac{0.001}{1.011}$ or $\frac{1}{1000}$.

* Buret correction.

† Note that 1.000 ml base = 1.011 ml acid.

STANDARDIZATION

Potassium Acid Phthalate

When carbonate-free base is used, potassium acid phthalate is one of the best primary standards. It is readily available in pure form (from the Bureau of Standards or several chemical manufacturers), is non-

hygroscopic, is stable on drying, has a high equivalent weight, and is about the same acid strength as the common organic acids such as acetic acid. Phenolphthalein and thymol blue are suitable indicators for the titration.

Procedure. Put 4 g (trip scale) potassium acid phthalate (KHP) of assay value 99.95 per cent or higher in a clean weighing bottle, and dry in an oven at 110°C for an hour or more. Stopper the bottle, and store in a desiccator. Weigh into 250-ml wide-mouth Erlenmeyer flasks three portions of 0.7–0.9 g KHP with an accuracy of 0.5 mg, and dissolve in about 50 ml distilled water. Add a drop of phenolphthalein indicator, and titrate with base solution (if the buret has been filled with water remember to rinse well with the solution), as in the comparison of acid and base. Try to stop the titration just at the end point. If the end point is over-run, do not discard the determination, but back-titrate with the acid which has previously been compared with the base. If this is done, compute the volume of base equivalent to the acid used in back titration, and subtract from the total volume of base to get the net volume required to titrate the KHP.

Record the data for the weight of the samples and the buret readings on the left-hand page of the notebook as the measurements are made. Apply buret corrections and summarize the data on the right-hand page of the notebook, as shown in Table 13. Compute the normality of the base solution for each sample and the average value. The equivalent weight of potassium acid phthalate is 204.2. From the average value and the previously determined ratio of acid to base compute the normality of the acid.[1] The average deviation for the separate samples should not be greater than 1–2 parts per 1000.

Mark the average normality values on the labels of the acid and base bottles. Present the notebook to the instructor for approval.

Errors. Since this is the first quantitative determination for most students, it is advisable to review the sources of error (see page 94). We may classify these as *general* errors applying to all volumetric determinations and as *specific* for this particular determination.

The most probable general errors are:

1. Loss of sample or of solution, by leaky burets, faulty transfer, and so on.

2. Contamination or dilution of solutions because of failure to rinse burets.

[1] A student error of frequent occurrence is to use the wrong value for the acid–base ratio. From the comparison titrations, note whether the acid or base is the stronger, and take care to use the proper ratio to give a higher or lower acid normality, as the case may be. If 1.000 ml base = 1.011 ml acid, the base is stronger. Therefore the acid normality is less than that of the base.

TABLE 13

STANDARDIZATION OF BASE AND ACID SOLUTIONS WITH POTASSIUM ACID PHTHALATE

Notebook Record

Sample No.	*I*	*II*	*III*
Weight KHP	0.7835	0.8460	0.8035
Corrected weight (for purity)	0.7831	0.8456	0.8031
Corrected volume of base	40.35	42.00	39.96
Corrected volume of acid in back titration	1.52	0.00	0.00
Volume base = volume acid used	1.50	0.00	0.00
Net volume base	38.85	42.00	39.96
Milliequivalents KHP	3.835	4.141	3.933
Normality of base	0.0987	0.0986	0.0984
Average normality	0.0986		
Deviation	0.0001	0.0000	0.0002
Average deviation	0.0001 or 1/985		
Normality of acid	0.0975		

Purity of KHP, 99.95%
1.000 ml base = 1.011 ml acid

3. Purity of standard. An error from this source will not be shown in the data since it will affect all the duplicate results in the same manner. Failure to dry the potassium acid phthalate will of course affect the purity factor.

4. Weighing errors.

5. Faulty reading of burets.

6. Failure to allow time for drainage before reading the burets, or improper calibration values for the burets. Errors from these sources will in general not exceed 0.1 ml and will not greatly affect the results.

The specific error of most frequent occurrence is the presence of carbonate in the base solution. As shown in the next chapter, carbonate is only half neutralized at the *p*H of the phenolphthalein end point and if present will buffer the solution so that a sharp change in *p*H will not be obtained with a drop of solution. Consequently the end point is not sharp if much carbonate is present.

A certain amount of carbonate is always present in a base solution prepared in this manner, but it is usually not enough to affect the sharpness of the end point. Although it is only half-neutralized at the phenolphthalein end point, this causes no error because the solution is used for the analysis of samples in exactly the same way as in the standardization. Therefore, the neutralization equivalent of a milliliter of solu-

tion is the amounts of NaOH and Na_2CO_3 that have reacted when the phenolphthalein end point is reached.

It may be pointed out that the normality value obtained for the HCl solution is not dependent on the presence or absence of carbonate in the base solution. In effect, the HCl solution is compared with a weighed sample of potassium acid phthalate by means of the amount of base which under the same conditions reacts with unit quantities of acid and phthalate.

Sodium Carbonate

If properly used, sodium carbonate is a very reliable primary standard. It is cheap, readily available in high purity and known assay value, stable on drying, and non-hygroscopic. An advantage is that it may be used for direct standardization of acid solutions which are to be used for the analysis of carbonate samples, thus giving the same type of end points in standardization that will be obtained in the analysis. A disadvantage is that direct titration of sodium carbonate with 0.1 *N* acids does not give a good end point unless the solution is boiled to expel carbon dioxide.

Before carrying out this standardization, the student should read the discussion of carbonate titrations on page 135.

Procedure. Place about 1.5 g sodium carbonate of known assay value in a weighing bottle, and dry at 110°C. Stopper the bottle, and cool in a desiccator.

Weigh out to the closest 0.1 mg three samples of 0.2 to 0.25 g and transfer to wide-mouth 250-ml Erlenmeyer flasks. Dissolve in about 50 ml distilled water, and titrate according to the procedure of page 136, beginning with the star. Use the previously compared NaOH solution for back titration.

Record all data as taken on the left-hand page of the notebook, and make a summary table on the right-hand page like that shown in Table 13, substituting Na_2CO_3 for KHP. In the computation of the normality determine the net volume of HCl used for reaction with the carbonate by subtracting from the total volume the amount of HCl required to react with the NaOH used in back titration. (Apply buret corrections to all readings.) From the net volume of HCl and the weight and purity of Na_2CO_3 used, compute the milliequivalents per milliliter of HCl.

Errors. General titration errors are discussed on page 94. The only probable specific errors are loss of acid in boiling the solution, if too large an excess has been added, and failure to cool the solution to room temperature before the titration is completed.

Constant-boiling Hydrochloric Acid

Standardization by this method is not widely used as a student exercise because of the time required to set up equipment and distil the acid. This is a very useful method for the commercial laboratory, however, because it is convenient to prepare and keep a large quantity of the constant-boiling solution as a stock solution which can be diluted readily to give a solution of any desired concentration. The constant-boiling solution keeps well because liquid and vapor are of the same composition, and evaporation does not change the strength.

A convenient student exercise is the preparation of a standard 0.1 *N* solution from stock solution supplied by the instructor.

Procedure. Preparation of Stock Solution. Set up a distillation outfit as shown in Fig. 18, page 142, but replacing the Kjeldahl flask with a 2-l. round-bottom boiling flask. With a hydrometer determine the density of the concentrated HCl supplied, and by reference to a handbook determine the percentage composition of this solution. Compute the volume of concentrated HCl required to make 1 l. of acid with density 1.10. Measure out the computed volume, and add sufficient water to dilute it to a liter. Pour the diluted solution into the flask, connect to the condenser, and distil at a constant rate of 3–4 ml per minute. When about 350 ml of distillate has been collected, pour it into the side shelf bottle labeled 7 *N* HCl, then continue the distillation, and collect as sample the next 350 ml. This completes the distillation. Pour the remainder of the acid in the boiling flask into the 7 *N* HCl bottle (for use as laboratory reagent). Record the barometric pressure at regular intervals during the distillation. Preserve the 350-ml sample of distillate (middle portion) in a dry glass-stoppered bottle.

From the average barometric pressure, compute from the data of Table 14 the composition of the distillate. Interpolate as described on

TABLE 14

COMPOSITION OF CONSTANT-BOILING HYDROCHLORIC ACID

Pressure (*mm Hg*)	*Weight (in Air) of Distillate per mole* HCl (*grams*)	*Difference in Weight per 10-mm Pressure* (*grams*)
770	180.407	
760	180.193	0.214
750	179.979	0.214
740	179.766	0.213
730	179.555	0.211

Foulk and Hollingsworth, *J. Am. Chem. Soc.*, **45**, 1220 (1923).

page 118 for the exact pressure and composition. Label the stock bottle showing the weight of distillate to contain 1 mole of HCl (weight in air).

Procedure. Preparation of 0.1 *N* Solution from Stock Solution. Weigh a small glass-stoppered bottle to the nearest milligram (preferably a weighing bottle if it has sufficient capacity). Clean and *dry* a small graduated cylinder, and rinse once with 2 ml of the stock solution prepared in the previous exercise. Measure out a volume of 16–18 ml stock solution, and pour into the bottle. Stopper, and weigh to the nearest milligram.

Transfer the weighed solution quantitatively (see page 86) to a 1-l. volumetric flask. Wash out the bottle thoroughly, taking care to avoid any loss of washings. Dilute to the mark of the volumetric flask, and mix thoroughly. Compute the exact normality of the solution.

Label the diluted solution. It may be stored in the volumetric flask or transferred to a dry glass-stoppered bottle.

A 0.1 *N* base solution can be standardized by comparison with the standard HCl previously prepared. If the base is carbonate-free, follow the procedure of page 128. If carbonate has not been removed from the base, titrate as described on page 136, beginning with the marginal star.

Gravimetric Standardization

Hydrochloric acid can be conveniently and accurately standardized gravimetrically by precipitation of AgCl which is filtered out, dried, and weighed. In fact, most of the standard substances have been tested at one time or another by comparison with the results of gravimetric standardization. Ordinarily this method is not required in student training, but it is one which every analyst should know, for use when other methods are lacking.

Procedure. Prepare approximately 0.1 *N* HCl by dilution of concentrated HCl from a freshly opened bottle which has not been exposed to ammonia fumes. Since this method determines the total chloride, it is essential that all the chloride ion be that from HCl. Precipitate and weigh the chloride as AgCl, following the procedure of page 381. From the weight of AgCl obtained, compute the milliequivalents of chloride per milliliter.

ANALYSES

The analyses of this section illustrate the most common types of acid–base determinations; they are: (1) determination of weak acids, (2) determination of carbonate or other salts of weak acids, and (3)

analysis of concentrated solutions. The determination of strong acids and bases has been illustrated in the comparison of the acid and base solutions.

Determination of Weak Acids

The procedures of this section are applicable to the analysis of any sample of strong acid or any weak acid whose ionization constant is not less than about 10^{-6}. For such acids, it is better to titrate a salt of the acid with a strong acid, as in the determination of carbonates.

Analyzed Sample of Potassium Acid Phthalate. Obtain the sample in a weighing bottle according to laboratory instructions for student unknowns. Dry in an oven overnight. Stopper the bottle, and keep in a desiccator.

Procedure. Weigh out to the nearest milligram three portions of 1–4 g each (notes 1, 2) and dissolve in 50–75 ml distilled water in a 250-ml wide-mouth Erlenmeyer flask. Titrate with standard 0.1 *N* base solution, just as in the standardization. Use standard HCl solution to back-titrate if the end point is over-run, but avoid this if possible.

TABLE 15

SAMPLE REPORT CARD FOR SOLID ACID UNKNOWN

Date *Name* *Acid Unknown*

Normality of base = 0.1032

Wt. Sample	*Vol. Base*	*% KHP*	*Deviation*
3.175 g	38.73	25.70	0.05
3.562	43.36	25.65	0.00
3.485	42.34	25.60	0.05
		Average 25.65	0.03

$$\text{Average deviation} = \frac{0.03}{25.65} \text{ which is } \frac{1.2}{1000}$$

Apply buret corrections for all volumes. Correct the volume of base for the amount of acid used in back titration (if any). From the net volume and normality of the base compute (1) the milliequivalents of potassium acid phthalate in the sample, (2) the weight of KHP, and (3) the percentage of KHP. Report your results on a plain 3x5-in. card as shown in Table 15. The average deviation should not exceed 2–3 parts per 1000. Present the notebook to the instructor for approval.

Notes. 1. Prepared samples may range from about 20 to 90 per cent KHP. The size of sample should be so chosen that titration will require 30–45 ml. The instructor will specify the size to use.

2. For samples of this size, it is not necessary to weigh to the nearest tenth of a milligram.

Errors. The same errors may occur as in the standardization. In addition, any determinate errors in the value for the normality of the base will affect all samples. Lack of homogeneity in the unknown sample will cause variations in the individual determinations. If it is suspected that the sample is inhomogeneous, the analysis may be repeated using a single sample of five times the weight of individual samples. This is dissolved, diluted to 250 ml, and 50-ml aliquot portions are analyzed.

Prepared Acid Solution. The sample, obtained in a stoppered bottle or flask, is a measured volume of 0.5 *N* acid. It is quantitatively diluted to 250 ml, and aliquot portions are separately analyzed. The report shows the milliequivalents of acid received in the total sample.

Procedure. Obtain the sample as directed by the instructor. Transfer quantitatively to a 250-ml volumetric flask which has been calibrated relative to a 50-ml pipet. Dilute to the mark, and mix thoroughly. Rinse the pipet with small portions of the solution, and then pipet out four 50-ml portions into 250-ml wide-mouth Erlenmeyer flasks. Titrate with standard base solution, as in the standardization with potassium acid phthalate, using phenolphthalein indicator. Apply buret corrections, correct the total volume of base for the amount of acid used in

TABLE 16

SAMPLE REPORT CARD FOR ACID SOLUTION

Date *Name* *Acid Unknown*

Volume of aliquot portion = $\frac{1}{5}$ total
N of base = 0.1005

ml Base	*m e Acid*	*Deviation*
42.35	4.256	0.005
42.25	4.246	0.005
42.29	4.250	0.001
	Average 4.251	0.004

Total m e received = $5 \times 4.251 = 21.26$

Average deviation = $\frac{0.004}{4.251}$ which is $\frac{1}{1000}$

back titration (if any), and compute the total number of milliequivalents received. Report the results on a plain 3x5-in. card, following the arrangement shown in Table 16. The average deviation should not exceed 1–2 parts per 1000. Present the notebook for approval.

Errors. The same errors may occur as in standardization. Any error of standardization will of course affect all the analyses to the same extent. The most frequent student error is failure to mix the solution well before taking the aliquot portions.

Analysis of Bases Which Contain Carbonate

It is shown in the next chapter that a weak acid of ionization constant much less than 10^{-6} cannot be directly titrated by a base, because a sharp end point cannot be obtained. In such cases it is possible to titrate a salt of the weak acid by a strong acid, provided the proper indicator is used.

The analysis of carbonates by titration with strong acids is of frequent occurrence. In this titration, the following reactions occur:

$$CO_3^{=} + H^+ = HCO_3^- \quad p\text{H near } 8$$

$$HCO_3^- + H^+ = H_2CO_3 \quad p\text{H near } 4$$

Reference to the table of indicators on page 166 shows that, at the stoichiometric point for the first reaction, phenolphthalein changes color and, at the *p*H of the second reaction, a methyl orange end point is obtained. However, at the phenolphthalein end point, the solution is buffered, and one does not obtain a sharp end point such as was received in the titration of weak acids by sodium hydroxide. At the methyl orange end point, the solution contains carbonic acid which decomposes into CO_2 and H_2O to an extent depending on the temperature and the degree of agitation. Therefore, the exact amount of carbonic acid present is not known. Further, in titrations with dilute acids (below 0.5 *N*), the methyl orange end point is difficult to recognize. It is therefore better to remove the carbonic acid from solution and to employ an indicator which will give a sharper color change than methyl orange. Carbon dioxide can be removed by boiling the solution or by vigorous agitation [2] after sufficient acid is added to neutralize all the carbonate. After removal of CO_2, there remains an unbuffered solution of NaCl and any excess acid. This excess can now be back-titrated with standard base, using any indicator which will serve for titration of strong acids and bases.

[2] R. K. McAlpine, *J. Chem. Ed.*, **21**, 589 (1944).

Determination of the Basic Strength of Soda Ash. The analysis of soda ash, crude sodium carbonate, has for many years been a standard student exercise in acidimetry. Titration with HCl to the proper end point gives the total basic strength, regardless of whether the sample contains NaOH, $NaHCO_3$, or Na_2CO_3. The results are generally reported as the percentage of Na_2CO_3 in the sample, but they might just as well be reported as Na_2O or as NaOH; the report represents merely the method of computation, and it does not imply that the basic material of the sample is in the form reported.

The following procedure may be used for the analysis of carbonate samples, for standardization of acids by Na_2CO_3, and for the analysis of base solutions which contain carbonates. After preparation of the samples all these analyses are alike.

Procedure. Obtain the sample in a weighing bottle, and dry in the oven. Preserve in a desiccator until needed. Weigh out three (note 1) samples of 0.4 to 1.5 g as directed by the instructor (note 2). Transfer each to a 250-ml wide-mouth Erlenmeyer flask and dissolve in about 50 ml distilled water.

* Add 1 drop methyl orange indicator (note 3) and titrate with standard HCl until a definite color change is obtained, and then add about 1 ml in excess. Do not take a buret reading at this point since more acid is required to complete the titration.

Place the flask on a wire gauze and heat over a free flame until the solution comes to a boil (note 4), and then boil gently for about 1 minute (note 5). Cool in tap water *to room temperature*, add 2–4 drops bromcresol green–methyl red mixed indicator, and titrate slowly with standard NaOH solution until a green color is obtained. Now back-titrate with acid to a pink color, then add base a drop at a time until one drop gives a sharp change to green. It is advisable to approach the end point by addition of base in every titration. Read both burets, and record. No indicator blank is needed.

Apply buret corrections for all readings and compute the volumes of acid and base used. From these and the normalities compute the milliequivalents of each. Subtract the milliequivalents of base from those of acid to obtain the milliequivalents of acid used in neutralization of the sample. From the net m e acid and the m e weight of Na_2CO_3, compute the weight and the percentage of Na_2CO_3 in the sample. Report on a 3x5-in. card, showing the percentages for the individual samples, the average, and the deviations for each sample. Average deviation should not exceed 3/1000 unless the sample is very inhomogeneous.

Notes. 1. Optionally the instructor may direct to weigh out a single sample and use aliquot portions for the separate analyses, to avoid difficulties due to inhomogeneity of the sample.

2. About 4 m e or 0.2 g Na_2CO_3 should be in each portion, but since the percentage purity may vary from 20 to 80 the instructor will specify what size of sample to employ.

3. Methyl orange indicator is used to show when sufficient acid is added to neutralize the carbonate completely. It is not a good indicator for use in the final end point, because its color change is difficult to see when 0.1 *N* solutions are used. Presence of the methyl orange does not affect the sharpness of the final end point of the mixed indicator. If the mixed indicator is used for the first part of the titration, it does not show when the carbonate is neutralized since its color change occurs prior to complete neutralization.

4. According to McAlpine,[2] vigorous swirling will remove most of the CO_2. His paper should be consulted for details if one wishes to omit the boiling, which does take some time.

5. Some 97 per cent of the CO_2 is removed by 1 minute's boiling.[2]

Errors. Review the discussion of errors in comparison and standardization of the solutions. Any error in the normality of the solutions will cause a corresponding error in the analysis.

If the deviations between the samples are large, the analysis should be repeated with a single large sample and aliquot portions.

There should not be too great an excess of acid when the solution is boiled. This may cause loss of HCl by vaporization.

The solution should be cooled to near room temperature after boiling, before the titration is completed. This is important.

Analysis of Prepared Solution

The sample is a measured volume of 0.5 *N* sodium hydroxide and sodium carbonate solution. It is diluted to 250 ml, and aliquot portions are analyzed for total basic strength. The total number of milliequivalents received is reported.

Procedure. Obtain the sample in a stoppered bottle or flask as directed. Transfer quantitatively to a 250-ml volumetric flask, dilute to volume, mix thoroughly, and pipet out four 50-ml aliquot portions after properly rinsing the pipet. Titrate as directed in the preceding exercise, beginning at the star.

Report the total milliequivalents of base received, following the general arrangement shown in Table 16. Duplicate results should agree within 1–3 parts per 1000.

Simultaneous Determination of Carbonate and Hydroxide

It is often necessary to determine the carbonate content of an alkali solution or to determine carbonate and bicarbonate in the presence of one another. Several methods may be used for these analyses. It is

shown in the following chapter that, in the titration of carbonate solutions, there are two points at which the addition of a small amount of acid will cause a large change in the hydrogen-ion concentration. The first of these occurs at the point where the carbonate is converted into bicarbonate, or one equivalent of hydrogen ion is added per mole of carbonate. The second occurs when the carbonate is completely converted into carbonic acid.

If a solution contains both carbonate and hydroxide, titration to the phenolphthalein end point will neutralize all the hydroxide and convert all the carbonate to bicarbonate. Titration to the methyl orange end point will neutralize all the hydroxide and all the carbonate. If the same solution is first titrated to the phenolphthalein end point, then methyl orange is added, and the titration continued to its end point, the volume of acid required to go from the phenolphthalein to the methyl orange end point will represent one-half the total volume required for titration of the carbonate. Therefore it is readily determined what volume of acid is used for each constituent. This method has the disadvantage that the phenolphthalein end point obtained is not sharp. It is necessary to prepare a standard color by adding indicator to a solution of sodium bicarbonate and then match this color in the titration.

A preferable method is to determine the total basic strength, according to the procedure given for the standardization of acid by sodium carbonate, by titration of an aliquot portion of the solution. In another portion the carbonate is removed by precipitation with barium ion, and the hydroxide is determined by titration with standard acid, using phenolphthalein indicator. It is not necessary to remove the precipitate of barium carbonate before making the titration, if phenolphthalein indicator is used, because the color change is obtained before the hydrogen-ion concentration becomes large enough to cause a reaction with the precipitate.

Mixtures of carbonate and bicarbonate are analyzed by determining the total alkalinity on one fraction. On another fraction the solution is treated with a measured excess of standard base to convert all bicarbonate to carbonate, the carbonate is removed by precipitation with barium chloride, and the remaining base is determined by titration with standard acid to the phenolphthalein end point.

Procedure. Obtain the unknown sample in a stoppered bottle or flask. Transfer to a 500-ml volumetric flask, and dilute to volume. Mix well. Withdraw six 50-ml aliquot portions by a calibrated 50-ml pipet.

Determine the total basic strength on three of the portions, following the procedure on page 136.

Prepare a solution of barium chloride containing about 5 g crystals per 50 ml water. Add a drop of phenolphthalein indicator, and make the solution just neutral by addition of base or acid as needed.

To each of the remaining three aliquot portions of the sample, add barium chloride solution, drop by drop from a pipet, until no further precipitation occurs. It may be necessary to allow the precipitate to settle after each addition of barium chloride, to determine when precipitation is complete. No harm is done if there is a slight excess of barium chloride added.

To each portion add phenolphthalein indicator, and titrate with standard HCl. If the end point is over-run, back-titrate with carbonate-free base.

From the net amount of acid used for the samples treated with barium chloride, compute the milliequivalents of NaOH. The difference between the total basic strength as previously determined and the milliequivalents of NaOH gives the millequivalents of carbonate. Report the total milliequivalents of NaOH and Na_2CO_3 in the sample.

Analysis of Concentrated Solutions of Acids or Bases

The analysis of concentrated solutions utilizes the same types of titrations as the dilute solutions previously described. The only difference is in the methods of preparation of samples. The analysis of a typical sample may be illustrated by the determination of the strength of a concentrated ammonia solution of density near 0.90. This determination also illustrates the titration of a weak base by a strong acid. Methyl red is used as indicator because the color change corresponds to the *p*H of ammonium chloride, which is formed in the titration.

Procedure. Accurately weigh a small dry stoppered bottle. Add from a graduated cylinder about 7 ml concentrated ammonium hydroxide solution, stopper the bottle, and reweigh. Transfer the solution quantitatively to a 1-l. volumetric flask, dilute to the mark, and mix thoroughly. Fill a buret with the diluted solution, and measure out 35–45 ml into an Erlenmeyer flask. Titrate with standard 0.1 *N* HCl solution, using methyl red as indicator.

Compute the total weight of NH_3 in the sample and the percentage by weight.

Obtain a hydrometer from the instructor, and determine the density of the concentrated ammonia from which the sample was taken. From the percentage by weight and the density, compute the normality of the concentrated solution.

KJELDAHL-GUNNING METHOD FOR THE DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS

Nitrogen in the form of amines or amides may be quantitatively determined by being converted into an ammonium salt and analyzed by the usual volumetric procedures. The process of conversion into ammonium salts is accomplished by digesting the organic compound with concentrated sulfuric acid. Carbon and hydrogen are oxidized to carbon dioxide and water, respectively, while nitrogen is converted into ammonium sulfate. After digestion is complete, as shown by the disappearance of carbon, the solution is made alkaline with sodium hydroxide, and the liberated ammonia is distilled into a measured volume of standard sulfuric acid solution. The amount of ammonia is estimated by titrating the remaining sulfuric acid with a standard base solution. This method for the determination of nitrogen is known as the Kjeldahl process. Nitrogen present as azo compounds or as nitro derivatives is not detected in analyses performed by the method as outlined, but, if the sample is first reduced, so as to convert the nitrogen into an amine, the Kjeldahl method may be used. Nitrates may be included in a regular Kjeldahl analysis, if means are provided for preventing the escape of nitric acid and reducing the nitrogen to ammonia. Treatment of the sample with a salicylic acid–sulfuric acid mixture serves to prevent escape of nitric acid, because salicylic acid reacts with the nitric acid liberated, giving nitrated derivatives. After fixation of the nitrogen in this manner, it may be reduced by treating the sulfuric acid solution with sodium thiosulfate, prior to digestion. The thiosulfate serves to reduce the nitrated salicylic acid to corresponding amine derivatives.

Many modifications of the Kjeldahl method have been proposed, and many catalysts have been used to accelerate the digestion process.[3] In the Gunning modification, which is widely used, no catalyst is employed, but the sulfuric acid solution is nearly saturated with sodium or potassium sulfate. The salt elevates the boiling point, and thus, by permitting higher digestion temperatures to be employed, accelerates the process.

Directions are given in the following procedures for the analysis of dried-blood samples. They do not contain nitrates. If commercial fertilizers or other samples which may contain nitrates are to be analyzed, modifications of the procedure are necessary. See standard reference books, such as *Official and Tentative Methods of Analysis* of the

[3] See, for example, C. F. Poe and M. E. Nalder, *Ind. Eng. Chem., Anal. Ed.*, **7**, 189 (1935). A method which eliminates the distillation has been suggested by K. Marcali and W. Rieman, *Anal. Chem.*, **18**, 709 (1946).

adapter. Titrate the remaining sulfuric acid with standard 0.1 *N* NaOH, using methyl red indicator. From this titration and the amount of acid originally present, compute the milliequivalents of acid neutralized by the ammonia which was liberated from the sample. Run a blank (note 6) determination by digesting and analyzing a 1-g sample of some non-nitrogenous organic substance such as sugar. Subtract the milliequivalents of acid neutralized in the blank from the amount found in the analysis. Multiply the net milliequivalents of acid by the atomic weight of nitrogen in order to obtain the weight of nitrogen in milligrams. Compute the percentage of nitrogen in the sample. Duplicate results should agree within 0.3 per cent (note 7).

Notes. 1. If it is available, use "sodium hydroxide flake, 76 per cent for nitrogen determination." This is considerably cheaper than the reagent-grade pellets and is just as satisfactory.

2. All manipulations, after the alkali solution is mixed, should be performed rapidly in order to prevent loss of ammonia. For this reason also the solutions must be cold before mixing.

3. Granulated zinc aids in preventing bumping during distillation.

4. The test is very important for beginning students. Often too much acid is used, and an attempt is made to distil ammonia from a solution which is still acidic.

5. This is to prevent the solution from sucking back into the Kjeldahl flask as it cools.

6. A blank is essential, since contamination of reagents or absorption of ammonia during the analysis may readily lead to results far too high.

7. The precision to be desired is not 3 parts per 1000, but rather an agreement of 0.3 per cent in the percentage of nitrogen in the sample. Thus, 7.60 and 7.90 per cent represent acceptable results, although the agreement among these results is only 30 parts per 790, or 38 parts per 1000.

Errors. The more frequent errors, in addition to those common to all acidimetric determinations, are due to the following mistakes:

1. Spray is carried over into the receiver from the alkaline solution in the digestion flask. If a very high result is obtained, it is almost certain to be due to this error.

2. Ammonia may be absorbed during digestion of the sample or by the standard sulfuric acid during the distillation.

3. If the initial distillation is made too rapidly, ammonia may escape through the acid solution without being absorbed. See H. S. Miller, *Ind. Eng. Chem., Anal. Ed.*, **8**, 50 (1936), for a discussion of this error. Steam distillation minimizes this source of error.

Boric Acid Modification. This method, suggested by Winkler [4] in 1913, has in recent years received very favorable attention. It appears to be fully as accurate as the older method of absorption of ammonia in

[4] L. W. Winkler, *Z. angew. Chem.*, **26**, 231 (1913).

a measured volume of sulfuric acid, and it saves a great deal of time. In this method, the liberated ammonia is absorbed in a 4 per cent boric acid solution, the volume and concentration of which need not be accurately determined. The amount of ammonium borate formed is determined by titration with standard hydrochloric acid. The indicator used, bromcresol green, gives an end point at a hydrogen-ion concentration corresponding to a solution of ammonium chloride. Boric acid itself is so weak that it has no appreciable influence on the hydrogen-ion concentration. The reactions are:

$$NH_3 + HBO_2 = NH_4^+ + BO_2^-$$

$$H^+ + BO_2^- = HBO_2$$

Procedure. Carry out digestion, distillation, and so on, just as in the preceding directions, but replace the sulfuric acid absorbent with approximately 50 ml 4 per cent boric acid solution. When the distillation is complete, remove the absorption flask, as previously directed, and titrate with standard 0.1 *N* hydrochloric acid, using bromcresol green indicator.

Determination of Ammonia in Soluble Salts

Ammonia, in the form of a soluble salt, may be determined by a modification of the Kjeldahl procedure. No digestion is needed. The solution is placed in a Kjeldahl flask, treated with excess sodium hydroxide solution, and the liberated ammonia is distilled into a measured volume of standard sulfuric acid. The excess acid is then determined by titration with a standard base solution. The boric acid method may advantageously be used if desired (see previous paragraph). This exercise is often substituted for a Kjeldahl determination in elementary courses because no digestion is needed; the sample can be a measured solution of ammonium sulfate of known concentration.

Procedure. Dilute the sample, which contains 20–25 m e of ammonium sulfate, to a volume of 250 ml, and measure out three 50-ml aliquot portions with a pipet. Add to each portion 150 ml water, and place each portion in a 500-ml Kjeldahl flask. Set up a distillation apparatus as described in the preceding section, with a measured 50-ml portion of 0.2 *N* sulfuric acid (or boric acid) in the receiving vessel. Pour into the Kjeldahl flask a solution of 10 g sodium hydroxide in 50 ml water, mix by shaking, and immediately connect the flask to the distilling apparatus. Slowly distil over about half of the solution, and complete the analysis as described in the preceding exercise. Compute the total number of milliequivalents ammonium salt received.

QUESTIONS

1. Should unused portions of liquid be returned from a buret to the stock bottle? Why?

2. Compute the probable error, in milliliters, in making four buret readings and in locating the end point of a titration. Sum these to obtain the total error that might be introduced in these operations. What precision, in parts per 1000, is indicated when the volume of the standard solution is 10 ml? When the volume is 45 ml?

3. Does the volume of water in which the KHP is dissolved for titration influence the normality determined for the NaOH?

4. HCl is standardized by Na_2CO_3 using methyl orange indicator and titrated cold. Is an indicator blank required? Why?

5. An organic acid has a molecular weight of approximately 200. It is water-soluble. Give detailed directions for the determination of its equivalent weight. How is it necessary to modify the procedure if the acid is not readily soluble in water? If the equivalent weight is found to be 98.7, what can be said about the molecular weight and the structure of the acid? Give illustrative calculations for this determination, assuming that the equivalent weight is 98.7.

6. Give a detailed procedure for the determination of the percentage of ammonia in crude ammonium sulfate. Illustrate your procedure by a typical computation.

7. Although in the standard Kjeldahl procedure the titration which follows the distillation is that of a strong acid *vs.* a strong base, a serious error will result if phenolphthalein is selected as the indicator. Explain.

8. Could the total nitrogen content of NH_4NO_3 be measured by the procedure described in the text?

9. Concentrated sulfuric acid, which contains about 95 per cent acid by weight, is to be analyzed by use of a 0.1 *N* base solution. Give detailed directions, including approximate weights and volumes, for this determination. How would the directions be modified if the standard base solution were 1 *N*?

10. A sample may be one of the following: NaOH, Na_2CO_3, $NaHCO_3$, NaOH and Na_2CO_3, or $NaHCO_3$ and Na_2CO_3. If A represents the milliliters of standard acid to reach the phenolphthalein end point and B the volume of acid to go from this end point to the methyl red end point, state the composition of the sample for each of the following cases:

(*a*) $B = 0$
(*b*) $A = 0$
(*c*) $A = B$
(*d*) $A > B$

PROBLEMS

1. A solution of sodium hydroxide is standardized by potassium acid phthalate of assay value 99.95 per cent. From the following data compute the normality of the base:

Weight potassium acid phthalate	0.8573 g
Buret reading before titration	0.00
Buret reading after titration	45.53
Buret correction	−0.03

Is an indicator blank necessary in this titration? Explain.

2. The base solution of Problem 1 was compared with an acid (HCl) solution. From the following data compute the normality of the acid.

Readings:	*Acid Buret*	*Base Buret*
	45.63	43.25
	0.17	0.00
Correction:	0.06	−0.03

Phenolphthalein indicator was used. The blank required 0.02 ml of the base solution.

3. Acid and base solutions were standardized by use of sodium carbonate. From the following data compute the normality of the two solutions:

Comparison of acid and base, with methyl orange indicator

Readings:	*Acid Buret*	*Base Buret*
	38.85	42.46
	0.14	0.12
Correction:	0.04	0.03

The indicator blank requires 0.23 ml of the acid solution.

Weight of sodium carbonate = 0.2547 g
Purity of sodium carbonate = 99.9 per cent

Back titration is used; the buret readings are as follows in the standardization, which employs methyl orange indicator.

Readings:	*Acid Buret*	*Base Buret*
	44.35	0.57
	0.04	0.06
Correction:	0.06	0.00

The solution is boiled to expel carbon dioxide, and the indicator blank correction is applied.

4. Acid and base solutions are standardized by use of sulfamic acid, which is assumed to be pure. From the following data compute the normality of the solutions:

Comparison: 47.88 ml of the acid solution = 45.33 ml of the base solution, after corrections are applied for buret calibration and indicator blank.

Standardization: 0.3501 g sulfamic acid is titrated with 44.25 ml of the base solution; 1.15 ml of the acid solution is needed for back titration.

5. A sodium hydroxide solution is standardized with benzoic acid. A 1.8810-g sample of the acid is neutralized by 32.25 ml of the base solution. What is the normality?

6. How much of the base solution of Problem 5 is needed to prepare 500.0 ml of the base solution of Problem 1?

7. A weighed crystal of calcite, $CaCO_3$, is dissolved in excess HCl and the solution boiled to remove carbon dioxide. The unneutralized acid is then titrated by a base solution which has previously been compared with the acid solution. From the following data compute the normality of the acid and base solutions:

Weight calcite	2.100 g
Volume HCl added	47.00 ml
Volume NaOH used in back titration	15.75 ml
Comparison of acid and base	40.15 ml acid = 30.00 ml base

Methyl orange indicator is used, but no indicator blank is needed because of the strength of the solutions (less than 0.02 ml of acid is used in the blank).

8. The following normalities were found for a solution which contains 5.000 m e of H_2SO_4 in 20.00 ml:

0.2452, 0.2450, 0.2454.

Which of the following errors are likely to be involved in this analysis?

(*a*) Failure to apply an indicator blank.
(*b*) Erratic end points.
(*c*) Spilling a few drops of solution in one titration.
(*d*) Use of an uncalibrated volumetric flask.
(*e*) Parallax.

9. A 0.8350-g sample of KHP was incorrectly recorded in the notebook as 0.8530 g. 37.16 ml of NaOH was required for titration. By how many parts per thousand does the apparent value of the normality differ from the true value?

10. 37.93 ml of a 0.1157 *N* HCl is required to titrate the Na_2CO_3 in a sample. The end point is over-run by three drops (0.12 ml). What error is made in terms of milligrams of Na_2CO_3 reported?

11. Would a 0.5000-g sample of Na_2CO_3 be of a satisfactory size for the standardization of half normal HCl? Explain.

12. What range of sample weights would you suggest for the standardization of 0.5 *N* NaOH by use of KHP? How carefully should these samples be weighed?

13. What size sample of sulfamic acid should be used for the standardization of 0.01 *N* KOH? Would you suggest using individual samples or taking aliquots of a large sample?

14. A sample contains approximately 4 per cent Na_2CO_3, and the remainder is inert material. How large a sample should be taken for analysis if the titration is to be carried out with 0.1 *N* HCl? How carefully should the sample be weighed?

15. What is the succinic acid ($H_2C_4H_4O_4$) titer of 0.025 *M* $Ba(OH)_2$ on the basis of complete neutralization?

16. What weight of a barium hydroxide sample shall be taken for analysis so that each milliliter of 0.1000 *N* HCl represents 0.5000 per cent $Ba(OH)_2$ in the sample?

17. What is the normality of a solution of H_2SO_4 such that each milliliter is equivalent to 2.000 per cent Na_2O in a 0.2500-g sample of soda ash?

18. 8.993 g of constant-boiling HCl prepared at 755 mm is diluted to 500 ml. 21.65 ml of this acid is equivalent to 38.73 ml of NaOH. What are the normalities of the acid and base solutions?

19. What weight of constant-boiling HCl prepared at 740 mm should be weighed out to prepare 250.0 ml of 0.2000 *N* solution?

20. A 16.24-ml sample of vinegar of density 1.060 requires 48.24 ml of 0.3564 *N* base for titration. What is the percentage by weight of acetic acid in the vinegar?

21. From the following data calculate the percentage purity of a sample of $KHSO_4$:

Weight of sample	1.2118 g
Volume of NaOH used	26.28 ml
Volume of HCl used	1.53 ml

1.000 ml HCl = 1.206 ml NaOH
1.000 ml HCl = 0.02198 g Na_2CO_3 (99.5% pure)

22. A solution of HCl is of such strength that 50.00 ml react with 0.2600 g calcite. This acid is used to determine the percentage purity of a sample of $Ba(OH)_2$ from the following data:

Weight of sample	0.4213 g
Volume of HCl used	34.51 ml
Volume of NaOH used	2.44 ml
1.100 ml HCl = 1.220 ml NaOH	

23. Obtain the percentage of CaO in a sample of limestone from the following data:

Weight of sample	1.5000 g
Volume of HCl used	40.00 ml
Volume of NaOH used	3.00 ml
1.000 ml HCl = 1.500 ml NaOH	
Normality of the NaOH	0.3333

24. Express the results of Problem 23 as percentage of $CaCO_3$ in the limestone.

25. From the following data calculate the percentage purity of a sample of succinic acid, $H_2(C_4H_4O_4)$:

Weight of sample	0.2462 g
Volume of base	38.46 ml
Volume of acid	2.00 ml
Normality of base	0.1120
1.000 ml acid = 1.500 ml base	

26. The analysis of a mixture of sodium chloride and partially hydrated sodium carbonate produced the following data. Calculate the percentages of NaCl, Na_2CO_3 and H_2O in the sample.

Weight of sample as received	1.2000 g
Weight after drying at 110°C	1.1000 g
Volume of acid	43.65 ml
Volume of base	3.65 ml
Normality of acid	0.1000
Normality of base	0.1250

27. From the following data decide whether the sample is $H_2C_2O_4 \cdot 2H_2O$, KHP, or citric acid, $H_3(C_6H_5O_7)$:

Weight of sample	0.2245 g
Volume of NaOH used	30.00 ml
31.75 ml NaOH = 35.11 ml of 0.1056 *N* HCl	

28. 9.05 g of a NH_3 solution is treated with 50.00 ml of 0.4982 *N* H_2SO_4; 21.64 ml of 0.1016 *N* NaOH is required for back titration. What is the percentage of NH_3 in the solution?

29. 45.50 ml of 0.2020 *N* NaOH is required to neutralize a 0.5000-g sample of a crystalline organic acid. What is the equivalent weight of the acid? If the acid is dibasic and completely neutralized in the titration, how many grams of it are required to prepare 300 ml of a 0.400 *M* solution?

30. The "saponification number" of a fat or oil is defined as the number of milligrams of KOH required to saponify 1 g of fat or oil. To a sample of butter weighing 2.010 g is added 25.00 ml of 0.4900 *N* KOH solution. After saponification is complete, 8.13 ml of 0.5000 *N* HCl is found to be required to neutralize the excess alkali. What is the "saponification number" of butter?

31. 50.00 ml of HCl solution yielded a precipitate of AgCl which weighed 1.1200 g.

(*a*) How many milliliters of the HCl solution are needed to prepare 100.0 ml of 0.1000 *N* solution?

(*b*) To what volume should 100.0 ml of the HCl solution be diluted to prepare a 0.1500 *N* solution?

32. A solution of H_2SO_4 which is approximately 52 per cent by weight is in equilibrium with air of average moisture content and is recommended as a stock solution to be prepared, standardized, and preserved for the preparation of standard solutions of desired concentrations.

(*a*) By reference to a handbook, what is the approximate specific gravity to which concentrated sulfuric acid should be diluted to prepare the acid?

(*b*) How many grams of water should be added to 100 g of 95 per cent H_2SO_4 to prepare the solution?

(*c*) If 1.000 g of an approximate 52 per cent solution gave a precipitate of $BaSO_4$ which weighed 1.245 g, what weight of solution should be taken to prepare 500.0 ml of exactly 0.1000 *N* solution?

33. How many milliliters of 0.5193 *N* NaOH should be added to exactly 1 l. of 0.0975 *N* NaOH to make a 0.1000 *N* solution?

34. To what volume must 50.00 ml concentrated nitric acid, density 1.4450 g per milliliter containing 78.00 per cent HNO_3 by weight, be diluted to contain exactly 10 g HNO_3 per 100 ml (10 weight–volume per cent)?

35. Compute the percentage by weight in the diluted nitric acid solution of Problem 34. Use a handbook for the necessary density table, interpolating if necessary.

36 How much water must be added to 50.00 ml of the concentrated nitric acid solution of Problem 34 to prepare a solution which is exactly 10 per cent by weight?

37. 1.000 g of a crude ammonium salt is treated with concentrated KOH, and the liberated NH_3 is distilled and collected in 50.00 ml of 0.5000 *N* HCl. 1.50 ml of 0.5010 *N* NaOH is required for back titration. Compute the percentage of NH_3 in the sample.

38. A 0.5000-g sample of urea, $CO(NH_2)_2$, is treated by the Kjeldahl procedure and the NH_3 distilled into 50.00 ml of 0.4861 *N* H_2SO_4. How much 0.4967 *N* KOH will be required for back titration?

39. If the NH_3 of Problem 38 had been absorbed in boric acid, what volume of an HCl solution made by diluting 80.00 g of constant-boiling HCl distilled at 746 mm to 1.000 l. will be required to reach the bromcresol green end point?

40. What weight of sample should be taken for a Kjeldahl analysis by the boric acid modification so that the volume of 0.5051 *N* H_2SO_4 used will be equal to the percentage of nitrogen in the sample?

41. A fertilizer sample is known to contain about 5 per cent nitrogen. A Kjeldahl analysis is to be made, using boric acid as the absorbent for ammonia. If the available acid solution is 0.1 *N*, what weight of sample will be taken for the analysis? Would it be desirable to weigh out a large sample for the digestion, and to use a $\frac{1}{5}$ aliquot portion for the distillation? Explain your answer.

42. Nitrates may be determined by a procedure similar to that of the Kjeldahl method. The sample, dissolved in sodium hydroxide solution, is treated with Davorda's alloy (50 per cent Cu, 5 per cent Zn, 45 per cent Al), which reduces the nitrogen to ammonia. The ammonia is distilled from the sodium hydroxide solution and absorbed in an acid solution, just as in the Kjeldahl analysis. From the following data compute the percentage of potassium nitrate in a sample:

Weight of sample	2.123 g
Volume of acid	50.00 ml
Normality of acid	0.5000
Base for back titration	12.01 ml, 0.4620 *N*

43. A sample of sodium hydroxide contains 95.0 per cent NaOH and 3.00 per cent sodium carbonate. If 4.25 g of this material is dissolved and diluted to exactly 1 l., (*a*) what is the normality of the solution when it is employed in titrations with phenolphthalein indicator; (*b*) what is the normality when methyl orange indicator is used?

44. A sample contains sodium hydroxide and sodium carbonate: 20.00 ml of 0.1000 *N* acid is needed to titrate it to the phenolphthalein end point and an additional 5.00 ml of acid to complete the titration from the phenolphthalein to the methyl orange end point. How many grams of each constituent are present in the sample?

45. If the sample of Problem 44 contains sodium hydroxide and sodium bicarbonate, how many grams of each substance are present?

46. A sample which weighed 1.1179 g contains Na_2CO_3, NaOH, and NaCl. It is dissolved and titrated with 0.3000 *N* HCl. 38.16 ml of acid is required to reach the phenolphthalein end point, and an additional 24.08 ml of acid is needed to reach the methyl red end point. Calculate the percentages of each constituent in the sample.

47. A solution of crude caustic soda contains 5.000 g in 500.0 ml; 50 ml of this solution is titrated by 26.42 ml of 0.3760 *N* acid to the methyl orange end point. Another 50.00-ml portion, after addition of barium chloride, required 22.48 ml of acid for titration to the phenolphthalein end point. Calculate the percentages of sodium hydroxide and sodium carbonate in the sample.

48. From the following data find the percentages of Na_2CO_3 and $NaHCO_3$ in a mixture of these chemicals and inert constituents:

(*a*) A 0.5000-g sample required 45.50 ml of 0.1050 *N* HCl to reach the methyl red end point.

(*b*) 25.00 ml of 0.1000 *N* KOH is added to 0.2500 g of the sample; $BaCl_2$ is added to precipitate the $BaCO_3$, and 12.00 ml of 0.1050 *N* HCl is required to reach the phenolphthalein end point.

49. To 50.00 ml of a H_2CO_3 solution is added 25.00 ml of 0.0500 *N* $Ba(OH)_2$. 13.25 ml of 0.0510 *N* HCl is required to titrate to the phenolphthalein end point. What is the molarity of the H_2CO_3 solution?

50. Titration of Na_3PO_4 with HCl to the phenolphthalein end point produces Na_2HPO_4; subsequent titration to the methyl orange end point produces NaH_2PO_4. Find the milligrams of Na_3PO_4 and Na_2HPO_4 present in a sample which required 25.00 ml of 0.1200 *N* H_2SO_4 to reach the phenolphthalein end point and an additional 35.00 ml of the acid to attain the methyl orange end point.

51. State the composition of a dry mixture of Na_2HPO_4 and NaOH which would behave in solution similarly to the mixture of Problem 50.

52. A base solution was prepared in the usual manner for removal of carbonate. It was found, however, that some carbonate was present. The following titration data were obtained:

49.00 ml of an acid solution is needed to titrate 50.00 ml of the base solution to the phenolphthalein end point.

49.50 ml of the acid solution is needed to titrate 50.00 ml of the base solution to the methyl orange end point.

The volume of acid is corrected for the indicator blank.

47.50 ml of the acid solution is needed to titrate a solution of 0.2125 g pure sodium carbonate in 50 ml water to the methyl orange end point. No indicator blank is taken; the titration is made in the cold.

(*a*) Compute the normality of the base solution when it is used with methyl orange indicator.

(*b*) Compute the normality of the base solution when it is used with phenolphthalein indicator.

(*c*) The base solution is separately standardized by potassium acid phthalate of assay value 95.5 per cent. What weight of phthalate will react with 50.00 ml of the base?

53. An acid is 0.1000 *N* at 20°C. What is its normality at 30°C if it is assumed that the density of the solution is the same as that of water?

To solve the following problems reference must be made to the section on indirect analysis on page 332.

54. A mixture contains only $CaCO_3$ and $MgCO_3$. 0.5000 g of the mixture is dissolved in 50.00 ml of 0.2500 *N* H_2SO_4, and 15.00 ml of 0.0960 *N* KOH is needed for back titration. Find the composition of the mixture.

55. Oleum or fuming sulfuric acid is a mixture of H_2SO_4 and SO_3. If 1.5000 g of oleum require 32.63 ml of 0.998 *N* NaOH for titration, what is the composition of the sample?

CHAPTER

9

Theory of Neutralization Reactions

To date we have discussed only laboratory techniques and the computations needed for standardization of solutions and analysis of samples. There is more to analytical chemistry than the ability to manipulate equipment and perform the necessary computations. The really competent chemist must understand *why* things are done as they are. Specifically, for neutralization analyses one should know which titrations of acids and bases can be made and which ones cannot, the factors which determine the feasibility of titrations, how acid–base indicators work, and how to select the proper indicator for a given titration. These factors are discussed in this chapter. This discussion is based on the chemical equilibria involved in dissociation of acids and bases and in hydrolysis of salts. In modern curricula the student has studied these topics in previous courses, but, since it is necessary to make new applications of the theory, we shall first of all review the basic concepts. The student who finds this review too brief or too condensed will profitably refer to his previous textbooks for a more complete discussion. A thorough understanding of the use of logarithms is also necessary for the work of this chapter.

REVIEW OF PRINCIPLES OF CHEMICAL EQUILIBRIUM

For a chemical reaction at equilibrium, such as

$$n\mathrm{A} + m\mathrm{B} = p\mathrm{D} + q\mathrm{E}$$

the concentrations of the reactants are related by the mathematical expression:

$$\frac{[\mathrm{D}]^p[\mathrm{E}]^q}{[\mathrm{A}]^n[\mathrm{B}]^m} = K_e$$

In this expression all concentrations are expressed in terms of moles per liter, designated by the brackets [ ]. Each molar concentration is raised to a power numerically equal to the number of molecules appearing in the balanced chemical equation. Conventionally, the concentrations of reaction products appear in the numerator and of starting materials in the denominator. Thus it is always necessary to write the chemical equation for which the equilibrium constant is given. For every reaction there are two constants, one of which is the reciprocal of the other. For example, the constant for the reaction,

$$2HI = H_2 + I_2$$

is

$$\frac{[H_2][I_2]}{[HI]^2} = K_c$$

For the reaction,

$$H_2 + I_2 = 2HI$$

the constant is

$$\frac{[HI]^2}{[H_2][I_2]} = K_c' = \frac{1}{K_c}$$

The constant K_c is known in general as the equilibrium constant. Its dimensions are moles per liter raised to some power, or if the number of molecules is the same on both sides of the chemical equation the constant may be dimensionless, that is, only a number. For a specific type of reaction, such as ionization of a weak electrolyte, the constant is usually referred to as the ionization constant.

The equilibrium constant is applicable only at constant temperature. In all reactions a change in temperature will shift the equilibrium so as to change the concentrations of the reactants; therefore at T_2 a new constant will apply.

Ionization of Acids, Bases, and Salts

The law of chemical equilibrium applies to any type of reaction, regardless of the physical state of the reactants. Some of the more important applications are to gas-phase reactions of industrial importance. In the present discussion, however, we shall limit the field to the ionization of acids, bases, and salts in aqueous solution and the equilibria which are brought about by these ionizations.

It may be recalled that all acids, bases, and salts belong to the class of substances known as electrolytes. When dissolved in water they give charged ions which will conduct an electric current. Further, elec-

trolytes are of two classes, strong and weak, depending on whether a large or small fraction of the dissolved molecules dissociate into ions. Most salts, the common inorganic acids, and all bases, except ammonium hydroxide and its derivatives, are strong electrolytes. The majority of organic acids are weak electrolytes. Some substances which can ionize in two or more stages may belong in both classes. Phosphoric acid, for example, is a moderately strong acid for dissociation of one hydrogen but weak for dissociation of the second and third hydrogen ions.

Ionization Constant for Weak Electrolytes. If one measures the degree of ionization for a weak electrolyte, such as acetic acid, the ionization constant is readily computed from the data. There are various methods for measuring the degree of dissociation of a solute. The most common ones are by the electrical conductivity of the solution, which depends on the number and type of ions present, and by the *p*H of the solution, which depends on the hydrogen-ion concentration.

Measurement shows that, if one prepares a one-tenth molar solution of acetic acid, the hydrogen-ion concentration is 0.00134 mole per liter. This is due to dissociation of the acid according to the equation,

$$HAc = H^+ + Ac^-$$

Here the abbreviation Ac^- is used to represent the acetate ion, $C_2H_3O_2^-$.

Since an acetate ion is produced for each hydrogen ion formed by the dissociation, the concentration of acetate ion is also 0.00134 *M*. Further, since 0.00134 mole per liter of HAc molecules has dissociated, the remaining concentration of HAc is 0.1000 − 0.00134 or 0.09866 moles per liter.

Application of the equilibrium equation to the ionization of HAc gives

$$\frac{[H^+][Ac^-]}{[HAc]} = K_i$$

On substitution of the values for the concentrations of the components, we have

$$\frac{(0.00134)^2}{0.09866} = 0.000018 \quad \text{or} \quad 1.8 \times 10^{-5}$$

This constant is known as the ionization constant for acetic acid.

If now similar measurements are made for other concentrations of acetic acid and the constant is computed for each, it is found that over a wide range of concentrations a value of 1.8×10^{-5} is obtained for the ionization constant. In other words, the law of chemical equilibrium applies to this reaction.

Once the ionization constant has been determined for a given dissociation one can compute, by methods shown later, the hydrogen-ion concentration for any concentration of the weak electrolyte. Thus, the ionization constant is a convenient method for tabulating the hydrogen-ion concentration.

Ionization of Strong Electrolytes. If one attempts to measure the ionization of 0.1 *M* HCl solution by any experimental method, it is found that apparently well over 90 per cent of the acid is ionized. Consequently, the apparent value for the ionization constant is a large number instead of a very small one such as was found for acetic acid. Further, if measurements are made at various initial concentrations of hydrochloric acid, it is found that the apparent ionization constant changes for each initial concentration. It is obvious then that the law of chemical equilibrium does not apply, or at least not without the introduction of correction terms. For many years a great deal of work was done in an attempt to ascertain why the equilibrium law did not apply to strong electrolytes, whose apparent degree of dissociation was large but which seemed to change with dilution of the solution. This work led to the modern view that strong electrolytes are completely dissociated in aqueous solution; there are no undissociated HCl molecules in a 0.1 *M* solution of HCl. Rather, there is a 0.1 *M* solution of H^+ and of Cl^- ions. The measurement of hydrogen-ion concentration leads to the conclusion that the concentration is not 0.1 *M* but is near 0.09 *M*; thus the apparent degree of dissociation is near 90 per cent. This effect is attributed to the electrostatic attractive forces between the ions that keep them from behaving as completely independent particles. Regardless of the apparent 90 per cent ionization, we believe that it is complete, or 100 per cent. Therefore there is no equilibrium constant for a strong electrolyte.

In this text we shall disregard the apparent degree of dissociation of strong electrolytes and in every case shall consider the strong electrolyte as completely dissociated. Thus, in a 0.1 *M* NaOH solution the hydroxide-ion concentration is taken as 0.1 *M*, and in a 0.1 *M* NaAc solution the concentrations of Na^+ and Ac^- ions are each 0.1 *M*.

Activity and Activity Coefficient. We have stated previously that a constant value of the concentration product is obtained for acetic acid solutions of various dilutions. This is not strictly true. Although the constant has roughly the value 1.8×10^{-5} at room temperature, accurate measurements show that with increasing dilution the constant changes slightly. The theory as previously given is overly simplified. In the simple statement of the law of chemical equilibrium it is tacitly assumed that each ion or molecule in a solution is completely independent of other ions or molecules and is not at all affected by their presence

This is not true except in very dilute solutions, just as the perfect-gas laws are not strictly valid for actual gases except at very low pressures. The various solute particles of a solution attract or otherwise influence one another. Therefore the effective concentrations of solute particles may differ from the actual concentrations, and the law of chemical equilibrium is not strictly obeyed.

Because of these effects it is customary in more advanced work to deal with the activity or effective concentration of ions or molecules rather than with the actual concentrations. The activity a is a function of the concentration C and is related by the expression,

$$a = \gamma C$$

where γ is known as the activity coefficient.

The activity coefficient γ is not a constant for a given substance but depends on many factors, chief among which is the total concentration of ions in a solution. Because of the complexity of the factors which influence γ, the knowledge of numerical values for this term is limited. In dilute solution, where the ions are relatively far apart, the activity is practically the same as the concentration; that is, γ approaches unity; but in more concentrated solutions the activity may be greater or less than the concentration. Since few numerical values are known for γ, it is often necessary, for purposes of calculation, to ignore the deviations of γ from unity, that is, to consider the activity as equal to the concentration. This assumption is made in all equilibrium calculations of this text. Because of the assumption, the calculations to be made will give results which are only approximately true. More exact results could be obtained by use of activities, which are not as yet generally known.

Use of Equilibrium Constant to Compute Hydrogen-ion Concentrations of Solutions

In considering the feasibility of titrations and the selection of neutralization indicators, it is necessary to know how the hydrogen-ion concentration of the solution varies during the titration. By proper use of ionization and hydrolysis constants one can compute, for any aqueous solution of an acid, base, salt, or mixture thereof, the hydrogen-ion concentration. The methods for doing this are briefly reviewed.

***p*H.** In any aqueous solution the product of hydrogen- and hydroxide-ion concentrations is a constant, or, at room temperature,

$$[H^+][OH^-] = K_w = 1 \times 10^{-14}$$

In a 0.1 M HCl solution the hydrogen-ion concentration is 0.1 M. But

in a 0.1 M NaOH solution the hydroxide-ion concentration is 0.1 M, and therefore the hydrogen-ion concentration is 1×10^{-13} M. Thus, in passing from a basic to an acid solution the hydrogen-ion concentration may change by a factor of 10^{12} or a million million times. Numbers of this magnitude are too large for convenient representation, and in particular the change is too great to be represented in any type of plot. In scientific work it is customary to compress the scale for plotting purposes, in dealing with such large numbers, by taking the logarithms of the numbers. But, since the hydrogen-ion concentrations generally range from 10^{-13} to 10^{-1}, the logarithms are negative numbers. Therefore it is convenient instead of hydrogen-ion concentrations to deal with a function known as the pH which is defined by the relation:

$$p\text{H} = -\log [\text{H}^+]$$

Anyone familiar with the use of logarithms can readily make the transformation from hydrogen-ion concentration to pH or the reverse transformation. The methods are illustrated in the following examples:

Problem. The hydrogen-ion concentration of a solution is 4×10^{-5} M. What is the pH of the solution?

Solution:

$$\text{Log } 4 \times 10^{-5} = \log 4 + \log 10^{-5}$$

$$= 0.60 - 5 = -4.40$$

$$p\text{H} = -\log [\text{H}^+] = -(-4.40) = 4.40$$

In a problem of this type it is most convenient to express the number whose logarithm is to be found as the product of a number between 1 and 10 and some power of 10. This transformation is made by suitable change of the exponent. For example, the hydrogen-ion concentration of 0.1 M HAc solution, 0.00134 M, is written as 1.34×10^{-3}. The log of 1.34 is 0.13 (to two decimal places, which is usually sufficient in pH computation), and the pH is $-(0.13 - 3)$ or 2.87.

Problem. What is the hydrogen-ion concentration which corresponds to a pH of 5.70?

Solution: Since $5.70 = -\log [\text{H}^+]$,

$$[\text{H}^+] = 10^{-5.70} \quad \text{or} \quad 10^{-0.70} \times 10^{-5}$$

It is apparent to one who understands logarithms that the antilogarithm of $10^{-0.70}$ cannot be obtained from a log table, all the values of which are positive numbers. Therefore it is necessary to rewrite the number to get a positive mantissa:

$$10^{-5.70} = 10^{+0.30} \times 10^{-6}$$

Now, taking the antilogs, we get

$$[\text{H}^+] = 2.0 \times 10^{-6}$$

Other terms frequently used in the same manner as the pH of solutions are defined as follows:

$$p\text{OH} = -\log [\text{OH}^-]$$

$$pK = -\log K_e$$

$$p\text{H} + p\text{OH} = 14 \text{ (for aqueous solutions at room temperature)}$$

This last follows from the relation of hydrogen- and hydroxide-ion concentrations in water.

pH of Aqueous Solutions. The types of solutions most frequently encountered in titrations may be summarized as follows:

A. The solution contains an excess of strong acid or base, with or without a salt.

B. The solution contains a weak acid or base and no other electrolyte.

C. The solution contains a weak acid or base together with a salt of the weak acid or base.

D. The solution contains a salt of a weak acid or base.

E. The solution contains a salt of a strong acid and strong base.

We shall in the following sections review by illustrative computations the methods for determining the pH of the various types of solutions.

A. Whenever a solution contains an excess of strong acid or base, the hydrogen- or hydroxide-ion concentration is determined solely by the concentration of the acid or base, regardless of salts which may be present.[1] Since strong acids and bases are completely dissociated, the presence of salts has no effect on the pH. To determine the pH it is only necessary to determine the concentration of the acid or base present.

Problem. If 50 ml 0.1 M NaOH is added to 75 ml 0.1 M HCl, what is the pH of the solution?

Solution: Since acid is in excess, all the NaOH is neutralized, with formation of NaCl and water. There remains 25 ml of the original 0.1 M HCl, in a total volume of 125 ml. Therefore,

$$[\text{H}^+] = [\text{HCl}] = \frac{25 \times 0.1}{125} = 0.02\ M = 2 \times 10^{-2}\ M$$

$$p\text{H} = -\log (2 \times 10^{-2}) = -(0.30 - 2) = 1.70$$

B. In a solution of weak acid HA there is the equilibrium:

$$\text{HA} = \text{H}^+ + \text{A}^-$$

[1] This statement is only approximately correct when salts are present which hydrolyze. For example, in a mixture of NaOH and NaAc the salt contributes a slight amount of hydroxide ion by hydrolysis. This amount of hydrolysis is so small that it is completely justifiable to neglect it.

Mathematically,

$$\frac{[H^+][A^-]}{[HA]} = K_i$$

The value for K_i is known for most common acids (see Appendix). From the constant the pH is readily computed for a solution of weak acid or base of any concentration.

Problem. K_i for HA (a hypothetical acid) is 2×10^{-6}. What is the pH of a 0.15 M solution of HA?

Solution: Write the chemical equation. Over each term indicate the concentration which is present at equilibrium.

$$\overset{0.15-X}{HA} = \overset{X}{H^+} + \overset{X}{A^-}$$

Note that X represents the concentration of both the H^+ and A^- ions, since both ions are formed in equimolar amounts by dissociation of HA.

Substitute the concentrations in the mathematical relation given above.

$$\frac{X^2}{0.15 - X} = 2 \times 10^{-6}$$

This equation may be solved by the general method for quadratic equations. It is simpler, however, and sufficiently exact to use an approximate solution by letting $0.15 - X \cong 0.15$, since X is obviously small in comparison with 0.15. This gives

$$\frac{X^2}{0.15} \cong 2 \times 10^{-6}$$

$$X^2 = 3.0 \times 10^{-7}$$

We may complete the solution by extracting the square root to solve for X and then taking $-\log X$, which is pH. The mathematical operations are shortened, however, by taking $-\log X^2$ at this point and dividing by 2 to get the pH.

$$-\log X^2 = -(\log 3.0 + \log 10^{-7})$$

$$= -(0.48 - 7) = 6.52$$

$$-\log X = -\log [H^+] = \frac{6.52}{2} = 3.26 = p\text{H}$$

For a solution of a weak base we may proceed in a similar manner except that pOH is determined. Subtraction of pOH from 14 gives pH.

Problem. K_i for BOH is 5×10^{-5}. What is pH of a 0.14 M solution of BOH?

Solution:

$$\overset{0.14-X}{BOH} = \overset{X}{B^+} + \overset{X}{OH^-}$$

$$\frac{X^2}{0.14} \cong 5 \times 10^{-5}$$

$$X^2 = 0.7 \times 10^{-5} = 7 \times 10^{-6}$$

$$-\log X^2 = -(0.85 - 6) = 5.15 = 2p\text{OH}$$

$$p\text{OH} = \frac{5.15}{2} = 2.58$$

$$p\text{H} = 14 - 2.58 = 11.42$$

C. When a solution contains a salt of a weak acid or base, together with excess acid or base, ionization is repressed by the common-ion effect. The *p*H is computed by the same relations as in the preceding section, but account must be taken of the effect of the common ion provided by the salt.

Problem. A 0.05 *M* solution of acetic acid contains sodium acetate at a concentration of 0.15 molar. Find the *p*H.

Solution: Write (always this is the first step) the chemical equation:

$$\text{HAc} = \text{H}^+ + \text{Ac}^-$$

Let

$$X = [\text{H}^+] \text{ at equilibrium}$$

$$0.05 - X = [\text{HAc}]$$

$$0.15 + X = [\text{Ac}^-]$$

Acetate ion is furnished both by the salt which is completely dissociated and by the molecules of acid which dissociate.

Substitution of these concentrations into the equilibrium expression gives

$$\frac{(X)(0.15 + X)}{0.05 - X} = 1.8 \times 10^{-5}$$

Neglecting X when added to or subtracted from a much larger number, we have

$$\frac{0.15X}{0.05} \cong 1.8 \times 10^{-5}$$

$$3X = 1.8 \times 10^{-5}$$

$$X = 0.6 \times 10^{-5} = 6.0 \times 10^{-6}$$

$$p\text{H} = -\log (6.0 \times 10^{-6}) = -(0.78 - 6) = 5.22$$

When a solution of acetic acid is partially neutralized by a strong base, the salt represses the ionization of the remaining acid, just as in the preceding example.

Problem. What is the *p*H of a solution made by adding 30 ml 0.1 *M* NaOH to 50 ml 0.15 *M* HAc?

Solution: First find the concentrations of the constituents of the solution. Since acetic acid is in excess, the final solution will contain unneutralized acid plus salt equivalent to the amount of base added. Originally there were 50 × 0.15 or 7.5 m mol acid. To this 30 × 0.1 or 3 m mol base were added. Therefore, the solution

now contains 7.5 − 3.0 or 4.5 m mol acid. Since each millimole base formed a millimole salt, there are 3 m mol salt (NaAc) present. Then,

$[H^+] = X$

$[HAc] = 4.5/80$ since the final volume is 80 ml (Concentration = m mol/ml)

$[NaAc] = 3.0/80$

Substituting, we have

$$\frac{X(3.0/80)}{4.5/80} \cong 1.8 \times 10^{-5}$$

from which the pH is determined as in the preceding examples.

D. A salt of a weak acid or base or of both hydrolyzes (reacts with ions of water) in the following ways:

1. Weak acid—strong base. Sodium borate may be taken as an example.

$$Na^+ + BO_2^- + H_2O = HBO_2 + OH^- + Na^+$$

Application of the equilibrium relation gives

$$\frac{[HBO_2][OH^-]}{[BO_2^-]} = K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.1 \times 10^{-9}}$$

which may be used to compute the pH of a salt solution of specified concentration.

Problem. Find the pH of a 0.05 M sodium borate solution.

Solution: Let $X = [HBO_2]$ and $[OH^-]$ since both are formed from the reaction above, in equimolar amounts. Then $0.05 - X$ is $[BO_2^-]$. Substituting these values and neglecting X when subtracted from the much larger number, 0.05, we have

$$\frac{X^2}{0.05} \cong \frac{1 \times 10^{-14}}{1.1 \times 10^{-9}}$$

$$X^2 = \frac{5 \times 10^{-16}}{1.1 \times 10^{-9}} = 4.6 \times 10^{-7}$$

$$2p\text{OH} = -\log X^2 = -\log (4.6 \times 10^{-7}) = -(0.66 - 7) = 6.34$$

$$p\text{OH} = \frac{6.34}{2} = 3.17$$

$$p\text{H} = 10.83$$

2. Weak base—strong acid. Ammonium chloride may be taken as example.

$$NH_4^+ + H_2O = NH_4OH + H^+$$

$$\frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{1 \times 10^{-14}}{K_b} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$$

Problem. Compute the pH of a 0.05 M solution of NH_4Cl.
Solution: Let $X = [H^+] = [NH_4OH]$ and $(0.05 - X) = [NH_4^+]$. Then,

$$\frac{X^2}{0.05} \cong \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$$

This equation is solved in the usual manner.

3. Weak base—weak acid. Ammonium borate is an example. Since both the anion and cation react with ions of water to give undissociated molecules, hydrolysis is much more extensive than in the previous examples. The chemical equation is

$$NH_4^+ + BO_2^- + H_2O = NH_4OH + HBO_2$$

which gives the equilibrium expression,

$$\frac{[NH_4OH][HBO_2]}{[NH_4^+][BO_2^-]} = \frac{K_w}{K_aK_b} = \frac{1 \times 10^{-14}}{1.1 \times 10^{-9} \times 1.8 \times 10^{-5}}$$

Problem. What is the pH of a 0.05 M solution of ammonium borate?
Solution: Let $X = [NH_4OH] = [HBO_2]$

$$0.05 - X = [NH_4^+] = [BO_2^-]$$

In view of the large value for the hydrolysis constant, it is not permitted to neglect X in comparison with 0.05.

Substitution in the equilibrium expression gives

$$\frac{X^2}{(0.05 - X)^2} = 0.5$$

The simplest solution is to extract the square root of both sides of the equation. This gives

$$\frac{X}{0.05 - X} = 0.7$$

To get the pH of the solution we must now substitute the value of $X/(0.05 - X)$ in the ionization expression for NH_4OH or HBO_2. That is,

$$[H^+] = K_a \frac{[HBO_2]}{[BO_2^-]} \quad \text{or} \quad [OH^-] = K_b \frac{[NH_4OH]}{[NH_4^+]}$$

Since X is $[HBO_2]$ and $0.05 - X$ is $[BO_2^-]$, the ratio $[HBO_2]/[BO_2^-]$ is the previously found value for $X/0.05 - X$ or 0.7. Therefore $[H^+]$ is given by the equation,

$$[H^+] = 1.1 \times 10^{-9} \times 0.7 = 7.7 \times 10^{-10}$$

and pH is 9.11.

In this example the acid is weaker than the base, and consequently more hydrogen ion is removed from water than hydroxide ion. If the computation is made for ammonium acetate hydrolysis, where the acid and base are of the same strength, it is found that the pH of the solution is the same as that of water, 7.

E. When a salt of a strong acid and strong base is dissolved, neither of the ions can unite with an ion of water. Consequently, there is no hydrolysis, and the *p*H is that of water, or 7, provided the water contains no carbon dioxide. If carbon dioxide is present, the *p*H is about 5.7 (see top line, Table 17).

Bronsted Definitions in Neutralization Equilibria

In the preceding section the terms acid and base have been used in the classical sense for aqueous solution; an acid is a substance that furnishes hydrogen ion, and a base is a substance that furnishes hydroxide ion. The classical definition has been broadened by Bronsted [2] in order to take into account the variations in strength of acids in various solvents and the role of the solvent in ionization. According to the newer definitions an acid is a substance which furnishes a proton (positively charged hydrogen atom), and a base is a substance which can accept or unite with a proton. In the reaction,

$$\underset{\text{acid}}{HA} = \underset{\text{proton}}{H^+} + \underset{\text{base}}{A^-}$$

HA is known as an acid, and A^- is known as the conjugate base of the acid HA. The reaction which occurs when an acid is placed in water is written

$$\underset{\text{acid 1}}{HA} + \underset{\text{base 2}}{H_2O} = \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 1}}{A^-}$$

This equation emphasizes the facts that: (*a*) Water acts as a base, accepting a proton to form the hydrate H_3O^+ which is known as the hydronium ion and (*b*) there is competition between the two bases A^- and H_2O for the proton. If HA is a weak acid, the base A^- is a stronger base than H_2O, since A^- holds the proton so tightly that the dissociation is slight. On the other hand, when HA is largely dissociated, we consider that A^- is a weaker base than H_2O, that is, that H_2O holds the proton more tightly than does A^-.

An advantage of this formulation is that it emphasizes the role of the solvent in dissociation, that is, the attraction of the solvent molecule for the proton. A disadvantage is that the formulation does not take into account the fact that other ions are also hydrated (combined with water molecules); hydration is indicated only for the proton.

[2] J. N. Bronsted, *Rec. trav. chim*, **42**, 718 (1923); *J. Phys. Chem.*, **30**, 777 (1926); *Trans. Faraday Soc.*, **25**, 59 (1929); *Z. angewand. Chem.*, **43**, 229 (1930); *Z. physik. Chem.*, **169A**, 52 (1934); *Physical Chemistry*, translated by R. P. Bell, Heinmann, London, 1937, pp. 202–28; *Chem. Rev.*, **5**, 231 (1923).

In dealing with aqueous solutions there is little difference between the classical and the Bronsted formulations of acid–base equilibria. The chief points of difference are the substitution of hydronium ion for hydrogen ion and the change in definitions of acids, bases, and salts. The mathematical treatment of neutralization equilibria is essentially the same for either notation. As for terminology, it makes little difference which system is used, provided that the meaning of the words is clearly understood. Sodium carbonate is a salt in the classical system, whereas carbonate ion is a base in the Bronsted system. But using the classical system we can still recognize the basic properties of carbonate ion; in fact, sodium carbonate is widely used as a primary standard for acids.

For comparison we may formulate the equilibria of the preceding section by means of the Bronsted notation.

1. Ionization of weak acid. The chemical equation is written

$$HAc + H_2O = H_3O^+ + Ac^-$$

Mathematically,

$$\frac{[H_3O^+][Ac^-]}{[HAc][H_2O]} = K_e$$

but, since $[H_2O]$ is constant, we may write

$$\frac{[H_3O^+][Ac^-]}{[HAc]} = K_a$$

This is the conventional ionization constant for acetic acid if we represent the same concept by the two symbols H_3O^+ and H^+.

2. Ionization of weak bases. Since all the common weak bases are ammonia derivatives, we may select ammonia as an example. The chemical equation is written

$$NH_3 + H_2O = NH_4^+ + OH^-$$

This is preferable to the older system,

$$NH_3 + H_2O = NH_4OH = NH_4^+ + OH^-$$

because it eliminates the necessity for postulation of an intermediate NH_4OH. The equation as written emphasizes the fact that ammonia will compete with the hydroxide ion for a proton. In following the classical system it is implied that the dissolved ammonia is united with water to form ammonium hydroxide and that this ionizes to give the ammonium and hydroxide ions.[3] Mathematically,

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = K_b$$

[3] The hypothetical carbonic acid is likewise omitted, in the Bronsted formulation, for the equilibrium between carbon dioxide and carbonate or bicarbonate ions.

$$CO_2 + 2H_2O = H_3O^+ + HCO_3^-$$

which differs from the older equation only in the substitution of the concentration of dissolved ammonia for the concentration of ammonium hydroxide.

3. Ionization of water. The chemical equation is written

$$H_2O + H_2O = H_3O^+ + OH^-$$

which implies that one molecule of water acts as an acceptor for a proton donated by another molecule. Mathematically,

$$\frac{[H_3O^+][OH^-]}{[H_2O]^2} = K_e$$

or

$$[H_3O^+][OH^-] = K_w = 10^{-14}$$

4. Hydrolysis. The hydrolysis of acetate ion is represented by the proton exchange between two bases.

$$Ac^- + H_2O = HAc + OH^-$$

The hydrolysis of ammonium ion is represented by the equations:

$$NH_4^+ + H_2O = NH_3 + H_3O^+$$

and the mathematical formulation is

$$\frac{[H_3O^+][NH_3]}{[NH_4^+]} = K_h = \frac{K_w}{K_b}$$

This differs from the classical treatment by the replacement of H^+ by H_3O^+ and of NH_4OH by NH_3.

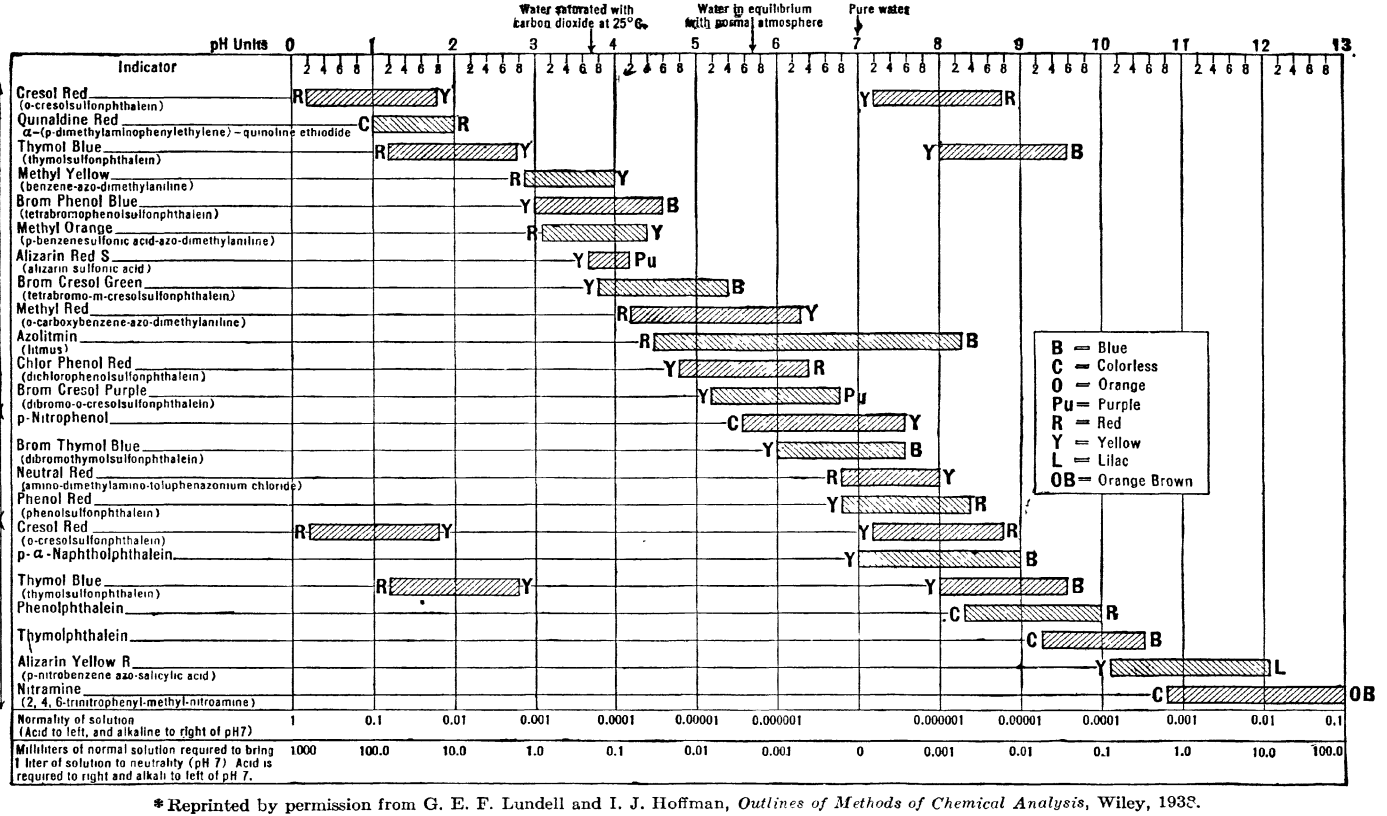
From the parallelism in the two treatments it is apparent that for neutralization equilibria in aqueous solution either system of notation is satisfactory. The classical notation is preferred in this book because of long-established usage, because it is somewhat misleading to indicate hydration for the proton without reference to the hydration of other ions, and because of simplicity in terminology. But in applying the classical notation it is not implied that the symbol H^+ refers to a hydrogen atom which has lost an electron; the symbol is understood to mean a *dissolved* and *hydrated* proton, or a hydrogen ion.

PROPERTIES OF INDICATORS

Acid–base indicators are highly colored organic dyes which exhibit a change in color when the *p*H of a solution is changed between certain limits. The *p*H at which this color change occurs differs for various indicators; this is a fortunate situation for the analyst, since he thereby is enabled to select the indicator whose color change most nearly corresponds to the *p*H of the stoichiometric point for a given titration. A partial list of indicators is given in Table 17.

TABLE 17*

*p*H Ranges of Hydrogen-Ion Indicators



* Reprinted by permission from G. E. F. Lundell and I. J. Hoffman, *Outlines of Methods of Chemical Analysis*, Wiley, 1938.

It may be noted in Table 17 that the various indicators do not abruptly change color at a definite *p*H value, but that the color change occurs when the *p*H is varied over a narrow range, usually about two units. The reason for this phenomenon, as well as the mechanism of the color change, is considered in the following sections.

Equilibria of Colored Forms of Indicators. The organic dyes used for neutralization indicators are either weak organic acids or bases, whose ionization may be, respectively, represented by the following equations:

$$\underset{\text{(color A)}}{HIn} = H^+ + \underset{\text{(color B)}}{In^-}$$

$$InOH = In^+ + OH^-$$

The two colors given by an indicator are the colors, respectively, of the undissociated molecule and of the ion.[4] An acid indicator will, therefore, exhibit color A when in acid solution, because the ionization of the weak indicator acid will be repressed. In basic solution the indicator acid is neutralized to form a salt, and the color of the ion will be shown. The opposite situation is found for a base indicator; in basic solution the undissociated molecule is formed, whereas the ion is formed in acid solution.

Application of the law of chemical equilibrium to the ionization of an acid indicator gives the expression,

$$\frac{[H^+][In^-]}{[HIn]} = K_{ind}$$

which can be rearranged to the form,

$$[H^+] = K_{ind}\frac{[HIn]}{[In^-]}$$

It is evident from this equation that the ratio in the concentrations of the two colored forms of the indicator will vary continuously as the hydrogen-ion concentration is changed.

The color changes that the eye observes depend on the colors of the two different forms of the indicator and on their relative concentrations. If, for example, HIn is yellow and In^- is red, the solution will appear red when In^- is in great excess and yellow when HIn is in great excess.

[4] This is a simplified statement of indicator behavior. Actually, several other reversible changes are involved. For a more complete discussion, see A. A. Noyes, *J. Am. Chem. Soc.*, **32**, 815 (1910).

When the two are present at about the same concentration, the solution is neither yellow nor red, but is orange.

If we assume that in the mixture of colors for In^- and HIn the solution appears red when $[In^-]$ is ten times or more [HIn] and that the color is yellow when [HIn] is ten times or more $[In^-]$, we can readily show that to change the solution from one color to the other will require a *p*H change of 2 units or more. If the ionization constant has the value 10^{-8}, we have

$$[H^+] = (\tfrac{1}{10}) \cdot 10^{-8} \text{ or } 10^{-9} \text{ when the solution is red}$$

$$[H^+] = (\tfrac{10}{1}) \cdot 10^{-8} \text{ or } 10^{-7} \text{ when the solution is yellow}$$

Thus, at *p*H above 9 the solution is red, and at *p*H below 7 it is yellow. In the intermediate region, between *p*H 7 and 9, the solution is neither yellow nor red, but it goes through various shades of orange as the *p*H is changed. If the computation is made for some other ionization constant than 10^{-8}, the transition interval is still 2 *p*H units, but it is at different values from those we have just computed.

Actually, many indicators do have a transition interval of about 2 *p*H units, although some are considerably smaller and some larger. This indicates that, for the eye to see the change from one color to the other, the excess must be, as previously assumed, at least tenfold in most cases.

It is not necessary, however, to have a *p*H change of 2 units to see an end point in a titration. Many indicators are of such colors that the eye recognizes a change when the *p*H is changed only a few tenths of a unit. This is particularly true of some of the mixed indicators.

The apparent sharpness of an indicator end point depends on factors other than the contrast afforded by the colored forms of the indicator; most important is the concentration of the solution used for the titration. The more concentrated the solution, the greater the change in *p*H when one drop of reagent is added, and therefore the sharper the color change. Methyl orange, for example, requires a *p*H change of about 2 units to give a sharp end point. If titration is made with solutions much stronger than 0.1 *N*, one drop will cause such a *p*H change and give a sharp end point. But solutions of the order of 0.1 *N* or weaker will not give a sharp end point because each drop causes too little change in *p*H. It is for this reason that use of mixed methyl red–bromcresol green indicator was recommended in the titration of carbonates in the previous chapter.

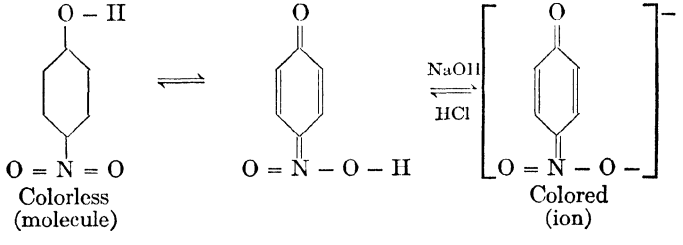
In some titrations, where there is a somewhat continuous change of indicator color near the end point, it is better to titrate to a definite color tint rather than to a sharp change. For such titrations there is

prepared a color standard made by adjusting a comparison solution to the *p*H which should prevail at the end point and adding indicator to this. Each sample is then titrated to match the color of the standard.

Chemistry of Indicators. Two questions arise concerning the use of indicators: (*a*) what volume of titration reagent is required for reaction with the titration indicator, and (*b*) what chemical change in the indicator accompanies the color change?

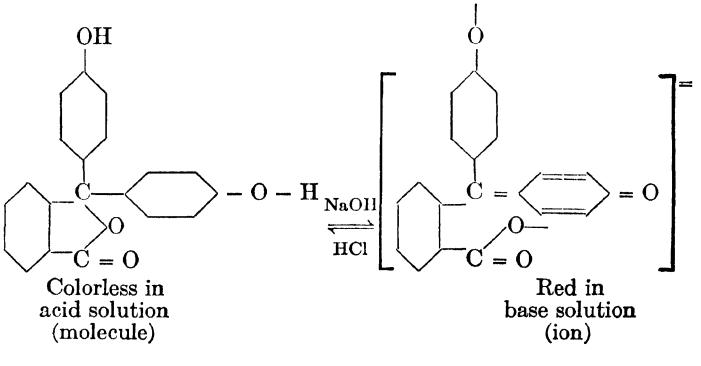
The amount of indicator required to give the necessary intensity of color is so small that a negligible amount of reagent is required for reaction with the indicator. At most, less than 10^{-3} m mol of indicator is employed, and not more than 0.01 ml of 0.1 *N* acid or base is required to neutralize the indicator.

The mechanism of indicator color change has been widely investigated. The generally accepted theory is that the formation of an indicator ion is attended by a molecular rearrangement which gives rise to a chromophoric, or color-forming, group. Paranitrophenol may be cited as an example. In acid solution this is colorless, but in basic solution it is yellow. The structural formulas for the colorless molecule and colored ion are as follows:

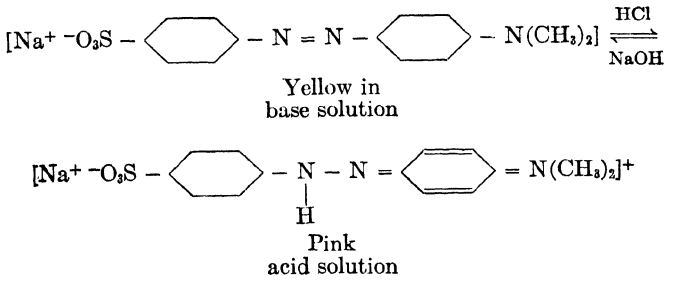


The structural changes in phenolphthalein and methyl orange are more complicated.

Phenolphthalein:



Methyl orange:



Mixed Indicators. The transformation range of an indicator may often be decreased and the sharpness of the color change increased by the addition of a suitable dye.[5] The added dye may be either a second indicator or an inert substance whose color does not change with *p*H. The addition of xylene cyanole FF to methyl orange is an example of the use of an inert dye.

The effect of the added substance is to decrease the range of wavelengths transmitted by the solution, so that the light transmitted by the two colored forms of the indicator is not masked by light of other wavelengths. Methyl orange in alkaline solution transmits light of the violet, green, yellow, orange, and red regions. The observed color is yellow. Xylene cyanole absorbs strongly in the yellow–orange region. When the dye is added to methyl orange the predominating color in the transmitted light is now green, which is the observed color of the solution. In acid solution the indicator absorbs in the green, the dye (as before) in the yellow–orange region. The resulting color, due to light transmitted in the blue and red regions, is magenta. The mixed indicator is almost colorless in the transition region, near *p*H 3.8, owing to transmission of colors that are nearly complementary to one another.

TITRATION CURVES

In order to understand the principles which govern the selection of indicators for a titration one should know how the *p*H changes during a titration. These changes are best shown by titration curves in which the *p*H of the solution is plotted against the volume of reagent added. Titration curves may be constructed by experimental measurement with a hydrogen or glass electrode, or they may be made from values calculated by application of the equilibrium law. In this section the

[5] See I. M. Kolthoff and C. Rosenblum, *Acid-Base Indicators*, Macmillan, 1937, page 172, for a list of mixed indicators and their transition intervals.

calculations are shown for two simple cases. In addition, curves are shown for other titrations of common occurrence.

Titration of Strong Acid with Strong Base. As an example, the titration of 25 ml 0.1 *M* HCl by 0.1 *M* NaOH is taken. The volume is assumed to be 100 ml at the beginning of the titration; after addition of base the volume is 100 ml plus the volume of base added. The concentration of hydrogen ion is calculated for the addition of various quantities of base, in order to obtain a sufficient number of points to plot the neutralization curve. The calculated values are shown in Table 18.

TABLE 18

CONSTRUCTION OF TITRATION CURVE FOR HCl *vs.* NaOH

25 ml 0.1 *M* HCl Diluted to 100 ml and Titrated with 0.1 *M* NaOH

ml NaOH	*Volume of Solution*	$[H^+]$	*p*H
0.00	100	0.0250	1.60
5.00	105	0.0190	1.72
10.00	110.0	0.0136	1.87
15.00	115.0	0.00870	2.06
20.00	120.00	0.00416	2.38
22.50	122.5	0.00204	2.69
23.0	123.0	0.00163	2.79
23.5	123.5	0.00122	2.92
24.0	124.0	0.000806	3.09
24.5	124.5	0.000402	3.40
24.75	124.8	0.000200	3.70
24.85	124.9	0.000120	3.92
24.95	125.0	0.000040	4.40
24.99	125.0	0.000008	5.10
25.00	125.0	10^{-7}	7.00
25.01	125.0	1.25×10^{-9}	8.90
25.025	125.0	5.0×10^{-10}	9.30
25.10	125.1	1.25×10^{-10}	9.90
25.20	125.2	6.25×10^{-11}	10.20
25.50	125.5	2.51×10^{-11}	10.60
26.00	126.0	1.26×10^{-11}	10.90
28.00	128.0	4.27×10^{-12}	11.37
30.00	130.0	2.60×10^{-12}	11.59
32.50	132.5	1.77×10^{-12}	11.75
35.00	135.0	1.35×10^{-12}	11.87

The actual calculation may be repeated for a few representative points in order to illustrate the method employed. Since HCl is a strong acid, the concentrations of its ions are numerically equal to the concentration of the total acid present. At the start of the titration,

$$[H^+] = \frac{25 \times 0.1}{100} = 0.025\ M$$

When 10 ml NaOH has been added, the solution contains 15 ml unneutralized 0.1 *M* acid and the equivalent of 10 ml 0.1 *M* NaCl. The salt, however, does not affect the HCl ionization. The calculation is

$$[H^+] = \frac{15 \times 0.1}{100 + 10} = 0.0136\ M$$

At the stoichiometric point the solution contains NaCl at a concentration of 0.02 *M*. Since NaCl does not hydrolyze, the solution is neutral, or

$$[H^+] = 10^{-7}\ M$$

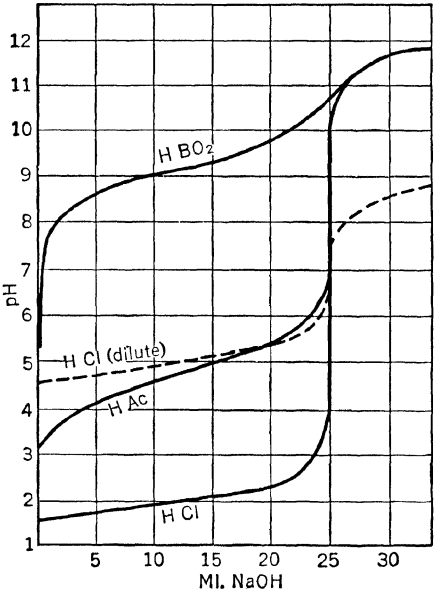


FIG. 19. Titration curves for acids.

At additions past the stoichiometric point, the solution contains excess base. For example, after 30 ml NaOH has been added, there is 5 ml excess base, and

$$[OH^-] = \frac{5 \times 0.1}{130} = 3.85 \times 10^{-3}\ M$$

$$[H^+] = \frac{10^{-14}}{3.85 \times 10^{-3}} = 2.60 \times 10^{-12}\ M$$

The *p*H values for the various points are listed in the last column of Table 18. A plot of *p*H *vs.* ml NaOH is shown in Fig. 19.

Titration of Weak Acid with Strong Base. Computation of the *p*H values for a titration curve for HAc–NaOH is somewhat more laborious than for the previous titration, because (*a*) the acid is not completely dissociated, (*b*) the presence of the salt NaAc represses the

ionization of the acid, and (*c*) the salt hydrolyzes. As before, the titration of 25 ml 0.1 *M* acid with 0.1 *M* NaOH is assumed. The initial volume is 100 ml. The results of the calculation are tabulated in Table 19, and the plotted titration curve is shown in Fig. 19.

The method of calculating may be illustrated by a few representative points.

1. At the start of the titration the solution contains HAc at a concentration of

$$\frac{25 \times 0.1}{100} = 0.025\ M$$

The hydrogen-ion concentration of such a solution is calculated as on page 160. Let

$$X = [H^+] = [Ac^-]$$

$$0.025 - X = [HAc]$$

$$\frac{X^2}{0.025 - X} = 1.8 \times 10^{-5}$$

$$X \cong 6.7 \times 10^{-4} = [H^+]$$

Therefore,

$$p\text{H} = 3.17$$

2. When base has been added, the solution contains HAc and NaAc. For example, when 10 ml NaOH is added, the solution contains 1.5 m mol unneutralized acid and 1.0 m mol sodium acetate solution formed by neutralization of the 10 ml of added base (see page 160 for a similar calculation).

$$[H^+] = X$$

$$[Ac^-] = \frac{1.0}{110} + X$$

$$[HAc] = \frac{1.5}{110} - X$$

$$\frac{X\left(\frac{1.0}{110} + X\right)}{\frac{1.5}{110} - X} = 1.8 \times 10^{-5}$$

$$X\left(\frac{1.0}{1.5}\right) \cong 1.8 \times 10^{-5}$$

$$X = 2.7 \times 10^{-5}$$

$$p\text{H} = 4.57$$

A similar computation is made for all points where both acid and salt are present.

3. At the stoichiometric point the solution contains NaAc at a concentration of 0.02 *M* (2.5 m mol NaAc per 125 ml). The *p*H of the solution is not 7 as in the

HCl–NaOH titration, but is that due to hydrolysis of Ac^-. It is calculated by a method similar to that shown on page 161.

4. After the stoichiometric point is passed, the solution contains NaAc, and NaOH in excess. Under these conditions hydrolysis is repressed, and the *p*H is that due to the excess base present. In this region the HAc titration curve coincides with the HCl curve.

TABLE 19

CONSTRUCTION OF TITRATION CURVE FOR HAc *vs.* NaOH

25 ml 0.1 *M* HAc Diluted to 100 ml and Titrated with 0.1 *M* NaOH

ml NaOH	*Volume of Solution*	$[H^+]$	*p*H
0.00	100.0	6.71×10^{-4}	3.17
1.00	101.0	3.21×10^{-4}	3.49
2.50	102.5	1.62×10^{-4}	3.79
5.00	105.0	7.20×10^{-5}	4.14
10.00	110.0	2.70×10^{-5}	4.57
15.00	115.0	1.20×10^{-5}	4.92
20.00	120.0	4.50×10^{-6}	5.35
22.50	122.5	2.00×10^{-6}	5.70
23.00	123.0	1.56×10^{-6}	5.81
24.00	124.0	7.50×10^{-7}	6.12
24.50	124.5	3.67×10^{-7}	6 44
24.75	124.8	1.82×10^{-7}	6.74
24.90	124.9	7.24×10^{-8}	7.14
24.95	125.0	3.66×10^{-8}	7.44
24.98	125.0	1.54×10^{-8}	7.82
24.99	125.0	8.16×10^{-9}	8.08
24.995	125.0	6.43×10^{-9}	8.19
25.00	125.0	3.00×10^{-9}	8.52
25.025	125.0	5.0×10^{-10}	9.30
25.10	125.1	1.25×10^{-10}	9.90
25.20	125.2	6.25×10^{-11}	10.20
25.50	125.5	2.51×10^{-11}	10.60
26.00	126.0	1.26×10^{-11}	10.90
28.00	128.0	4.27×10^{-12}	11.37
30.00	130.0	2.60×10^{-12}	11.59

Comparison of the HCl with the HAc titration curve shows several points of interest.

1. The magnitude of the break in the acetic acid curve is not nearly so great as it is for the hydrochloric acid curve. The *p*H range of suitable indicators is restricted to the region 7.5–10.

2. The acetic acid curve shows a minor inflection point after a few milliliters of base have been added. This inflection is due to the effect of the salt, sodium acetate, in repressing the ionization of the acid. The solution in the region where both salt and acid are present is said to be

buffered, since the combined action of the salt and acid gives a solution which is very resistant to change in hydrogen-ion concentration.

3. After the stoichiometric point is passed, the two titration curves coincide. In one titration the solution contains sodium hydroxide in the presence of sodium chloride; in the other it contains sodium hydroxide in the presence of sodium acetate. The presence of excess base prevents an appreciable amount of hydrolysis of the acetate. The *p*H of the solution is, therefore, in both cases, due only to the excess base.

Other Titrations. Titration curves [6] for several bases are shown in Fig. 20 and for H_2SO_4 and H_3PO_4 in Fig. 21. Each student should redraw all these curves to scale as he studies the various points enumerated below, so that from memory a reasonably accurate curve can be drawn for any common titration. The following points in relation to titration curves should be noted:

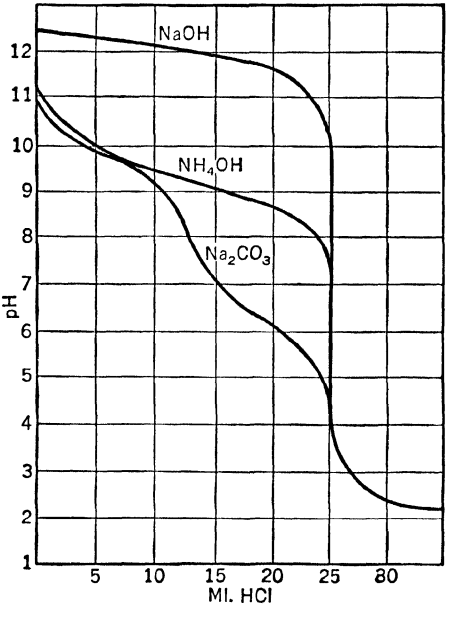


FIG. 20. Titration curves for bases. NaOH and NH_4OH, calculated. Na_2CO_3, by electrometric titration.

1. The curves for bases and for acids have an inverse relation.

2. Strong bases and acids give *p*H curves with long vertical portions near the stoichiometric point. As the strength decreases, the length of the vertical portion also decreases, and the *p*H of the stoichiometric point (center of vertical portion) changes. Very weak acids and bases, such as boric acid, give no vertical region in the titration curve.

3. In the titration of a weak base or acid there is at first a very abrupt *p*H change followed by a region of comparatively little change, where the solution is buffered by the presence of the weak electrolyte and its salt.

4. The curve for sodium carbonate shows two inflection points, corresponding, respectively, to formation of HCO_3^- and H_2CO_3.

[6] See Davis, Oakes, and Salisbury, *Ind. Eng. Chem.*, **15**, 182 (1923) for typical electrometric titration curves.

5. Sulfuric acid, although dibasic, gives a curve with only one break. The reason for this is that both hydrogens are ionized and titrate as strong acids. Actually the constant for the reaction,

$$HSO_4^- = H^+ + SO_4^=$$

has a value near 0.01, which makes the bisulfate ion quite strong in comparison with such acids as acetic.

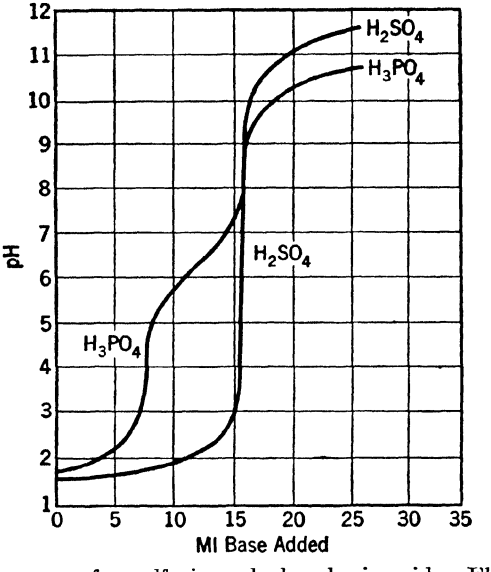


FIG. 21. Titration curves for sulfuric and phosphoric acids. Electrometric titration. Note the buffer effect of phosphate ion after the stoichiometric point is passed.

6. Phosphoric acid gives a curve with two breaks corresponding, respectively, to neutralization of the first and second hydrogen ions. The third hydrogen is so slightly dissociated that it is not neutralized in titration.

7. The sharpness of the break in a titration curve is influenced by the concentration of the reagents. Unit volume of a very dilute solution will cause less *p*H change than the same volume of a more concentrated solution. This effect is apparent in the dotted curve of Fig. 19, which shows the titration of 10^{-4} *N* HCl by 10^{-4} *N* NaOH. The vertical portion of the curve covers a *p*H range of only 1 unit.

SELECTION OF INDICATOR FOR TITRATION

We are now in position to make practical application of the principles of the preceding sections, to the problem of selecting the proper indica-

tor for a titration. The basic principle has been brought out in the discussion of titration curves; namely: *the indicator should undergo a color change at the pH of the stoichiometric point* (or so near this value that a negligibly small volume of reagent is used to go from the stoichiometric point to the end point).

If the titration curve has been plotted, one need only pick out the indicator whose transition range falls on the vertical portion of the curve. For example, in the HCl–NaOH titration with 0.1 *N* reagent any of the indicators whose color change occurs in the range 4 to 10 will give a satisfactory end point. For the HAc–NaOH titration, however, the indicator must change color in the much smaller range of 7.5 to 10. Phenolphthalein is the indicator usually employed.

Usually the titration curve is not prepared for a given analysis. In this case the *p*H of the stoichiometric point is computed, and the indicator whose transition range includes this *p*H is used. Computation of the *p*H at the stoichiometric point is done by the methods of the previous sections. To make this computation one must recognize what substances are present in the solution at the stoichiometric point and must use the concentrations that prevail under the conditions of the analysis. Several examples may be given:

1. Titration of 0.1 N HCl *by 0.1 N* NaOH. Unless further dilution is done by adding water, the solution contains NaCl at a concentration of 0.05 *N* at the stoichiometric point. Therefore the *p*H is 7.

2. Titration of 0.1 N HAc *by 0.1 N* NaOH. At the stoichiometric point the solution contains NaAc at a concentration of 0.05 *N*. The *p*H is computed from the equation for hydrolysis, page 161.

3. Titration of 0.1 N $NaBO_2$ *by 0.1 N* HCl. The reaction is

$$BO_2^- + H^+ = HBO_2$$

If no further dilution is made, the *p*H is computed for 0.05 *N* HBO_2 solution, as shown on page 159.

4. Titration of salt of very weak bases, such as phenyl ammonium chloride, by NaOH. At the stoichiometric point the solution contains phenyl ammonium hydroxide at concentration 0.05 *N* if the titration is done with 0.1 *N* reagents, and no further dilution is made. The *p*H is computed from the ionization constant of this weak base.

The student should make the indicated computations for each of the typical cases above and should select the proper indicator to use.

Feasibility of Titrations. Before making a titration an analyst should not only select the indicator that turns at the proper *p*H, but, in addition, make certain that the titration is feasible. By this we mean that the rate of change of *p*H is sufficiently rapid that addition of a

small volume of reagent, say 0.1 ml or two drops, will span the *p*H range required for the indicator to show a definite change in color shade. In other words, the titration curve must be nearly vertical at the stoichiometric point. In the titrations of Fig. 19 the acetic and hydrochloric acid curves indicate feasibility, but the boric acid titration is not feasible because there is not a sharp break in the curve as reagent is added. An indicator turning at *p*H about 10.7 would be selected on the basis of a *p*H computation; however, if the titration is attempted, it is found that the color change occurs very gradually as base is added and that no sharp end point is obtained. About 5 ml NaOH are required to give a *p*H change of 1 unit.

There are several criteria by which one may estimate whether a titration will give a sharp end point:

1. The titration curve is plotted, and the height in *p*H units of the vertical portion is determined. Usually this method is not used because of the labor involved in computing the number of points needed.

2. A comparison is made with known titrations. For example, one would not question the feasibility of titrating an acid of ionization constant 10^{-5} by 0.1 *N* NaOH because the acid is about as strong as acetic acid whose titration is known to be feasible. Likewise, titration of a base of ionization constant 10^{-5} or greater by 0.1 *N* HCl is feasible. Titration of acids or bases of ionization constant 10^{-6} is doubtful, and, when K_i is less than 10^{-6}, the titration is not feasible. This method of comparing with known cases is not reliable except when the concentrations of the reactants are of the same magnitude as those usually employed.

3. The most reliable quick method is to compute (*a*) the *p*H at the stoichiometric point and (*b*) the *p*H when two drops (0.10 ml) reagent is added in excess of the stoichiometric point. If the *p*H range is 1 or greater, the titration is feasible, and, if the range is much less than 0.5 *p*H unit, a sharp end point will not be obtained with most indicators.

To illustrate, we may compute the feasibility of titrating 50 ml 0.1 *N* NaAc by 0.1 *N* HCl. At the stoichiometric point the solution contains 0.05 *N* HAc, if there has been no further dilution during the titration. The equilibrium concentrations are represented above the chemical equation.

$$\underset{0.05-X}{\mathrm{HAc}} = \underset{X}{\mathrm{H^+}} + \underset{X}{\mathrm{Ac^-}}$$

By use of the usual approximation, the mathematical expression to be solved is

$$\frac{X^2}{0.05} \cong 1.8 \times 10^{-5}$$

$$X^2 = 9 \times 10^{-7}$$

$$-\log X^2 = -(0.95 - 7) = 6.05 = 2p\text{H}$$

$$p\text{H} = 3.03$$

When 2 drops (0.10 ml) HCl is added in excess of the stoichiometric volume of acid,

$$[\text{HCl}] = \frac{0.1 \times 0.1}{100.1} = 10^{-4}$$

This calculation shows that the hydrogen ion furnished by the 0.1 ml excess HCl is less than that of the HAc solution, whose pH is 3.03. The actual hydrogen-ion concentration would have to be determined from the relation,

$$\frac{(10^{-4} + X)(X)}{(0.05 - X)} = 1.8 \times 10^{-5}$$

It is apparent, however, that little change in pH is caused by a 0.1 ml excess of HCl; *the titration is not feasible.*

Frequently in analysis of organic acids it is desired to titrate with very dilute carbonate-free NaOH. For example, 50 ml of a 0.01 N solution of benzoic acid may be titrated by 0.01 N NaOH. We may compute the feasibility, assuming a stoichiometric volume of 100 ml.

At the stoichiometric point,

$$[\text{NaBz}] = 0.005$$

We have

$$\overset{0.005-X}{\text{Bz}} + \text{H}_2\text{O} = \overset{X}{\text{HBz}} + \overset{X}{\text{OH}^-}$$

$$\frac{X^2}{0.005 - X} = \frac{1 \times 10^{-14}}{6.6 \times 10^{-5}}$$

$$X^2 \cong \frac{5 \times 10^{-17}}{6.6 \times 10^{-5}} = 7.6 \times 10^{-13}$$

$$p\text{OH} = 6.06$$

$$p\text{H} = 7.94$$

When 0.1 ml 0.01 N NaOH is in excess of the stoichiometric amount,

$$[\text{NaOH}] = [\text{OH}^-] = \frac{0.1 \times 0.01}{100.1} = 10^{-5}$$

$$p\text{OH} = 5$$

$$p\text{H} = 9$$

Thus it appears that the titration is feasible since 0.1 ml NaOH has caused a pH change of 1 unit. In practice, it has been found that a reproducible and moderately sharp end point can be obtained, thus verifying the result of the computation.

TITRATION OF SALTS

It has already been mentioned that numerous analyses are made by titrating the salt of a weak acid by a strong acid. Examples are

$$Na^+ + BO_2^- + H^+ + Cl^- = HBO_2 + Na^+ + Cl^-$$

$$2Na^+ + CO_3^= + 2H^+ + 2Cl^- = H_2CO_3 + 2Na^+ + 2Cl^-$$

$$Na^+ + CN^- + H^+ + Cl^- = HCN + Na^+ + Cl^-$$

Similarly, salts of weak bases may be titrated by strong bases.

$$(C_6H_5NH_3)^+ + Cl^- + Na^+ + OH^- = C_6H_5NH_3OH + Na^+ + Cl^-$$

In all such titrations the stoichiometric *p*H may be computed from the ionization constant of the weak acid or base present in known concentration at the stoichiometric point.

TABLE 20

FEASIBILITY OF ACID-BASE AND SALT-ACID TITRATIONS USING 0.1 *N* REAGENTS

Material Being Titrated	*Titrating Reagent*	*Approximate pH at Stoichiometric Point*	*Feasibility*
HAc	NaOH	8	Feasible
NaAc	HCl	3	Not feasible
HBO_2	NaOH	11	Not feasible
$NaBO_2$	HCl	5	Feasible
H_2CO_3	NaOH	11	Not feasible
Na_2CO_3	HCl	5	Feasible

An interesting example of this type of titration was used in the Kjeldahl determination of nitrogen, page 143. Ammonia is distilled from an alkaline solution and absorbed in a solution of boric acid, where it forms ammonium borate. The ammonium borate is titrated by HCl, in presence of excess boric acid, by using an indicator which changes color at the *p*H of boric acid solutions, about 5. It is not necessary to know either the amount or the concentration of the boric acid. When the stoichiometric point is passed, there is a sharp drop in *p*H due to presence of excess HCl.

When an acid is too weak for direct titration, as boric acid, titration of the salt by a strong acid is feasible. Conversely, where the acid can be titrated by a strong base, the salt titration is not feasible. One can readily tell, by computing the stoichiometric *p*H, which titration is more feasible. The one whose stoichiometric *p*H lies nearer 7 gives the sharper end point. This is illustrated in Table 20.

The most common salt titration, that of carbonate, has been studied in the preceding chapters. The titration curve is shown in Fig. 20. There are two breaks, at *p*H near 8.6 and 4, respectively, which correspond to phenolphthalein and methyl orange end points. The phenolphthalein end point is not sharp, since the solution is buffered on both sides of the stoichiometric point. The second break is quite sharp and gives a good end point. Since, however, methyl orange is a poor indicator for use with dilute HCl solutions (because the color intensity is low), it is preferable in this titration to add excess acid, boil off CO_2, and back-titrate by an indicator whose color change is sharp, as described in the procedure on page 136. After removal of CO_2, the stoichiometric *p*H is that of the NaCl in solution, or 7. The end point with the mixed indicator used occurs at about *p*H 5.

The reason for using carbonate-free NaOH for titrations with phenolphthalein indicator is that, if carbonate is present, the solution is buffered by formation of bicarbonate; this causes an obscure and fading end point. A small amount of carbonate can be tolerated, since not enough buffer is formed to cause end point difficulty. However, if there is any carbonate, it must be kept in mind that the normality is not the same when the solution is used with methyl orange indicator as when used with phenolphthalein. For example, assume that 50 ml solution contains 5 m mol NaOH and 0.25 m mol carbonate. At the phenolphthalein end point all the NaOH is neutralized, and the carbonate has been converted to bicarbonate. The total number of basic milliequivalents is 5.25, and thus the phenolphthalein normality is 5.25 m e/50 ml or 0.105. At the methyl orange end point both the carbonate and hydroxide are completely neutralized, and the total number of basic milliequivalents is 5.50, or the methyl orange normality is 5.5 m e per 50 ml, or 0.110.

INDICATOR BLANK

The need for indicator blanks is readily seen from a consideration of the titration curves of the preceding sections. If the end point does not coincide with the stoichiometric point, it is necessary to determine the amount of acid or base required to go from the stoichiometric to the end point. This volume should be subtracted from the total volume used in the titration. Thus, if an HCl–NaOH titration with 0.1 *N* reagents is made with methyl orange, the end point occurs near *p*H 4. The data of Table 18 show that *p*H 4 is reached when 24.85 ml 0.1000 *N* NaOH is added to 25.00 ml 0.1000 *N* HCl, or when 0.15 ml HCl is unneutralized. Subtraction of this value from the total HCl volume gives

as the net volume 24.85 ml HCl which reacts with 24.85 ml NaOH. Phenolphthalein gives an end point so close to neutrality that the volume of 0.1 *N* NaOH consumed is negligible. If, however, a very dilute NaOH solution is used, the blank may be appreciable even with phenolphthalein.

Whenever possible the use of indicator blanks is avoided by selecting the indicator so that the end point coincides with the stoichiometric point.

BUFFER SOLUTIONS

It has been pointed out in connection with various titration curves that certain solutions are buffered. A buffer solution is defined as one which contains constituents that react with either acid or base, so that it is resistant to changes in *p*H. In general, a buffer consists of a weak electrolyte and its salt. A common type is represented by a solution of acetic acid and sodium acetate. When an acid is added, it reacts with sodium acetate to form more acetic acid. A base reacts with acetic acid to form more acetate. Since the *p*H is governed by the ionization of the acetic acid, a change in the ratio of salt to acid does not cause any great change in *p*H until one or the other constituent is nearly used up.

Buffers are very important both in pure chemistry and the chemical processes of living matter. In the human body the *p*H of blood and body fluids remains remarkably constant, regardless of the type of diet used, because of the buffer effects of bicarbonate, phosphates, and other salts.

To illustrate the effect of a buffer we may consider the effect produced by adding a small amount of acid or base to (1) an unbuffered solution of NaCl and (2) to a solution buffered by presence of acetic acid and sodium acetate. Consider addition of 1 m e HCl to 10 ml 1 *N* NaCl. Before addition of HCl the *p*H is 7. After addition,

$$[H^+] = \frac{1 \text{ m e}}{10 \text{ ml}} = 0.1$$

$$p\text{H} = 1$$

If the same amount of HCl is added to a buffer which is 1 *N* with respect to HAc and NaAc, the 1 m e HCl reacts with 1 m e NaAc to form 1 m e HAc. Before addition of HCl 10 ml of the solution contains 10 m e HAc and 10 m e NaAc. After addition, the same solution contains 9 m e NaAc and 11 m e HAc. The *p*H for the two cases is readily computed:

Before addition,

$$[H^+] = 1.8 \times 10^{-5} \times \tfrac{10}{10} = 1.8 \times 10^{-5}$$

$$p\text{H} = 4.75$$

After addition of HCl,

$$[H^+] = 1.8 \times 10^{-5} \times \tfrac{1}{9} = 2.2 \times 10^{-6}$$

$$p\text{H} = 4.66$$

Thus it is seen that the same amount of HCl that changes the *p*H 6 units when added to an unbuffered solution will cause a change of only 0.09 *p*H unit when added to a buffered solution. If we had added 1 m e NaOH, respectively, to the buffered and unbuffered solutions, a similar resistance to change would have been found.

Examination of the titration curves of this chapter shows that all have a buffered region in which there is little change in *p*H as reagent is added. In all cases except the strong-acid–strong-base titration the buffer region is where the solution contains either a weak acid and its salt or a weak base and its salt. The HCl–NaOH titration curve shows a region of little change in *p*H, when strong acid is present in large excess. This is not, strictly speaking, a case of buffer action in the sense that some constituent reacts with added acid or base to maintain the *p*H nearly constant. Rather it is due to the fact that, when there is a large concentration of acid present, there must be added a large amount to change the hydrogen-ion concentration by a significant amount. That is, when the hydrogen-ion concentration is of the order of 0.1 *M*, it requires a large amount to change it by a factor of 10, which is required for a *p*H change of 1 unit.

The *p*H of a weak electrolyte–salt buffer can be computed by the relations:

$$\frac{[H^+][\text{salt}]}{[\text{acid}]} = K_i \quad \text{for an acid buffer}$$

$$\frac{[OH^-][\text{salt}]}{[\text{base}]} = K_i \quad \text{for a base buffer}$$

These relations can be used to compute the relative amounts of weak electrolyte and its salt to employ for making up a buffer solution of a given *p*H. In general, to prepare such a solution it is desirable to select the acid or base whose ionization constant most nearly equals the hydrogen- or hydroxide-ion concentration desired for the buffer, so that the acid/salt or base/salt ratio can be made as near unity as possible. When the ratio is unity, the buffer has maximum capacity to take up either acid or base. For example, if it is desired to prepare a buffer of *p*H 9 (or *p*OH 5), one uses a mixture of ammonium hydroxide and ammonium chloride. Then,

$$\frac{[OH^-][NH_4]}{[NH_4OH]} = 1.8 \times 10^{-5}$$

Since $[OH^-] = 10^{-5}$,

$$\frac{[NH_4^+]}{[NH_4OH]} = \frac{1.8 \times 10^{-5}}{10^{-5}} = 1.8$$

To prepare this buffer it is only necessary to mix an ammonium salt with ammonium hydroxide in such proportions that the molar concentrations of salt and hydroxide are in the ratio 1.8 to 1.

Lists of standard buffers covering the whole *p*H range have been prepared (see references at end of this chapter or any handbook of chemistry). A few typical ones covering a limited *p*H range are shown in Table 21.

TABLE 21

TYPICAL SERIES OF BUFFERS ACCORDING TO CLARK AND LUBS

*p*H *Range*	*Reagents Required*	*p*H *of a Typical Mixture*	*Composition of Typical Mixture (per 100 ml Solution)*	*Equilibrium which Controls p*H
1–2.2	0.2 *N* HCl 0.2 *N* KCl	2.0	10.6 ml HCl * 50.0 ml KCl *	
2.2– 3.8	0.1 *N* HCl 0.1 *M* $KHC_8H_4O_4$	3.4	9.90 ml HCl 50.0 ml $KHC_8H_4O_4$	Ionization of $H_2C_8H_4O_4$
4.0– 6.0	0.1 *N* NaOH 0.1 *M* $KHC_8H_4O_4$	5.8	43.00 ml NaOH 50.0 ml $KHC_8H_4O_4$	Ionization of $HC_8H_4O_4^-$
6.0– 8.0	0.1 *N* NaOH 0.1 *M* KH_2PO_4	7.4	39.50 ml NaOH 50.0 ml KH_2PO_4	Ionization of $H_2PO_4^-$
8.0–10.0	0.1 *N* NaOH { 0.1 *M* H_3BO_3 { 0.1 *M* KCl }	9.2	27.60 ml NaOH 50.0 ml H_3BO_3–KCl	Ionization of H_3BO_3

* Per 200 ml solution.

REFERENCES

I. M. KOLTHOFF (translated by C. Rosenblum), *Acid-Base Indicators*, Macmillan, 1937.

W. M. CLARK, *The Determination of Hydrogen Ion*, 3d Ed., Williams and Wilkins, 1928.

QUESTIONS

1. What experimental data would you need to decide whether an electrolyte is strong or weak?

2. How would you decide when to neglect an X term which is added to or subtracted from another number in a quadratic equation?

3. Why does acetic acid have a higher *p*H than hydrochloric acid of the same normality? How does the *p*H of hydrochloric and sulfuric acids of the same normality compare? Of the same molarity?

4. Derive an expression for the hydrolysis of ammonium acetate.

5. Is a solution which appears "neutral" to methyl red, that is, has a color intermediate between red and yellow, neutral in the sense that the *p*H of the solution is 7?

6. Explain why an indicator does not show a continuous change of color throughout the *p*H range from 0 to 14.

7. What colors will the following indicators have at *p*H values of: 2, 3.3, 6.7, 7, 9, 11?

(*a*) Bromthymol blue.

(*b*) Methyl orange.

(*c*) Litmus.

(*d*) Phenolphthalein.

8. What colors will the indicators, methyl yellow cresol red, and thymolphthalein, have in solutions of the following *p*H values?

3.5, 7.5, 10.0.

9. Why is a titration curve plotted in terms of *p*H instead of hydrogen-ion concentration?

10. Why do the titration curves given for hydrochloric and acetic acids coincide after the stoichiometric point is passed?

11. Plot, on the same coordinates, the approximate titration curves for

(*a*) 0.1 *N* NaOH *vs.* 0.1 *N* HCl; 1 *N* NaOH *vs.* 1 *N* HCl.

(*b*) 0.1 *N* HAc *vs.* 0.1 *N* NaOH; 1 *N* HAc *vs.* 1 *N* NaOH.

12. Draw approximate titration curves on which are indicated the line for *p*H 7 and the stoichiometric volume for

(*a*) 25 ml of 0.1 *M* HCN titrated by 0.1 *M* KOH.

(*b*) 25 ml of 0.1 *M* HNO_3 titrated by 0.1 *M* NaOH.

(*c*) 50 ml of 0.1 *M* NH_4OH titrated by 0.2 *M* HCl.

(*d*) 15 ml of 0.1 *M* Na_3PO_4 titrated by 0.1 *M* HCl.

13. Discuss the feasibility of titrating HCN to a point of color change of an indicator. How might the titration be accomplished?

14. What factors must be considered in selecting an indicator for a titration? What factors affect the feasibility of a titration?

15. Draw an approximate curve for the titration of sodium sulfide by hydrochloric acid. No computations should be made.

16. Why is not methyl red a suitable indicator for the titration of 0.001 *N* HCl by 0.001 *N* NaOH?

17. Which reaction is more feasible for titration?

(*a*) $HAsO_4^{=} + OH^- = AsO_4^{\equiv}$

(*b*) $AsO_4^{\equiv} + H^+ = HAsO_4^{=}$

(K_i for $HAsO_4^{=} = 6 \times 10^{-10}$)

18. Why cannot orthophosphoric acid be titrated directly as a tribasic acid?

19. In which of the following cases should an indicator blank correction be applied?

(*a*) NaOH (carbonate-free) titrated with HCl using phenolphthalein.

(*b*) NaOH (containing carbonate) titrated with HCl using methyl red and boiling.

(*c*) NaOH (containing carbonate) titrated with HCl using methyl red and not boiling.

20. For which of the following titrations is phenolphthalein a suitable indicator without the application of an indicator blank?

(*a*) Na_2CO_3 titrated to complete neutralization with HCl in a cold solution.
(*b*) Acetic acid titrated by carbonate-free base.
(*c*) Hydrochloric acid titrated by ammonium hydroxide.
(*d*) 0.001 *N* HCl titrated by 0.001 *N* NaOH, carbonate-free.
(*e*) 0.2 *N* H_2SO_4 titrated by 0.2 *N* NaOH in the Kjeldahl determination.

21. A base which contains carbonate is standardized by the use of methyl red as indicator; the solution is boiled before the end point is determined, and an indicator blank is applied. Could the normality so determined be used for the titration of an acetic acid solution? Explain.

22. A base which is carbonate-free is standardized, methyl orange being used as indicator, but no indicator blank correction is applied. Could the normality so determined be used in the titration of an acetic acid solution? Explain.

23. Why is NaCl used in the determination of the indicator blank correction when methyl red is used as an indicator?

24. The ionization constants for an acid H_3Z are 10^{-3}, 10^{-7}, and 10^{-13}. Would it be feasible to titrate this acid as a monobasic, dibasic, or tribasic acid?

25. Which of the following can be feasibly titrated with 0.1 *N* NaOH? In the case of polybasic acids specify whether the acid is titratable as monobasic, dibasic, etc.

$$H_2SO_4,\ H_2C_2O_4,\ H_3PO_4,\ HBO_2,\ HCN.$$

26. Which of the following can be feasibly titrated with 0.1 *N* HCl?

$$Na_2S,\ NaC_2H_3O_2,\ NaCN,\ NaBO_2,\ C_6H_5NH_3OH.$$

27. A base solution is prepared nearly free of carbonate. This solution is standardized with potassium acid phthalate, using phenolphthalein indicator. The base is now used to standardize a hydrochloric acid solution, with phenolphthalein indicator. If the acid and base solutions are used for titrations with methyl orange indicator, which has the more accurately known concentration? Explain. If a titration is made with methyl orange indicator, will the acid solution have the same normality with this indicator as the value originally determined by means of phenolphthalein indicator? Explain. How may the true normality of the base solution, for use with methyl orange indicator, be determined?

28. What is a buffer solution? Under what condition does a buffer solution have the greatest capacity to absorb acid or base without appreciable change in *p*H?

PROBLEMS

1. Convert to *p*H values:

(*a*) $[H^+] = 0.0003$
(*b*) $[H^+] = 18 \times 10^{-6}$
(*c*) $[H^+] = 0.45 \times 10^{-9}$
(*d*) $[H^+] = 1.25$
(*e*) $[H^+] = 10$
(*f*) $[H^+] = 0.50$
(*g*) *p*OH = 8.50
(*h*) $[OH^-] = 0.0000072$
(*i*) $[OH^-] = 10^{-12}$

2. Find the H^+ which correspond to the following:

(*a*) *p*H = 8.95
(*b*) *p*H = 12.00
(*c*) *p*H = −1
(*d*) *p*H = 3.85
(*e*) *p*H = 0.00
(*f*) *p*OH = 4.50
(*g*) *p*OH = 15.0
(*h*) *p*OH = 0.30

3. Find the $[OH^-]$ which correspond to the values in Problem 2.

4. At 100°C K_w is 5.8×10^{-13}. What is the pH of a neutral solution at 100°C?

5. At 0°C K_w is 1.2×10^{-15}. Is a solution whose pH at 0°C is 7 neutral, acidic, or basic?

6. Calculate the pH of the following solutions:
   (*a*) 0.001 *M* HCl.
   (*b*) 0.001 *M* HNO_2.
   (*c*) 0.01 *M* KNO_2.

7. Find the pH of the following solutions:
   (*a*) 50 ml of 0.0001 *M* NaOH.
   (*b*) 10 ml of 2.0 *M* HCl.
   (*c*) 100 ml of 0.01 *M* $Ba(OH)_2$ (assume complete ionization).
   (*d*) 75 ml of 0.1 *M* KNO_3.
   (*e*) 25 ml of 0.01 *M* H_2SO_4 (assume complete ionization).
   (*f*) 100 ml of 0.2 *M* sodium benzoate.
   (*g*) 5 g of Na_2SO_4 in 250 ml of solution.
   (*h*) 5 m mol NH_4Cl added to 200 ml 0.1 *M* NH_4OH.
   (*i*) 0.025 mole KOH in 125 ml solution.
   (*j*) 1 g HAc in 100 ml.
   (*k*) 1 g HCl in 100 ml.
   (*l*) 1 g HCl and 1 g KCl in 100 ml.
   (*m*) 1 g HAc and 1 g KAc in 100 ml.

8. 50 ml of 0.1 *M* NH_4OH is mixed with 100 ml 0.1 *M* HCl. What is the pH of the resulting mixture?

9. Repeat Problem 8, but use 50 ml of 0.1 *M* HCl and 100 ml of 0.1 *M* NH_4OH.

10. How many grams of KOH must be dissolved in 400 ml to produce a solution whose pH is 9.95?

11. Repeat Problem 10, but use NH_3 in place of KOH.

12. If the solution of Problems 10 and 11 are mixed, what is the pH of the mixture?

13. How many milliliters of 0.1000 *M* HCl must be diluted to 250.0 ml to produce a solution of pH 2.50?

14. How many drops of 0.1 *M* HCl must be added to 100 ml of water to change the pH from 7 to 4? Repeat the calculation using 1 *N* acid.

15. If 100 per cent ionization is assumed, is it possible to prepare a solution of pH -2.3 from concentrated sulfuric acid?

16. Is it possible at room temperature to prepare a NaOH solution whose pH is 15?

17. 10 ml of 0.2 *M* HCl is added to 100 ml of 0.1 *M* HCl. What is the pH of the mixture?

18. 25 ml of 0.2 *M* HAc is diluted to 75 ml and titrated with 0.1 *M* NaOH. Find the pH when half the acid has been neutralized.

19. What color will each of the following indicators have in the solutions of Problem 6? Bromphenol blue, methyl red, phenol red.

20. An indicator which is a weak monobasic acid is blue in a strongly acid solution and yellow in a strongly basic one. If the K_{ind} is 10^{-10}, what is the pH when 40 per cent of the indicator is in the yellow form? What color would this indicator have in a solution of pH 7?

21. The K_{ind} for an indicator which is a weak monoacidic base is 10^{-5}. What is the pH when the indicator is equally divided between its two colored forms?

22. What is the concentration of HCl present in solution when methyl red shows its intermediate color?

23. Repeat Problem 22, but use HAc.

24. What is the *p*H at the stoichiometric point when 50 ml of 0.1 *M* HCl is diluted to 75 ml and titrated with 0.2 *M* NaOH?

25. Repeat Problem 24, but use HAc.

26. What is the *p*H at the stoichiometric point in the titration of 5 m mol of KHP dissolved in 100 ml of water and titrated with 0.1 *M* NaOH? (Neglect anything but the first step of the hydrolysis.)

27. 0.025 mole Na_2CO_3 is dissolved in 150 ml of water and titrated with 1.0 *M* HCl using methyl red as the indicator. Find the approximate *p*H at the stoichiometric point.

28. Select an indicator for the titration of 50 ml of 0.1 *M* benzoic acid in a volume of 225 ml and titrated by 0.2 *M* KOH.

29. The acid HA has an ionization constant of 10^{-5}. If 50 ml of 0.1 *N* HA is diluted to 200 ml and titrated with 0.1 *N* NaOH:

(*a*) Find the *p*H before any base is added.

(*b*) Find the *p*H when 25 ml base has been added.

(*c*) Find the *p*H at the stoichiometric point.

(*d*) What indicator should be used?

(*e*) Draw the approximate titration curve, using the points for which the *p*H has been computed.

(*f*) Give reasons for thinking that the titration is feasible, without computing the *p*H at points near the stoichiometric point.

30. The base BOH has an ionization constant of 10^{-6}. If 50 ml 0.1 *N* BOH is titrated with 0.1 *N* HCl:

(*a*) Find the *p*H before any acid is added.

(*b*) Find the *p*H at the stoichiometric point.

(*c*) Find the *p*H when the base is two-fifths neutralized.

(*d*) Draw the approximate titration curve.

(*e*) What indicator should be used?

31. Repeat the calculations of Problem 29 for the neutralization of 50 ml 0.001 *N* HA by 0.001 *N* NaOH, assuming an initial volume of 200 ml.

32. From the data given in this chapter, plot on a large scale the titration curve for 0.1 *N* HCl and NaOH.

33. In a titration 25 ml 0.001 *N* HCl is diluted to 100 ml and titrated by 0.001 *N* NaOH. Compute the *p*H for the addition of 0, 5, 20, 24, 26, 30 ml base. Plot the results on the same sheet, and compare with the plot of Problem 32.

34. 50 ml of 0.1 *M* HX ($K_i = 10^{-7}$) is diluted to 75 ml and titrated with 0.2 *M* KOH.

(*a*) What color will the indicator methyl red exhibit when enough base has been added to neutralize half the acid present?

(*b*) Select an indicator for the titration.

(*c*) Draw the approximate titration curve, and discuss the feasibility of the titration.

35. A 0.05 *M* solution of a salt BCl has a *p*H of 4.35. What is the ionization constant of BOH?

36. It is found that 50.00 ml of a carbonate-free base is neutralized to the phenolphthalein end point by 50.00 ml of 0.1000 *N* HCl.

(*a*) What volume of HCl is needed to neutralize 50.00 ml of the base to the methyl orange end point, *p*H 3.80?

(*b*) What is the normality of the base solution when used with phenolphthalein indicator?

(*c*) What is the normality of the base solution when used with methyl orange indicator without an indicator blank, assuming an end point at *p*H 3.80?

37. An acid HA has an ionization constant of 5×10^{-6}. If 50 ml of a 0.1 *M* solution of the acid is diluted to 200 ml and titrated with 0.1 *N* NaOH:

(*a*) Compute the *p*H when 49.95 ml of base has been added.

(*b*) Compute the *p*H when 50.05 ml of base has been added.

38. (*a*) How many grams of NaAc must be added to 300 ml of 0.01 *M* HAc to produce a buffer of *p*H 6.50?

(*b*) 2.00 m mol NaOH is added to the above buffer. What is the *p*H after the addition of the base?

(*c*) What would happen to the buffer if 2.00 m mol NaOH additional were introduced?

39. 10 ml of 0.1 *M* HCl is added to 100 ml of a solution which is 0.1 *M* both in HAc and NaAc. By how many units does the *p*H change because of the HCl addition?

40. What is the *p*H of a solution which produces a slight greenish color when bromthymol blue is added as an indicator? What must be the ratio of $[Ac^-]/[HAc]$ to produce a solution of this *p*H?

41. Find the *p*H of a buffer made by dissolving 3 m mol NaCN and 5 m mol HCN in 250 ml solution.

42. What is the *p*H of a buffer which has been prepared by mixing 250 mg of NH_4Cl and 200 ml of 0.1 *M* NH_4OH solution? What is the *p*H of this after 10 m mol HCl has been added? The addition of the acid dilutes the mixture to 250 ml.

43. What is the *p*H of a buffer made by mixing 43.00 ml of 0.1000 *N* NaOH with 50.00 ml of 0.1000 *M* KHP and diluting to a volume of 100 ml?

44. Estimate the *p*H of a buffer made by adding 10 g of $NaHCO_3$ to 250 ml of a solution which is saturated with CO_2 and is 0.032 *M* in H_2CO_3.

45. Estimate the *p*H of a buffer made by mixing 50 ml of 0.1 *M* KH_2PO_4 and 25 ml of 0.1 *M* NaOH and diluting to 200 ml.

CHAPTER

10

Complex Equilibria

In the preceding chapter we have discussed the effects of ionization of weak electrolytes and of hydrolysis on acid–base titrations. A simplified treatment was used which was adequate for the mathematical formulation of the equilibria considered. This simplified treatment has, however, certain limitations when applied to complex equilibria or to very dilute solutions where the contribution of the hydrogen or hydroxide ions from water may be of significance. For example, if one computes the *p*H of a 10^{-6} *M* solution of an acid whose ionization constant is 10^{-10}, by the previously described method, there is obtained the expression,

$$\frac{[H^+][A^-]}{[HA]} = 10^{-10}$$

or, by use of the customary approximation,

$$\frac{[H^+]^2}{10^{-6}} = 10^{-10}$$

Solution of this gives

$$[H^+] = 10^{-8}$$

This is, of course, an absurd answer. The fallacy of the treatment is that we have neglected the contribution from the ionization of water, which will by itself give a hydrogen-ion concentration of 10^{-7}.

We shall in this chapter outline a general method which can be applied to any set of equilibria. The equations as set up are often too complicated for ready solution, and it is frequently necessary to make simplifying assumptions before solving them. However, when this is done, the worker is aware of what assumptions have been made, whereas in using the simpler methods of Chapter 9 he may readily lose sight of the tacit assumptions involved.

We may illustrate the general method by consideration of the hydrolysis of acetate ion from NaAc solution whose initial concentration is C. The various equilibria to be considered are:

$$\begin{matrix} & X & Y \\ H_2O = & H^+ & + OH \end{matrix}$$

$$\begin{matrix} Z & X & C-Z \\ HAc = & H^+ & + Ac^- \end{matrix}$$

The equilibrium concentrations are indicated by the algebraic symbols above the chemical formulas. The concentration of acetate ion is $C - Z$, because C is the initial concentration, and Z is the concentration of the portion that has reacted to form HAc.

Mathematically, we have

$$XY = K_w$$

$$\frac{X(C - Z)}{Z} = K_a$$

Here we have two equations involving three unknowns. To get a third relation, we equate the sum of the plus charges in solution to the sum of the negative charges, since the solution is electrically neutral.

$$\begin{matrix} C & X & C-Z & Y \\ [Na^+] + & [H^+] = & [Ac^-] + & [OH^-] \end{matrix}$$

or

$$X = Y - Z$$

To solve, we make the simplifying assumption that $C - Z = C$, or that Z is small in relation to C. The validity of the assumption is tested later by comparing the value of Z with that of C after a preliminary solution has been obtained. We now have

$$XY = K_w$$

$$CX = ZK_a$$

$$X = Y - Z$$

Eliminating Y, which is K_w/X, we have

$$CX = ZK_a$$

$$X = \frac{K_w}{X} - Z$$

Substitution of CX/K_a for Z gives

$$X = \frac{K_w}{X} - \frac{CX}{K_a}$$

Rearranging gives

$$K_a X^2 = K_a K_w - CX^2$$

Solving, we get

$$X = \sqrt{\frac{K_a K_w}{C + K_a}}$$

When $C \gg K_a$, this reduces to

$$X = \sqrt{\frac{K_a K_w}{C}}$$

This is identical with the solution obtained by the classical methods of Chapter 9. When C is of the same magnitude as K_a (in very dilute solutions), the complete equation must be used.

To check the validity of the simplifying assumptions made, we solve for Z:

$$Z = \frac{CX}{K_a} = \frac{C}{K_a}\sqrt{\frac{K_a K_w}{C + K_a}}$$

When $C \gg K_a$,

$$Z = \frac{C}{K_a}\sqrt{\frac{K_a K_w}{C}} = \sqrt{\frac{CK_w}{K_a}}$$

Since K_w/K_a is $10^{-14}/1.8 \times 10^{-5}$ or 5.5×10^{-10}, the value of Z is much smaller than that for C, and the assumption that $C - Z = C$ is justifiable.

Ionization of Weak Acid. The complete equilibria for the ionization of a weak acid HA in a solution of concentration C are:

$$\underset{C-Z}{HA} = \underset{X}{H^+} + \underset{Z}{A^-}$$

$$\underset{}{H_2O} = \underset{X}{H^+} + \underset{Y}{OH^-}$$

The mathematical relations for these equilibria are:

$$\frac{XZ}{C - Z} = K_a$$

$$XY = K_w$$

Summation of charges gives

$$\underset{X}{[H^+]} = \underset{Y}{[OH^-]} + \underset{Z}{[A^-]}$$

$$X = Y + Z$$

To solve, assume $C - Z = C$. Then,

$$XZ = CK_a$$

$$XY = K_w$$

$$X = Y + Z$$

Eliminating Y gives

$$XZ = CK_a$$

$$X = \frac{K_w}{X} + Z$$

Eliminating Z gives

$$X = \frac{K_w}{X} + \frac{CK_a}{X}$$

$$X^2 = K_w + CK_a$$

$$X = \sqrt{K_w + CK_a}$$

When $CK_a \gg K_w$,

$$X = \sqrt{CK_a}$$

This is the usual expression for the hydrogen-ion concentration in a solution of a weak acid.

In extremely dilute solutions, where C is very small, the degree of ionization becomes large and one cannot assume $C - Z = C$. For this case the complete solution is necessary to get an exact formula. An approximation can be made by assuming ionization is complete and that the total hydrogen ion is that contributed by the acid and the water.

Hydrolysis of Salt of Weak Base and Weak Acid. To illustrate, we may consider the pH of a 0.1 M solution of ammonium borate. The equilibria are:

$$\underset{}{H_2O} = \overset{X}{H^+} + \overset{Y}{OH^-}$$

$$\underset{Z}{HBO_2} = \overset{X}{H^+} + \overset{C-Z}{BO_2^-}$$

$$\underset{P}{NH_4OH} = \overset{C-P}{NH_4^+} + \overset{Y}{OH^-}$$

The mathematical relations are:

(1) $$XY = K_w$$

(2) $$\frac{X(C - Z)}{Z} = K_a$$

$$\frac{Y(C-P)}{P} = K_b \tag{3}$$

Summation of charges gives

$$\overset{C-P}{[NH_4^+]} + \overset{X}{[H^+]} = \overset{C-Z}{[BO_2^-]} + \overset{Y}{[OH^-]}$$

$$X - P = Y - Z \tag{4}$$

Here we cannot assume $C - P$ or $C - Z \sim C$, since we know that extensive hydrolysis occurs. As a first approximation, we shall assume $P = Z$. Then,

$$X(C - Z) = K_aZ \tag{5}$$

$$Y(C - Z) = K_bZ \tag{6}$$

Combining (5) and (6) gives

$$\frac{X(C-Z)}{K_a} = \frac{Y(C-Z)}{K_b}$$

or

$$\frac{X}{K_a} = \frac{Y}{K_b}$$

If we eliminate Y by (1), then,

$$\frac{X}{K_a} = \frac{K_w}{XK_b}$$

$$X^2 = \frac{K_aK_w}{K_b}$$

$$X = \sqrt{\frac{K_aK_w}{K_b}}$$

To test the validity of the assumption that $P = Z$, we substitute values for the constants K_a, K_b, and K_w and solve. Then

$$[H^+] = X = \sqrt{\frac{1.1 \times 10^{-9} \times 10^{-14}}{1.8 \times 10^{-5}}} = 7.85 \times 10^{-10}$$

From (1), we have

$$[OH^-] = 1.27 \times 10^{-5}$$

From (2), we have

$$\frac{C-Z}{Z} = \frac{1.1 \times 10^{-9}}{7.8 \times 10^{-10}} = 1.40$$

If C is taken as 0.1 M, solution for Z gives

$$Z = 0.0415$$

From (3),

$$\frac{C - P}{P} = \frac{1.8 \times 10^{-5}}{1.27 \times 10^{-5}} = 1.42$$

If $C = 0.1$, $P = 0.0412$, or $P \sim Z$.

It should be noted that pH of the solution does not depend on the concentration. A salt of a weak base and weak acid is a good buffer for the pH value determined by the relative values of K_a and K_b. When the acid is stronger than the base, the solution is acidic, and, when the base is stronger, the solution is basic. When $K_a = K_b$, the solution is neutral. A solution of ammonium acetate is therefore a neutral buffer.

Sodium Bicarbonate Solutions. One cannot use the simple hydrolysis equation discussed in Chapter 9 to compute the pH of a solution of bicarbonate ion because there occurs in such a solution two different reactions. Bicarbonate ion (1) hydrolyzes to carbonic acid and (2) ionizes to hydrogen and carbonate ions. The reactions and the concentrations present at equilibrium in a $NaHCO_3$ solution of concentration C are:

$$\underset{}{H_2O} = \overset{X}{H^+} + \overset{Y}{OH^-}$$

$$\overset{P}{H_2CO_3} = \overset{X}{H^+} + \overset{C-P-Z}{HCO_3^-}$$

$$\overset{C-P-Z}{HCO_3^-} = \overset{X}{H^+} + \overset{Z}{CO_3^=}$$

The mathematical relations are:

(1) $$XY = K_w$$

(2) $$\frac{X(C - P - Z)}{P} = K_1$$

(3) $$\frac{XZ}{C - P - Z} = K_2$$

Summation of charges gives

$$\overset{X}{[H^+]} + \overset{C}{[Na^+]} = \overset{Y}{[OH^-]} + \overset{C-P-Z}{[HCO_3^-]} + \overset{2Z}{2[CO_3^=]}$$

We note that the negative charges associated with carbonate ions are twice the molar concentration of the ion, since it is doubly charged. This gives

(4) $$X = Y - P + Z$$

As a first approximation, assume $C - P - Z = C$. Then

$$CX = PK_1 \tag{5}$$

$$XZ = CK_2 \tag{6}$$

Eliminating Y gives

$$CX = PK_1$$

$$ZX = CK_2$$

$$X - \frac{K_w}{X} = Z - P$$

Eliminating Z gives

$$CX = PK_1$$

$$X - \frac{K_w}{X} = \frac{CK_2}{X} - P$$

Eliminating P gives, $$X - \frac{K_w}{X} = \frac{CK_2}{X} - \frac{CX}{K_1}$$

Solving for X, we have

$$K_1X^2 - K_wK_1 = CK_1K_2 - CX^2$$

$$X^2(C + K_1) = CK_1K_2 + K_1K_w$$

$$X = \sqrt{\frac{CK_1K_2 + K_1K_w}{C + K_1}}$$

Since $K_1 \gg K_2 \gg K_w$ and C is usually large in comparison with K_1, this reduces to

$$X = \sqrt{K_1K_2}$$

or

$$[H^+] = \sqrt{3 \times 10^{-7} \times 7 \times 10^{-11}}$$

$$= 4.6 \times 10^{-9}$$

PROBLEMS

1. A solution contains the following ions at the stated concentrations:

$[Fe^{+++}] = 0.1\ M$ $[H^+] = 0.1\ M$ $[SO_4^{=}] = 0.2\ M$ $[Cl^-] = 0.1\ M$

From the viewpoint of the electrical neutrality of solutions must any other ions also be present?

2. How many equations would have to be set up to determine precisely the pH of a 0.1 M K_2HPO_4 solution?

3. Find the pH of a solution made by diluting one drop (0.04 ml) of 0.10 N HCl to 10 l.

4. Repeat Problem 3, but use HAc.

5. Find the pH of 0.1 M solutions of:

(*a*) $NaHSO_3$.

(*b*) KHS.

(*c*) NH_4NO_2.

6. Find the pH at the stoichiometric point in the titration of 50 ml of 0.1 M NH_4OH by 0.1 M HAc if the total volume at the end of the titration is 200 ml.

7. Repeat Problem 6, but use HCN.

8. Compute the degree of hydrolysis for 10^{-1}, 10^{-3}, 10^{-5}, 10^{-7} M solutions of sodium acetate. Construct a curve showing α as a function of pC ($-$ log concentration). The degree of hydrolysis is the ratio of the concentration of acetic acid to the original concentration of salt present.

9. Make a computation similar to that of Problem 8 for the hydrolysis of ammonium chloride and plot a curve showing α as a function of pC.

CHAPTER

11

Oxidation–reduction I. General Discussion

Analytical methods which are based on the oxidation or reduction of a constituent of the sample by an ion of a standard solution are known as oxidation–reduction or redox methods. A great variety of such methods is used in analytical chemistry, because a large number of the elements give ions that can readily be oxidized or reduced. Consequently, redox methods are used for more different types of analyses than are all other volumetric methods combined.

Definitions. *Oxidation* is an increase in positive valence due to loss of an electron from an atom, ion, or molecule. *Reduction* is the opposite process, a gain of an electron or loss of positive valence. In the reaction.

$$2\ Fe^{+++} + 2I^- = 2\ Fe^{++} + I_2$$

iodide ion is oxidized to iodine, and ferric ion is reduced to ferrous ion. The *oxidizing agent* is the electron acceptor, in this case ferric ion, and the *reducing agent* is the electron donor, the iodide ion.

Since all solutions are at all times electrically neutral, an oxidation or reduction will not occur singly; when one substance takes up electrons and is reduced, another substance furnishes the electrons and is oxidized.

Standard Solutions. Fortunately one does not need specific reagents for each individual redox reaction. With a standard solution of a strong oxidizing agent such as potassium permanganate and a solution of a reducing agent such as sodium thiosulfate, practically any oxidation or reduction analysis can be performed. The strong oxidizing agent is used for analysis of samples which contain reducing agents. Samples which contain oxidizing agents can be analyzed by treating

with an excess of potassium iodide and titrating the liberated iodine with standard thiosulfate solution.

Other reagents which are suitable for use as standard solutions are ceric sulfate, a strong oxidizing agent; potassium dichromate, a moderately strong oxidizing agent; iodine, a weak oxidizer; and arsenious

TABLE 22

A Partial List of Determinations That May Be Made by Oxidation or Reduction Methods

Substance Determined	*Standard Reagent*	*Method of Analysis*
Antimony, H_3SbO_3	I_2	Titrate in neutral solution
Arsenic, H_3AsO_3	I_2	Titrate in neutral solution
Bromine, Br_2	$Na_2S_2O_3$	Treat with KI. Titrate liberated I_2
Bromate, BrO_3^-	$Na_2S_2O_3$	Treat with KI. Titrate liberated I_2
Calcium, $CaC_2O_4 \cdot H_2O$	$KMnO_4$	Dissolve in acid. Titrate $H_2C_2O_4$
Chlorine, Cl_2	$Na_2S_2O_3$	As Br_2
Chlorate, ClO_3^-	$Na_2S_2O_3$	As BrO_3^-
Chromium, $Cr_2O_7^=$	$Na_2S_2O_3$	Treat with KI in acid solution. Titrate I_2
Copper, Cu^{++}	$Na_2S_2O_3$	Treat with KI in HAc solution. Titrate I_2
H_2S	I_2	Direct titration, acid solution
H_2O_2	$KMnO_4$	Direct titration, acid solution
Iodine, I_2	$Na_2S_2O_3$	Direct titration
Iodate, IO_3^-	$Na_2S_2O_3$	As BrO_3^-
Iron, Fe^{++}	$KMnO_4$	Direct titration, acid solution
Iron, Total	$KMnO_4$	Reduce to Fe^{++}. Titrate as above
Manganese, MnO_2	$KMnO_4$	Treat with $H_2C_2O_4$. Titrate excess
Molybdenum, MoO_3	$KMnO_4$	Reduce in Jones reductor to Mo^{+++} Titrate in acid solution
Nitrites, HNO_2	$KMnO_4$	Titrate in acid solution
Oxalates, $H_2C_2O_4$	$KMnO_4$	Titrate in acid solution
Sulfites, H_2SO_3	$KMnO_4$	Titrate in acid solution
Thiosulfate, $S_2O_3^=$	I_2	Direct titration

oxide, a reducing agent. Sometimes the oxygen salts of the halogens, such as potassium bromate, are used. Many oxidizing agents, such as HNO_3, Cl_2, Br_2, and H_2O_2, which are used in qualitative analyses, are not suitable for use as quantitative reagents because they do not give a single reaction or because a suitable end-point indicator is not available. However, the versatility of the reagents listed is so great that there is little need for other reagents—practically all redox analyses can be performed with the reagents listed.

In the following chapters the preparation, standardization, and use of the more common redox reagents are discussed. Although these exercises cannot cover all possible applications, they do illustrate the

general properties of the reagents, and the student should have no difficulty in applying the methods to other analyses.

A list of the more common determinations that are made by redox methods is given in Table 22. In studying this list, the student should classify the sample as oxidizing or reducing, to understand why the particular reagent is chosen.

In every redox analysis it is essential that all of the substance to be determined be in the proper oxidation state prior to the titration. For example, all the iron in a sample must be present as ferrous ion before the sample is titrated with permanganate or other oxidizing agent. Further, there must not be in the solution any oxidizing or reducing agent other than the ion to be determined which will react with the titrating agent. In many analyses it is necessary to oxidize or reduce the sample, prior to the titration, to insure that the sought constituent is in the proper valence state. In the iron analysis, the preliminary reduction to the ferrous state is done by treating the sample with stannous chloride or with metallic zinc. It is of course necessary to remove any excess of the reducing agent from the solution before the iron is titrated.

Indicators. In neutralization titrations, the indicator is itself an acid or base which undergoes a color change on neutralization. For a particular titration, that indicator is selected which will be neutralized at the desired *p*H to correspond with the stoichiometric point of the titration.

Similarly, there are available redox indicators which undergo a color change on oxidation or reduction. For a particular titration with an oxidizing agent the indicator should be one which is not oxidized until practically all the sample has reacted, so that the end point will coincide with the stoichiometric point. The two most widely used of such redox indicators are diphenylamine sulfonic acid and orthophenanthroline. Diphenylamine sulfonic acid is the more readily oxidized of the two, and it is used with the weaker oxidizing reagents. Orthophenanthroline is used with the strong oxidizers such as potassium permanganate and ceric sulfate. The theory of the use of redox indicators is discussed in a later chapter.

Besides the general redox indicators, there are a number of specific ones, suitable for a particular reagent. These indicators were in use for many years before the general redox indicators had been developed, and many of them are still standard. The more common of these are:

1. Potassium permanganate. Permanganate ion is so highly colored that, when it is used as oxidizing agent, the stoichiometric point is recognized by the color imparted by a slight excess of the reagent. A

somewhat more sensitive end point can be obtained by use of orthophenanthroline, but this is not necessary except when very dilute permanganate solutions are used. One drop of 0.1 N $KMnO_4$ will impart a distinct pink tinge to several hundred milliliters of solution.

2. Starch has for many years been the standard indicator for the presence of free iodine; the deep blue color developed by iodine and starch is familiar to all. This indicator is reversible; that is, the color will appear with excess iodine and disappear with excess of reducing agent which removes the iodine.

3. Potentiometric methods are wisely used to detect redox end points, as discussed in Chapter 24. An electric cell is set up in such a manner that the voltage depends on the concentration of the ion which is being titrated; measurement of the voltage shows when the point is reached at which the reaction is complete. In the course of the titration, the voltage changes in the same manner as the pH curves of Chapter 9 change with volume of reagent added.

4. Spot-test indicators. When no internal indicator is available, it is sometimes possible to employ a spot-test indicator. At intervals during the titration, drops of solution are withdrawn and tested for the presence of a constituent of the reaction. The end point is indicated when a drop shows an abrupt change from the previously withdrawn drop. An example is the use of potassium ferricyanide as indicator for ferrous ion. Prior to the stoichiometric point, a drop of the solution gives the blue color typical of ferrous ferricyanide, but, when the end point is reached, the color no longer appears, since ferrous ion has been used up. Spot-test titrations are tedious and are not employed whenever other indicators are available.

Completeness of Oxidation Reactions. All oxidations are under proper conditions reversible. For example, the reaction,

$$Fe^{++} = Fe^{+++} + \text{electron}$$

may go in either direction, depending on the presence of other substances which will furnish or take up electrons. With permanganate ion ferrous ion is a reducing agent, but with iodide ion ferric ion is an oxidizing agent. In general, if there are in a solution two ions which can change in valence, the one with the greater tendency to take up electrons will do so at the expense of the other.

The elements and their ions can be arranged in a table which shows the relative tendencies to give up electrons. The student is already familiar with a simplified arrangement of this type, the electrochemical series of the metals. It may be recalled that the metals in this series are so arranged that each one will displace from solution those metals

which lie below it. For example, iron will react with cupric ion to give ferrous ion and metallic copper, or cupric ion will oxidize iron to ferrous ion.

A more comprehensive form of the electrochemical series is shown in Table 25 on page 270. It includes not only metals, in the order in which they will displace one another from solution, but also ions and molecules that may exist in more than one valence state, and non-metals such as the halogens. As arranged in the table, the reducing agents are at the top and the oxidizing agents at the bottom. Any substance will tend to oxidize all substances above it in the table, provided they are present at the same concentration.

In Table 25 numerical values are given for every half reaction. These values are known as the oxidation potentials of the atoms or ions. The meaning and use of these potentials is discussed in Chapter 15. For the present it is sufficient to state that the potentials provide a quantitative measure of the tendency of a material to give up an electron, with reference to an arbitrarily chosen standard of reference. When the potential is given a positive sign, the substance is a stronger reducing agent than the reference material (hydrogen), and, when the potential has a negative sign, the substance is a stronger oxidizing agent than the reference (hydrogen ion). When two substances are brought together, the one with the lower potential will tend to oxidize the other, if they are at the same concentrations. Thus for the ferrous–ferric and iodide–iodine systems the potentials are:

$$Fe^{++} = Fe^{+++} + e \qquad E^0 = -0.77$$

$$2I^- = I_2 + 2e \qquad E^0 = -0.53$$

The tendency of ferric ion to take up an electron is greater than that of iodine, and consequently ferric ion will oxidize iodide ion.

An important consideration in oxidation–reduction reactions is the degree of completeness attained. Actually, since all oxidations are reversible, no reaction ever goes entirely to completion. Practically, however, a reaction can be said to be complete when the amount of original substance which has not reacted is below the limits of sensitivity of the measuring instruments used. Oxidation of ferrous ion can be said to be complete when the unoxidized portion does not exceed 0.1 mg ferrous ion, since the analytical balance will not detect amounts below 0.1 mg.

A consideration of the quantitative relations governing the completeness of redox reactions is given in Chapter 15. There it is shown how to compute from the oxidation potentials the equilibrium constant

for oxidation–reduction reactions. Pending this discussion, we can speak only qualitatively of the completeness of redox reactions. Qualitatively it can be said that, when two reactants lie far apart in the oxidation potential table, their reaction will be essentially complete, and, when two substances have potentials of nearly the same value, their reaction will not be complete. Permanganate ion is a strong oxidizer, as shown by the potential:

$$4H_2O + Mn^{++} = MnO_4^- + 8H^+ + 5e \qquad E^0 = -1.52$$

In acid solution permanganate will oxidize ferrous ion so completely that, when there is an excess of one drop 0.1 N permanganate solution, the remaining ferrous ion is negligibly small—this reaction goes essentially to completion. On the other hand, ferric ion will not oxidize iodide ion in the same quantitative manner—when stoichiometric amounts of the two are brought together, the reaction is far from complete. Here the differences in the potentials are small. This reaction can be made complete only by adding a large excess of one or the other of the reactants.

STOICHIOMETRY

The stoichiometric computations of oxidation–reduction analyses are essentially the same as for neutralization reactions. The basic rule is that the equivalents or milliequivalents of oxidizing constituent must equal the equivalents or milliequivalents of reducing constituent. In acidimetry–alkalimetry the equivalent weight was defined in terms of the number of gram-atomic weights of hydrogen ion involved per mole of substance in the titration reaction since the exchange of H^+ is common to virtually all neutralization processes. The equivalent weight of an oxidizer or reducer is defined in terms of the number of electrons gained or lost in the reaction; that amount of any oxidizer which gains one electron is always equivalent to that of reducer which loses one electron. The definition we shall use is:

$$\text{Equivalent weight} = \frac{\text{molecular weight}}{\left\{\begin{array}{c}\text{number of electrons gained or lost as deter-} \\ \text{mined from the reaction of titration}\end{array}\right\}}$$

Since the oxidation of a hydrogen atom or the reduction of a hydrogen ion requires one electron, it can be seen that there is a fundamental relation between the foregoing definition and the use of the element hydrogen as the basis for equivalent weight systems.

The volumetric determination of iron involves the reaction,

$$Fe^{++} = Fe^{+++} + e$$

and the equivalent weight of iron is the same as its atomic weight, 55.85. If we want to evaluate the equivalent weight of Fe_3O_4 as related to the determination of iron by the same process, we note that each molecule of Fe_3O_4 is capable of furnishing 3 molecules of Fe^{++} in a

TABLE 23

EQUIVALENT WEIGHTS OF SOME OXIDIZING AND REDUCING SUBSTANCES

Substance	*Essential Change in Titration Reaction*	*Electron Gain or Loss Per Mole of Substance*	*Equivalent Weight*	*Normality of a 0.1 M Solution*
$K_2Cr_2O_7$	$Cr_2O_7^{=} \rightarrow 2Cr^{+++}$	6	$\frac{294.21}{6}$	0.6
H_2S	$H_2S \rightarrow S$	2	$\frac{34.08}{2}$	0.2
$Na_2S_2O_3 \cdot 5H_2O$	$2S_2O_3^{=} \rightarrow S_4O_6^{=}$	1	$\frac{248.21}{1}$	0.1
As_2O_3	$H_2AsO_3^{-} \rightarrow H_2AsO_4^{-}$	4	$\frac{197.82}{4}$	Insoluble in water; but 0.1 mole As_2O_3 dissolved in NaOH and diluted to 1 l. would prepare a 0.4 *N* $NaAsO_2$ solution

chemical process which would dissolve Fe_3O_4 and reduce all the iron to the ferrous state. Each of the three molecules of Fe^{++} would lose one electron in the reaction of titration or a total of three electrons for all the iron furnished by one molecule of Fe_3O_4. The equivalent weight of Fe_3O_4 under these circumstances is 231.55/3.

As is the case, for example, with H_3PO_4 in neutralization reactions (see page 110), the same oxidizing or reducing agent has different equivalent weights for various titration conditions. When $KMnO_4$ is used in acid solution, the change is from MnO_4^{-} to Mn^{++} which involves 5 electrons per molecule of $KMnO_4$, and the equivalent weight is 158.03/5. Used in basic solution the reaction involves the reduction of MnO_4^{-} to MnO_2, a change of 3 electrons per molecule of $KMnO_4$, and the equivalent weight is 158.03/3.

Table 23 will serve to illustrate further the foregoing definitions.

Balancing Equations. Before the stoichiometric computations can be made for an oxidation reaction, it is necessary to write the chemical equation, to know the number of electrons involved per molecule of each reactant. Methods for writing such equations have been studied in general chemistry; they need only be reviewed here.

TABLE 24

A Partial List of Oxidizing and Reducing Agents

	Products	*Remarks*
Oxidizing Agents		
$MnO_4^- + H^+$	$Mn^{++} + H_2O$	Acid solution
$Cr_2O_7^= + H^+$	$Cr^{+++} + H_2O$	Acid solution
Ce^{++++}	Ce^{+++}	Acid solution
$ClO_3^- + H^+$	$Cl^- + H_2O$	Acid solution
$BrO_3^- + H^+$	$Br^- + H_2O$	Acid solution
$IO_3^- + H^+$	$I^- + H_2O$	Acid solution
$NO_3^- + H^+$	$NO + H_2O$	Many side reactions
Cl_2	Cl^-	
$MnO_2 + H^+$	$Mn^{++} + H_2O$	Acid solution
$H_2O_2 + H^+$	H_2O	Acid solution
Reducing Agents		
$HNO_2 + H_2O$	$NO_3^- + H^+$	
I^-	I_2	
H_2O_2	$O_2 + H^+$	
$H_2C_2O_4$	$CO_2 + H^+$	
H_2S	$S + H^+$	
$H_2SO_3 + H_2O$	$SO_4^= + H^+$	
$S_2O_3^=$	$S_4O_6^=$	When oxidized by I_2
Sn^{++}	Sn^{++++}	
Metals	Metal ion	
Fe^{++}	Fe^{+++}	
$H_3AsO_3(As_2O_3) + H_2O$	$H_3AsO_4 + H^+$	

The first step in balancing an equation is to write down the starting materials and the reaction products. The student is expected to know these, just as he knows the valences of the common elements. A brief list of the more common oxidizing and reducing agents is given in Table 24, which should be memorized if not already known.

We may take as example the oxidation of oxalic acid by potassium permanganate in acid solution. As in previous sections, only the essential ions are shown in the equation, and ions which are present but do not participate in the reaction are omitted. The starting materials and reaction products are

$$MnO_4^- + H^+ + H_2C_2O_4 = CO_2 + H_2O + Mn^{++}$$

Next we indicate the electron changes. Obviously the Mn and C atoms are the ones involved. To compute the electron changes, we first compute the valence number (oxidation state) or average valence of each atom before and after reaction. In this computation the H atom is assigned a valence number of +1 and the O atom a number of −2 (except in peroxides, where O has a valence of −1). In the MnO_4^- ion there are 4 × 2 negative valences. Since the over-all charge is −1, the Mn atom must have a valence number of +7. After reaction, the charge of the Mn atom is +2. Therefore the MnO_4^- ion must take up 5 electrons. This is indicated in the equation by an upward arrow.

In $H_2C_2O_4$ the average valence of the C atom is +3 since the molecule contains 4 × 2 negative valences for the oxygen atoms and 2 × 1 positive valences for the hydrogen atoms. Hence the two carbon atoms contribute +6 charges, or +3 for each one. After reaction the valence of carbon in CO_2 is +4. Each carbon atom gives up 1 electron, or the molecule gives 2 electrons. This is indicated by a downward arrow in the unbalanced equation, which now becomes

$$\overset{+7}{MnO_4^-} + H^+ + \overset{+3}{H_2C_2O_4} = \overset{+4}{CO_2} + H_2O + \overset{+2}{Mn^{++}}$$

$$\uparrow 5e \qquad \downarrow 2e$$

Next the electrons are balanced. It requires 2 MnO_4^- and 5 $H_2C_2O_4$ molecules for this, giving a total of 10 electrons used and 10 electrons furnished. The partial equation now reads

$$2MnO_4^- + H^+ + 5H_2C_2O_4 = CO_2 + H_2O + Mn^{++}$$

We now proceed to balance the other atoms in the usual manner. The 2 MnO_4^- ions yield 2 Mn^{++} ions, and the 5 $H_2C_2O_4$ molecules yield 10 CO_2 molecules.

$$2MnO_4^- + H^+ + 5H_2C_2O_4 = 10CO_2 + H_2O + 2Mn^{++}$$

To complete, we balance the oxygen atoms and finally the hydrogen atoms. On the left there are 28 oxygen atoms, and on the right only 20. The remaining 8 oxygen atoms appear as water. This requires 16 hydrogen atoms. On the left there are 10, in the 5 molecules of $H_2C_2O_2$. An additional $6H^+$ is needed. Writing in these numbers gives the completed equation:

$$2MnO_4^- + 6H^+ + 5H_2C_2O_4 = 10CO_2 + 8H_2O + 2Mn^{++}$$

As the last step we check the accuracy of the work by summing up the electric charges on each side. On the left there are 2 negative and

6 positive or a sum of +4 charges. On the right there are $2 \times +2$ or +4 charges, which balances.

For comparison we may write the same equation in the molecular form, including all atoms which are present in the solution. If potassium permanganate, sulfuric acid, and oxalic acid had been used, the equation is

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 = 10CO_2 + 8H_2O + 2MnSO_4 + K_2SO_4$$

or

$$2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 = 10CO_2 + 8H_2O + 2MnSO_4 + K_2SO_4 + 5Na_2SO_4$$

if sodium oxalate had been used instead of oxalic acid. Comparison of these with the ionic form previously given shows the greater simplicity of the ionic form.

As another illustration, we may write the equation for the reaction of nitric acid with copper to yield NO.

$$H^+ + \overset{+5}{NO_3^-} + Cu^0 = Cu^{++} + \overset{+2}{NO} + H_2O$$

$\uparrow 3e$ $\downarrow 2e$

Balancing electrons gives

$$H^+ + 2NO_3^- + 3Cu = 3Cu^{++} + 2NO + H_2O$$

Now balancing the H and O atoms gives

$$8H^+ + 2NO_3^- + 3Cu = 3Cu^{++} + 2NO + 4H_2O$$

The same equation in the molecular form is

$$8HNO_3 + 3Cu = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

The equation for oxidation of H_2O_2 by permanganate in acid solution is sometimes confusing. Here the valence number of the oxygen is minus 1, and the reaction product is O_2, with valence number of zero. Therefore each molecule of H_2O_2 loses 2 electrons. The balanced equation is

$$2MnO_4^- + 6H^+ + 5H_2O_2 = 2Mn^{++} + 5O_2 + 8H_2O$$

$\uparrow 5e$ $\downarrow 2e$

It should be emphasized that the valence number represents only the *average* valence; it may or may not be the actual valence. Thus in Fe_3O_4 the valence number of Fe is $2\frac{2}{3}$. In $S_4O_6^=$ the valence number of S is $2\frac{1}{2}$.

Typical Calculations

Problem. Concentration of Solutions. What weight of pure potassium dichromate is needed for the preparation of 500 ml 0.1000 *N* solution?

Solution: When potassium dichromate is used as an oxidizing agent, the change of valence is 6 units per molecule, or 6 electrons are gained per molecule. The equivalent weight is, therefore,

$$\frac{K_2Cr_2O_7}{6} = \frac{294.22}{6} = 49.04 \text{ g}$$

The milliequivalent weight is 49.04 mg. In 500 ml 0.1000 *N* solution the total number of milliequivalents is

$$500 \times 0.1000 = 50.00 \text{ m e}$$

Since the weight of 1 m e is 49.04 mg, the total weight in milligrams is given by the product,

$$50.00 \times 49.04 = 2452 \text{ mg or } 2.452 \text{ g}$$

Problem. Standardization of Solution. A solution of permanganate is standardized by comparison with sodium oxalate. From the following data calculate the normality of the permanganate.

Volume of permanganate	= 40.41 ml
Weight sodium oxalate	= 0.2538 g
Purity of oxalate	= 99.60%

Solution: The reaction proceeds according to the equation given above. Although the standard is weighed as sodium oxalate, it reacts like an equivalent weight of oxalic acid, since, when it is put into acid solution, oxalic acid is formed.

Weight pure sodium oxalate = 0.2538×0.996 = 0.2528 g
= 252.8 mg
Weight of 1 m e sodium oxalate = 134.0/2 = 67.0
Milliequivalents of sodium oxalate = 252.8/67.0 = 3.773
Normality of permanganate = milliequivalents per milliliter = 3.773/40.41
= 0.0934

Problem. Analysis of Sample. A sample which contains iron is dissolved, all the iron is reduced to the ferrous condition, and the resulting solution is titrated with standard permanganate solution. From the following data calculate the percentage of iron, as ferric oxide, in the sample.

Weight of sample	= 1.097 g
Volume of permanganate solution	= 37.63 ml
Normality of permanganate solution	= 0.1050

Solution: The equation for the reaction is

$$MnO_4^- + 8H^+ + 5Fe^{++} = Mn^{++} + 4H_2O + 5Fe^{+++}$$

Milliequivalents iron = milliequivalents permanganate = $37.63 \times 0.1050 = 3.951$

Each atom of iron changes valence by one unit in titration; there are two atoms per molecule. Therefore, the milliequivalent weight of ferric oxide is given by the equation:

$$\text{Milliequivalent weight of ferric oxide} = \frac{Fe_2O_3}{2} = 79.84 \text{ mg}$$

$$\text{Weight ferric oxide} = 3.951 \times 79.84 \text{ mg} = 315.4 \text{ mg} = 0.3154 \text{ g}$$

$$\text{Percentage ferric oxide} = \frac{0.3154}{1.097} \times 100 = 28.75\%$$

This type of problem is often confusing, when encountered for the first time. Although iron as ferric oxide cannot be titrated by an oxidizing agent, since the iron is already in an oxidized condition, we have expressed the equivalent weight in terms of ferric oxide. An alternative method of solving would be to compute the weight of iron titrated by the given volume of permanganate solution, and from the weight of iron to compute the weight of ferric oxide. Such a solution is unnecessarily long. Since each atom of iron present in the form of ferric oxide gives an atom of ferrous ion when the sample is prepared for analysis, it is obvious that a mole of ferric oxide will give two equivalents of ferrous ion. Therefore the most direct method for the solution of the problem is to compute the weight of ferric oxide from the number of milliequivalents, as was done previously.

Problem. Indirect Oxidation Titration. A solution of permanganate is 0.1000 *N*; 40.00 ml of this solution is added to an acidified solution which contains excess potassium iodide. The iodine liberated is titrated by 35.00 ml sodium thiosulfate solution. What is the normality of the latter?

Solution: The reactions involved are:

$$2MnO_4^- + 16H^+ + 10I^- = 2Mn^{++} + 5I_2 + 8H_2O$$
$$I_2 + 2S_2O_3^{=} = S_4O_6^{=} + 2I^-$$

milliequivalents $KMnO_4 = 40.00 \times 0.1000 = 4.000$
= milliequivalents I_2 liberated
= milliequivalents $Na_2S_2O_3$

Therefore, milliequivalents $Na_2S_2O_3$ = milliequivalents $KMnO_4$
= 4.000

N of $Na_2S_2O_3 = 4.000/35.00 = 0.1143$

Problem. Oxidation Equivalence *vs.* Acidimetric Equivalence. A solution of potassium acid oxalate, KHC_2O_4, is found to be 0.1200 *N* when standardized by titration with sodium hydroxide, phenolphthalein being the indicator. If 42.15 ml of this solution require 38.26 ml potassium permanganate solution for titration, what is the normality of the permanganate?

Solution: In the acidimetric reaction, the equivalent weight of KHC_2O_4 is the molecular weight, since there is only one hydrogen atom per molecule. As a reducing agent, the equivalent weight of KHC_2O_4 is one-half the molecular weight, since the change in valence number is two electrons per molecule. Accordingly, the normality as a reducing agent is *twice* the normality as an acid.

$$\text{Normality of the } KMnO_4 = 0.1200 \times 2 \times \frac{42.15}{38\ 26} = 0.2644$$

QUESTIONS

1. Define the following terms: oxidation, reduction, reducing agent, oxidizing agent, valence, valence number.
2. List examples of atoms for which the valence number is not the actual valence of an atom.
3. Complete and balance the following:

$$MnO_4^- + H_2O_2 + H^+ =$$
$$Cr_2O_7^= + H_2S + H^+ =$$
$$Ce^{++++} + H_2C_2O_4 =$$
$$BrO_3^- + I^- + H^+ =$$
$$MnO_4^- + H_2SO_3 =$$
$$ClO_3^- + Sn^{++} + H^+ =$$
$$IO_3^- + HNO_2 =$$
$$Ag + NO_3^- + H^+ =$$
$$BrO_3^- + H_3AsO_3 =$$
$$Cr_2O_7^= + Fe^{++} + H^+ =$$
$$S_2O_3^= + I_2 =$$
$$H_2O_2 + Sn^{++} + H^+ =$$
$$MnO_4^- + HNO_2 + H^+ =$$
$$Cr_2O_7^= + I^- + H^+ =$$
$$I_2 + H_2S =$$
$$VO_3^- + Fe^{++} + H^+ = VO^{++} +$$

4. When is a reversible reaction said to be quantitative?
5. Why is nitric acid not a suitable oxidizing agent for volumetric determinations?
6. Give an example of an oxidation–reduction determination using each of the types of indicators discussed in this chapter.
7. Tell how ferric ion may be quantitatively reduced by iodide ion although the reaction is not suitable for direct titration of iodide ion by ferric ion. Explain.

PROBLEMS

1. Arrange in tabular form (*a*) the molecular weight, (*b*) the equivalent weight, and (*c*) the milligrams per milliliter of 0.1250 *N* solution for the following substances: $KMnO_4$ (used in acid solution), $K_2Cr_2O_7$, $Na_2S_2O_3 \cdot 5H_2O$, H_2SO_3, SO_2, HNO_2 (as a reducing agent), $Ce(SO_4)_2$, $Na_2C_2O_4$.
2. What is the equivalent weight of each of the following metallic oxides? The reactions by which the determinations are made are given in parentheses in unbalanced form.

As_2O_3 ($H_2AsO_3^- + I_2 + H_2O = H_2AsO_4^- + I^- + H^+$)
Fe_3O_4 ($Fe^{++} + Ce^{++++} = Fe^{+++} + Ce^{+++}$)
Cu_2O ($Cu^{++} + I^- = CuI + I_2$)
V_2O_5 ($VO^{++} + MnO_4^- + H_2O = VO_3^- + Mn^{++} + H^+$)
Mo_2O_3 ($Mo^{+++} + MnO_4^- + H_2O = MoO_4^= + Mn^{++} + H^+$)

3. (*a*) How many milligrams of $K_2Cr_2O_7$ are present in 400.0 ml of 0.1037 *N* solution? What is the molarity of the solution?

(*b*) How many grams of $Na_2S_2O_3 \cdot 5H_2O$ need to be dissolved in 650 ml to prepare a 0.200 *N* solution?

4. How much of substance *B* will react with the stated amount of substance *A*?

A	*B*
(*a*) 50.00 ml of 0.1200 *N* H_2S	____ ml of 0.01200 *M* $K_2Cr_2O_7$
(*b*) 25.00 ml of 0.0400 *M* $KMnO_4$	____ mg Fe_3O_4
(*c*) 30.00 ml 0.01000 *M* H_2S	____ ml 0.05000 *N* $KMnO_4$
(*d*) 55.85 mg Fe	____ ml 0.02000 *N* Ce^{++++}
(*e*) 25.00 ml of 0.1000 *N* I_2	____ mg As_2O_3
(*f*) 35.00 ml of 0.1200 *N* $KMnO_4$	____ g H_2O_2
(*g*) 3.000 m mol KHC_2O_4	____ ml 0.2000 *N* KOH
	____ ml 0.1000 *N* $KMnO_4$
(*h*) 0.2000 g CaC_2O_4	____ ml 0.1500 *N* $KMnO_4$

5. What is the Fe_2O_3 titer of 0.1125 *N* $Ce(HSO_4)_4$ solution?

6. How many milliliters of a solution of 25.00 g of $KMnO_4$ per liter will react with 3.400 g of $FeSO_4 \cdot 7H_2O$?

7. What is the iron titer of a solution made by dissolving 5.017 g $K_2Cr_2O_7$ in 1.750 l.?

8. How many grams of As_2O_3 must be dissolved in concentrated NaOH to produce 500.0 ml of a solution which is 0.05000 *N* in $NaAsO_2$?

9. From the following data compute the normalities and molarities of the permanganate and ferrous solutions:

Weight of $Na_2C_2O_4$	0.2000 g
Volume of $KMnO_4$	42.00 ml
Volume of $FeSO_4$	5.00 ml
30.00 ml $KMnO_4$	= 35.00 ml $FeSO_4$

10. What is the percentage of iron in an ore sample which weighs 0.5250 g and which requires 40.00 ml of 0.1193 *N* ceric sulfate solution for titration?

11. How many milliliters of 0.0973 *N* $K_2Cr_2O_7$ solution are needed to titrate a 0.3563-g sample of an iron ore which is 78.33 per cent Fe_2O_3?

12. How many milliliters of 0.1000 *M* $KMnO_4$ are equivalent in oxidizing power to 50.00 ml of 0.1200 *M* $K_2Cr_2O_7$ solution? Both reagents are to be used in acid solution.

13. 40.00 ml of 0.1000 *N* $KMnO_4$ is equivalent to 35.00 ml of KHC_2O_4 solution; how many milliliters of 0.1000 *N* KOH are needed to titrate 50.00 ml of the KHC_2O_4 solution?

14. 20.00 ml of $KHC_2O_4 \cdot H_2C_2O_4$ solution reacts with 30.00 ml of 0.2000 *N* NaOH solution. How many milliliters of 0.1000 *N* ceric sulfate solution will react with 40.00 ml of the oxalate solution?

15. What is the molarity of a $KMnO_4$ solution if 25.00 ml of it react with 50.00 ml of a 0.1250 *M* KHC_2O_4 solution?

16. From the following calculate the normality of the permanganate and thiosulfate solutions:

25.00 ml of HCl = 0.5465 g AgCl
24.36 ml HCl = 27.22 ml NaOH
24.62 ml NaOH = 30.17 ml KHC_2O_4
41.54 ml KHC_2O_4 = 37.82 ml $KMnO_4$
40.00 ml of the $KMnO_4$ is added to 100 ml of a molar KI solution, and the liberated I_2 requires 35.17 ml of $Na_2S_2O_3$

Additional problems on redox stoichiometry are at the ends of Chapters 12, 13, and 14.

CHAPTER

12

Oxidation–reduction II. Potassium Permanganate

Potassium permanganate has for over a hundred years been the most widely used oxidizing agent in analytical chemistry. Today it is to some extent replaced by other agents, but it is still one of the most important reagents. Several reasons have led to this widespread use of permanganate. It is readily available and low in cost. Used in acid solution, it has a high oxidation potential, about 1.5 volts, and will quantitatively oxidize most reducing agents when added in stoichiometric amounts. It requires no indicator, since the MnO_4^- ion is so highly colored that it acts as its own indicator. Prior to the recent development of oxidation indicators, the color was perhaps the chief reason for use of permanganate in preference to other strong oxidizing agents such as chlorates, bromates, and dichromates—until fairly recently there were no satisfactory indicators for these other agents, and it was necessary to use spot-test end points.

Permanganate has some disadvantages. Solutions must be prepared free of reducing agents, or else a precipitate of MnO_2 will be formed in the solution. If this occurs, the precipitated MnO_2 acts as a catalyst for autodecomposition of the solution, and the strength will vary with time. Acid solutions of permanganate are not stable; the analytical reagent is a neutral solution which can be kept without decomposition if properly prepared. Light appears to facilitate decomposition, and solutions for permanent use should be stored in dark bottles. In many of the reactions with reducing agents, care must be taken to avoid side reactions.

Because of these disadvantages, there has been recently, since the discovery of good redox indicators, a trend towards the use of other

oxidizing agents in applications where permanganate was formerly employed. Chief among the newer reagents is ceric sulfate which is more stable than permanganate and less likely to have side reactions.

Permanganate is used in acid, neutral, or basic solutions. In acid media, the reaction is a reduction to Mn^{++}. In neutral or basic solutions, reduction proceeds only to the tetravalent state because MnO_2 precipitates. In presence of barium ion in neutral solutions, reduction is only to a hexavalent state, at which $BaMnO_4$ precipitates. This reaction has been used for the determination of cyanides, alcohols, aldehydes, glycol, and sugars, whose quantitative oxidation in acid solution is difficult.[1]

PREPARATION AND STANDARDIZATION OF SOLUTIONS

Permanganate solutions are ordinarily used at a concentration of about 0.1 *N* (0.02 *M*), but solutions as dilute as 0.01 *N* are employed on occasion. When the very dilute solutions are used, it is advisable to employ an indicator such as orthophenanthroline since the permanganate color no longer provides a sensitive end point.

Procedure. Preparation of 0.1 *N* Permanganate Solution. Weigh on a watch glass approximately 3.2 g (note 1) reagent-grade potassium permanganate crystals. Dissolve in 1 l. of distilled water, and heat in a covered beaker for 2 hours (note 2) on a steam bath. Allow the covered beaker to stand overnight in the desk, filter (note 3) through an asbestos mat (notes 4, 5), and store in a clean glass-stoppered bottle. Keep in the dark except when in use. Subsequent decomposition of the solution can be recognized by the appearance of a brown coating on the walls and bottom of the bottle.

Notes. 1. The equivalent weight is 158.03/5, or 31.61 g.

2. Distilled water contains organic matter which will reduce permanganate. The solution is heated in order to hasten the oxidation of this material and to coagulate the precipitate of manganese dioxide which forms as a reduction product. In neutral solution the reaction is

$$MnO_4^- + \text{reducing agent} = MnO_2 + \text{oxidation product}$$

3. All particles of manganese dioxide should be removed since these particles catalyze further decomposition of the solution.

4. Filter paper should not be used, since particles of the paper suspended in the solution would lead to further reduction.

5. Prepare the asbestos mat in a Gooch crucible according to directions on page 73. Reject the first 50-ml portion of filtrate.

[1] R. E. Oesper, *Newer Methods of Volumetric Analysis*, D. Van Nostrand, 1938.

Standards

The most readily available standards for permanganate are sodium oxalate, arsenious oxide, iron wire, and oxalic acid. Both sodium oxalate and arsenious oxide are sold and recommended by the Bureau of Standards. Arsenious oxide is particularly advantageous, because it also serves as primary standard for iodine solutions. Iron wire prepared for use as a primary standard is excellent, but ordinary iron should not be used since it contains an unknown amount of carbon in the form of carbides, which will react with permanganate. Oxalic acid crystals are not recommended because they contain water of hydration and tend to decompose on drying. Oxalic acid solutions previously standardized by acidimetric methods are a convenient and reliable standard; their use permits an interrelation of the oxidation and acidimetric solutions of a laboratory.

Standardization

Arsenious Oxide. Analyzed grade As_2O_3 with an assay value of 99.97 per cent is commercially available. The authors recommend this primary standard because the titrations are easy to perform and high precision and accuracy are obtained.[2] Student results with it have been considerably better than those with sodium oxalate standardization.

The weighed sample of arsenious oxide is dissolved in sodium hydroxide solution. This solution is acidified with hydrochloric acid, and the acid solution of arsenious acid is titrated with permanganate. Permanganate oxidizes arsenious acid slowly if no catalyst is used, but addition of a trace of iodide or iodate ion causes the reaction to proceed rapidly, and each drop of permanganate is quickly decolorized. This type of catalysis is frequently encountered in oxidation reactions. Apparently the electron transfer between permanganate ion and arsenious acid does not occur readily, and the iodide acts as a carrier. Possibly the mechanism is that permanganate oxidizes iodide ion to iodine which then reacts rapidly with arsenious acid and is reduced to iodide ion, which in turn is reoxidized by permanganate. The titration of arsenious acid can be made in the presence of moderate amounts of HCl without oxidation of chloride ion. The reactions are:

$$As_2O_3 + 2OH^- + H_2O = 2H_2AsO_3^-$$

$$H_2AsO_3^- + H^+ = H_3AsO_3$$

$$2MnO_4^- + 5H_3AsO_3 + 6H^+ = 2Mn^{++} + 5H_3AsO_4 + 3H_2O$$

[2] H. A. Bright, *Ind. Eng. Chem. Anal. Ed.*, **9**, 577 (1937).

Procedure. Dissolve 20 g reagent-grade NaOH pellets in 80 ml water, and cool to room temperature. Weigh out to the closest 0.1 mg three 0.2-g portions (note 1) of dried arsenious oxide of known purity into 250-ml wide-mouth Erlenmeyer flasks. Add 10 ml of the cooled sodium hydroxide solution, and allow to stand 8–10 minutes with occasional swirling, or until the sample is all dissolved. Dilute to 100 ml, and add 10 ml concentrated hydrochloric acid and 1 drop 0.002 *M* potassium iodide or iodate solution (note 2). Titrate with permanganate solution until a faint pink color persists for 30 seconds or more (note 3). Run a blank determination (note 4). From the net volume of permanganate, corrected for buret calibrations and the blank, and from the weight and purity of the standard, compute the normality of the permanganate. The average deviation should not exceed $\frac{1}{1000}$.

Notes. 1. The equivalent weight is $As_2O_3/4$ or 49.45 g.

2. Prepare the solution by dissolving about 0.3 g potassium iodide or iodate in 1 l. distilled water. The exact amount of catalyst used is not important provided care is taken not to add enough to react with a detectable volume of the permanganate. It is immaterial whether iodide or iodate is used. If iodate is used, it is immediately reduced to iodide by the arsenious acid.

3. A more sensitive end point can be obtained by use of ferrous orthophenanthroline indicator, but for ordinary work this is not necessary. One drop of 0.025 *M* indicator solution should be used. It is added when it appears that the end point is near, as shown by the slowness with which each drop of permanganate is decolorized. The indicator gives a color change from pink to a very faint blue.

4. A blank is necessary to insure that the NaOH is free of reducing agents. Carry out the determination just as in the standardization except that no As_2O_3 is present. The first drop of permanganate should impart a detectable color.

Errors. Guard against the usual volumetric errors (page 94). Insufficient acidity will cause error, but, if instructions are followed, the solution should contain excess acid at a concentration of about 0.5 *N*.

Iron Wire. An analyzed grade wire, labeled "for standardization," should be used.

Procedure. Obtain a spool of analyzed wire from the instructor. It should be bright and free of rust. Weigh out to the closest 0.1 mg three portions of about 0.2 g (note 1), and place in small beakers (note 2). Add 10 ml concentrated HCl and 10 ml water, and heat on the steam bath until all the iron is dissolved. A slight residue of carbon may be disregarded.

Follow the procedure on page 221, beginning at the star and continuing to the double star.

From the volume of permanganate, corrected for the blank and for buret calibrations, and from the weight and purity of the iron, compute the normality of the permanganate. The average deviation should not exceed $\frac{2}{1000}$.

Notes. 1. Since the valence change of iron is one, from +2 to +3, the equivalent weight is 55.85 g.

2. The sample is originally placed in a beaker instead of the final titration flask, because it should be evaporated to small volume prior to reduction with stannous chloride. Evaporations cannot be done efficiently from Erlenmeyer flasks.

Errors. Aside from purity of standard and the usual volumetric errors, the errors of this method are those of the Zimmermann–Reinhardt procedure. Read the discussion on page 220.

Sodium Oxalate. For many years sodium oxalate was the almost universally used primary standard for permanganate solutions. It is readily available in high purity, is stable on drying, and is non-hygroscopic. It has, however, the disadvantage that titration must be made at elevated temperature and that, unless precautions are taken, side reactions may occur. Student results with sodium oxalate show considerably greater deviations than when arsenious oxide is used.

The over-all reaction of permanganate with sodium oxalate in acid solution is given by the equations:

$$2Na^+ + C_2O_4^= + 2H^+ = H_2C_2O_4 + 2Na^+$$

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ = 2Mn^{++} + 10CO_2 + 8H_2O$$

The mechanism of the reaction is complicated and not at all like what the equations would indicate.[3] The reaction is catalyzed by manganous salts; the first portions of permanganate added react slowly, but, after some manganous ion is formed, succeeding portions of permanganate are decolorized almost instantaneously. If manganous ion is added prior to the titration, the reaction is rapid from the start. The reaction is slow at room temperature, and it is necessary to carry out the last portions of the titration, at least, at elevated temperatures so that the reaction is sufficiently fast to enable the analyst to determine when the end point is reached.

In the McBride procedure,[3] which has been standard for many years, the acidified solution is heated to near 80° and is titrated slowly by permanganate until a permanent faint pink tinge is obtained. In 1935 Fowler and Bright [3] showed that this method leads to a small error which can be avoided by adding the bulk of the permanganate rapidly to the cold solution of the sample and allowing it to decolorize slowly without stirring, then completing the titration at elevated temperature. The Fowler–Bright procedure was given in the previous edition of this text, but experience has shown that in student hands it often causes

[3] I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II, Interscience, 1946. R. S. McBride, *J. Am. Chem. Soc.*, **34**, 393 (1912). R. M. Fowler and H. A. Bright, *J. Research Bur. Standards*, **15**, 493 (1935). H. F. Launer and D. M. Yost, *J. Am. Chem. Soc.*, **56**, 2571 (1934).

more difficulties than the less exact McBride procedure which gives sufficiently good results.

Procedure. Weigh out to the closest 0.1 mg three 0.25-g samples (note 1) of dry $Na_2C_2O_4$, and transfer to wide-mouth 250-ml Erlenmeyer flasks. Prepare approximately 1.5 *N* sulfuric acid solution by pouring 15 ml concentrated H_2SO_4 into 300 ml water. Dissolve the sodium oxalate sample in 75 ml of the 1.5 *N* sulfuric acid solution.

* Heat the solution (note 2) to 80–90°C, and titrate slowly with permanganate, with constant swirling. The end point is a faint permanent pink color. The temperature should not fall below 60° during the titration. Obtain a blank by heating 75 ml 1 *N* sulfuric acid to 80° and titrating with permanganate. From the corrected volume of permanganate and the weight and purity of the standard, compute the normality of the permanganate. The average deviation should not exceed 1–2/1000.

Notes. 1. The equivalent weight is 134.01/2 or 67.00 g.

2. Place a thermometer in the flask for accurate measurement of the temperature. Remove and rinse off the thermometer with a small stream of water before the titration. Recheck the temperature just before the end point is reached, and if necessary reheat.

Errors. In addition to the usual volumetric errors there is danger of error due to insufficient acidity of the solution. If the permanganate is added rapidly, the hydrogen ions may be exhausted locally. When this happens, a brown color is obtained resulting from precipitation of colloidal manganese dioxide. A determination should be discarded if this occurs. Care must be taken to keep the temperature above 60°.

DETERMINATIONS BY PERMANGANATE

The high oxidation potential of permanganate in acid solutions makes it a suitable reagent for the quantitative titration of many ions of lower potential. A partial list of the more widely used permanganate analyses follows:

$$Fe^{++} = Fe^{+++}$$
$$H_3SbO_3 = H_3SbO_4$$
$$H_3AsO_3 = H_3AsO_4$$
$$Sn^{++} = Sn^{++++}$$
$$Ti^{+++} = Ti^{++++}$$
$$Mo^{+++} = MoO_3$$
$$U^{++++} = (UO_2)^{++}$$
$$H_2SO_3 = SO_4^{=} + 2H^{+}$$

$$VO^{++} = VO_3^-$$
$$H_2S = S + 2H^+$$
$$H_2O_2 = H_2O + O_2$$
$$H_2C_2O_4 = H_2O + CO_2$$
$$HNO_2 = NO_3^- + 2H^+$$

All of these are made in acid solutions. Hydrochloric and sulfuric acids are the ones usually employed.

In the determination of metals which can exist as ions of different valence states, it is necessary to reduce to the lower valence state prior to the titration by permanganate. The reduction must be carried out in such a manner that any excess of reducing agent is removed from the solution. A number of methods may be used for the reduction. Among them are:

1. Reduction by metals, such as zinc, cadmium, aluminum, or silver. The metal may be used in the form of a spiral coil, which is immersed in the sample solution until reduction is complete, or it may be in the form of granules packed in a column through which the sample solution is passed. The Jones reductor, described later, is an example.

2. Reduction by stannous chloride, followed by removal of excess stannous ion by reaction with mercuric chloride:

$$Sn^{++} + 2HgCl_2 = Sn^{++++} + Hg_2Cl_2 + 2Cl^-$$

The mercurous chloride formed in this reaction is insoluble and is not reoxidized during the titration, since it is present as solid. This method is used chiefly for reduction of ferric ion to ferrous ion, as in the Zimmermann–Reinhardt procedure.

3. Reduction by gases, such as SO_2 and H_2S. The excess of reducing gas is removed from the solution by boiling. In general, this method is not widely used because reaction proceeds slowly, and it is difficult to determine when reduction is complete.

To illustrate the applications of permanganimetric methods, procedures are given for the types of sample most often used as student exercises. The principles therein illustrated are applicable to many other determinations.

IRON

Titration of ferrous ion by permanganate is the most widely used method for analysis of iron ores or ferrous alloys for the percentage of iron present. The reaction is

$$MnO_4^- + 8H^+ + 5Fe^{++} = Mn^{++} + 4H_2O + 5Fe^{+++}$$

The titration may be made in either sulfuric or hydrochloric acid solutions. When the latter is used, it is necessary to employ *preventive* solution to prevent oxidation of chloride ion.

Prior to the titration any ferric ion present must be quantitatively reduced to the ferrous condition by one of the methods previously listed. When the sample is in sulfuric acid solution, the Jones reductor method is convenient, but in hydrochloric acid solution the stannous chloride method is used. This is the more common method commercially because the sample is most often dissolved in hydrochloric acid.

Iron ores of commercial importance contain high percentages of iron oxides along with silicates and oxides of many other metals such as titanium, manganese, vanadium, and chromium. Organic matter may also be present. When reduction is done by stannous chloride, only organic matter and vanadium cause interference. Organic matter can be removed by ignition prior to solution of the sample, and vanadium interference can be avoided by using potassium dichromate instead of permanganate for the oxidation (dichromate has a smaller oxidation potential than permanganate and will not oxidize the vanadyl ion, VO^{++}). Student samples will not in general contain interfering substances. If such are present, the instructor will advise of modifications to be employed. If commercial samples are to be analyzed, standard reference books should be consulted regarding possible interfering substances and methods for avoiding this interference.

Analysis of Soluble Samples by Zimmermann–Reinhardt Process. The procedure illustrated in these exercises is very widely used commercially for iron analyses, particularly for ores. The basis for the method is reduction of iron by stannous chloride and the use of preventive solution to inhibit oxidation of chloride ion by permanganate. Ordinarily, in solutions of about 1 *N* HCl, permanganate will not oxidize chloride ion when present in the small excess required to give an end point. However, in presence of ferric ion, there is an appreciable oxidation of chloride ion before the stoichiometric point for the iron titration is reached. Consequently too much permanganate may be consumed in the titration, and the analysis may give high results. Further, the reaction with chloride ion is slow, and the apparent end point may "fade" so that it is difficult to say when it is reached. Preventive solution and use of proper technique avoids these effects and permits accurate titrations. This solution contains manganous ion, which inhibits oxidation of chloride ion, and phosphoric acid, which forms a complex ion with ferric ion. This complex formation serves a dual purpose; the potential required for complete oxidation of ferrous ion is

lowered by removal of the product, ferric ion, and the end point is made sharper by removal of the yellow color of ferric ion (the complex ferric phosphate ion is nearly colorless).

The student sample may be either an analyzed soluble iron salt or a solution made by dissolving a known weight of iron wire in hydrochloric acid. The instructor will designate which procedure to follow.

Procedure. Solution of Iron Sample. Obtain the sample in a 250-ml volumetric flask which has been calibrated relative to the 50-ml pipet. The sample is an accurately weighed portion of iron wire (1–2 g) dissolved in 30–50 ml concentrated HCl. If the sample has not dissolved completely, remove the stopper from the flask, and place it on the steam bath until solution is complete (disregard a small residue of carbon particles which may be present). Cool to room temperature, and dilute to volume with distilled water. Mix thoroughly by repeated inversion and shaking.

After properly rinsing the pipet, withdraw four 50-ml aliquot portions by a calibrated pipet, and deliver into small beakers (note 1). Use three samples for the analysis, and keep the fourth as reserve in case of accident.

* Place the beaker on the steam bath, and evaporate to a volume of about 10 ml (note 2). The solution will by now, because of air oxidation, probably show the pronounced yellow color of ferric ion, which is intensified in hydrochloric acid solution because of formation of a chloride complex. If there is not a pronounced color, partially oxidize the iron by adding a small crystal of permanganate and leaving the beaker on the steam bath for a few minutes longer (note 3).

Reduce ferric ion to the ferrous condition by adding stannous chloride solution (note 4) dropwise from a pipet to the hot iron solution until the color of the solution changes from yellow to light green (almost colorless). With care a sharp color change can be observed. Add 2 drops stannous chloride solution in excess after the color change is observed. Cool the solution to room temperature, and pour in rapidly 20 ml mercuric chloride solution (notes 5, 6). Allow to stand 5 minutes (note 7), then wash the contents of the beaker quantitatively into a 500-ml Erlenmeyer flask, and add water to bring the volume to about 300 ml. Add 20–25 ml preventive solution (note 8), and titrate immediately with permanganate. Run the solution in slowly, with constant swirling. The end point is a faint pink color which pervades the entire solution when it is thoroughly mixed.

Determine a blank by adding 2 drops stannous chloride solution to 10 ml 1:1 hydrochloric acid in a 500-ml Erlenmeyer flask and proceeding with addition of mercuric chloride, water, and preventive solution,

just as in the iron determination. Add permanganate drop by drop until an end point is reached.**

Subtract the volume of permanganate used for the blank from the titration volume (corrected for buret calibration). From the net volume of permanganate and the normality, compute the millicquivalents and the weight of iron in each aliquot portion and the total weight in the sample. Report the total weight of iron received, showing the value based on each titration and the average value. Duplicate results should agree within 2–3/1000.

Notes. 1. Since the sample is to be concentrated by evaporation, it is placed in a beaker. Evaporation from an Erlenmeyer flask is very slow.

2. Estimate the volume by comparison with 10 ml water in a similar beaker. Reduction by stannous chloride must be carried out in a relatively concentrated solution in order that the point at which reaction is complete can be determined by the change in color.

3. It is easier to recognize the point at which reduction is complete if the solution is distinctly yellow at the start.

4. If the reagent is not provided, prepare the necessary amount by dissolving 3 g stannous chloride in 10 ml concentrated HCl and diluting to 20 ml with water. The solution should be reasonably fresh; on long standing it is oxidized by air to $SnCl_4$.

5. A saturated solution of $HgCl_2$ in water.

6. If the reagent is not added all at once, there may be a local excess of stannous ion which will cause reduction of $HgCl_2$ to mercury rather than to Hg_2Cl_2.

7. The precipitate should be small in amount and of a pure white color. A grayish precipitate indicates reduction to mercury. This reacts slowly with permanganate and will not give true titration values. If no precipitate appears, it is indication that not enough stannous chloride has been added. If a small white precipitate is not obtained, the sample is spoiled and should be discarded.

8. If the preventive solution is not provided, prepare as follows: Dissolve 20 g $MnSO_4 \cdot 4H_2O$ in 100 ml water, and add a cooled mixture of 40 ml sulfuric acid, 120 ml water, and 40 ml sirupy phosphoric acid.

Errors. In addition to the usual volumetric errors, the following may cause trouble in this determination:

1. Incomplete reduction of ferric ion.

2. Use of too much excess stannous chloride.

3. Inability to recognize the end point. Some practice is required before one is certain of this end point. Even with preventive solution there is some fading of color, and it requires skill to titrate at just the right speed and stop just at the end point.

Procedure. Soluble Salt. Obtain the sample in a stoppered weighing bottle. Do not dry unless the instructor so directs (note 1). Weigh out three portions of proper size to furnish about 0.2 g iron (note 2), place in small beakers, and add 10 ml HCl and 10 ml water. Follow the

procedure of page 221, beginning with the star and going to the double star.

From the net volume of permanganate used and its normality, compute the grams of iron and the percentage of iron in the sample. Express the results as percentage of both Fe and of Fe_2O_3.

Notes. 1. The sample may be a hydrated salt which decomposes on drying. If so the analysis is reported on an "as-received" basis. Keep the sample in a stoppered bottle to prevent loss of water.

2. Depending on the type of sample used, the percentage of iron may vary widely. The instructor will give the approximate percentage, as a basis for selection of the proper size of sample.

Errors. See discussion on page 222.

Iron Ore

The most difficult part of an ore analysis is bringing the sample into solution. In general the samples used for student unknowns are decomposed by hydrochloric acid, but some naturally occurring samples dissolve with great difficulty.

The sample is treated with concentrated hydrochloric acid, with or without a little stannous chloride, and heated in a covered beaker or flask on the steam bath. When decomposition is complete, there will be a colorless residue of silica. If HCl treatment does not dissolve all but the silica, the sample is treated with a mixture of nitric and hydrochloric acids and then evaporated to dryness to destroy nitrates. Should the mixed acid treatment not effect complete solution, it is necessary to filter out the silica, fuse it with sodium carbonate, and then treat with hydrochloric acid. The fusion converts the insoluble silicate into sodium silicate and permits the iron to be brought into solution. Student samples will not require this treatment unless specific instructions are given to do so.

Procedure. Obtain the sample in a weighing bottle. Grind (note 1) about 2 g in an agate mortar. Effective grinding is obtained only by use of small portions, each of which is ground until no gritty particles can be felt in the powder. Following this grinding the entire 2-g sample is ground together for a short time to insure thorough mixing. Dry the ground sample at 110°, and store in a weighing bottle.

Weigh out accurately three samples of 0.3 to 0.6 g (note 2), and transfer to small beakers. Add 10–15 ml HCl, cover the beaker with a watch glass, and place on the steam bath until the sample is disintegrated, as shown by a white residue. This will usually require 30–60 minutes. When disintegration is complete, rinse off the watch-glass

cover with a little water, and permit the solution to evaporate to a volume of about 10 ml on the steam bath. Follow the procedure of page 221, beginning with the star and proceeding to the double star.

From the net volume of permanganate and its normality, compute the weight of iron and its percentage in each sample.

Notes. 1. Grinding may be omitted when it is known that the samples can be decomposed without further grinding. Consult instructor.

2. The amount of iron in ores usually lies in the range 30 to 60 per cent. The instructor will specify what size of sample to use.

Errors. Read the discussion of page 222. Additional errors in the mineral analyses are:

1. Incomplete decomposition of the sample.
2. Presence of other reducing agents besides iron in the sample.

Jones Reductor Method

Despite the fact that it is not widely used in commercial iron analyses, the Jones reductor method is often given as a student exercise because it illustrates the methods and techniques employed in any reduction by metals. Such procedures are of value in many special analyses.

The sample may be either a solution containing a known weight of iron dissolved in dilute sulfuric acid or a soluble salt. After preparation of the solution, the procedure is the same in either case.

For samples which are soluble in dilute sulfuric acid, the Jones reductor method has one great advantage over the Zimmermann–Reinhardt process, namely, the absence of chloride ion and the side reactions caused by chloride ion.

Procedure. Analysis of Iron Solution by Jones Reductor Method. Arrange a reductor (note 1) as shown in Fig. 22. If it is not charged, when obtained from the store room, prepare for use as follows: Place a perforated porcelain disk or a plug of glass wool in the bottom of the empty tube, and make a tight filter by pouring a suspension of acid-washed asbestos fiber through the tube until a retentive filter mat is formed, as in the preparation of a Gooch crucible. See page 73. The mat should be porous enough to permit water to flow through at a rate of 75–100 ml per minute without the use of suction. Amalgamate (note 2) a quantity of 10–20 mesh analyzed-grade zinc by stirring it for 5–10 minutes in a solution of 0.1 *M* mercuric chloride in 1 *M* hydrochloric acid; wash the zinc thoroughly by decantation, and pack it into the reductor column. The zinc column should be about 1.5–2 cm in diameter and 35–50 cm in length. Wash the column several

times with water, applying gentle suction, and then wash with 1 *N* sulfuric acid (note 3), taking care that the liquid level never falls below the top of the zinc column (note 4). Continue the washing until a 250-ml portion of acid will not require more than 2 drops of permanganate solution to impart a distinct pink tinge. The reductor is now ready for use.

If the reductor is already filled with zinc when obtained, it is only necessary to rinse with acid until a satisfactory blank is obtained, before proceeding with the reduction of the samples for analysis. Obtain the blank by passing a 250-ml portion of 1 *N* sulfuric acid through the column of zinc at a rate of 50–75 ml per minute. Pour the acid in at the top at such a rate that the liquid level stands just above the zinc surface, but take care never to allow the level to fall below the surface so that air can come into contact with the zinc. After the 250-ml portion of acid has run through, rinse with 100 ml water. Add the water in several portions, letting the level fall to a point just above the zinc surface for each portion. Remove the filter flask, and add permanganate from a buret until a barely perceptible pink color is imparted to the solution. If the volume of permanganate needed is greater than 2 drops, repeat the blank until a satisfactory value is obtained. Proceed immediately with the reduction of the analysis samples, after a satisfactory blank is obtained.

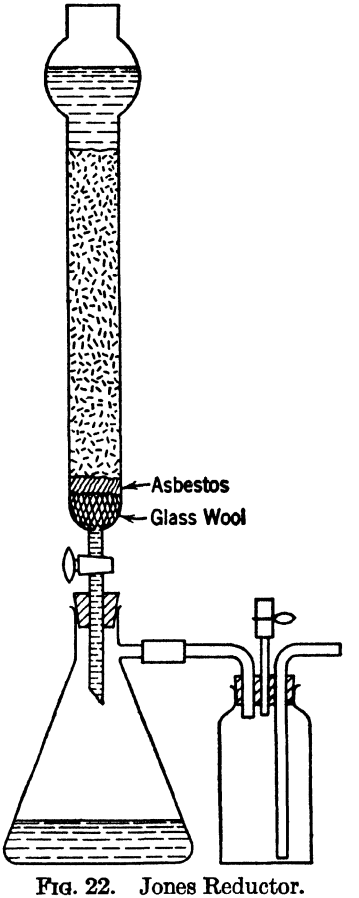


FIG. 22. Jones Reductor.

Obtain a sample of iron in a 250-ml calibrated flask. The sample is a weighed portion of iron wire to which 50 ml 2 *N* sulfuric acid has been added. Heat the flask on a steam bath until all the iron has dissolved, cool, dilute to the mark, and mix well. From a calibrated pipet, measure four 50-ml portions of the iron solution into 250-ml beakers. Add 5 ml concentrated sulfuric acid to each, and dilute to approximately 100 ml.

Pour the sample solution through the reductor, at a rate of about 50 ml per minute. Use suction, and control the rate of flow by the stop-

cock at the bottom of the reductor. Guide the solution into the funnel with a stirring rod held against the lip of the beaker. Allow sample to run through until the liquid level is just above the zinc surface, then close the stopcock, add about 50 ml 1 *N* sulfuric acid to the beaker, pour this into the reductor, and allow the acid to run through until the level is just above the zinc surface. In this manner use four 50-ml wash portions. Finally, rinse with 100 ml distilled water (note 5). Remove the suction flask, and titrate the solution immediately, in the suction flask. Permanganate may be added rapidly until the end point is approached, but final addition should be made dropwise so that the end point is not over-run. Subtract from the total volume of permanganate the volume used in the blank (note 6). Compute the weight of iron received. Duplicate aliquot portions should agree within 1–2 parts per 1000.

Notes. 1. Zinc, cadmium, or aluminum may be used as reducing agents, either in the form of a column or as a spiral which may be introduced into the solution and withdrawn after reduction. Use of the column is recommended because of the certainty of complete reduction. The reaction is

$$Zn + 2Fe^{+++} = Zn^{++} + 2Fe^{++}$$

2. Amalgamated zinc does not react so rapidly with 1 *N* sulfuric acid as the pure metal, but it will reduce ferric ion rapidly and quantitatively. The inhibiting effect of amalgamation is probably due to the high overvoltage of hydrogen on a mercury surface. Zinc displaces mercuric ion according to the reaction,

$$Zn + Hg^{++} = Zn^{++} + Hg$$

The liberated mercury amalgamates the zinc surface.

3. A large quantity of 1 *N* sulfuric acid should be prepared. Slowly stir 30 ml concentrated sulfuric acid into a liter of water, and set aside to cool.

4. It is very important to exclude air from a prepared reductor, since hydrogen peroxide is formed by the reaction of oxygen and the liberated hydrogen. Hydrogen peroxide reduces permanganate according to the equation,

$$5H_2O_2 + 2MnO_4^- + 6H^+ = 2Mn^{++} + 8H_2O + 5O_2$$

thereby leading to high results.

5. An acid solution should not be left in the reductor because it will dissolve the zinc.

6. A blank is necessary because of reducing constituents, particularly iron, that may be present in the zinc. It is important that the quantity of solution and the rate of flow for the blank be the same as those employed in analyses. If a satisfactory blank is not obtained, impure zinc is indicated, and the reductor must be refilled with zinc of a good grade.

Errors. In addition to the usual volumetric errors this determination is subject to several specific ones:

1. Incomplete reduction, because of too rapid passage of solution over the zinc, or use of too short a column of zinc.

2. Reoxidation of iron by air. This is not appreciable if the titration is made immediately after reduction.

3. Hydrogen peroxide, formed by air in the reductor.

4. The presence of interfering substances such as titanium, vanadium, chromium, molybdenum, uranium, arsenic, nitrates, and certain nitrogenous compounds. Of the metals which are likely to occur in iron ores—titanium, vanadium, and chromium—only vanadium will interfere in the stannous chloride reduction, whereas all interfere in reduction by zinc. Nitrates are reduced by zinc to hydroxylamine which reacts with permanganate. If nitrates are present, the solution of the sample should be evaporated until fumes of sulfur trioxide are evolved, then cooled, diluted, and passed through the reductor. Organic compounds are oxidized by this procedure.

5. Loss of sample, by incomplete washing from the reductor.

6. Air in the reductor.

OTHER DETERMINATIONS

The following procedures, which are based on analyzed samples available for student use, illustrate various applications of permanganimetric analysis.

Oxalates

Oxalates can be dissolved in dilute sulfuric acid and the oxalic acid determined by titration with permanganate as described previously in sodium oxalate standardization.

Procedure. Soluble Oxalate. Obtain the sample in a stoppered weighing bottle, and dry at 110°. Weigh out three portions of about 1 g and transfer to 250-ml Erlenmeyer flasks. Add 75 ml 1.5 *N* sulfuric acid, and titrate according to the procedure of page 218, beginning with the star. Report the percentage of $Na_2C_2O_4$ in the sample.

Read the notes and discussion of page 218.

Calcium. In gravimetric analyses calcium is normally precipitated as the oxalate $CaC_2O_4 \cdot H_2O$. The precipitate may be ignited to the oxide for weighing, or it may be washed free of soluble oxalates and dissolved in sulfuric acid, and the amount of calcium determined by means of the permanganimetric titration of the oxalate. The volumetric method compares favorably with the gravimetric one in speed and accuracy.

In computation of the weight of CaO which corresponds to the milliequivalents of permanganate used, the equivalent weight of CaO is one-

half the molecular weight. Each CaO yields one molecule of $H_2C_2O_4$, which undergoes a 2-electron valence change.

A procedure for this method is given on page 430, in connection with the determination of calcium in limestone.

Arsenic and Antimony

Both arsenic and antimony may be determined by permanganate titration, as in standardization by arsenious oxide.

Other oxidizing agents which can be used for the determination of arsenic and antimony are bromate and iodine. Directions for the use of iodine are given in the following chapter.

Procedure. Soluble Arsenic. Dry the sample and weigh out three 0.5- to 2-g portions as directed by the instructor. Dissolve the sample in NaOH, and determine according to the procedure of page 216.

Report the percentage of As_2O_3 in the sample.

Antimony Ore. Antimony trisulfide ore, stibnite, provides an excellent student exercise in the use of permanganate oxidimetry. The ore should be free of other reducing constituents than antimony; samples suitable for use in iodometric determinations (see page 246) are also suitable for use in the permanganimetric method.

The finely ground ore is treated with concentrated sulfuric acid and heated until sulfur and hydrogen sulfide are completely removed. A little potassium sulfate is sometimes added, to facilitate the decomposition. Antimony usually is not oxidized by the hot acid treatment, but is brought into solution in the trivalent form. After the sample is completely dissolved, the solution is diluted, hydrochloric acid is added, and the antimony is determined by titration with standard permanganate solution at a temperature not above 10°C.

If it is doubtful that all the antimony is in the trivalent condition at the start of the titration, the solution should be saturated with sulfur dioxide while in a 1:1 sulfuric acid medium, and the excess sulfur dioxide expelled by boiling before hydrochloric acid is added. This precaution is not generally necessary in student analyses unless the sulfuric acid treatment for solution of the sample has been unduly prolonged.

If an ore of unknown content, which might contain arsenic and other reducing constituents, is to be analyzed, it is necessary to make preliminary separations before the antimony determination can be carried out. Reference books in mineral analysis should be consulted if this is necessary.

Procedure. Weigh out three 0.7- to 2-g samples of the dried ore (note 1), and transfer to 150-ml beakers. Add 15 ml concentrated

H_2SO_4 and a small crystal of potassium sulfate. Place the beaker on a wire gauze, and boil the liquid over an open flame, taking care to avoid spattering (*Hood*). When the solution becomes clear (note 2), cool, and cautiously add 20 ml water. Boil until fumes of sulfur trioxide are evolved. Cool, cautiously add 50 ml water, and then quantitatively transfer the solution from the beaker to a 500-ml Erlenmeyer flask. Add 20 ml hydrochloric acid, and dilute to a total volume about 200 ml. Cool in ice water to a temperature below 10°. Titrate while cold with standard permanganate solution. Report the percentage of antimony in the ore. The equivalent weight is half the atomic weight.

Notes. 1. The usual samples run from 10 to 30 per cent Sb. The instructor will state what size sample to employ.

2. If the ore is not well disintegrated in the acid treatment, it should be more finely ground before the samples are taken. Usually no further grinding is necessary for student samples.

Determination of Oxidizing Agents

In addition to its use for the analysis of substances that are reducing agents, a standard solution of permanganate can also be used as the reagent for analysis of some oxidizing materials, by the employment of an indirect method. A weighed portion of sample is treated with an excess known amount of a reducing agent, and the excess remaining after reaction is determined by titration with permanganate. Although this procedure may at first sight seem roundabout and involved, it is often preferable to direct titration of the oxidizing agent with a standard reducing agent. This is true because of (1) the difficulty in preserving standard solutions of strong reducing agents, and (2) the fact that the materials which are determined by this procedure are in solid form and cannot be directly titrated since reaction does not occur instantaneously. In the indirect method time is allowed for complete reaction of the sample with the reducing agent; then the titration of the excess reducing agent is a normal oxidimetric procedure.

The chief applications of this method are in the analysis of higher oxides of lead or manganese dioxide. Several reducing agents can be used, including ferrous sulfate, oxalic acid, and arsenious oxide. The last is preferred since it is not oxidized by air as is ferrous sulfate and since the permanganate titration of it is simpler than that of oxalic acid.

Determination of Available Oxygen in Manganese Ore. The oxidizing power of a manganese ore which contains MnO_2 (pyrolusite) can be determined by the indirect method previously outlined. The result of the analysis is expressed as the percentage of available oxygen

in the sample. This is computed by multiplying the milliequivalents of oxidizing agent in the sample by the milliequivalent weight of oxygen, 8.00 mg.

Procedure. Prepare an approximately 0.1 *N* solution of arsenious acid by dissolving 5 g As_2O_3 in 5 g NaOH dissolved in 15 ml water. When the As_2O_3 has dissolved, dilute to 50 ml, neutralize with 6 *N* HCl to the methyl orange end point, and dilute to 1 l.

Weigh out three 0.25- to 1-g samples (note 1) of the finely ground ore and transfer to 1-l. Erlenmeyer flasks. Pipet into each flask exactly 50 ml of the arsenious acid solution. Add 10 ml concentrated H_2SO_4, and boil gently (note 2) until the sample is decomposed, as shown by absence of colored particles in the siliceous residue. Cool the solution, wash down the sides of the flask with a little water (note 3), and add 100 ml water, 5 ml hydrochloric acid, and a drop of 0.002 *M* potassium iodide solution (note 4). Titrate with permanganate as in the procedure of page 216.

Determine the permanganate value of the arsenious acid solution by measuring out three 50-ml portions, adding the same reagents as previously, and titrating with permanganate. The difference in the volume of permanganate required for the solutions without sample and those with sample represents the milliequivalents of oxidizing agent in the sample. From this value compute the percentage of available oxygen in the sample.

Notes. 1. The percentage of available oxygen may range from 2 to 10. The instructor will specify the size of sample to use.

2. Arsenic trichloride is volatile and may be lost during the heating if much chloride ion is present. Use of the large flask minimizes the possibility of loss, since the walls act as a condenser. A cold trap, consisting of a test tube through which tap water is passed, may be suspended in the neck of the flask for further precaution against loss, if desired. The tube has a two-hole stopper with glass inlet tube extending to the bottom and outlet tube reaching only through the stopper. If the cold trap is used, remove it and rinse off after the sample is decomposed.

3. If the residue is large in amount, it is advisable to filter before the titration. Use a Gooch crucible with suction.

4. Prepare according to note 2, page 216.

Procedure. Soluble Chromate. Prepare a solution of 40 g ferrous ammonium sulfate in 950 ml water and add 50 ml concentrated H_2SO_4. Obtain the sample in a stoppered weighing bottle. Dry and weigh out three 0.5–1-g portions (note 1). Transfer to 250-ml Erlenmeyer flasks, and add from a pipet exactly 50 ml of the ferrous solution. Add about 4 ml H_2SO_4, and swirl until the sample is dissolved. Titrate immediately (note 2) with standard permanganate (note 3).

Determine the permanganate value of the ferrous solution by measuring out three 50-ml portions and carrying through the procedure above,

but without sample added. The difference in the permanganate values with and without sample represents the oxidizing equivalents in the sample. Report the percentage of Cr in the sample. The equivalent weight is 52.01/3, or 17.34 g, since chromium undergoes a valence change of three in this reaction.

Notes. 1. Consult instructor as to size of sample.

2. If the sample is allowed to stand atmospheric oxidation of ferrous ion may occur.

3. A better end point is obtained by use of orthophenanthroline indicator, since the green color of chromic ion obscures the permanganate end point somewhat.

QUESTIONS

1. Write the ionic equations for the titration reaction with MnO_4^- in acid solution for each of the following:

$$H_3SbO_3,\ Ti^{+++},\ HNO_2,\ H_2S.$$

•2. Which of the following could be determined by titration with $KMnO_4$ without treatment of the unknown before titration?

$$Fe^{++},\ Sn,\ Cl^-,\ H_2C_2O_4,\ S_2O_3^=.$$

3. Why must acid be present during permanganimetric titrations? What concentration of acid is usually employed?

4. Discuss the suitability of the various standards for permanganate.

5. A solution of $KMnO_4$ is standardized with $Na_2C_2O_4$. Predict the effect on the determined normality if:

(*a*) The temperature falls below 50°C during the titration.

(*b*) H_2O_2, an intermediate product, escapes during the course of the titration.

6. What would be the effect on the normality of $KMnO_4$ if in the standardization with As_2O_3 the KI or KIO_3 were not added?

7. Why is reduction of iron by stannous chloride carried out in hot solutions. Why is mercuric chloride not added while the solution is hot? Why is the solution diluted and cooled before titration? What error is introduced if too much stannous chloride is used? How is this condition recognized?

8. Explain the purpose of each of the components of preventive solution.

9. Draw a diagram of the Jones reductor, and explain its operation.

10. List the advantages and disadvantages of several different methods for reducing iron to the ferrous condition before titration with permanganate.

11. Predict the effects on the result of an analysis of an iron sample by the Zimmermann–Reinhardt procedure of each of the following:

(*a*) Failure to add mercuric chloride.

(*b*) Titration of a sample in which a gray precipitate formed after the addition of mercuric chloride.

(*c*) Carrying out the reduction with stannous chloride at room temperature.

(*d*) Failure to add preventive solution.

12. Predict the effect of the result of the analysis of an iron-ore sample by the use of a Jones reductor of each of the following:

(*a*) Passing the solution through the reductor too rapidly.

(*b*) Admitting air to the reductor.

(*c*) The presence of vanadium in the ore.

13. Which of the following constituents, if present in large amounts, will interfere in permanganimetric determinations of iron: silica, aluminum, magnesium, manganese, calcium, alkalies, chromium, sulfur, titanium, vanadium?

14. How may both the ferrous iron and the total iron be determined in the analysis of a sample of magnetite, Fe_3O_4?

PROBLEMS

1. Tabulate the titer of 0.1275 *N* $KMnO_4$ in terms of: Fe, FeO, Fe_2O_3, Fe_3O_4, H_2S, H_2O_2, $Na_2C_2O_4$, SO_2, Sb_2O_3, HNO_2, Sn, UO_2SO_4, V_2O_5.

2. Find the normalities of the following solutions of $KMnO_4$:

(*a*) 31.38 ml $KMnO_4$ is equivalent to 0.1947 g As_2O_3.

(*b*) 41.47 ml $KMnO_4$ is equivalent to 0.2500 g Fe.

(*c*) 35.62 ml $KMnO_4$ is equivalent to a 1/5 aliquot of 1.5000 g $Na_2C_2O_4$ dissolved in 250.0 ml.

3. What is the normality of a 0.300 molar $KMnO_4$ solution under each of the following circumstances:

(*a*) It is used as an oxidizing agent in strongly acid solution.

(*b*) It is used as an oxidizing agent in basic solution.

(*c*) It is used as an oxidizing agent in a reaction whereby it is converted to $MnO_4^{=}$.

4. How many milligrams of $H_2C_2O_4 \cdot 2H_2O$ are required to decolorize 50.00 ml of 0.0400 *M* $KMnO_4$?

5. How many milliliters of 0.1000 *N* NaOH are needed to neutralize 35.00 ml of KHC_2O_4 solution if 35.00 ml of the oxalate solution are equivalent to 40.00 ml of 0.1000 *N* $KMnO_4$?

6. How many milliliters of 0.1500 *N* $KMnO_4$ are needed to titrate 1.5968 g Fe_2O_3?

7. How many milligrams of As_2O_3 will react with the amount of $KMnO_4$ required in Problem 6?

8. How many grams per liter of potassium permanganate should be used to prepare a solution equivalent to a potassium dichromate solution containing 4.2060 g per liter?

9. 0.2030 g 99.0 per cent pure $Na_2C_2O_4$ was titrated beyond the end point by 34.60 ml $KMnO_4$ solution. 4.50 ml $FeSO_4$ solution was added for back titration, and 0.40 ml of $KMnO_4$ was used to establish the end point. Find the normalities and molarities of both solutions if 1.000 ml $KMnO_4$ is equivalent to 0.900 ml $FeSO_4$.

10. If the iron in a 0.1500-g sample of ore is reduced and subsequently requires 15.03 ml 0.1000 *N* $KMnO_4$ for titration, what is the purity of the ore expressed as percentage of: Fe, FeO, Fe_2O_3?

11. What is the percentage purity of a sample of sodium oxalate if a 0.2203-g sample requires 29.30 ml of $KMnO_4$ of which 1.000 ml is equivalent to 0.006023 g Fe?

12. Calculate the percentage of iron in a sample from the following data:

Weight of sample: 0.5862 g.

Volume of 0.1105 *N* permanganate: 32.43 ml.

Volume of 0.0942 *N* ferrous sulfate used for back titration: 3.42 ml.

13. The precipitated CaC_2O_4 from a 0.4207-g sample of limestone was dissolved in H_2SO_4 and required 43.08 ml of 0.0958 *N* $KMnO_4$ for titration. Find the percentages of calcium as CaO and $CaCO_3$.

14. Calcium in blood is often determined by precipitating it as the oxalate, dissolving the precipitate in sulfuric acid and titrating with standard permanganate. Find the milligrams of calcium per 100 ml blood from the following:

5.00 ml blood is diluted to 50.00 ml; 10.00 ml of this solution requires 1.15 ml of 0.0100 *N* $KMnO_4$.

15. A student unknown is a mixture of $NaAsO_2$ and NaCl. What is the percentage of NaCl in a sample if 0.3500 g of sample require 40.13 ml of 0.1105 *N* $KMnO_4$? What is the percentage of As_2O_3 in the sample?

16. What volume of 0.1155 *N* $FeSO_4$ solution should be added to a 0.5000-g sample of $K_2Cr_2O_7$ so that at least 10 ml of 0.0956 *N* $KMnO_4$ will be used for back titration?

17. By what number should the iron titer of a $KMnO_4$ solution be multiplied to give the antimony titer of the same solution?

18. If the purity factor in the illustrative problem on standardization of solution on page 208 had been neglected, by how many parts per thousand would the apparent normality differ from the true normality?

19. What size sample of $Na_2C_2O_4$ should be taken for standardization of 0.01 *N* $KMnO_4$? Should individual samples of standard be used?

20. Suggest a range of sample weights for an iron ore which is approximately 60 per cent Fe_2O_3 and is to be analyzed with 0.2000 *N* $KMnO_4$.

21. If 10.00 ml of commercial hydrogen peroxide, density 1.010, requires 36.82 ml 0.1200 *N* permanganate for titration, calculate the percentage by weight of H_2O_2 in the solution.

22. A sample of pyrolusite which weighs 0.4000 g is treated with 50.00 ml 0.2000 *N* $H_2C_2O_4$; 10.55 ml 0.1152 *N* $KMnO_4$ is required for back titration. What is the percentage purity of the ore?

23. Find the percentage of available oxygen in a pyrolusite sample from the following data:

Normality of $KMnO_4$ 0.0953

50.00 ml $NaAsO_2$ solution = 45.50 ml $KMnO_4$ solution

A sample of 0.5000 g is treated with 50.00 ml $NaAsO_2$ and requires 15.00 ml $KMnO_4$ for back titration.

24. Molybdenum in the +6 oxidation state is reduced to the +3 state in a Jones reductor. In this state it is caught in a ferric solution, and an amount of Fe^{++} is liberated which is equivalent to the molybdenum which is reoxidized to the +6 state. What volume of 0.1126 *N* $KMnO_4$ is needed to titrate the Fe^{++} liberated by 0.2000 g 99.9 per cent pure Na_2MoO_4? How many milligrams of Fe^{+++} were consumed by the molybdenum?

25. 1.500 g pure Pb_3O_4 is treated with 50.00 ml 0.1056 *N* $H_2C_2O_4$ solution. How many milliliters of $KMnO_4$ whose As_2O_3 titer is 5.000 mg are needed for back titration?

$$Pb_3O_4 + H_2C_2O_4 + 3SO_4^{=} + 6H^+ = 3PbSO_4 + 2CO_2 + 4H_2O$$

26. In the Volhard method manganese is determined by titration with standard permanganate solution, according to the reaction,

$$2MnO_4^- + 3Mn^{++} + 2H_2O = 5MnO_2 + 4H^+$$

(In practice manganese dioxide is not precipitated, but a zinc salt is added to the solution, and a precipitate of basic zinc manganite is obtained. The manganese, however, is in the tetravalent state.)

A 1.1246-g sample of manganese ore was dissolved and the solution diluted to 250 ml; 50.00 ml of this solution required 45.15 ml of permanganate solution, 1.000 ml of which is equivalent to 8.423 mg sodium oxalate. Calculate the percentage of manganese in the sample.

Note that the permanganate solution is standardized in acid solution, against sodium oxalate, but in the Volhard process permanganate is used in basic solution, where it undergoes a valence-number change of three.

27. A 0.2643-g sample of stibnite (Sb_2S_3) is brought into solution, the sulfide removed, and the antimony, which is in the trivalent condition, is titrated to the pentavalent condition by standard permanganate solution, 25.23 ml of 0.1042 *N* permanganate being used. Find the percentage of antimony in the ore.

28. What should be the normality of a $KMnO_4$ solution so that the number of milliliters used in titration divided by two gives the percentage of iron in a 0.3000-g sample of ore? What volume of 0.1108 *N* $KMnO_4$ solution is required to produce exactly 1 l. of the above solution?

29. What weight of sample should be taken for analysis so that each 1.000 ml of 0.2000 *N* $KMnO_4$ solution represents 0.500 per cent H_2O_2 in the sample?

30. What weight of material must be taken for analysis so that each 1.000 ml 0.2000 *N* $KMnO_4$ represents 2.000 per cent Fe_3O_4 in the sample?

CHAPTER

13

Oxidation–reduction III. Iodine Methods

Iodine is a weak oxidizing agent, and iodide ion is a fairly strong reducing agent since the potential for the reaction,

$$2I^- = I_2 + 2e$$

is −0.53 volt. This places iodide ion above ferrous ion, trivalent arsenic, and antimony as a reducing agent.

In the development of analytical chemistry several factors led to an early utilization of iodine methods. They are: (1) a sensitive indicator, starch, has long been known, and (2) a reagent, sodium thiosulfate, is available for quantitative titration of free iodine. Because of these conditions a large number of analytical methods has been developed about the iodine–iodide-ion equilibrium.

There are two types of iodine methods, direct and indirect. In the first, known as the iodimetric method, iodine solutions are used for titration of reducing agents which can be quantitatively oxidized at the stoichiometric point. The number of such reactions is limited because iodine is itself a weak oxidizing agent; further, most of these determinations can today be better done by some other method than by use of iodine. Thiosulfate alone, of the common reducing agents, must be determined by oxidation with iodine. It happens that the stronger oxidizing agents give side reactions with thiosulfate, whereas iodine oxidizes it quantitatively to tetrathionate ion, $S_4O_6^{=}$. The oxidations which can well be done by iodine are represented in the following equations:

$$H_2S + I_2 = 2H^+ + S + 2I^-$$

$$H_2SO_3 + I_2 + H_2O = SO_4^{=} + 2I^- + 4H^+$$

$$H_2AsO_3^- + I_2 + H_2O = H_2AsO_4^- + 2I^- + 2H^+$$

$$H(SbO)C_4H_4O_6 + I_2 + H_2O = H(SbO_2)C_4H_4O_6 + 2I^- + 2H^+$$

$$Sn^{++} + I_2 = Sn^{++++} + 2I^-$$

$$2S_2O_3^{=} + I_2 = S_4O_6^{=} + 2I^-$$

In indirect or iodometric methods the oxidizing agent which is to be analyzed is treated with an excess of iodide ion under suitable conditions. Iodine is liberated quantitatively, and it is titrated by a standard solution of sodium thiosulfate or arsenious acid. These methods can be used for the analysis of almost any strong oxidizing agent; consequently, there are many more applications than there are for iodimetric methods. The following equations indicate some that are widely used:

$$2MnO_4^- + 16H^+ + 10I^- = 2Mn^{++} + 5I_2 + 8H_2O$$

$$Cr_2O_7^{=} + 6I^- + 14H^+ = 2Cr^{+++} + 3I_2 + 7H_2O$$

$$BrO_3^- + 6H^+ + 6I^- = Br^- + 3I_2 + 3H_2O$$

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

$$ClO_3^- + 6H^+ + 6I^- = Cl^- + 3I_2 + 3H_2O$$

$$2HNO_2 + 2I^- + 2H^+ = 2NO + I_2 + 2H_2O$$

$$2Cu^{++} + 4I^- = 2CuI + I_2$$

$$HOCl + H^+ + 2I^- = Cl^- + H_2O + I_2$$

INDICATORS

In both iodimetric and iodometric methods the end point is based on the presence of free iodine. This can be detected by starch or by extraction of iodine from water by an immiscible organic solvent.

Starch. Starch does not dissolve as a true solution, but it is readily dispersed as a colloid. With iodine it gives a deep blue color which is formed on the surface of the colloid particles when iodine is adsorbed and is discharged when the iodine is reduced to iodide ion. The color change is reversible and may be approached from either direction. The presence of iodide ion is necessary for development of a good color. Anything that tends to coagulate the colloidal starch or to interfere with adsorption of iodine by the colloid will cause indicator interference. In general, heat, strong solutions of electrolytes, and organic materials such as alcohol are to be avoided.

When dispersed in water, starch is very susceptible to bacterial action which causes its decomposition and makes the solution ineffective as an

indicator. A solution prepared without any preservative will in general not be good for more than 2 or 3 days. Addition of a preservative inhibits this bacterial action, and it is possible to make preparations that can be stored for weeks or months. Recommended methods for preserving are (1) addition of a little mercuric iodide, (2) use of 1 g boric acid [1] per 100 ml and (3) use of 0.1 g furoic acid [2] per 100 ml.

In the titration of iodine the starch should not be added until just prior to the end point, when the iodine color is beginning to fade. When the starch is added to a high concentration of iodine, there is a tendency to formation of a reddish color which is not readily discharged at the end point. When the titration is made with iodine, the starch may be added at any time, since iodine is not in excess until the end point is reached.

Procedure. Preparation of Starch Indicator. Triturate 1–2 g soluble starch with cold water to make a thick paste. Slowly pour this paste into 100 ml boiling water in which 1 g boric acid crystals has been dissolved. Continue boiling for 1 minute, then cool, and store in a stoppered bottle. Discard the preparation when it becomes cloudy or when it begins to give a reddish color with iodine.

Recently the authors have been provided with samples of A-Fraction from starch, through courtesy of the Corn Products Refining Company, and have tested this material as an iodine indicator. According to the recommendations of the Corn Products staff it has been dispersed in 15 per cent KCl solution. It gives a sharp color change with an intense blue, comparable to that obtained from the best samples of soluble starch, and keeps in the KCl solution for a matter of weeks without coagulation or breakdown. We have used the same procedure for preparation as given in the last paragraph except that the paste is stirred into 15 per cent KCl solution, and boric acid has not been used.

Detection of End Point by Extraction. In certain titrations, where conditions are not suitable for the use of starch indicator, the end point may be determined by an extraction method. In this method a non-miscible organic liquid, such as carbon tetrachloride or carbon disulfide, is added to the titration solution. The heavier organic liquid forms a layer at the bottom; because of the greater solubility of iodine in the organic solvent, the concentration of the iodine is much greater in the organic than in the aqueous layer, and the color is more intense. The end point of the titration is marked by the disappearance of the iodine color in the bottom layer. After each addition of reagent, the solution is shaken up and then allowed to stand until the organic layer

[1] See Hillebrand and Lundell, *Applied Inorganic Analysis*, page 148.

[2] A. M. Platow, *Chem. Analyst*, June 1939.

has settled out. This method compares favorably in sensitivity with the starch-indicator method, but titrations made with an extraction end point require more time than those made with the starch indicator.

CHEMICAL REACTIONS AND EQUILIBRIA OF IODINE METHODS

Before studying specific determinations by iodine methods, one should understand the chemistry of the processes and the factors which affect the complex equilibria which are encountered in many reactions.

Reactions of Thiosulfate. The reaction of thiosulfate ion with iodine in acid or neutral solutions is given by the equation,

$$2S_2O_3^{=} + I_2 = S_4O_6^{=} + 2I^-$$

This reaction is essentially complete at the stoichiometric point. In basic solutions the oxidation may proceed further, according to the equation,

$$S_2O_3^{=} + 4I_2 + 5H_2O = 2SO_4^{=} + 8I^- + 10H^+$$

This reaction is not quantitative, since the one above may also occur. Consequently, the titration of iodine by thiosulfate must always be made in acid or neutral solution.

In strongly acid solutions thiosulfate decomposes according to the equation,

$$S_2O_3^{=} + 2H^+ = H_2S_2O_3 = S + H_2O + SO_2$$

It may be recalled that this reaction is the basis for a qualitative test for thiosulfate ion.

The equivalent weight of thiosulfate is a mole or 248.21 g if the pentahydrate is used. This hydrate is not suitable for preparation of standard solutions because of its water of crystallization, but the anhydrous salt has been suggested as a primary standard.[3] It is customary to make an approximate 0.1 *N* solution and to standardize by comparison with some primary standard.

Iodine. Iodine is sparingly soluble in water but dissolves readily in potassium iodide solutions because of formation of the complex I_3^- ion by the reaction,

$$I_2 + I^- = I_3^-$$

A large excess of iodide ion is used to shift the equilibrium to the right. Even with high concentrations of iodide ion, the vapor pressure of iodine over the solution is appreciable, and care must be taken to prevent loss of iodine by vaporization.

[3] H. M. Tomlinson and F. G. Ciapetta, *Ind. Eng. Chem., Anal. Ed.*, **13**, 539 (1941)

Iodine reacts with water, just as do other halogens, according to the equation,

$$I_2 + H_2O = H^+ + I^- + HIO$$

Acids tend to shift the equilibrium to the left and bases to the right. Consequently, iodine titrations are never made in strongly basic solutions.

Light accelerates the hydrolysis of iodine by causing decomposition of hypoiodous acid:

$$2HIO = 2H^+ + 2I^- + O_2$$

Standard solutions of iodine should be preserved in dark bottles or kept inside the desk to protect them from direct sunlight.

Iodide ion in acid solution may be oxidized by air:

$$4I^- + 4H^+ + O_2 = 2I_2 + 2H_2O$$

Bècause of this it is necessary to guard against access of air in iodometric determinations where the oxidizing agent is treated with KI in strongly acid solutions. The presence of certain ions accelerates this atmospheric oxidation of iodide ion. For example, nitrites give the reaction,

$$2HNO_2 + 2I^- + 2H^+ = 2NO + I_2 + 2H_2O$$

This is followed by oxidation of NO to NO_2, which yields more HNO_2 and causes further oxidation. Certain metal ions, such as cuprous, can also act as oxygen carriers to oxidize iodide ion.

Arsenites. The potential of the couple,

$$H_2AsO_3^- + H_2O = H_2AsO_4^- + 2H^+ + 2e$$

is -0.56 volt, or about the same as that of iodine. Nevertheless, by proper choice of conditions the equilibrium can be so displaced that the reaction,

$$I_2 + H_2AsO_3^- + H_2O = 2I^- + H_2AsO_4^- + 2H^+$$

proceeds quantitatively to the right. This is effected by removal of hydrogen ion as it is formed, which is accomplished by reaction with bicarbonate ion. The titration is carried out in a buffered nearly neutral solution. Enough bicarbonate or other buffer ion must be present to keep the *p*H near 8. If the buffer is exhausted, the hydrogen-ion concentration rises, and the reaction does not go to completion.

In the titration of trivalent antimony with iodine, there is a similar condition, and the solution must be buffered and nearly neutral. Basic antimony salts will precipitate in neutral solutions unless a substance is

added which will form a soluble complex ion with trivalent antimony. Tartrates may be used for this purpose.

Standard solutions of sodium arsenite (arsenious acid) are often used instead of thiosulfate for titration of iodine. These have the advantage that they keep better than thiosulfate solutions and that a solution of known strength is prepared by dissolving a known weight of arsenious oxide and making up to definite volume. Arsenious oxide is dissolved in excess sodium hydroxide,

$$As_2O_3 + H_2O + 2OH^- = 2H_2AsO_3^- \quad \text{or}$$

$$As_2O_3 + 2OH^- = 2AsO_2^- + H_2O$$

Excess hydroxide is neutralized with HCl or H_2SO_4, since one cannot employ a basic solution for iodine titrations.

Effect of *p*H. Since the hydrogen ion of the solution has such a variety of effects in determinations that involve the reactions of iodine, it is desirable to summarize in one place the various kinds of effects that may be encountered:

1. In iodometry it is often necessary to employ a high concentration of acid for the reaction of KI with the oxidizing constituent of the sample. This is always the case for samples which contain oxygen salts, such as permanganates, chlorates, and chromates, since hydrogen ion is one of the reactants with such oxidizing agents. Subsequent titration of iodine with thiosulfate or arsenite cannot be carried out in solutions of such high acidity. Therefore, after reduction of the oxidizing constituent by iodide ion, it is customary to dilute the solution before making the iodine titration.

2. Standard iodine solutions must be neutral or acidic. Basic solutions are not stable.

3. The reaction of thiosulfate with iodine must be carried out in neutral or acid solution, never in basic solution.

4. The titration of trivalent arsenic or antimony with iodine must be done in buffered solutions of *p*H 5 to 9.

5. Solutions of KI must be protected against atmospheric oxidation when in strongly acid media.

PREPARATION AND STANDARDIZATION OF SOLUTIONS

The solutions needed will depend on the samples to be analyzed. If only iodometric procedures are employed, a standard solution of sodium thiosulfate will suffice. If iodimetric analyses are required, it is necessary to have a standard solution of iodine. In the latter case it is also advisable to prepare a solution of sodium arsenite which serves both as

the primary standard for the iodine solution and as a reagent for back titration when this is needed. Iodine may be directly prepared of known strength, but this is not recommended since solutions do not keep well, and frequent restandardization is required.

Potassium iodide is required in all iodine analysis methods. A good-quality analyzed-grade reagent should be used, and every lot should be tested to see that it is free of iodates. If iodates are present, they react with iodide ion when the solution is acidified, releasing iodine according to the equation:

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

Test for iodates as follows: Dissolve 0.5 g KI in 10 ml water, add 1 ml 6 *N* sulfuric acid and 2 ml starch solution. Presence of iodates is shown by immediate appearance of a blue color. Disregard a blue color which forms slowly; this is due to air oxidation of KI.

Procedure. Preparation of 0.1 *N* Iodine Solution. Weigh out 12 g iodate-free potassium iodide crystals (note) on the trip scale, and dissolve in 10 ml water in a small beaker. Add 6.5 g resublimed iodine to the KI solution, and stir until it is all dissolved. Transfer the solution to a glass-stoppered bottle, and dilute to approximately 500 ml.

Note. Directions are for preparation of 500 ml solution, which is enough for standardization and for analysis of one unknown. If a larger volume of solution is required, use proportionally larger quantities of reagents.

Procedure. Preparation of Standard Iodine Solution. It is necessary to purify iodine if it is used for direct preparation of a standard solution. Weigh out 8–10 g resublimed iodine, and grind in a small mortar with 5 g potassium iodide and 2 g ignited lime (note 1). Transfer the ground mixture to a dry 600-ml lipless beaker, and place on top of the beaker a large round-bottom flask filled with cold water, which serves as a condenser. Sublime the iodine by heating the beaker with a small flame, holding the burner in the hand, and moving the flame about constantly. When it appears that most of the iodine has been sublimed, stop the heating, remove the flask, and scrape the iodine crystals onto a dry watch glass. Keep in a stoppered weighing bottle.

Dissolve 12 g iodate-free potassium iodide in 10 ml water in a glass-stoppered weighing bottle (note 2). When the KI has all dissolved and the solution is about at room temperature, weigh the bottle and solution to the nearest milligram. Weigh out on the trip scale about 6.3 g of the resublimed iodine, and transfer to the bottle which holds the KI solution. Quickly restopper the bottle, and reweigh to the nearest milligram. The difference in weight gives the weight of iodine added.

When the iodine has all dissolved, quantitatively transfer the solution to a 500-ml volumetric flask, dilute to volume, and mix well. From the weight of iodine compute the exact normality. The equivalent weight is 126.92 g.

Notes. 1. Iodine may be contaminated with other halogens and with water. Heating with KI causes other halogens to react by displacing iodine from KI. Water is removed by the lime. This should be freshly prepared before use by ignition in a crucible.

2. The iodine is weighed in potassium iodide solution to prevent loss by vaporization during subsequent transfer. The vapor pressure of I_2 from a solution in KI is considerably less than from pure crystals of solid iodine.

Procedure. Preparation of Standard Arsenious Oxide (Sodium Arsenite) Solution. Accurately weigh out a 4.5- to 5-g portion of dry analyzed-grade arsenious oxide, and transfer to a 400-ml beaker. Add 5–10 g reagent-grade NaOH pellets and 10 ml water. Stir, adding a little water if necessary, until all the sodium hydroxide and arsenious oxide have dissolved. Dilute to 100 ml, and neutralize with 6 *N* HCl, using methyl orange or methyl red indicator. When the solution is distinctly acid add about 5 g $NaHCO_3$.

Transfer the solution *quantitatively* to a 1-l. volumetric flask, dilute to volume, and mix well. From the weight and purity of As_2O_3 taken, compute the exact normality. The equivalent weight is $As_2O_3/4$ or 49.45 g.

Procedure. Preparation of Approximately 0.1 *N* Thiosulfate Solution. Clean a 1-l. glass-stoppered bottle with cleaning solution and *rinse thoroughly.* Boil 1 l. of distilled water, and while still hot transfer to the cleaned bottle. Stopper, and allow to cool. Add 25 g reagent-grade sodium thiosulfate crystals, $Na_2S_2O_3 \cdot 5H_2O$, and 2–3 g borax crystals (note). Stopper the bottle, and shake until all the solid is dissolved.

Note. $Na_2S_2O_3$ solutions may decompose on standing as is evidenced by the appearance of milky colloidal sulfur. The precaution of using boiled water which is free of dissolved O_2 and CO_2 and of bacteria, as well as the addition of borax as preservative, leads to the preparation of a fairly stable solution. Other recommended preservatives are sodium carbonate and sodium furoate.

Standardization of Thiosulfate by Iodine. If a standard solution of iodine has been prepared by dissolving a weighed amount, as previously described, this may be used to standardize the thiosulfate solution.

Procedure. Accurately measure out about 40 ml of the thiosulfate solution into a titration flask. Add 3–5 ml starch, and titrate with standard iodine solution. At the end point a drop of iodine imparts a

blue color that pervades the whole solution. If the end point is over-run, back-titrate with thiosulfate. From the normality and volume of iodine solution compute the normality of the thiosulfate. Obtain three results which have an average deviation not greater than $\frac{1}{1000}$.

Standardization of Iodine and Thiosulfate by Arsenious Oxide. This is the recommended method because it gives high accuracy and illustrates both arsenite–iodine and iodine–thiosulfate titrations.

Procedure. Determine by direct titration the relative strength of the iodine and thiosulfate solutions.

Dry at 110°C about 2 g primary standard-grade arsenious oxide. Weigh accurately three samples of about 0.2 g each, and transfer to 250-ml Erlenmeyer flasks. Add to each flask 10–15 ml 1 *N* NaOH (note 1), and warm to hasten solution of the arsenious oxide. Cool in tap water, add a drop of methyl orange or methyl red indicator, and neutralize with 1 *N* HCl solution (note 2) until the solution is distinctly acid. Add about 3 g solid $NaHCO_3$, and swirl the solution until the bicarbonate is all dissolved (note 3). Dilute to 100 ml, add 3 ml starch indicator, and titrate with iodine solution to the appearance of a deep-blue color. If the end point is over-run, back-titrate with thiosulfate solution that has been compared with the iodine. Run a blank (note 4). From the weight and purity of arsenious oxide and the net volume of iodine compute the normality. The equivalent weight of As_2O_3 is 49.45 g. The average deviation for three determinations should not exceed $\frac{2}{1000}$.

From the comparison values for iodine and thiosulfate and the normality of iodine, compute the normality of thiosulfate.

Notes. 1. Prepare by dissolving 2 g reagent-grade pellets in 50 ml distilled water.

2. Prepare by diluting 8 ml concentrated acid to 100 ml.

3. If the end point was not over-run by a large amount in neutralization of the NaOH with HCl, 3 g $NaHCO_3$ is sufficient to neutralize all excess acid and provide a reserve amount to act as a buffer in the iodine titration. As previously shown, hydrogen ion is liberated in the titration, and a buffer is needed to react with it. Write the equation. It is advisable to add another pinch of bicarbonate after the original 3 g is dissolved and note whether effervescence occurs. If so, it shows that the solution is still acid, and more bicarbonate is needed. An excess will do no harm.

4. For the blank add 1–1.5 g potassium iodide to 100 ml water, then add 5 drops hydrochloric acid, 2–3 g sodium bicarbonate, and 2–3 ml starch solution. Titrate with iodine solution to a permanent blue color. Potassium iodide is added in the blank in order to have the amount present that will ordinarily be present in an analysis (because of the use of approximately 40 ml of iodine reagent which contains potassium iodide).

Errors. The chief source of error in this titration is failure to use sufficient bicarbonate to neutralize all the excess acid. If there is in-

sufficient bicarbonate present, the end point appears prematurely, and too little iodine is added. See chemical equation.

Standardization of Thiosulfate by Dichromate. This exercise illustrates the iodometric method for analysis of strong oxidizing agents which must be reduced in solutions of high acidity. A known weight of pure dichromate crystals is treated with excess potassium iodide in sulfuric acid solution, and the liberated iodine is titrated with the solution to be standardized. The reactions are:

$$Cr_2O_7^{=} + 14H^+ + 6I^- = 3I_2 + 2Cr^{+++} + 7H_2O$$

$$3I_2 + 6S_2O_3^{=} = 6I^- + 3S_4O_6^{=}$$

Thus 1 molecule of $K_2Cr_2O_7$ requires 6 $S_2O_3^{=}$ ions, and the equivalent weight of potassium dichromate is 49.04 g.

Reagent-grade potassium dichromate is usually of sufficient purity for student requirements. A small portion should be ground and dried by heating in an evaporating dish at 175–200° for 30 minutes (heat in a sand bath, with a thermometer bulb imbedded in the powder).

Procedure. Accurately weigh out three portions of about 0.2 g of the dry powdered crystals. Transfer to a 500-ml Erlenmeyer flask, and dissolve in 100 ml 2 *N* sulfuric acid (note 1).

★ Add to the solution in small portions and with constant swirling 2 g powdered sodium carbonate (note 2), and then pour in a solution of 10 g iodate-free potassium iodide dissolved in 10 ml water. Swirl to mix. Cover the flask with a watch glass, to exclude air, and allow to stand 5–10 minutes (note 3). Dilute to 350 ml (note 4), and titrate with thiosulfate solution until the brown color of iodine begins to fade, then add 3–5 ml starch solution and complete the titration. At the end point the blue color of starch–iodine disappears, leaving the green color of chromic ion.★★

From the weight of dichromate used and the volume of thiosulfate, compute the normality of the latter. Duplicate results should agree with an average deviation of $\frac{2}{1000}$.

Notes. 1. Prepare by adding 30 ml concentrated H_2SO_4 to 500 ml water. Mix well.

2. The carbon dioxide evolved displaces air, thereby preventing air oxidation of iodide ion in the acid solution. Swirl gently to mix, but avoid vigorous agitation. Use the specified weight of Na_2CO_3; too much will exhaust the acid.

3. Time must be allowed for complete reaction. Longer standing is undesirable because of the possibility of air oxidation.

4. The final concentration of acid is about 0.4 *N*.

Errors. In addition to ordinary volumetric errors, the following may affect this titration:

1. Oxidation of iodide ion by air.

2. Insufficient acidity, which causes incomplete reduction of dichromate by iodide ion.

3. Loss of iodine vapor. The flask should be kept closed except during the titration. Avoid vigorous shaking.

4. Premature addition of starch. See the discussion of the use of starch.

5. Presence of iodate in the potassium iodide. If the test outlined on page 241 shows that iodate is present, a blank should be determined and a correction made for the volume of thiosulfate consumed in the blank.

Standardization of Thiosulfate by Copper. The reaction of copper with iodide ion and the iodometric determination of copper are discussed in the following sections. Commercial copper wire and sheet are of high purity and are often used as primary standards for thiosulfate solutions. The chief difficulty is in the end point, which is difficult to obtain accurately until some experience is gained.

Procedure. Clean a small piece of copper sheet or wire by immersing briefly in dilute nitric acid, washing, and drying. Weigh accurately three portions of about 0.3 g (note 1). Place each portion in a 250-ml Erlenmeyer flask and add 1.5 ml concentrated nitric acid and 5 ml water. Set the flask on the steam bath, and allow to stand until the copper has all dissolved (note 2); then dilute to 30–50 ml.

Follow the procedure given on page 248, beginning with the star.

From the weight of copper and volume of thiosulfate compute the normality of the latter. The average deviation in three determinations should not exceed $\frac{2}{1000}$.

Notes. 1. The equivalent weight of copper in this reaction is its atomic weight, 63.54 g.

2. Do not leave on the bath after the copper has dissolved, since, if the acid evaporates, the copper nitrate may not readily redissolve.

Errors. See discussion on page 249.

ANALYSES

Cr in Soluble Chromate. Obtain the sample in a stoppered weighing bottle. Dry in the oven. Weigh out accurately three 0.5- to 1-g samples as directed by the instructor, and transfer to 500-ml Erlenmeyer flasks. Dissolve in 100 ml 2 *N* sulfuric acid. Follow the procedure on page 244, beginning with the star and ending with the double star. From the volume and normality of the thiosulfate solution com-

pute the weight and percentage of Cr in the sample. Read the notes and discussions of errors on page 244.

Sb in Soluble Antimony Sample. Obtain the sample in a stoppered weighing bottle, and dry in the oven. Weigh out accurately three 1-g samples (note 1), and transfer to 250-ml Erlenmeyer flasks. Dissolve in a solution of 5 ml HCl in 50 ml water. Add 3 g powdered tartaric acid (note 2), and carefully neutralize with 1 *N* NaOH (note 3), using methyl red or methyl orange indicator. If the end point is overrun bring the solution back to the acid side by a few drops of HCl, taking care to avoid any large excess. When the solution is barely acid, add 3 g powdered $NaHCO_3$, and swirl until the bicarbonate is dissolved. Add 3–5 ml starch solution, and titrate immediately with a standard iodine solution. Compute the percentage of Sb in the sample. The equivalent weight is Sb/2.

Notes. 1. Based upon Sb percentages of 15–25.

2. Tartaric acid forms the complex $H(SbO)C_4H_4O_6$ which is soluble. This prevents precipitation of basic antimony salts when the solution is neutralized. If tartar emetic is used as student sample (see instructor), it may not be necessary to add tartaric acid.

3. Prepare by dissolving 4 g reagent-grade NaOH in 100 ml water.

Antimony in Stibnite. The analysis of stibnite, an ore which consists chiefly of antimony sulfide along with a little silica, is a common student exercise. If arsenic and iron are present, it is necessary to use a complicated procedure for the separation of antimony, but in the absence of interfering substances it is sufficient to bring the ore into solution and titrate the trivalent antimony without any separations.

The ore is disintegrated in concentrated hydrochloric acid and the solution heated to expel hydrogen sulfide. Potassium chloride is added prior to the acid treatment to prevent loss of antimony trichloride by volatilization. Excess chloride ion gives the complex $SbCl_4^-$ ion which is not volatile. After removal of hydrogen sulfide, the solution is diluted, neutralized, and buffered by addition of sodium bicarbonate. Trivalent antimony is titrated in the buffered solution with iodine. Precipitation of basic antimony salts is prevented by addition of tartaric acid, which forms the complex $H(SbO)C_4H_4O_6$.

Procedure. If the ore is not well ground as received, it should be ground to a fine powder (not usually necessary with student samples). Dry the sample at 110°. Weigh out accurately three 0.5- to 3-g samples (consult instructor as to approximate percentage of antimony), and transfer to dry 250-ml beakers. Add about 0.3 g potassium chloride crystals, which have been ground to a fine powder. Pour 10 ml hydrochloric acid over the sample, cover the beaker with a watch glass, and

set on the steam bath for disintegration of the sulfide. At the end of 15 minutes the disintegration should be complete; the residue (silica) should be white.

When decomposition is complete, add 3 g powdered tartaric acid, and continue heating on the steam bath for 10–15 minutes. Dilute to 100 ml by slowly adding water from a pipet. If a red precipitate of antimony sulfide appears, stop the addition of water, and place the beaker on the steam bath until the precipitate redissolves and all hydrogen sulfide is expelled from the solution. If a white precipitate of basic antimony salts appears, discard the determination. Such a precipitate once formed is difficult to redissolve.

Add a drop of methyl orange or methyl red indicator (or a strip of litmus paper), and neutralize the solution by slow addition of 6 *N* NaOH solution (note 1). Try to avoid a large excess of NaOH. Add 6 *N* HCl solution (note 2) until the solution is distinctly acid, but avoid a large excess. Now add about 3 g powdered $NaHCO_3$, and stir until it is dissolved. At this point the acid should be all neutralized, and sufficient bicarbonate should be present to buffer the solution during the subsequent titration. Test for excess bicarbonate by adding another pinch of powder and noting whether there is further evolution of CO_2. If there is, add more bicarbonate.

Quantitatively transfer the solution to a 500-ml Erlenmeyer flask, and titrate with standard iodine solution, using 3–5 ml starch indicator. From the volume and normality of iodine used compute the percentage of antimony in the ore. The equivalent weight is Sb/2 or 60.88 g.

Notes. 1. Prepare by adding 6 g reagent-grade pellets to 25 ml water.
2. Prepare by adding 10 ml concentrated HCl to 10 ml water.

Errors. The chief source of error is due to insufficient bicarbonate to buffer the solution completely. When this occurs, the end point fades badly.

Copper. Two methods are widely used for the determination of copper, electrolytic deposition and titrimetric by iodometry. The latter is based on the reaction,

$$2Cu^{++} + 4I^- = 2CuI + I_2$$

This reaction goes to completion because cuprous iodide is precipitated. The iodine liberated is titrated, without removal of the CuI precipitate, with standard thiosulfate solution.

The reactions are carried out in acid solution, for the reasons discussed on page 240. Strongly acid solutions cannot be used because air oxidation of iodide ion (catalyzed by cuprous ion) is favored. Moreover,

thiosulfate titrations should not be made in too strongly acid a solution. The copper analysis is best done at a *p*H of about 3–4; a buffered acetic acid solution is ordinarily employed. The chief interfering substances are oxides of nitrogen and the elements such as trivalent or pentavalent arsenic and antimony, which react with iodine or with iodide ion. Since copper samples are usually dissolved in nitric acid, special precautions must be taken to remove oxides of nitrogen. This may be done by evaporation in the presence of sulfuric acid until all nitrates are expelled, or more simply by using only a slight excess of nitric acid and removing the oxides of nitrogen by adding to the solution a little urea which reacts rapidly and quantitatively with nitrous acid. Use of too great an excess of urea causes the end point of the titration to be uncertain.

The presence of a precipitate of cuprous iodide causes some difficulty in recognition of the end point. Much of this is avoided if starch is not added until practically all the iodine has reacted. With a little experience this point is readily recognized by the fading of the iodine color. When starch is added prematurely, it is adsorbed on the surface of the precipitate and is not readily decolorized. The end point may be made sharper by adding 1–2 g ammonium or potassium thiocyanate just prior to the addition of starch. Thiocyanate ion is adsorbed by cuprous iodide and displaces adsorbed iodine.[4] The same effect can also be obtained by adding a few drops of nitrobenzene.

Procedure. Copper Solution. The sample is a weighed portion of copper sheet or wire dissolved in 7–8 ml HNO_3. Obtain in a 250-ml volumetric flask. If the sample has not all dissolved, place the flask (unstoppered) on the steam bath until solution is complete. Dilute to the mark, and mix thoroughly. Properly rinse the pipet, and pipet out four 50-ml aliquot portions; deliver them into 250-ml Erlenmeyer flasks.

★ Heat the solution to boiling, and add 5 ml of a solution which contains 1 g urea per 25 ml. Boil for 1 minute. Cool in tap water, and neutralize with 1:4 ammonium hydroxide until a blue–green precipitate of cupric hydroxide begins to form. Avoid sufficient excess ammonium hydroxide to give the blue color of the cupric ammonia ion (note 1). Add to the neutral solution 5 ml glacial acetic acid, cool to room temperature if warm, and add a solution of 5 g potassium iodide in 10 ml water. Cover the flask with a watch glass, and allow to stand 2 minutes. Titrate with standard thiosulfate solution. When the color of iodine begins to fade, and the precipitate appears almost pure white (note 2), add 5 ml starch solution, and complete the titration until one drop of thiosulfate causes disappearance of the blue color. Optionally,

[4] H. W. Foote and J. E. Vance, *Ind. Eng. Chem., Anal. Ed.*, **8**, 119 (1936); *J. Am. Chem. Soc.*, **57**, 845 (1935).

2 g ammonium or potassium thiocyanate (note 3) may be added just before addition of starch and the solution swirled until all the thiocyanate is dissolved; then starch may be added and the titration completed.

Compute the weight of copper in each aliquot portion, and report the total weight received. The equivalent weight is 63.54 g.

Notes. 1. If any appreciable concentration of ammonium salts is present, the hydroxide-ion concentration is so repressed that the cupric hydroxide precipitate does not form. The use of too much nitric acid or urea may lead to this condition. If too much ammonium hydroxide is used (blue color of cupric ammonia complex), it is neutralized by the acetic acid, leading to formation of an ammonium acetate buffer. This condition causes poor end points. Careful control of *p*H is important.

2. It often happens that students spoil the first sample by failure to recognize the proper point at which to add starch. Use of four samples is specified so that three good values may be obtained even if the first is spoiled.

3. A blank should be run on the thiocyanate to establish the absence of reducing-agent impurities (often sulfides) in the reagent which might react with iodine. Dissolve 2 g of reagent in a small amount of water, add 5 ml starch indicator, and determine the volume of standard I_2 solution to produce the blue color.

Errors. In addition to the usual volumetric errors, the following may occur:

1. Presence of oxides of nitrogen, leading to excess oxidation of iodide ion.
2. Incorrect *p*H, due to use of too much nitric acid, urea, or ammonia.
3. Difficulty in determination of end point.
4. Air oxidation, because of too slow titration.
5. Loss of iodine from the solution, due to vigorous swirling.

Copper Ore. Copper ores usually contain iron, arsenic, and antimony. All these can cause interference in the iodometric determination of copper unless the copper is isolated or unless the titration is carried out under conditions that will prevent interference. The copper can be isolated by dissolving the sample in nitric acid, converting to a sulfuric acid solution, and precipitating the copper with zinc or aluminum. The precipitated copper is then dissolved in nitric acid and determined according to the procedures given previously. In the Park method [5] no separations are made. Interference from ferric iron is prevented by addition of ammonium bifluoride, which causes formation of the stable complex, $FeF_6^{\equiv}$. Arsenic and antimony are oxidized to the pentavalent condition by the procedure used for bringing the sample into solution. In this form they cause no interference provided that the *p*H of the solution is carefully regulated at a value of about 3.5. A phthalate buffer serves for *p*H regulation.

[5] B. Park, *Ind. Eng. Chem., Anal. Ed.*, **3**, 77 (1931).

Procedure. Weigh out sufficient sample to furnish about 0.2 g Cu (instructor), and transfer to 150-ml beaker. Add 20 ml nitric acid, and heat on the steam bath until all copper is in solution. Evaporate on steam bath to a volume of about 5 ml. Add 5 ml urea solution (1 g in 25 ml), and heat for a few minutes, then dilute to 30 ml, place the beaker on a wire gauze, and bring the solution to a boil (avoid spattering). Filter while hot, and wash the residue well with hot dilute nitric acid (1:100), catching the washings with the filtrate in a wide-mouth Erlenmeyer flask. Place the filtrate on the steam bath, and evaporate to about 30 ml. Cool and add 6 *N* ammonium hydroxide to precipitate the iron. When a precipitate begins to appear, add the hydroxide a drop at a time, testing after each addition for the smell of ammonia above the solution. When ammonia is faintly detectable by smell, after residual gas is blown away from above the surface, the iron is all precipitated. There should not be sufficient excess ammonia at this point to give the deep-blue color of the cupric ammonia complex. Add exactly 2.0 g ammonium bifluoride, and swirl until it is dissolved; then add 1.0 g potassium acid phthalate, and swirl until dissolved. Add 3.0 g potassium iodide, and swirl gently until dissolved. Titrate at once with standard thiosulfate solution, as directed in the preceding exercise. Report the percentage of copper in the ore.

Iodide Ion. The amount of iodide ion in a sample can be determined by quantitative oxidation to iodine and titration of the iodine with thiosulfate. It is, of course, necessary to remove all excess of oxidizing agent before the thiosulfate titration. This limits the choice of oxidizing agents that can be used. Sodium nitrite in dilute sulfuric acid solution is a convenient oxidizer; the excess of nitrite can be removed by urea, as described in the iodometric method for copper. Bromine or chlorine cannot be used unless care is taken to oxidize all the iodine to iodic acid, since otherwise there is uncertainty as to the equivalents of iodine formed. When the amount of iodine in a sample is very small, an acid solution may be treated with bromine and boiled until all bromine is expelled. This oxidizes iodine quantitatively to iodic acid. The sample is now treated with an excess of potassium iodide, and iodine is liberated. The liberated iodine is titrated with standard thiosulfate. This method has the advantage that each equivalent of iodide ion originally present gives six equivalents of titratable iodine. The reactions are:

$$I^- + 3Br_2 + 3H_2O = IO_3^- + 6Br^- + 6H^+$$

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

This method is often used for the determination of iodine in biological samples.

QUESTIONS

1. Write ionic equations to represent all the reactions involved in the following; include reactions used to dissolve materials, etc.

(*a*) The iodimetric determination of sulfur present as H_2S.

(*b*) The standardization of I_2 solution with As_2O_3.

(*c*) The standardization of $Na_2S_2O_3$ solution with Cu.

2. Why have so many volumetric redox methods been developed which involve iodine?

3. What errors arise in iodometric procedures from:

(*a*) Too low a *p*H at the time of titration?

(*b*) Addition of starch at the beginning of the titration?

(*c*) Use of partially decomposed starch solution?

4. Why is borax or sodium carbonate sometimes added to thiosulfate solutions?

5. Why is starch often an unsatisfactory indicator if a solution contains a high concentration of electrolytes?

6. Describe a method whereby a thiosulfate solution could be standardized by pure iron wire.

7. In the standardization of thiosulfate with permanganate, dichromate, etc., why is the standard added to a strongly acid solution? Why is the solution later diluted before titration with thiosulfate? Why cannot thiosulfate be directly titrated against such oxidizing agents as permanganate?

8. Why must the iodimetric determination of As^{+++} or Sb^{+++} be made in buffered solutions? What *p*H is employed?

9. Predict the effects of the following errors on the specified determinations:

(*a*) In the standardization of $Na_2S_2O_3$ with $K_2Cr_2O_7$ sodium carbonate is not added.

(*b*) In the analysis for Cu urea is not added.

(*c*) Atmospheric oxidation takes place during the standardization of $Na_2S_2O_3$ with Cu.

(*d*) A blank is not run on the KI which contains a small amount of KIO_3; the KI is used in an analysis of a soluble chromate sample.

10. In the stibnite determination what would be the effect on the result if:

(*a*) The H_2S were not all boiled out of solution?

(*b*) The $NaHCO_3$ were not added?

11. Why is it advisable, in indirect iodine determinations, to prepare *four* samples, instead of the three samples ordinarily employed for other volumetric analyses?

12. List the errors which may result from the incorrect use of starch solution.

13. List the errors common to all indirect analyses involving iodine.

14. Describe a method for standardization of a thiosulfate solution by indirect comparison with a standard sodium hydroxide solution. Give equations for each reaction involved. What indicator should be used for each titration?

PROBLEMS

1. Express the strength of a 0.0900 *N* iodine solution in terms of the titer for the following substances: As, As_2O_3, As_2O_5, H_2S, H_2SO_3, S, CdS.

2. What is the titer of 0.1000 *N* thiosulfate solution for each of the following substances: I, Cu, Fe, $K_2Cr_2O_7$, Cr_2O_3, $KMnO_4$?

3. How much of the substance in column *B* will react with the stated amount of reagent in column *A*?

A	*B*
30.00 ml 0.1000 *N* I_2	____ g As_2O_3
35.00 ml 0.2000 *N* $Na_2S_2O_3$	____ mg $K_2Cr_2O_7$
150.0 mg Cu	____ ml 0.0950 *M* $Na_2S_2O_3$
40.00 ml 0.1000 *M* $KMnO_4$	____ ml 0.1000 *M* $Na_2S_2O_3$

4. Calculate the normalities of the following thiosulfate solutions:

(*a*) 31.67 ml $Na_2S_2O_3$ is equivalent to 0.3500 g pure I_2.

(*b*) 35.15 ml $Na_2S_2O_3$ is equivalent to 0.2500 g electrolytic Cu.

(*c*) 41.22 ml $Na_2S_2O_3$ is equivalent to 37.84 ml I_2; 35.62 ml I_2 is equivalent to 0.2750 g As_2O_3.

(*d*) 29.08 ml $Na_2S_2O_3$ is equivalent to 0.1000 g $KBrO_3$.

(*e*) 36.52 ml $Na_2S_2O_3$ is equivalent to 0.2982 g KIO_3.

5. A solution of thiosulfate is standardized with pure potassium dichromate. From the following data calculate the normality of the solution.

Buret readings: after	41.73 ml
before	0.51 ml
Weight sample plus container	16.3852 g
Weight container	16.1731 g
Buret readings for the blank: after	0.15 ml
before	0.07 ml

6. 1.000 ml $K_2Cr_2O_7$ is equivalent to 0.005585 g Fe; 20.00 ml $K_2Cr_2O_7$ liberate the iodine which is titrated by 32.46 ml $Na_2S_2O_3$. What is the normality of the latter solution?

7. Find the copper titer of a thiosulfate solution from the following data:

40.16 ml $KMnO_4$ is equivalent to 200.0 mg As_2O_3.

35.79 ml $KMnO_4$ liberates iodine which is titrated by 41.07 ml $Na_2S_2O_3$.

8. To a mixture of 97.31 ml of 0.1096 *N* I_2 and 97.21 ml 0.1098 *N* $Na_2S_2O_3$ a drop of starch is added. Is the mixture blue or colorless?

9. How many milligrams of As_2O_3 will react with the I_2 equivalent to 35.00 ml $Na_2S_2O_3$ solution if 40.00 ml $Na_2S_2O_3$ solution is equivalent to 3.000 m mol metallic copper?

10. What range of weights of $K_2Cr_2O_7$ as a primary standard should be used for the standardization of a 0.0500 *N* $Na_2S_2O_3$ solution? Should individual samples or aliquot portions be used?

11. How many grams of $KIO_3 \cdot HIO_3$ (potassium biniodate) are contained in 500 ml of 0.1000 *N* solution?

12. A soluble chromate is treated with excess KI in the presence of strong acid; after dilution 35.00 ml 0.1600 *N* $Na_2S_2O_3$ is required to titrate the liberated I_2. What is the weight of Cr in the sample?

13. Calculate the percentage of CuO in an ore from the following:

weight of sample	0.4217 g
volume of $Na_2S_2O_3$	35.16 ml

41.22 ml $Na_2S_2O_3$ is equivalent to 0.2121 g $K_2Cr_2O_7$

14. Find the percentage of Cu_2O in an ore from the following:

30.10 ml I_2 is equivalent to 0.2475 g As_2O_3.

50.00 ml $Na_2S_2O_3$ is equivalent to 30.10 ml I_2.

0.6092 g ore requires 30.46 ml $Na_2S_2O_3$.

15. What would be a satisfactory range of sample weights for the analysis of an unknown which is approximately 15 per cent As_2O_3 by titration with 0.1250 N I_2?

16. 18.00 ml 0.1000 M $KMnO_4$ reacts with excess KI to liberate a quantity of I_2 which in turn requires 45.00 ml $Na_2S_2O_3$ for titration. 30.00 ml of the thiosulfate solution is needed to titrate the iodine liberated by a copper sample. Calculate the milligrams of copper in the sample.

17. The As_2O_3 titer of an I_2 solution is 5.100 mg per milliliter. Find the percentage purity of a stibnite ore which required 27.50 ml I_2 to titrate a 0.5000-g sample.

18. What is the percentage purity of a sample of tartar emetic, $K(SbO)C_4H_4O_6$ if 0.5063 g requires 38.63 ml of an I_2 solution for titration in the presence of $NaHCO_3$. The As_2O_3 titer of the I_2 is 1.000 mg per milliliter.

19. The reaction between IO_3^-, I^- and H^+ to form I_2 and the reaction of the latter with $S_2O_3^=$ may be used to standardize an acid. A weighed sample of iodate is dissolved in a solution which contains an excess of KI and $Na_2S_2O_3$. The solution is titrated with the acid until all the iodate is used up and H^+ is in excess as shown by methyl orange indicator. In such a standardization 32.56 ml of an acid was needed to titrate a solution containing 0.5455 g pure KIO_3. What is the normality of the acid?

20. A 0.2352-g sample of pyrolusite (MnO_2) is heated with excess hydrochloric acid, and the distillate is passed into excess potassium iodide solution. The iodine liberated requires 47.82 ml 0.1123 N thiosulfate solution for titration. Calculate the percentage of manganese dioxide in the pyrolusite.

21. An iron sample contains 0.05 per cent of S, present as sulfide. If a 1.000-g sample is analyzed iodimetrically, what concentration of iodine solution should be used in order that the volume of solution be 30 ml or greater?

22. What weight of potassium bromate is required to liberate sufficient iodine to react with 30.00 ml thiosulfate solution, 42.56 ml of which is equivalent to 37.95 ml of an iodine solution; 30.00 ml of the iodine solution is equivalent to 0.1575 g pure arsenious oxide.

23. Lead may be estimated volumetrically by electrolyzing to convert the lead to the dioxide PbO_2, dissolving the dioxide in an acid solution of potassium iodide, and titrating the liberated iodine with thiosulfate; 0.5670 g of an ore required 36.23 ml 0.0998 N thiosulfate for titration of the liberated iodine. Calculate the percentage of lead in the ore.

$$PbO_2 + H^+ + I^- = Pb^{++} + I_2 + H_2O \text{ (unbalanced)}$$

24. Lead can be determined by precipitating it as $PbCrO_4$, dissolving in acid, adding excess KI, and titrating with $Na_2S_2O_3$. What volume of 0.1400 N $Na_2S_2O_3$ would be required to titrate the iodine liberated by the sample of Problem 23? Often the acidified chromate solution is directly titrated with $FeSO_4$ solution. What volume of 0.1250 N $FeSO_4$ solution would be required to titrate the sample of Problem 23?

25. Calculate the normality of a $Na_2S_2O_3$ solution from the following:

Normality of NaOH = 0.1000
21.29 ml NaOH is equivalent to 32.15 ml KHC_2O_4.
32.15 ml KHC_2O_4 is equivalent to 54.60 ml $KMnO_4$.
27.30 ml $KMnO_4$ is equivalent to 21.29 ml $Na_2S_2O_3$.

26. A 3.565-g sample of bleaching powder is shaken thoroughly with water and diluted to 500 ml. 25.00 ml of this required 29.62 ml 0.1042 N $Na_2S_2O_3$ to titrate

the I_2 liberated when the bleaching powder solution is mixed with KI. Find the percentage of available chlorine in the bleaching powder.

27. How many milliliters of a solution which contains 1.500 g 99.5 per cent As_2O_3 in 250 ml are needed to directly titrate a 50.00-ml aliquot of the bleaching powder solution of Problem 26?

28. Small amounts of gold are estimated by an iodometric procedure whereby the iodine producing reaction is:

$$AuCl_3 + 3KI = AuI + I_2 + 3KCl$$

What volume of $N/1000$ $Na_2S_2O_3$ is needed to titrate the iodine liberated by the gold in 1.000-g ore which contains 0.030 per cent Au?

29. 0.5000 g of a sample of KI is added to 50.00 ml of 0.1000 N KIO_3 which is acidified; the mixture is boiled until the I_2 is expelled. The solution is cooled, and 2–3 g KI is added. It requires 21.21 ml 0.0956 N $Na_2S_2O_3$ to titrate. Find the percentage purity of the KI.

30. The Hinman method for the volumetric determination of sulfate involves the addition of an acidified solution of $BaCrO_4$ to the unknown. After the $BaSO_4$ has precipitated, the solution is made basic, and the excess $BaCrO_4$ precipitates. One mole of $CrO_4^=$ is left in solution for each mole of $SO_4^=$ precipitated. The precipitate is removed by filtration, and the solution is acidified, treated with KI, and titrated with $Na_2S_2O_3$. How many milliliters of 0.1108 N $Na_2S_2O_3$ are needed to titrate a 0.1500-g sample of $(NH_4)_2SO_4$ treated as described?

31. What weight of steel must be taken for analysis so that each 1.000 ml of 0.0100 N I_2 solution represents 0.0100 per cent S in the sample?

CHAPTER

14

Oxidation–reduction IV. Other Oxidizing Agents

Until recently the majority of oxidation–reduction determinations were made either with permanganate or by the methods involving iodine, because of lack of an indicator for use with other oxidizing agents. The development of general oxidation–reduction indicators has given impetus to the use of other oxidizing agents.

CERIC SULFATE[1]

Ceric sulfate has about the same oxidation potential as potassium permanganate, and it may replace permanganate in all titrations. In certain reactions, however, which proceed readily with permanganate, a catalyst must be employed with ceric sulfate. Examples of this are the titration of oxalate, usually catalyzed by iodine monochloride, and the titration of arsenious acid, catalyzed by osmium tetroxide. Ceric sulfate must be employed for titration in acid solution; ceric salts are hydrolyzed in basic or neutral solutions. The advantages of ceric sulfate are the following:

1. Stability. Solutions of concentration from 0.01 N to 0.1 N or stronger are stable, both hot and cold, and may be preserved indefinitely.

2. Ceric sulfate may be used in the presence of rather high concentration of hydrochloric acid without any oxidation of chloride ion. Because of this, ceric sulfate is a much better reagent than permanganate for the determination of iron by the Zimmermann–Reinhardt process.

3. Ceric ion can undergo, in acid solution, but one reaction:

$$Ce^{++++} = Ce^{+++}$$

[1] See the various publications appearing in the *Journal of the American Chemical Society* and in *Industrial and Engineering Chemistry, Analytical Edition.*

4. The color of ceric solutions does not obstruct observation of the position of the meniscus in solutions of concentration not greater than 0.1 *N*.

5. The product of the reaction of ceric ion, cerous ion, is colorless.

6. A ceric salt suitable for a primary standard is available. This salt is the complex hexanitrato ammonium cerate,[2] $(NH_4)_2Ce(NO_3)_6$. It may be used for direct preparation of solutions of known concentration by being dissolved in dilute sulfuric acid, evaporated until the nitrate complex is decomposed and the nitric acid is volatilized, and then diluted to volume.

Other Ceric Salts.[3] Recent work [4] has shown that other ceric salts behave somewhat differently from ceric sulfate. The oxidation potential of tetravalent cerium is to a high degree dependent on the acid anion present. This suggests that we are not dealing with the simple Ce^{++++} ion, but with complex anions, probably of the composition $CeX_6^{=}$. To each complex ion there can be assigned an oxidation potential, which depends on the degree of stability of the complex, just as the oxidizing power of heptavalent manganese is expressed in terms of the oxidizing potential of the stable complex, MnO_4^{-}. The oxidation potential is least for hydrochloric acid solutions and increases in order with the series sulfuric, nitric, and perchloric acids. The fact that ceric salts do not oxidize chlorides in the Zimmermann-Reinhardt process, whereas permanganate does oxidize chlorides under the same conditions, is probably due to the low oxidizing potential in a hydrochloric acid medium. The high potentials obtained in nitric and perchloric acid media provide the analyst with a superoxidizing agent. Smith and Getz (*loc. cit.*) have shown that oxalates can be titrated quantitatively *in the cold* by nitric or perchloric acid solutions of ceric salts, without a catalyst. This same titration with ceric sulfate requires a catalyst and an elevated temperature. The high-potential ceric salts are not so stable in solution as ceric sulfate, because of the great tendency to gain an electron, but they are sufficiently stable that the solutions may be satisfactory if restandardized occasionally. These high-potential oxidizers will doubtless broaden the field of oxidation determinations, as further studies are made.

Indicator. The oxidation indicator for most ceric ion titrations is orthophenanthroline ferrous complex, $Fe(C_{12}H_8N_2)_3^{++}$, which is pre-

[2] G. F. Smith, V. R. Sullivan, and G. Frank, *Ind. Eng. Chem., Anal. Ed.*, **8**, 449 (1936).

[3] A knowledge of oxidation–reduction theory, as given in Chapter 15, is necessary before this section is studied.

[4] G. F. Smith and G. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191, 304 (1938).

pared by adding a solution of orthophenanthroline to a ferrous salt. On oxidation the ferrous complex is converted into the ferric complex, $Fe(C_{12}H_8N_2)_3^{+++}$. The color change is from an intense red to a faint blue color.[5] This change is apparently caused by a molecular rearrangement within the complex ion when the iron atom is oxidized.

The indicator is purchased under the trade name of "Ferroin" as a 0.025 *M* solution of the ferrous complex. One drop is used for a titration volume of 100–150 ml.

Preparation of Ceric Sulfate Solution. Dissolve 63 g reagent-grade ammonium tetrasulfato cerate dihydrate (notes 1, 2) or an equivalent amount of other reagent-grade ceric sulfate compound in 500 ml 2 *N* sulfuric acid, and dilute to 1 l. Store in a glass-stoppered bottle. If the solution becomes turbid on standing, owing to slow precipitation of ceric phosphate, filter through a Gooch or Selas crucible. The solution is approximately 0.1 *N*.

Notes. 1. The formula of this salt is $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$, and the molecular weight 632.53.

2. Other salts are $Ce(SO_4)_2$ and $H_4Ce(SO_4)_4$.

Standardization. Sodium oxalate, arsenious oxide, and iron wire of known assay value may be used for standardization. With the first two it is necessary to employ a catalyst; iron wire [6] is preferable, since the most frequent use of ceric sulfate is in the analysis of iron samples.

Procedure. Iron Wire. Weigh accurately three 0.25-g samples of clean bright wire, and transfer to 500-ml Erlenmeyer flasks. Dissolve in 10 ml hydrochloric acid (note 1). Heat the solution nearly to boiling, and add stannous chloride solution (note 2), drop by drop, until the sample is decolorized (note 3). Avoid an excess of more than 1 drop. Cool completely, and pour in rapidly 10 ml mercuric chloride solution (note 4). Allow to stand 3–5 minutes, then add 10 ml hydrochloric acid, dilute to 300 ml, add 1–2 drops "Ferroin" indicator, and titrate to a sharp color change. Calculate the normality of the ceric sulfate solution. No indicator blank is employed.

Notes. 1. When solution is complete, there may still be a residue of small pieces of carbon floating in the liquid. This may be disregarded.

[5] When used in an iron titration the color change will be to green which results from the blue of the indicator and the yellow of the Fe solution.

[6] Iron wire labeled "for standardization" has been repeatedly tested by comparison with primary standard-grade sodium oxalate and found to be reliable. Ordinary wire is unsuitable because of the carbides present. If a suitable grade of wire is not available, the solution may be standardized by comparison with an iron ore of known analysis.

2. For preparation of the stannous chloride and mercuric chloride solutions, see Zimmermann–Reinhardt process, page 222.

3. The first drop added may cause decolorization, since there is little opportunity for oxidation during solution of the sample.

4. No preventive solution is needed when ceric sulfate is used as oxidizing agent.

Procedure. Analysis of Iron Ore. Read carefully the directions of page 223 for the Zimmermann–Reinhardt process. The ceric sulfate determination is identical with the permanganate one except for the preventive solution and the indicator used.

Proceed as on page 223 with solution of the sample and reduction by stannous chloride. Cool, and add rapidly 10 ml mercuric chloride solution. Allow to stand 3–5 minutes, then add 300 ml cold distilled water and 1–2 drops ferrous orthophenanthroline indicator. Titrate as in the standardization. Compute the percentage of iron in the ore.

POTASSIUM DICHROMATE

Potassium dichromate has been used for the analysis of iron ores for many years because of the fact that hydrochloric acid solutions of the sample can be titrated accurately without the occurrence of side reactions between the oxidizing agent and chloride ion. The procedure followed in the past, however, was very tedious because of the lack of a suitable internal indicator. The titration was performed by aid of a spot-test indicator, a solution of potassium ferricyanide serving to indicate the point at which ferrous ion disappeared from the solution being titrated. The use of dichromate has received fresh impetus with the discovery of suitable internal oxidation indicators. It possesses the advantages of cheapness and non-reduction by chloride ion.

Indicator. Since the oxidation potential of dichromate is somewhat lower than that of permanganate and ceric ions, it is advisable to employ as indicator a lower oxidation potential substance than that of the ferrous orthophenanthroline complex. The latter will give an accurate end point (near the stoichiometric point) with dichromate titrations of iron only if the acidity of the solution is very high. A better indicator is the sodium or barium salt of diphenylamine sulfonic acid. The color change obtained is sharp, the indicator turning from colorless to a deep purple. The amount of dichromate required for oxidation of the indicator is negligible, when 0.1 N solutions are employed, but with more dilute solutions the indicator should be partially oxidized before use.[7]

Preparation and Standardization of Solution. Although potassium dichromate is usually obtained in sufficient purity for use as a

[7] H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, **5**, 154 (1933).

primary standard,[8] it is necessary to standardize the solutions used for the analysis of iron ores with iron wire. The end point obtained in iron titrations does not agree with the stoichiometric point as shown by electrometric titrations, but comes somewhat after the stoichiometric point. The deviation from the stoichiometric point cannot be compensated by an indicator blank, because the presence of iron is essential. If standardization is made by use of iron samples the end-point error will cancel in the analysis of iron samples.

Procedure. Weigh out approximately 5 g potassium dichromate, dissolve, and dilute to 1 l. Weigh accurately three 0.25-g portions of primary standard-grade iron wire, and transfer to 500-ml Erlenmeyer flasks. Dissolve in 10 ml hydrochloric acid. Heat the solution nearly to boiling, and add stannous chloride[9] solution, drop by drop, until the sample is decolorized. Avoid an excess of more than 1 drop. Cool completely, and pour in rapidly 10 ml mercuric chloride[9] solution. Allow to stand 3–5 minutes. Pour in 300 ml of a solution containing 40 ml sulfuric acid and 15 ml 85 per cent phosphoric acid per liter. Add 6–8 drops diphenylamine sulfonic acid indicator, and titrate with dichromate solution, adding the reagent very slowly and with constant swirling of the solution in the flask. When the color begins to change, add dichromate a drop at a time. The end point is marked by the first appearance of a purple or violet tinge. Compute the iron titer of the solution.

Analysis of Iron Ore. Read carefully the directions of page 223 for the Zimmermann-Reinhardt process. The dichromate process is almost identical with the permanganate determination.

Proceed as on page 223 with solution of the sample, reduction by stannous chloride, and addition of mercuric chloride solution. After the mercuric chloride is added, allow to stand 3–5 minutes, and then add 300 ml of a well-cooled solution containing 40 ml sulfuric acid and 15 ml 85 per cent phosphoric acid per liter. Titrate immediately with standard dichromate solution according to the directions given previously for standardization. Report the percentage of iron in the ore.

POTASSIUM BROMATE

Potassium bromate is a somewhat different type of oxidizing agent from those previously described. Although it has a high oxidation potential, it is not usually employed for the common reducing agents because the usual redox indicators will not give a correct end point.

[8] H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, **7**, 57 (1935).

[9] See page 222 for preparation of stannous chloride and mercuric chloride solutions.

Reduction of BrO_3^- in acid solution proceeds according to the equation,

$$BrO_3^- + 6H^+ + 6e = Br^- + 3H_2O$$

but this is followed by reaction with bromide ion,

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$$

The liberated bromine reacts irreversibly with the indicator.

It is possible to titrate certain reducing agents (such as trivalent arsenic and antimony) with bromate by using as indicator a dye that is readily brominated by the Br_2 set free when there is an excess of $KBrO_3$ present. In most of such determinations, however, it is preferable to employ one of the oxidizing agents that can be used with the standard redox indicators. The unique uses of $KBrO_3$ are based on reactions of the Br_2 which is quantitatively liberated when $KBrO_3$ is added to an acidified solution of KBr. Certain organic compounds, such as the phenols, take up bromine rapidly and quantitatively, and they can be determined by the amount of Br_2 taken up. Potassium bromate provides a convenient method for adding Br_2 in known amount (use of a bromine solution is not feasible because of its volatility).

It has been found that a number of dyes can be used as indicators [10] in bromate titrations; a requirement is that the dye molecule take up bromine rapidly and that on bromination it undergo a color change. In titrations using this type of indicator it is necessary, of course, that the sample be a stronger reducing agent than bromide ion, so that no bromine is liberated until the stoichiometric point is passed. Considerable skill is required in titrations made with indicators of this type. Reagent must be added slowly as the end point is approached, to avoid local excess of reagent and permit time for bromination to occur. Usually it is preferable not to seek a deadstop end point but to add an excess of $KBrO_3$ and to determine the amount of the excess of Br_2 or $KBrO_3$ iodometrically by adding KI and titrating the liberated iodine with standard thiosulfate, using starch indicator. This procedure gives good end points and reproducible titrations.

The most important application of potassium bromate as an oxidation reagent is for indirect determinations of metals that can be precipitated with 8-hydroxyquinoline (abbreviated 8HQ). The metal is precipitated as described on page 402. After filtration and washing, the precipitate is dissolved in hydrochloric acid, and the amount of 8HQ is determined

[10] Smith and Bliss, *J. Am. Chem. Soc.*, **53**, 2091 (1931) have investigated many dyes. They list those found most suitable.

by bromate titration. The reactions are, if Mg is used as example,

$$Mg(C_9H_6ON)_2 + 2H^+ = Mg^{++} + 2C_9H_7ON$$

$$2C_9H_7ON + 4Br_2 = 2C_9H_5ONBr_2 + 4H^+ + 4Br^-$$

It is seen from the equation that each mole of Mg requires eight equivalents of bromine which in turn are liberated by eight equivalents of bromate. Therefore, the equivalent weight of Mg is the atomic weight divided by eight. The equivalent weight of $KBrO_3$ is of course $KBrO_3/6$.

Procedure. Preparation of Standard Solution. Solutions of $KBrO_3$ can be standardized by titration against weighed portions of arsenious oxide, but because of the indicator difficulty previously mentioned it is preferable to make up the solution of known normality by dissolving a weighed portion of recrystallized $KBrO_3$ which has been dried at 150–170°C.

Recrystallize 5 g reagent-grade $KBrO_3$, and dry at 150°C in an oven. Accurately weigh out a sample of about 2.8 g, and make up in a volumetric flask to exactly 1 l. Compute the normality. The equivalent weight is 167.01/6 or 27.835 g.

Procedure. Determination of Magnesium by Bromate Titration of 8-Hydroxyquinoline Precipitate. Precipitate, filter, and wash as described on page 402, using a Selas or Gooch crucible. When washing is complete, replace the filter flask by a clean one. With suction off, fill the crucible about half full with 2 *N* HCl solution. After a moment turn on the suction, and suck dry. Repeat until the liquid comes through colorless.

Compute from the weight and approximate percentage of the sample the weight of magnesium [11] in the solution. Transfer the solution to a volumetric flask, and take an aliquot portion of proper size to contain 10–14 mg of magnesium. Put the portions in glass-stoppered flasks for titration.

Add 1 g powdered KBr and a few drops of methyl red indicator. Titrate slowly with standard bromate solution until there is a distinct color change, and then add 0.5 to 1 ml additional. Stopper the flask, and allow to stand 2 minutes. Read the buret. Add 1 g KI, and restopper the flask. Swirl the liquid until the KI dissolves. A precipitate of an iodine compound with the bromination product of 8-hydroxyquinoline forms at this point, but it disappears when the iodine is removed by titration. Titrate with standard thiosulfate solution until

[11] In a dolomite analysis the approximate weight of MgO can be gotten by difference after the percentages of the other constituents are known.

the color of iodine begins to fade, then add starch indicator, and complete the titration.

Compute the milliequivalents of $KBrO_3$ and $Na_2S_2O_3$ used. The difference gives the milliequivalents of magnesium in the aliquot portion. Report the percentage of MgO in the sample.

QUESTIONS

1. What are the advantages in the use of ceric sulfate or potassium dichromate for the determination of iron?
2. What are the requirements of a redox indicator? What redox indicator should be used for ceric titrations? For dichromate titrations?
3. List the standards that may be used for ceric sulfate solutions. Why is it preferable to use iron for the standardization if the solution is to be used for iron analyses? Why cannot ordinary commercial iron be used for the standardization? How might pure ferric oxide, prepared by precipitation from C. P. ferrous ammonium sulfate, be used for the standardization?
4. Why should dichromate solutions be standardized by iron if intended for use in iron analyses?
5. Why is phosphoric acid added in dichromate titration of iron? Why is it not necessary to use preventive solution?
6. List several solutions for which As_2O_3 is a satisfactory standard.

PROBLEMS

1. What is the normality of a ceric sulfate solution if 42.75 ml is required to titrate 0.2500 g 99.3 per cent $Na_2C_2O_4$? What weight of pure As_2O_3 would react with 35.00 ml of the ceric solution?
2. How many milliliters of 0.1000 *M* $Ce(HSO_4)_4$ solution are equivalent in oxidizing power to 25.00 ml 0.02000 *M* $K_2Cr_2O_7$ solution?
3. What are the normality and molarity of a $K_2Cr_2O_7$ solution, 35.5 ml of which is equivalent to 0.4162 g 99.7 per cent pure Fe?
4. What weight of sample should be taken for analysis so that each 2.000 ml 0.1000 *N* ceric solution represents 1.000 per cent Fe_2O_3 in an ore?
5. From the following data calculate the percentage of Fe_2O_3 in a sample of limonite:

Weight of sample	0.6170 g
Volume of $K_2Cr_2O_7$	47.56 ml
Volume of $FeSO_4$	2.85 ml

1.000 ml $FeSO_4$ is equivalent to 1.021 ml $K_2Cr_2O_7$
The Fe titer of $K_2Cr_2O_7$ is 6.299 mg per milliliter

6. What is the percentage of iron in the limonite sample of Problem 5?
7. A 0.2620-g sample of chromite ($FeO \cdot Cr_2O_3$) was fused with sodium peroxide, and the resulting chromate solution was treated with 49.21 ml 0.1422 *N* ferrous sulfate solution; 4.08 ml of 0.0711 *N* dichromate solution was required to titrate the excess ferrous sulfate. Calculate the percentage of chromium in the ore.

8. What is the normality of a solution of potassium dichromate of such strength that the volume of solution used (in milliliters) gives the percentage of iron in the sample, when the analysis is performed on a 0.5000-g sample. If this solution is used for the analysis of a 0.7500-g sample, how is the volume of solution related to the percentage of iron in the sample?

9. Calculate the percentage of iron in a limonite sample, 0.4216 g of which requires 43.16 ml of 0.01687 *M* dichromate solution.

10. What is the largest weight of iron ore containing 20 per cent of limonite ($2Fe_2O_3 \cdot 3H_2O$) and 30 per cent of siderite ($FeCO_3$) that can be taken for analysis without refilling a 50-ml buret with 0.0962 *N* ceric sulfate solution?

11. How many milligrams of As_2O_3 will react with a 1/5 aliquot of a solution made by dissolving 5.000 g $KBrO_3$ in 250.0 ml?

12. How many grams of $KBrO_3$ are present in 0.700 l. of 0.2000 *N* solution?

13. What is the equivalent weight of aluminum in the estimation of the metal by the bromometric titration of the hydroxyquinoline precipitate? The precipitate is $Al(oxine)_3$.

14. Find the percentage of MgO in a 0.5000-g sample of limestone from the following:

Normality of $KBrO_3$	0.1100
Normality of $Na_2S_2O_3$	0.1200
Volume of $KBrO_3$	25.00 ml
Volume of $Na_2S_2O_3$	1.25 ml

CHAPTER

15

Equilibria in Oxidation–reduction Reactions

It was shown in Chapter 11 that the various oxidizing and reducing agents vary in their tendencies to take up or lose electrons and that in general the substances which possess the greatest tendencies to take up electrons will oxidize substances whose electrons can be readily removed. It was pointed out that oxidizing and reducing agents can be arranged in such an order that each substance will oxidize those above it and reduce each substance below it. Such an arrangement is shown in Table 25. A condensed form of this table has been discussed in general chemistry under the title "Electromotive Series of the Metals."

In the present chapter we shall consider the quantitative relations which determine the equilibrium conditions for oxidation–reduction or "redox" reactions. Every oxidation–reduction is a reversible reaction, and therefore none goes entirely to completion. For all practical purposes many such reactions are essentially complete, but even in an extreme case, the oxidation of sodium metal by hydrogen ion,

$$Na + H^+ = Na^+ + \tfrac{1}{2}H_2$$

the concentration of hydrogen ion does not become zero; it has a finite but small value when equilibrium is reached.

OXIDATION-REDUCTION POTENTIALS

The tendency of a given atom or ion to acquire electrons may be evaluated numerically in a number of ways. All these are based on the measurement of an electric potential which is set up when two oxidation–reduction systems are so arranged that the electron transfer must take place through a conductor. The arrangement of such a system is shown

in Fig. 23. A solution of an oxidizing agent is placed in one beaker and a solution of a reducing agent in the other beaker. A conducting electrode is placed in each beaker, and the two solutions are connected by a salt bridge, an inverted U-tube filled with a solution of an electrolyte.

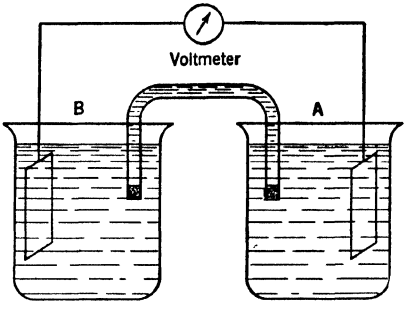


FIG. 23. Electric potential of oxidation–reduction system.

The operation of the system is readily followed by considering a specific example. Let us assume that *A* is a solution of copper sulfate in contact with a copper electrode and that *B* contains a zinc electrode in a zinc sulfate solution. Zinc atoms tend to lose electrons and become zinc ions. When this occurs, electrons are given up, and they flow through the conductor to the copper electrode, where they unite with cupric ions to form copper metal. The electrode reactions are:

$$Zn = Zn^{++} + 2e$$

$$Cu^{++} + 2e = Cu$$

and the over-all reaction is

$$Zn + Cu^{++} = Zn^{++} + Cu$$

The salt bridge is an essential part of the system since it provides a means for the transfer of ions from one solution to the other. The cell cannot operate without the transfer of ions, for otherwise zinc ions will accumulate in one beaker and sulfate ions in the other—which would lead to an impossible condition, because in any solution the sum of the positive charges must equal the sum of the negative charges. As the cell operates, negative ions migrate from the copper solution to the zinc solution, and positive ions from the zinc to the copper solution.

It is, of course, obvious that the oxidation of zinc by cupric ions can also take place by direct electron transfer if a strip of zinc is immersed in a copper sulfate solution. Then the reaction is the same as in the operation of the battery, but no electric work is done. An electric battery is merely an arrangement to carry out the oxidation and the reduction separately. Any oxidation–reduction reaction may be used for the production of electric energy.

When an oxidation–reduction reaction is carried out as previously described, a potential difference exists between the two electrodes. It

is this difference in potential which causes the electrons to travel from zinc to copper (flow of current). This potential difference can be measured by attaching the electrodes to the terminals of a voltmeter or potentiometer (see page 467). The unit of potential, in practical work, is the *volt* which is the difference in potential that causes a current of 1 ampere to flow through a resistance of 1 ohm.

The magnitude of the potential difference between the zinc and copper electrodes depends on several factors:

1. Most important is the relative tendency of the zinc atom to lose electrons and the tendency of the copper ion to gain electrons. If zinc is replaced by iron, the voltage of the cell is decreased because iron atoms have less tendency to lose electrons than zinc atoms. Conversely, if the copper–copper-ion system is replaced by a silver–silver-ion system, the voltage is increased because silver ion is a stronger oxidizing agent than cupric ion.

2. The concentrations of the zinc and cupric ions in the solutions affect the potentials. Since zinc goes into solution as the cell operates, it can be predicted from the principle of Le Chatelier that a decrease in the zinc-ion concentration will increase the tendency of the atoms to go into solution and increase the voltage of the cell. Conversely, since cupric ion goes out of solution, an increase in its concentration will increase the voltage and a decrease in cupric-ion concentration will reduce the voltage. These effects can be readily shown experimentally. If hydrogen sulfide is added to the zinc solution, the potential rises because precipitation of ZnS reduces the zinc-ion concentration. Addition of hydrogen sulfide to the cupric sulfate solution causes a decrease in the voltage. Addition of KCN solution to the cupric half-cell will cause the cupric-ion concentration to become so low that the voltage of the cell will change in sign, and copper now goes into solution while zinc goes out of solution. The reaction is

$$Cu^{++} + 3CN^- = Cu(CN)_2^- + \tfrac{1}{2}C_2N_2$$

3. Other factors, of minor importance in the present discussion, are the effects of temperature and of the potential difference which exists at the boundary between two solutions of electrolytes. We shall confine the present discussion to systems at constant temperature, 25°C, and shall neglect the small contribution of the liquid junction potential to the over-all voltage of the cell.

SINGLE ELECTRODE POTENTIAL

The tendency of any oxidation–reduction reaction to proceed may be quantitatively evaluated by separating the oxidizing and reducing

agents and measuring the potential difference between electrodes immersed in the two solutions. It is not necessary that the electrodes participate in the reactions, as in the zinc–copper system previously mentioned. If the oxidation and reduction involve only a change in valence of ions, the electrode may be any inert conductor, which acts merely to receive or supply electrons. For example, a cell may be set up to give the reaction:

$$Ce^{++++} + Fe^{++} = Ce^{+++} + Fe^{+++}$$

Ceric ions are placed in one of the beakers and ferrous ions in the other. Inert platinum electrodes are immersed in the two solutions, and a salt bridge is used to connect them. At one electrode ferrous ions give up electrons which flow through the conductor to the other electrode where they react with ceric ions.

$$Fe^{++} - e = Fe^{+++}$$

$$Ce^{++++} + e = Ce^{+++}$$

The over-all reaction is as given above. The electrode immersed in the ceric salt solution is the positive one since electrons flow in the conductor to this electrode.

From the potential of an oxidation–reduction cell, such as described in the preceding sections, the equilibrium constant for the chemical reaction can be computed. It is not necessary, however, to set up a cell and make the measurement. It may be recalled that in the equilibria of neutralization reactions the ionization constants for the weak electrolytes could be used to compute the *p*H values for any solutions of any concentration. Similarly, it is possible to compute the potentials and the equilibrium constants for any desired oxidation–reduction system from tabulated data. The data in this case are the *single electrode* or *half-cell* potentials. A half-cell must contain both the reduced and oxidized form of the reagent involved, plus an inert electrode if one of the forms of the reagent is not itself a conductor. Thus a half-cell which refers to copper as an oxidizing agent consists of a strip of metallic copper bathed by a solution of a cupric salt; the metal is the reduced form of the oxidation–reduction half reaction (or couple) of which Cu^{++} is the oxidized form. A half-cell which involves the ferrous–ferric ion equilibrium contains platinum or other inert conductor immersed in a solution which has both ferrous and ferric ions.

When a cell is set up as described in the preceding sections, the over-all potential is the difference between the single-electrode potentials of the two half-cells,

$$E_{1-2} = E_1 - E_2$$

It is not possible to measure the single-electrode potential experimentally, since to make a measurement one needs two electrodes so arranged that a current can flow from one to the other. For the system electrode-solution there is only one electrode. What one can measure is the difference in single-electrode potentials, by setting up a complete cell consisting of two half-cells, and measuring the over-all emf. If, however, some single-electrode potential is arbitrarily selected as standard and given a value of zero, then the value of any other single-electrode potential can be determined with reference to the standard by combining the desired cell with the selected reference cell and measuring the over-all potential. For example, the potential of the copper–zinc cell is about 1.10 volts. If the zinc half-cell were selected as standard and given a value of 0.00 volt, then the emf of the copper cell would be given by the relation,

$$1.10 = E_{Zn} - E_{Cu}$$

or

$$E_{Cu} = -1.10 \text{ volts}$$

The standard electrode to which all single-electrode values are referred is the "normal hydrogen electrode." It consists of a platinum electrode in contact with hydrogen gas at a pressure of 1 atmosphere and hydrogen ion at a concentration of one molal (strictly speaking, the gas and solution are both at unit activity, but essentially the pressure and concentration are both unity). Equilibrium between the gas and solution is brought about by use of an electrode coated with a deposit of finely divided platinum which serves as a catalyst for the reaction,

$$H^+ + e = \tfrac{1}{2}H_2$$

CONVENTIONS

There are two numerical potential values associated with every half-cell, one *positive* and one *negative*, just as a dry cell may be said to have a voltage of $+1.5$ or -1.5 volts, depending on how the terminals are connected to a voltmeter. It is, therefore, necessary to specify conventions in regard to the sign of potentials and to follow these conventions at all times. It is immaterial what conventions are used so long as one is consistent; inspection of various books shows some variations. We shall in this text follow the conventions [1] which are most widely used in more advanced works, but the student should realize that in using data from other books he should note the author's conventions.

[1] See W. M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, Prentice-Hall, 1938.

Before giving the electrical conventions, we should summarize the notations used to represent cells and half-cells. A half-cell is written as

$$\text{Electrode, solution } (xM)$$

where the comma indicates a phase boundary. If there are more than two phases, as in a gas–solid–liquid system, commas are used for each junction. Thus

$$\text{Pt, } H_2\text{(gas), } H^+ \text{ solution}$$

is used to represent the hydrogen electrode.

When two half-cells are combined, the second is written in reverse order. If a liquid junction between two solutions is present, it is represented by two vertical lines. Thus the copper–zinc cell previously discussed is written as

$$\text{Zn, } Zn^{++}(xM) \,\|\, Cu^{++}(yM), \text{ Cu}$$

Potentials of half-cells are represented by the symbol E, or, if the reactants are at standard state, by $E°$. Over-all potentials of whole cells are given as E_{1-2} or $E°_{1-2}$.

The conventions of this book are as follows:

1. Each couple or half-cell is written with the electron on the right-hand side. That is:

$$Li = Li^+ + e \qquad E° = 3.02 \text{ volts}$$

If the half-cell is written in reverse order, the voltage is given the opposite sign,

$$Li^+ + e = Li \qquad E° = -3.02$$

2. A + value for $E°$ when the cell is written with the electron on the *right-hand* side shows that the reduced form of the reactant is a better reducing agent than H_2. Conversely a − sign indicates that the oxidized form of the reactant is a better oxidizing agent than H^+. In general, any ion is a better oxidizing agent than the ions above it in Table 25.

3. In combining two half-cells to obtain the over-all emf of a whole cell,

(*a*) Write each half-cell reaction as in Table 25.

(*b*) Subtract the half-cell reaction of the right-hand electrode from that of the left-hand electrode; also subtract the half-cell potentials.

For example, to find the standard-state potential of the cell,

$$\text{Cu, } Cu^{++}(1\ M) \,\|\, Zn^{++}(1\ M), \text{ Zn}$$

TABLE 25

STANDARD OXIDATION-REDUCTION POTENTIALS

All values have been rounded off to one or two figures after the decimal point and without relation as to how accurately they are known. For a more complete table and more precise values see *Oxidation Potentials*.

Couple	E°
$Li = Li^+ + e$	3.02
$Cs = Cs^+ + e$	3.02
$K = K^+ + e$	2.92
$Ba = Ba^{++} + 2e$	2.90
$Sr = Sr^{++} + 2e$	2.89
$Ca = Ca^{++} + 2e$	2.87
$Na = Na^+ + e$	2.71
$2OH^- + Mg = Mg(OH)_2 + 2e$	2.67
$Mg = Mg^{++} + 2e$	2.34
$H^- = \frac{1}{2}H_2 + e$	2.23
$Al = Al^{+++} + 3e$	1.67
$Mn = Mn^{++} + 2e$	1.05
$Zn = Zn^{++} + 2e$	0.76
$S^= + 2Ag = Ag_2S + 2e$	0.71
$Cr = Cr^{+++} + 3e$	0.71
$S^= + Hg = HgS + 2e$	0.70
$S^= = S + 2e$	0.51
$H_2C_2O_4\ (aq) = 2CO_2\ (gas) + 2H^+ + 2e$	0.49
$Fe = Fe^{++} + 2e$	0.44
$H_2 = 2H^+\ (10^{-7}\ M)$	0.41
$Cr^{++} = Cr^{+++} + e$	0.41
$Cd = Cd^{++} + 2e$	0.40
$2I^- + Pb = PbI_2 + 2e$	0.37
$2Br^- + Pb = PbBr_2 + 2e$	0.28
$Co = Co^{++} + 2e$	0.28
$2Cl^- + Pb = PbCl_2 + 2e$	0.27
$Ni = Ni^{++} + 2e$	0.25
$V^{++} = V^{+++} + e$	0.25
$I^- + Cu = CuI + e$	0.19
$I^- + Ag = AgI$	0.15
$Sn = Sn^{++} + 2e$	0.14
$Pb = Pb^{++} + 2e$	0.13
$2I^- + 2Hg = Hg_2I_2 + 2e$	0.04
$4I^- + Hg = HgI_4^= + 2e$	0.04
$Fe = Fe^{+++} + 3e$	0.04
$2I^- + Cu = CuI_2^- + e$	0.00
$H_2 = 2H^+ + 2e$	0.00
$Br^- + Ag = AgBr + e$	−0.07
$H_2S = S + 2H^+ + 2e$	−0.14
$Sn^{++} = Sn^{++++} + 2e$	−0.15

TABLE 25 (*Continued*)

STANDARD OXIDATION–REDUCTION POTENTIALS

Couple	E°
$Cu^{+} = Cu^{++} + e$	−0.17
$Cl^{-} + Ag = AgCl + e$	−0.22
$6OH^{-} + I^{-} = IO_3^{-} + 3H_2O + 6e$	−0.26
$2Cl^{-} + 2Hg = Hg_2Cl_2 + 2e$	−0.27
$2Cl^{-}$ (1 *M*) $+ 2Hg = Hg_2Cl_2 + 2e$ (normal calomel electrode)	−0.28
$H_2O + V^{+++} = VO^{++} + H^{+} + e$	−0.31
$Cu = Cu^{++} + 2e$	−0.34
$Fe(CN)_6^{\equiv} = Fe(CN)_6^{\equiv} + e$	−0.36
$2NH_3$ (aq) $+ Ag = Ag(NH_3)_2^{+} + e$	−0.37
$Cu = Cu^{+} + e$	−0.52
$2I^{-} = I_2 + 2e$	−0.53
$3I^{-} = I_3^{-} + 2e$	−0.53
$2H_2O + HAsO_2 = H_3AsO_4 + 2H^{+} + 2e$	−0.56
$4OH^{-} + MnO_2 = MnO_4^{-} + 2H_2O + 3e$	−0.57
$H_2O_2 = O_2 + 2H^{+} + 2e$	−0.68
$Fe^{++} = Fe^{+++} + e$	−0.77
$2Hg = Hg_2^{++} + 2e$	−0.80
$Ag = Ag^{+} + e$	−0.80
$Hg = Hg^{++} + 2e$	−0.85
$CuI = Cu^{++} + I^{-} + e$	−0.88
$Hg_2^{++} = 2Hg^{++} + 2e$	−0.91
$HNO_2 + H_2O = NO_3^{-} + 3H^{+} + 2e$	−0.94
$2H_2O + NO = NO_3^{-} + 4H^{+} + 3e$	−0.96
$2Br^{-} = Br_2$ (liq) $+ 2e$	−1.06
$2Br^{-} = Br_2$ (aq) $+ 2e$	−1.09
$\frac{1}{2}I_2 + 3H_2O = IO_3^{-} + 6H^{+} + 5e$	−1.20
$2H_2O = O_2 + 4H^{+} + 4e$	−1.23
$2H_2O + Mn^{++} = MnO_2 + 4H^{+} + 2e$	−1.28
$Cl^{-} = \frac{1}{2}Cl_2$ (gas) $+ e$	−1.35
$7H_2O + 2Cr^{+++} = Cr_2O_7^{=} + 14H^{+} + 6e$	−1.36
$3H_2O + Br^{-} = BrO_3^{-} + 6H^{+} + 6e$	−1.44
$3H_2O + Cl^{-} = ClO_3^{-} + 6H^{+} + 6e$	−1.45
$3H_2O + Pb^{++} = PbO_2 + 4H^{+} + 2e$	−1.46
$\frac{1}{2}Cl_2$ (gas) $+ 3H_2O = ClO_3^{-} + 6H^{+} + 5e$	−1.47
$Mn^{++} = Mn^{+++} + e$	−1.51
$\frac{1}{2}Br_2$ (liq) $+ 3H_2O = BrO_3^{-} + 6H^{+} + 5e$	−1.52
$4H_2O + Mn^{++} = MnO_4^{-} + 8H^{+} + 5e$	−1.52
$Ce^{+++} = Ce^{++++} + e$	−1.61
$2H_2O + MnO_2 = MnO_4^{-} + 4H^{+} + 3e$	−1.67
$Pb^{++} = Pb^{++++} + 2e$	−1.69
$O_2 + H_2O = O_3 + 2H^{+} + 2e$	−2.07
$2F^{-} = F_2$ (gas) $+ 2e$	−2.85

write the half-cell reactions, and subtract.

$$\begin{array}{rl} Cu = Cu^{++} + 2e & E^\circ = -0.34 \text{ volt} \\ Zn = Zn^{++} + 2e & E^\circ = \ \ 0.76 \text{ volt} \\ \hline Cu + Zn^{++} = Cu^{++} + Zn & E^\circ_{1-2} = -1.10 \text{ volts} \end{array}$$

If it is known in advance which is the reducing agent, it is preferable to set up the cell with the reducing agent on the left, so that the sign of the over-all emf is positive. That is, the cell above should be set up as

$$Zn, Zn^{++} \,||\, Cu^{++}, Cu$$

and the emf is then found to be +1.10 volts. It is obvious that the two ways are equivalent.

4. When the two half-cell reactions are combined as in (3), the sign of the over-all emf indicates the polarity of the right-hand electrode. Thus, by either of the formulations above it is found that Cu is the positive electrode. This means that in the external circuit connecting the two electrodes the electrons flow towards the copper pole.

5. A + value of the over-all emf indicates that the chemical reaction obtained by combination of the half-cell reactions will go from left to right. Conversely a − sign indicates spontaneity of the reaction from right to left. Thus, when all substances are at standard state (see below) the reaction of the Zn–Cu cell is

$$Zn + Cu^{++} = Zn^{++} + Cu$$

STANDARD POTENTIALS

In order to tabulate reference values for half-cell potentials one must specify the concentrations of all reactants since the value of cell emf depends on the concentrations.

In all tables of standard electrode potentials all reactants are at unit activity unless otherwise stated. By *activity* is meant the effective concentration, expressed as the ratio to the concentration that has been arbitrarily chosen for standard state. It is beyond the scope of this text to explain the various methods used to relate actual concentrations to activities, since our purpose is not to make exact computations but rather to show how approximate values of equilibrium constants can be computed from potential values. For our purposes unit activity may be defined as follows:

1. A pure liquid or solid is at unit activity. When it is not pure, the effective concentration is given by the mole fraction, as defined by the relation:

$$\text{Mole fraction of } A = \frac{\text{number of moles } A}{\text{total number of moles}}$$

Thus, if 23 g Na is dissolved in 200 g Hg, the mole fraction of each constituent is 0.5. In a 1 M solution H_2O has a mole fraction of 55.5/56.5, but usually in computations it is taken as 1.

2. A gas is at unit activity when at a pressure of 1 atm. The partial pressure of a gas, in atmospheres, is taken as its effective concentration when it is not at unit activity. Thus the effective concentration of oxygen in the atmosphere is approximately 0.2 since its partial pressure is about 0.2 atm.

3. A solute is at unit activity when the concentration is 1 molar (more exact is when the concentration is 1 mole per 1000 g of solvent, but, since neither takes account of deviations from the laws of perfect solutions, we will use 1 molar as an approximation). At other concentrations the activity is considered to be the molarity.

The value of the activity to be used for a saturated solution depends on the standard state employed for the standard potential. It may be either the molar concentration, if standard state were taken for a 1 M solution, or unity, if standard state were taken for pure solid. For example, $E°$ for the cell,

$$\text{Hg, } Hg_2Cl_2, \text{ KCl (1 } M\text{)}$$

is for solid Hg_2Cl_2 in equilibrium with its saturated solution in 1 M KCl.

Standard half-cell potentials for a variety of oxidation–reduction reactions are given in Table 25. These are for a temperature of 25°C and with all reactants at unit activity.

The values of Table 25 are not absolute, for as previously stated the absolute values are not known. All that can be determined by present experimental methods is the relative value of the potential of a given half-cell in relation to some other half-cell, since the measurement of potential requires that a whole cell be used. It is conventional to express all relative half-cell potentials in terms of the standard hydrogen electrode which is arbitrarily given a value of zero. To determine any other half-cell potential it is necessary only to measure the potential of the cell,

$$\text{Unknown cell} \parallel H^+ \text{ (unit activity), } H_2 \text{ (unit pressure), Pt}$$

and, since the right-hand side is given a value of zero, the over-all emf is the numerical value of the left-hand side.

In practice, it is not easy to construct a hydrogen electrode with all reactants at unit activity. Consequently, it is customary to employ a reference electrode whose emf is accurately known in relation to a standard hydrogen half-cell. Several such reference electrodes are used. All employ the system,

Metal, insoluble salt, solution with ion common to salt

This has the advantage that it is easily reproduced from one laboratory to another since the amount of metal ion in solution, which determines the emf, is governed by the solubility-product principle. The two most widely used of the reference electrodes are the couples:

Ag, AgCl, HCl

Hg, Hg_2Cl_2, KCl

The most common Ag, AgCl, HCl reference half-cell contains 0.1000 N HCl. At 25°C its voltage is −0.2221 volt. If a cell,

Ag, AgCl, HCl (0.1 N) || unknown half-cell

is set up, the voltage E_x of the unknown half-cell is related to the over-all cell voltage E_{1-2} by

$$E_x = -0.2221 - E_{1-2}$$

wherein the algebraic sign of E_{1-2} is determined by the polarity of the unknown half-cell.

The calomel half-cell reference electrode commonly employs three different concentrations of KCl, namely: saturated, normal, and decinormal. The voltages of the calomel reference half-cells at 25°C are:

Saturated KCl	−0.2458
Normal	−0.2847
Decinormal	−0.3376

ANALYTICAL APPLICATIONS

Many useful computations may be made with the aid of a table of oxidation–reduction potentials. Some of the more important applications to analytical chemistry are illustrated in the following sections.

Direction of Reaction. Since all oxidation–reduction reactions are reversible, a given substance may function as either an oxidizing or a

reducing agent, depending on whether it takes up or gives off electrons. The standard potentials of Table 25 enable one to compute what reaction will occur when two reagents are brought together. This is done by formulating a cell involving the reagents in question (so that, as the cell operates, the reagents interact) and computing the emf of the cell. We will consider first the case that all constituents are at standard state. To illustrate, consider the reaction of Fe^{+++} with Cl^-. In which direction will the following reaction go?

$$Fe^{+++} + Cl^- = \tfrac{1}{2}Cl_2 + Fe^{++}$$

Solution: Set up a cell to give the desired reaction,

$$Pt,\ Cl_2\ (gas),\ Cl^- \parallel Fe^{++} + Fe^{+++},\ Pt$$

Write down the two half-cell reactions as given in Table 25, and subtract the one for the right-hand side from the one for the left.

$$\begin{array}{lll} Cl^- = \tfrac{1}{2}Cl_2 + e & E^\circ & = -1.35 \\ Fe^{++} = Fe^{+++} + e & E^\circ & = -0.77 \\ \hline Cl^- + Fe^{+++} = \tfrac{1}{2}Cl_2 + Fe^{++} & E^\circ_{1-2} & = -0.58 \end{array}$$

Reference to the conventions of page 268 shows that (1) the chlorine electrode is positive, and (2) the reaction goes from right to left, or Cl_2 oxidizes Fe^{++}. Note that, if the reaction had been written in the opposite way, the same interpretation would have resulted. It makes no difference which of the half-cells is set down on the left-hand side.

In the more general case all reactants are not at standard state, and allowance must be made for the effect of the concentrations on the direction of the reaction.

The relation of concentration to the emf of a cell is given by the classical Nernst equation,

$$E_{1-2} = E^\circ_{1-2} - \frac{0.059}{n} \log_{10} Q$$

where n is the number of electrons involved in the reaction, the constant 0.059 is a composite value for several constants when the temperature is 25°C, and Q is the product of the activities of reaction products divided by the product of the activities of the starting substances, each activity raised to a numerical power equal to the coefficient of the number of molecules involved in the chemical equation.

This equation may for illustration be used to compute the emf of the ferrous ion–chlorine system at given concentrations of the various reactants. For example, will Cl_2 gas at 1 atm oxidize Fe^{++} when its con-

centration is 0.01 M, in a solution in which the concentrations of Fe^{+++} and Cl^- are each 2 M?

Solution:

$$E_{1-2} = E^\circ_{1-2} - \frac{0.059}{1} \log \frac{(a_{Cl_2})^{1/2}(a_{Fe^{++}})}{(a_{Cl^-})(a_{Fe^{+++}})}$$

Since we are using the concentrations as approximate values of the activities, we can substitute the values previously given. Then

$$\begin{aligned} E_{1-2} &= -0.58 - 0.059 \log \frac{(1)^{1/2}(0.01)}{(2)(2)} \\ &= -0.58 - 0.059 \log 2.5 \times 10^{-3} \\ &= -0.58 - 0.059(0.40 - 3) \\ &= -0.43 \end{aligned}$$

The negative value indicates that the reaction will proceed from right to left, as written when the standard cells were combined. The smaller value of E_{1-2} shows that there is less tendency for the reaction to go at the specified concentrations than when all reactants are at standard state. In other words, the increase in concentration of Cl^- and Fe^{+++} inhibits the tendency of the reaction to proceed, and the decrease of the reactant Fe^{++} aids in this effect. Had we made the concentrations of Fe^{+++} and Cl^- very large and the concentration of Fe^{++} very small, it would have been found that the reaction goes spontaneously in the opposite direction, or that Fe^{+++} will oxidize Cl^-.

Equilibrium Constant for Redox Reactions. If a cell is short-circuited by the electrodes being connected with a conducting wire, reaction will proceed until the voltage becomes zero. At this point the concentrations of reactants have, of course, changed, and the reaction has reached a condition of equilibrium. The product term Q is then the equilibrium constant K_e. That is, at equilibrium E_{1-2} is zero, and

$$0 = E^\circ_{1-2} - \frac{0.059}{n} \log K_e$$

$$\log K_e = \frac{nE^\circ_{1-2}}{0.059}$$

We may, therefore, use the single-electrode potentials to compute the equilibrium constant for an oxidation–reduction reaction. To illustrate, consider the reaction,

$$Zn + Cu^{++} = Zn^{++} + Cu$$

Solution: Set up cell to give the reaction, and solve for $E°_{1-2}$.

$$\text{Zn, } Zn^{++} \parallel Cu^{++}\text{, Cu}$$

$$\begin{aligned} Zn &= Zn^{++} + 2e \qquad E° = 0.76 \\ Cu &= Cu^{++} + 2e \qquad E° = -0.34 \end{aligned}$$

$$Zn + Cu^{++} = Zn^{++} + Cu \qquad E°_{1-2} = 1.10$$

At equilibrium,

$$0 = 1.10 - \frac{0.059}{2} \log \frac{[Zn^{++}]}{[Cu^{++}]}$$

$$= 1.10 - \frac{0.059}{2} \log K_e$$

Solving gives

$$\log K_e = \frac{1.10 \times 2}{0.059} = 37.3$$

$$K_e = 10^{37.3} = 10^{0.3} \times 10^{37}$$

$$= 2.0 \times 10^{37}$$

Completeness of Reaction. The evaluation of K_e for a redox reaction makes it possible to compute the completeness of the reaction under specified conditions. This is important in analytical procedures, for frequently we wish to know how completely a sought ion is oxidized when the stoichiometric amount of reagent has been added in a titration. To illustrate, we will first consider the oxidation of ferrous ion by permanganate in acid solution, which we already know from experience to be a feasible laboratory determination. For the computation we shall arbitrarily select conditions outlined in the following problem.

Problem. A 5 m mol sample of Fe^{++} is titrated with $KMnO_4$ in acid solution, with a final volume of 200 ml at the stoichiometric point. Concentration of H^+ is 1 *M*.

We shall compute the concentration of Fe^{++} remaining unoxidized at the stoichiometric point.

Solution: First formulate a cell to give the desired reaction. It is convenient always to put the reducing agent on the left-hand side:

$$\text{Pt, } Fe^{++} + Fe^{+++} \parallel MnO_4^- + H^+\text{, Pt}$$

Write down the half-cell reactions, and subtract in the usual manner to obtain the value of $E°_{1-2}$ associated with the chemical reaction. Before the subtraction is made, it is necessary to balance the two half-cell reactions so that the same number of electrons is involved in each. In so doing we do not change the value of $E°$ for the half-cell but merely change the number of moles involved in the reaction. The emf does not depend on the number of moles present, but merely on the concentrations of the reactants.

$$5Fe^{++} = 5Fe^{+++} + 5e \qquad E^\circ = -0.77$$
$$Mn^{++} + 4H_2O = MnO_4^- + 8H^+ + 5e \qquad E^\circ = -1.52$$

$$5Fe^{++} + MnO_4^- + 8H^+ = 5Fe^{+++} + Mn^{++} + 4H_2O \qquad E^\circ_{1-2} = 0.75$$

Then, at equilibrium,

$$0 = 0.75 - \frac{0.059}{5} \log \frac{(a_{Fe^{+++}})^5(a_{Mn^{++}})(a_{H_2O})^4}{(a_{Fe^{++}})^5(a_{MnO_4^-})(a_{H^+})^8}$$

$$= 0.75 - \frac{0.059}{5} \log K_e$$

Solving gives

$$K_e = 10^{63.6}$$

It is now necessary to evaluate the concentrations in the solution and as an approximation to substitute these concentrations for the activities. It should again be emphasized that such a procedure is at best an approximation, since the activities are not the same as the molar concentrations, but for our purposes this approximation is justified.

$[Fe^{+++}] = 5/200 = 2.5 \times 10^{-2}$. Practically all of the original 5 m mol Fe^{++} is oxidized when the stoichiometric point is reached.

$[H_2O] = 1$. Here and in future we shall represent all activities by the concentration symbol, since for many substances we are using the concentrations for activities. Actually the concentration of water is 1000/18 or 55.5 moles per liter, but it will be recalled that in the treatment of oxidation equilibria each activity must be given in terms of the value that has been selected as standard state in the determination of E°. Standard state for water is as the pure liquid. Here again an approximation has been introduced for in the titration solution the mole fraction of water is not unity. Actually it is near 55.5/56.5 since the concentration of hydrogen ion is 1 M and other ions are present in low concentration. But the value is so near unity that the approximation is justified.

$[Mn^{++}] = 1/200 = 0.005$. For each 5 moles of Fe^{+++} formed in the reaction there is 1 mole Mn^{++} (see equation).

$[MnO_4^-] = X$.

$[Fe^{++}] = 5X$. We see from the equation that, when stoichiometric amounts of MnO_4^- and Fe^{++} are mixed, the number of moles of Fe^{++} remaining unoxidized is 5 times the number of moles of MnO_4^-.

$[H^+] = 1$. This is the concentration specified in the statement of the problem and is about the final concentration present in actual permanganate titrations.

Substitution of these values gives

$$\frac{(2.5 \times 10^{-2})^5(5 \times 10^{-3})(1)^4}{(5X)^5(X)(1)^8} = 10^{63.6}$$

Solving, we have

$$X = 10^{-13.80} = 10^{0.20} \times 10^{-14}$$

$$= 1.6 \times 10^{-14}$$

Therefore,

$$[Fe^{++}] = 8.0 \times 10^{-14}$$

This computation shows that the concentration of ferrous ion remaining unoxidized at the stoichiometric point of the titration is negligibly small or that the reaction is quantitatively complete. Actually the calculation is not at all exact, for we have ignored another reaction that occurs simultaneously, namely, the removal of ferric ion as a complex with chloride and phosphate ions that are present in the solution. The effect of these side reactions is to make oxidation of ferrous ion even more quantitative than is indicated in the present computation.

As a second case we will consider the oxidation of chloride ion by permanganate ion.

Problem. Five millimoles of Cl^- is titrated by 0.02 M permanganate. The final volume is 250 ml. What is the concentration of Cl^- when 1 drop (0.05 ml) of permanganate is present in excess? Assume a hydrogen-ion concentration of 1 M.

Solution: Set up the cell,

$$Pt, Cl_2, Cl^- \,||\, Mn^{++}, MnO_4^-, H^+, Pt$$

$$5Cl^- = \tfrac{5}{2}Cl_2 + 5e \qquad E^\circ = -1.35$$

$$Mn^{++} + 4H_2O = MnO_4^- + 8H^+ + 5e \qquad E^\circ = -1.52$$

$$MnO_4^- + 8H^+ + 5Cl^- = \tfrac{5}{2}Cl_2 + Mn^{++} + 4H_2O \qquad E^\circ_{1-2} = 0.17$$

At equilibrium,

$$0 = 0.17 - \frac{0.0591}{5} \log \frac{[Cl_2]^{5/2}[Mn^{++}][H_2O]^4}{[MnO_4^-][H^+]^8[Cl^-]^5}$$

$$K_e = 10^{14.38}$$

Substitute the concentration values: The molar concentration of chlorine is 0.01 (2.5 m mol Cl_2 in 250 ml) if it is assumed for the calculation that all the Cl^- ion is oxidized. But since the standard state for Cl_2 is a gas at 1 atm, it is necessary to state the activity in the same terms. The solubility of Cl_2 is given as 0.0618 M, at a partial pressure of 1 atm. Therefore a solution in which the concentration is 10^{-2} M is in equilibrium with gas at a pressure of $10^{-2}/0.0618$ or 0.16 atm, or $a_{Cl_2} \cong [Cl_2] = 0.16$.

$$[Mn^{++}] = 4 \times 10^{-3}$$

$$[H_2O] = 1$$

$$[H^+] = 1$$

$$[MnO_4^-] = 4 \times 10^{-6}$$

$$[Cl^-] = X$$

$$\frac{(4 \times 10^{-3})(0.16)^{5/2}(1)^4}{(4 \times 10^{-6})(1)^8(X)^5} = 10^{14.38}$$

$$\frac{(0.16)^{5/2}}{10^{-3}(X)^5} = 10^{14.38}$$

$$\frac{(0.16)^{5/2}}{(X)^5} = 10^{11.38}$$

$$\frac{(0.16)^{1/2}}{X} = 10^{2.28}$$

$$\frac{0.4}{X} = 10^{2.28} = 1.91 \times 10^{2}$$

$$X = 2.1 \times 10^{-3}$$

The result of this calculation shows that the original assumption of complete oxidation of Cl^- was not justified. If a more exact solution were desired, it would be necessary to make a correction for the unoxidized chloride ion, the concentration of Cl_2 becoming $10^{-2} - X/2$, and to solve the equation again. This is hardly necessary, since the computation has shown that the concentration of Cl^- remaining in solution is so large that the titration cannot be quantitative.

If it is desired to make a similar computation for the completeness of oxidation of bromine ion by permanganate, it is necessary to express the concentration of Br_2 as the degree of saturation of the solution. The solubility of bromine is about 0.16 *M*. In a 0.01 *M* solution, therefore, the activity of Br_2 is 0.01/0.16 or 0.062. All other activities in the bromine computation would appear just as in the chlorine computation.

REDOX INDICATORS

It may be recalled that acid–base indicators are weak organic acids or bases which exhibit a color change when salt formation takes place through neutralization. Similarly, redox indicators are highly colored organic substances which change in color when oxidized or reduced. As is true of any other oxidizing agent, an oxidation potential is associated with each indicator. The standard potentials for some of the more widely used indicators are given in Table 26. When hydrogen ion takes part in the indicator reaction, the standard potentials are given for unit activity of hydrogen ion.

TABLE 26

PARTIAL LIST OF OXIDATION–REDUCTION POTENTIALS FOR REDOX INDICATORS

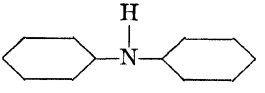
Indicator	*Color Change on Oxidation*	*Transition Emf in volts*
Diphenylamine	Colorless to violet	−0.76
Barium diphenylamine sulfonate	Lightgreen or colorless to red–violet	−0.84
Ferroin (Orthophenanthroline ferrous complex)	Red to faint blue	−1.14
Nitro-Ferroin	Red to faint blue	−1.25

For a more complete list see *Products and Prices*, G. Frederick Smith Company. Columbus, Ohio.

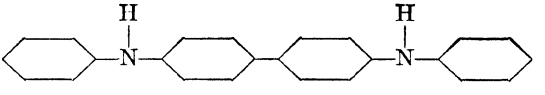
The mechanism of the color change for redox indicators has not been clearly established. It is probable that in some cases, at least, the color formation is due to a quinoidal structure of some part of the molecule. With some of the indicators the presence of a metal ion is necessary for color formation.

A number of oxidation–reduction indicators has been developed, with normal potentials ranging from -0.76 to -1.25. The most widely used ones are diphenylamine and its derivatives, and orthophenanthroline, which is used in the form of a complex ion with ferrous ion.

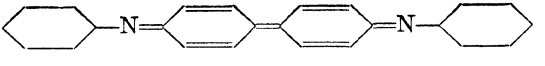
Diphenylamine was one of the first redox indicators to be widely used; the chief application has been for the titration of ferrous ion by dichromate. The indicator has the formula,



The first stage of the oxidation, which occurs at a low potential, is the formation of diphenylbenzidine,



Diphenylbenzidine is on oxidation converted into diphenylbenzidine violet.



The oxidized and reduced forms are present in equal concentration at a potential of -0.76 volt.

Diphenylamine and diphenylbenzidine are sparingly soluble in water, but are soluble in sulfuric acid. The indicator solution used contains 1 g diphenylamine in 100 ml concentrated sulfuric acid. A few drops of this solution suffice for a titration in a volume of 200–300 ml.

Recently diphenylamine has largely been replaced by a derivative, diphenylamine sulfonic acid. This derivative, in the form of a sodium or barium salt, is readily soluble. A further advantage is that the sulfonic acid can be used in the presence of tungstates, with which diphenylamine forms a precipitate. The color change occurs at a potential of -0.84 volt. In the reduced form the solution is green while the oxidized indicator is reddish violet. The intensity of color is sufficiently high that the color change can readily be seen in chromate titrations, where the solution is colored by the green Cr^{+++} ion.

Orthophenanthroline is used in the form of the ferrous complex, $Fe(C_{12}H_8N_2)_3^{++}$, which goes by the trade name "Ferroin." On oxidation it is converted into a corresponding ferric complex. The standard potential is given as -1.14 volts. Ferroin indicator is prepared by dissolving 1.45 g orthophenanthroline monohydrate in 100 ml 0.025 *M* ferrous sulfate solution.

An indicator of still higher oxidation potential than Ferroin is obtained from the ferrous complex of nitro-orthophenanthroline. This indicator, known as "Nitro-Ferroin" has an oxidation potential of -1.25 volts. The color change is the same as that of Ferroin.

Selection of Indicator for Titration

The sections of Chapter 24 which deal with oxidation–reduction titrations should be studied in connection with this section.

Just as in neutralization titrations, it is necessary to select a redox indicator so that the end point will correspond to the stoichiometric point. In neutralization titrations the determining factor in the selection of an indicator is the *p*H of the solution at the stoichiometric point. In oxidation–reduction titrations the oxidation potential at the stoichiometric point is the basis on which the suitable indicator is selected.

The computation of the oxidation potential for a redox indicator may be made by consideration of either the equilibrium between the indicator and the substance which is titrated or the oxidation potential which exists in the titration system at the stoichiometric point. Both methods are illustrated in the following sections.

Equilibrium between Indicator and Reductant. In the titration of ferrous ion it is desired that the indicator used shall show an end point when the concentration of unoxidized ferrous ion has become negligibly small. If, for example, 5 m mol of ferrous ion is titrated by a suitable oxidizing agent, we may compute the oxidation potential of an indicator which will show a color change when the concentration of ferrous ion has become 10^{-5} *M*. If we assume a final volume of 200 ml, a concentration of 10^{-5} *M* corresponds to about 0.1 mg unoxidized ferrous ion in the solution. The system which will give the desired equilibrium is represented in the cell,

$$\text{Pt, Ind}^+ + \text{Ind} \parallel \text{Fe}^{++} + \text{Fe}^{+++}, \text{Pt}$$

where Ind symbolizes the reduced form of the indicator and Ind^+ the oxidized form of the indicator when only one electron is involved in the oxidation.

Treating this cell in the usual manner, we have

$$\begin{array}{lll} \text{Ind} = \text{Ind}^+ + e & E^\circ & = X \\ \text{Fe}^{++} = \text{Fe}^{+++} + e & E^\circ & = -0.77 \\ \hline \text{Ind} + \text{Fe}^{+++} = \text{Ind}^+ + \text{Fe}^{++} & E^\circ_{1\text{-}2} & = X + 0.77 \end{array}$$

At equilibrium,

$$0 = X + 0.77 - 0.059 \log \frac{[\text{Ind}^+][\text{Fe}^{++}]}{[\text{Ind}][\text{Fe}^{+++}]}$$

According to the conditions of the problem, $[\text{Fe}^{+++}]$ is 5/200 or $0.025\,M$ since practically all the original ferrous ion has been oxidized and $[\text{Fe}^{++}]$ is $10^{-5}\,M$. Lacking knowledge of what fraction of the indicator is oxidized when the color change occurs, we assume that the two forms are present in equal concentration or that the ratio $\text{Ind}^+/\text{Ind} = 1$. Substitution of these values for the activities of the reactants in the previous equation gives

$$0 = X + 0.77 - 0.059 \log \frac{(1)(10^{-5})}{(1)(2.5 \times 10^{-2})}$$

$$X = -0.97 \text{ volt}$$

The computed E° value for the indicator lies between that of diphenylamine sulfonic acid and Ferroin. In practice either of these indicators can be used, the diphenylamine end point appearing when the concentration of ferrous ion is somewhat greater than the value assumed in the computation, and the Ferroin end point appearing when the concentration of ferrous ion has been reduced to a very small value. The computation does not take into account the oxidizing agent for the titration of ferrous ion, because it makes no difference what oxidizing agent is used provided that it has a sufficiently high potential to oxidize the ferrous ion to the specified degree of completeness.

Oxidation Potential of Titration System. If the potential difference is measured between a hydrogen electrode and a platinum electrode immersed in a solution containing ferrous and ferric ions, the observed potential depends on the ratio of the concentrations of ferrous and ferric ions. If the emf of such a system is measured during the course of a titration of ferrous ion by an oxidizing agent, there are obtained data from which a titration curve such as shown in Chapter 24 may be plotted. The emf at the stoichiometric point of the titration is the oxidation potential at which a suitable indicator should give a color change. This emf may be computed as follows:

The cell is

$$\text{Pt, normal hydrogen electrode} \parallel \text{Fe}^{++} + \text{Fe}^{+++}, \text{Pt}$$

The emf of the system is given by the expression,

$$\begin{array}{rll} \tfrac{1}{2}H_2 = H^+ + e & E^\circ & = 0.00 \\ Fe^{++} = Fe^{+++} + e & E^\circ & = -0.77 \\ \hline \tfrac{1}{2}H_2 + Fe^{+++} = H^+ + Fe^{++} & E^\circ_{1\text{-}2} = & 0.77 \end{array}$$

$$E_{1\text{-}2} = 0.77 - 0.059 \log \frac{[Fe^{++}]}{[Fe^{+++}]}$$

$$= 0.77 + 0.059 \log \frac{[Fe^{+++}]}{[Fe^{++}]}$$

since H_2 and H^+ are at unit activity.

To find the value of $E_{1\text{-}2}$ at the stoichiometric point, which is the emf at which the indicator color change should appear, we must take into consideration the oxidizing agent used in order to evaluate the ratio Fe^{+++}/Fe^{++}. To illustrate we shall make the computation for the titration of 5 m mol ferrous ion by ceric sulfate solution. It is not necessary to specify the volume of the solution since the ratio Fe^{+++}/Fe^{++} is independent of volume.

Set up the cell,

$$Pt,\ Fe^{++} + Fe^{+++} \parallel Ce^{+++} + Ce^{++++},\ Pt$$

$$\begin{array}{rll} Fe^{++} = Fe^{+++} + e & E^\circ & = -0.77 \\ Ce^{+++} = Ce^{++++} + e & E^\circ & = -1.61 \\ \hline Ce^{++++} + Fe^{++} = Ce^{+++} + Fe^{+++} & E^\circ_{1\text{-}2} = & 0.84 \end{array}$$

At equilibrium,

$$0 = 0.84 - 0.059 \log \frac{[Ce^{+++}][Fe^{+++}]}{[Ce^{++++}][Fe^{++}]}$$

At the stoichiometric point it follows from the chemical equation that $[Ce^{++++}] = [Fe^{++}]$ and $[Ce^{+++}] = [Fe^{+++}]$. Therefore,

$$0 = 0.84 - 0.059 \log \frac{[Fe^{+++}]^2}{[Fe^{++}]^2}$$

$$\log \frac{Fe^{+++}}{Fe^{++}} = 7.12$$

$$\frac{Fe^{+++}}{Fe^{++}} = 10^{7.12}$$

Substitution of this value in the previous equation for the emf of the titration system at the stoichiometric point gives

$$E_{1\text{-}2} = 0.77 + 0.059 \log 10^{7.12}$$

$$= 1.19 \text{ volts}$$

This is the emf which the proper indicator for the titration should give if we set up the system.

Pt, normal hydrogen electrode $\|$ $Ind^+ + Ind$, Pt

$$\begin{array}{rll} \frac{1}{2}H_2 = H^+ + e & E^\circ & = 0.00 \\ Ind = Ind^+ + e & E^\circ & = X \\ \hline \frac{1}{2}H_2 + Ind^+ = H^+ + Ind & E^\circ_{1-2} & = -X \end{array}$$

Since E is found above to be 1.19 volts, we have

$$1.19 = -X - 0.059 \log \frac{[Ind]}{[Ind^+]}$$

If the color change occurs when the two forms of the indicator are in equimolar concentrations,

$$1.19 = -X \quad \text{or} \quad X = -1.19 \text{ volts}$$

In this titration, with ceric sulfate as the oxidizing agent, the indicator should have about the same oxidation potential as Ferroin, which is widely used.

OTHER APPLICATIONS

It should by now be apparent that proper setting up of cells and measurement of emf makes possible indirect determinations of very small concentrations of ions in solution. This method therefore is the basis for data by which many of the equilibrium constants of analytical and physical chemistry are determined. A few illustrations will illustrate the general method.

1. Ionization Constant of Weak Acid. A cell may be so set up that the emf depends on the hydrogen-ion concentration of a solution of a weak acid whose ionization constant is to be determined (another method is to use a salt of a weak acid and determine the concentration of hydrogen ion due to hydrolysis, from which one may compute the ionization constant). From the known concentration of acid or salt and the measured hydrogen-ion concentration, the ionization constant is readily computed. For example, it is found that the emf of the cell,

$$Pt, H_2 \text{ (1 atm)}, HA \text{ (0.1 } M\text{)} \| KCl \text{ (1 } M\text{)}, Hg_2Cl_2, Hg$$

is 0.58 volt. We compute first the concentration of hydrogen ion in 0.1 M HA and then the value of K_i.

$$\begin{array}{rll} H_2 = 2H^+ + 2e & E^\circ & = 0.00 \\ 2Hg + 2Cl^- = Hg_2Cl_2 + 2e & E^\circ & = -0.28 \\ \hline H_2 + Hg_2Cl_2 = 2H^+ + 2Hg + 2Cl^- & E^\circ_{1-2} & = 0.28 \end{array}$$

$$0.58 = 0.28 - \frac{0.059}{2} \log [H^+]^2$$

$$= 0.28 - 0.059 \log [H^+]$$

since all other constituents are at standard state.

Solving, we have

$$[H^+] = 10^{-5.08} = 10^{0.92} \times 10^{-6}$$

$$= 8.3 \times 10^{-6}$$

Now we have

$$\begin{array}{cccc} & 0.1 & 8.3\times10^{-6} & 8.3\times10^{-6} \\ HA & = & H^+ + & A^- \end{array}$$

$$K_i = \frac{(8.3 \times 10^{-6})^2}{10^{-1}} = 6.9 \times 10^{-10}$$

It should be noted that this measurement is not rigorously exact because the cell as set up has a liquid junction whose emf is not taken into consideration. This effect does not greatly change the value of the ionization constant, however, in most measurements.

2. Solubility-product Constant. Measurement of emf may be used to measure the concentration of metal ion present in a saturated solution of an insoluble salt of the metal, thus giving data for computation of the solubility-product constant. For example, it is found that the cell,

$$M, MCl \text{ (solid)}, KCl \text{ (1 } M\text{)}, AgCl, Ag$$

has an emf of 0.05 volt. The metal M has the half-cell potential

$$M = M^+ + e \qquad E^\circ = -0.40$$

To compute K_{SP},

$$\begin{array}{rll} M = M^+ + e & E^\circ & = -0.40 \\ Ag + Cl^- = AgCl + e & E^\circ & = -0.22 \\ \hline M + AgCl = M^+ + Cl^- + Ag & E^\circ_{1\text{-}2} & = -0.18 \end{array}$$

$$0.05 = -0.18 - 0.059 \log [M^+][Cl^-]$$

$$= -0.18 - 0.059 \log K_{SP}$$

$$K_{SP} = 10^{-3.9} = 1.25 \times 10^{-4}$$

3. Dissociation Constant for Complex Ions. The principle is exactly the same as in the previous examples. A cell is so set up that measurement of the emf gives data for determination of the concentration of ion furnished by the desired dissociation. For example, to determine the dissociation constant for the silver ammonia complex there is set up the cell,

$$Ag, Ag^+ (xM) + NH_3 (yM) \parallel \text{reference electrode}$$

The emf is measured, and from this there is computed the concentration of silver ion in the ammoniacal solution of known strength.

QUESTIONS

1. Define the terms volt, ampere, ohm.
2. What is meant by the statement that a potential difference exists between two electrodes?
3. Describe cells whereby the following chemical reactions could be made to produce electric energy:
   (*a*) $Zn + 2H^+ = Zn^{++} + H_2$
   (*b*) $Pb + 2Ag^+ = Pb^{++} + 2Ag$
   (*c*) $Cl_2 + 2I^- = 2Cl^- + I_2$
4. If the normal calomel electrode were taken as the reference standard for single-electrode potentials, with assigned value of zero, how would the values of the standard electrode potentials be changed?
5. Why are calomel and silver–silver chloride electrodes better experimental standard reference electrodes than the hydrogen electrode?
6. Describe an experimental procedure for determining the standard electrode potentials of the following half-cells. Specify the concentrations to be employed.
   (*a*) Cu, Cu^{++}
   (*b*) Pt, $Fe^{+++} + Fe^{++}$
   (*c*) Pt, Cl_2, Cl^-
   (*d*) Pt, Br_2, Br^-
   (*e*) Pt, I_2, I^-
7. What effect will addition of hydrogen sulfide to the left-hand portion of the cell,

$$Cu,\ Cu^{++} \parallel Zn^{++},\ Zn$$

have on the emf? What effect will the addition of hydrogen sulfide to the right-hand half-cell have on the emf? The addition of potassium cyanide to the left-hand half-cell will cause the polarity of the cell to reverse. Explain.

8. In practice the copper–zinc cell is often used without a mechanical salt bridge. Consult a physics textbook for the design employed. Explain the operation of this cell if both the copper and zinc solutions are in the same container.
9. Formulate cells which may be used to evaluate the following equilibrium constants:
   (*a*) The solubility product of silver iodide.
   (*b*) The dissociation constant of the argentocyanide complex ion.
   (*c*) The ion product constant for water.
   (*d*) The hydrolysis constant for sodium cyanide.
   (*e*) The ionization constant of a weak acid.
   (*f*) The constant for the reaction of permanganate with ferrous ion.

PROBLEMS

1. In which direction will the following reactions proceed if all substances are at standard state:
   (*a*) $Sn^{++++} + Cd = Sn^{++} + Cd^{++}$
   (*b*) $Ce^{++++} + Br^- = Ce^{+++} + \frac{1}{2}Br_2$
   (*c*) $2Fe^{+++} + Cd = 2Fe^{++} + Cd^{++}$
   (*d*) $Sn^{+4} + 2Ce^{+++} = Sn^{++} + 2Ce^{+4}$
   (*e*) $S^= + 2Cr^{+++} = S + 2Cr^{++}$
   (*f*) $2MnO_4^- + 5O_2 + 6H^+ = 5O_3 + 3H_2O + 2Mn^{++}$
   (*g*) $5Cl_2 + I_2 + 6H_2O = 2IO_3^- + 10Cl^- + 12H^+$

2. Compute the voltage of each of the following cells. Designate the polarity of the electrodes.

(*a*) Cu, Cu^{++} (0.001 *M*) || Zn^{++} (0.1 *M*), Zn

(*b*) Ag, Ag^{+}(10^{-10} *M*) || KCl (1 *M*), Hg_2Cl_2, Hg

(*c*) Pt, H_2 (0.90 atm), H^{+} (0.01 *M*) || KCl (0.05 *M*), Hg_2Cl_2, Hg

(*d*) Pt, H_2 (1 atm), HCl (0.005 *M*), Cl_2 (1 atm), Pt

(*e*) Pt, H_2 (0.5 atm), HBr (0.1 *M*), Br_2 (liquid), Pt

(*f*) Pt, Ce^{++++} (0.1 *M*) + Ce^{+++} (0.2 *M*) || Fe^{+++} (0.01 *M*) + Fe^{++} (0.05 *M*), Pt

3. What is the voltage of the cell:

$$Ag,\ Ag^{+}\ (1\ M)\ ||\ H^{+}\ (1\ M),\ H_2\ (1\ atm),\ Pt$$

What is the spontaneous cell reaction? Which is the + pole of the cell? Of what practical value is the voltage of this cell?

4. For the cell,

$$Pt,\ Fe^{++}\ (10^{-2}\ M),\ Fe^{+++}\ (10^{-5}\ M)\ ||\ I^{-}\ (10^{-3}\ M),\ I_2,\ Pt$$

(*a*) What is the numerical magnitude of the cell voltage?

(*b*) Which is the negative electrode?

(*c*) If Fe^{++}, Fe^{+++}, and I^{-} are mixed together in solution at the above concentrations and the solution is kept in contact with solid I_2, will Fe^{+++} oxidize I^{-} or will Fe^{++} reduce I_2?

5. (*a*) Compute the equilibrium constant for the reaction,

$$Fe + Cu^{++} = Fe^{++} + Cu$$

(*b*) Compute the equilibrium constant for the reaction,

$$Fe + Cd^{++} = Fe^{++} + Cd$$

(*c*) A solution contains cupric and cadmium ions at a concentration of 0.05 *M*. Iron is added and the solution shaken until equilibrium is reached. Compute the final concentration of the cupric and cadmium ions, assuming a final concentration of 0.3 *M* for the ferrous ion (a considerable quantity of ferrous ion is formed by the reaction of iron with hydrogen ion).

(*d*) Compute the equilibrium constant for the reaction,

$$Cd + Cu^{++} = Cd^{++} + Cu$$

(*e*) What is the ratio of Cu^{++} to Cd^{++} at equilibrium?

6. A solution containing ferrous and hydrogen ions at concentrations of 0.1 *M* each is brought into contact with a strip of pure iron. What pressure of hydrogen gas must be applied to prevent liberation of hydrogen by the action of iron on hydrogen ion?

7. A 0.1 *M* solution of copper sulfate is treated with zinc dust. What is the final concentration of cupric ion remaining in solution? (*Note:* The final concentration of zinc ion may be assumed to be 0.1 *M*. Explain.)

8. If a 0.1 *M* solution of ferrous sulfate of *p*H 7 is treated with pure iron, should any hydrogen be evolved? At what concentration of hydrogen ion is hydrogen gas liberated at a pressure of 1 atm?

9. Metallic silver is shaken with a 0.1 *M* Fe^{+++} solution. Find the ratio $[Fe^{+++}]/[Fe^{++}]$ at equilibrium.

10. Find the equilibrium constant and the ratio $[Sn^{+4}]/[Sn^{++}]$ at equilibrium for the reaction:

$$2Ce^{++++} + Sn^{++} = 2Ce^{+++} + Sn^{++++}$$

if 1 m mol Sn^{++} and 2 m mol Ce^{++++} are mixed in a volume of 100 ml.

11. Compute the equilibrium constant for the reaction,

$$Fe^{+++} + I^- = Fe^{++} + \tfrac{1}{2}I_2$$

12. Ferric nitrate is added to a solution of potassium iodide until the final concentration of ferric ion is 10^{-5} *M*. Compute the equilibrium concentration of iodide ion, assuming the solution to be saturated with iodine, and the final concentration of Fe^{++} to be 0.1 *M*. Would you conclude that iodide ion may be determined by titration with ferric ion?

13. A solution of potassium iodide is treated with excess ferric nitrate so that the final concentration of Fe^{+++} is 0.1 *M*. Assuming the final concentration of Fe^{++} to be 0.1 *M* and the solution to be saturated with iodine, compute the equilibrium concentration of iodide ion.

14. Find the concentrations of Fe^{+++}, Fe^{++} and I^- present when equilibrium is reached in the mixture described in the cell of Problem 4. Assume that solid I_2 is always in contact with the solution.

15. 4 m mol Br^- is titrated by 0.02 *M* Ce^{++++} solution. The final volume of the solution is 300 ml. What is the concentration of Br^- when 0.05 ml of ceric solution is added in excess of the stoichiometric amount? Is the reaction between ceric and bromide ions suitable for volumetric purposes? (A saturated solution of bromine water is 0.16 *M*.)

16. 5 m mol $FeSO_4$ is dissolved in 100 ml water and titrated with 0.1000 *N* $KMnO_4$ until two drops (0.10 ml) have been added in excess. Assume the $[H^+] = 1$, and calculate the milligrams of ferrous sulfate which have not reacted with the $KMnO_4$.

17. Compute the equilibrium constant for the reaction,

$$MnO_4^- + H^+ + Sn^{++} = Mn^{++} + Sn^{++++} + H_2O$$

18. If 5 m mol Sn^{++} is titrated with permanganate in acid solution, what is the concentration of Sn^{++} at the stoichiometric point? Assume the following conditions:

Final volume of solution: 100 ml
$[Sn^{++++}] = 0.05$, since practically all the stannous ion is oxidized
$[Mn^{++}] = 0.02$, since 2 moles Mn^{++} are formed for 5 moles Sn^{++++}
$[Sn^{++}] = X$
$[MnO_4^-] = 0.4X$ (see equation)
$[H_2O] = 1$
$[H^+] = 1$

19. If the titration of Problem 18 is made to an end point, with 0.05 ml 0.02 *M* permanganate present in excess, what is the final concentration of Sn^{++}? Assume all concentrations except that of permanganate to be the same as in Problem 18.

20. What should be the standard oxidation potential of a redox indicator suitable for use in the titration of Problem 18? Assume that the indicator shows a color change when it is half oxidized and that one electron is involved per mole of indicator.

21. Compute the E° value for an indicator to be used in the titration of Fe^{++} by Ce^{+4}; assume that the indicator loses 2 electrons per mole of it which is oxidized and that the color change is observed when 70 per cent of the indicator is in its oxidized form

22. Compute the oxidation potential of a redox indicator that will be half oxidized when in a solution which contains ferric and ferrous ions at concentrations, respectively, of 0.02 M and 10^{-6} M if 2 electrons are used per mole of indicator oxidized.

23. Compute the oxidation potential of a redox indicator that will be 10 per cent oxidized at the point that a ferrous sulfate solution is 99.99 per cent oxidized if one electron is used per mole of indicator oxidized.

24. A solution of ferrous sulfate contains 10^{-5} per cent of the iron in the ferric condition. What is the half-cell potential of this solution?

25. What is the half-cell potential of a ferric salt solution in which 10^{-5} per cent of the iron is in the ferrous condition?

26. The solubility product of AgCl is 1×10^{-10}. Compute the emf of the cell

$$\text{Ag, AgCl, KCl (0.05 } M\text{), } Hg_2Cl_2\text{, Hg}$$

27. (*a*) From the standard silver–silver ion potential compute the potential of the half-cell,

$$\text{Ag, AgCl, KCl (1 } M\text{)}$$

(*b*) Compute the potential of the half-cell,

$$\text{Ag, AgCl, KCl (0.01 } M\text{)}$$

28. From the two half-cell potentials,

$$2Hg = Hg_2^{++} + 2e \qquad E^\circ = -0.80 \text{ volt}$$

$$2Hg + 2Cl^- = Hg_2Cl_2 + 2e \qquad E^\circ = -0.28 \text{ volt}$$

compute the solubility product for mercurous chloride, Hg_2Cl_2.

29. The emf of the cell,

$$\text{Ag, AgX, KX (0.05 } M\text{) } \| \text{ KCl (1 } M\text{), } Hg_2Cl_2\text{, Hg}$$

is +0.30 volt. What is the solubility product for AgX?

30. E° for $Pb + SO_4^{=} = PbSO_4 + 2e$ is 0.31 volt. From this and the table of standard electrode potentials compute the K_{SP} for $PbSO_4$.

31. From a table of standard electrode potentials and the K_{SP} for $Cu(OH)_2$ develop a value of E° for

$$Cu + 2OH^- = Cu(OH)_2 + 2e$$

32. From a table of standard electrode potentials compute the following:

(*a*) K_{inst} for $HgI_4^{=}$.

(*b*) K_{SP} for AgI.

(*c*) K_{SP} for $Mg(OH)_2$.

33. The ionization constant of the acid HA is 5×10^{-6}. Compute the emf of the cell,

$$\text{Hg, } Hg_2Cl_2\text{, KCl (1 } M\text{) } \| \text{ HA (0.1 } M\text{), } H_2 \text{ (1 atm), Pt}$$

34. What is the emf of the cell,

$$\text{Normal calomel electrode } \| \text{ NaA (0.05 } M\text{), } H_2 \text{ (1 atm), Pt}$$

when NaA is a salt of the acid HA of Problem 33?

35. Using the data of Table 4, Appendix II, compute the emf of the cells:

(*a*) Zn, $ZnCl_2$ (0.01 M) + NH_4OH (0.1 M) $\|$ Normal hydrogen electrode

(*b*) Ag, AgCl, KCl (0.01 M) $\|$ KCN (1 M) + $AgNO_3$ (0.1 M), Ag

36. The emf of the cell,

Normal calomel electrode || MCl (0.1 *M*), H_2 (1 atm), Pt

is —0.52 volt. What is the ionization constant of the base MOH?

37. Compute the potential of the half-cells:

(*a*) Hg + Na (1 g Na per 200.6 g Hg), NaCl (0.1 *M*)

(*b*) Hg + Na (1 mole per cent Na), NaCl (0.1 *M*)

(*c*) Pt, Cl_2 + H_2O (Cl_2 at a concentration of 0.01 *M*), Cl^- (1 *M*)

(*d*) Pt, Br_2 + H_2O (Br_2 at a concentration of 0.01 *M*), Br^- (0.1 *M*)

(The solubility of bromine in water is about 0.16 *M*.)

CHAPTER

16

Volumetric Precipitation Methods

[The sections of Chapters 18 and 19 which relate to the solubility-product principle and to the behavior of colloids should be studied before the material of this chapter.]

It may be recalled that a determination may be made by volumetric methods if (*a*) the reaction goes rapidly to completion, (*b*) there is only one reaction, (*c*) there is a marked change in some property of the solution at the stoichiometric point, and (*d*) an indicator is available which will show the change at the stoichiometric point. Most precipitation reactions fulfill the first three requirements: the reactions, since they are ionic, proceed rapidly to completion; the conditions are usually so adjusted that only one insoluble substance forms; finally, there is a marked change in the concentration of the ions of the precipitate at the stoichiometric point. Unfortunately, no indicators are available for most precipitation reactions, and consequently comparatively few volumetric precipitation methods are employed in quantitative analysis.

PRECIPITATION INDICATORS

1. Formation of a Colored Precipitate

In certain titrations the formation of a colored precipitate may be used to indicate the end point. It is necessary that the precipitate formed in the analysis be colorless and that a colored precipitate of the ion which is used for the titration be made to form at or near the stoichiometric point. The best-known example of this method is the use of silver chromate as indicator in the titration of chlorides with silver nitrate solution. It is known as the Mohr method and is based on the principle of fractional precipitation.

Fractional Precipitation. If an ion is added to a solution containing two ions which may form a precipitate with the added ion, that substance will precipitate first whose solubility product is first exceeded. In the Mohr titration silver ion is added to a solution which contains a relatively high concentration of chloride ion and a small concentration (usually about 0.002 *M*) of chromate ion. The two solubility products are

$$[Ag^+][Cl^-] = 10^{-10}$$

$$[Ag^+]^2[CrO_4^=] = 9 \times 10^{-12}$$

A precipitate of silver chloride forms as soon as reagent is added, but silver chromate does not begin to precipitate until the concentration of silver ion reaches the value given by the equation,

$$[Ag^+]^2 = \frac{K_{SP}}{[CrO_4^=]} = \frac{9 \times 10^{-12}}{2 \times 10^{-3}}$$

$$[Ag^+] = 7 \times 10^{-5}$$

The point at which silver chromate begins to appear is taken as the end point in the titration; it is recognized by means of the color of the silver chromate precipitate. At the stoichiometric point for the precipitation of silver chloride, the silver-ion concentration is given by the expression,

$$[Ag^+] = [Cl^-] = \sqrt{10^{-10}} = 10^{-5}$$

Error in Mohr Method. Since the concentration of silver ion present at the end point is greater than the concentration at the stoichiometric point, there is an inherent error in the method, due to the excess of silver nitrate reagent which must be added after the stoichiometric point is reached. This error is very small, however, as may be shown by a simple calculation:

Assume the titration of 50 ml 0.1 *M* sodium chloride solution. The total volume at the end point is 150 ml. At the end point the millimoles of silver nitrate present are given by the equation,

$$7 \times 10^{-5} \times 150 = 10.5 \times 10^{-3} \text{ m mol}$$

At the stoichiometric point there are present, as shown by a similar calculation, 1.5×10^{-3} m mol. The excess of silver nitrate amounts to 9×10^{-3} m mol or 9×10^{-2} ml of 0.1 *M* solution. The percentage error is given by the expression,

$$\text{Percentage error} = \frac{\text{excess volume of reagent}}{\text{stoichiometric volume}} \times 100$$

$$= \frac{9 \times 10^{-2}}{50.0} \times 100 = 0.18\%$$

The actual error caused by the excess of reagent is negligible when standardization follows the same procedure as the analysis, because of the cancelation of the end-point error.

In view of the previous calculation a question may be raised as to the possibility of using such a concentration of chromate ion that the end point shall appear at the concentration of silver ion which corresponds to the stoichiometric point. At the stoichiometric point the concentration of silver ion is 10^{-5} M. Substitution of this value into the expression for the solubility product of silver chromate gives for the chromate-ion concentration the value 9×10^{-2} M. This concentration is not used in practice, because the intensity of color in such a solution is so great that the formation of silver chromate precipitate is not readily observed. In practice, a concentration of 0.001–0.003 M is used.

If the concentration of chromate ion is made much smaller than 0.001 M, a serious error may be introduced, since a large excess of silver ion will be required before the product of the ionic concentrations of silver and chromate ions reaches the solubility-product value. It is for this reason that the Mohr titration cannot be carried out in strongly acid solution. The ionization constant of the acid $HCrO_4^-$ is very small. In the presence of strong acids little free chromate ion exists, most of the chromium being present as the bichromate ion. In practice, the Mohr titration must be carried out in a solution whose pH lies between 6 and 10. Solutions of $p\text{H} > 10$ cannot be used because at high pH silver oxide precipitates.

2. Formation of a Soluble Colored Compound

In the Volhard method, solutions containing silver ion are titrated with a standard solution of potassium thiocyanate. Silver thiocyanate is precipitated,

$$Ag^+ + SCN^- = AgSCN \text{ (white precipitate)}$$

When the stoichiometric point is passed, the concentration of thiocyanate increases to such an extent that the ion may be detected by means of the reaction,

$$Fe^{+++} + 6SCN^- = Fe(SCN)_6^{\equiv} \text{ (colored)}$$

Ferric alum is usually employed as indicator. This titration may be made in nitric acid solution.

3. Appearance of Turbidity

Certain titrations utilize the initial appearance of turbidity in a solution as the end point. This method requires that the reagent ion which

is used for the titration form a stable soluble complex with the analyzed ion. The concentration of reagent ion, therefore, remains very small until the stoichiometric amount is added, after which it rapidly increases. The most widely used application of this principle is in the Liebig method for cyanides. Solutions of cyanide ion are titrated with standard silver nitrate solution. A soluble complex ion is formed, according to the equation,

$$Ag^+ + 2CN^- = Ag(CN)_2^-$$

As the stoichiometric point is passed, there is a large increase in the concentration of silver ion, and a precipitate forms,

$$Ag^+ + Ag(CN)_2^- = Ag[Ag(CN)_2] \text{ (precipitate)}$$

4. Adsorption Indicators

Fajans [1] and others have shown that certain organic dyes may be used as indicators for volumetric-precipitation reactions. The action of these indicators is due to the fact that at the stoichiometric point the indicator is adsorbed by the precipitate. In the process of adsorption a change occurs in the indicator which causes the production of a substance of different color.

The theory of the action of the adsorption indicators is based on the properties of colloids. At the surface of a colloidal particle is a layer of that ion of the lattice which predominates in the surrounding solution. This *primarily adsorbed layer* holds by *secondary* adsorption oppositely charged ions which are present in the solution. See Fig. 31, page 365. The ion which is most strongly held by secondary adsorption is the ion of the solution whose compound with the primarily adsorbed ion is least soluble. An adsorption indicator is an organic *ion* which is strongly held by secondary adsorption *only* when the primarily adsorbed ion is the reagent used in the titration.

In the titration of chlorides by silver nitrate the fluorescein negative ion serves as indicator. Before the stoichiometric point is reached, the primary adsorption is one of chloride ions, as this is the lattice ion which is in excess. Since the chloride ion is negatively charged, the primary adsorbed layer does not attract the negative fluorescein ion. Just at the stoichiometric point the concentration of silver ion rises while the concentration of chloride ion decreases, and as a result the electric charge

[1] For reviews of adsorption indicators see I. M. Kolthoff, *Chem. Rev.*, **16**, 87 (1935); A. W. Welling, *School Sci. Rev.* (London), **17**, 181 (1935). See also K. Fajans and others, *Z. Electrochem.*, **29**, 495 (1923); *Z. physik. Chem.*, **125**, 309 (1927); *Z. anorg. allgem. Chem.*, **137**, 221 (1924).

on the surface of dispersed particles is changed; silver ion is now primarily adsorbed instead of chloride ion, giving a positively charged particle which holds negative ions by secondary adsorption. In particular, the fluorescein ion is strongly adsorbed by the positively charged particle. The forces which cause the adsorption of fluorescein ion induce a rearrangement of the structure of the ion and thereby cause the formation of a colored substance.

Successful use of adsorption indicators requires the following conditions:

1. The indicator ion must be of opposite charge to the ion used for the titration reagent.

2. The indicator ion must be specifically adsorbed to such an extent that the color change appears immediately after the stoichiometric point.

3. The indicator ion must not be too strongly adsorbed by the precipitate. If this occurs, the adsorption of indicator may be a *primary* process which takes place before the stoichiometric point is reached. For example, in the silver–chloride titration, if eosin (tetrabromofluorescein) is used as the indicator, the color change occurs before the stoichiometric point is reached. The premature color change is probably due to the fact that the indicator is primarily adsorbed by the precipitate instead of chloride ion, when the concentration of the chloride ion becomes small.

4. The precipitate formed in the titration should be highly dispersed throughout the titration. Since the color change occurs only at the surface of precipitated particles, the visibility of the change depends on the number of particles. In chloride–silver-ion titrations a protective colloid, dextrin, is often added to prevent coagulation of the sol.

The indicators most used for the titration of halides with silver are derivatives of fluorescein, a weak organic acid. Since the negative ion of the indicator is the substance adsorbed, the efficiency of the indicator action is decreased by the presence of hydrogen ion, which represses the concentration of fluorescein ion. Because of this, titrations with fluorescein indicator must be carried out in neutral or slightly basic solutions (pH 7–10). Kolthoff [2] has shown that derivatives of fluorescein which are stronger acids than fluorescein itself may be advantageously substituted for it, thus permitting the titration to be made in acid solutions. Eosin may be used for the titration of bromides or iodides in solutions whose pH is as low as 2, but it is unsuitable for chloride determinations, as previously mentioned. Dichlorofluorescein is very useful for the titration of chlorides, where it can be used at pH as low as 4.

A list of the more widely used adsorption indicators is given in Table 27.

[2] I. M. Kolthoff, W. M. Lauer, and C. J. Sunde, *J. Am. Chem. Soc.*, **51**, 3273 (1929).

TABLE 27

A Partial List of Adsorption Indicators for Volumetric Precipitations

Titration of	*Titrating Ion*	*Indicator*	*Notes*
Cl^-	Ag^+	Dichlorofluorescein	pH > 4
Br^-	Ag^+	Eosin	pH > 2 Best in acetic acid solution
I^-	Ag^+	Eosin	as Br^-
SCN^-	Ag^+	Eosin	as Br^-
CN^-	Ag^+	Diphenyl carbazide	
Ag^+	Br^-	Rhodamine 6 G	In 0.5 N HNO_3
OH^-	Pb^{++}	Fluorescein	Quite sharp in 0.01 and 0.1 N solutions
BO_2^-, $B_4O_7^=$	Pb^{++}	Dichlorofluorescein	Accurate in neutral solution
$SO_4^=$	Pb^{++}	Dibromofluorescein	A better method is based on fractional precipitation *

* See W. C. Schroeder, *Ind. Eng. Chem., Anal. Ed.*, **5**, 403 (1933), and Sheen, Kahler, and Cline, *ibid.*, **9**, 69 (1937).

5. Spot-test Indicators

Spot-test or external indicators may often be employed when no internal indicator is available which can be added to the solution in which a titration is made. A spot-test indicator is a reagent which will react with one of the constituents involved in the titration to give either a precipitate or a colored compound. In making a spot-test titration the reagent is added without testing until the end point is approached (a semi-quantitative titration is first made to determine the approximate volume of reagent needed). Near the end point a drop of solution is withdrawn on a stirring rod after each addition of reagent, and this drop is tested by adding to it a drop of indicator solution. The end point is located by the point at which the tested drop first shows absence of the substance titrated or excess of titrating reagent. An example of this type of titration is the volumetric determination of zinc by titration with potassium ferrocyanide. Potassium zinc ferrocyanide is precipitated quantitatively when the reagents are mixed. Solutions of uranyl salts or of ammonium molybdate are employed as spot-test indicators. A deep color is developed in the spot test when ferrocyanide is present in excess.

STOICHIOMETRY

The concentrations of the standard solutions employed for precipitation reactions are expressed as either the titer or the molarity. The normality basis for concentration is not usually employed, since this

would require a new definition of the equivalent weight; it may be recalled that the equivalent weight has been defined in terms of the neutralization or reduction of hydrogen ion which is not a reactant in most precipitation reactions.

The titer method is most convenient when the reagent is standardized by means of the constituent whose analysis is later to be made. For example, silver nitrate solutions are standardized by titration of weighed samples of pure sodium chloride; the strength is conveniently expressed in terms of the milligrams of chloride ion per milliliter of standard solution.

Illustrative Problem. A 0.2500-g sample of pure NaCl requires 40.00 ml of $AgNO_3$ solution. What is the Cl^- titer of the solution?

Solution:

$$1 \text{ ml } AgNO_3 \text{ titrates } \frac{250.0 \text{ mg NaCl}}{40.00 \text{ ml } AgNO_3} = 6.250 \frac{\text{mg NaCl}}{\text{ml } AgNO_3}$$

In 6.250 mg NaCl (mol wt = 58.46) there are $6.250 \times (35.46/58.46) = 3.791$ mg Cl^- (mol wt = 35.46).

Therefore, the Cl^- titer is 3.791 mg per milliliter.

When this solution is used for the analysis of a sample, it is only necessary to multiply the volume of $AgNO_3$ solution (in milliliters) by the titer, to obtain the weight of Cl^- in the sample (in milligrams).

Illustrative Problem. A 0.3000-g sample is analyzed by titration with 45.00 ml of the silver nitrate solution given above. What is the percentage of Cl^- in the sample?

Solution:

$$\text{Weight } Cl^- \text{ in milligrams} = 45.00 \text{ ml} \times 3.791 \text{ mg per milliliter} = 170.6 \text{ mg}$$

$$\text{Percentage } Cl^- = \frac{170.6}{300.0} \times 100 = 56.87\%$$

When a given reagent is to be used for the analysis of several different constituents, it is convenient to express the concentration in terms of molarity rather than as titer. The conversion from one unit to the other is readily made.

Illustrative Problem. What is the molarity of the $AgNO_3$ solution of the preceding section?

Solution: It may be recalled that a 1 *M* solution contains 1 mole per liter or 1 m mol per milliliter. Since the titer of the solution is given in terms of milligrams per milliliter, it is convenient to consider the millimoles of solute. According to the equation,

$$Ag^+ + Cl^- = AgCl$$

the moles of Ag^+ per unit volume are the same as the number of moles of Cl^- that will be titrated by unit volume. Therefore the molarity is obtained by converting the Cl^- titer into the number of millimoles of Cl^- per milliliter of solution.

$$\frac{3.791 \dfrac{\text{mg}}{\text{ml}}}{35.46 \dfrac{\text{mg}}{\text{m mol}}} = 0.1069 \frac{\text{m mol}}{\text{ml}} = \text{molarity}$$

If this silver nitrate solution is used for determination of the bromide ion in a sample, the computation is as follows.

Illustrative Problem. A 0.7000-g sample of Br^- is titrated by 33.00 ml of the above solution. What is the percentage of Br^- in the sample?

Solution: Since millimoles Br^- = millimoles Ag^+, the total number of millimoles is given by the expression,

$$33.00 \text{ ml} \times 0.1069 \frac{\text{m mol}}{\text{ml}} = 3.528 \text{ m mol}$$

Therefore, the weight of Br^- is

$$\text{Milligrams } Br^- = 3.528 \text{ m mol} \times 79.92 \frac{\text{mg}}{\text{m mol}} = 282.0 \text{ mg}$$

$$\text{Per cent } Br^- = \frac{282.0 \text{ mg}}{700.0 \text{ mg}} \times 100 = 40.28\%$$

DETERMINATIONS

Chloride by Adsorption Indicator Method

Preparation and Standardization of Silver Nitrate Solution. Procedure. Weigh out on the trip scale about 8.5 g reagent-grade silver nitrate crystals. Transfer to a glass-stoppered bottle, and add 500 ml distilled water which has first been tested for presence of chlorides. Mix well, and store in the desk when not in use, to protect from direct sunlight.

Dry about 2 g reagent-grade sodium chloride at 120°C. Weigh out three samples of about 0.25 g, and transfer to titration flasks. Dissolve each in 25–50 ml distilled water. Add about 0.3 ml dichlorofluorescein indicator and 0.1 g dextrin, and titrate with the silver nitrate solution. Do not allow direct sunlight to shine on the titration flask since this causes a rapid darkening of the precipitate when in the presence of dichlorofluorescein. The end point is a sudden change from white to pink in the color of the AgCl particles. It is reversible, and back titration can be done if a standard sodium chloride solution is available.

From the weight of NaCl and volume of $AgNO_3$ used compute the molarity of the $AgNO_3$ solution. Compute also the Cl^- titer of the solution.

Determination of Percentage Chlorine in Soluble Chloride. Procedure. Dry the sample at 120°C. Weigh out three samples of 0.25 to 1.0 g, as directed by the instructor. Dissolve each in a little distilled water, and titrate as in the standardization. Report the percentage of chlorine in the sample.

Errors. The usual volumetric errors may be encountered. The solution must not be at *p*H less than 4, nor greater than 10. Other anions which form insoluble silver salts must be absent. High concentrations of electrolytes may interfere because of flocculation of the sol. Strong light must be avoided.

Other Applications. The procedure is the same for bromides, iodides, and thiocyanates. Silver solutions may be analyzed by using them to titrate solutions containing a known amount of chloride, just as in the standardization.

Chloride by Volhard Method

The Volhard method is applicable for the determination of halides or of silver in nitric acid solution and is consequently widely used because the other titrimetric methods must be carried out in nearly neutral solutions. Copper (up to 70 per cent), arsenic, antimony, cadmium, bismuth, lead, iron, zinc, manganese, cobalt, and nickel do not interfere unless they are present in such amount that the color of their ions interferes with detection of the end point.

The method is based on the insolubility of silver thiocyanate and the use of ferric ion as indicator to show when excess thiocyanate is present. Nitric acid in large excess does not interfere, but it is essential that nitrous acid be absent. When the sample has been oxidized by nitric acid, it is necessary to boil until all oxides of nitrogen are removed before making the titration.

In the analysis of silver the sample, in the form of silver ion, is titrated directly. In the analysis of halides a measured excess of standard silver solution is added to the sample, and the excess silver is titrated by a standard solution of thiocyanate. When chloride is present, an equilibrium is established between silver chloride and silver thiocyanate; the solubility products are such that some of the chloride is converted into thiocyanate during the titration, according to the equation,

$$AgCl + SCN^- = AgSCN + Cl^-$$

Application of the equilibrium law leads to the relation,

$$\frac{[Ag^+][Cl^-]}{[Ag^+][SCN^-]} = \frac{K_{SP \text{ for AgCl}}}{K_{SP \text{ for AgSCN}}}$$

$$= \frac{1 \times 10^{-10}}{1.2 \times 10^{-12}}$$

Or, since it is the same concentration of Ag^+ that appears in both the numerator and denominator of the expression,

$$\frac{[Cl^-]}{[SCN^-]} = 0.8 \times 10^2$$

Therefore, when thiocyanate is present in sufficient excess to give an end point, a considerable amount of chloride ion has been brought back into solution, and a corresponding amount of thiocyanate has been used in reaction with the silver chloride. This undesired reaction may be prevented by filtering the solution before making the thiocyanate titration or by adding nitrobenzene [3] after precipitation of the silver chloride. The nitrobenzene forms an oily coating on the particles of silver chloride and prevents reaction with the thiocyanate. Other silver halides (bromide and iodide) are so insoluble that no appreciable amount of reaction occurs with thiocyanate, and filtration is not needed prior to the thiocyanate titration.

In the analysis of halides it is necessary to know the concentration of the silver nitrate solution and to know the strength of the thiocyanate solution relative to that of the silver nitrate solution, in order that the volume of thiocyanate used can be converted into the corresponding amount of silver solution. For halide analysis, standardization is best made by a pure halide sample, as in the adsorption indicator method. In the analysis of silver it is only necessary to know the concentration of the thiocyanate solution. This is best standardized by use of pure silver. A weighed amount of the silver is dissolved in nitric acid, and the solution boiled to remove oxides of nitrogen, diluted to a suitable volume, and titrated directly with the thiocyanate solution.

Procedure. Standardization. Prepare approximately 0.1 *M* solutions of silver nitrate and potassium thiocyanate (500 ml each), and 50 ml of a saturated solution of ferric ammonium sulfate dissolved in 1 *N* nitric acid. Dilute 25 ml nitric acid with an equal volume of water, and boil in an Erlenmeyer flask until the solution is colorless, to remove nitrous acid. Keep this reagent in the dark until needed.

[3] J. R. Caldwell and H. V. Meyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

Determine the relative strength of the silver nitrate and the thiocyanate solutions. Measure, from a buret, 35–40 ml of the silver solution into a 250-ml Erlenmeyer flask. Add 5 ml of the nitric acid solution and 1 ml of the indicator solution. Titrate (note 1) with thiocyanate to the appearance of a brownish tinge (note 2) which is permanent on shaking. Determine the indicator blank by adding 1 ml indicator to 75 ml water acidified with 5 ml of the nitric acid solution, and titrating with thiocyanate. Subtract the volume of thiocyanate required for the blank from the total volume used. Compute the ratio $\frac{\text{ml thiocyanate}}{\text{ml silver}}$. Duplicate results should agree within 1–2 parts per 1000.

Accurately weigh a 1.1- to 1.2-g sample of pure dry sodium chloride, transfer to a 250-ml volumetric flask, dissolve, and dilute to volume. Withdraw, by a pipet, one-fifth aliquot portions and introduce into 250-ml Erlenmeyer flasks. Add 5 ml of the nitric acid solution, and then add silver nitrate solution from a buret until it is in excess (note 3). Add 1–3 ml nitrobenzene (note 4) and 1 ml of the indicator solution, shake, and then titrate with thiocyanate. From the volume of thiocyanate used compute the volume of silver nitrate in excess, and deduct this from the total volume to obtain the net volume required for precipitation of the chloride. From the net volume and the weight of chloride sample employed compute the Cl^- titer of the solution. Duplicate results should agree within 1–2 parts per 1000.

Notes. 1. Care must be taken to avoid the addition of too little thiocyanate. Near the end point the reagent must be added dropwise and the solution thoroughly shaken before the next addition.

2. The end-point color is due to the formation of the complex $Fe(SCN)_6^{=}$ ion.

3. Near the stoichiometric point the precipitate will coagulate. After this occurs, shake well, allow to stand a moment, and add a little silver nitrate to the clear supernatant liquid. If precipitation is complete, no marked cloudiness will occur. Continue until it is certain that silver nitrate is in excess.

4. Optionally, instead of adding nitrobenzene, filter the solution through a Gooch crucible, wash with a little water, and titrate the clear filtrate with thiocyanate solution. This method has the advantage that at the end point only a little precipitate is in the solution.

Analysis of Chloride Samples. Prepare a solution of the sample as directed in the previous methods. Analyze aliquot portions, following the procedures employed for standardization. Report the percentage of chlorine in the sample. Alternatively, weigh out three 0.25- to 1.0-g samples as directed. Dissolve each, add excess standard $AgNO_3$, and complete the titration with standard KSCN, as in the standardization.

Errors and interfering substances. The usual volumetric errors are encountered. In addition, the beginner is prone to undertitrate on adding thiocyanate. The necessity for removal of silver chloride has been emphasized. Other substances which form insoluble silver salts must be absent, as must bivalent mercury which forms a stable complex ion with thiocyanate ion. Nitrous acid and oxides of nitrogen must be boiled off, since they attack thiocyanic acid, causing a premature red color in the solution. The amount of excess silver nitrate should be kept small, thereby reducing the volume required in back titration.

Procedure. Analysis of Silver Alloy. Prepare solutions as directed above. Standardize the thiocyanate solution as follows: Accurately weigh 0.3–0.4 g pure silver sheet or foil, and dissolve in an Erlenmeyer flask in 5–10 ml 1:1 nitric acid. Boil the solution until oxides of nitrogen are expelled. Dilute to 100 ml, add ferric indicator, and titrate with thiocyanate, as directed in the preceding exercise. Compute the Ag^+ titer of the thiocyanate.

In the analysis of an alloy proceed just as in the standardization. Report the percentage of silver.

Mohr Method

The theory of this method has been given on page 293. The titration is made in neutral solution to an end point which is shown by the formation of a colored precipitate of silver chromate. Because of the intense color of the chromate ion the theoretical amount of potassium chromate is not used; therefore an excess of silver ion, past the stoichiometric point, is required. The amount of excess cannot be accurately evaluated by means of a blank, but any error from this cause can be avoided by standardization of the silver nitrate solution under the same conditions as those under which the analysis is performed.

Procedure. Standardization. Accurately weigh a 1.1- to 1.2-g sample of pure dry sodium chloride, transfer to a 250-ml volumetric flask, and dilute to volume. Withdraw one-fifth aliquot portions by a pipet, and deliver into 250-ml porcelain casseroles (note). Add 2 ml 0.1 *M* potassium chromate solution, and titrate, without further dilution, with silver nitrate solution prepared according to directions on page 299. The end point is marked by the first appearance of a permanent colored precipitate of silver chromate. Compute the Cl^- titer of the silver nitrate solution.

Note. The end point for this titration is more readily detectable in a casserole than in a flask. Stir the solution with a short glass stirring rod.

Analysis of Soluble Chloride. Accurately weigh 1.5–2 g, and make up to a volume of 250 ml in a calibrated flask. Titrate aliquot portions (note) according to the procedure used in standardization. Calculate the percentage chlorine in the sample.

Note. Test the solution of the sample with litmus paper after the aliquot portion is measured. If it is acid, add chloride-free sodium bicarbonate until the solution shows a neutral reaction, or neutralize, using phenolphthalein indicator, with chloride-free base. If the sample is strongly basic, neutralize with chloride-free nitric acid to the phenolphthalein end point. Optionally, the sample may be made slightly basic with sodium or ammonium hydroxide, and then made just acid to phenolphthalein by addition of dilute acetic acid.

Errors and interfering substances. All the errors common to volumetric determinations may be encountered. The solution must be nearly neutral. The chief difficulty in using this method lies in the technique of determining the end point. Interfering cations are those which are colored, such as copper and nickel; those which give precipitates with chromates, such as lead and barium; and those which precipitate as basic chlorides in neutral solution, such as bismuth and tin. Interfering anions are those whose silver salts are insoluble in neutral solution, such as phosphate, arsenate, and sulfide., $C_2O_4^-$

Other Applications. The Mohr method may be used for the determination of bromides, but is not satisfactory for iodides and thiocyanates because adsorption by the precipitate causes an unsatisfactory end point. Since the introduction of adsorption indicators, the Mohr method is not widely used, even for chlorides, for the end point is difficult to detect, and the titration is tedious. The method, however, is capable of high accuracy in the hands of an experienced analyst.

Liebig Method for Cyanides

Titration of cyanide solutions with silver nitrate is the standard method for the volumetric determination of cyanides. The method is listed here, not as a recommended student exercise,[4] but because of its commercial importance. It is also useful for the determination of silver in the presence of halogens.

In cyanide analyses silver nitrate may be added to a cyanide solution until addition of a drop of reagent causes turbidity in the solution. The chemistry of the determination is as follows: Prior to the stoichiometric point, a soluble silver cyanide complex ion is formed,

$$Ag^+ + 2CN^- = Ag(CN)_2^-$$

[4] The very poisonous nature of potassium cyanide and the liberation of hydrocyanic acid, when cyanide solutions are acidified, render its use dangerous.

When the stoichiometric point is reached, the insoluble silver salt of this complex ion begins to precipitate; the appearance of the precipitate may be taken as the end point. There is danger, however, that some precipitate may form locally before the stoichiometric point is reached, and a better end point is obtained by adding to the solution ammonium hydroxide and iodide ion. Formation of a complex silver ammonia ion prevents the precipitation of silver argentocyanide. Ammonia does not interfere with precipitation of silver iodide after the stoichiometric point has been passed, since silver iodide is extremely insoluble. The appearance of this precipitate, therefore, marks the end point. In the stoichiometry of the method it must be remembered that two cyanide ions are equivalent to one silver ion.

Procedure. To the dissolved sample (note 1) which should contain 6–8 m mol of cyanide ion, add 30–40 m mol of ammonium hydroxide and 0.1–0.2 g potassium iodide, and dilute to a volume of 100 ml. Titrate with standard 0.1 *M* silver nitrate until the addition of 1 drop of reagent causes the appearance of a permanent turbidity in the solution (note 2).

Notes. 1. Keep constantly in mind the very poisonous nature of potassium cyanide. Be sure to wash out the solution with a large quantity of water at the conclusion of the determination. Do not allow any waste cyanide to stand in a sink where it may come into contact with acids and evolve hydrogen cyanide gas.

2. The method may be used for the determination of silver in the presence of halides. Add to the sample a measured excess of cyanide solution whose strength is accurately known, and back-titrate according to the above procedure with standard silver nitrate.

QUESTIONS

1. Is the strength of a silver nitrate solution as determined by the Mohr method greater than, equal to, or less than the strength as determined by an adsorption indicator titration, pure sodium chloride being used as the primary standard in each case?

2. When a solution of hydrochloric acid is to be standardized by the Mohr method, the acid is first neutralized. What indicator should be used? What reagent would you employ for the neutralization?

3. Is it necessary to neutralize a hydrochloric acid solution if it is to be standardized by silver nitrate titration by the adsorption indicator method? If the solution is neutralized, what indicator should be employed? What would be the effect on the normality if the neutralization were not carried out?

4. What relation must exist between the charge on the indicator ion and the charge on the titrating ion when an adsorption indicator is used?

5. Why is dextrin used in the chloride determination with dichlorofluorescein as indicator?

6. In a Volhard analysis for Cl^- the AgCl was not removed by filtration before the back titration with SCN^-. Was the determined percentage of chloride too high or too low?

7. Explain how I^- can serve as indicator in the titration of CN^- by Ag^+.

8. If an excess of $AgNO_3$ were added to a mixture of NaCN and NaCl, what would have precipitated?

9. Why is it not required to filter off the silver iodide in the determination of iodine by the Volhard procedure?

10. Describe a procedure for determining the silver present in a sample of photographic emulsion which contains silver, bromine, and organic matter.

PROBLEMS

1. What is the molarity of a NH_4SCN solution 25.75 ml of which is required to titrate 215.3 mg 99.9 per cent pure Ag after the metal has been dissolved in HNO_3?

2. How many grams of $AgNO_3$ should be present per liter of solution so that each milliliter is equivalent to 1.000 mg Cl^-?

3. How many milliliters of 0.1500 *M* $AgNO_3$ are needed to titrate:
   (*a*) 4.000 m mol $BaCl_2 \cdot 2H_2O$?
   (*b*) 0.5000 g KCN?
   (*c*) 35.5 ml 0.1571 *M* KSCN?

4. A sample of silver alloy is dissolved in nitric acid and the silver determined by a Volhard titration. If 38.62 ml of 0.1175 *M* KSCN solution is required for the titration, how many grams of silver are in the sample?

5. How many milliliters of 0.1200 *M* KSCN will be needed in the back titration after the addition of 30.00 ml 0.1100 *M* $AgNO_3$ solution to 0.3655 g KI dissolved in 100 ml water?

6. An iodide sample which weighs 3.000 g is analyzed by the Volhard process; 49.50 ml 0.2000 *M* $AgNO_3$ is added, and 6.50 ml 0.1000 *M* KSCN is needed to titrate the excess silver. Calculate the percentage of iodide in the sample.

7. A sample contains NaBr and inert material. A 1/5 aliquot is dissolved in water and 50.00 ml 0.1050 *M* $AgNO_3$ is added; 8.00 ml KSCN solution is required to produce the red color with the ferric alum indicator. Calculate the grams of NaBr present if 1.000 ml $AgNO_3$ is equivalent to 1.250 ml KSCN.

8. 40.00 ml 0.1000 *M* $AgNO_3$ is added to 0.3300 g of a sample which contains 1.300 m mol $BaCl_2 \cdot 2H_2O$ and impurities inert to $AgNO_3$. How many milliliters of 0.1200 *M* KSCN solution will be required for back titration?

9. From the following data determine the percentage of chloride in a sample:

Standardization:	Weight of NaCl	0.2500 g
	Volume of $AgNO_3$	63.46 ml
	Volume of KSCN	3.79 ml

37.90 ml KSCN is equivalent to 50.00 ml $AgNO_3$.

Analysis:	Weight of sample	0.6250 g
	Volume of $AgNO_3$	35.00 ml
	Volume of KSCN	7.58 ml

10. A 3.500-g portion of a sample containing NaBr and Na_2SO_4 is dissolved and diluted to 250.0 ml. One-fifth aliquot portions are titrated by silver nitrate, an average of 42.50 ml of solution being required for the aliquot portion. In standardization 1.000 ml of $AgNO_3$ is found to be equivalent to 0.01250 g KBr. Compute the percentage of Br in the sample. How many grams sodium sulfate are present in the sample?

11. In a cyanide determination 35.66 ml of silver nitrate solution is needed to titrate to the appearance of turbidity. If 1.000 ml $AgNO_3$ = 0.002875 g KCl, how many grams of cyanide, computed as NaCN, are present in the sample?

12. A small amount of KI is added to a solution of NaCN. 35.00 ml 0.1200 *M* $AgNO_3$ is required to produce a precipitate of AgI. Find the milligrams of NaCN present.

13. 25.00 ml $AgNO_3$ reacts with 5.000 m mol NaCl; 35.00 ml of the silver solution is required to titrate a sample of $ZnCl_2 \cdot 6H_2O$. How many milligrams of the hydrate are present in the sample?

14. Mercury can be precipitated as $Hg(SCN)_2$ and determined by a procedure similar to the Volhard process. What is the percentage of mercury in an alloy 0.7500 g of which required 45.10 ml of a KSCN solution whose Ag titer is 9.542 mg per milliliter?

15. A 0.5216-g sample of a zinc ore was brought into solution and the zinc separated and titrated with ferrocyanide solution, 23.21 ml being required; 32.00 ml of this solution was required for 0.2613 g of pure zinc oxide in the standardization. Find the percentage of zinc in the ore. The reaction is

$$2K_4Fe(CN)_6 + 3ZnCl_2 = K_2Zn_3[Fe(CN)_6]_2 + 6KCl$$

16. In an aqueous solution of 0.2100 g of a mixture containing potassium cyanide and chloride, 14.56 ml of 0.1000 *M* silver nitrate was required to produce a faint permanent turbidity; 30.00 ml more of the silver nitrate was added and the precipitate of AgCl and AgCN filtered off from the solution. The filtrate and washings were titrated with 13.06 ml of 0.1000 *M* thiocyanate solution. Calculate the percentages of KCl and KCN in the sample.

17. Nickel is determined volumetrically by the addition of a known amount of cyanide to an ammoniacal solution of the sample. The excess of cyanide is titrated by standard silver solution. Potassium iodide is often added as an indicator. (Silver iodide precipitates as soon as there is any silver in excess.)

$$Ni^{++} + 4CN^- = Ni(CN)_4^=$$
$$Ag^+ + 2CN^- = Ag(CN)_2^-$$
$$Ag^+ + I^- = AgI$$

How much potassium cyanide should be added to a solution of 0.2500 g of nickel ore containing 20.00 per cent nickel in order that at least 15.00 ml 0.1100 *M* silver nitrate will be used in the back titration?

18. If 5.0 m mol of sodium chloride is dissolved in 150 ml of water, calculate the concentration of chloride ion after the addition of the following volumes of 0.1000 *M* silver nitrate solution: 0, 10, 20, 30, 40, 45, 48, 49, 49.3, 49.5, 49.9, 50, 55. Plot the negative logarithm of chloride-ion concentration (*p*Cl) against the milliliters of silver nitrate added. Compare this curve with the titration curves of Chapter 9.

19. The solubility product for silver chloride is 10^{-10}, and for silver thiocyanate 10^{-12}. If the concentration of thiocyanate ion which is needed to affect the ferric ion indicator is 10^{-5} *M*, what concentration of chloride ion will be in equilibrium at the end point in a solution which is in contact with both silver chloride and silver thiocyanate? What volume of 0.1 *M* thiocyanate solution will need to be added to 100 ml of solution in order to bring this amount of chloride into solution, according to the equation,

$$AgCl + SCN^- = AgSCN + Cl^-$$

If the stoichiometric volume of thiocyanate required in the Volhard determination of chloride is 15.00 ml, what is the percentage of error introduced if the silver chloride is not removed by filtration?

20. Calculate the theoretical error in a Mohr titration in which 50.00 ml 0.1 M silver nitrate solution is needed at the stoichiometric point, and the concentration of chromate ion is 10^{-4} M. Assume a final volume of 100 ml.

21. What should be the concentration of chromate ion so that there will be no theoretical error in the determination of Br^- by the Mohr method? Is it possible to use such a concentration?

22. Sulfate may be determined by titration with standard lead nitrate solution. Potassium iodide is used as a spot-test indicator. What concentration of iodide ion should be used in order that the spot test show a turbidity at the stoichiometric point in a sulfate titration? Use the solubility-product values in the Appendix.

PART THREE

Gravimetric Analysis

CHAPTER

17

Methods and Operations

A gravimetric analysis is one in which the desired constituent is weighed in some form after separation from other constituents of the sample. There are obviously three major requirements for such analyses:

1. Separation must be complete.
2. The substance weighed must be of definite known composition so that weight relations can be applied to compute from the weight of precipitate the weight of the sought element.
3. The weighed material must be pure, that is, not contaminated with other substances.

In practice, these conditions are seldom attained completely, and the success of a gravimetric analysis depends on the degree to which they are realized. In the following chapters we shall discuss the factors which affect the completeness of precipitation and the purity and composition of the precipitate.

A variety of methods are used for separating the desired constituent of the sample preliminary to weighing. The more important of these are:

1. *Precipitation as an insoluble compound, such as* AgCl, $BaSO_4$, hydrated Fe_2O_3. This is by far the most widely used method.
2. *Deposition by electrolysis, for metals such as* Cu, Ag.
3. *Volatilization.* Gases such as CO_2, NH_3, H_2S may be isolated by treatment of the sample with a suitable reagent and subsequent absorption of the gas. The increase in weight of the absorbent measures the quantity of liberated gas.

4. *Extraction.* This method is seldom used to obtain the constituent in final form but is useful for separation of a complex mixture into subgroups. For example, large amounts of ferric ion can be removed from small amounts of Ni, Co, Al, Mn, Cr, etc., by extraction with ether. Ferric chloride is more soluble in ether than in water whereas the other chlorides are insoluble in ether.

In this text the chief emphasis is placed on precipitation analyses, since these are of most frequent occurrence. Electrodeposition is illustrated by the determination of copper, and volatilization is used for the determination of carbon dioxide in a dolomite.

The operations employed in gravimetric analyses by precipitation methods are:

1. Preparation of a suitable solution of the sample.
2. Precipitation. In many cases precipitation of other constituents must precede the precipitation of the desired constituent.
3. Digestion of the precipitate.
4. Filtration.
5. Washing.
6. Conversion of the precipitate into a form suitable for weighing.
7. Weighing.

General directions for these operations are given in this chapter. These directions should be carefully studied before the determinations of Chapters 21 and 22 are begun. The theoretical principles on which the operations are based are discussed in the following chapters.

OPERATIONS

Preparation of the Solution

General directions for the preparation of a sample solution have been given in Chapter 5. The methods therein described apply for both gravimetric and volumetric analyses. When it happens that a single constituent remains in insoluble form during the preparation of a solution, it is often possible to utilize this insolubility to make a gravimetric determination of that constituent. For example, certain rocks are decomposed by acid treatment. Any silica present is left in rather pure form as an insoluble residue. This residue is separated by filtration, washed, ignited, and weighed as SiO_2. Similarly, in the analysis of brass or bronze, any tin present is left as an insoluble residue when the sample is dissolved in nitric acid. The residue is separated, washed, ignited, and weighed as pure SnO_2.

Methods for preparation of the solution in analyses of frequent occurrence are as follows:

1. *Silicate rocks.* In general the rock is not decomposed by acid treatment. The entire sample is fused with sodium carbonate and the fused mass dissolved in hydrochloric acid. Silica remains as an insoluble residue.

2. *Carbonate rocks.* Many carbonate rocks are completely decomposed by treatment with hydrochloric acid. A residue of nearly pure silica is left after the acid treatment. If the decomposition is not complete, it is necessary to fuse the residue with sodium carbonate, and then to treat the fused residue with hydrochloric acid. All constituents except silica are then brought into solution.

3. *Iron ores.* Most ores can be decomposed, and all constituents except silica brought into solution, by prolonged treatment with hydrochloric acid. When the residue after the acid treatment is colored, indicating incomplete decomposition, it is necessary to fuse this residue with sodium carbonate, and then to treat again with acid.

4. *Brass and bronze.* The sample is usually dissolved in 1:1 nitric acid. Any tin present is left as an insoluble residue of metastannic acid (hydrated stannic oxide).

5. *Iron, steel, and ferroalloys.* The sample is usually dissolved in hydrochloric, nitric, sulfuric, 70 per cent perchloric, or a mixture of hydrochloric and nitric acids. Directions as to the most suitable solvent are given with the analytical procedures for specific analyses.

Evaporation

In the majority of gravimetric analyses the volume of solution present must at some stage be reduced by evaporation, and frequently the solution must be evaporated to dryness. Evaporations are made on gas or electric hot plates or on a steam bath. Because of the higher temperature, hot-plate evaporations proceed somewhat faster than those on a steam bath, but also because of the higher temperature there is danger that an evaporation on a hot plate may cause the solution to spatter as it approaches dryness.

Evaporations are usually carried out in beakers. Erlenmeyer flasks are undesirable, because steam condenses on the upper part of the wall, and the condensate runs back into the liquid. Occasionally it is desirable to replace the beaker by a porcelain evaporating dish or a casserole, but usually the liquid to be evaporated is in a beaker, and it is better to make the evaporation in the same container rather than to risk the danger of loss during a transfer to another vessel.

During an evaporation the beaker must at all times be covered, to prevent foreign matter falling into the solution. At the same time it is necessary to allow space for the ready escape of steam. Both these objectives can be attained by covering the beaker with a watch glass elevated on glass supports, as shown in Fig. 24. The glass must be

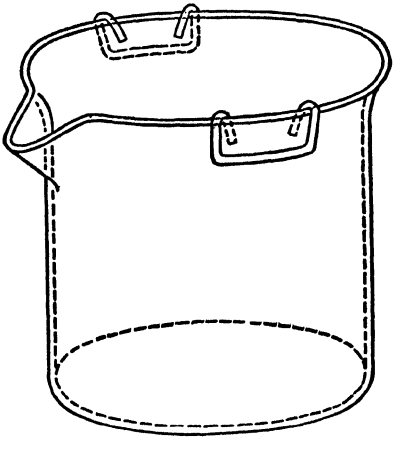


FIG. 24. Supports for cover glass.

large enough to cover the beaker, but should not be unduly large, as this would require too much space.

Precipitation

Separation by precipitation is the oldest form of exact chemical analysis. Even so, precipitation methods are often inadequate, and there is today a constant search for reagents which will precipitate certain constituents specifically or which will give precipitates of greater purity than are now obtainable.

Precipitation reagents may be divided into two classes, group reagents and final precipitants. Group reagents are those such as hydrogen sulfide, which will separate a group of constituents from other constituents of the sample. The chief requirements of a group reagent are that it effect nearly complete precipitation of the desired group of ions and precipitate none of the other ions present. Final precipitants are the reagents used to isolate a single constituent in a form which is suitable for weighing or which can readily be converted into a form suitable for weighing. The reagent used for the final precipitation should satisfy the following requirements:

1. The precipitate should be quantitatively insoluble; that is, the amount which remains in solution to satisfy the solubility-product equilibrium should be less than the limit of weight which the balance in use can detect. For ordinary student instruments this limit is 0.2 mg.

2. The precipitate must be readily filterable and should be in a form which is easy to wash free of the precipitating reagent and other ions in solution.

3. The precipitate must be one which can be dried or ignited to a directly weighable substance, that is, a substance of definite composition.

4. The precipitating agent must be specific; that is, it must effect a separation of the particular constituent sought from the others in solution.

5. The precipitating agent should not contain ions which contaminate the precipitate.

It is not always possible to find a single reagent which will satisfy all requirements; it may happen that a reagent which will give a precipitate of definite composition, suitable for weighing, will not effect separation of the desired constituent from other ions in the solution. For example, phosphates are separated from other ions by precipitation as ammonium phosphomolybdate. This precipitate is not of sufficiently definite composition for the final weighing. It is customary, therefore, in this analysis to dissolve the separated phosphomolybdate precipitate and to reprecipitate the phosphate ion as magnesium ammonium phosphate, which is readily converted into magnesium pyrophosphate for weighing.

Many of the precipitants for group separations are the ones employed in qualitative analysis. For example, in the analysis of a rock the following group separations are made:

1. Insoluble in HCl (Si).
2. Precipitated by NH_4OH (Al, Fe, P, Zr, Cr, V).
3. Precipitated by $(NH_4)_2S$ (Mn, Co, Ni, Zn).
4. Precipitated by $(NH_4)_2C_2O_4$ (Ca, Sr).
5. Precipitated by $(NH_4)_2HPO_4$ (Mg, Ba).
6. Not precipitated in general separation (Na, K, H, O, Li, C, N, S, Cl, F).

The same precipitant used for group separations may also be used for final precipitations when the conditions outlined above are met and when other ions than the desired constituent are absent. For example, in the analysis of a limestone, where strontium is generally absent, ammonium oxalate serves as the final precipitant for calcium.

In addition to the inorganic precipitants, a number of organic reagents [1] are widely used in quantitative analysis. Important among these are dimethylglyoxime, cupferron, and 8-hydroxyquinoline. Dimethylglyoxime is a specific precipitant for nickel, used in most of the ASTM methods of analysis. Cupferron gives precipitates with a num-

TABLE 28

GRAVIMETRIC ANALYSES OF FREQUENT OCCURRENCE

Element	*Precipitated as*	*Filtration Medium*	*Wash Liquid*	*Ignition Temperature (Centigrade)*	*Weighed as*
Ag (Halogens)	AgCl	Gooch	Dilute HNO_3	100–110°	AgCl
Ca	CaC_2O_4	Fine paper	$(NH_4)_2C_2O_4$	Blast lamp	$CaO(CaSO_4)$
Cu	Cu (electrolysis)	—	Acetone	100°	Cu
Fe (Al, Cr, Ti)	$Fe(OH)_3$	Coarse paper	1% NH_4NO_3	Blast lamp	Fe_2O_3
K	K_2PtCl_6	Gooch	80% Alcohol	130°	K_2PtCl_6
Mg (Mn)	$MgNH_4PO_4$	Gooch or paper	Dilute NH_4OH	800–1200°	$Mg_2P_2O_7$
Ni	$Ni(C_4H_7O_2N_2)_2$ (dimethylglyoxime)	Gooch	Hot H_2O	100–110°	$Ni(C_4H_7O_2N_2)_2$
P	$(NH_4)_3PO_4 \cdot 12MoO_3$	Paper	HNO_3 NH_4NO_3	Converted to $MgNH_4PO_4$	$Mg_2P_2O_7$
Pb	PbO_2 (electrolysis)	—	Alcohol	180–200°	PbO_2
	$PbSO_4$	Gooch	H_2SO_4 Alcohol	500°	$PbSO_4$
S (Ba)	$BaSO_4$	Gooch (paper)	Hot H_2O	800°	$BaSO_4$
Si	$SiO_2 \cdot H_2O$	Coarse paper	Dilute HCl	Blast lamp	SiO_2
Sn	$SnO_2 \cdot H_2O$	Coarse paper	1% NH_4NO_3	Blast lamp	SnO_2
Zn	$ZnNH_4PO_4$	Gooch	1% $(NH_4)_2HPO_4$ 50% Alcohol	105° (900°)	$ZnNH_4PO_4$ ($Zn_2P_2O_7$)

ber of metals from acid solutions. An important application is in the separation of Fe, V, Ti, Zr, and Sn from other elements such as Al, Cr, Mn, Ni, Co, and Zn. The reagent 8-hydroxyquinoline will form insoluble compounds with many of the metal ions from neutral or alkaline solutions. One of the widely used applications is for the precipitation of magnesium from a solution containing no other metal ions except those of the alkalies.

[1] See Lundell and Hoffman, *Outlines of Methods of Chemical Analysis*, for an excellent summary of these reagents; also, Yoe and Sarver, *Organic Analytical Reagents*, Wiley, 1941; Mellon, *Organic Reagents in Inorganic Analysis*, Blakiston, 1941; Welcher, *Organic Analytical Reagents*, Van Nostrand, 1947.

In general, the precipitations of quantitative analysis are made from aqueous solution, just as in qualitative analysis. In special cases, where it happens that the sought constituent does not give any precipitate of sufficiently low solubility, a separation may be made from some solvent other than water. Often used is a mixture of alcohol and water. A common example is the precipitation of potassium chloroplatinate from an 80 per cent alcohol solution, to separate potassium from sodium.

A few of the more common precipitates of gravimetric analysis are listed in Table 28. The contents of this table should be learned by every chemistry student, since the determinations listed are those of very frequent occurrence.

Technique. Precipitations are usually made in low-form lipped beakers, because of the ease of removal of the solid from such vessels. Each beaker is equipped with a stirring rod of such length that it projects 4–6 cm from the edge, when the rod rests on the bottom of the beaker. The beaker should be of such size that it is not more than two thirds full at the completion of the operation. The precipitating reagent is usually added from a buret or pipet, seldom from a beaker or graduated cylinder. A pipet is used for precipitations which need not be made exceedingly slowly, but a buret is preferable for those analyses that require very slow addition of reagent. In such cases, the buret is mounted above the beaker, in a slanting position, and the stopcock is opened just enough to allow a dropwise flow of solution. If the precipitation is to be made in hot solution, the beaker rests on a stand, so that it may be heated.

Mechanical stirring is recommended for precipitations which require as much as 10 minutes, since this insures better mixing than can be achieved when the solution is stirred by hand. Many types of good mechanical stirrers are available for this purpose. Usually an all-glass propeller or agitator is best, to prevent possible reaction with the solution.

Before the addition of reagent the approximate amount required should be calculated, on the basis of previous knowledge of the composition of the sample. About 5 per cent in excess of the calculated amount should be added (as a dilute solution), and then the stirring should be interrupted and the precipitate allowed to settle. A drop of reagent is then added to the clear supernatant liquid; if a further precipitate is formed, more reagent should be added. After filtration the liquid should again be tested for complete precipitation.

In many analyses the precipitate first obtained is dissolved in acid or other suitable solvent, and a second precipitation is made. The purpose of the reprecipitation is to obtain a purer precipitate.

Digestion

After precipitation is complete, the solution is, in most analyses, placed on a steam bath and allowed to stand for a time before filtration. The purpose of this operation, which is known as digestion, is to improve the filterability and purity of the precipitate. A discussion of the changes which occur during digestion is given in Chapter 19.

Digestion is not always necessary or desirable. Some precipitates, such as magnesium ammonium phosphate, are unstable in hot solution and cannot be digested. Some are too soluble in hot solution. In general, digestion is of no benefit for gelatinous precipitates, such as hydrous ferric oxide. With this substance a few minutes' boiling of the solution will effect all the coagulation that could be obtained from prolonged digestion. The analytical procedure will in all cases specify the time and temperature of digestion.

Filtration

Beginning students encounter more difficulty in filtration than in any other operation of gravimetric analysis. Improperly performed, this operation can waste many hours time; at best, it is tedious and slow. The student should learn proper techniques at the start and should never attempt short cuts which only lead to trouble.

Filtering Media. The filtering media used depend on the nature of the precipitate and on the treatment needed to convert the precipitate into a form suitable for weighing. The most common filters are:

1. Paper.
2. Gooch crucible.
3. Sintered-glass crucible.
4. Porous-porcelain crucible.
5. Munroe crucible.

Filter paper is suitable when the precipitate is not easily reduced by the action of the carbon of the paper and when a high ignition temperature is needed. Paper must be used for gelatinous precipitates, since they clog the pores of the various other types of filters. The Gooch crucible, the sintered-glass crucible, and the porous-porcelain crucible are all used for precipitates which are easily reduced by the carbon of paper. When only drying is desired, sintered-glass or porous-porcelain crucibles are recommended, because they require less preliminary preparation than the Gooch crucible. When the precipitate must be ignited to dull redness, the Gooch or porous-porcelain crucible must be used, since sintered-

glass crucibles will not withstand high temperatures. Even with the porcelain crucibles, ignition must be carefully performed, as described subsequently. The Munroe crucible,[2] because of its expense, is seldom employed in student work. It is in construction similar to the Gooch crucible (described below), but the filtering mat is of platinum. Consequently, it may be heated to the highest attainable ignition temperatures.

Filter Paper. A special grade of "ash-free" paper must be used for all precipitates which are to be ignited and weighed. Ordinary paper such as used in qualitative analysis may contain as many as several milligrams of ash per circle, enough to invalidate completely the results of an analysis. Ash-free paper is acid-treated in manufacture, to remove most of the inorganic constituents, and the weight of ash per circle of paper is negligible.

TABLE 29

QUANTITATIVE FILTER PAPERS

W	*S&S*	*JG*	*Porosity*	*Speed*	*Use for*	*Approximate Weight of Ash per 9-Cm Circle*
41	589–1	801	Coarse	Very rapid	Gelatinous precipitates	<0.1 mg
40	589–2	802	Medium	Rapid	Ordinary crystalline precipitates	<0.1
42	589–3	803	Fine	Slow	Finest crystalline precipitates	<0.1

Quantitative paper is manufactured in several degrees of porosity. It is important to select the proper grade for a given precipitate. Use of too coarse a paper will permit small crystals to pass through the funnel while use of too fine a paper will make filtration unduly slow. In Table 29 there are given the manufacturers recommendations for Whatman (W), Schleicher and Schull (S&S) and J. Green (JG) quantitative papers. Other makes are just as reliable as these, which have been listed because of their general availability. In addition to the three degrees of porosity shown in Table 29 all manufacturers also provide quantitative paper for special purposes, such as papers to withstand moderate suction or the action of alkalies.

[2] The Munroe crucible, which is made of platinum with a perforated base on which a mat of platinum is formed, is used for very high-temperature ignition with reducible precipitates and for other special applications. See W. B. Snelling, *J. Am. Chem. Soc.*, **31,** 456 (1909), and O. O. Swett, *ibid.*, **31,** 928 (1909).

Technique of Filtration with Paper. The size of the paper should be governed by the amount of precipitate to be retained and not by the amount of filtered liquid. The paper should be about one third filled with the precipitate at the end of the filtration. The funnel should match the paper in size. The folded paper should come within 1–2 cm of the top of the funnel, but never closer than 1 cm. The funnel should be of exactly 60° angle. It should have a long stem, with a constriction at the upper end of the stem. This constriction will facilitate maintenance of a solid column of water in the stem, thereby accelerating the speed of filtration. The funnel should be held in a rigidly mounted funnel holder, with the stem reaching into the beaker which received the filtrate. The stem should touch the side of the beaker, so that a column of liquid runs down the side; this arrangement prevents splashing.

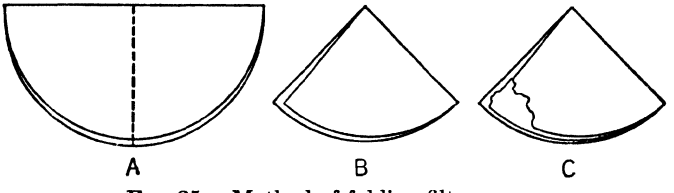


FIG. 25. Method of folding filter paper.

The operation of folding the paper and fitting it into the funnel is most important. The circle of paper is commonly folded exactly in half and folded again in quarters. The folded paper is then opened so that a 60°-angle cone is formed, with three thicknesses of paper on one side and a single thickness on the other. The paper is adjusted to fit the funnel exactly, and the corner of the outside fold is torn off as shown in Fig. 25, in order to give a tighter fit. The paper is then placed in the funnel, moistened, pressed down tightly to the sides of the funnel, and filled with water. The stem of the funnel will fill with a continuous column of liquid if the paper fits properly. This liquid column promotes a gentle suction which accelerates filtration. Much time can be saved in the operation of filtration if care is taken to choose good funnels (with 60° angles and with long stems) and to fit the paper to the funnel correctly.

The experienced analyst often folds the paper so that it does not fit the funnel tightly except at the top. To do this, the second fold is made so that the angle is slightly greater than 60°. During filtration, liquid passing through the paper is free to run down the side of the funnel between the paper and glass. Care must be taken that papers so fitted do not pull loose from the funnel, thereby allowing air to enter

and the liquid column to break. Funnels with 58° angle are available to use with 60° paper cones, so that the paper fits only at the top. Another type of funnel has grooves extending radially from the bottom, to provide more rapid filtration.

After the paper is fitted and the receiving vessel is in place, the filtration may be started. The beaker of solution is held just above the funnel. A stirring rod is held against the lip of the beaker, to guide the column of liquid into the funnel, and to prevent drops of liquid from running down the outside of the beaker (see Fig. 16, page 86). Solution is poured into the filter until it is filled nearly to the top of the paper. *Care must be taken not to over-run the paper.* If the liquid runs through the paper very rapidly, the beaker is held in the pouring position, and liquid is added to the funnel as rapidly as it can be accommodated. In most filtrations some time is needed for the filled paper to empty, so that several filtrations may be in progress simultaneously. Care must be taken to prevent mixing of filtrates. Each beaker with solution is numbered, and the receiving beaker carries a corresponding number. Care must be taken to prevent loss of solution on the outside of the beaker lip, as the beaker is set upright after pouring.

The precipitate is retained in the beaker during filtration. When no more liquid can be poured off the precipitate without transferring the precipitate to the paper, the filtration is interrupted, and the receiving beaker is replaced by an empty one. This is done in order that if any precipitate passes through the filter it will not be necessary to refilter the entire bulk of solution. The last of the mother liquor is removed from the precipitate in the operation of washing, described below.

When filtration is completed, test for completeness of precipitation by adding 1–2 ml of the precipitant solution to the filtrate. If more precipitate is formed, the solution must be refiltered.

Whenever the solubility of the precipitate permits, it is advantageous to filter solutions while hot. Because of lowered viscosity, hot solutions will run through a paper much faster than cold solutions. Instructions are given in the analytical procedures when the filtration can be made with hot solutions.

Use of Suction. When suction is applied to the ordinary filter paper, the paper ruptures at its point of least strength, the apex of the cone. If a perforated platinum filter cone is put into the funnel beneath the paper to reinforce the apex or, if specially hardened paper is used, a moderate degree of suction may be employed to reduce the time required for filtration. The papers are fitted to the funnels (containing the cones)

in the customary manner, and the funnel is inserted into a suction flask (Fig. 26), which is then connected to the water aspirator pump through a safety bottle (to prevent water from backing up from the pump and contaminating the filtrate). The stem of the funnel must project below the side arm of the flask to prevent loss of the filtrate. Speed of filtration may be controlled by a screw clamp on the side tube which is inserted in the rubber stopper along with the funnel. If the filtrate is to be subjected to further analysis, care must be exercised to rinse it completely out of the suction flask, or to arrange the apparatus so that the filtrate is caught in a beaker. To do this, the funnel is mounted in the top section of a vacuum desiccator (or bell jar), the beaker is placed in the lower portion of the desiccator beneath the funnel, and the assembly is evacuated through an opening in the lower portion.

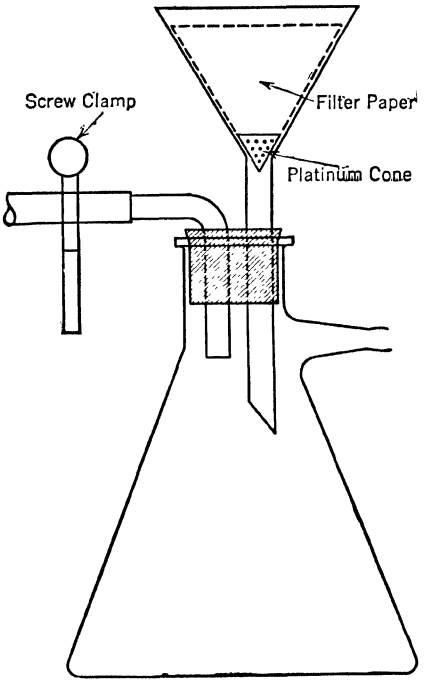


FIG. 26. Filtration with suction, using platinum filter cone.

Filtration by suction is advantageous when the precipitate is crystalline, but it cannot be employed for gelatinous precipitates. With such precipitates suction draws particles into the pores of the paper, clogging it until no liquid will pass.

Macerated Filter Paper. Addition of a suspension of macerated filter paper is often advantageous in the filtration of gelatinous precipitates, which tend to clog the pores of filter paper. When a suspension of paper fibers is added to such a precipitate, the fibers serve to keep the gelatinous precipitate in a condition more permeable toward water. Macerated filter-paper tablets may be purchased ready for use, or the papers may be prepared by disintegrating ashless filter paper with concentrated hydrochloric acid for a few minutes, washing out the acid, and storing in distilled water. A bulk of macerated paper approximately that of the gelatinous precipitate is added immediately after precipitation, and the solution stirred up so as to mix thoroughly the macerated paper and the precipitate.

Gooch Crucible. As previously stated, the Gooch crucible is advantageous (*a*) when the precipitate is readily reduced by carbon of the paper on ignition, and (*b*) when extremely high ignition temperatures are not necessary. The use of the Gooch crucible or of paper is a matter of choice in many determinations, where the paper can be ignited without danger of reduction of the precipitate, but in others, as in those involving silver halide precipitates, a filtering crucible is essential.

The Gooch crucible is a porcelain thimble with a perforated base. The filtering medium is a mat of asbestos fiber which covers the bottom of the crucible. Preparation and use of asbestos mats for qualitative filtrations have been described on page 73. To prepare a mat for quantitative use, proceed as follows: Place the crucible in its holder, as shown in Fig. 12, page 73. The receiving test tube is omitted. Prepare a suspension of acid-washed asbestos fiber in a beaker of water. With the suction disconnected, pour enough of the suspension into the crucible to make an asbestos mat at the bottom. After a moment, when some of the fiber has settled under the influence of gravity, turn on the suction, and drain all water from the crucible. With continued suction slowly pour asbestos suspension into the crucible until a mat $\frac{1}{2}$–1 mm in thickness is formed. With a properly prepared mat one can just discern the perforations in the bottom of the crucible if it is held with the bottom towards the light and observed from the open end.

When a suitable mat is formed, wash with water, with suction applied, to remove loose particles. The water should be poured into the crucible gently, with the aid of a stirring rod. If a porcelain plate is supplied, place this on top of the mat before washing (an advantage of the plate is that it prevents disruption of the mat by liquids which are poured into the crucible). Wash the mat until the following test for loose fibers indicates their complete removal. Test by collecting a portion of the wash water in a clean test tube and observing the presence or absence of fine asbestos fibers as the tube is viewed in a strong light. Remove the crucible from the holder, place in a small beaker, and heat at the temperature to be used for drying or igniting the precipitate. Cool in a desiccator, and weigh. Replace in the holder, and repeat the process of washing, drying, and weighing. The weight should remain constant within 0.3 mg. When this constancy is attained, the crucible is ready for use.

In filtration with a Gooch crucible clean the filter flask, place the crucible in its holder, turn on the suction (a safety bottle must be used to keep tap water from the filter flask), and pour the liquid through the filter in a continuous stream. Take care to prevent rupture of the mat by the liquid; pouring should be done with the aid of a stirring rod, and

the stream should be directed against the center of the mat. Suction should be applied before the filtration begins, to hold the fibers in place. The bulk of the precipitate is retained in the beaker, as directed for filtration with paper.

Gooch crucibles are cleaned by scraping out the mat and adhering precipitates and re-forming another mat. Since it takes considerable time to prepare a mat and bring it to constant weight, it is often desirable to use a crucible for several filtrations before removing the precipitate and making a new mat. Successive filtrations in the same crucible can be made when the precipitate is very insoluble, so that weighable amounts of previous precipitates do not pass into solution when a new filtration is made.

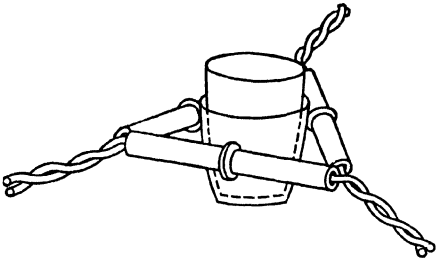


FIG. 27. Ignition of precipitate in Gooch crucible.

Crucibles with Permanent Mats. For several years there has been a trend toward replacement of Gooch crucibles by some type of porous-bottom crucible which needs no asbestos mat. A shortage of long-fiber asbestos during the war has accelerated this change, and today few industrial laboratories use Gooch crucibles for gravimetric filtrations.

As previously stated, filtering crucibles are made with glass and porous-porcelain mats. The latter, such as the American-made Selas [3] crucible, are now more widely used than glass crucibles because they can be ignited to the same temperature as other types of porcelain crucibles.

The general techniques of using the filtering crucibles are like those for Gooch crucibles except that no mat is formed. The crucible is cleaned and brought to constant weight at the temperature to be used for ignition of the precipitate. Filtration and washing are done exactly as described for the Gooch. Ignition of Selas crucibles is done either by flame or in a muffle furnace. In either case the crucible should be placed within an ignition thimble or plain porcelain crucible, as in Fig. 27. (The Selas Corporation provides ignition thimbles for this use.) Care must be taken to avoid a tight fit of the two crucibles, which will cause breakage when they cool.

[3] Manufactured by the Selas Corporation of America, Philadelphia, Pa. Available through most supply houses.

Filtering crucibles, both glass and porcelain, are cleaned by dissolving the precipitate in a suitable reagent. The following are commonly used:

Precipitate	*Reagent*
Barium sulfate	Conc. sulfuric acid or cleaning solution
Silver chloride	Ammonia solution
Fats, organic compounds	Cleaning solution or ignition (for porcelain)
Metal sulfides	Aqua regia

Cleaning may be done either by immersing the crucible in a beaker of the reagent or by "back washing" with the reagent. In back washing the liquid is poured through the mat in the reverse direction. The instructor will provide directions for this operation, based on the type of crucible in use.[4]

Certain precautions are applicable to both glass and porcelain crucibles:

1. Do not ignite glass crucibles at temperatures above those of the drying oven. Ignite porcelain crucibles only within a protecting crucible.

2. Never filter concentrated alkalies through a porous crucible. Even a short contact with alkali will enlarge the pores and spoil the mat.

3. Fusions cannot be made in filtering crucibles.

4. Never scrape the precipitate from a filtering crucible. The mats are fragile and easily punctured.

Washing

Immediately after filtration all precipitates must be washed free of soluble impurities. If the precipitate is allowed to dry in the paper, it will cake in such a manner that complete washing will be impossible. The wash liquid is chosen on the basis of the following requirements:

1. The wash liquid should leave no residue when it is evaporated as the precipitate is ignited.

2. A common ion should often be present to reduce the solubility of the precipitate. This factor is especially important with rather soluble precipitates such as magnesium ammonium phosphate.

3. An ion should be present to prevent the hydrolysis of salts such as those of iron and aluminum which may hydrolyze into insoluble basic salts.

[4] Apparatus for cleaning Selas crucibles is described in *Ind. Eng. Chem., Anal. Ed.*, **16**, 277, 539 (1944).

4. The liquid should contain a volatile electrolyte to prevent the peptization of colloids.

5. Hot wash liquids should be used if the solubility permits.

In order to reduce solubility losses the quantities of wash liquid should be as small as possible. Most efficient washing is obtained, with a given volume of water, if the wash liquid is added in small portions and each portion is allowed to drain completely before the next one is added. Since a certain amount of liquid is always retained by the precipitate, the fraction of the impurity removed in a single washing is the ratio of the volume retained to the total volume used. If, for example, 1 ml is retained in the precipitate, the fraction of the impurity retained in a washing with a 50-ml portion is $\frac{1}{50}$. If 50 ml of wash liquid is added in 10-ml portions and each portion allowed to drain before addition of the next, the first washing will leave $\frac{1}{10}$ the total impurity, the second washing $\frac{1}{10}$ the amount left in the first, and so on. Washing with five 10-ml portions will, therefore, reduce the amount of impurity to $(\frac{1}{10})^5$ or to 1/100,000 the original amount.

Technique. The precipitate is partially washed by decantation before it is transferred to the filter. After the bulk of the mother liquor is removed, and no more liquid can be poured off from the precipitate, a small portion (10–30 ml) of wash liquid is added, the precipitate is thoroughly stirred up in the wash liquid and then allowed to settle, and the supernatant liquid is poured through the filter. Generally, the receiver is replaced by an empty flask or beaker before washing is begun. When no more liquid can be poured from the precipitate, another portion of wash liquid is added, and the process is repeated. After two or three washings by decantation the precipitate is transferred to the filter, and washing is completed there. In the transfer as much of the precipitate as possible is poured into the filter along with the last portions of liquid. While the beaker is still above the filter, a stream of water from the wash bottle (see Fig. 16, page 86) is used to dislodge additional precipitate and wash it into the filter. Finally a policeman is used to rub adhering particles from the walls of the beaker. Particles are washed from the policeman directly into the filter by a stream of water from the wash bottle. Sometimes the last portions of precipitate adhere so strongly to the walls of the beaker that they must be wiped out with a piece of ashless filter paper, which is then ignited with the precipitate.

In filtration with paper the wash liquid must always be added from a wash bottle fitted with a tip of small bore. The stream of liquid is never directed at the precipitate but around the upper edge of the filter paper so that, as it runs down, it will wash the precipitate to the apex of the cone. With a Gooch crucible a different technique is employed.

Small portions of wash liquid are poured onto the center of the mat with the aid of a stirring rod. Here it is necessary to exercise care that the mat is not disrupted by the addition of wash liquid.

Completeness of washing must be tested in every analysis. The test is performed by collecting 5–10 ml of the filtrate in a test tube and making a simple qualitative test for some readily identified ion, such as chloride or sulfate, which is present in the solution at the time of filtration. It is seldom advisable to make tests before six to eight portions of wash liquid have been used. When suction is used for filtration, a test tube is placed inside the filter flask to catch the test portion. The tube is suspended by a wire which runs beneath the stopper.

Ignition

The last stage in a gravimetric analysis is the conversion of the precipitate into a form suitable for weighing. This conversion may require only the removal of water, or it may require ignition at a high temperature to effect a partial decomposition of the precipitate. (Sometimes high-temperature ignition may be needed for removal of water, when the water is partially combined as in the precipitation of ferric hydroxide.)

In all analyses it is necessary to bring the crucible to constant weight *at the same temperature* as that employed for ignition of the precipitate. If this is not done, there may be loss in weight of the crucible itself during ignition. To bring a crucible to constant weight, clean it and ignite for 5–10 minutes. Cool in a desiccator, and weigh accurately. Reignite for a 5–10-minute period, cool, and reweigh. Continue the process until the weight is constant within 0.3 mg after successive heating periods.

The technique of ignition varies widely with the different types of filtration employed. Gooch crucibles may be dried in an oven, or they may require ignition at 600–800°C. Filter paper may be ignited in porcelain, silica, or platinum crucibles. Porcelain crucibles can be heated to 1200°C without danger of breaking but are subject to attack by alkaline carbonates, alkalies, and hydrofluoric acid. Platinum is inert to attack by many reagents and can be heated as high as 1700°C. In any ignition (except for substances which attack it), platinum is to be preferred because its high thermal conductivity permits rapid attainment of temperature equilibrium. In flames, precipitates in platinum attain a much higher temperature than in porcelain, but in muffle furnaces both types of crucibles attain the same temperature.

Choice of Burner. Commonly available in all analytical laboratories are Tirrill (double regulator Bunsen-type burners), Meker, and blast burners. The temperatures which can be attained with these

various sources may be seen in Table 30. These temperatures are, of course, only approximate, because there are many variable factors, such as thickness of the crucibles and composition of the fuel gas. In general, Meker burners are preferred to blast lamps, because the flame of the former is free of reducing gases which may permeate the platinum at high temperatures and thus cause damage to the crucible.

A rough measure of the temperature obtained by a crucible may be made by observation of the color. A platinum crucible appears dull red at temperatures of 600–850°C. The color is cherry red in the range 850–1000°C, orange in the range 1000–1100°C, and yellow in the range 1100–1200°C. Above 1200°C the color becomes a very bright yellow,

TABLE 30

APPROXIMATE BURNER TEMPERATURES

Burner	*Covered Platinum Crucible*	*Covered Porcelain Crucible*
Tirrill	1050–1150	600– 700
Meker	1100–1250	725– 900
Blast	1100–1300	900–1000

which gradually shifts to white with rising temperature. The white color is beyond the range of the burners employed in the laboratory.

Drying Precipitates to Constant Weight in Filtering Crucibles. After washing is completed, the crucible is sucked dry on the filter flask and placed in an electric oven at 110–130°C. After drying for 1–3 hours, the crucible is cooled in a desiccator and weighed. It is then redried, cooled, and reweighed. The second weight is usually found to agree with the first one.

Ignition of Gooch and Selas Crucibles. The crucible and contents are dried in an oven and then ignited inside another crucible or ignition thimble as shown in Fig. 27. The two crucibles must not fit too tightly together, since uneven expansion will cause breakage. With a Meker burner or blast lamp a temperature near 900°C may be attained.

Ignition When Filter Paper Is Used. There are many correct methods for performing an ignition. The following directions will serve as a guide, but they may be modified as circumstances require:

1. Bring the crucible to constant weight. See above.

2. Transfer the precipitate to the crucible. After the filter paper is well drained in the funnel, fold over the top portion so as to enclose the precipitate completely. Lift the bundle from the funnel, and place it point down in the crucible. Press it well down to the bottom of the crucible to facilitate drying and charring.

3. Dry the paper and precipitate. Time may be saved by doing this in an oven overnight. If a wet paper is to be ignited immediately, proceed as follows: Put the crucible in a triangle as shown in Fig. 28, but put the cover on the crucible instead of slanting it as shown. Place a *small* flame beneath the crucible at a point about midway along the lower side. The tip of the flame must not reach the crucible. Heat until the paper and precipitate are entirely dry.

4. Char the paper. Move the flame back until it is beneath the bottom of the crucible, as shown in Fig. 28. Slightly increase the size of flame, and continue to heat until all organic matter is distilled from the paper. The cover should be slanted as in Fig. 28 during this operation. Take care that the flame does not strike the cover and deflect reducing gases onto the precipitate. If the escaping gas bursts into flame, reduce the rate of heating.

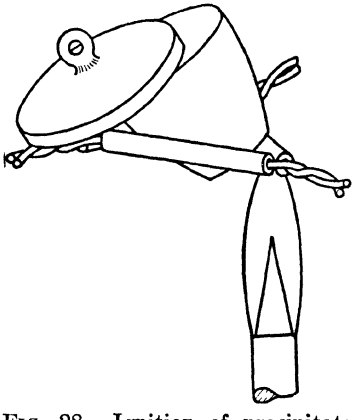


FIG. 28. Ignition of precipitate with access of air.

5. Oxidize carbon. Increase the size of the flame until the bottom of the crucible is heated to redness. Continue to heat until the carbon residue is burned away. From time to time the crucible should be turned, so as to expose a fresh portion to the heat

6. Ignition. Place the crucible upright, remove the cover so as to permit free access of air, and ignite at the prescribed temperature. With some precipitates it is advisable to crush the solid lump before ignition, so as to obtain better heat transfer. This is done with a blunt stirring rod. Any adhering powder is wiped from the rod with a small piece of ashless filter paper which is then placed in the crucible and burned. Do not crush the precipitate unless this is approved by the instructor.

Ignition in a Muffle Furnace. A muffle furnace is an enclosed chamber which can be heated by electricity to the high temperatures (800–1000°C) needed in ashing samples and igniting precipitates. Temperature control is provided by means of a rheostat, and often a pyrometer is attached to indicate the temperature. If such furnaces are available, they greatly increase the efficiency of the ignition process.

If a precipitate which has been collected in a filtering crucible is to be ignited in a muffle furnace, the crucible containing the precipitate is first dried in an oven at 110°C; it is then set inside an ignition thimble,

and the two are placed in a muffle furnace which has been preheated to the proper ignition temperature. The filtering crucible should previously have been brought to constant weight by ignition in the furnace.

For precipitates which have been collected on a filter paper and the paper placed in a porcelain or platinum crucible, the operations of charring the paper (see steps 3 and 4, page 327) should be performed. The crucible is then placed directly in a muffle furnace which has been heated to the proper ignition temperature. The crucibles should have been previously brought to constant weight in the furnace.

Care of Platinum. Platinum crucibles are expensive and should have special care. The following rules are to be observed:

1. Protect from mechanical damage. Platinum is very soft and pliable. Crucibles may be reshaped on wooden or metal forms if dented or bent.

2. Never use with oxidizing agents, such as aqua regia, chlorine, bromine, or ferric chloride, which react with the metal.

3. Do not ignite compounds of sulfur, phosphorus, arsenic, selenium, mercury, lead, bismuth, silver, tin, or antimony in platinum, since these elements (sometimes formed by reduction of the precipitates containing their compounds) alloy with it.

4. Strong bases or salts which decompose into strong bases, for example, barium or lithium carbonates, must not be heated in platinum. It is perfectly safe to fuse the carbonates of sodium and potassium.

5. Never heat platinum ware in a reducing flame since this causes the formation of a crystalline deposit on the metal. In time such a deposit penetrates the wall of the crucible, causing it to become brittle.

6. Hot platinum ware should always be handled with platinum-tipped or nichrome forceps. Iron forceps must never be used for crucibles which are at a temperature above 500°C, because iron will alloy with the platinum. Platinum or silica triangles should be used. Ordinary clay triangles often contain enough iron to damage platinum if they are used for ignitions.

7. The surface of platinum must always be kept shiny by scouring with talc or sea sand. HCl is the best cleansing agent. Certain metallic stains, especially iron, can be removed by low-temperature fusion with potassium acid sulfate. The molten solid should not be allowed to solidify in the crucible, but should be poured onto a dry stone or iron slab.

Platinum iridium alloys (such as are often used for crucibles) undergo an appreciable loss in weight when heated at temperatures of 1000°C or above. The magnitude of this loss is shown in Table 31. Since a 25-ml

platinum crucible has an area of about 80–100 sq cm, the error due to volatility may be appreciable if the crucible is made of an alloy high in iridium.

Not all crucibles will change appreciably in weight, but the student should at all times be aware of this possibility.

Cooling. All precipitates which have been heated should be cooled in a desiccator. Even those precipitates which are not hygroscopic will take up some surface moisture if cooled in a moist atmosphere. The general use of desiccators has been discussed in Chapter 2; this material should be read again before gravimetric determinations are attempted.

Very hot crucibles are not put into desiccators. The crucible is allowed to cool, in the air, for a short time. The cover should be in

TABLE 31

APPROXIMATE LOSS IN WEIGHT OF CRUCIBLES

Mg/100 Cm^2/Hour, at Temperature Indicated *

Temperature, °C	*Pure* Pt	*1%* Ir— *99%* Pt	*2.5%* Ir— *97.5%* Pt
900	0	0	0
1000	0.08	0.30	0.57
1200	0.81	1.2	2.5

* G. K. Burgess and R. G. Waltenburg, *Bur. Standards Sci. Paper*, 280 (1916).

place during this period. When the temperature has fallen to 100–300°C, the crucible is placed in the desiccator. The cover of the desiccator is left slightly open for a few moments, so that heated air may escape from the interior; then the cover is closed and the crucible allowed to stand until it is completely cool. Platinum crucibles will cool in 10–15 minutes, if the desiccator itself is thoroughly cool, but porcelain crucibles require a somewhat longer time.

Care must be exercised in opening the desiccator. The expansion of heated air and subsequent cooling may leave a partial vacuum within the chamber, and, if the lid is opened suddenly, a rush of air may blow a portion of the contents from the crucibles. Always slide the cover to one side very gradually, so that the first opening is on the side opposite the crucible. It is not advisable to cool several crucibles at once because the repeated opening of the desiccator, to remove the crucibles for weighing, permits the crucibles to stand in a not thoroughly dried atmosphere. Rather, several desiccators should be used if many ignitions are in progress simultaneously.

Weighing

Ignited precipitates should be weighed in covered crucibles, to prevent contact of the precipitate with moist air. This precaution is particularly to be observed with precipitates which can take up carbon dioxide. Even with covered crucibles, it is sometimes found that a precipitate will show an appreciable gain in weight while on the balance pan. In this event the precipitate should be reignited. For the next weighing, the approximate weight should be placed on the balance pan before the crucible is removed from the desiccator. Observation of the first swing or set of swings will then enable the analyst to compute the exact weight, while exposing the precipitate to the air for only a few seconds to make the observation. It is necessary, of course, to determine the sensitivity of the balance during the process of determining the approximate weight, before the final ignition.

Sometimes, when the ignition is prolonged, the loss in weight of platinum crucibles becomes appreciable, and the question arises as to what is the proper weight for the crucible when the precipitate has attained constant weight. *In this case the weight of the empty crucible should be determined after the ignition*, not before, as in the usual procedure. The precipitate is removed from the crucible, and the crucible is washed, dried by brief ignition, cooled, and weighed.

CALCULATIONS

The calculations of a gravimetric analysis are in general somewhat simpler than those of volumetric analysis. From the weight of precipitate obtained the amount of the desired constituent present in the sample is computed. It often happens that the weight of the precipitate is the weight of the constituent in the desired form. For example, calcium is weighed as CaO; usually the results of the analysis are expressed in terms of the percentage of CaO. When the precipitate is not the constituent sought, a *gravimetric factor* is used to compute the amount of the desired constituent. This gravimetric factor is a number which expresses the weight of the desired constituent present in 1 g of the substance weighed, or equivalent to 1 g of the substance weighed. Therefore, multiplication of the weight of the precipitate (in grams) by the gravimetric factor gives the weight of the sought constituent (in grams). If the weight of precipitate is expressed in other units than grams, the weight of constituent is obtained in the same units.

For illustration we may compute the gravimetric factor for chlorine when silver chloride is weighed. Since 1 mole of AgCl is formed from

1 mole of Cl^- ion, a gram-mole of AgCl or 107.88 + 35.46 g is equivalent to 35.46 g of Cl^- ion. Therefore, 1 g AgCl is equivalent to 35.46/143.34 g of Cl^- ion. The number 35.46/143.34 or 0.2474 is the gravimetric factor.

The following rules must be observed in the use of gravimetric factors:

1. The *constituent weighed* appears in the denominator and the *constituent sought* in the numerator.

2. The number of molecules in the numerator and denominator must be arranged so that they contain the same number of atoms of the elements sought for in the analysis.

A few examples of factors will clarify these rules.

Weighed	*Sought*	*Factor*
$BaSO_4$	S	$S/BaSO_4$
$BaSO_4$	SO_3	$SO_3/BaSO_4$
$Mg_2P_2O_7$	MgO	$2MgO/Mg_2P_2O_7$
Fe_2O_3	Fe_3O_4	$2Fe_3O_4/3Fe_2O_3$

It is not essential that the substance sought appear in the final precipitate, provided that there is a stoichiometric relation between the sought substance and the substance weighed. For example, the amount of sodium oxalate in a sample might be determined by precipitating as calcium oxalate, igniting the precipitate to calcium oxide, and weighing the oxide. The gravimetric factor should give the weight of sodium oxalate, $Na_2C_2O_4$, equivalent to 1 g CaO. Since 1 mole sodium oxalate gives 1 mole calcium oxalate, which in turn gives 1 mole calcium oxide, or

$$Na_2C_2O_4 = CaC_2O_4 = CaO$$

the gravimetric factor is $Na_2C_2O_4/CaO$.

All chemistry handbooks give tables of gravimetric factors and their logarithms. Use of these tables will save considerable time.

Illustrative Problems. 1. A sample of impure magnetite (Fe_3O_4) weighing 1.542 g is dissolved by fusion with $KHSO_4$; the iron is oxidized to Fe^{+++} and precipitated with NH_4OH. The $Fe(OH)_3$ precipitate is ignited to Fe_2O_3 and weighed. The weight is 1.485 g. Calculate the percentage of iron as Fe and as Fe_3O_4.[5]

Solution:

$$\text{Per cent Fe} = \frac{1.485 \times \dfrac{2Fe}{Fe_2O_3} \times 100}{1.542} = 67.35\%$$

$$\text{Per cent } Fe_3O_4 = \frac{1.485 \times \dfrac{2Fe_3O_4}{3Fe_2O_3} \times 100}{1.542} = 93.09\%$$

[5] Beginning students are frequently confused by this operation. It should be kept in mind that we are not computing the amount of Fe_3O_4 present. We are computing the weight which would be present if the iron were all combined as Fe_3O_4.

2. How many milliliters of ammonium hydroxide (density 0.926 g per milliliter, 20.00 per cent NH_3 by weight) will be required to precipitate the iron in an impure sample of $FeCl_3$ which weighs 1.500 g?

Solution: Grams of NH_3 per milliliter = $0.926 \times 0.20 = 0.1852$.

Each molecule $FeCl_3$ requires 3 molecules of NH_4OH (or of NH_3) for precipitation. On the assumption that the $FeCl_3$ is pure,

$$\text{Grams } NH_3 \text{ required} = 1.500 \times \frac{3NH_3}{FeCl_3}$$

$$= 1.500 \times \frac{51.09}{162.2} = 0.4725 \text{ g}$$

$$\text{Milliliters } NH_4OH = \frac{0.4725}{0.1852} = 2.55 \text{ ml}$$

3. How many milliliters of a 0.150 M $BaCl_2$ solution are needed to precipitate the sulfate from a 0.500-g sample of potassium alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, mol wt 948.8, if a 10 per cent excess is to be used?

Solution: Each m mol of alum contains 4 m mol $SO_4^=$ and requires 4 m mol $BaCl_2$.

$$\text{M mol } BaCl_2 = \frac{500}{948.8} \times 4 = 2.11$$

$$\text{Stoichiometric volume } BaCl_2 = \frac{2.11 \text{ m mol}}{0.150 \dfrac{\text{m mol}}{\text{ml}}} = 14.1 \text{ ml}$$

$$\text{Volume } BaCl_2 \text{ to be added} = 14.1 \times 1.1 = 15.5 \text{ ml}$$

Indirect Analysis. When a sample contains two constituents that are separated with difficulty, it is often advantageous to make two determinations that will provide data for simultaneous equations involving the amounts of the two constituents and by solution of these equations to compute the amount of each. This procedure may be illustrated by the analysis of a mixture of chloride and bromide. By precipitation and weighing of the combined silver salts (as AgCl and AgBr), and by an independent determination on another aliquot portion of the amount of silver needed for a Mohr or Fajans determination, data are obtained for the two simultaneous equations needed.

Problem. Aliquot portions weighing 1.000 g each of a sample containing chloride and bromide are analyzed as follows:

(*a*) The mixed halides are precipitated, dried in a Gooch crucible, and weighed. The weight of combined AgCl and AgBr is 0.8055 g.

(*b*) In a Fajans titration 50.00 ml of 0.1000 M silver nitrate solution is needed to titrate the chloride and bromide.

Solution: Let X represent the millimoles of Cl^- and Y the millimoles of Br^- present in a 1.000-g portion of the sample. Since 50.00×0.1000 or 5.00 m mol of

Ag^+ are needed in the titration, the sum,

$$X + Y = 5.00$$

is obtained. This is one of the necessary equations.

Since there are X m mol of Cl^- in the sample portion, there are X m mol of AgCl in the halide precipitate. Similarly, there are Y m mol of AgBr in this precipitate. Therefore,

$$143.3\ X = \text{mg AgCl} \quad (143.3 \text{ is the molecular weight})$$

$$187.8\ Y = \text{mg AgBr}$$

The second equation is

$$143.3\ X + 187.8\ Y = 805.5 \text{ mg}$$

Solving the two equations simultaneously gives

$$X = 3.000$$

$$Y = 2.000$$

The percentage of Cl^- is given by the equation,

$$\text{Per cent } Cl^- = \frac{3.000 \times 35.46 \times 100}{1000} = 10.64\%$$

and the percentage of Br^- by the equation,

$$\text{Per cent } Br^- = \frac{2.000 \times 79.92 \times 100}{1000} = 15.98\%$$

It should be noted that this indirect computation will give good results only when the molecular weights involved are quite far apart. If the coefficients of X and Y in the second equation have about the same values, the effect will be to magnify any experimental errors, and the computed composition may be greatly in error. An indirect determination of SCN^- and Br^- will not give such good results as those for Cl^- and Br^-, because the molecular weight of AgSCN is 165.96 and of AgBr is 187.80.

A simpler case of indirect analysis involves samples which are mixtures of only two substances. In such cases only one analytical determination is necessary, and only one algebraic equation has to be solved.

Problem. 0.5000 g of sample which is a mixture of NaCl and KCl yields a precipitate of AgCl which weighs 0.9815 g. What is the percentage of KCl in the mixture?

Solution: Let X = g KCl present, and, because of the composition of the sample, $0.5000 - X$ = g NaCl

$$\text{grams AgCl furnished by KCl} = X \times \frac{\text{AgCl}}{\text{KCl}} = X \times 1.923$$

$$\text{grams AgCl furnished by NaCl} = (0.5000 - X) \times \frac{\text{AgCl}}{\text{NaCl}} = (0.5000 - X) \times 2.452$$

The equation to be solved is

$$1.923X + 2.452(0.5000 - X) = 0.9815$$

$$X = 0.4621$$

$$\text{Per cent KCl} = \frac{0.4621}{0.5000} \times 100 = 92.4\%$$

QUESTIONS

1. What methods are commonly employed for isolation of the desired constituent in gravimetric analysis?
2. List the conditions that must be fulfilled in successful gravimetric analyses.
3. How would you prepare the solution for analysis in each of the following examples? If any insoluble residue is obtained in bringing the sample into solution, tell what constituents are in the residue.

An iron ore.
A limestone.
A sample of steel.
A sample of grass.
A sample of glass.

4. List the requirements needed in the reagent used for obtaining the final precipitate.
5. A sample is obtained in a nitric acid solution. The following constituents are present: Na, Ca, Fe, Co, Al, Cu. Describe the group separations that would be used. What constituents will be found with each group?
6. What organic precipitants have you used in qualitative analysis? For what determinations?
7. List the various common methods for filtration. Tell when each is desirable. Which method would you choose for each of the following precipitates: barium sulfate, ferric hydroxide, silver chloride, magnesium ammonium phosphate, zinc sulfide?
8. What is digestion of a precipitate? Is this procedure always employed? Explain.
9. When is it advantageous to employ suction with filter paper? Describe the arrangement necessary to use suction with paper.
10. Describe the preparation of a Gooch crucible.
11. Why should washing be done by the addition of several small portions of liquid rather than by a smaller number of larger portions, provided that the same total volume of liquid is used in each method?
12. For which of the following would HCl be a satisfactory wash solution?
    (*a*) AgCl precipitated by $AgNO_3$ in a Cl^- determination.
    (*b*) AgCl precipitated by NaCl in a Ag^+ determination.
    (*c*) Hydrated ferric oxide.
    (*d*) Calcium oxalate.
    (*e*) Hydrated silica.
    (*f*) Lead sulfate.
13. According to the color scale of temperature given, what temperature do you estimate is attainable with the burner available in your desk?

14. Describe the various steps employed in the ignition of a precipitate in filter paper.

15. Name three gravimetric determinations in which the material is weighed in the same form that it is precipitated.

16. Why should ignited precipitates be cooled in a desiccator?

17. What may occur if the desiccator cover is suddenly removed after an ignited precipitate has been cooled?

18. Make a list of more common errors in gravimetric analysis. Compare this list with the one given in the book.

19. In which of the following determinations is no gravimetric factor required in the calculation?

(*a*) Lead reported as Pb and determined by anodic deposition.
(*b*) Aluminum reported as Al_2O_3.
(*c*) Silver reported as Ag_2O.
(*d*) Copper reported as Cu and determined by electrodeposition.
(*e*) Tin reported as Sn.

PROBLEMS

1. Calculate the chemical factors:

Weighed	*Sought*	*Factor*
$(NH_4)_2PtCl_6$	NH_3	_____
AgCl	$Mg(ClO_4)_2$	_____
K_2PtCl_6	K_2O	_____
Cu_2S	CuO	_____
K_2PtCl_6	K	_____
Pb_3O_4	Pb	_____
$BaSO_4$	FeS_2	_____
CaO	$H_2C_2O_4 \cdot 2H_2O$	_____

2. Calculate by factors the following:

(*a*) The tons of limestone ($CaCO_3$) needed for the preparation of 5 tons of lime (CaO).

(*b*) The pounds of $BaCl_2$ needed to furnish 1.50 lb of chlorine by an electrolytic process.

(*c*) The weight of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) in milligrams needed to precipitate the calcium in a 0.5000-g sample of phosphate rock of the composition $Ca_3(PO_4)_2$.

(*d*) The weight of pyrites, FeS_2, in kilograms that must be burned to produce 3.60 kg sulfuric acid.

(*e*) The milligrams of Mn_3O_4 which can be obtained by strongly heating 0.2500 g MnO_2.

3. A 0.8000-g sample of pyrolusite (MnO_2) yielded 1.282 g $Mn_2P_2O_7$. What is the percentage purity of the ore?

4. What is the percentage purity of a sample of $Al_2(SO_4)_3$ if a 0.5000-g sample produced a precipitate of $BaSO_4$ weighing 1.000 g?

5. A 2.350-g sample of K_2CrO_4 yielded an ignited precipitate of Cr_2O_3 which weighed 0.9055 g. Calculate the percentage Cr and the percentage purity of the salt.

6. A 0.8050-g sample of brass, on analysis, yields 0.2537 g of SnO_2, 1.0752 g of $Zn_2P_2O_7$, and 0.1571 g of copper. Calculate the percentage of copper, tin, and zinc in the sample.

7. An impure sample of Na_2SO_4 weighed 1.562 g. A $BaSO_4$ precipitate from this sample weighed 2.496 g. Calculate the percentage of sulfur and the percentage purity of the salt.

8. What is the percentage of Fe_3O_4 in an ore sample which weighed 0.5350 g? The sample was dissolved by fusion with $KHSO_4$, oxidized by Br_2 water, and the iron was precipitated as hydrous ferric oxide. The ignited ferric oxide weighed 0.5178 g.

9. A 0.8500-g sample of pyrites, FeS_2, was fused and the sulfur oxidized to $SO_4^=$. The precipitate of $BaSO_4$ weighed 1.4300 g. What is the percentage of pyrites in the ore?

10. A chromium ore was brought into solution by an oxidizing flux. 0.5000 g of the ore produced a precipitate of $BaCrO_4$ weighing 0.5000 g. What is the percentage of Cr_2O_3 in the ore?

11. A sample of rock taken for analysis weighs 1.0000 g on an air-dry basis. After drying for one hour at 110°C the sample weighs 0.9437 g. The calcium is precipitated as oxalate but weighed as $CaSO_4$; this weighs 0.5000 g. The magnesium is precipitated as $MgNH_4PO_4$ which ignited to 0.5000 g $Mg_2P_2O_7$. Find the percentages of CaO and MgO on an oven-dry basis and the percentages of these as well as of H_2O on an air-dry basis.

12. In a steel analysis the CO_2 from the combustion of carbon is absorbed in "ascarite." If the gain in weight of the absorbent for a 0.5000-g sample of steel is 15.6 mg, what is the percentage of C in the steel?

13. A 0.5000-g sample of FeO is ignited to Fe_2O_3; what is the percentage gain in weight?

14. A 0.7650-g sample of clay, containing 20.50 per cent moisture, gave a precipitate of potassium perchlorate weighing 0.3822 g. What is the percentage of K_2O in the clay on a dry basis?

15. A metallic alloy which is 60 per cent Co and 40 per cent Ni is analyzed by determining the cobalt by electrodeposition and the nickel by precipitation with dimethylglyoxime. What weight of precipitates will be obtained from a 0.6000-g sample of alloy?

16. A limestone sample weighing 0.7735 g gave a precipitate of CaC_2O_4 which was ignited to CaO and weighed 0.3135 g.

(*a*) Express the percentages of the following in the dolomite: CaO, $CaCO_3$, $CaSiO_3$, and $Ca_2Si_2O_7$, on the assumption that all the calcium in the rock is present as the specified constituent.

(*b*) What would the ignited precipitate have weighed had it been ignited to: $CaCO_3$, $CaSO_4$?

(*c*) If the precipitated CaC_2O_4 had been dissolved in H_2SO_4, what volume of 0.1000 *N* $KMnO_4$ would have been required for titration?

17. What weight of sample which contains 56.15 per cent Cl was taken for analysis if the precipitated AgCl weighed 0.5017 g?

18. What size sample of a mixture which is approximately 15 per cent S should be taken for analysis in order that the proportionate error in determining the weight of the precipitate on an ordinary analytical balance does not exceed 1/1000? (The precipitate is weighed as $BaSO_4$).

19. •A sample of pure $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ weighs 1.215 g.

(*a*) What volume of NH_3 solution (density = 0.9 g/ml, 28% NH_3) is needed for precipitation?

(*b*) What weight of ignited Al_2O_3 will be obtained from the precipitate in (*a*)?

20. How many milliliters of NH_3 (density = 0.91 g/ml, 25% NH_3) are needed to precipitate the iron as hydrated ferric oxide from a 0.1262-g sample of $FeCl_2$?

21. How many milliliters of saturated bromine water (0.16 *M*) are needed to oxidize the iron in Problem 20 to the ferric state?

22. How many milliliters of 0.1 *M* NH_3 solution are needed to precipitate the iron as ferric hydroxide from a 2.000-g sample of ore which is approximately 80 per cent Fe_3O_4?

23. How many milliliters of HNO_3 of specific gravity 1.10 (consult handbook for composition) are needed to dissolve 0.5000 g Ag if the reduction product is NO_2?

24. How many milliliters of a solution which contains 1.0 g $AgNO_3$ per 20.0 ml are needed to precipitate the AgCl from a 0.5000-g sample of $BaCl_2 \cdot 2H_2O$ if a 5 per cent excess is to be used?

25. If a 10 per cent excess is to be used, how many milliliters of 0.15 *M* $AgNO_3$ are needed to precipitate the AgCl from a sample which weighs 0.5000 g and contains 3.00 m mol $ZnCl_2$?

26. How much 0.15 *M* Na_2SO_4 solution is needed to precipitate the $BaSO_4$ from the sample of Problem 24 if no excess is to be used?

27. Find the number of milliliters of a solution which contains 0.2000 mole of $BaCl_2$ in 500-ml solution which are needed to precipitate $SO_4^{=}$ from 3.00 m mol $Al_2(SO_4)_3$ as $BaSO_4$.

28. How many milliliters of a solution of 2.0 g $Ba(NO_3)_2$ in 100 ml of solution are needed to precipitate the $BaSO_4$ from a 0.5000-g sample of $Fe_2(SO_4)_3 \cdot 9H_2O$ if a 20 per cent excess is to be used? Would you advise the procedure?

29. A sample is known to be NaCl, KCl, or $MgCl_2$, or a mixture of these constituents. What is the smallest volume of 0.2 *M* $AgNO_3$ that will insure the complete precipitation of AgCl, regardless of the composition of the sample?

30. How many milliliters of a 1.00 per cent alcoholic solution of dimethylglyoxime are needed to precipitate the nickel contained in a 0.750-g sample of ore which is approximately 35 per cent Ni?

31. What volume of a solution which contains 1.2 g $(NH_4)_2C_2O_4$ per 100 ml is needed to precipitate the calcium from a 1.0-g sample of phosphate rock which is essentially tertiary calcium orthophosphate?

32. How many milliliters of a 20 per cent by weight solution of $(NH_4)_2Cr_2O_7$ are needed for the precipitation of barium as chromate from a 1 g sample of mixture which is 50 per cent $Ba(NO_3)_2$ and 50 per cent $Sr(NO_3)_2$. The precipitation reaction is

$$2Ba^{++} + Cr_2O_7^{=} + H_2O + 2Ac^{-} = 2BaCrO_4 + 2HAc$$

33. What weight of sample should be taken for analysis so that each 10.0 mg precipitated AgCl represents 1.000 per cent Ag_2O in the original sample?

34. What weight of sample should be taken for analysis so that exactly twice the weight in mg of precipitated $BaSO_4$ is the percentage of SO_3 in the original sample?

35. A 0.5000-g sample of an alloy gave a precipitate of Fe_2O_3 and Al_2O_3 which weighed 0.2000 g. The alloy contained 5.00 per cent Al. How much 0.1000 *N* $KMnO_4$ is needed for titration of the ignited precipitate after fusion with $K_2S_2O_7$ and reduction in a Jones reductor?

36. A 1.000-g sample of a mixture which consists only of NaCl and KCl gave a precipitate of AgCl which weighed 2.000 g. What are the percentages of Na and K in the mixture?

37. A sample contains both Cl^- and Br^-. The precipitate of mixed silver halides obtained from a 1.0175-g portion weighs 0.8845 g. The precipitate is reduced in a

stream of hydrogen, the silver dissolved in nitric acid and determined by the Volhard procedure, 48.14 ml of 0.1010 *M* thiocyanate solution being used for the titration. Compute the percentage of chlorine and bromine in the sample.

38. A mixture of only AgCl and AgI is heated in a current of chlorine, thereby converting the AgI to AgCl. This conversion causes a loss of 6.00 per cent of the original weight. Find the percentage of Cl in the mixture.

39. In what proportions should potassium and ammonium bromides be mixed to make a salt mixture which is 70.00 per cent Br?

40. How many grams of KCl should be added to 100 g NaCl to make a mixture which contains 55.0 per cent Cl?

41. A mixture of $BaCl_2$ and KCl contains 40.00 per cent Cl. What is the percentage of barium in the mixture? How many grams of $BaCl_2$ should be mixed with 0.5000 g KCl to produce the mixture?

42. What is the percentage composition of a mixture of KCl and NH_4Cl which has the same percentage of Cl as NaCl? If 0.5000 g of the mixture is strongly ignited, what is the weight of the residue?

CHAPTER

18

Equilibria in Precipitation Reactions

In this chapter we shall discuss the equilibria between precipitates and their ions and the factors which govern the completeness of precipitations. This material is an extension to a two-phase system of the law of chemical equilibrium which was previously discussed in Chapter 9. It is, of course, possible to carry out gravimetric analyses by merely following the laboratory precedures without understanding the principles on which the procedures are based. However, one who wishes to be more than a routine technician must understand these principles so that he can avoid errors or can develop new methods as needed.

In the first portion of this chapter we shall consider simple systems in which only one substance may precipitate. This is followed by a discussion of the more complex equilibria that are involved in separations of one constituent from other components of a sample.

COMPLETENESS OF PRECIPITATION

Solubility. Before discussing the phenomena of precipitation we should review the subject of solubility. At first thought this appears to be a simple matter; a solid is placed in water and goes into solution until an equilibrium condition is reached when the solution becomes saturated. But what makes the solid dissolve? Why are some substances more soluble than others? Why is the solubility different for different solvents? Answers to these and other questions are not known completely. We can only indicate in a qualitative manner some partial answers.

Solubility is in a broad sense an indication that attractive forces exist between solute and solvent ions or molecules. If solute molecules are

not attracted more strongly by solvent molecules than by their own type of molecules, a solution is not formed. For example, oil and water are very slightly soluble in one another because oil molecules are attracted to one another more strongly than to water molecules and water molecules are attracted to one another more strongly than to oil molecules. Therefore, if oil and water are shaken together to form an emulsion, there soon results on standing a two-phase system, as oil molecules are squeezed out of the water phase and water molecules are squeezed out from the oil phase. Quite different is the behavior of water and alcohol, whose molecules attract one another strongly. Not only are these liquids miscible in all proportions, but so strong are the attractive forces between the molecules that there is a contraction in volume when alcohol and water are mixed.

We do not know the exact nature of the attractive forces that cause molecules or ions to go into solution. In some ways the attraction must be like the forces that cause two molecules to react with one another, since the forces of solution are specific for certain molecules or ions. In organic chemistry a rule-of-thumb guide to predict when solubility will occur is "Like dissolves like," which means that compounds of similar groups or structures will dissolve in one another.

When a solid is immersed in a liquid, solution can occur only if atoms, ions, or molecules of the solid are strongly enough attracted by the liquid so that the forces which hold the particles in the solid are overcome. These forces in the solid state are quite strong. Most pure solids are crystalline in nature, and the atoms or ions are arranged in a regular network, as illustrated in Fig. 29, page 360, so that every particle has exactly the same surroundings as every other like particle. In a sodium chloride crystal, for example, each sodium ion is surrounded by 6 chloride ions and each chloride ion by 6 sodium ions. When such a crystalline solid is heated, each lattice particle vibrates about its equilibrium position with increased amplitude. The crystal structure is not broken down until the amplitude of the vibrations becomes sufficiently great to remove particles completely from the lattice positions. At this temperature the solid becomes a liquid or melts. The melting point for most inorganic crystals is quite high, which indicates that considerable energy is required to overcome the forces which hold the particles in the crystal lattice.

If now a crystal goes into solution, energy is likewise required to break down the crystal structure. This energy must be furnished by the energy of combination of solvent molecules with the lattice particles which go into solution. We reason therefore that in view of the thermal stability of crystals the energy of solution must be quite large.

Most inorganic compounds have crystals of the ionic type; the lattic positions are occupied by ions as in the NaCl crystal previously described. When such crystals dissolve, they go into solution as positive and negative ions rather than as molecules. A sodium chloride crystal gives a solution of Na^+ and Cl^- ions, not NaCl molecules. There are reasons to believe that all such ions are hydrated or combined with water molecules. Thus the Na^+ ion is really $Na(H_2O)_x^+$ and the Cl^- ion is really $Cl(H_2O)_y^-$.

Every known inorganic ion is soluble unless it occurs with some other ion that prevents its going into solution. Both Ag^+ and Cl^- ions are soluble since both $AgNO_3$ and NaCl are soluble. Yet AgCl is only slightly soluble. This must mean that Ag^+ and Cl^- ions are so tightly held in the crystal lattice that the attractive force between these ions and water molecules is weaker than the crystal-lattice forces. Why this is true for AgCl and not for $AgNO_3$ is something we cannot explain. The facts of solubility must be accepted as empirical. Crystals such as $AgNO_3$, $BaCl_2$, $FeCl_3$, $MgSO_4$ are soluble, whereas other combinations of the same ions, such as AgCl, $BaSO_4$, Fe_2O_3, are insoluble.

EQUILIBRIA BETWEEN PRECIPITATE AND SOLUTION

Solubility-product Constant. At room temperature the solubility of AgCl is about 0.0015 g per liter or approximately 1×10^{-5} mole per liter. In solution the following equilibrium exists:

$$AgCl_{(solid)} = Ag^+ + Cl^-$$

Since each mole that dissolves yields a mole each of Ag^+ and Cl^- ions, the concentration of each ion in a saturated solution is 1×10^{-5} molar. Application of the law of chemical equilibrium gives

$$\frac{[Ag^+][Cl^-]}{[AgCl_{(solid)}]} = \text{a constant}$$

Since [AgCl] refers to the crystal, whose concentration does not change, the expression can be simplified to

$$[Ag^+][Cl^-] = K_{SP}$$

where the constant is known as the solubility-product constant. In a saturated solution $[Ag^+] = 1 \times 10^{-5}$ and $[Cl^-]$ is the same. We can evaluate K_{SP} by substitution of these values, or

$$[Ag^+][Cl^-] = (1 \times 10^{-5})(1 \times 10^{-5}) = 1 \times 10^{-10} = K_{SP}$$

Similarly, in a saturated solution of barium sulfate we have the relation,

$$[Ba^{++}][SO_4^{=}] = K_{SP}$$

For a polyvalent insoluble substance, such as $Mg(OH)_2$, we have the equilibrium,

$$Mg(OH)_{2\,(solid)} = Mg^{++} + 2OH^-$$

The solubility-product expression is

$$[Mg^{++}][OH^-]^2 = K_{SP}$$

For the general case,

$$M_xN_y = xM \text{ ions} + yN \text{ ions}$$

the solubility-product expression is

$$[M \text{ ion}]^x[N \text{ ion}]^y = K_{SP}$$

It should be noted that in the K_{SP} expressions, just as in other chemical equilibria of solutions, *all concentrations are expressed in moles per liter.* The reason is that the equilibria depend on the number of molecules per unit volume of the solution, which in turn determines the number of collisions per unit time.

Relation of Solubility to K_{SP}. It is obvious from the preceding discussion that the value of the K_{SP} constant may be computed from the measured solubility, or, conversely, the solubility may be computed from the value of the constant. These computations are illustrated in the following examples.

1. The value of K_{SP} for barium sulfate is 1.1×10^{-10} (see Appendix). Compute the solubility in grams per 100 ml.

Solution: Write the chemical equation,

$$BaSO_{4\,(solid)} = Ba^{++} + SO_4^{=}$$

We may denote by X the molar concentrations of barium and sulfate ions. Then

$$X^2 = K_{SP} = 1.1 \times 10^{-10}$$

Solution of this equation gives

$$X = \sqrt{1.1 \times 10^{-10}} = 1.05 \times 10^{-5}$$

Since each mole of barium sulfate which dissolves yields a mole each of barium and sulfate ions, X represents the number of moles of $BaSO_4$ which go into solution in 1 l. The weight dissolved per liter is then the product of the molecular weight by the number of moles per liter, or

$$\text{Weight in grams per liter} = 1.05 \times 10^{-5} \times 233$$

$$= 245 \times 10^{-5} \text{ g per liter}$$

From this value we may compute the grams per 100 ml:

$$\text{Grams per 100 ml} = 245 \times 10^{-5} \times 0.1$$
$$= 24.5 \times 10^{-5}$$
$$= 2.45 \times 10^{-4}$$

2. The solubility of $Mg(OH)_2$ is 0.0009 g per 100 ml. Compute the solubility-product value.

Solution: The molar solubility is not given, but it may be calculated by dividing the solubility in grams per liter by the molecular weight, 58.34. Since the solubility is 0.0009 g per 100 ml, the solubility in grams per liter is $1000/100 \times 0.0009 = 0.009$ g per liter. Division by 58.34 gives 1.54×10^{-4} as the molar solubility.

From the chemical equation, it is obvious that each mole which dissolves yields 1 mole of magnesium ion and 2 moles of hydroxide ion. The concentration of magnesium ion is, therefore, 1.54×10^{-4}, and the concentration of hydroxide ion is $2 \times 1.54 \times 10^{-4}$. Substitution of these values into the solubility-product equation gives

$$(1.54 \times 10^{-4})\ (2 \times 1.54 \times 10^{-4})^2 = K_{SP} = 14.6 \times 10^{-12}$$

3. The solubility product for silver chromate is 9×10^{-12}. Calculate the solubility in grams per 100 ml.

Solution: Here there is extensive hydrolysis of one constituent, the chromate ion, but the effect is ignored in the calculation. The chemical equation is

$$Ag_2CrO_{4\,(solid)} = 2Ag^+ + CrO_4^=$$

The solubility-product equation has the form,

$$[Ag^+]^2[CrO_4^=] = K_{SP} = 9 \times 10^{-12}$$

Each mole of salt, on dissolving, yields 2 moles of silver ion and 1 mole of chromate ion. If the number of moles dissolved in a liter is denoted by X, the concentration of silver ion is $2X$, while that of chromate ion is X. Substitution of these values in the solubility-product expression gives the equation:

$$(2X)^2(X) = 9 \times 10^{-12}$$
$$4X^3 = 9 \times 10^{-12}$$
$$X = 1.3 \times 10^{-4} \text{ mole per liter}$$

In order to determine the concentration in grams per 100 ml, the molar concentration is multiplied by the number of liters, and the product is multiplied by the molecular weight, 332.

$$\text{Grams per 100 ml} = (1.3 \times 10^{-4} \times 100/1000) \times 332 = 4.3 \times 10^{-3}$$

Common-ion Effect. It is obvious, from the solubility-product expression, that, if the concentration of one ion is increased in a solution which is in equilibrium with a precipitate, the concentration of another ion of the precipitate must be decreased in order to maintain equilibrium. Therefore, addition of one ion of a precipitate to a saturated solution will cause the formation of more of the solid phase. A familiar example is the precipitation of sodium chloride from a saturated solution

by the addition of hydrogen chloride. As HCl gas is passed into the solution, the concentration of chloride ion is increased, and equilibrium is maintained by precipitation of sodium chloride, which lowers the concentration of sodium ion. The effect of an ion of the precipitate on the solubility is known as the *common-ion effect.*

Advantage is taken of the common-ion effect to reduce the solubility of precipitates. By addition of an excess of precipitant, the amount of the ion sought which remains in solution may be greatly reduced. For example, in a saturated solution of silver chloride the concentration of chloride ion is 10^{-5} M, or 35.46×10^{-5} g of chloride ion remain in solu-

TABLE 32

EFFECT OF TEMPERATURE ON SOLUBILITY

Precipitate	*Solubility in Grams per 100 Ml*	
	Cold	*Hot*
AgBr	8×10^{-6}	4×10^{-4} (100°)
Ag_2CO_3	3.4×10^{-3} (15°)	5×10^{-2} (100°)
AgCl	8.9×10^{-5} (10°)	2.17×10^{-3} (100°)
$AgIO_3$	3×10^{-3} (10°)	1.8×10^{-2} (60°)
$BaSO_4$	1.15×10^{-4} (0°)	2.85×10^{-4} (30°)
$BaCO_3$	2.2×10^{-3} (18°)	6.5×10^{-3} (100°)
CaC_2O_4	6.7×10^{-4} (13°)	1.4×10^{-3} (95°)
$CaCO_3$	6.5×10^{-3} (20°)	2×10^{-3} (100°)

tion per liter. If an excess of silver ion is added to bring the final silver-ion concentration to 10^{-3} M, the chloride-ion concentration is correspondingly reduced, as shown in the computation,

$$[Cl^-] = \frac{K_{SP}}{[Ag^+]} = \frac{10^{-10}}{10^{-3}} = 10^{-7}$$

and the grams chloride ion per liter are reduced to 35.46×10^{-7}.

Factors Affecting Solubility. In the preceding discussions the solubility is taken as that in pure water, at room temperature. These conditions do not always apply, and the analyst should know of the factors which may affect solubilities and the K_{SP} values of precipitates. The more important of these are the effects of temperature, change in solvent, and the neutral-salt effect.

In general, an increase in temperature will increase solubility, sometimes to a very marked degree. In some cases, however, there is little change in solubility with increase in temperature. In Table 32 there are listed some typical solubility data at various temperatures. Inspection of these data reveals that in extreme cases there may be a 50- to 100-fold increase in solubility when the solution is heated. Conse-

quently, care must be exercised in the application of computations based on room-temperature data to a system at a different temperature.

A change in solvent will usually cause a large change in solubility, and, in general, most inorganic salts are less soluble in organic solvents than in pure water. Occasionally advantage is taken of this behavior to separate ions whose differences in solubility in water are not sufficiently great to achieve the separation. For example, strontium is often precipitated as $SrCrO_4$ in an alcohol–water solution, in the qualitative separation from calcium. The perchlorate method for quantitative determination of sodium is based on the fact that potassium perchlorate is only slightly soluble in organic liquids such as absolute alcohol or ethyl acetate while sodium perchlorate is soluble. It is probable that analysts will more and more turn to the use of non-aqueous solvents to effect separations that cannot at present be made from water solutions, because of lack of suitable insoluble compounds.

The neutral-salt effect is an increase in solubility when neutral salts with no common ion are added to a saturated solution of a slightly soluble substance. For example, $BaSO_4$ is over twice as soluble in dilute KNO_3 solution as in pure water,[1] and $CaC_2O_4 \cdot H_2O$ is about 4 times as soluble in 0.6 N NaCl as in water alone. The effect of the neutral salt is to increase the attraction of the solvent for lattice ions of the precipitate, presumably by the electrostatic attraction of the neutral-salt ions. In general, the magnitude of the neutral-salt effect is not large unless there are present very large concentrations of the salt, a condition which is otherwise undesirable because of the increased possibility of contamination of the precipitate. The analyst should, however, keep in mind the possibility that an excess of electrolytes in the liquid may to some extent increase his solubility losses.

Applications in Analysis. We may now summarize the applications of the law of chemical equilibrium to precipitation equilibria and show how account is taken of these equilibria in the analytical procedures.

1. Precipitation is never complete. Since the solubility-product equation for a salt in which both ions have the same valence has the form of a hyperbola (xy = a constant), it is not possible to reduce the concentration of one ion to zero unless the concentration of another ion becomes infinite. However, for practical purposes precipitation is complete when the amount of substance remaining in solution is less than the limits of weighing, or about 0.1 mg.

[1] E. W. Neumann, *J. Am. Chem. Soc.*, **55**, 879 (1933). Kolthoff and Sandell, *Textbook of Quantitative Inorganic Analysis*, page 57.

Most of the gravimetric procedures are based on precipitates of such low solubility that errors due to incomplete removal of ions from solution are negligibly small. Incomplete precipitation is generally the least important source of error. There are, however, occasional analyses which employ precipitates of appreciable solubility because more insoluble ones are not known; in such analyses solubility losses may become appreciable if care is not taken to use minimum volumes of solution and otherwise keep solubility losses as low as possible.

2. Use of a common ion in precipitation decreases the amount of the sought ion which remains in solution. Use of an unduly large excess of common ion is not desirable, because it may increase the degree of contamination of the precipitate and may even cause increased solubility because of the neutral-salt effect.

3. A common ion is advantageously used in washing precipitates of appreciable solubility. To be suitable for such use the common ion must be one of the precipitant, not of the sought constituent, and must be provided in a form such that any excess is removed by volatilization when the precipitate is ignited or dried.

In the majority of analyses it is not possible to find a volatile common ion which is suitable for use, and washing is done with pure water or with water which contains a small amount of an electrolyte to prevent the precipitate from becoming colloidal. There is more danger of appreciable solubility losses in the wash water than in the precipitating solution when no common ion can be used, and, if care is not taken to use a minimum volume of wash liquid, the loss due to solubility may become appreciable.

4. The solubility-product relation may be used to compute the weight of precipitate which is lost by solubility. We may illustrate by computation of the loss of AgCl in precipitation and washing.

(*a*) Loss in mother liquor. As shown previously, the solubility of AgCl is at room temperature about 0.00015 g per 100 ml or 1.5×10^{-3} g per liter. The molar solubility is about 1×10^{-5} moles per liter and the K_{SP} value about 1×10^{-10}. If 3 m mol NaCl is treated with 3.5 m mol $AgNO_3$ in a total volume of 200 ml, there is an excess of 0.5 m mol of silver ion over that required for complete reaction with the chloride ion (3.5 m mol $Ag^+ - 3.0$ m mol $Cl^- = 0.5$). Therefore the concentration of Ag^+ in excess of the stoichiometric amount is 0.5/0.200 or 2.5 m mol per liter $= 2.5 \times 10^{-3}$ mole per liter.

Since the amount of Ag^+ contributed by the solubility of AgCl is negligible with respect to the $[Ag^+]$ in excess, the $[Ag^+]$ in excess may be substituted directly into the solubility-product expression to compute the $[Cl^-]$.

$$(2.5 \times 10^{-3})[Cl^-] = 1 \times 10^{-10}$$

or

$$[Cl^-] = \frac{1 \times 10^{-10}}{2.5 \times 10^{-3}} = 0.4 \times 10^{-7}$$

The number of millimoles of chloride ion remaining in solution is the volume–molarity product:

$$\text{Millimoles } Cl^- \text{ lost} = 200 \times 0.4 \times 10^{-7}$$

$$= 80 \times 10^{-7}$$

The percentage of the chloride ion lost is given by

$$\text{Per cent loss} = \frac{80 \times 10^{-7}}{3} \times 100 = 0.00027\%$$

Thus the error due to solubility loss is negligible.

On a weight basis the loss of chloride ion is given by

$$\text{Milligrams } Cl^- \text{ in solution} = 200 \times 0.4 \times 10^{-7} \times 35.46$$

$$= 28 \times 10^{-5} \text{ mg}$$

(*b*) Loss in wash liquid. In the chloride determination it is not feasible to use a common ion in the wash liquid (why?). Consequently the solubility is that of AgCl in pure water, or 1×10^{-5} mole per liter. If 200 ml wash water is used, the solubility loss is $0.200 \times 1 \times 10^{-5}$ mole per liter, and the loss in grams of chloride ion is

$$\text{Weight chloride ion in solution} = 0.200 \times 10^{-5} \times 35.46$$

$$= 0.000071 \text{ or } 0.071 \text{ mg}$$

This loss, too, is negligible.

If precipitation and washing are done at 100°C, the losses are greater. According to the data of Table 32, the solubility of AgCl at 100°C is 0.00217 g per 100 ml or 1.5×10^{-4} mole per liter, and the K_{SP} value is 2.25×10^{-8}. Computation as above shows that loss of chloride ion in the mother liquor is about 0.07 mg, and in 200 ml wash liquid is about 1 mg.

It must be realized that the magnitudes of the losses caused by solubility in the wash water which have just been calculated represent hypothetical maxima. It is unlikely that wash water remains in contact with a precipitate long enough to form a saturated solution. Furthermore, in a chloride analysis some of the excess silver nitrate used in the precipitation adheres to the solid silver chloride, and the Ag^+ so remaining acts as a common ion in the early stages of washing.

COMPLEX EQUILIBRIA IN PRECIPITATION

In many gravimetric separations it is necessary to consider the combined effects of precipitation equilibria and other equilibria. We shall in this section discuss a few such cases, to illustrate the general type of treatment and to point out some of the more common analytical applications of complex equilibria.

Separations by Control of *p*H. Many of the precipitations of analytical chemistry utilize the insolubility of hydroxides, sulfides, phosphates, carbonates, oxalates, and salts of other weak acids. In all these precipitations the *p*H of the solution will affect the completeness of precipitation, because the hydrogen-ion concentration of the solution determines the concentration of the precipitant ion. In the hydrogen sulfide precipitations of qualitative analysis, for example, there are the equilibria:

$$H_2S = H^+ + HS^-$$

$$HS^- = H^+ + S^=$$

Application of the equilibrium law gives the expressions:

$$\frac{[H^+][HS^-]}{[H_2S]} = K_1 = 9 \times 10^{-8}$$

$$\frac{[H^+][S^=]}{[HS^-]} = K_2 = 1 \times 10^{-15}$$

Combining these gives

$$\frac{[H^+]^2[S^=]}{[H_2S]} = K_1K_2 = 9 \times 10^{-23}$$

If a saturated solution of hydrogen sulfide (approximately 0.1 M) is acidified with hydrochloric acid at a concentration of 0.2 M, the sulfide-ion concentration is computed by means of the last equation:

$$\frac{(0.2)^2[S^=]}{(0.1)} = 9 \times 10^{-23}$$

$$[S^=] = 2 \times 10^{-22}$$

The solubility product for CuS is given as 3.5×10^{-38} (see Appendix). Substitution of the value for the sulfide-ion concentration, as previously calculated, gives

$$[Cu^{++}] = \frac{3.5 \times 10^{-38}}{2 \times 10^{-22}} = 1.7 \times 10^{-16}$$

Therefore, the precipitation of CuS by hydrogen sulfide in a 0.2 M hydrochloric acid solution is quantitative. But for ZnS, whose solubility product is 1.2×10^{-23}, a similar computation shows that the concentration of zinc ion remaining in solution is 0.06 M. Treatment of a mixture of copper and zinc salts with hydrogen sulfide gives precipitation of the copper while the zinc is left in solution. In order to precipitate ZnS it is necessary to decrease the hydrogen-ion concentration, by neutralization, thus permitting the sulfide-ion concentration to increase to such an extent that the solubility product for ZnS is exceeded.

The equilibria of the preceding computations may be used to show that, if a mixture of copper and zinc sulfides is treated with an acid, the zinc sulfide will dissolve while the copper sulfide will be unaffected. Zinc dissolves because the equilibrium,

$$ZnS_{(solid)} = Zn^{++} + S^{=}$$

is shifted as sulfide ion is removed to form undissociated hydrogen sulfide. In the case of the copper sulfide the formation of hydrogen sulfide does not repress the sulfide-ion concentration to a sufficient degree that any appreciable amount of cupric ion can go into solution. It may be recalled that to bring cupric sulfide into solution it is necessary to remove sulfide ion completely, by oxidation with hot nitric acid or a mixture of hydrochloric acid and potassium chlorate.

Several examples of the effect of pH on precipitations involving the anion of a weak acid may be cited, in addition to the hydrogen sulfide separations of qualitative analysis:

1. Phosphates are often present along with calcium and magnesium ions. In the determination of phosphate it is necessary to make the precipitation from acid solution, since, if the solution is basic, the concentration of phosphate ion will be increased to such an extent that the solubility products of both calcium and magnesium phosphates will be exceeded. It happens that ammonium phosphomolybdate is so insoluble that complete precipitation of phosphates is obtained even from quite strongly acid solutions, where no precipitation of calcium or magnesium phosphate occurs.

2. Magnesium (zinc and manganese behave similarly) is usually precipitated as magnesium ammonium phosphate. This precipitate will not form in acid solution, because the concentration of phosphate ion is kept so low that the solubility product cannot be reached, that is:

$$[Mg^{++}][NH_4^{+}][PO_4^{\equiv}] < K_{SP}$$

In an ammoniacal solution the concentration of hydrogen ion is reduced, and consequently the concentration of phosphate ion is increased to such an extent that precipitation takes place.

3. Calcium is usually precipitated as the oxalate. Since oxalic acid is a weak acid, this precipitate cannot be formed in a strongly acid solution. It is customary to add oxalic acid to a hydrochloric acid solution of the calcium ion, and then to neutralize with ammonium hydroxide. As the concentration of hydrogen ion is reduced, the concentration of oxalate ion is increased, and precipitation occurs.

The hydroxides of many metals are insoluble, and the solubility-product values vary over a wide range. Consequently many separations are made by precipitation of hydroxides from solutions of carefully controlled *p*H. (As shown in Chapter 9, the concentration of the hydroxide ion in aqueous solutions is inversely proportional to the hydrogen-ion concentration, or $p\text{H} + p\text{OH} = 14$.) Of the common metals, the hydroxides of iron (ferric) and aluminum are least soluble, whereas the hydroxides of zinc and magnesium are of considerably higher solubility. On the basis of this it should be possible to precipitate ferric and aluminum hydroxides while leaving the hydroxides of zinc and magnesium in solution. Such is actually the case. The principle of the separation may be illustrated by a simple computation.

Problem. The solubility product for magnesium hydroxide is 1.5×10^{-11} (see page 343), and the solubility product for ferric hydroxide is 1.5×10^{-36}. At what *p*H will each of these hydroxides begin to precipitate? Assume a metal-ion concentration of 0.1 *M* in each case.

Solution: Since

$$[\text{Mg}^{++}][\text{OH}^-]^2 = 1.5 \times 10^{-11}$$

the hydroxide-ion concentration is given by the expression,

$$[\text{OH}^-]^2 = \frac{1.5 \times 10^{-11}}{0.1} = 1.5 \times 10^{-10}$$

when the magnesium-ion concentration is 0.1 *M*. Solving gives

$$[\text{OH}^-] = 1.2 \times 10^{-5} \quad \text{and} \quad p\text{H} = 9.08$$

Similarly, for ferric hydroxide,

$$[\text{OH}^-]^3 = \frac{1.5 \times 10^{-36}}{0.1} = 15 \times 10^{-36}$$

Solving, we have

$$[\text{OH}^-] = 2.5 \times 10^{-12} \quad \text{and} \quad p\text{H} = 2.40$$

If an acid solution containing Fe^{+++} and Mg^{++} ions is neutralized, ferric hydroxide will begin to precipitate when the *p*H gets above 2.4, whereas no precipitation of magnesium hydroxide occurs until the *p*H reaches a value of 9–10. Magnesium may be held completely in solution if neutralization is done by ammonium hydroxide in the presence of

an ammonium salt, which represses the ionization of the hydroxide. The effect may be shown by a simple computation.

Problem. A solution contains Fe^{+++} and Mg^{++} ions at a concentration of 0.1 *M*. Sufficient ammonium hydroxide and ammonium chloride are added to make a concentration of 0.1 *M* for each. What will precipitate?

Solution: It is first necessary to compute the concentration of hydroxide ion. Since OH^- ion is furnished by the ionization of ammonium hydroxide,

$$NH_4OH = NH_4^+ + OH^-$$

The equilibrium expression is

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

Let

$$X = [OH^-]$$

$$0.1 + X = [NH_4^+] \quad \text{or} \quad \text{approximately } 0.1$$

$$0.1 - X = [NH_4OH] \quad \text{or} \quad \text{approximately } 0.1$$

Substituting, we have

$$\frac{(X)(0.1)}{(0.1)} = 1.8 \times 10^{-5}$$

Solving gives

$$X = 1.8 \times 10^{-5}$$

Substituting the value for the ferric ion and for the hydroxide ion in the solubility-product expression gives

$$(0.1)(1.8 \times 10^{-5})^3 = 5.8 \times 10^{-16}$$

Since this value is much greater than the solubility product, precipitation of ferric hydroxide will occur.

Substitution of the ionic concentrations in the solubility-product expression for magnesium hydroxide gives

$$(0.1)(1.8 \times 10^{-5})^2 = 3.2 \times 10^{-11}$$

This value is just slightly in excess of the solubility product for magnesium hydroxide; if any precipitation occurs, it will be very slight. As a matter of fact, it is usually necessary to exceed the solubility product by a wide margin before precipitation begins, because of the tendency towards the formation of supersaturated solutions.

In the separation of metals whose solubility products lie much closer together than those of ferric and magnesium hydroxides, it is not feasible to attempt to control the addition of a weak base so that the hydroxide-ion concentration will become large enough for the precipitation of one ion but not for the other. Rather, it is necessary to fix the hydroxide-ion concentration carefully by suitable buffering of the solution, so that during the addition of the base there can occur no local high concentration of hydroxide ion that will cause precipitation of both ions. An

example of this technique for precipitation at carefully controlled *p*H is the basic acetate method for the separation of ferric iron from cobalt, copper, or zinc. In this method a solution in hydrochloric acid is carefully neutralized by ammonium hydroxide until the *p*H is near that at which ferric hydroxide begins to precipitate. Neutralization is continued by the addition of ammonium carbonate until the addition of one more drop of solution will cause some precipitation. The solution is now boiled, and sodium acetate is added to remove the hydrogen ion formed in the hydrolysis of ferric ion,

$$Fe^{+++} + H_2O = Fe(OH)^{++} + H^+$$

$$Ac^- + H^+ = HAc$$

The basic ferric ion, $Fe(OH)^{++}$, forms with acetate ion the precipitate, $Fe(OH)Ac_2$. The solution is boiled for a twofold purpose: Boiling increases the extent of hydrolysis, because of the increased ionization of water at elevated temperatures, and boiling causes the colloidal precipitate to coagulate.

Numerous other methods are used for controlling the *p*H during precipitation of hydroxides. Among these may be mentioned:

1. Precipitation by urea. If a nearly neutral solution containing urea is boiled, the urea hydrolyzes according to the equation,

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3$$

and the *p*H slowly rises during the course of the hydrolysis. This reaction may be used to effect precipitation of insoluble hydroxides.

2. Precipitation by barium carbonate. When solid barium carbonate is added to a slightly acid solution, hydrogen ion is neutralized,

$$BaCO_{3\,(solid)} = Ba^{++} + CO_3^{=}$$

$$CO_3^{=} + 2H^+ = H_2CO_3$$

and the *p*H becomes that of a carbonic acid solution. If there is present an ion, such as ferric ion, that is readily hydrolyzed,

$$Fe^{+++} + 3H_2O = Fe(OH)_3 + 3H^+$$

the liberated hydrogen ion reacts with carbonate ion from the solid barium carbonate and the hydrolysis reaction proceeds towards the right, with precipitation of ferric hydroxide. The hydroxides of Fe^{+++}, Al^{+++}, and Cr^{+++} may be precipitated in this manner, by shaking a slightly acid solution with freshly precipitated barium carbonate. It is, of course, necessary to make certain that the barium carbonate contains no hydroxide. Why?

3. Precipitation of small amounts of aluminum in the presence of large amounts of iron by phenylhydrazine. If a hydrochloric acid solution of ferric and aluminum salts is treated with sulfur dioxide, the iron is reduced to the ferrous condition, in which form the hydroxide is much more soluble than that of ferric iron. If phenylhydrazine, $C_6H_5NHNH_2$, is added and the solution boiled, aluminum hydroxide is precipitated. The function of phenylhydrazine is to remove hydrogen ion, formed in the hydrolysis of the aluminum ion.

$$Al^{+++} + 3H_2O = Al(OH)_3 + 3H^+$$

$$H^+ + C_6H_5NHNH_2 = C_6H_5NHNH_3^+$$

Complex Ions. Ions other than hydrogen may affect the solubility of precipitates, by formation of complex ions. A familiar example, from qualitative analysis, is the solubility of silver chloride in ammonium hydroxide. If solid silver chloride is treated with ammonium hydroxide, the concentration of silver ion is reduced because of formation of the complex, $Ag(NH_3)_2^+$. The magnitude of the effect of complex-ion formation on the solubility may be shown by a simple calculation.

Problem. Solid silver chloride is treated with 100 ml 1 *M* ammonium hydroxide. How many grams will dissolve?

Solution: By reference to the tables of equilibrium constants in the Appendix the following values are found:

$$[Ag^+][Cl^-] = 1 \times 10^{-10}$$

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6.8 \times 10^{-8}$$

If X = molar concentration of the silver chloride which dissolves, it follows that $X = [Cl^-] = [Ag(NH_3)_2]^+$. The concentration of silver ion is given by the expression,

$$[Ag^+] = \frac{K_{SP}}{[Cl^-]} = \frac{1 \times 10^{-10}}{X}$$

Since each mole of salt which passes into solution reacts with 2 moles of ammonia, the concentration of ammonia is the original amount minus the amount which has reacted, or $1 - 2X$.

Substitution of the preceding concentration values into the expression for the dissociation of the complex ion gives

$$\frac{\left(\frac{1 \times 10^{-10}}{X}\right)(1 - 2X)^2}{X} = 6.8 \times 10^{-8}$$

$$\frac{(1 - 2X)^2}{X^2} = 6.8 \times 10^2$$

$$X = 0.036\ M$$

X was defined as the molar concentration of silver chloride which dissolves. The weight of salt is obtained from the expression

$$\text{Weight of AgCl} = \text{volume in liters} \times \text{molarity} \times \text{molecular weight}$$

$$= \tfrac{100}{1000} \times 0.036 \times 143 = 0.51 \text{ g}$$

Several complex ions which may affect the completeness of precipitations may be mentioned. Copper, as cuprous ion, forms a very stable complex ion with the cyanide ion. Silver also forms a complex cyanide ion; this is the basis for the Liebig method for the volumetric determination of cyanides by titration with standard silver nitrate solution (see page 304). Lead forms a complex ion with acetate; this reaction is often used in qualitative analysis for bringing a precipitate of lead sulfate into solution. The solubility of amphoteric hydroxides in strong bases may be regarded as due to formation of complex anions with the cation of the hydroxide. An example is the solubility of aluminum hydroxide in sodium hydroxide by means of the formation of the aluminate ion, AlO_2^-. Similarly, the solubility of arsenic group sulfides in sodium or ammonium sulfide solution is due to formation of complex ions of the metal with the sulfide ion, as the $AsS_4^{\equiv}$ ion. Cadmium forms a chloride, possibly $CdCl_4^{=}$, of such stability that cadmium is with difficulty precipitated as sulfide from solutions of high chloride-ion concentration. Many of the polyhydric alcohols and the hydroxy acids form complex ions with metals, but, since organic matter is usually removed in the preparation of a sample, this is not likely to cause difficulty in quantitative determinations. The solubility of lead sulfate in very dilute nitric acid solutions is probably due both to the formation of complex lead ions, and to the formation of HSO_4^- ions.

QUESTIONS

1. Can the solubility product for a salt ever be equal to the cube of the molar solubility?

2. By means of the concepts of activity and activity coefficient explain why silver chloride is slightly more soluble in a potassium nitrate solution than in pure water.

3. What types of precipitates are more soluble in acid than in neutral solutions? Explain, for one example, the nature of the effect of acid on the solubility.

4. Describe some of the methods of regulating the pH of the solution for the precipitation of hydroxides.

5. Make a list of the constituents which are precipitated by the basic acetate method (see reference books).

6. List some of the complex ions that have been studied in qualitative analysis.

PROBLEMS

1. From the solubility-product values in the appendix find the solubility expressed in millimoles per milliliter and in grams per 100 ml for:

(*a*) PbI_2.

(*b*) Hg_2Cl_2.

(*c*) $MgCO_3$.

2. What is the percentage increase in the solubility product for CaC_2O_4 between 13° and 95°C?

3. Find the number of milligrams of AgCl which are left unprecipitated in 200 ml of solution in which the excess concentration of Ag^+ is 10^{-2} *M*.

4. A precipitate of CaC_2O_4 is digested in a volume of 300 ml. Calculate the percentage loss (in terms of a theoretical weight of precipitate of 0.2500 g) caused by solubility in the precipitating solution if:

(*a*) No excess of precipitant had been added.

(*b*) The supernatant liquid contains an excess of 5.0 ml of 0.10 *M* $(NH_4)_2C_2O_4$.

5. The solubility of Ag_2CrO_4 is 2×10^{-5} mole per 100 ml.

(*a*) If the possibility of supersaturation is neglected, what is the minimum volume of water required to dissolve 0.5 mg Ag_2CrO_4?

(*b*) How many milligrams of Ag_2CrO_4 remain unprecipitated in 200 ml of solution in which there is a stoichiometric excess of 1.00 m mol $CrO_4^=$?

6. The precipitate AB_2 (molecular weight = 100) is soluble to the extent of 10^{-4} moles per liter.

(*a*) How many milligrams of AB_2 remain unprecipitated in 250 ml of solution in which the concentration of excess A^{++} ion is 0.001 *M*?

(*b*) What is the maximum number of milligrams of AB_2 which can dissolve in 200 ml of wash water?

(*c*) 3.00 m mol BaB_2 is dissolved in 100 ml water, and 10 per cent in excess of the stoichiometric amount of 0.10 *M* $A(NO_3)_2$ is added. How many milligrams of AB_2 remain unprecipitated?

7. The solid M_2N (molecular weight = 75) is soluble to the extent of 0.00015 g per 100 ml.

(*a*) Find the solubility product for M_2N.

(*b*) Calculate the milligrams of M_2N which remain unprecipitated in 300 ml of solution in which the excess concentration of M^+ is 10^{-3} *M*.

(*c*) Calculate the milligrams of M_2N which could be lost in 250 ml wash water.

(*d*) Is the actual loss in washing likely to equal the amount found in (*c*)?

8. The solubility of silver chloride is 10^{-5} moles per liter. How much wash water may be used in an analysis if the loss of chloride ion in the wash water is not permitted to exceed 0.1 mg?

9. A sample which weighs 0.5000 g contains 40.00 per cent Cl^-. This sample is dissolved in 200 ml water, and an amount of 0.100 *M* $AgNO_3$ solution is added which is equivalent to the Cl^- in the sample and 5.00 ml in excess. Find the percentage error due to solubility in the precipitating solution. The precipitate is drained free from supernatant solution and washed with 300 ml 0.05 *M* HNO_3. Find the maximum percentage error due to solubility in the wash water.

10. What will be the weight of the precipitated AgCl from 0.2000 g of a sample which is 50.00 per cent Cl if the losses caused by solubility in the precipitating solu-

tion and wash water are taken into account? The conditions of precipitation and washing are:

Final volume of precipitating solution	200 ml
Excess 0.1 *M* $AgNO_3$ present	1.0 ml
Volume of wash water used	500 ml

11. 0.5000 g $AgNO_3$ and 0.7000 g $KBrO_3$ are added to 250 ml water. The precipitated $AgBrO_3$ is collected on a filter and washed with 250 ml water. After drying in an oven how much does the precipitated $AgBrO_3$ weigh?

12. Find the milligrams of Cl^- left in solution if 50 ml 0.1 *M* $AgNO_3$ is added to 200 ml of solution which contain 0.2500 g NaCl.

13. 40.00 ml 0.5000 *M* $AgNO_3$ is added to 230 ml of water which contain 1.942 g K_2CrO_4. What percentage of chromium remains unprecipitated?

14. $M(OH)_2$ is a slightly soluble strong base which dissolves to the extent of 10^{-6} mole per 100 ml. To 200 ml of 0.1 *M* MSO_4, solid NaOH is added.

(*a*) How many grams of NaOH have been added before a precipitate begins to form?

(*b*) What is the *p*H when 75 per cent of M^{++} has precipitated?

15. The solubility of a hydroxide, $X(OH)_2$, is 0.003 g per liter. The molecular weight is 150.

(*a*) Compute the solubility product.

(*b*) At what *p*H will a precipitate begin to form if an acid solution of 0.01 *M* X^{++} is neutralized?

(*c*) If 1.0 g XSO_4 and 1.0 g NH_4Cl are added to 100 ml 0.1 *M* NH_4OH, will a precipitate be obtained? Justify the answer by a computation of the product $[X^{++}][OH^-]^2$ and comparison of the value with the solubility-product value.

16. At what *p*H will magnesium hydroxide begin to precipitate from a 0.01 *M* magnesium sulfate solution?

17. If 25 mg magnesium chloride is added to 100 ml of 0.1 *N* ammonium hydroxide, will a precipitate be formed?

18. If 1 g of ammonium chloride is added to the solution above, will a precipitate be obtained?

19. How many milliliters of 2 *M* HNO_3 must be diluted to 400 ml so that 2.00 g silver acetate will completely dissolve in this volume?

20. 50 ml 0.4 *M* $MgSO_4$ and 50 ml 1.0 *M* NaAc solutions are mixed. Is there any precipitation of $Mg(OH)_2$?

21. Would $Fe(OH)_3$ precipitate from a solution which is 0.1 *M* in KOH and 0.2 *M* in $K_3Fe(CN)_6$? ($K_{inst.}$ for $Fe(CN)_6^{\equiv}$ is approximately 10^{-44})

22. What concentrations of Fe^{+++} and Zn^{++} ions can remain in equilibrium with a buffer made by adding 20 g NaAc to 150 ml 0.15 *M* HAc?

23. Consider the effect of the ionization of water and make a reasonable approximation of the solubility of cupric hydroxide from its solubility product.

24. A solution contains hydrogen, copper, and zinc ions at a concentration of 0.1 *M*. This solution is saturated with hydrogen sulfide, to make a final concentration of 0.1 *M*. Compute the concentration of copper and zinc ions remaining in solution. (Note: as the sulfide precipitates, the hydrogen-ion concentration of the solution increases. Account must be taken of this.)

25. Can manganous sulfide, MnS, be quantitatively precipitated by saturating a 0.05 *M* $MnCl_2$ solution with H_2S? Take in account the hydrogen ion produced by the reaction: $Mn^{++} + H_2S = MnS + 2H^+$.

26. Calculate the *p*H of a buffer which will permit all but 0.1 mg of Zn^{++} to be precipitated from 200 ml of 0.1 *M* $ZnSO_4$ solution when it is saturated with H_2S. How many grams of formic acid and sodium formate should be added to the solution to prepare this buffer? (Neglect the effects of dilution; use sufficient sodium formate to have 50 per cent in excess of the amount required for the H^+ produced by the precipitation.)

27. How much silver iodide will dissolve if the solid salt is shaken with 250 ml of concentrated ammonium hydroxide (15 *M*)?

CHAPTER

19

Colloids and the Formation and Properties of Precipitates

Introduction. It will be recalled that two conditions are necessary for accurate gravimetric analyses by precipitation methods: (1) essentially all of the sought constituent must be removed from the solution and weighed in a suitable form, and (2) the substance which is weighed must be pure and of known composition. The error due to the first of these, incomplete precipitation, is in most cases negligibly small because gravimetric methods are based chiefly on precipitates of very low solubility. Errors due to lack of purity and definite composition of the precipitate are far more serious than are those due to solubility losses. All precipitations are made from solutions which contain ions other than those of the precipitate, and some of these ions are frequently dragged down with the precipitate.

The dragging down of impurities by a precipitate is known as *coprecipitation* (or occlusion). The amount of coprecipitation varies with the nature of the precipitate and the conditions under which it is formed. Under favorable conditions errors from this source can be made negligibly small, but under unfavorable conditions such errors may completely invalidate an analysis. Further, such errors may be totally unsuspected, since duplicate samples are analyzed under fixed conditions, and the same error may occur for each portion. Thus the attainment of good precision in a gravimetric analysis is no guarantee of high accuracy.

We shall discuss in this chapter the factors which cause coprecipitation, the methods which are employed to minimize or avoid errors from this source, and other types of errors which may lead to impure precipitates. We shall also discuss the factors which govern the particle size of precipitates and therefore influence the ease of filtering and washing the precipitate.

PROPERTIES OF COLLOIDS

Definitions. Before proceeding with the discussion of factors which affect coprecipitation, it is necessary to consider the properties of colloids in more detail than has been done in previous courses. In every precipitation the particles first formed are of colloidal size before they become large enough to settle out of the solution. It is usually in the colloidal stage that coprecipitation occurs.

It may be recalled that colloids are dispersions of matter in such a finely divided state that gravitational forces will not cause the suspended phase to settle out; the particles are of such small mass that molecular motion in the gas or liquid in which the particles are suspended can cause the particle to move about against the force of gravity. There are many types of colloids; in gravimetric analysis the ones of interest are dispersions of solids in aqueous solutions. These may be of two general types known, respectively, as *suspensoids* and *emulsoids*. The former have low viscosity, about the same as that of water, and have little affinity for water. When coagulated they do not retain water which is difficult to remove on drying. Because of their resemblance in physical properties to solutions they are known as *sols* or in water as *hydrosols*. Familiar examples of this type are dispersions of metals and salts in water. Emulsoids are, as the name implies, like emulsions (colloidal dispersions of a liquid in a liquid) in physical properties. They have high viscosity, and when coagulated they yield a jelly-like mass. They have a high affinity for water, and on coagulation they retain large amounts of water which cannot be removed by ordinary drying at 110°. They are commonly called *gels* or if in water, *hydrogels*.

Size of Colloid Particles. Dispersions of solids in water may be of three classes, depending on the size of the particles in the dispersed phase. These classes are solutions, colloids, and suspensions. In a solution the particles are single molecules or ions. The individual particles are only a few angstrom units [1] in diameter or about the same size as the individual molecules of the solvent. Individual particles in a solution cannot be observed by any physical method. In a colloid the particles are of the order of 10 to 2000 A in diameter, and each one may consist of many molecules. The individual particles are too small to be seen by an ordinary microscope, but they may be observed by an ultra-

[1] An angstrom unit (A) is 10^{-8} cm. Other units used to describe small particles are the micron μ or 10^{-4} cm and the millimicron mμ which is 10^{-7} cm. The wavelengths of X-rays are of the order of an angstrom unit, and the wavelengths of visible light cover the range 4000–7000 A.

microscope.[2] The only difference between a colloid and a suspension is the size of the particles, which are in a colloid of such small mass that the particles do not settle out under the influence of gravity. The particles exhibit Brownian motion; that is, they move about haphazardly in the liquid because of the bombardment by molecules of the liquid. If gravitational forces are increased manyfold by use of a centrifuge, the effect of the molecular motion can be overcome, and the particles will settle out of the liquid.

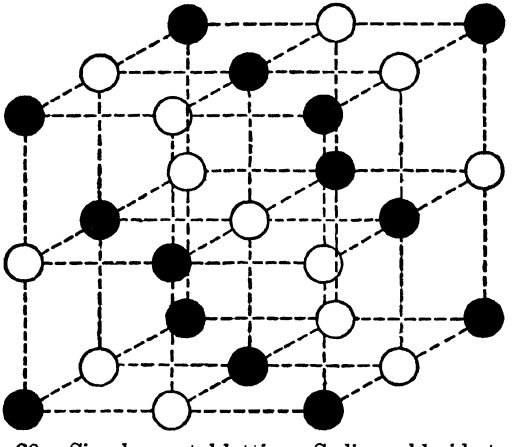


FIG. 29. Simple crystal lattice. Sodium chloride type.

Surfaces of Colloid Particles. The unique properties of colloids, as compared with larger particles of the same substances, are due wholly to the differences in the amount of surface area per unit mass. When particles are small, as in colloids, the surface per unit mass is many times greater than when the particles are of microscopic size or larger. This is illustrated by consideration of progressive subdivision of a cube measuring 1 cm on an edge. The surface area is 6 cm^2. If it is subdivided into cubes of colloidal size, say 10^{-6} cm on an edge, the surface is 6×10^6 cm^2. Thus, the properties which are associated with phenomena at surfaces are very much more pronounced for particles of colloidal size.

The properties of surfaces are due to the exposed atoms or ions lying on the surface. Inside a crystal each ion is surrounded by ions of opposite charge. A typical arrangement is shown in Fig. 29, where the black circles represent the centers of one kind of ion, and the white circles the

[2] An ultramicroscope is so arranged that the sample is viewed through a high-power microscope at right angles to a sharply defined and intense beam of light which is passed through it. One sees not the particles themselves but the light scattered by the particles. The same phenomenon is frequently observed when a beam of sunlight passes through a darkened room. In the light beam one may observe dust particles which cannot be seen in ordinary light.

centers of the ions of opposite charges. (This arrangement is schematic only, to show the relative positions of the ions—actually the ions probably touch one another, and there is no vacant space between them.) At the surface of the crystal there are ions or atoms which are not surrounded by other atoms. These surface ions or atoms can attract and hold other ions or atoms with which they come in contact. This holding of foreign atoms at a surface is known as *adsorption.*

Adsorption occurs at every surface, regardless of whether the particle is large or small. Every crystal has on the surface an adsorbed layer of foreign material. The amount adsorbed per unit area is so small, however, that it is only possible to detect adsorption when the adsorbate is so finely divided that it presents a very large surface area. Thus adsorption is primarily a property of matter in the colloidal state, or when it is in such a form that the surface area is large. In a crystal of colloidal size a large fraction of the atoms or ions may lie in the surface. For example, a cube whose edge is 10 atomic diameters in length will contain 10^3 or 1000 atoms. But $2 \times 100 + 2 \times 80 + 2 \times 64$ or 488 of these atoms will lie in the surface. If each of these can hold a foreign atom by adsorption, the total adsorption per unit mass is many times greater than when the same unit mass is in the form of larger crystals.

The phenomenon of adsorption is an important and widespread one, which has many applications. The removal of poison gases by a gas-mask canister, the clarification of sugar sirup by removal of colored impurities, the recovery of volatile solvents, the application of granular catalysts to vapor- and liquid-phase reactions, all are effective because of adsorption at surfaces.

The forces which cause foreign atoms to be held at surfaces may be either electrostatic, as when the surface is composed of ions which attract and hold ions of opposite charge, or van der Waals forces which depend on the attraction of masses for one another. There is a certain degree of specificity in both kinds of forces so that a given adsorbent will hold some adsorbates more tightly than others. Charcoal, for example, will hold organic molecules more tightly than water molecules.

A surface composed of ions will hold ions of opposite charge, but to differing degrees. This is to be expected since we know that in crystallization each crystal takes from the solution only its own kind of ions. For example, if K^+, Na^+, Cl^-, and NO_3^- ions are all in the same solution, we may obtain crystals of KNO_3, KCl, $NaNO_3$, and NaCl, but not crystals in which the anions or cations are mixed. The specificity in crystallization is probably due to the sizes of the various ions. In the building up of a crystal lattice only ions of proper size will fit into the lattice, and we can obtain isomorphous crystals only in case of two ions of the same charge and size, such as in the alums where Fe^{+++} or

Cr^{+++} ions can replace Al^{+++} in the crystal of $KAl(SO_4)_2 \cdot 12H_2O$. Probably the same considerations apply to the holding of an ion by adsorption at the surface of a crystal. If the ion is of proper size to fit into the crystal lattice, it should be drawn more closely and held more tightly than another ion of the same charge but of improper size to fit into the lattice. It is found experimentally that those ions are best adsorbed by crystal surfaces which form with ions of the crystal the least soluble crystals (rule of Paneth–Fajans–Hahn). Thus, if $BaSO_4$ crystals are in a solution which contains Pb^{++}, Fe^{++}, Na^{+}, and H^{+} ions, the Pb^{++}

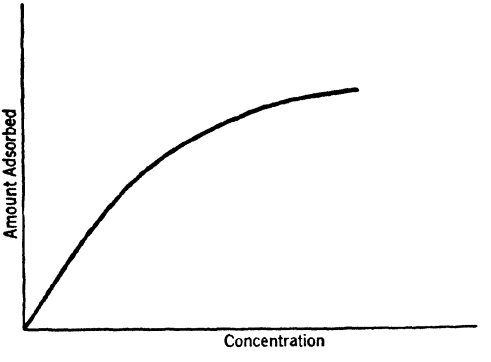


FIG. 30. Effect of concentration on amount adsorbed.

ion is most strongly adsorbed; this ion forms with the $SO_4^{=}$ ion of the crystal a very insoluble compound as compared with the sulfates of the other positive ions of the solution.

Effect of Concentration on Adsorption. When adsorption takes place from solution, the amount adsorbed per unit weight of adsorbent is related to the concentration by a curve of the general shape shown in Fig. 30. Such a curve, if determined at constant temperature, is known as an *adsorption isotherm*. It is characteristic of all isotherms that the amount adsorbed increases rapidly with concentration at first and that at higher concentrations the curve tends to flatten out. This effect of concentration on the amount of adsorption is of practical importance in relation to contamination of precipitates, as discussed in a later section.

Charge and Stability of Colloid Particles. The phenomenon of adsorption is responsible for the existence of stable colloidal dispersions of solids in water. Both hydrosols and hydrogels are charged, owing to adsorption of ions from solution. The existence of such charges can be shown experimentally by placing in the colloidal dispersion charged electrodes and observing the motion of the particles. It is found that all the colloid particles will migrate toward one of the electrodes, sometimes

toward the cathode and sometimes toward the anode. This phenomenon is called electrophoresis.

A given substance can be dispersed either as a positive- or as a negative-charged colloid, depending on the sign of the ion that is adsorbed; this can be controlled by the conditions of dispersal of the colloid. For example, if silver chloride is precipitated by addition of silver nitrate to a sodium chloride solution, the colloidal particles first formed, when chloride ion is in excess in the solution, will be negatively charged. Such particles may be represented by the formula $AgCl:Cl^-$, indicating that the AgCl particle has adsorbed chloride ions. Conversely, if the precipitate is formed by addition of sodium chloride to a silver nitrate solution, the particles will be positively charged because of adsorption of Ag^+ ions; they are represented by the formula $AgCl:Ag^+$.

The stability of colloidal dispersions in water is attributed to the action of the electric charges in preventing collisions of the particles. Since all particles have like charges, they will repel one another, and collisions are much less frequent than if the particles were uncharged. Therefore, *coagulation*, the condensation of several colloidal particles to form a particle large enough to be affected by gravity, is prevented.

Coagulation of Colloids. Since the charge on colloidal particles prevents their collisions and coalescence, it is an obvious deduction that, if one adds to a colloid ions which can be strongly adsorbed by the charged particles and which will neutralize the previously adsorbed charges, then the particles may become electrically neutral and may collide and coalesce. Actually this is a simplified statement of what happens in the coagulation of colloids. In the preceding section it was shown that AgCl colloids could be prepared with either positive or negative charges, depending on whether Ag^+ or Cl^- ions are adsorbed. If one slowly adds $AgNO_3$ solution to NaCl solution, a fine cloudy dispersion is first obtained, whose particles are of colloidal size. If the addition of $AgNO_3$ is continued, it is observed that near the stoichiometric point the colloid appears to coagulate. As soon as Ag^+ ions are in excess in the solution, they are adsorbed by the particles, which previously have been negatively charged because of adsorption of Cl^- ions. This adsorption of positively charged ions has the effect of neutralizing the negative charge, and the particles become neutral or nearly so. At this point they can coagulate.

One may well ask at this point: "If Ag^+ ions are adsorbed by the colloid particles, why cannot Na^+ ions also be adsorbed since they are present in the solution from which the AgCl is precipitated?" No thoroughly satisfactory explanation can be given as to why the AgCl colloid is coagulated by a small excess of silver ions whereas it is stable in a

large excess of sodium ions. We can only give the generally accepted explanation of today, which is in part conjecture.

Before consideration of the mechanism of coagulation of colloids we shall first list some of the known facts in regard to the effects of different kinds of ions in effecting coagulation.

1. The ions which effect coagulation of colloids are of opposite charge to the ions which impart the charges to the particles.

TABLE 33

COAGULATING VALUES OF ELECTROLYTES FOR NEGATIVELY CHARGED ARSENIC TRISULFIDE SOL

Electrolyte	*m mol per liter*
LiCl	58
NaCl	51
KNO_3	50
KCl	50
NH_4Cl	42
HCl	31
$MgCl_2$	0.72
$MgSO_4$	0.81
$CaCl_2$	0.65
$SrCl_2$	0.64
$BaCl_2$	0.69
$AlCl_3$	0.093
$Al(NO_3)_3$	0.095
$Ce(NO_3)_3$	0.080

Values taken from H. B. Weiser, *Colloid Chemistry*, Wiley, 1939, page 224.

2. Ions of the same valence and charge differ among themselves in the concentrations required for coagulation of a given dispersion. Those which are most effective in coagulation are those which are most strongly adsorbed. It may be recalled that the ions which are most strongly adsorbed are those which form with the oppositely charged ion of the solid the most insoluble substance (see page 362). This partially explains why Ag^+ is more effective in coagulation of $AgCl:Cl^-$ than is Na^+ ion. Silver ion forms a more insoluble compound with the charge-imparting ion, chloride ion, than does sodium ion. It may be that silver ion, since it is one of the constituents of the crystal, is of proper size to fit more closely to the surface of the crystal than sodium ion can.

3. As a general rule the higher the valence of the precipitating ion, the more effective it is for coagulation; that is, the smaller concentration is required for coagulation of a given amount of colloid. This rule does

not hold when it conflicts with the requirements of the preceding paragraph. The ion which forms the most insoluble compound with the charge-imparting ion is usually most effective in coagulation, regardless of its valence. Silver ion is a more effective coagulant for $AgCl:Cl^-$ than Ca^{++} or Al^{+++} ions even though it has lower valence.

When the coagulating ions do not form very insoluble compounds with the precipitate ion, the valence of the coagulating ion may have a great effect on its coagulating power. This is illustrated in Table 33.

4. The ion which causes coagulation of a colloid is not dragged down in amounts equivalent to the amount of charged ion first adsorbed. This is shown by the vast differences in the coagulating power of ions of different valence. However, after coagulation the precipitate has no charge or is electrically neutral. This must mean that, as coagulation proceeds, the charged particles drag down equivalent amounts of oppositely charged ions from the solution, including the coagulating ions.

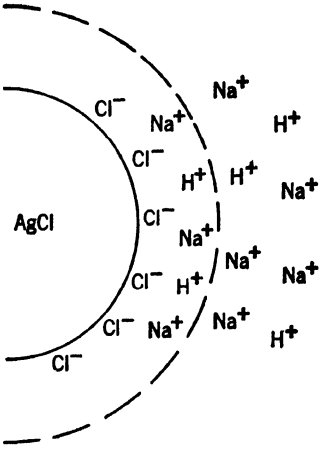


FIG. 31. Adsorption at the surface of a colloidal particle of AgCl. The particle is formed in excess chloride ion.

To explain these facts we must consider the present picture of a charged ionic crystal in contact with a solution of electrolytes. Adsorption is considered [3] to be of two kinds, primary adsorption of the charge-imparting or stabilizing ion and secondary adsorption of a diffusely held layer of counter ions of opposite charge to the stabilizing ion. The surface of the particle is surrounded by a double layer of charge, as represented in Fig. 31. This shows the condition assumed to exist at the surface of a $AgCl:Cl^-$ particle formed as described previously. The Cl^- ions are adsorbed tightly to the crystal lattice and hold some positive ions, Na^+ and H^+ tightly. The over-all result is an excess of negative charges on the surface, and, if a potential is applied, the particle migrates toward the positive electrode. The portion of the particle which migrates as a unit is shown inside the dotted lines. Surrounding the charged particle there is a diffuse cloud of positive ions, which are known as *counter ions*. When the particle is coagulated, the counter ions are dragged down with it in sufficient amounts to just neutralize the chloride ions.

[3] See H. B. Weiser, *loc. cit.*

Any effect which will cause the diffuse layer of counter ions to be more closely drawn to the surface will cause a decrease in the effective density of the negative charge on the surface. Silver ion, which can be adsorbed in equivalent amount by the surface chloride ions, will neutralize the charge completely. This explains the effect of an ion which forms an insoluble compound with the stabilizing ion. The effects of ions which do not form an insoluble compound and the valence effects are not so easy to understand. The valence effect is probably due to the greater density of electric charge in ions of higher valence. A barium ion or an aluminum ion in the counter-ion layer may be pulled more closely to the surface by the electrostatic charge of the chloride ions than such univalent ions as sodium and hydrogen, because the doubly and triply charged ions have greater charge density than univalent ions. This may cause the layer of counter ions to be drawn in so that the negative charge is partially neutralized. It is not necessary to have complete neutralization, merely that the charge effect be so reduced that particles may collide.

Whether the explanation is valid or not is for present purposes not important. The important things to remember are (1) the known effects of various ions on coagulation of precipitates and (2) the fact that on coagulation the precipitate will drag down ions of opposite charge from the solution.

The dragging down of counter ions by a precipitate is responsible for one type of coprecipitation. To prevent contamination from this effect the analyst should so arrange his conditions of precipitation that the counter ion will be an ion of the precipitate or else will be some material which can be volatilized when the precipitate is ignited. Thus H^+ and NH_4^+ are preferred as counter ions to accompany Cl^- ion in preference to Na^+ and K^+, since the chlorides of the former are volatile whereas those of the latter are not.

Peptization. The dispersal of an insoluble material into a liquid medium as a colloid is known as *peptization*. This may sometimes occur in the washing of a precipitate if the counter ions which effected coagulation are dissolved in the wash water and the particles become charged again. When this happens, the precipitate passes through the filter, as a colloid. It is frequently necessary, in washing a precipitate, to add an electrolyte to the wash water, to supply a counter ion to maintain the neutralization of the electric charge of the particles. An example is in the determination of chloride as AgCl. The original counter ions may be Ag^+, Na^+, and H^+. If these are removed on washing, peptization occurs. Dilute nitric acid is added to the wash water to provide H^+ ions at the surface of the precipitate and thereby prevent peptization.

RELATION OF COLLOIDS TO THE FORMATION OF PRECIPITATES

The process of crystallization is complex, and it is not yet thoroughly understood. When solutions of two ions which may form a precipitate are brought together, the K_{SP} value is exceeded, and the solution becomes supersaturated. After a time, which may vary from a fraction of a second to several years, crystallization begins with formation of particles of colloidal size. Just how the first particles are formed is not known. Possibly the process is aided by adsorption of ions on the surface of dust particles or other foreign material which will always be present in the solutions. Or perhaps the chance juxtaposition of a number of ions leads to a clumping together to form a crystal nucleus on which further ions may deposit. In any event it is known that the number of nuclei which appears depends on the relative degree of supersaturation of the solution, as expressed by the Von Weimarn ratio

$$\text{Degree of supersaturation} = \frac{Q - L}{L}$$

where Q is the total concentration of the salt in solution, and L is the equilibrium solubility of the salt. If the relative supersaturation is large, many nuclei appear, but, if it is small, there are fewer nuclei formed.

After the initial appearance of crystal nuclei further precipitation may occur by (1) coagulation and clumping together of colloidal particles and (2) deposition of ions from the solution to build up the crystal lattice of the nuclei. Usually both processes occur simultaneously; the extent to which one or the other process predominates depends on the conditions of the precipitation and the ease of coagulation of the colloidal particles. Growth of the original nuclei by deposition of ions from the solution is favored by slow mixing of the reagents so that at all times the degree of supersaturation is kept small. Rapid mixing of reagents leads to increased supersaturation and formation of more nuclei.

It is possible, within limits, to vary the size of crystals obtained in a precipitation. Obviously, it is advantageous to obtain fewer and larger crystals, since these have a smaller surface than if the precipitate is made up of many smaller crystals, and, consequently, the adsorption of impurities is minimized. Further, large crystals are more readily filtered and washed than small ones.

Von Weimarn's experiments with precipitation of barium sulfate under varying conditions are classical illustrations of the effects of the relative supersaturation on the size of crystals. When precipitation was effected by rapid mixing of 3 to 7 N solutions, a gelatinous precipitate

was formed instantly. The gel consisted of very fine colloid particles, combined with water, and was so stiff that it could not be poured from the beaker. At concentrations of 0.75 to 3 N the precipitate was curdy, formed by coagulation and coalescence of colloid particles. Large crystalline particles were obtained from concentrations of 0.05 N and below. At concentrations such that the solubility product was barely exceeded by a factor of 2–3, no precipitate appeared until after a month's time.

Any condition which reduces the degree of supersaturation at the moment when crystallization begins favors the formation of fewer nuclei. Precipitations are commonly made from hot solutions to take advantage of this effect, since the solubilities of most salts rise with increasing temperature. At higher temperatures a given concentration of ions in solution creates less supersaturation than at lower temperatures, since the solubility L is less at the lower temperature. Precipitation from hot solutions has the further advantage that recrystallization by exchange of ions between the solution and the crystal surface is speeded up, and consequently the amount of surface impurities is decreased, as discussed in a later section.

Another widely used method for decreasing the degree of supersaturation is to add to the solution a chemical which increases the solubility, and then to remove this chemical slowly by vaporization or neutralization. For example, calcium oxalate is best precipitated by adding ammonium oxalate to an acidified solution of a calcium salt and then slowly neutralizing the acid with ammonium hydroxide. As neutralization proceeds, crystals begin to form, under conditions of maximum solubility. The final product consists of coarse crystals. If ammonium oxalate is added to an ammoniacal solution of calcium ion, there is obtained a precipitate of such small crystals that filtration is almost impossible. Similarly, silver chloride crystals may be obtained by slow evaporation of an ammoniacal solution, in which AgCl is soluble. Slow removal of ammonia permits the crystals to grow slowly, whereas in the usual precipitation no single crystals are obtained; rather the precipitate is a curdy mass composed of agglomerated colloidal particles.

Under the same conditions of precipitation some substances give much more crystalline products than others. For example, the hydrated oxides of iron and aluminum come down as gels made up of coalesced colloid particles combined with water, silver chloride gives a curdy precipitate, whereas barium sulfate, magnesium ammonium phosphate, and calcium oxalate give well-developed crystals. The atoms and ions of all these precipitates are in a crystalline arrangement, but the external forms are widely different.

CONTAMINATION OF PRECIPITATES

On the basis of the preceding discussion we may now point out the various ways in which precipitates may become contaminated during the process of formation:

1. The precipitate may be made up of coagulated colloid particles which clump together as coagulation proceeds. Each individual particle of the colloid may retain its adsorbed counter ions so that the foreign salt is occluded throughout the particle of precipitate. The amount of impurity will depend on the size and extent of surface of the individual colloid particles which make up the clump and on whether the counter ions are ions of the precipitate or foreign ions. When the coagulation is effected by ions of the precipitate, the amount of foreign substance dragged down may be small, even though the precipitate is made up of minute colloidal particles. To illustrate, when AgCl is precipitated by addition of Ag^+ to Cl^- ions, the colloid at first is $AgCl:Cl^-$. Coagulation occurs very near the stoichiometric point, and it appears that it is due to neutralization of the charge on the particle by adsorption of positively charged Ag^+ ions. Thus there is no large amount of foreign ion dragged down.

2. After the precipitate has formed, there may be a slow precipitation of a second insoluble substance if adsorption at the surface creates favorable conditions. For example, magnesium oxalate may post-precipitate at the surface of a calcium oxalate precipitate. This phenomenon is due to adsorption of oxalate ions by the precipitate, followed by adsorption of magnesium ions. Concentrations of magnesium and oxalate ions at the adsorbed layer are higher than in the solution, and this favors precipitation of the slightly soluble magnesium oxalate. This type of contamination has been designated as *postprecipitation*. It occurs only when the supernatant solution contains an ion which may form a compound of low solubility with an ion of the primary precipitate.

3. Mixed crystal formation may occur during the formation of the precipitate if the solution contains two ions of the same charge and size which may replace one another in a crystal lattice. The alums, such as $KAl(SO_4)_2 \cdot 12H_2O$, may form isomorphous crystals with Cr^{+++} or Fe^{+++} ions replacing Al^{+++}. Mixed crystal formation is of infrequent occurrence in student analyses where the samples are simple mixtures, but in some mineral analyses mixed crystal formation may lead to serious errors.

AGING OF PRECIPITATES

Much of the impurity dragged down as counter ions by a precipitate can be made to redissolve by proper *digestion* or aging of the precipitate

in contact with the mother liquor. At the same time other beneficial changes occur in the crystals of the precipitate. Consequently, in almost all procedures, after precipitation is completed, the solution is heated and allowed to stand. This step is omitted only where (1) the nature of the precipitate is such that no improvement is obtained on digestion, as in the case of gelatinous precipitates, (2) the precipitate is soluble or decomposes in hot solution, and (3) postprecipitation may be favored by digestion. Kolthoff and his coworkers [4] have made extensive studies of the changes which occur during aging. They have shown that the beneficial effects obtained are due to a dissolving and reprecipitation of ions from the crystal. This process goes very much more rapidly for a fresh precipitate than for an aged one. Because of it the following changes occur:

1. Small crystals dissolve, and the ions reprecipitate on the surface of larger ones. It is well established that small crystals are, because of the large surface area and surface tension effects at the crystal–liquid boundary, appreciably more soluble than larger ones. Whether this effect is very important in analysis is a disputed question, since the crystals first obtained may often be of such size that their solubility is the same as for larger ones.

2. The surface area of the precipitate is reduced, and some of the original counter ions are redissolved. The first precipitate often consists of aggregates made up of coagulated colloid particles. These may redissolve and the ions redeposit on larger and more perfect crystals. The net result is a diminution of surface area and a purification of the precipitate, because the counter ions originally dragged down remain in solution. At the same time the formation of larger and more perfect crystals improves the filterability of the precipitate and facilitates washing.

3. Exchange adsorption of counter ions occurs. This may under proper conditions lead to replacement of undesirable impurities by other ions which will be less harmful in the final weight of precipitate. When the colloid particle is first coagulated, it may drag down as counter ions those ions of opposite charge which predominate in the solution about the particle. On aging, these ions redissolve, and they may be replaced by other ions of the solution. The process is best illustrated by an example. A precipitate of silver chloride may drag down positive ions such as Na^+ and H^+. At the conclusion of precipitation there is an excess of Ag^+ ions. Since these are better adsorbed than the other positive ions, they may replace the others during the aging.

[4] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, Macmillan, 1943.

This leads to a better stoichiometric relation between silver and chloride ions in the precipitate.

Exchange of counter ions may lead to formation of a more impure precipitate, if there are in the solution ions which tend to form insoluble compounds with an ion of the precipitate. A precipitate of $BaSO_4$, for example, if aged in presence of Pb^{++} ions would adsorb $PbSO_4$. This is, of course, postprecipitation.

MINIMIZATION OF IMPURITIES

We may now summarize, on the basis of the preceding discussion, the methods used to minimize the effects of coprecipitation and postprecipitation.

1. Precipitation is made slowly from dilute solutions and under conditions of maximum solubility, which favor formation of large crystals with small surface areas.

2. The concentration of foreign ions which may be coprecipitated is kept low:

(*a*) Precipitation is made from dilute solutions. If it is known that either the sample or the precipitant contains an ion that is preferentially coprecipitated, the solution which contains the offending ion is added to the other one. This insures that at the time of formation of the precipitate the concentration of the offending ion is kept at a minimum.

(*b*) Reprecipitation is frequently used to reduce further the concentration of troublesome foreign ions. When the precipitate can readily be dissolved, the first precipitate is partially washed and then dissolved and reprecipitated. The amount of contaminant present in the first precipitate is but a fraction of that in the original sample, and on the second precipitation the concentration of the offending ion is only that amount which was dragged down with the first precipitate. Since the amount adsorbed varies with concentration as shown in Fig. 30, the contamination of the second precipitate is greatly reduced. Sometimes even a third precipitation is used, to reduce further the amount of impurity.

A further advantage of reprecipitation is that, after the first precipitate is dissolved, its ions are present in equivalent amounts, and only a known and slight excess of precipitant need be added; this permits closer control of the amount of foreign salts present. For example, postprecipitation of magnesium oxalate with calcium oxalate is greatly reduced by a second precipitation.

Reprecipitation is routinely used for the oxides of iron, aluminum, and chromium; for oxalates, phosphates; and, in general, for those precipitates which can readily be dissolved in dilute hydrochloric or nitric acids. It is not employed for such precipitates as silver chloride and barium sulfate, because these are not readily soluble in suitable reagents.

(*c*) Foreign ions may be removed by separation or by reaction prior to precipitation if they are particularly troublesome in a given determination. For example, ferric ion is badly coprecipitated with barium sulfate. If it is present in the sample, it may be removed by precipitation as ferric hydroxide, or it may be reduced to the ferrous condition.

3. The precipitate is, in many analyses, digested with the mother liquor. This leads to redissolving of coprecipitated counter ions and to a decrease in surface area, so that less impurity is adsorbed. Sometimes conditions are chosen so that on digestion harmful counter ions are replaced by readily volatile ones, such as NH_4^+ or H^+.

WASHING PRECIPITATES

After the precipitate has been formed, it may still become contaminated by retention of solids from the mother liquor if it is not properly washed. The procedure for this operation is described in Chapter 17. It may be recalled that washing is done with hot liquid when the solubility permits, that a volatile electrolyte is usually present, and that the quantity of wash liquid is kept at a minimum.

The purpose of washing is twofold. Most obvious is removal of all the mother liquor, with dissolved salts. In addition there is often an exchange adsorption of counter ions during washing; this may be used to replace a non-volatile counter ion with a volatile one.

The use of hot wash liquid is advantageous, because soluble impurities dissolve more quickly, the viscosity is reduced so that the wash water flows through the precipitate and filter more rapidly, and exchange adsorption is facilitated.

The advantage of using the minimum volume of wash liquid is obvious; the greater the volume, the greater are solubility losses. It has previously been stated that maximum effectiveness is gained by allowing the filter to drain rather completely after each filling. This is true for two reasons: (1) Time is allowed for attainment of solubility equilibrium, and (2) use of several small portions is more efficient than use of a single large portion, as shown on page 324.

IGNITION

The purpose of ignition is to convert the precipitate into a dry substance of definite composition. It is obvious that, if the precipitate is contaminated by foreign ions, one can never obtain a pure ignited product unless the foreign ions are volatile. Even when foreign substances other than water are not present, there may be errors in ignition unless the operation is properly performed. The chief errors are summarized below:

1. Ignition must be at a sufficiently high temperature for complete removal of water. Drying at 110°C will remove water from some precipitates, for example, AgCl, but others, such as hydrated ferric oxide, retain water tenaciously and may require heating to as high temperatures as 1000°C. The analytical procedures specify the required ignition temperatures.

2. Many precipitates are decomposed by ignition at too high a temperature. The specified conditions should be followed closely.

3. The chief source of error in ignition is reduction of the precipitate by carbon of the filter paper. Some precipitates, such as AgCl, are so readily reduced that they cannot at all conveniently be ignited with filter paper; filtering crucibles are essential for such. Other precipitates which are not readily reduced may be ignited with paper, but, if the paper is not properly burned off with a plentiful supply of air, some reduction may take place. Trouble from this source is frequently encountered in student analyses of sulfate, where the $BaSO_4$ is reduced to BaS, or iron, where reduction of Fe_2O_3 to Fe_3O_4 occurs.

4. Prolonged ignition at high temperature is required for complete conversion of some precipitates to the desired compound, and a frequent student error is underignition, particularly of calcium oxalate which must be converted to calcium oxide. The attainment of the final composition in such precipitates is facilitated if the precipitate is crushed after the paper is burned away, to give better contact of all particles of precipitate with the heated crucible walls. Directions for this operation are given on page 327.

QUESTIONS

1. Differentiate between a solution of sodium sulfide and a colloidal dispersion of arsenic trisulfide with respect to:
   (*a*) Size of the dispersed particles.
   (*b*) Charge on the particles.
   (*c*) Filterability of the dispersed material.
   (*d*) Effect of the addition of NH_4Cl.

2. Discuss the effect on the amount of adsorption of:

(*a*) Total surface area.

(*b*) Temperature.

(*c*) Concentration of the adsorbed ion.

(*d*) Solubility of the salt corresponding to the ions adsorbed primarily and secondarily.

(*e*) Valence of the secondarily adsorbed ion.

3. Hydrous ferric oxide is crystalline in internal arrangement. On what evidence is this statement based?

4. What is the origin of the electric charge found on the surface of colloidal particles?

5. If barium sulfate is precipitated by addition of barium chloride solution to a sulfuric acid solution, what charge would you expect to find on the particles while they are in the colloidal condition? What counter ion might be effective in neutralizing this charge? What substance would you expect to find dragged down with the precipitate because of the occlusion of the counter ion on coagulation of the sol?

6. Explain why silver chloride sol is coagulated just at the stoichiometric point in the addition of silver nitrate to sodium chloride.

7. How may the addition of an electrolyte to the wash water prevent peptization of a precipitate?

8. Could dichlorofluorescein (Chapter 16) serve as indicator for the titration of silver nitrate by sodium chloride? Explain, on the basis of the discussion given in this chapter.

9. A sample of Na_2SO_4 has appreciable amounts of NaCl and $NaNO_3$ impurities. In the analysis for the sulfate content by precipitation as $BaSO_4$ which of the following are advisable?

(*a*) Reprecipitation.

(*b*) Several evaporations to dryness with HCl.

(*c*) Addition of the unknown to $BaCl_2$ rather than the reverse.

10. Explain briefly how each of the following tends to minimize coprecipitation:

(*a*) Digestion or aging.

(*b*) Reprecipitation.

11. Give two reasons why most precipitations are conducted in hot dilute solution.

12. Give two reasons why a volatile electrolyte with an ion common to the precipitate is used in the wash water.

13. Name several separations in which postprecipitation may be important.

14. Draw a picture which represents the various adsorption layers on a colloidal particle of $BaSO_4$ which is formed by adding H_2SO_4 to a solution of $BaCl_2$.

15. Explain why slow addition of reagent will give a more filterable precipitate than rapid addition. Why is it not important to add reagent slowly in the precipitation of ferric hydroxide?

16. Why are many precipitations made by mixing the reagents in an acid solution and then slowly neutralizing the acid?

17. What is the purpose of reprecipitation? Under what conditions can reprecipitation be employed?

18. List the routine methods for minimization of coprecipitation.

19. What is the purpose of ignition of a precipitate? What factors govern the choice of ignition temperature?

PROBLEMS

1. How many ions are in the surface of a cubical colloidal particle which has 15 ions on an edge?

2. How many spherical colloidal oil particles 20 A in radius can be made from a spherical oil drop whose radius is 2 microns? The density of the oil is 0.9 g per milliliter. What is the percentage increase in surface?

3. If the molecular weight of the oil in Problem 2 is 150, how many molecules are contained in the particle of 20 A radius?

4. 0.5000 g Fe^{+++} is precipitated as hydrated ferric oxide. During ignition 90 per cent of the iron is converted to Fe_2O_3, and the remainder is present as Fe_3O_4. What does the ignited precipitate weigh? What should it have weighed if all the iron were in its proper form?

CHAPTER

20

Summary of Errors in Gravimetric Analyses

Introduction. In the preceding chapters we have discussed a number of errors that affect the accuracy of gravimetric analyses. These can be summarized under the three headings:

1. Loss of constituent.
2. Purity of precipitate.
3. Miscellaneous indeterminate errors.

ERRORS DUE TO LOSS OF SAMPLE OR PRECIPITATE

Errors of this type may occur in the following ways:

1. Loss in precipitating solution. Such losses may be caused by:

(*a*) The precipitate has an appreciable solubility. Most gravimetric methods are based on precipitates of very low solubility, and this condition is quite rare. It is, however, encountered occasionally, and in such cases every effort should be made to keep the volume of solution at a minimum.

(*b*) Insufficient precipitant is added. An error from this cause can occur only through carelessness, since in every precipitation one should test for completeness.

(*c*) Improper *p*H may cause precipitates which are quite insoluble, under the proper conditions, to become quite soluble. An example of this is the precipitation of magnesium ammonium phosphate which is quite soluble in even slightly acid solutions but sufficiently insoluble with proper control of *p*H.

(*d*) Ions are present that can form stable complexes with an ion of the precipitate. For example, cadmium forms a complex chloride ion

and is not precipitated completely from a solution that contains a high concentration of chloride ion.

(*e*) A constituent of a complex sample may be lost by coprecipitation with some other constituent. For example, in a limestone analysis calcium or magnesium may precipitate with the mixed oxides, or magnesium may precipitate with calcium if the separations are not carefully performed.

(*f*) The presence of interfering ions may lead to faulty separations in some analyses. For example, if phosphate ion is present in a mineral analysis, magnesium may precipitate when the solution is made basic for precipitation of the mixed oxides.

2. Loss in wash water. This may be due to:

(*a*) Peptization of the precipitate and loss as a colloid which passes through the filter.

(*b*) Solubility losses if too large a quantity of wash water is used or if a necessary common ion is omitted from the wash water.

3. Mechanical losses. These are due to:

(*a*) Loss of sample in transfer.

(*b*) Loss of small crystals which pass through the filter. The analyst should always note the appearance of the filtrate, and, if it is cloudy, he should refilter. Losses from this source may be appreciable if poor technique of precipitation is used or if a too porous filter paper or mat in the filtering crucible is used.

ERRORS DUE TO PURITY OF THE PRECIPITATE

In general, errors from this source are more serious than those due to loss of sample. The following sources of error may be encountered:

1. Coprecipitation of foreign ions with the precipitate. Methods for minimization of this error are discussed on page 371. In general, the individual analytical procedures are designed to give optimum conditions for avoidance of coprecipitation.

2. Postprecipitation of sparingly soluble foreign substances.

3. The precipitate may have the wrong composition if improperly formed. Magnesium, for example, may precipitate as $Mg_3(PO_4)_2$ rather than as $Mg(NH_4)PO_4$ if care is not taken to maintain the proper concentrations of all the constituents.

4. Insufficient washing for removal of soluble impurities. In all procedures directions are given to test for completeness of washing by a qualitative test for some readily identified ion of the mother liquor (frequently the chloride or sulfate ion).

5. Reduction of precipitate by carbon of the filter paper during ignition.

6. Incomplete ignition and failure to convert the precipitate to the anticipated composition or failure to remove all water from the precipitate.

7. Ignition at too high a temperature, which may cause partial decomposition of the precipitate. Silver chloride, for example, should not be heated to a high temperature. This will cause decomposition and loss of chlorine.

8. Error in weighing, due to adsorption of water or carbon dioxide by the precipitate.

INDETERMINATE ERRORS

The most probable indeterminate errors not previously listed are:

1. Errors in weighing of the sample or precipitate.

2. Failure to obtain constant weight for crucibles, prior to ignition of the precipitate.

3. Loss of asbestos from Gooch crucible mats.

4. Mixing of samples (this occurs all too frequently).

5. Spattering during evaporation or other loss of sample due to carelessness.

EFFECT OF ERRORS ON THE ANALYSIS

In closing this discussion of errors, the effects of some of the more important ones may be mentioned.

Loss of a constituent will, of course, make the values for that constituent low, but in a complete analysis there is the possibility that a constituent lost at some stage of the separation may come down at some other stage and make some other result high. For example, in student dolomite analyses, the values for mixed iron and aluminum oxides are nearly always too high because of coprecipitation of calcium or magnesium; consequently, the values for calcium or magnesium are often low. Silica also tends to be high because of occlusion of calcium, iron, and aluminum.

With respect to the errors arising from the purity of the precipitate it can be noted that the following usually lead to high results: Postprecipitation, insufficient washing, incomplete ignition, and errors in weighing due to adsorption of water or carbon dioxide. Reduction or decomposition during ignition most generally leads to low results.

Errors which arise from coprecipitation and wrong composition of precipitate must be considered for each case because they can lead to high or low results or even occasionally will not affect the results.

In the case of coprecipitation, we must consider three things: (*a*) what is coprecipitated, (*b*) what should it have been precipitated as, and (*c*) to what does the coprecipitated material ignite? Let us assume that in a sulfate analysis barium nitrate is coprecipitated with the $BaSO_4$. Actually the barium nitrate should not have precipitated at all, and, hence, it is extra material which ignites to BaO and is weighed along with $BaSO_4$, and the error arising from coprecipitation leads to high results. If, however, in a barium analysis, barium nitrate were coprecipitated, the results are different. In this case the barium ion combined with nitrate ion should be combined with sulfate ion. In the ignited product the BaO weighs much less than the $BaSO_4$ which it should be, and errors from coprecipitation lead to low results.

In an iron analysis $Fe_2(SO_4)_3$ may be coprecipitated with the $Fe(OH)_3$. On ignition both of these substances are converted to Fe_2O_3, and, hence, no error arises from this coprecipitation.

It has been pointed out on page 377 that magnesium may wrongly precipitate as $Mg_3(PO_4)_2$ rather than $MgNH_4PO_4 \cdot 6H_2O$. The latter ignites to $Mg_2P_2O_7$, whereas the former does not change in composition during ignition. In $Mg_2P_2O_7$ we are weighing per magnesium atom $PO_{3.5}$ or 87 atomic weight units; in $Mg_3(PO_4)_2$ we weigh per magnesium atom $P_{\frac{2}{3}}O_{\frac{8}{3}}$ or 73.4 atomic weight units. For each atom of Mg which precipitates as $Mg_3(PO_4)_2$ the final precipitate weighs less than if the Mg had precipitated as $MgNH_4PO_4 \cdot 6H_2O$.

Questions and Problems pertaining to the material summarized in this chapter are to be found at the ends of Chapters 17, 18, 19, 21 and 22.

CHAPTER

21

Gravimetric Analysis of Simple Mixtures

[To avoid repetition, the procedures for the determination of silica, calcium, magnesium, tin, lead, and other substances are given only in connection with the analysis of a limestone or brass. If it is desired to use these procedures for a simple mixture, they may be employed without modification, since each determination in the mineral or brass analysis is given as a separate unit.]

The number of substances whose analysis is made gravimetrically is so large that a comprehensive list of methods is beyond the scope of an elementary textbook. The determinations most frequently encountered are those of chlorine, iron, aluminum, sulfur, phosphorus, calcium, magnesium, silicon, copper, lead, nickel, zinc, and the alkalies. Procedures for these and other analyses are given in this and the following chapters. The methods given for the analysis of chlorine, iron, sulfur, and phosphorus pertain to the analysis of a simple mixture which contains no interfering substances. These are first studied in order that the student may master general technique by working with only one constituent of a sample before he undertakes the analysis of complex mixtures. The substances have been chosen with the object of illustrating the various types of precipitates most frequently encountered. In connection with each procedure a list is given of other determinations which may be made by this method.

CHLORINE (Br, I, Ag)

One of the simplest gravimetric determinations is that of chlorine in a soluble chloride. When a dilute solution of a chloride is treated with a silver nitrate solution, silver chloride is precipitated.

$$Ag^+ + Cl^- = AgCl$$

The precipitate is very insoluble, is easily obtained in a condition nearly

free of occluded impurities, is readily filtered and washed, and does not require ignition. For these reasons it is frequently chosen as the first exercise in gravimetric analysis.

Properties of Silver Chloride Precipitates. Silver chloride belongs to the class of curdy or agglomerated precipitates. When the reagents are first mixed, a colloidal suspension is obtained which coagulates readily, leaving a clear supernatant liquid. The coagulated mass forms in large lumps which are readily separated from the liquid by filtration. The precipitate does not greatly occlude foreign substances, especially when it is formed by the addition of silver nitrate to chloride solutions. Silver chloride is readily peptized on washing by pure water, but the addition of a little nitric acid to the wash water prevents this. The solubility is about 2 mg per liter at 25°C and 21 mg per liter at 100°C in pure water, but is much less in the presence of excess silver nitrate because of the common-ion effect.

Silver chloride cannot be ignited in the presence of organic matter, because at elevated temperatures it is readily reduced. Furthermore, a high temperature cannot be employed in ignition, because the melting point is 460°C, and on heating above this point there is considerable loss by volatilization. Because of this it is customary to filter through a filtering crucible so that ignition is not required. Drying at 110–130°C removes most of the water and is the method ordinarily employed. In the most precise work the precipitate is fused by heating in an electric oven in order to remove the last traces of moisture.

An outstanding characteristic of silver halide precipitates is their sensitivity to light. Direct sunlight, or even diffuse light, causes a darkening of the precipitate, due to decomposition into the elements. The halogen formed by the decomposition escapes, leaving silver dispersed within the precipitate. In the analysis of silver this decomposition leads to low results,[1] but in the analysis of chlorine the result is high if decomposition occurs before filtration because the liberated chlorine reacts with silver nitrate solution to form additional precipitate. Decomposition after filtration causes relatively little error, since only the comparatively light chlorine atom escapes, while the heavy silver atom remains. In all halogen analyses it is important to precipitate and digest in diffuse light and to avoid all exposure to direct sunlight.

Analysis of Soluble Chloride

Procedure. Wash three filtering crucibles, and bring to constant weight by drying at 110–130°C. (If filtering crucibles are not available,

[1] G. E. F. Lundell and J. I. Hoffman, *Bur. Standards J. Research*, **4**, 109 (1930).

prepare three Gooch crucibles as directed on page 321. Dry and weigh, then pass a small amount of water through the mat, and again dry and weigh. Repeat until a constant weight is obtained.)

The unknown substance is a mixture of soluble chlorides, which contains no interfering ions. Dry the sample at 100–120°C, and weigh three portions of 0.3–0.6 g (note 1). Transfer each portion to a 250-ml beaker, and dissolve in 100–150 ml water to which 1–2 ml nitric acid has been added (note 2). Calculate the weight of silver nitrate necessary for precipitation, assuming that the sample is sodium chloride. Prepare a solution containing approximately 20 mg silver nitrate per milliliter, and add the calculated amount of this solution, plus an excess of about 10 per cent, to each portion of sample. Add the silver nitrate from a pipet, keeping the solution well stirred during the addition. After addition is completed, heat the solution nearly to boiling, and keep at this temperature until the precipitate has coagulated. Allow the precipitate to settle, and then test for complete precipitation by adding a few drops of silver nitrate solution to the supernatant liquid. Continue the addition of silver nitrate, in small portions, until precipitation is complete. Cover the beaker with a watch glass, and allow it to stand in the desk (note 3) for 1–2 hours before filtration.

Place a filtering or Gooch crucible in the filtering apparatus, and apply suction. Carefully pour the clear supernatant liquid through the crucible, retaining as much of the solid in the beaker as possible. Use the technique described on page 324. Again test for complete precipitation by adding a few drops of silver nitrate solution to the filtrate. Wash with 0.01 *N* nitric acid as follows: Add 20–25 ml wash solution to the precipitate, stir well, allow the particles to settle, and decant the supernatant liquid through the filter. Repeat the washing by decantation three or four times; then transfer the precipitate to the crucible. With a stirring rod equipped with a policeman, rub all particles of precipitate from the walls of the beaker, and wash the particles into the crucible. Fill the crucible half full of wash solution, and allow it to drain completely. Repeat the process two or three times; then remove the funnel from the filter flask, insert a test tube in the flask as shown in Fig. 12, page 73, and collect a 5-ml sample of wash solution. Test this for completeness of washing by adding a little hydrochloric acid. If no appreciable cloudiness forms, washing may be assumed to be complete. If it is not complete, continue the washing until a satisfactory test is obtained. Remove the crucible from the funnel, place it in a small beaker, and dry in an oven at 110–130°C for 2–4 hours. Cool in a desiccator, and weigh; then redry, and reweigh. Repeat until a weight constant within 0.3 mg is obtained. The second period of drying usually gives a weight which agrees with the first one. From the weight of silver chlo-

ride obtained, calculate the weight of chlorine and the percentage of chlorine in the sample. Results should agree within 0.3 per cent for the percentage of chlorine present. Run a blank on the reagents (note 4).

Notes. 1. The weight of the final precipitate should be 0.4–0.5 g. Consult instructor.

2. Nitric acid is added to the solution as an aid in coagulating the precipitate, and in order to prevent precipitation of silver hydroxide, carbonate, etc.

3. As protection from light.

4. Add a few drops of silver nitrate solution to a nitric acid solution similar to that employed for solution of the sample. If any cloudiness appears, obtain chloride-free reagents.

Errors. The chief sources of error in addition to those listed on page 376 are the moisture retained on ignition and the decomposition of the precipitate under the action of light. Occlusion is not a source of great error, nor are the losses due to solubility. Interfering substances are the following:

1. Anions whose silver salts are insoluble in nitric acid, such as bromide, iodide, thiocyanate, sulfide.

2. Heavy metals whose chlorides are insoluble; in particular, mercurous and lead ions.

3. Substances which form complex ions with silver. If the solution is properly acidified, these substances are without effect.

Other Applications. The procedure may be employed with little modification for other determinations. The most widely used of these are:

1. *Bromine and iodine.* Because these ions are readily oxidized, it is important to use less nitric acid than in the chloride precipitation and to wash the precipitate nearly free of nitric acid before drying.

2. *The oxyhalogen acids and their salts.* These may be determined by reducing them to the halogen ion and precipitating with silver. The reduction may be made by treating a nitric acid solution of the sample with chloride-free sodium nitrite.

3. *Organic halogen compounds.* These may be analyzed if the halogen is first converted to the ion by fusion with sodium peroxide in a bomb or by heating with fuming nitric acid in a closed tube (Carius method).

4. *Silver.* Silver ion is determined gravimetrically by precipitating it with hydrochloric acid. A large excess of acid must be avoided, since silver chloride is appreciably soluble in hydrochloric acid.

5. *Mixtures of two halides.* A mixture of two halides may be analyzed by an indirect method. Two independent determinations are needed, which may be (*a*) the weight of combined silver salts and (*b*) the weight of silver in the precipitate. The former weight is determined by pre-

cipitating the combined halides, just as in the analysis of chloride. The weight of silver in the precipitate may be determined by reducing the precipitate in a stream of hydrogen and weighing the resulting residue of silver, or it may be found by titrating an aliquot portion of the sample with standard silver nitrate solution by the Fajans, Volhard, or Mohr method. From the volume of standard solution required the weight of silver used is computed.

Gravimetric Standardization of Hydrochloric Acid

Gravimetric standardization of hydrochloric acid, by precipitation of silver chloride, is a convenient and accurate method which has the advantage of being independent of the purity of any primary standard. The disadvantage of the method lies in the fact that the determination does not give the amount of hydrochloric acid, but the amount of chloride ion. If the acid is contaminated by ammonium chloride, this leads to error.

Procedure. Measure out accurately, from a buret or calibrated pipet, a 40- to 50-ml portion of the acid. Add a drop of methyl red indicator, and neutralize with 0.1 *N* sodium hydroxide solution (note). Add 1 ml nitric acid to the neutral solution, and determine the amount of chloride present according to the previous procedure. From the weight of precipitate obtained calculate the number of milliequivalents of chloride ion in the solution and the normality of the solution.

Note. Test the sodium hydroxide for chloride by acidifying a 5-ml portion with nitric acid and adding silver nitrate. Heat. If a perceptible precipitate appears, the sodium hydroxide is unsuitable for use. If chloride-free sodium hydroxide is not available, ammonium hydroxide may be used.

IRON (Al^{+++}, Cr^{+++}, Ti^{++++}, Zr^{++++})

Iron or steel samples are seldom analyzed by a gravimetric method because of the accuracy and convenience of volumetric methods. The gravimetric methods illustrated in this section are nevertheless very important, because in mineral analyses the separation of iron (and the related substances listed above) is always made by precipitation. These methods are also valuable in student training because they illustrate the technique of analysis with gelatinous precipitates. In the following section directions are given for iron analyses only, but the operations employed for filtration, washing, ignition, and so on, are applicable to all the other substances which precipitate as hydrous oxides on the addition of ammonium hydroxide to a solution of the ions.

When iron, in the ferric condition, is treated with ammonium hydroxide, it is quantitatively precipitated as hydrous ferric oxide according to the reaction:

$$2Fe^{+++} + 6NH_4OH + xH_2O = Fe_2O_3 \cdot yH_2O + 6NH_4^+$$

The precipitate is of indefinite composition because of the water which is more or less tightly bound with it. Such precipitates are known as *hydrous oxides,* rather than hydroxides, although the two terms are commonly used interchangeably. On ignition the precipitate yields ferric oxide, in which form it is weighed.

Properties of Hydrous Ferric Oxide. Hydrous ferric oxide is a very insoluble substance whose solubility product $[Fe^{+++}][OH^-]^3$ is approximately 10^{-36}. Because of this low solubility, precipitation is quantitative, even from slightly acid solutions. The precipitate first forms as a dispersed phase, but on heating in the presence of electrolytes it coagulates to a gelatinous mass which settles out of suspension. Prolonged boiling tends to break up the aggregates and cause the precipitate to become slimy. If the precipitate is well coagulated, it may be readily filtered and washed, provided a porous paper is employed, and washing is done by decantation. The use of suction is not recommended, for suction drags particles of the gel into the pores of the filtering medium, clogging it so that no liquid can be drawn through. The solubility of the hydrous oxide is so small that precipitation and washing can be carried out with hot solutions without any danger of loss. Electrolytes, usually ammonium salts, are added to the wash liquid in order to prevent dispersion of the coagulated gel.

As might be expected from their colloidal character, the hydrous oxides have a great tendency to adsorb other ions present. If precipitation is made from basic solution, the primarily adsorbed ion is the hydroxide ion, and this readily holds by secondary adsorption positive ions which may be present. If there is a large excess of ammonium ion in the precipitating and wash solutions, the adsorption of other positive ions can be kept at a minimum, and, since ammonium salts volatilize on ignition of the precipitate, little harm is caused by the adsorption. As might be expected from the general nature of adsorption, divalent ions are more strongly adsorbed than monovalent ones. Since the precipitates are readily dissolved by addition of acids, it is customary to employ reprecipitation in order to minimize the amount of coprecipitation.

The ignition of the hydrous oxides requires rather high temperatures in order to drive off water. Ferric oxide is made completely anhydrous by heating at 1000°C, but most of the water is expelled by heating at lower temperatures. Aluminum oxide requires still higher temperatures.

If the precipitate contains only iron, the final ignition may be made in a porcelain crucible over a Tirrill burner, but, if the precipitate is one of combined oxides, such as obtained in mineral analysis, it is advisable to ignite for a short time with a blast lamp. Iron oxide is readily reduced to the magnetic oxide Fe_3O_4 by carbon or reducing gases from the filter paper, and it is necessary to permit free access of air while burning off the paper. Should reduction occur, the product may be reoxidized by prolonged ignition, or by careful addition of a little concentrated nitric acid, evaporation, and reignition.

Analysis of Iron Solution

The samples used as student exercises for gravimetric iron analyses are usually (*a*) solutions of weighed iron samples, or (*b*) analyzed samples of ferrous ammonium sulfate. The former has the advantage that each student can be given an individual sample of accurately known weight of iron, with added constituents that make a double precipitation essential.

Procedure. Before beginning the analysis clean three porcelain crucibles (properly identified; see page 15), and bring to constant weight by ignition at the highest temperature of a Tirrill burner (or in the muffle furnace if one is provided). The second heating should give a weight in agreement with the first one.

Obtain the sample of weighed iron wire (note 1) in a 250-ml volumetric flask. Dilute to volume, mix well, and measure out three 50-ml aliquot portions from a pipet which has been calibrated with reference to the flask. Deliver the samples into 400- to 600-ml beakers. Do not begin the analysis unless a 2- to 3-hour period is available for work, since the filtration once started cannot be interrupted (note 2).

★ Heat the sample solution to boiling and add 1–2 ml concentrated nitric acid, a drop at a time, from a pipet (note 3). Continue boiling for a minute in order to expel oxides of nitrogen. Dilute the solution to 200–300 ml, heat to boiling, and slowly add, from a pipet, filtered 6 *N* ammonium hydroxide (note 4), stirring constantly and heating during the addition. After a precipitate begins to form, add the base in small portions until the odor of ammonia persists in the steam above the boiling solution. Continue to boil for about a minute after precipitation is complete, then remove the flame, allow the precipitate to settle, and test for complete precipitation by adding a few more drops of ammonium hydroxide. Note the color of the coagulated precipitate (note 5). Decant (note 6) the clear supernatant liquid through an open-texture filter paper (Whatman no. 41 or an equivalent grade), taking care to retain

the bulk of the precipitate in the beaker. Test the filtrate for completeness of precipitation by adding a little ammonium hydroxide solution. Add to the beaker which holds the bulk of the precipitate 25–30 ml ammonium nitrate wash solution (note 7), heat, and decant the hot solution through the filter paper. Wash twice in this manner.

Carefully remove the filter paper from the funnel, taking care that no precipitate is lost, and place it in the beaker that contains the bulk of precipitate. Pour in about 30 ml 3 *N* hydrochloric acid, and warm gently. Break up the filter paper with a stirring rod. All the precipitate should dissolve readily in the hot acid solution. After solution is complete, dilute to 100 ml, and precipitate by addition of ammonium hydroxide, as before. Filter through an open-texture ashless paper, wash twice by decantation, and then transfer all the precipitate to the filter. Wipe the beaker with a small piece of dry ashless filter paper to remove the last traces of precipitate, and add the filter paper to the precipitate in the funnel. Wash the precipitate in the funnel with hot ammonium nitrate solution until a 5-ml portion of wash water gives only a faint cloudiness when acidified and treated with silver nitrate solution (note 8). If only a faint cloudiness appears, washing may be assumed to be complete. Allow the filter paper to drain thoroughly, fold over the edges, transfer to a previously ignited and weighed porcelain crucible, and ignite according to the directions in Chapter 17. Complete the ignition by heating for 30 minutes at the highest temperature of the Tirrill burner (note 9). Cool the crucible in a desiccator for 20–25 minutes, weigh, and reignite for 20-minute periods until the weight is constant within 0.3 mg. Compute the weight of iron received.

Notes. 1. The sample weight is 0.7–1.0 g so that the weight of ferric oxide received from the aliquot portion will be 0.2–0.3 g. The sample is dissolved in 10–20 ml hydrochloric acid. Usually some inert impurity, such as sodium sulfate, is added to the flask, to make the analytical conditions comparable to those when ferrous sulfate samples are used.

2. The gelatinous precipitate obtained must not be allowed to dry on the paper before washing is completed. On drying, the precipitate breaks up into lumps, and in this condition it cannot be washed.

3. Ferrous ion is oxidized according to the reaction,

$$3Fe^{++} + NO_3^- + 4H^+ = 3Fe^{+++} + NO + 2H_2O$$

The solution darkens at first, owing to formation of the complex, $FeSO_4 \cdot NO$. As oxidation proceeds, the color changes to the bright yellow of the ferric ion. Bromine water may be substituted for nitric acid if desired. Add 10–15 ml saturated bromine water and boil until all bromine is expelled.

4. Filtered ammonia must be used in order to prevent the introduction of silica, which is often present as a suspension in alkaline solutions. If the ammonia solution is clear, filtration is not needed.

5. The precipitate should be reddish brown in color. If a dark-green precipitate is obtained, indicating ferrous hydroxide, dissolve the precipitate in hydrochloric acid, reoxidize with nitric acid, and reprecipitate. The precipitation of ferrous hydroxide is not complete in the presence of ammonium salts.

6. In the filtration of gelatinous precipitates it is important to use every precaution to insure a rapid flow. Read the directions of Chapter 17. Use an open-texture filter paper. Make certain that the paper fits the funnel tightly. Filter while hot.

7. The wash solution contains 8–10 g ammonium nitrate per liter. Prepare by dissolving solid ammonium nitrate or by adding ammonium hydroxide to a solution of 10 ml nitric acid per liter of water until it is neutral to litmus paper.

8. Chloride ion in small concentration is not harmful; its presence is used here as a convenient test for completeness of washing.

9. A blast lamp or Meker burner should be used for ignition if the usual burners do not give a flame sufficiently hot to heat the bottom of the crucible to bright redness. The crucibles must be brought to constant weight at the same temperature as that used for ignition of the precipitate. If a blast lamp or Meker burner is used, the precipitate need be ignited for only 10- to 15-minute periods.

Errors. See page 376 for general gravimetric errors. The interfering substances are the anions which yield precipitates in basic solution with ferric ion, such as phosphate and arsenate, and all the metals except those of the alkaline-earth and alkali group. If barium, calcium, and strontium are present, distilled ammonium hydroxide must be used to avoid the presence of carbonate, which would precipitate these metals as carbonates. Sufficient ammonium salts must be present to prevent the precipitation of magnesium if this is present. The errors due to incomplete oxidation and to drying of the precipitate have been mentioned. Incomplete washing leads to high results. Reduction is very likely to occur during ignition of the precipitate. Alkaline solutions, because they dissolve silica, should not be allowed to stand in contact with glass vessels for long periods of time. Reduction during ignition and incomplete ignition are probably the most frequent errors of beginning students.

Other Applications. Aluminum, trivalent chromium, zirconium, titanium, and trivalent manganese are precipitated as hydrous oxides by an excess of ammonium hydroxide. The more amphoteric ones, aluminum and chromium, are completely precipitated only in solutions of carefully controlled *p*H, since, if much excess ammonium hydroxide is added, the solubility is increased. (See determination of mixed oxides in limestone analysis.) Precipitation of manganese is complete only if it is first oxidized by treatment with bromine or persulfate.

Analysis of Ferrous Ammonium Sulfate

Since both iron and sulfur can be determined on the same sample, this is a widely used exercise. The samples are artificial mixtures of ferrous ammonium sulfate and ferrous sulfate or sodium sulfate.

Procedure. Obtain the sample in a stoppered weighing bottle. Do not dry unless specific instructions are given to do so. The analyzed samples usually supplied contain hydrated ferrous or ferrous ammonium sulfate.

Weigh out into 400–600-ml beakers three samples of 0.8 to 1 g each (note 1). Moisten with 5 ml concentrated hydrochloric acid, add 50 ml water, and heat until the sample is dissolved. Follow the procedure on page 386 for the iron determination, beginning with the star.

If a determination of sulfur is desired on the same sample (consult instructor), the filtrate and washings from both precipitations should be combined, evaporated, and reserved for the sulfur analysis. To the combined filtrate and washings add 15 ml concentrated HCl, and evaporate to dryness on the steam bath. Keep covered with a watch class suspended on glass hooks as shown on page 312. Moisten the residue with 10 ml HCl and again evaporate to dryness. After the second HCl evaporation dissolve the residue in 200 ml water, filter if any precipitate of silica is visible, and reserve the filtrate for the sulfur determination (note 2).

Notes. 1. Analyzed samples usually contain 2 to 8 per cent iron.

2. Evaporation with excess HCl destroys nitrate ion, which causes coprecipitation with barium sulfate. The presence of nitrates may be avoided by using bromine water for oxidation of ferrous ion before precipitation of ferric oxide. When this is done, the combined filtrate and washings from the iron precipitation need only be acidified with HCl, evaporated to 200 ml, and filtered if any precipitate of silica is observed.

SULFUR (Ba)

One of the most widely used (and at the same time least exact) gravimetric analyses is the determination of sulfur or barium ion by precipitation as barium sulfate. The ions react quantitatively according to the equation,

$$Ba^{++} + SO_4^{=} = BaSO_4$$

giving a precipitate whose solubility is only 3–4 mg per liter in pure water. Unfortunately, however, the precipitate is generally impure, and the accuracy of the analysis is never very great.

Properties of Barium Sulfate Precipitates. Barium sulfate crystals are usually so very finely divided that the analyst must use care in order to obtain a filterable product. Precipitation from concentrated and cold solutions gives such a fine-grained product that it passes through any obtainable filter paper, but, if precipitation is carried out from hot dilute solutions and a period of digestion is allowed, a coarser precipitate can be obtained which is readily separated by filtration.

The solubility of barium sulfate is slight and is decreased by excess of barium or sulfate ion. It is increased, however, by the presence of hydrogen ion. This is due to repression of the concentration of sulfate ion by formation of the bisulfate ion HSO_4^-, since the second ionization of sulfuric acid is rather small.[2] In the presence of 1 *N* hydrochloric acid the solubility is about 30 times greater than in pure water. Nevertheless, it is customary to carry out precipitation in weakly acid solutions, because the precipitates so obtained not only are less contaminated than those from neutral solutions but also consist of larger crystals and are therefore more easily filtered. The presence of acid also prevents the precipitation of barium carbonate, barium phosphate, and other barium salts which are insoluble in neutral solution. Because of the solubility of the precipitate, a high concentration of acid must be avoided. It is customary to employ 0.01–0.05 *N* solutions.

The coprecipitation of other salts with barium sulfate has been widely studied. Almost every constituent of the solution may be dragged down, even though the precipitate is formed under the most favorable conditions, that is, by the addition of barium chloride to sulfuric acid solutions. The chlorides and sulfates of the univalent cations are the least occluded foreign substances. Nitrate and chlorate ion should not be present because they are carried down as barium salts. The bivalent metals whose sulfates are soluble cause little more difficulty than the univalent metals, but the presence of any substances which have slightly soluble sulfates must be avoided. The only trivalent metals likely to be present are iron, aluminum, and chromium. Of these, iron is coprecipitated to a very large extent, usually as a basic sulfate, while chromium and aluminum are coprecipitated to a smaller extent. Chromium, however, should be avoided, because it may form a complex with sulfate ion.

The general method of reprecipitation cannot be employed in order to obtain purer precipitates of barium sulfate because no solvent is available in which the precipitate can be dissolved. Coprecipitation of certain substances is best prevented by removal of the offending ion, either by precipitation or by chemical reaction. Thus ferric ion, which is readily coprecipitated, may be reduced to ferrous ion, or it may be removed by precipitation as the hydroxide before precipitation of barium sulfate. Since not all substances can be removed (for example, the alkali and ammonium ions) their coprecipitation may only be minimized by proper conditions of formation of the precipitate and by digestion of the precipitate.

[2] The constant for the second ionization of sulfuric acid is approximately 0.01.

The error due to coprecipitation may make a result either high or low. In the determination of sulfate the occlusion of barium chloride leads to a high result, but the occlusion of sulfuric acid (either as the free acid or as barium acid sulfate) leads to a low result because sulfuric acid is volatilized during ignition. For the same reason the occlusion of ferric sulfate gives low results. Occlusion of barium chloride leads to low results in the determination of barium, but all foreign sulfates cause high results. Why?

The ignition of barium sulfate presents difficulties. If filter paper is used, it must be carefully burned away, with plentiful access of air, since the sulfate may be reduced by the filter paper according to the reaction,

$$BaSO_4 + 4C = BaS + 4CO$$

If a reduced precipitate is obtained, it may be reoxidized by treatment with sulfuric acid followed by volatilization of the acid and a brief reignition. A filtering crucible may advantageously be used for this determination, thereby eliminating any reduction of the precipitate; but, if this method is followed, the precipitate must be heated to a temperature of 600–900°C in order to remove occluded water.

Determination of Sulfur in a Soluble Sulfate

The samples ordinarily employed are mixtures of alkali sulfates and chlorides. They are free of the substances which are most extensively coprecipitated.

Procedure. Weigh out three 0.5-g portions (note 1) of the dried sample (note 2), and transfer to 400–600 ml beakers. Dissolve in a little water, add 1 ml hydrochloric acid, and dilute to 200–300 ml. Heat to boiling, and, with constant stirring and continued heating, add barium chloride solution (note 3) dropwise from a buret which is mounted in a slanting position with the tip above the precipitation beaker. After 15–20 ml have been added, interrupt the process, allow the precipitate to settle, and test for completeness of precipitation by adding a few more drops of barium chloride. If a further precipitate forms, add 5 ml of reagent, then again test for completeness of precipitation. Continue in this manner until an excess of reagent is present. Cover the beaker, and set it on the steam bath for an hour (note 4). The precipitate should be coarse enough to settle readily after stirring, and the supernatant liquid should be clear. If these conditions are not fulfilled, consult the instructor. Complete the determination by one of the following procedures.

***A.* Filter-paper Method.** Select an ashless filter paper according to the manufacturer's recommendations for barium sulfate precipitates (Whatman 42 or equivalent). Decant the hot supernatant liquid through the filter paper, and test the filtrate for complete precipitation. If no more precipitate forms, reject the filtrate (note 5), and replace the beaker beneath the funnel. Transfer the precipitate to the filter and wash with hot water until a test for chloride ion shows that little is present. After washing is complete, fold down the edges of the filter paper, and transfer the moist precipitate to a previously ignited and weighed porcelain crucible. Carefully burn off the filter paper, and ignite at the highest temperature of the Tirrill burner for 15–20 minutes after the paper is completely removed. Cool in a desiccator, and weigh. Repeat, with 15-minute ignitions until the weight is constant within 0.5 mg. Compute the percentage of sulfur as SO_3 in the sample.

***B.* Filtering Crucible.** Either a Gooch or porous-porcelain crucible may be used. Sintered glass is not satisfactory because of the ignition temperature required.

Prepare the crucible and bring to constant weight by ignition within a porcelain crucible at the highest temperature attainable from a Meker burner. Filter and wash in the usual manner, and dry in an oven at 110°C. Place the dried crucible inside a protecting crucible, and ignite over a Meker burner for 20-minute periods until constant weight is attained. Use of a muffle furnace is very advantageous in this determination if one is available.

Report the percentage of sulfur as SO_3.

Notes. 1. The amount of sample is chosen to yield 0.5–1.0 g of precipitate.

2. If hydrated sulfate samples are employed as student unknowns, they should not be dried before weighing.

3. Prepare an approximately 5 per cent solution by dissolving 5 g $BaCl_2 \cdot 2H_2O$ in 100 ml water.

4. One hour is a minimum period of digestion. A longer time is not harmful.

5. The bulk of the filtrate is removed before washing in order that only a small volume need be refiltered, should any precipitate go through the paper. Carefully examine the washings for suspended matter. If any is found, refilter through the same paper.

Errors. In addition to the errors listed on page 376 the determination of sulfur is subject to the following:

1. Loss by solubility because of strongly acid solution.
2. Impurity of precipitate. See preliminary discussion.
3. Reduction during ignition. This is a very frequent error in student analyses.
4. Interfering substances. All metals which form insoluble sulfates should be absent. Univalent and divalent metals whose sulfates are

soluble cause no trouble beyond occlusion. Ferric, nitrate, and chlorate ions, in particular, are to be avoided. Other ions which form insoluble barium salts must be absent.

5. Loss of solid during filtration. Because of the fineness of barium sulfate crystals, they often pass through the filter paper. Before the filtrate is discarded, it should be gently swirled, so as to collect solid matter at the center, and examined for suspended matter. If any marked cloudiness is seen, the filtrate should be digested for a time and refiltered through the same paper.

Other Applications. The method is applicable for the analysis of barium and for all sulfur compounds which can be quantitatively oxidized to sulfates. Organic sulfur compounds may be oxidized by fusion with sodium peroxide in a Parr bomb, or by treatment with fuming nitric acid in a sealed tube. Lead and strontium may be determined gravimetrically as the sulfates if the solubility of the precipitate is diminished by the addition of alcohol to the solution. The gravimetric method is not recommended for standardization of sulfuric acid solutions because of the errors due to coprecipitation.

Sulfur in Ferrous Ammonium Sulfate

Procedure. Iron is precipitated according to the procedure of page 389. The combined filtrate and washings after removal of iron are evaporated with hydrochloric acid to destroy nitrate ion.

Add to the solution obtained after destruction of nitrate ion (page 389) 1 ml hydrochloric acid, and determine sulfur according to the procedure of page 391. Compute the percentage of sulfur as SO_3.

A reasonably good sulfur determination may be obtained on a ferrous ammonium sulfate sample without removal of iron, provided precautions are taken to prevent the presence of ferric ion. The weighed sample is dissolved in 200 ml water to which 1 ml hydrochloric acid has been added, and a few drops of stannous chloride solution (see page 222) are added. Sulfur is then determined as in the preceding exercise.

Determination of Sulfur in Pyrites

Sulfur occurs commonly in nature as sulfides of iron, copper, lead, or zinc. The general method of analysis involves the oxidation of sulfur to sulfate, removal of interfering substances, and precipitation and determination as barium sulfate. Either a wet or dry method of oxidation may be employed. Each has advantages and disadvantages. In the wet method, the sample is treated with a strong oxidizing agent such as

aqua regia, fuming nitric acid, bromine, or potassium chlorate. The action is slow, and there is danger of incomplete oxidation. Nitrate or chlorate ion must be removed before precipitation of barium sulfate. Insoluble sulfates present may escape detection, since they are not attacked by the reagents. Silicate rocks are not decomposed by the wet treatment. The advantages of the wet method are that it introduces no new metal ions into the sample and that the sample so prepared may be used for the analysis both of sulfur and of the metals. Dry oxidation is carried out by fusing the sample with sodium carbonate and an oxidizing agent, such as potassium nitrate or sodium peroxide. This method effects rapid and complete decomposition of the sample, but it has the disadvantage that large amounts of sodium or potassium ion are introduced. In addition, the fusion mixture attacks the iron or nickel crucible used, bringing appreciable quantities of the metal into solution. Fused samples, therefore, are not suitable for the determination of the metal content of the sample. A further disadvantage of the fusion method is the danger of contamination by sulfur from the gas flames which heat the fusion crucible since sulfur dioxide in the gas from the flame is rapidly absorbed by the alkaline melt. Care must be taken to protect the crucible from the flame and, by a blank fusion, to insure the absence of sulfur in the reagents.

The analysis of pyrite is chosen as an example because of the ease of decomposition of this mineral and the widespread occurrence of sulfur in this form. The method given is a modification of the method of Allen and Bishop.[3] The coprecipitation of ferric ion is minimized by reduction with aluminum.

Procedure. Grind a sample of pyrite to pass an 80-mesh sieve, dry at 100–105°C (note 1) for 1 hour, and weigh out samples of 0.5 g. Transfer the samples to dry 200–300-ml beakers, add 10 ml of a mixture of two volumes of liquid bromine (note 2) to three volumes of carbon tetrachloride (Caution: Use a good hood), and cover with a watch glass. Allow the mixture to stand 15 minutes at room temperature, then add 15 ml nitric acid, and allow to stand another 15 minutes, shaking occasionally. Heat gently on a thick asbestos plate on top of a steam bath. When the reaction ceases, and most of the bromine is gone, place the beaker on the steam bath, elevate the cover by glass hooks, and evaporate to dryness. Add 10 ml hydrochloric acid, and again evaporate to dryness. Place the beaker in an oven at 110–120°C for an hour or longer in order to dehydrate silica (see Chapter 22). Drench the hot mass with 4 ml hydrochloric acid, add 100 ml hot water, digest for a

[3] W. S. Allen and H. B. Bishop, *8th Intern. Congr. Applied Chem.*, **1–2,** 48 (1912). See Hillebrand and Lundell, *Applied Inorganic Analysis*, page 571.

few minutes, and add 0.2 g powdered aluminum to reduce the iron (note 3). After the solution becomes colorless, cool and filter. Wash the beaker and filter paper with hot water. Dilute the filtrate and washings to 500–700 ml, add 1 drop stannous chloride solution (note 4), heat to boiling, and precipitate sulfur according to the procedure given previously.

Notes. 1. Drying at 100°C does not cause an appreciable oxidation of sulfides.

2. Sulfur is oxidized to a bromine compound in the carbon tetrachloride treatment. Subsequent addition of nitric acid causes the oxidation of this to sulfate. If nitric acid is added at first, the oxidation is slow because of separation of free sulfur which agglomerates in the hot solution and is but slowly attacked.

3. Many analysts prefer to precipitate the iron, as given in the analysis of iron samples, rather than to reduce by aluminum.

4. Stannous chloride is added to prevent reoxidation of ferrous ion by air.

PHOSPHORUS (Mg)

Phosphorus is determined by precipitation as the complex salt, magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4 \cdot 6H_2O$, from an ammoniacal solution. The precipitate may be dried at room temperature and weighed as the hexahydrate, or, by ignition at 1000–1100°C, it may be converted to the pyrophosphate $Mg_2P_2O_7$ and weighed in this form.

Properties of the Precipitate. Precipitation is carried out by slow neutralization of an acid solution which contains magnesium, ammonium, and acid phosphate ions. While acid is in excess, no precipitate is formed, but on neutralization the concentration of the phosphate ion is increased, and a supersaturated solution is obtained from which the hexahydrate slowly precipitates. After addition of ammonium hydroxide, the solution must be allowed to stand for several hours before filtration, in order that precipitation may be complete.

The equilibria involved in the formation of the precipitate are complex. Application of the solubility-product principle gives the expression,

$$[Mg^{++}][NH_4^{+}][PO_4^{\equiv}] = K_{SP}$$

Since the third ionization of phosphoric acid,

$$HPO_4^{=} = PO_4^{\equiv} + H^{+}$$

is very slight, the concentration of phosphate ion in an aqueous solution depends on the concentration of hydrogen ion. The solubility of the precipitate is therefore highly dependent on the *p*H of the solution. In pure water at room temperature it is quite soluble. Addition of am-

monium chloride increases the solubility rather than decreases it, according to the common-ion effect, since ammonium chloride gives by hydrolysis an acid solution which represses the concentration of phosphate ion. In ammonium hydroxide solution, however, the concentration of phosphate ion is increased, and the precipitate is less soluble. Precipitation is therefore carried out in an ammoniacal solution. Ammonium ion must be present, both for formation of the precipitate and to prevent precipitation of magnesium hydroxide (since ammonium ion decreases the hydroxide-ion concentration).

It is difficult to obtain a precipitate of the composition represented by the formula $MgNH_4PO_4$. Unless the concentrations of the various ions and the *p*H of the solution are held within narrow limits, the precipitate will be contaminated by phosphates of other composition, such as $MgHPO_4$ and $Mg_3(PO_4)_2$. Least contamination is observed if precipitation is carried out by slow neutralization of an acid solution, but even that will not insure a precipitate of the correct composition. In an analysis it is often impossible to know the concentration of all ions present when the determination has been preceded by removal of interfering ions, and it is usually necessary to use a double precipitation in order to obtain accurate results. The precipitate first obtained, of uncertain composition, is dissolved in acid, and the final precipitation is made from this solution under carefully determined conditions.[4]

The solution must be free of all metal ions other than those of magnesium, the alkalies, and ammonium. Salts of the alkali metals are occluded to a marked extent in the first precipitation, but a double precipitation will give accurate values except in the presence of potassium, which tends to form mixed crystals of the composition $Mg(NH_4,K)PO_4$. If potassium is present, three or more precipitations may be needed. In the determination of phosphorus a preliminary separation from the heavy metals is made by precipitation with ammonium molybdate, as described subsequently. In magnesium determinations other metals are first removed by precipitation, just as in the procedures of qualitative analysis.

The hexahydrate is rather stable at room temperature, and Worsham [5] has suggested drying by alcohol and ether and weighing in this form. The method, which is recommended by Fales [6] and Mehlig,[7] has been tested in student analyses by the present authors. Although drying at

[4] See A. Epperson, *J. Am. Chem. Soc.*, **50**, 321 (1928).

[5] W. A. Worsham, Jr., dissertation, Columbia University, 1923.

[6] H. A. Fales, *Inorganic Quantitative Analysis*, page 222, Century Co., New York, 1925.

[7] J. P. Mehlig, *J. Chem. Education*, **12**, 288 (1935).

room temperature is not in general an advisable procedure, because there is no criterion as to completeness, in this determination it is often advantageously employed because of the difficulties attendant on ignition of the precipitate. The composition of the precipitate is even more important when it is weighed as the hexahydrate than when it is ignited, since on ignition all volatile matter is expelled. Furthermore, the precipitate must not at any time be warmed, since at temperatures of 40–60°C the hexahydrate loses water and forms the monohydrate.

Hoffman and Lundell [8] have studied the ignition of the precipitate, and they recommend a temperature of 1100°C. At 1000°C constant weight is attained only slowly, and at 1200°C the pyrophosphate slowly decomposes. Results accurate enough for most determinations may be obtained by ignition at lower temperatures, even by blast-lamp ignition in a Gooch crucible which is heated within another porcelain crucible. The temperature thus reached is probably about 800–900°C. Ignition in a crucible, with filter paper, has the serious disadvantage that the precipitate is very easily reduced by the paper. Correct results can be obtained only by very slow charring of the filter paper and subsequent low-temperature heating, with plentiful access of air until the carbon of the paper is entirely consumed. Gases from the flame may also reduce the precipitate, and use of an electric muffle furnace is recommended if one is available. Detaching the dried precipitate from the paper and burning the paper in air so that the ash falls into the crucible are advantageous for the experienced analyst, but they often lead to difficulty with students because of danger of loss of the dried precipitate. A well-ignited precipitate gives a pure white compound of pyrophosphate, but that obtained in practice is often somewhat gray in color, because of enclosed carbon.

Determination of Phosphoric Anhydride in Phosphoric Acid

A very convenient student exercise is the analysis of phosphoric acid solutions, since the unknown sample is free of interfering substances and is of known strength. The sample issued is accurately measured into a volumetric flask. It is diluted to definite volume, and aliquot portions, of such size as to contain 125–200 mg phosphoric oxide, are analyzed.

Procedure. Obtain a sample (note 1) in a calibrated 250-ml volumetric flask, dilute to volume, mix thoroughly, and withdraw three 50-ml aliquot portions. Transfer the samples to 250-ml beakers, dilute to 100 ml, and add a drop of methyl red indicator and 15 ml of magnesia reagent (note 2).

[8] J. I. Hoffman and G. E. F. Lundell, *Bur. Standards J. Research*, **5**, 279 (1930).

* Cool in a dish of ice water, and, with constant stirring, slowly add a concentrated solution of filtered ammonium hydroxide until the indicator changes color. Avoid scratching the sides of the beaker while stirring (note 3). Continue stirring for a few minutes, until a precipitate has formed, then add 5 ml ammonium hydroxide, and allow the solution to stand in ice water for 4 hours (note 4). Filter the cold solution through a retentive filter paper, keeping the precipitate in the beaker; then wash once by decantation with 25 ml 1 *N* ammonium hydroxide which has been chilled. Discard the filtrate and washings. Place beneath the funnel the beaker which contains the precipitate, and dissolve the precipitate by slowly pouring 50 ml hot 1 *N* hydrochloric acid through the filter paper, taking care to wet all portions of the paper repeatedly. Wash the paper with a little hot water, catching all washings in the beaker which contains the sample. Discard the paper. Dilute the solution of the redissolved sample to 100 ml, add 2 ml magnesia mixture, and again precipitate as above. After standing, filter and ignite according to one of the following methods. From the weight of precipitate calculate the weight of phosphoric anhydride (P_2O_5) in the aliquot portion analyzed and the total weight received.

***A.* As Hexahydrate.** Prepare three Gooch or filtering crucibles, but instead of drying in an oven pass through the crucibles two 15-ml portions of 95 per cent alcohol followed by two 15-ml portions of ether. Continue to draw air through the crucible 5–10 minutes after the last portion of ether is added, then remove the crucible, dry the outside with a clean cambric towel, and let it stand in the balance case for 20 minutes before weighing. After weighing repeat the washing, and reweigh. The second weight should agree within 0.4 mg. Place the weighed crucible in its holder, apply suction, and decant the well-cooled supernatant liquid from the precipitate. Wash once by decantation with cold 1 *N* ammonium hydroxide, then transfer the precipitate to the crucible, and complete the washing, sucking the precipitate dry after each addition of liquid. The total volume of wash liquid need not exceed 50–75 ml. When washing is complete, as shown by a test for chlorides, dry the precipitate by passing alcohol and ether through the filter, as in the preparation of the crucible. Every detail in drying and weighing the precipitate should be exactly like the same operation in the preparation of the crucible in order to provide for a cancelation of errors. Weigh as the hexahydrate, $Mg(NH_4)PO_4 \cdot 6H_2O$. A second weighing is unnecessary.

***B.* Ignition in Filtering Crucible.** Prepare three filtering crucibles, and ignite to constant weight by a blast lamp or Meker burner. During ignition the crucible is placed within a porcelain crucible as

shown on page 322. Filter the sample, and wash with ammonium hydroxide, as directed previously; then dry the precipitate in an oven, and ignite for 20- to 30-minute periods until constant weight is obtained. Use a muffle if available. The final form of the precipitate is as the pyrophosphate $Mg_2P_2O_7$.

***C.* Filter Paper.** Decant the solution above the sample through a small ashless paper, and wash the residue twice with cold 1 *N* ammonium hydroxide by decantation; then transfer the precipitate to the paper, and continue washing until a test shows absence of chlorides. Use as little wash liquid as possible. Suction may advantageously be used for this filtration. See page 319. Allow the paper to drain thoroughly, transfer it to a previously ignited and weighed porcelain crucible, and very slowly dry and char the filter paper, leaving the crucible uncovered. When no more smoke escapes, set the crucible in a slanting position, and oxidize the carbon by a very small flame. When the carbon is oxidized, complete the ignition as usual, heating with a blast lamp for 20-minute periods until a constant weight is obtained.

Notes. 1. 30 to 40 ml of partially neutralized phosphoric acid solution which contains about 30 mg P_2O_5 per milliliter. After dilution the solution will contain 4–5 mg P_2O_5 per milliliter, and a 50-ml portion will give the desired amount for an analysis.

2. Preparation: To 50 g $MgCl_2 \cdot 6H_2O$, dissolved in 500 ml water, add 100 g NH_4Cl and a slight excess of NH_4OH. Allow to stand overnight, and filter if cloudy. Make slightly acid with HCl, and dilute to 1000 ml.

3. Crystals adhere very firmly to any scratched places on the wall of the beaker.

4. Standing overnight at room temperature is also satisfactory.

Errors. In addition to the errors listed on page 376, the most important ones in this determination are those mentioned in the introductory section. They are:

1. Loss by solubility. Negligible if directions are followed.

2. Incorrect composition of precipitate. If a double precipitation is carefully carried out, a precipitate of correct composition may be obtained. See Epperson, *loc. cit.*

3. Ignition errors. See previous discussion.

4. Solution of silica from glassware. When ammoniacal solutions are left in glass vessels, some silica is nearly always dissolved. It may be carried down by the precipitate. Only freshly filtered ammonia should be used for the precipitation.

5. Interfering substances. All common metal ions except those of magnesium and the alkalies must be absent. Arsenates if present are precipitated as magnesium ammonium arsenate.

Other Applications. Arsenates are determined by a similar procedure. Magnesium (see Chapter 22) is precipitated by addition of

ammonium phosphate solution. Manganese, cadmium, zinc, and cobalt form double phosphates similar to that of magnesium. This is a common method for the analysis of zinc.

Determination of Phosphoric Anhydride in a Mineral

The determination of phosphorus in a mineral is a much more complicated procedure than the simple analysis given above. The chief mineral sources of phosphorus are calcium phosphate rocks, in which calcium phosphates of varied composition are associated with large amounts of fluorine and smaller amounts of silicates, carbonates, aluminum, and magnesium. In nitric acid solution phosphates can be separated from the interfering constituents ordinarily present by precipitation as ammonium phosphomolybdate. This precipitate, which is approximately represented by the formula,

$$(NH_4)_3PO_4 \cdot 12MoO_3 \cdot H_2O$$

is not definite enough in composition to be used for a final weighing in exact analyses, but from the solution obtained by dissolving the precipitate in ammonium hydroxide the phosphorus may be precipitated as magnesium ammonium phosphate, as in the above analysis.

Because of the colloidal nature of ammonium phosphomolybdate, precipitation is best carried out in warm solutions. If, however, the temperature rises much above 60°C, the nitric acid solution of molybdic acid employed as reagent decomposes, and the precipitate is contaminated by molybdic anhydride, MoO_3. Large amounts of ammonium nitrate are necessary in formation of the precipitate, and a large excess of molybdic acid reagent is needed. The precipitate is readily peptized if washed with water, but remains as a gel in the presence of dilute ammonium nitrate solutions.

A number of interfering substances may cause difficulty in the precipitation of ammonium phosphomolybdate. Arsenic forms a complex molybdate and must be absent. Large amounts of sulfates, chlorides, fluorides, and organic substances retard formation of the precipitate, but these are not usually present in phosphate rocks in amounts sufficient to cause trouble. Silica must be removed prior to precipitation of phosphorus. Titanium, zirconium, and tin may lead to loss of phosphorus, by formation of insoluble compounds which remain in the silica precipitate. Iron and tin may cause loss of phosphorus at the time of dissolving the phosphomolybdate precipitate in ammonium hydroxide, but interference from this source may be eliminated by adding to the

ammonium hydroxide a small amount of ammonium citrate. This, by formation of complex ions with the metal ion, causes the solution of ferric or tin phosphates.

In analyses which do not require high accuracy the precipitate of ammonium phosphomolybdate may be dissolved in a measured volume of standard sodium hydroxide solution and the excess of base titrated with standard acid. The reaction is:

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 23NaOH$$
$$= 11Na_2MoO_4 + (NH_4)_2MoO_4 + NaNH_4HPO_4 + 11H_2O$$

Procedure. Weigh out duplicate samples of 0.3–0.4 g of the well-ground and dried mineral. Transfer to a small beaker, add 15 ml 6 *N* nitric acid, cover with a watch glass, and heat until the sample has dissolved (note 1), replacing acid if any evaporates. After solution of the sample, set the watch glass on glass hooks which hang on the rim of the beaker, and evaporate to dryness on the steam bath. Heat in an oven for 1 hour at 110–120°C (note 2), digest with 25 ml 6 *N* nitric acid to dissolve the soluble portions, filter off the silica (catching the filtrate in a 250-ml beaker), and wash with a little hot water. Test for completeness of washing by neutralizing a 5-ml portion of wash liquid with ammonium hydroxide. If calcium and phosphate ions are still present, a gelatinous precipitate of calcium phosphate will form. Should an appreciable precipitate form, add the tested portion to the solution, and continue washing.

To the filtrate and washings, which should not exceed 100 ml in volume, add 6 *N* ammonium hydroxide until a slight permanent precipitate is formed, then make slightly acid by addition of nitric acid until the precipitate dissolves. Avoid a large excess. Heat the solution to 60°C, stirring with a thermometer; then lower the flame so as to keep it at just this temperature, and add with stirring 75 ml warmed molybdate reagent (note 3). Digest at this temperature for half an hour, with frequent stirring, and then allow the solution to stand 4 hours at room temperature. Filter and wash several times by decantation with ammonium nitrate (note 4) solution. Set the beaker in which the bulk of precipitate remains beneath the funnel used for filtration, and dissolve the precipitate by pouring through the filter 20 ml 5 *N* ammonium hydroxide solution. Wash the filter with several portions of hot 0.5 *N* ammonium hydroxide and then with hot dilute hydrochloric acid solution, catching all washings in the beaker which holds the solution of the sample. The total volume should not exceed 100 ml. Add methyl red indicator to the solution, and carefully neutralize with 6 *N* hydrochloric acid. If

this operation is not done with care, a precipitate of phosphomolybdate may come down. Should this occur, add ammonium hydroxide until the precipitate is redissolved, and again neutralize. Add to the barely acid solution 15 ml magnesia reagent, and precipitate magnesium ammonium phosphate according to directions on page 398, starting at the star. A double precipitation is essential because of the presence of molybdate. Weigh the precipitate according to one of the methods described, and determine the percentage of P_2O_5 in the mineral.

Notes. 1. The reaction is

$$Ca_3(PO_4)_2 + 4H^+ = 3Ca^{++} + 2H_2PO_4^-$$

2. For dehydration of silica. See Chapter 22 for discussion.

3. Prepare the reagent as follows: Add 120 g molybdic acid (85 per cent MoO_3) to a solution of 80 ml concentrated ammonium hydroxide in 400 ml water, and stir until all has dissolved. Filter the cloudy solution, and pour the filtrate slowly and with constant agitation into a cold mixture of 400 ml concentrated nitric acid and 600 ml water. Filter before use, since nearly always there is a precipitate of molybdic anhydride.

4. 5 g per 100 ml.

ORGANIC PRECIPITANTS

The scope and applicability of gravimetric analytical methods have been extended by the somewhat recent introduction of organic precipitants that can be used for various metal ions (see page 314). Among the more important organic precipitants are:

Dimethylglyoxime, which is widely used for precipitation of nickel and will separate nickel from cobalt, manganese, iron, and other metals.

Cupferron, which is used to make a number of separations, particularly of iron, zirconium, and titanium from manganese and aluminum.

Nitron, which forms a precipitate with nitrate ion.

α-nitroso-β-naphthol, which precipitates copper, palladium, iron, and cobalt. An important application is precipitation of cobalt in presence of nickel.

8-hydroxyquinoline, which is most widely used for magnesium.

After precipitation with an organic reagent the analyst often has a choice of drying at about 105°C and determining the weight of the precipitate or of dissolving the precipitate and determining the amount of metal ion indirectly by a volumetric determination of the amount of organic reagent in the precipitate. Both methods are illustrated in the procedures given for determination of magnesium with 8-hydroxyquinoline.

Determination of Magnesium by 8-Hydroxyquinoline

The use of 8-hydroxyquinoline, or "oxine" as it is commonly called, began with studies of Berg in 1927. A number of metals form precipi-

tates with this reagent. The most widely used applications are for precipitation of magnesium in presence of alkali metal and ammonium salts and for separation of aluminum from magnesium and beryllium by precipitation from a buffered acetic acid solution.

The reagent has the formula C_9H_7ON, and it acts as a univalent ion, $C_9H_6ON^-$ in its combination with metals. It is a weak acid, and its precipitates are all soluble in strong acids. The precipitate with magnesium contains two molecules of water, having the formula $Mg(C_9H_6ON)_2 \cdot 2H_2O$.

It is shown, in a study by Miller and McLennan,[9] that formation of the magnesium precipitate is best made in an ammoniacal solution, that a large excess of oxine must be avoided, and that oxalates cause error. When magnesium is to be determined by precipitation with oxine in a mineral analysis it is preferable to destroy oxalates before precipitating the magnesium.

Analysis of Magnesium Sulfate. Procedure. Weigh out three samples of the dried material of such size that each will furnish 10–50 mg MgO. Transfer to 400-ml beakers, and dissolve in 100 ml water. Add 2 g NH_4Cl and 0.5 ml *o*-cresolphthalein indicator (0.2 per cent in alcohol), and neutralize with 6 *N* NH_4OH until a violet color is obtained (*p*H near 9.5); then add 2 ml NH_4OH in excess. Heat to 70–80°C, add very slowly and with constant stirring a 5 per cent solution of oxine in 2 *N* acetic acid to about 10 per cent excess above the calculated amount (see instructor). Avoid a large excess. Digest for 10 minutes on the steam bath, and then filter through a Selas or Gooch crucible. A trace of sodium tauroglycocholate if added at the time of digestion will reduce the tendency of the precipitate to stick to the walls of the beaker. Wash with small portions of hot water, using about 50 ml in all. Dry in an oven at 105°C, and weigh as $Mg(C_9H_6ON)_2 \cdot 2H_2O$. Alternatively the precipitate may be dissolved and the amount of oxine present determined by oxidation titration, as described on page 261.

QUESTIONS

A. Chloride

1. Why is a filtering crucible used for filtration?
2. Explain the following, and predict the effects on the analysis if the steps were omitted:
   (*a*) The addition of HNO_3 to the unknown solution.
   (*b*) The excess of $AgNO_3$ solution.
   (*c*) The presence of HNO_3 in the wash water.

[9] Miller and McLennan, *J. Chem. Soc. London*, 1940, p. 656.

3. List two metals and five anions which can be determined by slight modifications of the methods of this section.

4. What do you think of the determination of lead by precipitation as lead chloride?

5. An unknown contains a mixture of sodium carbonate and sodium chloride. Describe a method by which each constituent could be determined.

6. Why is *hot* 0.01 *N* HNO_3 solution not used to wash the AgCl?

7. How is completeness of washing tested?

8. What occluded substances might contaminate a precipitate of silver chloride? (Consider the adsorption conditions at the time of precipitation.) If this method were used for determination of silver what might be occluded?

9. Which of the following ions will interfere with a Cl^- determination: Hg^{++}, Hg_2^{++}, Co^{++}, Br^-, F^-, $SO_4^=$, NO_3^-?

10. During the determination of silver as AgCl the following substances were occluded. What effect do they have on the result if the ignition process consists of simply drying in the oven?

(*a*) NaCl
(*b*) $AgNO_3$

11. Why can washing be effectively done with a smaller volume of wash liquid when a Gooch crucible is used than when filter paper is used?

12. Outline a method for the analysis of a sample containing both chloride and chlorate.

13. How might the chlorine content of chloroform be determined?

14. How would you determine the bromine content of a photographic emulsion?

15. If a solution of hydrochloric acid is standardized gravimetrically, the value found for the concentration may be higher than that found by volumetric standardization. Suggest possible reasons for this.

16. List three methods for standardizing a solution of hydrochloric acid.

B. Iron

1. State the reason for using an electrolyte in the wash solution. Could NH_4Cl be used? HCl? ($FeCl_3$ is volatile at ignition temperatures.)

2. Explain briefly:
   (*a*) Why is the technique of reprecipitation employed?
   (*b*) Why is the precipitate washed with ammonium nitrate solution?
   (*c*) Why is paper chosen as the filtering medium? Why is the use of macerated filter paper recommended?
   (*d*) What other ions if present will interfere with the determination?

3. What effect on the observed percentage of iron will each of the following errors have? How can these errors be eliminated?
   (*a*) Incomplete oxidation to Fe^{+++}.
   (*b*) SiO_2 in the ammonium hydroxide.
   (*c*) Occlusion of $Fe(OH)SO_4$.
   (*d*) Reduction to Fe_3O_4 during the ignition.

4. Could $K_2Cr_2O_7$ be used as the agent to oxidize the iron to Fe^{+++}?

5. If Mg^{++} is present in the solution from which Fe and Al are to be precipitated as combined hydroxides, a fairly high concentration of ammonium chloride must be present. Why?

6. Why is the gravimetric method seldom used for the determination of iron in ores? Why, in rock analyses, are iron and aluminum precipitated gravimetrically?

7. Which would you expect to be most highly coprecipitated by hydrous ferric oxide, provided the two were present in equal concentration, Ba^{++} or K^{+}? Why?

8. Why is reprecipitation employed for iron but not for chlorine?

9. Show, by equations, that if sulfur, as a basic ferric sulfate, is occluded with ferric hydroxide the result of the analysis is not affected.

10. What error is introduced if an unwashed ferric hydroxide precipitate is allowed to dry in the filter before washing is completed?

C. Sulfur

1. What effect would the occlusion of each of the following have: $Ba(NO_3)_2$, Na_2SO_4, $Fe_2(SO_4)_3$

(*a*) On a sulfur determination in which the precipitate is collected in a filtering crucible and dried in oven?

(*b*) On a barium determination in which the precipitate is collected upon a filter paper and ignited to red heat?

2. How would each of the following affect the results of the analysis for sulfur?

(*a*) Use of hot wash water.

(*b*) Precipitation in a strongly acid solution.

(*c*) Occlusion of ferric chloride (the precipitate is ignited to red heat).

(*d*) Reduction to BaS during the ignition.

3. Which of the following have to be absent in the determination of Ba^{++} as $BaSO_4$: Mg^{++}, Pb^{++}, Na^{+}, NO_3^{-}, Cl^{-}, $PO_4^{\equiv}$?

4. Why is the solubility of barium sulfate increased by the presence of acids?

5. How would you analyze a sample of $BaSO_4$?

6. Outline a procedure for the analysis of PbS.

7. List the various ways of minimizing or avoiding occlusion. Which methods have been applied in the procedures of this chapter?

8. If Ba were present in a pyrite, what effect would it have on the determination of the percentage of sulfur determined (*a*) by the wet oxidation method, (*b*) by the fusion procedure?

D. Phosphorus

1. Describe the various methods which may be used for ignition of a precipitate of magnesium ammonium phosphate.

2. Why must phosphorus in apatite be precipitated by molybdate reagent before it is precipitated as the magnesium salt?

3. Show, by structural formulas, the relationship among ortho-, pyro-, and meta-phosphoric acid, and between phosphorus pentoxide and these acids.

4. List the most probable errors. How does each affect the result?

5. What is the effect on the result of an analysis for phosphorus if part of it precipitates as $Mg_3(PO_4)_2$ which ignites without change?

PROBLEMS

1. What is the percentage purity of a sample of $KClO_3$ which weighed 0.7440 g and yielded a precipitate of AgCl which weighed 0.8600 g?

2. In what proportions would KCl be mixed with NaCl or LiCl to produce a mixture which contains 65.00 per cent Cl?

3. How many milliliters HNO_3 (density 1.42, 69.8 per cent HNO_3 by weight) are needed to oxidize the iron in 50 ml of a solution which contains 10 mg of ferrous sulfate per milliliter:

(*a*) On the basis that the reduction product of HNO_3 is NO and that enough acid must be added to furnish both the necessary H^+ and NO_3^-?

(*b*) On the basis that NO is formed but that the solution is acidic and only enough HNO_3 must be added to furnish the necessary NO_3^-?

4. A mixture of iron and aluminum oxides weighs 0.0575 g and contains 15.0 per cent Al. How many milliliters of 0.0100 *N* $KMnO_4$ will be required to titrate the iron after the oxides have been dissolved and the iron reduced to the ferrous condition?

5. A mixture of 0.5000 g of FeO and 0.2500 g Fe_2O_3 is heated in air (FeO is oxidized to Fe_2O_3). What is the weight of the solid? A stream of hydrogen is passed over the heated solid to reduce the oxide to metallic iron. What is the weight of the metal?

6. A sample of Mohr's salt and impurities which are inert to both NH_3 and $BaCl_2$ yielded a precipitate of $BaSO_4$ which weighs 0.2500 g.

(*a*) What weight of Fe_2O_3 could be obtained from the sample?

(*b*) What is the percentage of Mohr's salt present if the sample weighed 0.5000 g?

7. What volume of 0.12 *M* $BaCl_2$ is required to precipitate the $BaSO_4$ after the oxidation of a sample of 0.1 g of ore which is approximately 80 per cent FeS_2?

8. What weight of pyrite must be taken for analysis so that each milligram of precipitated $BaSO_4$ shall represent 0.1 per cent sulfur in the sample?

9. A sample is a mixture of Mohr's salt [$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$] and $(NH_4)_2SO_4$. A 0.5000-g sample gave a precipitate of 0.7500 g $BaSO_4$. Calculate the percentage composition of the mixture. What weight of Fe_2O_3 would be obtained if 0.2000 g of the sample were ignited in air?

10. How many grams of Na_2O_2 are required to oxidize 0.4500 g ZnS to $ZnSO_4$?

11. What volume of 0.1 *N* KOH is used for titration of the molybdate precipitate obtained from 0.1 g P_2O_5?

12. A chloride mixture is prepared by grinding together pure $BaCl_2 \cdot 2H_2O$, KCl, and NaCl. What is the smallest volume of 0.15 *M* silver nitrate solution that may be used for complete precipitation of chloride from a 0.3-g sample of the mixture which may contain any or all of the above constituents?

13. What weight of iron ore must be taken for analysis in order that the weight of ferric oxide obtained in the analysis shall be multiplied by 50 to give the percentage of Fe_3O_4 in the sample? (Assume all the iron present in the ore as Fe_3O_4.)

14. Improper ignition of a ferric oxide precipitate gave a product containing both Fe_2O_3 and Fe_3O_4. The weight of the ignited residue was 0.2240 g. The precipitate was reduced, by a stream of hydrogen, to iron and reweighed, giving a residue of 0.1578 g. The original sample taken for analysis weighed 0.4500 g. What was the percentage of Fe_2O_3 reported on the basis of the ignited precipitate? What was the true percentage?

15. A 10.00-g soil sample was extracted with water and the solution diluted to 500.0 ml; 50.00 ml of this solution was used for a phosphorus determination. The precipitate of ammonium phosphomolybdate was dissolved in 25.00 ml of 0.1233 *N*

sodium hydroxide. To neutralize the excess base, 18.63 ml of 0.0683 N nitric acid was needed. Calculate the percentage of phosphorus pentoxide in the soil.

16. Cobalt is sometimes precipitated with α-nitroso-β-naphthol as $Co[C_{10}H_6O(NO)]_3$ and ignited in a stream of O_2 to Co_3O_4. At other times the precipitate is ignited in H_2 and weighed as Co. What weight of cobalt would have been obtained from the same weight of sample which produced 0.2125 g Co_3O_4?

17. A sample of $CaCO_3$ and $FeCO_3$ contains equal portions of each by weight. Strong ignition produces CaO and Fe_2O_3. What is the weight of a 1.000-g sample after thorough ignition?

18. A 0.7500-g sample of an alloy steel yielded on electrolysis 0.1532 g of a mixed deposit of Co and Ni. This is dissolved, and the precipitated nickel dimethylglyoxine weighs 0.3560 g. What are the percentages of the two metals in the alloy?

19. A student sample is prepared by mixing $Ca_3(PO_4)_2 \cdot CaCl_2$ with SiO_2. A 0.5000-g sample yields 0.1825 g $Mg_2P_2O_7$. What volume of an $(NH_4)_2C_2O_4$ solution of 40 mg per milliliter is needed to precipitate the calcium from a 1.000-g sample of the unknown?

20. What volume of NH_3 solution (density = 0.946 g/ml, 15% NH_3) is required to precipitate the iron as ferric hydroxide from a sample of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ which in turn required 0.30 ml HNO_3 (density = 1.350 g/ml, 55% HNO_3) to oxidize it? Assume that the HNO_3 is reduced to NO and that the 0.30 ml furnished both the needed NO_3^- and H^+.

21. What error in parts per thousand and in percentage of Cl present is made if 1.0 mg AgCl is mechanically lost in an analysis whereby a 0.3500-g sample produces a precipitate of AgCl which weighs 1.000 g?

22. I^- can be separated from other halides by precipitation as PdI_2 and weighed as such or reduced in a current of H_2 to Pd. A 0.5000-g sample of KI and NaCl and inert impurities gave a precipitate of mixed silver halides which weighed 0.8000 g. A 0.2000-g sample yielded 0.04250 g metallic palladium. Find the percentages of NaCl and KI in the sample.

23. A mixture of $KClO_4$ and $KClO_3$ can be analyzed as follows:

(*a*) The mixture is ignited with NH_4Cl and AgCl is precipitated from the residual KCl.

(*b*) The mixture is treated with SO_2 which reduces only the chlorate to chloride, and again the precipitated AgCl is weighed.

From the following data find the percentage of $KClO_4$ in a mixture:

Weight of sample	0.2610 g
Weight of AgCl from step 1	0.1490 g
Weight of AgCl from step 2	0.0745 g

CHAPTER

22

Analysis of Limestone

The complete analysis of a complex sample, involving the determination of several constituents, is an important exercise in the training of analytical chemists. The operations involved in the determination of each constituent are the same as in the determination of that constituent in a simple mixture, but a complete analysis is more difficult because errors introduced at any stage of the procedure will affect all subsequent determinations made on the sample. The material almost universally chosen for the first complete analysis is a dolomitic limestone rock. This mineral is chosen both because limestone is commercially important and because this analysis is typical of all mineral analyses. The analysis is one of the easiest of the complex mineral analyses because the samples are usually brought into solution readily, whereas many other minerals require great skill for this operation.

PART I. GENERAL DISCUSSION

A complete discussion of the field of mineral analysis is beyond the scope of an elementary textbook, but in connection with this analysis attention is called to methods which are of general application to other minerals. For more detailed discussion see the references listed in the Bibliography, and, in particular, *Applied Inorganic Analysis*, by Hillebrand and Lundell. Frequent reference is made to this publication in the following discussion.

Composition of Limestones. Hillebrand and Lundell discuss mineral analysis under the general classifications of silicate and carbonate rocks. The silicate rocks contain large amounts of silicates and can be brought into solution only by fusion with sodium carbonate, whereas carbonate rocks are those which contain relatively small amounts of silicates but large amounts of carbonates. The carbonates are, in general, more or less readily disintegrated by treatment with dilute acids.

These classifications are not absolute, nor are the analytical methods peculiar to one class or the other, since after solution of a sample the analysis of all minerals is very similar. Limestone rocks contain large amounts of carbon dioxide as carbonates of calcium and magnesium; nevertheless, it is often necessary to fuse the sample in order to effect solution.

The composition of dolomitic limestones may vary over wide ranges, as is shown in Table 34, which gives the approximate composition of the type of sample employed in student analyses. In addition to the constituents listed, there may be appreciable quantities of water, both

TABLE 34

APPROXIMATE COMPOSITION OF LIMESTONE

Constituent	*Percentage*
CO_2	30–45
SiO_2	1–20
Fe_2O_3	0– 2
Al_2O_3	0– 5
CaO	35–45
MgO	10–25
$Na_2O + K_2O$	0– 3

hygroscopic and combined; manganese, titanium, and phosphorus; and traces of lithium, sulfur, chlorine, molybdenum, and other substances.

Attention should be called to the method used for expressing the results of mineral analysis. It is customary to express the amount of each metal as its oxide, usually the higher one, and the amount of each anion as the anhydride of its most common acid. Thus, calcium is given in terms of percentage of CaO, and phosphorus as percentage of P_2O_5. Sulfur may be expressed either as percentage of S or of SO_3; often both sulfide and sulfate sulfur are separately determined. If the mineral is one which does not contain oxygen, this method is not followed, as for example in the analysis of iron pyrites FeS_2. The fact that the amount of a constituent is given as the oxide does not imply a determination of oxygen. Rather, the constituent is determined in the customary manner, and the amount present is calculated as if it were the oxide. The reason for this convention is probably based on the customs in vogue in the early days of analytical chemistry, when all formulas were written in dualistic style.[1] Today the usage persists because this is the most convenient method for including the oxygen content of a mineral in reporting an analysis. Furthermore, it is often impossible to assign a

[1] For example, sodium sulfate was denoted by the formula $Na_2O \cdot SO_3$.

definite chemical formula as the result of an analysis, and an attempt to do so might prove misleading. For example, if a mixture contains calcium, magnesium, silicon, and carbonate, the analyst cannot state which portion of the calcium is present as carbonate and which portion as silicate.

In the exact analysis of a limestone a determination is made for each constituent thought to be present; but, for many purposes, and in particular for the commercial analysis of limestones, a condensed or "proximate" analysis is made. In a proximate analysis the determinations are:

Loss on ignition.
Impure silica.
Combined oxides (Fe_2O_3, Al_2O_3, TiO_2, Mn_3O_4, and P_2O_5).
Calcium oxide.
Magnesium oxide.

All the constituents of the sample except sodium, potassium, chlorine, and sulfur are determined at some stage of the proximate analysis. The summation of the weights found in this analysis should therefore total the weight of sample used, except for the small amounts of the substances mentioned which escape detection. The term, proximate analysis, does not, therefore, indicate approximate accuracy but refers to the number of constituents measured. In the following procedures directions are given for a proximate analysis and also for the determination of the more important constituents which are not determined by this method. As previously mentioned, many of the methods used in limestone analysis are applicable to other minerals.

Preparation and Drying of Sample. The selection of a mineral sample depends on the purpose for which the analysis is made. If a single rock is to be analyzed, chips may be broken from various portions, and these may be combined to furnish a composite sample. If a commercial analysis is needed, as from a quarry, it is necessary to take samples systematically over a large area and to combine these by quartering, according to the directions on page 61. After a sample has been selected, it is crushed or ground until the particles are of a size suitable for dissolving. Since the heat generated by abrasion in grinding may alter the composition of some minerals, it is usually preferable to crush the sample by *striking* it with a hardened-steel hammer.[2] Hillebrand recommends that, if grinding is necessary, the sample be covered by some non-oxidizing liquid, such as absolute alcohol. Because of their hardness, agate mortars are commonly used for grinding. After crush-

[2] See Fig. 10, page 63.

ing or grinding the entire sample should be passed through a sieve of proper size, for, if only part of the sample is finely ground, there may be segregation of the harder portions. A sieve of 30–40 meshes to the linear centimeter is fine enough to give a readily soluble sample of most limestone rocks, although certain minerals require grinding to a powder which will pass a finer sieve. In very exact analyses the use of metal sieves is questionable, since the sample may abrade metal from the sieve; silk bolting cloth is substituted. Student samples of limestone have usually been ground in a ball mill before they are issued, in order to insure uniformity of composition, and usually they need no further grinding.

The type of drying employed depends on the purpose of the analysis. Most commercial analyses are made on samples which have been dried at 110°C; this plan is conventional for student samples. Care should be taken to prevent readsorption of moisture while dried samples are being weighed. The sample should be weighed only in a stoppered container, and a spoon should be used for withdrawal of the portions for analysis, so that the weighing bottle need not be kept open for any extended time.

Loss on Ignition. When limestones are ignited at high temperatures, all the combined carbon dioxide and water are expelled, and organic matter is oxidized. In addition, there are minor changes due to oxidation of sulfides and of ferrous salts, decomposition of sulfates, and volatilization of potassium chloride. Since the greater part of the loss on ignition is due to escape of carbon dioxide, the loss in weight is usually the only determination made for the carbon dioxide content of the sample. A more exact method for determination of carbon dioxide is given in a later section.

The readiness with which carbon dioxide is expelled depends on the composition of the sample. Magnesium carbonate is decomposed at quite low temperatures. If a sample containing magnesium carbonate is rapidly heated to a high temperature, the gas may be evolved so vigorously as to carry away solid particles. Calcium carbonate requires somewhat higher temperatures for complete decomposition. If ignition is completed at a temperature above 900°C, all carbon dioxide is driven off.

In addition to expelling carbon dioxide, ignition plays an important role in the subsequent analysis. Many silicates which originally cannot be decomposed by acids are converted by ignition into calcium and magnesium salts by reaction with the oxides of these elements. These salts are then readily decomposed by treatment with dilute hydrochloric acid.

The reactions which take place may be represented by the following equations (SiO_2 is used as illustration):

$$CaCO_3 = CaO + CO_2$$

$$SiO_2 + CaO = CaSiO_3$$

Solution of Sample and Determination of Silica. When decomposable silicates are treated with dilute acids, the reaction may be represented by the equation,

$$CaSiO_3 + 2H^+ + yH_2O = Ca^{++} + SiO_2 \cdot (y + 1)H_2O$$

The hydrated silicon dioxide, or silicic acid, is in the form of a dispersed gel. When the solution is evaporated, some of the water is driven off from the gel, and insoluble silicon dioxide, still somewhat hydrated, remains as a residue. When this residue is treated with water or dilute acids, a portion of the gel again passes into a dispersed condition. The tendency towards dispersion may be decreased by *dehydrating* the silica after evaporation. Ordinarily dehydration consists in heating the residue for a time at a temperature of 100–140°C. Higher temperatures may be employed, giving still better dehydration, but their use is not advantageous because at elevated temperature there is hydrolysis of hydrated iron salts to a basic substance which is not readily soluble in acids. More than one evaporation and dehydration, without an intervening filtration, does not decrease the amount of silica which passes into suspension. If, however, after the first evaporation and dehydration, the residue is extracted with acids (in order to dissolve soluble salts), the insoluble portion separated by filtration, and the solution again evaporated and dehydrated, most of the remaining silica is now recovered in an insoluble form. This is the procedure followed in analysis. In the insoluble form left after dehydration at 100–140°C, silicon dioxide still retains a large amount of water. This water is removed by high-temperature ignition, after which the sample is weighed as anhydrous silicon dioxide.

Even after two dehydrations, there is still a small amount of silica left in solution, but the error due to this is largely compensated by the amount of iron and aluminum oxides which contaminate the silica precipitate. In very exact analyses it is necessary to recover the silica which was left in solution by separating it from the precipitate of combined oxides obtained in the next operation. If this is done, it is also necessary to recover the impurities in the silica precipitate by treating the precipitate with hydrofluoric and sulfuric acids, evaporating the

solution to dryness, reigniting to decompose the residual sulfates, and weighing the residue. During this treatment silica is volatilized by formation of silicon tetrafluoride,

$$SiO_2 + 2H_2F_2 = SiF_4 + 2H_2O$$

The loss of weight represents the amount of pure silica present.

Not all silicates, even in dolomitic limestones, are decomposed by acid treatment. In general, it may be said that silicates in which the percentage of basic constituents (such as CaO and MgO) are high will be decomposed by an acid treatment which is preceded by a high-temperature ignition, whereas silicates which contain a high percentage of acidic constituents will not be decomposed by the acid treatment. Such silicates may be made soluble in acids by fusion with a basic flux; sodium carbonate is usually employed. The reaction which takes place is given by the equation (for SiO_2),

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2$$

If a large portion of the sample is not decomposed by acid treatment, it is advisable to fuse the original sample with sodium carbonate, but, if most of the sample is dissolved in acid, the fusion is conveniently made on the residue left after a preliminary acid treatment. This has the advantage that only a small amount of sodium carbonate is needed, and the amount of sodium salts in the solutions to be analyzed is kept at a minimum.

Combined Oxides. After a limestone sample is dissolved and the silica removed, the solution is treated with ammonium hydroxide. The precipitate formed consists of the hydrous oxides of iron, aluminum, and titanium (and of similar substances which may occasionally be present), along with the remaining silica in solution, phosphorus, and part of the manganese. If the manganese is first oxidized by treatment with ammonium persulfate or bromine, it is completely precipitated as hydrated Mn_2O_3 at this point, but otherwise a large portion remains in solution and is later precipitated with calcium or magnesium.

Because of the great tendency of the hydrous oxides to occlude other substances, it is necessary to employ a double precipitation in order to prevent loss of calcium and magnesium. There is also danger of precipitating calcium carbonate because of the presence of carbonate ion in the ammonium hydroxide solution used for precipitation of the combined oxides and because of the action of carbon dioxide of the air. This error, too, is minimized by a double precipitation.

In the procedure previously given for the determination of iron it was necessary only to add ammonium hydroxide in excess, boil the solution until the precipitate coagulated, and filter. More care is necessary in the present procedure. Aluminum hydroxide is somewhat amphoteric, and its solubility is increased in solutions of high *p*H value. Because of this, an excess of ammonia is avoided. The presence of ammonium salts is necessary, since they, by repressing the ionization of ammonium hydroxide, prevent the precipitation of magnesium hydroxide. These salts also aid in reducing the solubility of aluminum hydroxide. The presence of large amounts of phosphate may lead to error at this point, since, if the amount of phosphorus is more than that needed to combine with all the iron and aluminum present, there will be precipitation of calcium phosphate when the solution is made basic. No trouble from this source is encountered in a limestone analysis, since the phosphate content is low.

The precipitate of hydrous oxides is filtered, washed, and ignited, just as in the previous determination of iron. In a proximate analysis only the percentage of combined oxides, designated as R_2O_3, is reported. In an exact analysis the precipitate must be dissolved and the amount of each constituent determined. In the exact analysis, iron is determined by permanganate titration, titanium is determined colorimetrically, and the amount of aluminum is calculated by difference. Any silica present is left as a residue when the sample is dissolved. Solution of ignited oxides of iron and aluminum in acids proceeds with difficulty. For that reason the ignited precipitate is fused with potassium acid sulfate, $KHSO_4$, whereby the ignited oxides are converted into the readily soluble sulfates.

Calcium. After removal of the combined oxides, the solution contains only calcium, magnesium, sodium, potassium, and chloride ions. If fusion has been employed for solution of the sample, the amount of sodium is large; otherwise it is small. Magnesium is seldom present in greater concentration than calcium. Calcium may be precipitated from magnesium and the alkalies as the oxalate $CaC_2O_4 \cdot H_2O$, which is sparingly soluble in water but is practically insoluble in solutions containing oxalate ion. Two precipitations are necessary in order to obtain a moderately pure product, since occlusion of sodium, potassium, and magnesium oxalates occurs to a very large extent. After the second precipitation there is still some magnesium oxalate in the precipitate, but the error caused by this coprecipitation is largely compensated by the small amount of calcium which remains in solution and is later precipitated with magnesium.

The second ionization constant of oxalic acid is about the same as the constant for acetic acid, and consequently precipitates of calcium oxalate are soluble in strong acids. The oxalate may, however, be precipitated from slightly acid or neutral solutions. In limestone analyses a calcium precipitate of highest purity is obtained by adding ammonium oxalate reagent to a hot acidified solution of the sample and slowly neutralizing the acid with ammonium hydroxide. The greater portion of the precipitate forms while the solution is still slightly acid, with the result that large easily filterable crystals are obtained. In the analysis of calcium from solutions which contain much phosphate, it is often necessary to precipitate from buffered acetic acid solutions in order to prevent precipitation of calcium phosphate or of magnesium ammonium phosphate. If an excess of oxalate is added, a fairly complete precipitation may be achieved, even at a *p*H of 4–5.

Coprecipitation of the oxalates of sodium, potassium, and magnesium is very pronounced with calcium oxalate precipitates. Magnesium causes the greatest difficulty because magnesium oxalate is itself of limited solubility. Fortunately, however, magnesium forms complex salts with oxalate ion; moreover, magnesium oxalate readily forms quite stable supersaturated solutions. These two effects aid in keeping magnesium in solution during the precipitation of calcium. In the presence of magnesium it is necessary to employ a very large excess of oxalate, since part of the oxalate ion is removed from solution by reaction with magnesium. It is undesirable to allow the digestion period for the calcium precipitate to be longer than an hour, since long standing may bring about a postprecipitation of magnesium oxalate.

Several methods have been proposed for the ignition and weighing of calcium oxalate precipitates. The monohydrate itself is fairly stable at 100°C, and the precipitate is sometimes weighed in this form. At ignition temperatures of 450°–550°C there is complete conversion of the oxalate to carbonate; weighing in this form has been widely recommended. It is necessary, however, to control the temperature of ignition carefully because at still higher temperatures there is decomposition of the carbonate into the oxide. Despite the facts that complete conversion to the oxide requires a high temperature, and that the ignited oxide is very hygroscopic, complete ignition to the oxide is recommended if platinum crucibles are available, because there is no danger of overignition, and hence the analyst can be assured of correct results when the ignited precipitate is at constant weight. Another proposed method is weighing as the sulfate, after converting the precipitate to this form by treatment with sulfuric acid. This method is not desirable

for student use because of the difficulty involved in removal of excess sulfuric acid, and because of the possibility of incomplete conversion. A volumetric method has previously been mentioned, in Chapter 12. The well-washed precipitate of calcium oxalate is dissolved in sulfuric acid, and the oxalate is determined by titration with standard permanganate solution. This is the recommended procedure when platinum crucibles are not available.

Magnesium. After removal of all other metals except the alkalies, magnesium is precipitated as magnesium ammonium phosphate, and is weighed as the hexahydrate of this salt, or is ignited to the pyrophosphate. The properties of magnesium ammonium phosphate are discussed in Chapter 21. The precipitate is formed by slow neutralization of an acid solution which contains magnesium, ammonium, and orthophosphate ions. Two precipitations are needed to free the product of occluded salts of the alkalies if fusion has been employed. Oxalates prevent complete precipitation of magnesium, if present in large concentration, and they are destroyed, together with ammonium salts, prior to the first precipitation. This is accomplished by evaporation of the solution, which contains large amounts of chloride ion, with nitric acid. Under the action of nitrate and chloride ions, ammonium salts are oxidized to gaseous nitrogen, or to nitrous oxide, and oxalates are oxidized to carbon dioxide. The various methods for ignition and weighing of the precipitate are discussed in Chapter 21.

Magnesium can also be determined by precipitation with 8-hydroxyquinoline and weighed as $Mg(C_9H_6ON)_2$ (see page 403). The analysis can be completed volumetrically by the solution of the precipitate in acid, treatment with an excess of standard $KBrO_3$ solution, followed by back titration with $Na_2S_2O_3$ solution (see page 261).

Sodium and Potassium. Because of the small quantities present in limestones and the possibility of introduction of these elements during the preceding stages of the analysis, it is customary to determine the alkalies, sodium, and potassium, in an original sample, rather than in the sample from which other constituents have been removed. The method of J. Lawrence Smith is used to decompose silicates and to prepare a solution free of other metals. In this method the sample is strongly heated with a mixture of calcium carbonate and ammonium chloride, in a special platinum crucible. When the sintered mass is digested with water, there is obtained a solution of the alkali chlorides, together with calcium and a little magnesium. Other metals are for the most part left as insoluble oxides. The reactions in the decomposition of the mineral are complex, but proceed approximately as indicated in the following equations:

$$CaCO_3 = CaO + CO_2$$

$$CaO + 2NH_4Cl = CaCl_2 + 2NH_3 + H_2O$$

$$2KAlSi_3O_8 + CaCl_2 + 6CaCO_3 = 6CaSiO_3 + Ca(AlO_2)_2 + 2KCl + 6CO_2$$

After the residue is leached, the resulting solution is treated with ammonium carbonate and ammonium hydroxide in order to remove calcium. If the mineral contains sulfate, this will be in the solution and is removed by the addition of barium chloride prior to the carbonate treatment. The excess of barium ion introduced into this solution is precipitated as carbonate with the calcium. The precipitate of calcium carbonate is removed by filtration, the solution is evaporated to dryness, ammonium salts are removed by treatment with nitric and hydrochloric acids, and the residue is weighed, as mixed sodium and potassium chlorides. Other alkalies, if present in the sample, would also be in the mixed chloride residue, but in limestone their presence may generally be ignored.

The mixed chlorides are analyzed by either the chloroplatinate or perchlorate method, the latter being the more widely used because it requires less expensive reagents. In the chloroplatinate method, potassium (with rubidium and cesium) is precipitated as potassium chloroplatinate from an 80 per cent ethyl alcohol solution. The precipitate is dried at 135°C, and weighed as K_2PtCl_6. From the weight of precipitate the weight of potassium chloride is calculated. Subtraction of this weight from the weight of mixed chlorides gives the weight of sodium chloride (in the absence of lithium, which, if present, remains with the sodium). In the perchloric acid method, the mixed chlorides are treated with perchloric acid and the solution evaporated to dryness, thereby converting the metals to the perchlorate salts. Sodium perchlorate is then extracted with a mixture of *n*-butyl alcohol and ethyl acetate, and the residue, potassium perchlorate, is dried and weighed. Sodium may be determined by difference, or it may be precipitated as chloride from the extract and weighed. Lithium, if present, is extracted along with the sodium, while rubidium and cesium perchlorates are left with potassium perchlorate.

Laboratory procedures for the J. Lawrence Smith method are not given in this book because the necessary equipment and purified reagents are not generally available in the school laboratory. For detailed directions advanced reference books should be consulted.

Accuracy of the Analysis. When the proximate analysis is completed, a total of the individual percentage figures should be compiled for each sample analyzed. In the absence of appreciable amounts of sodium and potassium the total should be near 100 per cent. The accuracy of the analysis is often indicated by the agreement with this figure. If mistakes have occurred, there will be lack of agreement in the duplicate values for the various determinations and in the totals for the duplicate samples. It is possible, however, to obtain analyses whose total is near 100 per cent and whose individual determinations show good agreement in duplicate results, but which are still considerably in error.

TABLE 35

RESULTS OF COOPERATIVE ANALYSIS OF LIMESTONE

Constituent	*Probable Value, Per Cent*	*Extreme Results, Per Cent*	*Average Deviation from Probable Value, Per Cent*
SiO_2	18.15	17.6 –18.92	0.41
Al_2O_3	5.70	5.10– 7.35	0.73
Fe_2O_3	1.72	0.82– 2.70	0.32
CaO (SrO)	37.65	36.02–39.83	0.57
MgO	1.94	1.31– 3.04	0.24

Such a result indicates that careful work has been done but shows the presence of a systematic error. For example, in a certain student sample which was repeatedly analyzed, both with and without fusion with sodium carbonate, the results for silica varied from 9.99 per cent in the fused sample to 11.56 per cent in the non-fused sample. In all analyses the checks obtained were good, and the total was near 100 per cent. In those analyses which showed a high result for silica, the amount of R_2O_3 and CaO was low; conversely, the samples which gave low results for silica gave high results for R_2O_3 and CaO. It is obvious that in this case the low silica result is the correct one and that the use of a faulty method of analysis led to wrong results in the samples which were not fused.

The difficulties inherent in a good mineral analysis are well illustrated by the results quoted in Table 35, which is compiled from a number of cooperative analyses on a limestone sample. These analyses were conducted under the auspices of the American Chemical Society committee on uniformity in technical analysis.[3] The extreme results in this table are far from the most probable values, and for several constituents the average value for many determinations is considerably in error. Thus, the average deviation for Al_2O_3 is 0.73 per cent in a total of only 5.70 per cent. This is 73 parts per 570 in error.

[3] *J. Am. Chem. Soc.*, **28**, 223 (1906).

PART II. PROCEDURES FOR PROXIMATE ANALYSIS OF DOLOMITIC LIMESTONE

If platinum crucibles are available they should be used for the determination of loss on ignition and for the ignition of the calcium oxalate precipitate. Either platinum or porcelain crucibles may be used for the ignition of silica and of mixed oxides. The ignition of the magnesium ammonium phosphate precipitate should be done only in porcelain crucibles (or by the optional methods listed in Chapter 21). If platinum crucibles are not available, all the ignitions except that of calcium oxalate may be done with porcelain or silica crucibles; calcium is in this event determined volumetrically. Meker burners may, if available, be substituted for the blast lamp, particularly if platinum crucibles are used. The use of a muffle furnace is recommended for all ignitions if one is available which will give a sufficiently high temperature.

Loss on Ignition

Procedure. Read page 329, regarding constancy of weight of ignited platinum crucibles. Clean two crucibles, ignite for 5 minutes at the highest temperature of the blast lamp (use silica triangles), allow to cool until no redness is visible, and transfer to a desiccator. Cool the crucibles for 15 minutes (note 1), and weigh accurately. Reignite for a 5-minute period, cool, and reweigh.

If the sample has gritty particles, which can be felt by rubbing a pinch of the powder between the fingers, grind thoroughly in an agate mortar (usually not required for student samples). Grind only a small portion at a time, then regrind in larger portions to assure complete mixing. Dry the well-ground sample overnight at 110–140°C, and store in a glass-stoppered weighing bottle which is fitted with a weighing spoon. Weigh out samples of 0.5–0.8 g (note 2), and transfer to crucibles which have previously been ignited and weighed. Cover the crucible and heat over a Tirrill burner, gradually increasing the size of the flame over a period of 5–10 minutes (note 3) until the bottom of the crucible is a dull red. Transfer to the blast lamp, and heat for 10 minutes at the highest temperature obtainable (note 4), directing the flame against the bottom and one side of the crucible, which is upright in its silica triangle. Cool, weigh, and reheat (note 5) for 10-minute periods until the weight is constant, or until the rate of change is approximately the rate at which the crucible loses weight. Compute the loss on ignition, (note 6), and calculate the percentage loss. Duplicate results should agree within 0.2 per cent.

Notes. 1. Since many of the precipitates in the analysis are very hygroscopic, it is important to observe the following precautions:

(*a*) Always cool ignited crucibles for the same length of time, with the desiccator in a cool place. This length of time should be the minimum time required to bring the crucible to room temperature, since, after removal of the cover, the atmosphere in a desiccator is for some time of practically the same humidity as the external atmosphere.

(*b*) Keep the crucible covered during the process of cooling and weighing.

(*c*) Make all weighings in as short a time as possible. On the second and subsequent weighings place the proper weights on the balance pan before the crucible is removed from the desiccator. After the crucible is on the balance pan, only one or two sets of swings should be needed in order to compute the exact weight.

2. The weight of sample used is governed by the amount of magnesium. Since this is often present in amounts as high as 20 per cent of MgO, it is not desirable to employ a sample larger than 0.5 g unless the approximate composition is known. In no case should the amount of magnesium greatly exceed 0.1 g of MgO. Use of small samples increases the relative error in the determination of the minor constituents (silicon and combined oxides) but nevertheless permits sufficient accuracy for these.

3. Heat should be gradually applied, in order to prevent too rapid decomposition of magnesium carbonate. If this occurs, there is danger of loss of sample; particles of magnesium oxide may be carried away by the escaping gas.

4. If this is the first time the blast lamp is used, ask an assistant to inspect the adjustment. A properly adjusted lamp will bring a platinum crucible nearly to white heat, or at least to a bright-yellow color.

5. Two or three periods of heating should be sufficient to expel carbon dioxide completely. If constant weight is not obtained on the third heating, crush the sample, as directed for calcium oxide on page 426, and reignite until the weight is constant. It often happens that the sample sinters into a lump which encloses undecomposed particles, thereby preventing complete decomposition.

6. It sometimes happens that attainment of constant weight requires such a long time that the student is in doubt as to the final weight of the crucible after the prolonged ignition. It is advisable to reweigh the crucible after the sample has been removed, and to use this weight as the final weight of the crucible, in order to obtain the corrected weight of sample after ignition. After removal of the sample it is necessary to heat only to redness (for removal of surface moisture) before weighing the empty crucible.

Silica

It is assumed that the sample does not require sodium carbonate fusion. If fusion is needed, the instructor will supply supplementary directions.

Procedure. Put about 10 ml of water (note 1) into a 400-ml beaker, and transfer the sample from the crucible to the beaker, taking care to prevent any loss. If any particles adhere to the crucible lid, brush them into the beaker. Remove adhering particles from the crucible by adding to it 1 ml hydrochloric acid (1:1), heating gently for a short time, and washing the solution into the beaker. Rinse the crucible thoroughly, while holding it over the beaker. Add to the beaker 15 ml hydrochloric acid, cover with a watch glass, and allow it to stand on the steam bath until the sample has completely disintegrated. The process may be hastened by breaking up the sintered mass of sample with a blunt stir-

ring rod, which is left in the solution until the final filtration. When the sample has completely disintegrated, rinse off the watch-glass cover, rinse down the sides of the beaker, and evaporate the solution to dryness on a steam bath. During the evaporation the beaker should be covered by a watch glass resting on bent glass hooks which hang on the rim of the beaker. When the residue is dry, allow it to cool, drench with 10 ml hydrochloric acid (note 2), digest on the steam bath for a short time, then add 20 ml water, and bring the solution to a boil. Decant the solution through a small ashless filter paper. Add to the residue in the beaker 20 ml dilute hydrochloric acid (1:9), and boil for 5 minutes. Filter, this time transferring the residue to the paper. Wash with dilute hydrochloric acid (1:100) ten times. Fold the filter paper, and reserve for ignition.

Evaporate the filtrate and washings to dryness on the steam bath. When no fumes of acid can be detected above the hot beaker, heat the residue for 1 hour at 120–140°C on an asbestos pad on a hot plate (note 3). Cool, drench with hydrochloric acid, digest, dilute, and filter (note 4), as previously directed. Catch the filtrate and washings in a 400- to 600-ml beaker, and reserve for the following determination. Place both filter papers in a previously ignited and weighed platinum or porcelain crucible, and ignite, completing this process by 10 minutes' heating with a blast lamp. Allow a plentiful access of air while smoking off and burning the paper. Otherwise a carbide of silicon is formed. Weigh, and reignite with a blast lamp until constant weight is obtained. Report the percentage of impure silica in the sample. Duplicate results should agree within 0.2 per cent.

Notes. 1. Too vigorous reaction may result if the ignited sample, which contains a large amount of calcium oxide, is added directly to an acid solution.

2. The sample is first drenched with concentrated acid since the salts of iron and aluminum present are more easily brought into solution in concentrated than in dilute acid.

3. The temperature used for baking the residue should not exceed 140°C, because at higher temperatures the oxides of iron present are rendered insoluble and are not redissolved during the digestion period. It is also claimed that, in the presence of magnesium, silica is rendered somewhat soluble by baking at elevated temperatures.

4. A fresh filter paper is used for the second filtration. If the original paper were used, some of the first residue might redissolve (disperse). A very small paper may be used for the second filtration, since the amount of silica obtained never exceeds a few milligrams.

Errors. 1. Incomplete disintegration of the sample.

2. Incomplete removal of iron and aluminum oxides from the silica. The error from this source is largely compensated by the amount of silica which passes into solution.

3. Introduction of silica from some reagent.

4. The presence of sodium chloride in the silica precipitate. It is essential that the solution obtained after the first dehydration following fusion be digested for some time before filtration so that all the sodium chloride is dissolved.

Decomposition of Silicate Rocks. When the amount of silica is very large, as in silicate rocks, it is necessary to fuse the original sample rather than first to decompose with acid. Weigh out on a watch glass a 4-g sample of anhydrous sodium carbonate, and put about 2 g of this into the platinum crucible which is to be used for the fusion. Accurately weigh a finely ground rock sample of 0.5–1.0 g, and transfer it to the crucible. Mix well by stirring with a glass rod, and then clean the rod by rubbing it in the unmixed sodium carbonate. Transfer the remainder of the sodium carbonate to the crucible, brushing the particles from the watch glass with a camel's-hair brush. Cover the crucible, place it vertically in a triangle, and heat, very gently at first, with a Tirrill burner. Increase the heat over a period of 5–10 minutes until the bottom of the crucible is a dull red. Lift the cover with platinum forceps, and examine the contents. If the flux is not melted, raise the temperature until the entire mass is liquid. Hold at this temperature for 30 minutes, and then heat with a Meker burner for 10 minutes. Remove the burner, and allow the crucible to cool; as it cools, hold the crucible in platinum-tipped forceps, and slowly swirl the contents so that the melt solidifies in a thin layer which is spread about the inside of the crucible. Take care to avoid dipping the forceps into the melt during this process. When the melt has solidified, allow the crucible to cool *completely*, add water to fill it approximately one third full, and cautiously heat from one side with a small flame. Do not allow the water to boil. The flame should strike the crucible above the water level. If the melt does not loosen after a few minutes' heating, carefully pour the water into a 400-ml beaker, and rinse the outside of the crucible carefully, catching all rinsings in the beaker. Replace the crucible in the triangle, and again add water and heat. If two treatments of this kind do not cause the melt to loosen, place the crucible on its side in the beaker, add sufficient water to give a depth of 1 cm, cover the beaker, and boil the solution until the melt has disintegrated.

If the melt is loosened by the first treatment, pour it into a 400-ml beaker, rinse the crucible thoroughly, both inside and out, add 1 ml of hydrochloric acid (1:1), heat for a moment, and rinse the solution into the beaker. If it was necessary to place the crucible in the beaker, remove the crucible with platinum-tipped forceps after the melt has disintegrated, and rinse thoroughly with a stream of water, catching all rinsings in the beaker. Clean the crucible cover in the same manner.

After the melt is completely transferred to the beaker, cover the beaker with a watch glass, and add from a pipet 20 ml. of hydrochloric acid, running the acid down the side of the beaker at the lip while keeping the beaker well covered. Heat on a steam bath until the evolution of carbon dioxide has ceased, then proceed as in the previous directions with evaporation, dehydration, and so on.

Combined Oxides

Procedure. Prepare a quantity of distilled ammonium hydroxide as follows (several students may cooperate in the preparation of this solu-

TABLE 36

DENSITY AND COMPOSITION OF AQUEOUS AMMONIUM HYDROXIDE SOLUTIONS

Density	*Per Cent* NH_3 *by Weight*
0.960	10
0.953	12
0.946	14
0.939	16
0.933	18
0.926	20
0.920	22
0.914	24
0.908	26

tion): Set up a 500-ml distilling flask and condenser in the usual manner. The lower end of the condenser is attached to a bent adapter. The receiving vessel is an Erlenmeyer flask which is surrounded by a bath of ice water. Fifty milliliters of water is placed in this flask, which is so arranged that the tip of the adapter reaches just below the surface of the water. Place in the distilling flask 200–300 ml ammonium hydroxide, add a little barium or calcium oxide, and distil over approximately three fourths of the solution. The distillate may be preserved for several days in a stoppered Pyrex flask without its taking up appreciable amounts of carbon dioxide or silica. With a hydrometer (obtained from the store room) determine the density of the distillate, and calculate its composition with the aid of Table 36. Dilute with boiled water to make solutions of the desired strength.

Dilute the filtrate from the silica determination to 200 ml, and add sufficient hydrochloric acid to make its concentration 1–1.5 *M* (note 1), taking into account the amount of acid used in digestion and filtration after the second dehydration of silica. Add a few drops of methyl red

indicator, heat the solution to boiling, and neutralize with about 6 *N* distilled ammonium hydroxide (note 2). Boil 1–3 minutes, allow the precipitate to settle, and decant the solution through a rapid ashless filter paper (Whatman no. 41). Wash by decantation three times with 20-ml portions of hot ammonium chloride solution (2 g per 100 ml). Bring each portion to a boil before filtering. Reserve the combined filtrate and washings for the next determination. Carefully remove the filter paper from the funnel, taking care that no precipitate is lost, and place it (note 3) in the beaker which contains the bulk of precipitate. Add to the beaker 30 ml of hot 3 *N* hydrochloric acid, and break up the paper with a stirring rod. When all the precipitate is dissolved, dilute to 100 ml, bring the solution to a boil, and precipitate as before. Filter through an ashless paper, catching the filtrate in the beaker which holds the first filtrate, and taking care to keep most of the precipitate in the beaker. Wash twice by decantation with hot ammonium chloride solution, transfer the precipitate to the filter paper, and wash thoroughly with hot ammonium chloride solution. Make the combined filtrates and washings slightly acidic with hydrochloric acid, and place the solution on the steam bath for evaporation. Drain the paper, fold, transfer to a crucible, and ignite, finally bringing to constant weight by heating for 5–10-minute periods with a blast lamp. Report the percentage of mixed oxides, R_2O_3, in the sample. Duplicate results should agree within 0.2 per cent.

Notes. 1. Sufficient acid should be present to yield on neutralization a concentration of ammonium salts high enough to prevent precipitation of magnesium hydroxide.

2. If the precipitate is so voluminous that the indicator end point cannot be seen, add ammonia until it can be detected by the odor in the steam above the solution, and then boil until the odor of the ammonia is very faint. To make this test blow away the steam before smelling of the vapor. It is essential that the final concentration of ammonia be very small, in order to prevent loss of aluminum.

It is customary to oxidize manganese at this point, in order that it may precipitate with the mixed oxides, but the oxidation prevents the use of methyl red indicator, which is destroyed by excess of oxidizing agent. Usually the amount of manganese in student samples can be neglected. If a small amount is present, it will precipitate in part with the calcium and the remainder with magnesium. If it is thought to be present in significant amounts (consult instructor), treat the first filtrate, while still alkaline, with a little ammonium sulfide reagent, filter out the precipitate of manganous sulfide, and determine the amount by ignition to the oxide. An alternative method is to precipitate the manganese with the mixed oxides by adding to the solution which is made slightly alkaline with ammonia 1 g ammonium persulfate, boiling for a few minutes, then adding ammonium hydroxide until the solution is just alkaline to litmus paper.

3. The precipitate may be dissolved by pouring acid through the filter paper, but since the presence of macerated filter paper is advantageous in the final precipitation

the entire paper is added to the acid solution. The paper readily disintegrates to give a suspension of filter pulp.

Errors. 1. Salts of calcium and magnesium may be occluded in the precipitate of hydrous oxides. A double precipitation largely eliminates this error.

2. Calcium carbonate will precipitate if there is carbonate ion in the solution. Use only distilled ammonia, and do not allow the alkaline solution to stand in the presence of air.

3. Precipitation of aluminum may be incomplete if much excess ammonium hydroxide is used.

4. Magnesium hydroxide may precipitate if insufficient ammonium salts are present.

5. Any silica remaining in the solution is dragged down by the precipitate of hydrous oxides.

6. Incomplete ignition may cause the weight of precipitate to be too great. Aluminum hydroxide in particular requires a very high temperature for complete dehydration.

7. Iron oxide may be reduced by filter paper during the ignition. There should be a plentiful access of air during the early stages of ignition. Keep reducing gases from entering the crucible.

8. If phosphates are present in large amounts, calcium phosphate will precipitate from the ammoniacal solution.

Calcium

Evaporate the (acidified) combined filtrate and washings from the mixed oxide determination to 250 ml (note 1), add a few drops of methyl red indicator, bring the solution to a boil, and add 1 to 1.5 g oxalic acid or ammonium oxalate (dissolved in a little water). Add filtered or distilled 3 *N* ammonium hydroxide from a pipet, while continuing to boil the solution, until a precipitate of calcium oxalate begins to form. Complete the neutralization (note 2) over a period of 10 minutes by slowly adding ammonium hydroxide from a buret which is mounted above the beaker. The beaker is placed on a ring stand so that it may be constantly heated. Mechanical stirring is advisable if the facilities are available. When the indicator has just turned color, allow the precipitate to settle, and test for complete precipitation by adding a little ammonium oxalate solution. If no further precipitate forms, allow the solution to stand (note 3) for 1 hour. Filter, keeping the precipitate in the beaker as far as possible (note 4). Wash twice by decantation with ammonium oxalate solution (note 5). Acidify the filtrate and washings, and place on the steam bath for evaporation.

Place the beaker with the bulk of precipitate beneath the funnel, and dissolve the precipitate in 50 ml 2–3 *N* hot hydrochloric acid solution. Pour the acid solution through the paper, in order to dissolve any particles of precipitate which may be on the paper. Add the acid in small portions from a pipet, directing the stream about the upper edge of the paper. Wash the paper several times with hot water, catching all washings in the beaker in which the first precipitate has been dissolved. Discard the paper. Dilute the solution to 250 ml, add 0.5 g oxalic acid or ammonium oxalate, and again precipitate the calcium as before. Allow to stand 1 hour, and filter. *Add the filtrate and washings to those from the first precipitation.* The choice of filtering medium is governed by the method to be used for the final estimation. If platinum crucibles are available, filter with ashless paper (Whatman no. 40 or 42), and ignite in platinum to calcium oxide. If platinum is not available, filter in a Gooch crucible, and determine the calcium volumetrically according to the procedure given on page 430.

If the calcium is to be ignited to the oxide, filter with a suitable grade of quantitative paper, and wash thoroughly with ammonium oxalate solution (note 5), until a test for chlorides with a 5-ml portion gives only a slight cloudiness (note 6). Ignite in a platinum crucible. When the paper is completely oxidized, interrupt the heating, and crush the precipitate with a blunt stirring rod. Carefully wipe particles of precipitate from the rod with a piece of ashless filter paper, place the paper in the crucible, and burn it. After crushing, ignite for 15 minutes with the blast lamp, using the highest temperature attainable. Cool and weigh; then reignite for 10-minute periods until constant weight is obtained. Three periods are generally required to assure the attainment of constant weight. Report the percentage of calcium oxide in the sample. Duplicate results should agree within 0.3 per cent.

Notes. 1. The concentration of calcium should not exceed 1 mg CaO per milliliter.

2. Note that the precipitate is largely formed under conditions of greatest solubility, that is, in hot acid solution. Slow neutralization and efficient stirring are essential in order to minimize occlusion.

3. Prolonged standing is inadvisable since magnesium oxalate may in time precipitate.

4. If calcium is of be determined volumetrically use a Gooch crucible. Follow the directions of page 430.

5. The solution contains 1–2 g per liter.

6. The sample of wash water should be acidified with HNO_3 before addition of $AgNO_3$ to test for chloride; otherwise a precipitate of $Ag_2C_2O_4$ may be obtained.

Errors. 1. Calcium may be lost in preceding determinations.

2. Incomplete ignition. Unless the precipitate is broken up, it is difficult to obtain complete conversion to the oxide.

3. Readsorption of carbon dioxide and water during cooling and weighing. Keep the crucible covered, and make the weighings rapidly. The proper weights should be placed on the balance pan before the crucible is removed from the desiccator.

4. Occlusion of sodium or magnesium oxalates. Without a double precipitation this error may be quite large.

Magnesium

Procedure. Add 50 ml nitric acid to the combined filtrate and washings from the calcium determination, and evaporate to dryness (note 1) on the steam bath. If a large residue is obtained, add nitric and hydrochloric acids, and again evaporate. Add to the residue 2 ml hydrochloric acid and 50 ml water, and digest until all magnesium salts are in solution. A slight insoluble portion is probably silica. This will be removed in the first filtration. Dilute the solution to 150 ml, add 10 ml ammonium phosphate reagent (note 2) and a few drops of methyl red indicator, cool in a bath of ice water, and precipitate by slowly neutralizing with concentrated filtered ammonium hydroxide. After the solution is neutral, continue to stir vigorously for a few minutes, then add 5 ml ammonium hydroxide in excess, and allow the solution to stand 4 hours in ice water or overnight at room temperature. Filter the solution, retaining as much of the precipitate as possible in the beaker; wash twice by decantation with cold ammonium hydroxide (1:20). Reject the filtrate and washings. Place the beaker with precipitate beneath the funnel, dissolve the precipitate by pouring through the filter paper 50 ml warm hydrochloric acid (1:9), and wash the paper with several small portions of hot water. Discard the paper. Dilute the solution to 150 ml, add 0.5 ml ammonium phosphate reagent, and again precipitate as before. Follow one of the methods on page 398 for the final filtration and weighing; probably the hexahydrate method is preferable for student use. Calculate the weight of magnesium oxide in the precipitate and the percentage in the sample. Duplicate results should agree within 0.3 per cent.

Notes. 1. For destruction of ammonium salts and oxalic acid.

2. Prepare the reagent by dissolving 25 g diammonium hydrogen phosphate in 100 ml water. Filter if the solution is not clear.

Errors. See discussion in analysis of phosphorus. The errors in the determination of magnesium are chiefly the same as in the determination of phosphorus, except for the loss of magnesium which may occur during preceding stages of the analysis. This loss is most likely to

occur in the precipitation of calcium. The presence of sodium from fusion causes some occlusion, but two precipitations reduce the amount of this occluded impurity to a negligible value, as shown by Epperson.[4] Solubility losses may be important when dealing with such a soluble precipitate as that of magnesium ammonium phosphate, but, if precipitation and washing are properly done, the loss is negligible.[5] It is imperative to use only a small quantity of wash water and to keep the temperature low. Some mechanical loss may occur through failure to remove particles of precipitate which cling to the walls of the beaker. Scratching of the wall by the stirring rod should be carefully avoided. Any calcium and manganese which may remain in solution will be precipitated at this point, the former as the phosphate, the latter as manganese ammonium phosphate.

PART III. ADDITIONAL PROCEDURES EMPLOYED IN MINERAL ANALYSIS

Purification of Silica

As previously stated, the amount of silica which remains in solution after a second dehydration is largely compensated by the amount of iron and aluminum oxides which are retained by the silica precipitate. If allowance is to be made for the silica content of the mixed oxide precipitate, it is also necessary to determine the amount of impurity in the silica precipitate. Neither of these corrections should be applied alone.

Procedure. After ignition of silica to constant weight in a *platinum* crucible (platinum is necessary for the hydrofluoric acid treatment), moisten the precipitate with 1–2 ml water, adding this carefully from a pipet and allowing it to run slowly down the side of the crucible. Add in the same manner 0.5 ml sulfuric acid (1:2). Open a bottle of hydrofluoric acid by heating the sharp end of a *clean* file and making two holes in the top of the bottle with the heated iron. Pour through one hole 3–4 ml hydrofluoric acid. *Caution: Do not allow the acid to touch the skin. Carry out the entire operation in a good hood. Avoid breathing any hydrofluoric acid fumes.* Close the wax bottle by heating the wax with a hot file and allowing melted wax to run into the hole previously made. Make an air bath by bending the wire ends of a triangle and placing it within an iron crucible. The wires are bent to form hooks which engage the rim of the iron crucible. Place the platinum crucible within the air bath, and heat until all water is expelled and only sulfuric acid remains.

[4] A. Epperson, *J. Am. Chem. Soc.*, **50**, 321 (1928).

[5] R. F. Uncles and G. B. L. Smith, *Ind. Eng. Chem., Anal. Ed.*, **18**, 699 (1946). J. I. Hoffman and G. E. F. Lundell, *Bur. Standards J. Research*, **5**, 279 (1930).

Remove the crucible from the air bath, place it on a triangle, and heat cautiously with a free flame until the sulfuric acid is expelled, keeping the flame in motion throughout the operation. A ring or microburner is advised, if available. After the acid is expelled, gradually increase the size of the flame until the crucible is heated to redness, and then ignite for a short time with a Meker burner or blast lamp. Cool and weigh. The loss in weight is the weight of pure silica in the sample. After removal of silica in this manner compute the weight of combined oxides left in the crucible by subtracting from the final weight obtained the weight of the crucible. Add the weight of oxides recovered to the weight of combined oxides obtained in the analysis.

It is very important to test the hydrofluoric acid for purity. Evaporate in a platinum crucible a volume equal to that used in the analysis, and weigh the residue. If an appreciable residue is found the acid is not suitable for use.

Dehydration of Silica by Perchloric Acid

Willard and Cake [6] have shown that perchloric acid may be employed with advantage for the dehydration of silica, without evaporating the solution to dryness, as in the usual method when hydrochloric acid is employed. A hydrochloric acid solution of the sample is treated with perchloric acid, evaporated until most of the water is expelled, and boiled for a short time. After cooling, the solution is diluted with water and the silica removed by filtration. A single treatment suffices in all but the most exacting analyses. Fish and Taylor [7] give a procedure for the use of perchloric acid in the proximate analysis of dolomitic limestones and show that the presence of perchloric acid does not affect other determinations made after silica is removed.

Procedure. *Do not attempt this method without the advice of the instructor. Perchloric acid can cause violent explosions if improperly handled.* After bringing the ignited or fused sample into solution with hydrochloric acid, add 10 ml 60–70 per cent silica-free perchloric acid, cover the beaker with a watch glass resting on glass hooks, and evaporate on a hot plate until dense fumes of perchloric acid are evolved. Cover tightly with a watch glass, and boil over a free flame for 15 minutes, taking care that the solution does not solidify. Should this occur, add more perchloric acid. Cool, add about 50 ml water, boil for a few minutes, and filter off the silica. Wash the precipitate, and ignite in the usual manner. Reserve the filtrate and washings for subsequent determinations.

[6] H. H. Willard and W. E. Cake, *J. Am. Chem. Soc.*, **42**, 2208 (1920).

[7] F. H. Fish and F. M. Taylor, *J. Chem. Education*, **10**, 246 (1933).

Volumetric Determination of Calcium

Follow the directions of page 425 for precipitation and digestion. Prepare a Gooch crucible with a tight asbestos mat. It need not be weighed. After the first precipitation and digestion, filter through the Gooch crucible, with suction. Retain as much of the precipitate as possible in the beaker. Wash twice by decantation with ammonium oxalate solution (note 5, page 426). Remove the filtrate and washings from the suction flask, and reserve for the magnesium determination. Replace the Gooch crucible on the flask, and pour through the mat 50 ml hot 3 *N* hydrochloric acid solution. Wash with a little hot water. Carefully transfer the acid solution and washings to the beaker in which the bulk of the original precipitate remains. The precipitate should dissolve in the acid solution.

Carry out the second precipitation of calcium oxalate according to directions of page 426, and allow to stand 1 hour. Filter through the Gooch crucible used for the first precipitation. Wash twice by decantation with ammonium oxalate solution, and then transfer the precipitate to the Gooch crucible. Complete the washing with several 3–5 ml portions of ice-cold water, to remove excess ammonium oxalate. Interrupt the suction before adding each portion, and then suck dry before the next portion is added. Add the washings to the second filtrate, and reserve for the magnesium determination.

Remove the Gooch crucible from the holder, and place it in a 400-ml beaker. Add to the beaker 30 ml 4–5 *N* sulfuric acid, and warm to facilitate solution of the calcium oxalate. Break up the asbestos mat with a stirring rod, and remove the Gooch crucible, rinsing thoroughly with a stream of water from a wash bottle. Dilute the solution to about 80 ml, and heat to 80–90°C. Titrate with standard permanganate solution according to the procedure of page 218. A 0.2 normal solution should be used if available, since with the usual dolomite samples a volume of 70–80 ml of 0.1 *N* permanganate solution may be required. Determine a blank by diluting 30 ml 4–5 *N* sulfuric acid to 80 ml, heating, and titrating with permanganate to the appearance of a permanent color. Compute the weight and percentage of calcium as CaO in the sample. The equivalent weight is CaO/2 since each mole of CaO is equivalent to a mole of oxalic acid.

Carbon Dioxide by Gas Evolution

The loss on ignition is not an accurate measure of the carbon dioxide content of a limestone, because of the other changes which occur on ignition of a sample. A direct determination of carbon dioxide may be

made by treating the sample with acid and passing the evolved gas through an absorption train which removes in turn water vapor and carbon dioxide. The gain in weight of the absorption vessel gives the weight of carbon dioxide in the sample. The determination is not of particular importance in the analysis of limestones, but is included in quantitative analysis because it serves as an introduction to the general technique of gas-absorption determinations, which are very important in the analysis of organic compounds by combustion and in the determination of carbon in steel. The chief difficulties involved in the technique of this experiment are in obtaining an absolutely tight absorption train, in complete removal of water vapor and other impuri-

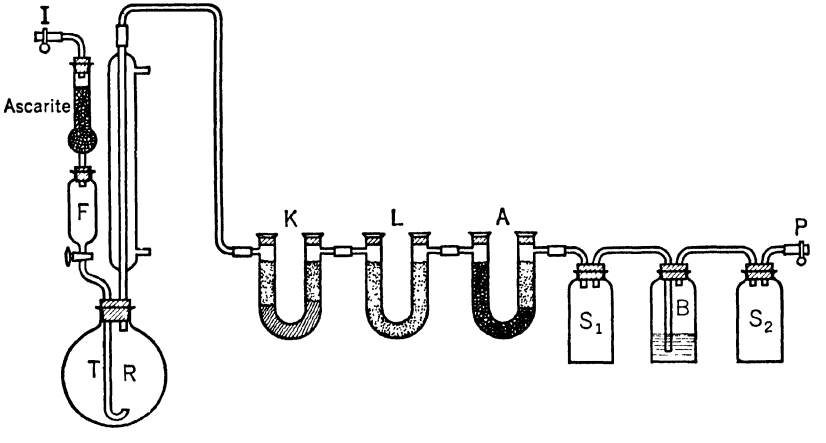


FIG. 32. Determination of carbon dioxide by gas evolution.

ties from the gas, in complete absorption of carbon dioxide, and in weighing the large glass apparatus used as absorbing vessels.

Many modifications of the absorption train may be introduced to conform with the apparatus available, but the essential principles are embodied in the apparatus described. A schematic diagram is shown in Fig. 32. The glass tubing should be of the same size throughout and should fit tightly into the rubber tubing used for connections. The side arms on all U-tubes [8] should be of the same size as the glass tubing employed for connections. The tops of the U-tubes are closed by corks, which are cut off flush with the top of the tube and covered with a layer of paraffin. All glass ends should be fire-polished, and the glass joints should touch one another. Rubber connections should be $1\frac{1}{2}$–2 in. long,

[8] Several types of absorption tubes now on the market are superior to the U-tubes as described and should be substituted for the U-tubes if available. The methods of operation are the same regardless of the type of absorption tube used.

to give gas-tight joints. The U-tubes must be closed, after removal from the train, by slipping over the side arms a piece of rubber tubing, sealed by a glass plug at the other end.

Formerly, calcium chloride was employed as absorbent for water vapor, and a 50 per cent solution of potassium hydroxide as absorbent for carbon dioxide. In modern practice calcium chloride is largely replaced by more efficient drying agents which may be regenerated by heat after they become saturated with water. Widely used are Dehydrite, $Mg(ClO_4)_2 \cdot 3H_2O$; Anhydrone, $Mg(ClO_4)_2$; Drierite, $CaSO_4$; Dessichlora, $Ba(ClO_4)_2$; and others of similar properties. All are efficient and satisfactory. Potassium hydroxide solution for carbon dioxide, which requires a fragile Geissler bulb, has been largely superseded by the introduction of solid carbon dioxide absorbents such as Ascarite, a mixture of sodium hydroxide with asbestos fiber.

The operation of accurately weighing a large glass vessel requires some care. Because of the large surface the amount of water vapor which is held by the glass varies with the humidity, and a variation of 1–2 mg may be noted in the weight of a U-tube on successive days if humidity conditions have changed. The effect of surface adsorption may be minimized by means of a counterpoise, a similar glass vessel which is always suspended from the right-hand arm of the balance when a weighing is made. Instead of the total weight of the absorption tube, only the difference in weight between the tube and the counterpoise is determined. The absorption tube and the counterpoise should be wiped with a damp cambric cloth 10 minutes before weighing and should be allowed to stand in the balance case until the weighing is made. By this procedure the amount of surface moisture on the two objects is made approximately the same. Use of a damp cloth for wiping prevents the glass from acquiring an electric charge. Closed glass vessels must be momentarily opened just before weighing, in order to insure pressure equalization within and without the vessel. With a counterpoise and the afore-mentioned precautions it is easy to reproduce weights, on even a large vessel, within 0.2–0.4 mg. It is convenient to select as counterpoise a vessel which weighs less than the absorption vessel, so that weights are added to the right-hand pan of the balance rather than to the object pan. If U-tubes are used for absorption, they may be equipped with hooks, made from copper wire, which suspend the tubes from the balance beam. Care must be taken to prevent swaying of the suspended tube during a weighing.

Procedure. Apparatus. The apparatus shown in Fig. 32 is made of readily available equipment. The reaction vessel *R* is a round-

bottomed flask with a wide mouth.[9] It is fitted with a two-hole rubber stopper. Acid is introduced from the dropping funnel F by means of the bent tube T. The lower end is bent upwards in order to prevent escape of gas through the acid funnel. Air used to sweep the apparatus is drawn in through this funnel, after first passing through a tube of Ascarite. The other hole of the stopper carries a small condenser, mounted vertically. Its function is to prevent a large amount of steam going over into the drying tubes.

After passing through the condenser, the evolved gas goes through two drying tubes K and L. The central portion of K is charged with anhydrous copper sulfate whose function is to remove hydrogen sulfide and hydrogen chloride from the gas. The remainder of K is charged with one of the drying agents previously mentioned. If none of these is available, calcium chloride may be used, provided that it is first saturated with carbon dioxide (because of the calcium oxide often present), and the excess carbon dioxide is removed by sweeping with purified air in the train. L is charged with the same drier as K. From L the gas passes into the U-tube A, which is filled with Ascarite for the first two thirds of its length. The final third is filled with drying agent to remove any water formed in the reaction of carbon dioxide with sodium hydroxide. Ascarite itself removes a large part of this water. All the U-tubes are fitted with cotton plugs at the two ends in order to prevent dust from the absorbents from being carried along by the gas stream.

From A the gas passes through a safety bottle S_1, a sulfuric acid bottle B, and another safety bottle S_2. The last is connected to a water aspirator pump by a length of suction tubing. The rate of flow is best regulated by a screw clamp P on the suction tubing. A pinch clamp on the inlet tube at I closes the apparatus when not in use.

Before use the apparatus must be tested for tightness. The rubber tube at I is tightly closed by a pinch clamp, and the clamp P is closed. Water is turned on at the aspirator pump, and the clamp P is opened to permit a steady stream of bubbles to pass through the sulfuric acid in B. If the train is gas-tight, the rate of flow decreases rapidly until only an occasional bubble may be seen in B. If not tight, the rate of flow continues to be rapid. At the conclusion of the test, close clamp P, and open the clamp at I. Never turn off the aspirator pump while the train is evacuated, since this would cause water to be drawn back into the apparatus.

Procedure. Blank. When the train is tight, make a blank run. Aspirate a current of air through the apparatus for about 10 minutes at

[9] A three-neck distilling flask (Pyrex no. 4945) of 200 ml capacity is advantageously used for the reaction vessel if available.

a rate of 2 bubbles per second. Stop the air current, remove the absorption bulb, close it with rubber tubes, and weigh with the aid of a counterpoise. Connect the absorption tube to the apparatus; put 30 ml of boiled water in the reaction flask and 50 ml of hydrochloric acid (1:1) in the dropping funnel. Connect the apparatus, remove the tube which leads to the aspirator, and slowly run most of the acid into the reaction flask at such a rate that 2–3 bubbles of gas pass through the sulfuric acid bottle per second. When nearly all the acid is added, close the stopcock in *F*, and heat the reaction flask with a small flame for a few minutes until the solution comes to a boil. Remove the flame, connect to the aspirator, open the stopcock on the dropping funnel, and begin to draw air through the apparatus at a rate of 2–3 bubbles per second, taking care to maintain a sufficient rate of gas flow to prevent sulfuric acid sucking backwards as the flask cools. Continue to draw air through the apparatus for 30 minutes. Remove and reweigh the absorption bulb. The weight should agree with the previous weight within 0.3–1.0 mg. When a satisfactory blank has been obtained, a determination may be started.

Procedure. Analysis. Sweep the system for 10 minutes, and weigh the absorption bulb (unless the weight is already known from a previous determination). Replace the bulb in position. Weigh out a 1-g sample, and introduce it into the reaction vessel. Add to the flask 30 ml of water, put in the dropping funnel 50 ml of hydrochloric acid (1:1), connect the train, and add the acid as in the blank, but more slowly because there will be evolution of carbon dioxide. When most of the acid is added, close the stopcock, and heat the flask until evolution of gas ceases. Connect the aspirator, and draw air through the apparatus for 30 minutes. Determine the gain in weight of the absorption tube, subtract from this the average gain in weight during a blank run, and compute the percentage of carbon dioxide in the limestone. Duplicate results should agree within 0.3 per cent. After one determination is completed, another may be started immediately, using the final weight of the absorption tube from the previous determination as the beginning weight for the new determination.

The chief errors are those mentioned in the introductory section. It is essential to have a tight train and to pass the gas slowly enough so that absorption is complete. If difficulty is encountered in obtaining a satisfactory blank, it may be due to incomplete removal of hydrochloric acid from the gas. In that case the amount of anhydrous copper sulfate may be increased. The Ascarite tube at *I* must be sufficiently long to remove all carbon dioxide from the entering gas.

QUESTIONS

1. Construct an outline for a scheme of qualitative analysis of a dolomitic limestone, considering only the major constituents.

2. If a limestone rock which contains SiO_2, CO_2, and metallic oxides of Fe, Al, Ca, Mg, and K is fused with sodium carbonate and the melt is extracted with water, what is the composition of the residue and of the solution?

3. What modification of the procedure given for limestone analysis would be needed for a silicate rock?

4. Suggest a method for the determination of ferrous iron, as FeO, in a rock analysis.

5. What does "loss on ignition" determine? Is it higher or lower than the CO_2 content of a limestone? Why does ignition aid in the subsequent acid decomposition of the sample?

6. What might cause the ignited silica to have a brownish tinge? How can this error be eliminated?

7. Under what circumstances might an analyst report a much higher percentage of silica than is actually present in a silicate rock?

8. What two factors lead to high results for silica?

9. Should the constituents of apatite, $Ca_5F(PO_4)_3$ be reported as the oxides? Why?

10. An analyst made the following errors in the procedure for mixed oxides. In each case tell what might happen because of the faulty procedure, and what effect it would have on the results.

(*a*) Use of undistilled ammonia.

(*b*) The presence of insufficient HCl in the solution before ammonia was added.

(*c*) The ignition of the precipitate under such conditions that there was an insufficient access of air.

11. If a mineral contains an amount of P_2O_5 considerably in excess of R_2O_3, could the separation of calcium and mixed oxides be accomplished by the methods of this chapter?

12. Why must a large excess of ammonia be avoided in precipitation of the mixed oxides?

13. An R_2O_3 precipitate is fused with $KHSO_4$ and the resulting mixture treated with water. If the precipitate is assumed to consist of Fe_2O_3, TiO_2, Al_2O_3, and SiO_2, what is the composition of the aqueous solution?

14. What are the difficulties involved in weighing calcium as the carbonate? As the sulfate? If platinum crucibles are not available, what method should be used for the determination of calcium?

15. Why must ammoniacal solutions never be allowed to stand in glass vessels during a mineral analysis?

16. If silica has been absorbed from glass vessels subsequent to the determination of the combined oxides, how may it affect the analysis? Can it be readily removed?

17. Why must the ammonium hydroxide used for the precipitation of combined oxides be distilled, whereas in other stages of the analysis it need only be filtered?

18. Why is the precipitation of calcium oxalate started in acid solution? Why is the process of reprecipitation used? Why is a period of digestion longer than several hours harmful? Discuss three ways in which the precipitate may be treated to determine the percentage of CaO.

19. What would be the effect on the percentage of CaO reported of each of the following errors?

(*a*) Incomplete decomposition of a complex calcium silicate.

(*b*) Ignition of precipitated CaC_2O_4 at too low a temperature.

(*c*) Postprecipitation of MgC_2O_4.

(*d*) Occlusion of Ca^{++} in the mixed oxides determination.

(*e*) Presence of CO_2 in the NH_3 used for mixed oxide determination.

(*f*) The R_2O_3 precipitate is allowed to stand overnight in equilibrium with its supernatant solution and the atmosphere.

20. What would be the effect on the reported percentage of MgO of each of the following errors?

(*a*) Too low a concentration of NH_4^+ during the R_2O_3 determination.

(*b*) Use of a hot ammonia solution for washing $MgNH_4PO_4$.

(*c*) Partial precipitation as $MgHPO_4$ instead of $MgNH_4PO_4 \cdot 6H_2O$, if the precipitate is weighed as the hydrate; if the precipitate is weighed after ignition to the pyrophosphate.

21. What should magnesium be precipitated as? weighed as? Why are the precipitations carried out in cold solution? Why is reprecipitation used? What is the purpose of evaporating the solution to dryness several times with HNO_3 before starting the magnesium precipitations?

22. List three places in limestone analysis other than in the actual determination of magnesium where one might account for a loss of magnesium.

23. A dolomite contains Ti, Zr, Cr, Ce, P, V, and Mn. State the formula for the precipitate given by each of these. Where, in the proximate analysis, will the precipitate be formed?

24. Why is the determination of sodium and potassium made on a portion of original sample rather than on a sample from which the other constituents have been removed?

PROBLEMS

1. A 1.000-g sample of limestone gave a precipitate of Fe_2O_3 and Al_2O_3, weighing 0.0800 g. The precipitate of mixed oxides was fused with $KHSO_4$, dissolved in sulfuric acid, and passed through a Jones reductor, and the iron was titrated with 20.00 ml of 0.0100 *N* permanganate solution. Calculate the percentage of FeO and of Al_2O_3 in the limestone (assume all iron present as FeO in the original sample).

2. Calculate the percentage of CaO in a limestone from the following data:

Weight of sample	0.7500 g
Volume of $KMnO_4$ to titrate acid solution of CaC_2O_4	15.00 ml

40.00 ml $KMnO_4$ is equivalent to 35.00 ml $Na_2S_2O_3$.

35.00 ml $Na_2S_2O_3$ is equivalent to 0.2300 g As_2O_3.

3. From a 0.8125-g sample of limestone there is obtained an impure ignited SiO_2 which weighed 0.0837 g. The residue after treatment of the SiO_2 with HF and H_2SO_4 weighed 0.0045 g.

(*a*) What is the reported percentage of SiO_2 without purification?

(*b*) What is the reported percentage of SiO_2 after purification?

(*c*) On the basis that the total impurity in the SiO_2 was calcium, which was weighed as CaO with the SiO_2 and as $CaSO_4$ after the purification, what error is made by not taking into account the differences in weight between the CaO and $CaSO_4$?

4. Because of insufficient ignition a supposed CaO precipitate from a 1.000-g sample of limestone weighs 0.4125 and contains 5.30 per cent of its own weight of $CaCO_3$. What is the reported percentage of CaO, and what is the true percentage of CaO?

5. 0.2000 g of a supposedly ignited precipitate of $Mg_2P_2O_7$ contains 10.0 per cent of its own weight of $Mg_3(PO_4)_2$. What should the ignited product have weighed had all the magnesium been properly precipitated as $MgNH_4PO_4 \cdot 6H_2O$? If it is assumed that all the magnesium is present in the mineral as $MgCO_3$, what is the correct percentage of this constituent in the sample which weighed 0.5000 g?

6. A 0.2564-g sample of a rock which contains only calcium and magnesium carbonates gives 0.1428 g of mixed oxides after ignition. What weight of rock will be needed to furnish 10 l. of carbon dioxide, measured at standard conditions?

7. If it is assumed that in a limestone all the calcium and magnesium are present as carbonates and that there are no other carbonates in the mineral, what is the percentage of CO_2 in a rock which analyzes 40.07 per cent CaO and 11.67 per cent MgO?

8. A sample is 20.00 per cent CaO and 25.00 per cent MgO. Could this sample be simply a mixture of $CaCO_3$ and $MgCO_3$ and nothing else?

9. A limestone analyzes as follows:

$CaCO_3$	91.7 %
$MgCO_3$	3.15%
SiO_2	1.75%
R_2O_3	1.32%
Volatile	1.84%

What is the composition of the resultant lime produced by strong ignition? Assume only the loss of CO_2 and volatile matter on heating.

10. A rock sample which weighed 0.5200 g gave a 0.0416-g residue of sodium and potassium chlorides. From this residue a 0.0648-g precipitate of potassium chloroplatinate was obtained. Calculate the percentages of sodium oxide and potassium oxide in the sample.

11. In the J. Lawrence Smith method for the estimation of K_2O and Na_2O a 0.7500-g sample of limestone gave a precipitate of mixed halides which weighed 0.0100 g and which on proper treatment yielded a precipitate of $KClO_4$ which weighed 0.0075 g. Find the percentages of K_2O and Na_2O in the rock. If the potassium had been separated as the chloroplatinate, what would the precipitate have weighed? If this latter precipitate had been strongly ignited and washed, what would it have weighed?

PART FOUR

Special Methods

CHAPTER

23

Analysis by Electrodeposition

THEORY

Electrolysis. The decomposition of a solution by passage of an electric current is known as *electrolysis.* During electrolysis positive ions migrate to the electrode connected to the negative terminal of the source of current, while negative ions migrate to the positive electrode. At the electrodes positive ions take up electrons and negative ions give up electrons. If there are in a solution several ions which may undergo electrolysis, the positive ion discharged is that with the greatest tendency to take up electrons, whereas the discharged negative ion is the one with the least tendency to hold electrons.

Laws of Electrolysis. The amount of an element set free by the passage of a current is proportional to the current which passes. Faraday's law states that "the same quantity of electricity sets free at the electrode the same number of equivalent weights of any substance." The practical unit of electricity is based on this law. One faraday of electricity, the unit quantity, will liberate one equivalent weight of any substance. The faraday is 96,500 *coulombs.*

The current passing through a solution is measured in *amperes,* that is, coulombs per second. The current is related to the applied potential and the resistance by Ohm's law,

$$\text{Effective emf} = \text{current} \times \text{resistance}$$

The effective emf is the applied emf minus the decomposition voltage

(see page 440), since the decomposition voltage is in effect an opposing emf. That is,

$$E_{\text{applied}} - E_{\text{decomp.}} = IR$$

The resistance R is measured in ohms. It is proportional to the distance between the electrodes and inversely proportional to the area of the electrodes.

Electrode Reactions. The reaction which occurs at an electrode depends on the ions present in solution and the nature of the electrode. In aqueous solution, with inert electrodes of platinum, hydrogen is liberated at the cathode (negative electrode) when the other positive ions present are substances above hydrogen in Table 25, but substances below hydrogen are preferentially reduced. Likewise, oxygen (from water) is liberated at the anode if other ions present have greater oxidation potential than the OH^- ion. If the charged electrode is readily oxidized or reduced, no element is liberated, but instead the electrode is attacked. A few examples will illustrate these statements.

Example 1. Silver nitrate is electrolyzed between silver electrodes.

At cathode $Ag^+ + e = Ag$

At anode $Ag - e = Ag^+$

Example 2. Silver nitrate is electrolyzed between platinum electrodes.

At cathode $Ag^+ + e = Ag$

At anode $2H_2O - 4e = O_2 + 4H^+$

Example 3. Sodium chloride is electrolyzed between a silver chloride cathode and a silver anode

At cathode $AgCl + e = Ag + Cl^-$

At anode $Cl^- + Ag - e = AgCl$

There may also occur at the electrodes a change in valence without liberation of an elementary substance. For example, Fe^{++} may be oxidized at an anode,

$$Fe^{++} - e = Fe^{+++}$$

and Fe^{+++} may be reduced at a cathode,

$$Fe^{+++} + e = Fe^{++}$$

Decomposition Potential. If current is passed through a solution, no appreciable decomposition occurs unless the voltage applied to the electrodes exceeds a certain minimum value, which is known as the de-

composition potential of the ions involved. The decomposition potential is related to the emf set up by the cell resulting from the electrolysis. Suppose, for example, that 1 M solution of zinc iodide is electrolyzed between platinum electrodes. Zinc and iodine are liberated:

$$Zn^{++} + 2e = Zn \quad \text{at } - \text{ electrode}$$

$$2I^- - 2e = I_2 \quad \text{at } + \text{ electrode}$$

As soon as this reaction occurs, there is built up the cell,

$$Zn,\ Zn^{++} + I^-,\ I_2,\ Pt$$

The potential of this cell is readily computed by the methods of Chapter 15.

$$\begin{array}{rll} Zn = Zn^{++} + 2e & E^\circ & = +0.76 \\ 2I^- = I_2 + 2e & E^\circ & = -0.53 \\ \hline Zn + I_2 = Zn^{++} + 2I^- & E^\circ_{1-2} & = +1.29 \end{array}$$

$$E_{1-2} = 1.29 - \frac{0.059}{2} \log [Zn^{++}][I^-]^2$$

In a 1 M solution of ZnI_2 the concentration of Zn^{++} is 1 and the concentration of I^- is 2 M. Substitution of these values for the concentrations of the ions gives

$$E_{1-2} = 1.29 - \frac{0.059}{2} \log (1)(2)^2$$

$$= 1.27 \text{ volts}$$

It is noted that in this cell the I_2 is the positive electrode and the Zn the negative. Thus the cell emf is in opposition to the applied emf, and in order to pass any current through this cell the applied emf must exceed the cell emf of 1.27 volts. The cell emf is therefore known as the theoretical decomposition voltage.

The student should at this point construct an electrical diagram for the electrolysis circuit and mark the voltage and polarity at each electrode, to understand that the cell emf opposes the applied emf.

Overvoltage. When the decomposition potential of a cell is computed, as previously, it is often found that application of the theoretical potential will not cause electrolysis. In some cases it may be necessary to exceed the theoretical potential by several volts before electrolysis will proceed. The excess potential, above the theoretical decomposition potential, is known as *overvoltage.*

Overvoltage is chiefly of importance at electrodes where a gas may be liberated; usually little or no overvoltage is found for the liberation of metals. The liberation of a diatomic gas (practically all those encoun-

tered in analytical depositions are diatomic) must take place in two steps:

$$X^+ + e = X \text{ (atoms)}$$

$$2X = X_2 \text{ (molecules)}$$

The theoretical explanations which have been proposed assume that one or the other of the two steps is a reaction which under certain conditions is retarded. A discussion of these theories is beyond the scope of an elementary book; only one is presented, and that is given chiefly to emphasize the factors which influence overvoltage. According to this theory, the second reaction, the combination of atoms to form gaseous

TABLE 37

APPROXIMATE HYDROGEN OVERVOLTAGES ON DIFFERENT METALS *

Current Density *amp per cm²*	*Platinized* Pt	*Smooth* Pt	Cu	Fe	Hg	Ni	Al
10^{-4}	0.003	—	0.35	0.22	0.28	—	0.50
10^{-3}	0.015	0.024	0.48	0.40	0.9	0.56	0.57
10^{-1}	0.038	0.19	0.80	0.82	1.06	1.05	1.0
1	0.048	0.68	1.25	1.29	1.13	1.24	1.29

* *International Critical Tables*, VI, 339–340.

molecules, is influenced by the metal on which the gas is liberated. Some metals catalyze the reaction markedly, others to a lesser extent. When there is an accumulation of atoms on the metal surface, there is a tendency for the liberated atoms to go back into solution, and therefore a higher voltage is required for further deposition.

Among the factors which influence overvoltage at gas electrodes are the following:

1. *Material of electrode.* As previously stated, there is a difference in the overvoltage found for different electrodes. Overvoltages for hydrogen and the halogens are practically zero at small current densities [1] when a platinized platinum [2] electrode is employed, whereas on mercury or metal amalgam surfaces the overvoltage of hydrogen is high.

Some approximate hydrogen overvoltages are shown in Table 37, to illustrate the variations with different metals.

[1] The current density at an electrode is the current passing per unit area of electrode surface. Usually the density is stated in amperes per square centimeter, N.D., or in amperes per square decimeter, $N.D._{100}$.

[2] A platinized platinum electrode is made of platinum covered by a coat of electrolytically deposited platinum. The term is used to differentiate the electrolytically deposited surface from the surface of a massive electrode. Platinized platinum electrodes are usually employed when equilibrium is sought between a gas and its ions.

2. *Nature of surface.* The condition of a surface will have some effect on overvoltages, particularly at high current densities. Probably this effect, as shown by comparison of the data for smooth and platinized platinum electrodes, is due to the extent of surface available for catalyzing the atomic reaction.

3. *Current density.* As the current density is increased, there is a rise in overvoltage for all metal surfaces and for all gases liberated. There is a tendency towards a limiting overvoltage at higher current densities; in general, the overvoltages on different metals tend to approach a common value at high current densities.

4. *Temperature.* Usually the overvoltages decrease as the temperature increases. The hydrogen overvoltage on platinized platinum is an exception, being apparently independent of temperature.

From the analytical chemist's viewpoint the overvoltages of importance are those of hydrogen and oxygen, particularly the former. In nearly all electrolyses there is some evolution of hydrogen at the cathode, due to local exhaustion of metal ions in the vicinity. If it were not for hydrogen overvoltage, this effect would predominate to such an extent that complete deposition of certain metals would be difficult. Often the analyst may by increasing the overvoltage make depositions that cannot otherwise be made. For example, a mercury cathode (a pool of mercury, connected to the negative terminal) is often employed to take advantage of the high hydrogen overvoltage on mercury. By means of the mercury cathode, iron and zinc can be completely separated from aluminum. The amalgamation of zinc for use in a Jones reductor prevents evolution of hydrogen because of the high overvoltage of hydrogen on mercury.

A striking illustration of the effect of overvoltage is provided in the familiar experiment of placing a strip of amalgamated zinc in dilute sulfuric acid and touching the zinc with a platinum wire. When the wire is removed, there is little evolution of hydrogen. When the wire is in contact with the zinc, there is copious evolution, but all the gas appears to come from the platinum wire. Because of the high overvoltage on the zinc surface the reaction,

$$H^+ + e = H$$

proceeds very slowly. When the platinum wire is touched to the zinc surface, the electrons released by the reaction,

$$Zn - 2e = Zn^{++}$$

may flow into the platinum wire; there, because of the low overvoltage, the deposition of hydrogen may proceed rapidly.

$$2H^+ + 2e = H_2$$

Separation by Electrolysis. If the decomposition voltages for two compounds in the same solution lie far apart, one of the substances may be almost completely deposited by application of a potential which is between the two decomposition voltages. For example, the decomposition voltage of a zinc sulfate solution is 2.55 volts, of a sulfuric acid solution 1.67 volts, and of a copper sulfate solution 1.49 volts. If a potential of 2.0 volts is applied to a sulfuric acid solution of zinc and copper sulfates, the copper is almost completely deposited, some hydrogen is liberated, but no zinc ion is deposited.

Because of overvoltage effects and the effect of *p*H on electrolysis (see below), the exact computation of decomposition voltages from aqueous solutions is complicated. The completeness of separation of two metals is, however, readily computed by a consideration of the equilibrium relations. For example, we may compute the concentration of cupric ion at which there will be simultaneous deposition of copper and zinc from a solution in which the concentration of zinc ion is 1 *M*.

The equilibrium is evaluated by means of the cell,

$$\mathrm{Zn},\ \mathrm{Zn^{++}} \parallel \mathrm{Cu^{++}},\ \mathrm{Cu}$$

Following the treatment of Chapter 15,

$$\begin{array}{lll} \mathrm{Zn} = \mathrm{Zn^{++}} + 2e & E^\circ & = +0.76 \\ \mathrm{Cu} = \mathrm{Cu^{++}} + 2e & E^\circ & = -0.34 \\ \hline \mathrm{Zn} + \mathrm{Cu^{++}} = \mathrm{Zn^{++}} + \mathrm{Cu} & E^\circ_{1\text{-}2} & = +1.10 \end{array}$$

At equilibrium,

$$0 = 1.10 - \frac{0.059}{2} \log \frac{[\mathrm{Zn^{++}}]}{[\mathrm{Cu^{++}}]}$$

Solving gives

$$\frac{[\mathrm{Zn^{++}}]}{[\mathrm{Cu^{++}}]} = 10^{37.3} = 2.0 \times 10^{37}$$

Before any Zn can deposit from a 1 *M* solution, the concentration of cupric ion must be reduced to $10^{-37.3}$.

Effect of Concentration on Decomposition Voltage. The decomposition voltage not only depends on the oxidation potentials of the products set free in the electrolysis, but in addition is influenced by the concentrations of the ions that are liberated. The relation between the theoretical decomposition voltage and concentration has been shown on page 440 for a zinc iodide solution. As the concentrations of zinc and iodide ions diminish, the voltage rises. For example, when the solution, originally specified to be 1 *M*, has been electrolyzed until the salt concentration is 10^{-5} *M*, the concentration of Zn^{++} is 10^{-5}, and the concentra-

tion of I^- is 2×10^{-5}. Substitution of these concentration values into the equation gives as the theoretical decomposition voltage 1.72 volts.

Concentration effects may cause incomplete separation of two metals by electrolysis, even though the decomposition potentials lie far apart. As electrolysis proceeds, there is local exhaustion of one ion in the vicinity of the electrode. Unless the applied voltage is carefully controlled, there is danger that because of this local effect another ion may be simultaneously deposited. For this reason it is difficult to make a complete separation of two ions unless they have oxidation potentials very far apart or unless the decomposition potential of hydrogen ion lies between those of the sought ions.

Part of the effectiveness of the mercury cathode in the electrolysis of ions that are otherwise difficult to deposit is due to the concentration effect. When an ion is reduced at a mercury cathode and the liberated metal dissolves in the mercury, its activity is lowered, and there is less tendency to redissolve. Consequently, the decomposition voltage is lowered. To compute the theoretical decomposition voltage when the deposited metal is dissolved in mercury, the mole fraction of the metal is taken as the activity.

Effect of *p*H. Since hydrogen ion is always present in aqueous solutions, the effect of *p*H must be taken into account in all electroanalyses. Metals which are below hydrogen in the oxidation-potential table may be deposited from acid solutions. At the same time there is some evolution of hydrogen, due to local exhaustion of metal ions in the vicinity of the electrode. Metals which lie above hydrogen cannot be deposited from acid solution except when the overvoltage of hydrogen is so great that its position in the oxidation-potential series is shifted to higher values. For deposition of metals which lie far above hydrogen it is necessary to reduce the hydrogen-ion concentration by making the solution alkaline. The separation of copper and nickel is an example of the effect of *p*H. Copper is deposited from acid solution. When the concentration of copper is locally depleted, no nickel is precipitated because of the plentiful supply of hydrogen ion in the vicinity of the electrode. After all the copper is removed, the solution is made alkaline with ammonia, and the nickel is then electrolyzed. Were it not for the effect of hydrogen ion, a complete separation of the two metals would be difficult, since it would be necessary to control carefully the applied potential to keep it below the decomposition potential for nickel sulfate until after deposition of copper was complete. In the presence of the acid no nickel is deposited.

The effect of overvoltage on the liberation of hydrogen may be quantitatively evaluated. For illustration we may compute the concentra-

tion of hydrogen ion that will permit deposition of zinc when the concentration of Zn^{++} is 10^{-6} M. We shall assume a hydrogen overvoltage of 0.50 volt. The oxidation potential of hydrogen ion is, therefore, +0.5 volts, since the effect of the overvoltage is to make a higher potential necessary for deposition of hydrogen. Because of the overvoltage hydrogen becomes more like the active metals such as zinc and sodium.

Solution: Set up the cell,

$$Zn, Zn^{++} \parallel H^+, H_2, Pt$$

$$\begin{aligned} Zn &= Zn^{++} + 2e \qquad E^\circ = +0.76 \\ H_2 &= 2H^+ + 2e \qquad E^\circ = +0.50 \end{aligned}$$

$$Zn + 2H^+ = Zn^{++} + H_2 \qquad E^\circ_{1-2} = +0.26$$

At equilibrium,

$$0 = 0.26 - \frac{0.059}{2} \log \frac{[Zn^{++}]}{[H^+]^2}$$

Solving yields

$$\frac{[H^+]^2}{[Zn^{++}]} = 10^{-8.8}$$

$$[H^+]^2 = 10^{-8.8} \times 10^{-6} = 10^{-14.8}$$

$$[H^+] = 10^{-7.4}$$

$$p\mathrm{H} = 7.4$$

Therefore zinc may be electrolyzed from a slightly basic solution, provided conditions are such that the hydrogen overvoltage is at least 0.5. The student should make a similar computation for the condition of no overvoltage.

Reactions at the Anode. In most of the electrolytic analyses encountered the only reaction observed at the anode is the oxidation of hydroxide ion,[3]

$$2OH^- - 4e = O_2 + 2H^+$$

If any ion that can be oxidized to a higher valence state is present in the solution, this reaction also will occur. No detectable change will take place, however (because the oxidized ion will be reduced at the cathode),

[3] Since the OH^- must be furnished by the ionization of water in acidic or neutral solutions, the actual process taking place is the sum of two equations:

$$\begin{aligned} 2H_2O &= 2H^+ + 2OH^- \\ 2OH^- - 4e &= O_2 + 2H^+ \end{aligned}$$

$$2H_2O - 4e = O_2 + 4H^+$$

unless some substance is present that will on oxidation form an insoluble precipitate. When lead (or manganese) is oxidized to the tetravalent form in acid solution, there results a precipitation of the dioxide.

$$Pb^{++} - 2e = Pb^{++++}$$

$$Pb^{++++} + 2H_2O = PbO_2 + 4H^+$$

This reaction is the basis for the electrolytic determination of lead. When it is carried out in high concentration of nitric acid, there is quantitative deposition of lead dioxide at the anode. The deposit is sufficiently firm and adherent that the electrode may be washed without loss of precipitate.

EXPERIMENTAL

Apparatus. The electric circuit used is shown in Fig. 33. Current is obtained from a 6- or 12-volt battery. Regulation is by a slide-wire resistance which must be able to carry the maximum current without overheating. A voltmeter *V* measures the potential across the electrodes, and an ammeter *A* measures the current. Since the resistance of the electrolytic cell is fixed, it is, of course, impossible to regulate separately the voltage and amperage of the system, but both meters are provided so that the student may accurately know the conditions employed.

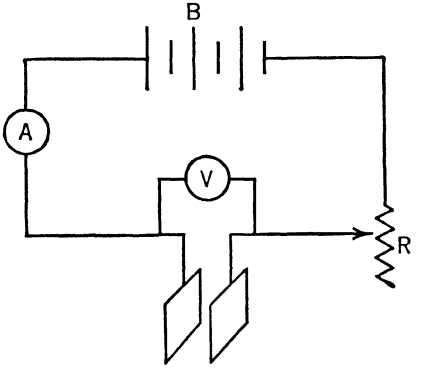


FIG. 33. Circuit employed for electrodeposition.

The electrodes are usually of platinum, although other metals may be employed for the cathode in special cases. Gauze electrodes are preferable, because of the large surface area. The cathode is a large cylinder, 2–3 cm in diameter and about 3 cm in length. It is supported by a heavy platinum-wire handle. The anode is a platinum-wire spiral, or preferably a small cylinder mounted so that it may be mechanically rotated. When gauze electrodes are not available, stationary electrodes may be employed. The inside surface of a platinum dish or crucible may be used as the cathode, while a flat spiral of platinum wire will serve as anode.

When gauze electrodes are used, they are mounted on a stand at a height such that the tall beaker for the electrolysis can be brought

beneath the electrodes and elevated into the desired position. A movable clamp supports the beaker in place.

Nature of Deposit. The most desirable condition is one in which the metal forms a fine-grained adherent deposit. Many factors affect the nature of the deposit obtained. Thus, silver may be obtained in forms varying from the fine grain of commercial silver plate to a very soft crystalline deposit which builds up in long needle-like crystals extending from the electrode. Only a few details as to the factors which affect a deposit are given here. More specific directions are given later in connection with the determinations listed.

1. *Concentration of ions.* If deposition is made from solutions of high concentration, the deposit is generally coarsely crystalline. It is often advantageous to electroplate metals from a bath in which the concentration of the ions is kept very low by means of a complex ion. Thus, silver plating is made from a cyanide bath, where the formation of $Ag(CN)_2^-$ keeps the concentration of free silver ion at a very low value.

2. *Nature of metal.* The properties of metals greatly affect the nature of the deposit obtained. Copper, for example, is readily plated out in an adherent deposit, whereas silver, under the same conditions, gives a very spongy non-adherent deposit. The material of the electrode, too, may affect the nature of deposit obtained. Many electroplating operations are performed by first plating on copper, which serves as a base for further deposition.

3. *Evolution of hydrogen.* Excessive evolution of gas causes a deposit to be brittle. All factors which decrease the amount of gas evolution aid in obtaining a better deposit. Chief among these are (*a*) mechanical stirring, (*b*) use of high temperature, (*c*) use of low current density, (*d*) decrease in acidity of solutions. In certain cases chemical depolarizers may also be used for reducing gas evolution. Thus, in the electrolysis of copper, the presence of nitric acid is helpful because it oxidizes hydrogen atoms at the cathode,

$$NO_3^- + 2H^+ + 8H = NH_4^+ + 3H_2O$$

Nitrate ion, however, is harmful in other depositions. Nickel cannot be electrolyzed from a solution which contains nitrates.

4. *Current density.* Because of its effect on the local concentration at the electrode surface, the current density is important. High current will cause excessive gassing. When the solution is vigorously stirred, by a rotating anode, high current may safely be used, because fresh solution is constantly brought into contact with the electrode surfaces.

Analysis of Copper Solution

One of the simplest electrical analyses is the determination of copper. The sample is a weighed portion of copper wire (0.5–1 g) dissolved in 5–7 ml HNO_3. It is obtained in a 250-ml volumetric flask. Aliquot portions are used for individual samples, and the total weight of copper received is reported.

Deposition is made from sulfuric acid solution. The small amount of nitric acid present from that used to dissolve the copper is advantageous, acting as a depolarizer to give a more adherent deposit.

Procedure. The following directions are for use of gauze electrodes, with rotating anode. If gauze electrodes are provided without stirring apparatus, the procedure is the same except that a current of 0.5 ampere is used overnight. If other types of apparatus are employed, it is necessary to consult the instructor as to the method of washing at the conclusion of the electrolysis and the current strength to be used.

Immerse the electrodes in concentrated nitric acid for 1 minute and then in dilute nitric acid (1:3) for 5–15 minutes. Rinse well in tap water, then in distilled water, and finally in a beaker of acetone. Place the cathode on a watch glass, and dry for 5 minutes in an electric oven at 110–120°C. Cool in a desiccator, and weigh accurately. Take care not to touch the gauze portion with the fingers after cleaning, because a grease film may be deposited that will cause formation of a non-adherent precipitate. Attach the electrodes to the apparatus so that the anode rotates freely inside the cathode. Test by hand for free rotation. *The electrodes will be ruined if they come in contact during rotation.*

Dilute the sample to 250 ml, mix thoroughly, and withdraw two one-fifth aliquot portions by a pipet which has been calibrated with respect to the flask. Place the samples in tall-form 200-ml beakers. Add to each sample 1.5 ml nitric acid, 2–3 ml sulfuric acid, and about 0.5 g urea (note).

* Dilute to 100 ml. Place the beaker on the shelf of the apparatus, and raise into position so that the bottom of the electrodes barely clears the bottom of the beaker. Cover the beaker with split watch glasses if they are provided, taking care that the glass does not come into contact with the rotating shaft of the anode. Start the stirring motor, connect the battery, and adjust the current to a strength of 1–2 amperes. Electrolyze for 20–30 minutes. If the solution appears colorless at the end of this time, stop the stirring motor, and put in sufficient water to raise the liquid level about 1 cm. Reduce the current to 0.5 ampere, and continue the electrolysis for a few minutes. If deposition is not complete, a film of copper will be seen on the upper portion

of the cathode stem, where the liquid level is raised. When deposition appears to be complete, pipet out a 1-ml portion, and make alkaline with ammonia. If the copper is not completely removed, the deep-blue color of the copper ammonia complex will be apparent. If deposition is not complete, return the test portion to the beaker, and continue the electrolysis for another 15 minutes.

When deposition is complete, slowly lower the beaker, without interrupting the current, meanwhile washing the cathode with a fine stream of water from a wash bottle. As soon as the beaker is completely removed, disconnect the current, replace the electrolysis beaker by one containing distilled water, and run the stirrer for a moment. Repeat this washing with another portion of distilled water, then disconnect the battery, remove the cathode, rinse it in a beaker of acetone, dry on a watch glass for 5 minutes in an oven at 110°C, cool in a desiccator, and weigh. The deposit should be bright yellow or orange in color. Duplicate results should agree within 0.5 mg for the aliquot portions or 2.5 mg for the total weight of copper received.

Note. Urea is added to remove nitrous acid, formed by reduction of nitrate iron in the acid solution. The reaction is

$$2HNO_2 + (NH_2)_2CO = 3H_2O + 2N_2 + CO_2$$

Errors. Deposition is incomplete if the acidity is too high. Chlorides must be absent, since they cause attack of the anode and deposition of platinum on the cathode. Other metals below hydrogen in Table 25 are deposited with the copper, if present. The most probable sources of error are oxidation due to incomplete washing and to prolonged drying, and mechanical loss of sample from the electrode.

Analysis of Copper–nickel Solution

This determination provides an excellent and simple demonstration of the technique of separation of two metals by electrolysis. The sample is a prepared solution containing copper and nickel sulfates in sulfuric acid. The concentrations are such that a weighed 10-g portion will contain 50–100 mg of each constituent. Copper is deposited from a sulfuric acid solution. Nitric acid is not added in this case, because nitrates prevent deposition of nickel; if the acid is used for the copper deposition, it must be removed by evaporation before nickel is determined. After the copper is completely removed, the solution is made alkaline with ammonium hydroxide, in order to repress the hydrogen-ion concentration to a sufficient degree to permit deposition of nickel, and the nickel is electrolyzed.

Procedure. Obtain 20–30 ml of sample solution in a dry glass-stoppered bottle. Weigh a weighing bottle to the nearest milligram, add 10 ml of sample solution by means of a dry pipet or graduated cylinder, stopper the bottle, and reweigh. Transfer the sample quantitatively to a tall-form 200-ml electrolytic beaker. Prepare the electrodes as directed in the preceding exercise. Add 2–3 ml sulfuric acid to the sample, and electrolyze the copper as directed on page 448, beginning with the star. Continue electrolysis until no further deposit is obtained when the liquid level is raised. (The color test cannot be used, since nickel gives a blue color with ammonia.) When deposition of copper is complete, remove the beaker, and wash the electrodes as in the preceding exercise, but take care to save all the solution and washings. Weigh the copper, and without removing the deposit return the electrode to the holder. Place a strip of litmus paper on the side of the beaker, so that it just dips into the liquid, neutralize the solution with concentrated ammonium hydroxide, and add 15–25 ml ammonium hydroxide in excess. If the volume of liquid is such that the beaker is nearly filled, transfer the solution to a larger beaker of such size that the height of liquid is sufficient to nearly cover the electrodes. Place the sample beaker in position, and electrolyze the nickel for 30–45 minutes, at a current of 1–2 amperes. At the end of this time test for complete deposition by withdrawing a 1-ml portion and adding ammonium sulfide solution. If any color is developed, discard the test portion, and continue the electrolysis until deposition is complete; then remove the solution as instructed for copper, washing the electrode with a stream of water as the beaker is withdrawn. Rinse twice in distilled water and once in acetone, dry the electrode 5 minutes, and weigh. Report the percentage of copper and nickel in the sample. Duplicate results should agree within 1 mg for the weight of each constituent. Clean the electrode (cathode) as previously directed before beginning another determination.

ANALYSIS OF BRASS

The analysis of brass is a good example of a combined chemical and electrolytic determination. Because of the commercial importance of brass, as well as the variety of methods utilized in its analysis, this determination is widely employed as a student exercise. The composition of brass is approximately the following:

Cu	60–90%
Zn	0–20
Sn	0–10
Pb	0–20
Fe	0– 3

Other elements may be present in small amounts, but they are seldom determined in the analysis.

Methods of Analysis

The methods given for brass may in general be used for the same constituents in other copper alloys, such as the bronzes. These methods are largely based on the procedures of the American Society for Testing Materials. In the ASTM methods separate samples are taken for the tin determination and for the copper–lead determination, because of the widely different amounts of these constituents; in student analyses all the constituents listed above may be determined from a single sample. If increased accuracy is desired for the tin analysis, a large portion may be taken to start the analysis, and after removal of tin one-fifth aliquot portions may be used for the other constituents.

Tin. The sample is dissolved in nitric acid. Tin forms hydrous stannic oxide $SnO_2 \cdot xH_2O$, which remains as a precipitate when the other constituents go into solution. It is separated by filtration, ignited, and weighed as the anhydrous oxide. The precipitate is always contaminated with some copper, lead, and iron. In exact analyses it is necessary to purify by fusing the precipitate with a mixture of sodium carbonate and sulfur, which converts the tin into soluble sodium sulfostannate, while leaving the impurities as sulfides. The fused sample is leached with water, the soluble sodium sulfostannate is brought into solution, and the sulfides are separated by filtration. They are ignited to oxides, and the weight is subtracted from the weight of impure stannic oxide. The recovered impurities are dissolved in nitric acid and added to the bulk of solution from which tin has been separated. An alternative method of purification is to mix the impure stannic oxide with ammonium iodide and heat. Stannic iodide is volatilized quantitatively, leaving the iodides of copper, lead, and iron. These are converted to the oxides by treatment with nitric acid, evaporation, and ignition.

Lead. In industrial laboratories lead is commonly determined by deposition as PbO_2 simultaneously with the deposition of Cu. This method is not recommended for student use; it is preferable to remove lead as the sulfate prior to electrolysis of copper. The sample solution, after removal of tin, is acidified with sulfuric acid and evaporated until all nitrates are removed. On dilution lead sulfate precipitates. It is separated by filtration with a porous-bottom crucible, since a filter paper cannot be used, and is dried and weighed as the sulfate.

Copper. Usually copper is determined electrolytically, after removal of lead, as described in the preceding section. When electrolytic equipment is not available, a gravimetric method based on precipitation as

cuprous thiocyanate may be used. This precipitate is very bulky, and, when this method is used, it is desirable to work with an aliquot portion rather than the whole sample.

In the thiocyanate method copper is reduced to cuprous ion by treatment in acid solution with bisulfite. CuSCN is then precipitated by addition of ammonium thiocyanate. The bulky precipitate is filtered out by means of a porous crucible, dried, and weighed as CuSCN. Alternatively, it may be dissolved in nitric acid and the copper determined iodometrically as described in Chapter 13.

Iron. After removal of copper, the solution is treated with bromine or nitric acid to oxidize the iron to the ferric state. Hydrous ferric oxide is precipitated by the addition of ammonium hydroxide. The precipitate may be ignited to the oxide and weighed, or dissolved and the iron determined volumetrically. Student samples frequently contain so little iron that this determination is often omitted. Consult the instructor before starting it.

Zinc. In many commercial analyses zinc is determined by difference. When an independent determination is desired, zinc may be precipitated as sulfide, after removal of the other constituents, converted to the sulfate, and weighed as such. Alternatively, the zinc may be precipitated as zinc ammonium phosphate and ignited to the pyrophosphate, as in the determination of magnesium.

Procedure

Tin. Wash the sample, which should be in the form of turnings, with ether or benzene to remove oil (not usually required for student samples). Dry with filter paper. Weigh out 1-g portions into 150-ml beakers, and slowly add to each 25 ml nitric acid (1:1), taking care that the reaction (note 1) does not become too violent. Cover the beaker with a watch glass supported on glass hooks, and evaporate on a steam bath to a volume of 10 ml. Dilute to 50 ml, digest (*do not boil*) at 80–90°C for 10 minutes, and filter while hot. Addition of macerated filter paper may prove advantageous if the amount of precipitate is large. Wash the precipitate 10–20 times with hot nitric acid (1:20). Reserve the filtrate and washings. Transfer the precipitate to a porcelain crucible, char the paper at a low temperature, and ignite. Complete the ignition to constant weight by use of a blast lamp or Meker burner for half-hour periods. From the weight of stannic oxide, SnO_2, calculate the percentage of tin in the sample (note 2).

Notes. 1. The reaction is

$$3Sn + 4NO_3^- + 4H^+ + yH_2O = 3SnO_2 \cdot xH_2O + 4NO$$

2. If purification of the stannic oxide is desired (consult instructor) proceed as follows: Mix the impure stannic oxide in the crucible with eight times its weight of a mixture of equal parts of anhydrous sodium carbonate and sulfur. Cover the crucible, and heat, with a small flame, until sulfur ceases to burn at the edge of the cover. Cool, place the crucible and cover in a 250-ml beaker, and add sufficient water to cover both. Warm until the fused mass is completely dissolved, remove the crucible and lid, and wash in a stream of water. Add 0.2–0.5 g sodium sulfite, and boil for a few minutes to decompose the polysulfides present. Filter through a small paper, and wash thoroughly with dilute ammonium sulfide solution which should contain no polysulfide. Transfer the paper and precipitate to a porcelain crucible, and ignite to constant weight. Deduct the weight of this precipitate from the total weight of impure stannic oxide. Dissolve the residue in dilute nitric acid, and add the solution to the main filtrate, which contains the other constituents.

Lead. Add 4 ml sulfuric acid to the filtrate from the tin precipitate, and expel nitric acid by evaporating (note 1) until fumes of sulfur trioxide are evolved. Cool, wash down the sides of the beaker with a little water, and again evaporate until fumes are evolved. Cool, add 25 ml water, and digest on the steam bath for 30 minutes (note 2), then add 50 ml water, and allow the solution to stand until it is at room temperature. Filter through an ignited and weighed filtering crucible (note 3), and wash with small portions of sulfuric acid (1:20). Reserve the filtrate and washings for the determination of copper. Ignite for 30 minutes by placing the filtering crucible inside a plain porcelain crucible and heating the porcelain crucible to dull redness. From the weight of lead sulfate, calculate the percentage of lead in the sample.

Notes. 1. The solution must be evaporated in order to remove nitric acid, which markedly increases the solubility of lead sulfate. Use a hot plate (*Hood*).

2. Prolonged digestion is necessary, after evaporation and dilution, in order to bring all sulfates other than lead into solution.

3. A filtering crucible is necessary for ignition of the precipitate of lead sulfate, since this precipitate is easily reduced by carbon if a filter paper is used. The ignition temperature must be sufficiently high to volatilize sulfuric acid and occluded water, but must not exceed 500°C since lead sulfate is decomposed above this temperature.

Copper. Evaporate the combined filtrate and washings from the lead determination to less than 100 ml, and transfer quantitatively to a 200-ml electrolytic beaker. Add 1 ml nitric acid, and electrolyze according to the procedure on page 448, beginning with the star. Report the percentage of copper in the sample. Reserve the solution for the zinc determination.

Iron. If this determination is desired (consult instructor), transfer the solution from the electrolytic beaker to a 400-ml beaker, and precipitate iron by addition of ammonium hydroxide following the procedure of page 386, beginning at the star. Ignite, and weigh as Fe_2O_3. Report the percentage of Fe. Reserve the filtrate and washings from both precipitations for the determination of zinc.

Zinc as Pyrophosphate. If iron was not determined (note 1), transfer the solution from the electrolytic beaker to a 400-ml beaker. Dilute to 150 ml, and neutralize with 6 *N* ammonium hydroxide to the methyl red end point. Heat nearly to boiling, and slowly add 30 ml of a solution prepared by adding 20 g diammonium hydrogen phosphate to 80 ml water (note 2). Digest one-half hour on the steam bath, with frequent stirring, allow to stand until the solution is at room temperature, and filter through a previously ignited and weighed Selas or Gooch crucible. Wash with dilute diammonium phosphate solution (note 3) until a test portion *acidified with* HNO_3 gives no precipitate with silver nitrate. Complete the washing by using several small portions of a mixture of equal volumes of alcohol and water, to remove the diammonium hydrogen phosphate from the precipitate. Allow the precipitate to suck dry after each addition of alcohol wash.

Dry the crucible and precipitate in an oven, and ignite over a Meker burner, inside a protecting crucible. Heat for 30-minute periods until constant weight is obtained. From the weight of $Zn_2P_2O_7$ compute the weight of Zn in the sample.

Notes. 1. If iron was determined, it is necessary to destroy ammonium salts before starting the zinc determination. Add to the combined filtrates from the first and second precipitations of iron 25 ml each nitric and hydrochloric acids, and evaporate until fumes of sulfur trioxide are evolved. Dilute to 150 ml, and proceed with the zinc determination.

2. The solution should be just neutral to phenolphthalein. Add a drop of indicator, and adjust if necessary by adding very dilute ammonium hydroxide until a faint pink color is obtained.

3. Prepare the wash liquid by diluting 1 volume of the 20 per cent solution with 20 volumes of water.

Alternative Procedure for Copper

Copper as Thiocyanate. Combine the filtrate and washings from the lead determination. Concentrate to about 200 ml if the volume is greater than this. Transfer quantitatively to a 250-ml volumetric flask, dilute to the mark, and mix. Withdraw two 50-ml aliquot portions into Erlenmeyer flasks.

Neutralize with sodium hydroxide until a precipitate just begins to form, and then add 30–50 m e sulfuric acid of any convenient strength. Pour in with stirring 20 ml approximately 0.5 *M* sodium or ammonium bisulfite solution, and then add (note 1) slowly from a pipet 10 ml approximately 1 *M* ammonium or potassium thiocyanate solution. Stopper the flask to prevent escape of SO_2, and allow to stand 1–2 hours. At the end of this time the precipitate should be white (note 2) and the liquid above it clear.

Filter through a Selas or Gooch crucible that has been brought to constant weight at 120°C. Wash 10 times with 10-ml portions of a solution which contains about 1 g per liter ammonium thiocyanate and 0.1 g per liter of ammonium bisulfite, and then wash 6 times with 10-ml portions of a solution containing 20 ml alcohol to 80 ml water. The washings need not be saved, for, if zinc is to be determined, a larger portion should be used than the one-fifth aliquot employed for the copper. Dry at 120°C, and weigh as CuSCN. Alternatively, the instructor may direct to dissolve the precipitate in nitric acid and determine the copper iodometrically.

Notes. 1. A more crystalline precipitate may be obtained by heating before the addition of thiocyanate, but precipitation in the cold followed by standing is usually recommended.

2. If the precipitate is dark colored, test the thiocyanate for presence of sulfide. A small amount of sulfide will darken the precipitate but not seriously affect the result of the analysis.

References

American Society for Testing Materials, *Methods of Chemical Analysis*, 1943.
N. H. Furman, *Scott's Standard Methods of Chemical Analysis*, Van Nostrand, 1939.
N. W. Lord and D. J. Demorest, *Metallurgical Analysis*, McGraw-Hill, 1924.

See also the references of the following chapter.

QUESTIONS

1. Define electrolyte, electrolysis, coulomb, ampere, volt, ohm, current density, cathode, cation, overvoltage, decomposition voltage.

2. In electrodepositions why
   (*a*) Are gauze electrodes used?
   (*b*) Are solutions stirred?
   (*c*) Does the current decrease as the electrolysis proceeds unless the applied voltage is raised?

3. How may direct current be obtained from a 110-volt a-c source? What equipment is needed?

4. Explain how the use of a mercury cathode permits deposition of ions which cannot be deposited on platinum cathodes.

5. Why is it desirable, in separations by electrolysis, that one substance be above hydrogen and the other below hydrogen in the electrochemical series? May any metals which are above hydrogen in the electrochemical series be deposited by electrolysis? Explain.

6. What are the products of the following electrolyses:

Cathode	*Electrolyte*	*Anode*
Pt	$NaNO_3$	Pt
Pt	KI	Pt
Pt	KI	Ag

7. Which of the following ions is likely to interfere in the electrolytic determination of copper: $PtCl_4^=$, K^+, Ag^+, Zn^{++}?

8. Why is the ignited SnO_2 precipitate sometimes tinged with color?

9. Why is the solution evaporated to SO_3 fumes in the determination of lead as sulfate?

10. What is the reducing agent in the determination of copper as thiocyanate?

PROBLEMS

1. A brass is 4.57 per cent Sn, 7.63 per cent Pb, 68.42 per cent Cu, and the remainder Zn. From a 0.5000-g sample:

(*a*) What weight of SnO_2 would be obtained?

(*b*) If the lead had been determined electrolytically, what would a Pt anode which weighs 17.6512 g weigh after deposition is complete?

(*c*) What weight of cuprous thiocyanate would be obtained?

2. What time will be required for the deposition of 1.1200 g lead as the metal, by a current of 3.000 amperes? What time will be required for the deposition of this amount of lead as the dioxide, using the same current?

3. A 0.7500-g sample of alloy yields by electrolysis 0.1532 g of a mixture of cobalt and nickel. The precipitate is dissolved and the nickel precipitated by addition of dimethylglyoxime, giving 0.3560 g $Ni(C_8H_{14}N_4O_4)$. Use the empirical factor 0.2032. Calculate the percentages of Co and Ni in the sample.

4. A current of 0.5 ampere is passed through a solution of copper sulfate between platinum electrodes 10 cm^2 in area for 1 hour. What is $N.D._{100}$ (assume that only one side of each electrode is effective)? How many grams of copper are deposited? How many milliliters of oxygen, at 25°C and 750 mm pressure, are evolved at the anode?

5. What is the current density if a current of 1 ampere is sent into a platinum leaf electrode which is 1×2.5 cm?

6. A solution is originally 0.1 *M* in Cu^{++} and has a *p*H of 1.2. What is the *p*H of the solution after 99.9 per cent of the copper has deposited and the corresponding amount of oxygen has been liberated at the anode? Assume no H_2 is liberated.

7. In the analysis of a solution which contains Cu^{++} and Pb^{++} the deposition of copper is followed by the liberation of H_2 and the deposition of PbO_2 by the liberation of O_2. In the analysis of a 100-ml portion of a solution whose density is 1.02 and which contains 6 per cent Cu and 5 per cent Pb, is H_2 or O_2 liberated first?

8. A solution is 0.1 *M* in Cu^{++}, 0.1 *M* in Pb^{++}, and 1 *M* in H^+. What is the concentration of H^+ when the deposition of Cu and PbO_2 is complete? Assume no evolution of hydrogen or oxygen.

9. The bivalent metals *A* and *B* are to be separated by electrolysis. What difference in the single-electrode potentials is necessary to permit the concentration of *B* to be reduced to 10^{-6} *M* while the concentration of *A* is 0.1 *M*? Compare the answer with the known potential differences for feasible electrolytic separations.

10. A solution contains Cu^{++}, Ag^+, and H^+, each at a concentration of 0.1 *M*. Neglect overvoltage, and

(*a*) Calculate the decomposition potential for the deposition of Ag and the liberation of O_2 at the anode.

(*b*) Calculate the decomposition potential for the deposition of copper and the liberation of O_2 at the anode.

(*c*) At what concentration of silver does the copper begin to deposit?

11. Find the decomposition potential for a 0.1 *M* $CuSO_4$ solution which is also 1 *M* in H_2SO_4 and is to be electrolyzed between smooth platinum electrodes at a current density such that the numerical magnitude of the overvoltage of oxygen is 0.5 volt.

12. Recalculate the decomposition potential for Problem 11 after 50 per cent of the copper has deposited. Include in the calculation the increase in hydrogen ion concentration.

13. If the overvoltage of hydrogen on copper is 0.8 volt, at what concentration of cupric ion will hydrogen begin to deposit at the cathode in the electrolysis described in Problem 11. For the purposes of estimating the hydrogen-ion concentration assume that the deposition of copper is essentially complete.

14. What is the minimum concentration of zinc ion that will permit the deposition of zinc from a solution of *p*H 7? Assume that a zinc cathode is used and that the overvoltage of hydrogen on it is 0.6 volt.

15. Calculate the concentration of hydrogen ion necessary to permit deposition of sodium from a solution of 0.01 *M* NaCl, assuming no hydrogen overvoltage. What overvoltage of hydrogen would be required, in order that sodium be deposited from a solution in which the concentration of hydrogen ion is 10^{-13} *M*? If a mercury cathode is used, how will it affect the results of the above calculations? At what concentration of hydrogen ion may sodium be deposited from a 0.001 *M* salt solution if the amalgam contains 0.1 g sodium per 50 g mercury and the overvoltage of hydrogen is 1 volt?

CHAPTER

24

Electrometric Titrations

Titrations in which the end point is determined by observation of the emf of an electric cell are known as electrometric titrations. In all electrometric titrations the solution being titrated forms a half-cell which is joined to a standard reference half-cell. If the half-cell composed of the electrode and the titration solution is one whose electrode potential depends on the concentration of an ion in the solution, the emf of the system provides a measure of the concentration of that ion.

Three types of electrometric titrations are widely used, corresponding to the three types of volumetric analyses.

1. *Acid–base titrations.* A hydrogen electrode dips into the titration solution. This together with a calomel half-cell forms the cell,

$$\text{Pt, } H_2, H^+(XM) \parallel \text{KCl } (1\ M), Hg_2Cl_2, \text{Hg}$$

whose emf is a function of the pH.

2. *Oxidation–reduction titrations.* The cell consists of the system

$$\text{Pt, oxidizing agent} + \text{reducing agent} \parallel \text{KCl, } Hg_2Cl_2, \text{Hg}$$

The emf depends on the relative concentrations of the oxidized and reduced forms of the substance which is titrated.

3. *Precipitation titrations.* The electrode is the metal whose ion is taking part in the formation of the precipitate. For example, in the cell,

$$\text{Ag, } Ag^+ \parallel \text{KCl, } Hg_2Cl_2, \text{Hg}$$

as precipitation of a silver salt takes place, the concentration of silver ion changes, thereby changing the emf of the cell.

THEORY

Acid–base Titrations

Hydrogen Electrode. The relation between pH and the emf of the cell may be shown by the methods of Chapter 15.

$$\begin{array}{rll} H_2 = 2H^+ + 2e & E^\circ & = 0.00 \\ 2Hg + 2Cl^- = Hg_2Cl_2 + 2e & E^\circ & = -0.28 \\ \hline H_2 + Hg_2Cl_2 = 2H^+ + 2Hg + 2Cl^- & E^\circ_{1\text{-}2} & = 0.28 \end{array}$$

$$E_{1\text{-}2} = 0.28 - \frac{0.059}{2} \log \frac{[H^+]^2[Hg]^2[Cl^-]^2}{[H_2][Hg_2Cl_2]}$$

Since everything except H^+ is at standard state, this reduces to

$$\begin{aligned} E_{1\text{-}2} &= 0.28 - \frac{0.059}{2} \log [H^+]^2 \\ &= 0.28 - 0.059 \log [H^+] \\ &= 0.28 + 0.059pH \end{aligned}$$

Solving, we have

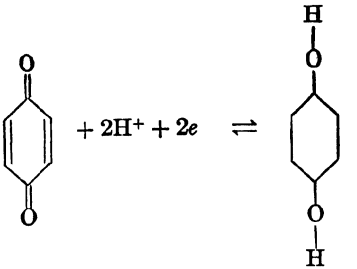
$$pH = \frac{E_{1\text{-}2} - 0.28}{0.059}$$

Since the equation involves a linear relation between emf and pH, it is obvious that the sharp rise in pH at the stoichiometric point of a titration is attended by a sharp rise in the emf of the hydrogen–calomel cell. The titration curves of Chapter 9 are readily converted into electrometric titration curves by transforming the y-axis into emf values corresponding to the pH values given.

Quinhydrone Electrode. The hydrogen electrode is not widely employed for actual electrometric titrations, because the platinized surface readily becomes poisoned, thereby giving rise to misleading emf values. Many substitutes for the hydrogen electrode have been used to give an emf which is proportional to the pH of the solution. Two of these are extensively used—the quinhydrone electrode and the glass electrode.

The quinhydrone electrode consists of a polished platinum electrode dipping into a solution which is saturated with quinhydrone. This is in reality an oxidation–reduction system, but a system in which the pH affects the emf. The relation is shown in the following section. A normal calomel electrode, as reference electrode, usually completes the circuit.

The oxidation–reduction system of the quinhydrone electrode is that of quinone and hydroquinone, as shown in the equations:



Quinone Hydroquinone

Quinhydrone, itself, is an equimolar compound of quinone and hydroquinone; therefore in a saturated solution of quinhydrone the concentrations of the oxidized form and the reduced form are equal, and the emf of the system

$$\text{Hg, } Hg_2Cl_2, \text{ KCl } (1\ M) \parallel Q + H_2Q, H^+, \text{ Pt}$$

depends only upon the concentration of hydrogen ion. The relation is readily shown:

$$\begin{aligned} 2Hg + 2Cl^- &= Hg_2Cl_2 + 2e & E^\circ &= -0.28 \\ H_2Q &= Q + 2H^+ + 2e & E^\circ &= -0.70 \end{aligned}$$

$$2Hg + 2Cl^- + Q + 2H^+ = Hg_2Cl_2 + H_2Q \qquad E^\circ_{1-2} = +0.42$$

$$E_{1-2} = 0.42 - \frac{0.059}{2} \log \frac{[Hg_2Cl_2][H_2Q]}{[Hg]^2[Cl^-]^2[Q][H^+]^2}$$

Since Q and H_2Q are present in equimolar quantities and everything but H^+ is at standard state, this reduces to

$$E_{1-2} = 0.42 - \frac{0.059}{2} \log \frac{1}{[H^+]^2}$$

$$= 0.42 - 0.059 \log \frac{1}{[H^+]}$$

$$= 0.42 - 0.059pH$$

$$pH = \frac{0.42 - E_{1-2}}{0.059}$$

It should be noted that according to this equation the emf becomes zero at a pH of 7.1. At higher pH values the emf becomes negative in sign; that is, the mercury electrode is then the positive electrode.

A disadvantage of the quinhydrone electrode is that it is not accurate at pH values above 8–9. Hydroquinone is a weak acid; in basic solutions the equilibrium between quinone and hydroquinone is shifted to the formation of soluble hydroquinone ion; the ratio H_2Q/Q is no longer equal to unity, and the derived pH equation is no longer valid. Excess

acid, on the other hand, does not disturb the Q–H_2Q ratio, because it merely represses the ionization of the hydroquinone present. The electrode cannot be used in solutions of high salt content because the solubilities of the two forms are affected to a different extent by the electrolyte.

Any other oxidation–reduction system in which hydrogen ion is a reactant may be used for *p*H determinations, provided the ratio of oxidized and reduced forms can be kept at a constant value; this, of course, means that the solution must be saturated with respect to both forms. It is this feature that gives the quinhydrone electrode its unique value.

Glass Electrode and *p*H Meter. The modern method for the determination of *p*H is by use of a special *p*H meter which is a potentiometer so arranged that the dial readings give *p*H units directly. The principle of operation is based on an emf developed at a glass membrane interposed between the solution whose *p*H is to be measured and a buffer solution of known *p*H. The electrode system as usually made up is

Reference electrode || solution of unknown *p*H, glass membrane, buffer of known *p*H || reference electrode

The instrument is so constructed that the solution whose *p*H is to be measured is placed in a small cup which is connected by a salt bridge to one of the reference electrodes. The glass electrode, which is a glass membrane of special composition sealed across the end of a small tube, is dipped into the cup and is connected through another salt bridge to the second reference electrode. Various types of reference electrodes are employed. Most common are silver–silver chloride–HCl and mercury–calomel–KCl, but occasionally a quinhydrone electrode in a buffer solution of known *p*H is used for reference.

To illustrate the principle of the glass-electrode *p*H measurements we shall develop the *p*H–emf equation for a typical setup. The cell whose emf is measured is

$$\text{Hg, } Hg_2Cl_2\text{, KCl (sat.) } \| \text{ } H^+(XM)\text{, glass, } H^+(10^{-7}\ M)$$

$$\| \text{ KCl (sat.), } Hg_2Cl_2\text{, Hg}$$

This cell may be treated as two separate cells operating in series, with the glass electrode replaced by two hydrogen electrodes whose platinum poles are joined so that electrons can flow from one to the other. The net result from the operation of such a system is the same as in the operation of the glass electrode; namely, hydrogen ions are transferred from one concentration to another, and the emf depends on the ratio of the

hydrogen ion concentrations in the two solutions. The cells equivalent to a glass electrode may be written as

$$\underbrace{\text{Hg, } Hg_2Cl_2\text{, KCl} \,\|\, H^+ (XM), H_2, \text{Pt}}_{\text{cell } A} \quad \underbrace{\text{Pt, } H_2, H^+ (10^{-7}\, M) \,\|\, \text{KCl, } Hg_2Cl_2\text{, Hg}}_{\text{cell } B}$$

Since the cells are connected in series the overall emf is the sum of the two or

$$E = E_A + E_B$$

The two separate emf values can be computed by the methods of Chapter 15, using as the $E°$ value of the saturated calomel electrode -0.246. This gives

$$E_A = -0.246 - 0.059\ p\text{H}$$

$$E_B = +0.659$$

Adding and solving for pH gives

$$p\text{H} = \frac{0.413 - E}{0.059}$$

In practice the value of pH is not determined by use of this or similar equations. Rather the potentiometer dial is calibrated to read directly the pH value, since this is a linear function of the emf. It is necessary to check pH meters by taking a reading with buffers of known pH value and correcting the dial setting to give the proper reading.

When used in solutions of high pH or with high concentrations of salts, particularly of sodium ion, it is necessary to apply a correction factor to the meter readings. The manufacturers of meters supply tables of salt corrections for various concentrations.

Oxidation–reduction Titrations

The course of an oxidation–reduction titration may be followed by measurement of the emf between a platinum electrode immersed in the titration solution and a calomel reference electrode, arranged as in Fig. 36 but with a plain platinum electrode in place of the hydrogen electrode. Reference to this system is made in Chapter 15, and it is shown that the emf changes with the ratio in concentrations of the oxidized and reduced forms of the substance that is being titrated. We may for illustration consider the cell,

Calomel electrode || ferrous–ferric ion solution, Pt

Following the methods of Chapter 15, the emf is related to the concentration as follows:

$$\begin{aligned} 2Hg + 2Cl^- &= Hg_2Cl_2 + 2e & E^\circ &= -0.28 \\ 2Fe^{++} &= 2Fe^{+++} + 2e & E^\circ &= -0.77 \end{aligned}$$

$$2Hg + 2Cl^- + 2Fe^{+++} = Hg_2Cl_2 + 2Fe^{++} \qquad E^\circ_{1-2} = +0.49$$

$$E_{1-2} = 0.49 - \frac{0.059}{2} \log \frac{[Hg_2Cl_2][Fe^{++}]^2}{[Hg]^2[Cl^-]^2[Fe^{+++}]^2}$$

Or, since everything else is at standard state except Fe^{++} and Fe^{+++},

$$E_{1-2} = 0.49 - \frac{0.059}{2} \log \frac{[Fe^{++}]^2}{[Fe^{+++}]^2}$$

$$= 0.49 - 0.059 \log \left[\frac{Fe^{++}}{Fe^{+++}}\right]$$

$$= 0.49 + 0.059 \log \left[\frac{Fe^{+++}}{Fe^{++}}\right]$$

From this equation we see that, as ferrous ion is oxidized, the voltage of the cell rises, and the course of the titration can be followed by a titration curve as shown in Fig. 34. The stoichiometric point is the midpoint of the vertical portion of the curve.

A given titration, say oxidation of ferrous ion, will give the same type of curve, regardless of the oxidizing agent used. The height of the vertical portion, however, is determined by the strength of the oxidizing agent. The stronger the oxidizing agent, the greater the length of this portion and the steeper the curve in the vicinity of the stoichiometric point. For a given oxidizing agent one can compute the potentials and construct a theoretical curve just as was done for neutralization titrations in Chapter 9.

For illustration we may consider the titration of 5 m mol ferrous ion by 0.1 *M* ceric sulfate solution; the volume of the titration solution is immaterial because we need only to know the ratio of ferric- to ferrous-ion concentrations. The computation of the emf values for various additions of oxidizing agent is made as follows:

1. *Beginning of the titration.* No computation can be made for this point, because we do not know the concentration of ferric ion in the solution before any oxidizing agent is added. (This amount will depend on the previous history of the ferrous solution used.) We do know that some ferric ion must be present, because otherwise the initial voltage of the cell would be minus infinity if the concentration of ferric ion were zero. Usually it is found that the cell has a small positive emf before any oxidizing agent is added and that the addition of the first drop of oxidizing agent causes a marked voltage rise.

2. *Partial oxidation.* For illustration we may compute the emf when 20 ml ceric sulfate solution has been added. At this point the solution contains 2 m mol ferric ion and 3 m mol ferrous ion. The ratio $[Fe^{+++}]/[Fe^{++}]$ has the value 0.67, and the emf is 0.48 volt.

3. *Half oxidation.* When the solution is half oxidized the concentration of ferrous ion is equal to the concentration of ferric ion, and the emf is that of the solutions at standard state or 0.49 volt.

4. *Stoichiometric point.* It was shown in Chapter 15 that at the stoichiometric point for this titration,

$$\left[\frac{Fe^{+++}}{Fe^{++}}\right] = 10^{7.12}$$

Therefore,[1]

$$E_{1-2} = 0.49 + 0.059 \log 10^{7.12}$$

$$= 0.91$$

5. *Past the stoichiometric point.* When excess ceric ion has been added, the ferric-ferrous ratio is computed from the equilibrium constant for the ceric-ferrous reaction. Substitution of this value for the ratio gives the emf at any desired point. For example we will compute the emf when 6 m mol Ce^{++++} has been added. The number of millimols of each substance is:

$Fe^{+++} = 5$
$Ce^{+++} = 5$
$Fe^{++} = X$
$Ce^{++++} = 1$ (since there is 1 m mol in excess of that required to react with all Fe^{++})

From Chapter 15 we have the relation that at equilibrium in this reaction,

$$0 = 0.84 - 0.059 \log \frac{[Ce^{+++}][Fe^{+++}]}{[Ce^{++++}][Fe^{++}]}$$

Then,

$$0 = 0.84 - 0.059 \log \frac{(5)(5)}{(1)(X)}$$

or

$$\log \left[\frac{Fe^{+++}}{Fe^{++}}\right] = \log \left(\frac{5}{X}\right) = \frac{0.84}{0.059} - \log 5$$

$$= 14.2 - 0.7 = 13.5$$

This gives

$$E_{1-2} = 0.49 + 0.059 \log 10^{13.5}$$

$$= 1.29 \text{ volts}$$

When computations are made in this manner for the complete titration and the curve is plotted, it is found that the results will not be identical with the results obtained experimentally. This happens be-

[1] In the computation of Chapter 15 we found a stoichiometric emf of 1.19 volts. The difference is that in the previous computation a normal hydrogen reference electrode was used and in the present case a calomel electrode is employed.

cause of the effects of other ions present in the solution, as explained in the following section.

Effect of Acids. It is shown in Chapter 15 that the concentration of hydrogen ion will affect the oxidation potential of any redox system in which hydrogen ion is a reactant. For example, in the expression for the potential of the permanganate–manganous system the concentra-

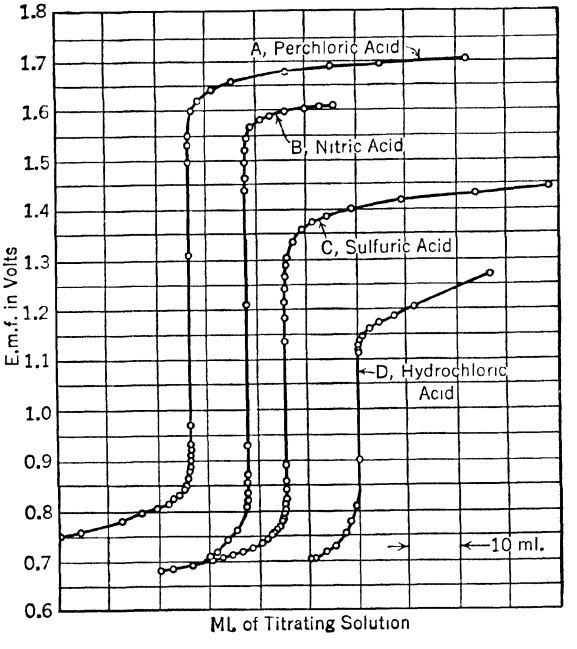


FIG. 34. Potentiometric titration of ferrous iron in normal perchloric, sulfuric, nitric, and hydrochloric acids. (Reproduced by permission of G. F. Smith and C. A. Getz, *Ind. Eng. Chem. Anal. Ed.* **10**, 191.)

tion of hydrogen ion appears as the eighth power. It might be expected that in redox systems that do not involve hydrogen ion the potential would be independent of the hydrogen-ion concentration or the presence of other ions. The curves of Fig. 34 show, however, that the oxidation potential of the ceric–cerous system is greatly affected by the kind of acid present and that the potential of the ferric–ferrous system is also affected. The first point shown on each of these curves gives the half-way potential, where ferrous and ferric ions are present in equal amount; therefore this point represents the *apparent* normal electrode potential. Likewise the last point on each curve gives the potential when ceric and cerous ions are present in equal amount. It may be noted that the apparent E° value for the $Fe^{++} - Fe^{+++}$ electrode varies from 0.68 to

0.75 and that the apparent $E°$ value for the $Ce^{++++} - Ce^{+++}$ electrode varies from 1.27 to 1.70. These variations may be due to two causes: either to large deviations of the activities of the ions from the stoichiometric concentrations, or to complex formation between the anions of the acids and the ions of the redox reagents. Possibly both effects are of importance. If complex ions are formed with the anions of the acids employed, the effect may be to increase or to decrease the apparent normal potential. From the equation,

$$E = E° + 0.0591 \log \frac{[Fe^{+++}]}{[Fe^{++}]}$$

we see that the emf should be the $E°$ value when ferrous and ferric ions are present in equal amount. When the ferrous-ion concentration is decreased, owing to complex-ion formation, the value of the ratio is increased, and the emf is greater than the true $E°$ value. On the contrary, when the concentration of ferric ion is decreased, through complex formation, the value of the ratio is decreased, and the emf is smaller than the true $E°$ value. The very large deviations found for the ceric–cerous potential in various media suggest that probably we are not dealing with the simple Ce^{++++} and Ce^{+++} ions at all, but that these ions are in solution as some form of complex. Because of this it is doubtful whether the true $E°$ value is known for the ceric–cerous potential.

Precipitation and Complex-formation Titrations

The course of precipitation and complex-formation titrations is readily followed by electrometric methods, provided there is available an electrode that will be at equilibrium with one of the ions involved in the reaction. As an example, we may take the precipitation of silver chloride by titration of silver ion with chloride ion. The cell is [2]

$$Ag,\ Ag^+\ (x\ M)\ \|\ KNO_3\ \|\ KCl\ (1\ M),\ Hg_2Cl_2,\ Hg$$

The silver electrode dips into the titration solution. As the concentration of silver ion is changed, the emf changes, according to the equation (readily derived by the methods of Chapter 15):

$$E = E°_{Ag} - E°_{calomel} - 0.0591 \log [Ag^+]$$

[2] An additional salt bridge of potassium nitrate is interposed between the silver solution and the potassium chloride solution, to prevent accidental introduction of chloride ion into the silver-ion solution.

At the stoichiometric point there is an abrupt change in the silver-ion concentration, and a corresponding change in voltage of the cell.

EXPERIMENTS

Potentiometer. The emf of cells must be measured by a potentiometer in order to make the measurement without withdrawing current. A simple form of potentiometer is shown in Fig. 35. The working battery W applies a potential to the slide-wire bridge R, which has a resistance of 200–1000 ohms. The cell to be measured, X, is connected so as to be of opposite polarity to W. The slide S is moved until the potential drop in R is equal and opposite to that of X. This potential drop is then determined by reading the voltmeter V. The condition of balance is found by noting the deflection of galvanometer G. The tapping key K should be closed only long enough to ascertain whether the potentials are in balance. The potential of the working battery W must be *greater* than the potential of the cell to be measured; otherwise no point of balance can be found as the slide is moved. For electrometric titrations the battery W usually consists of one or two dry cells of 1.5 volts each. The voltmeter used should give full-scale deflection at a potential of 1.5–3.0 volts. The galvanometer is usually a portable instrument of low sensitivity. Unless the slide wire contains very many turns, no advantage is gained by having a sensitive galvanometer, since even an instrument of low sensitivity will serve for detection of potential differences less than the drop between successive turns of the slide wire.

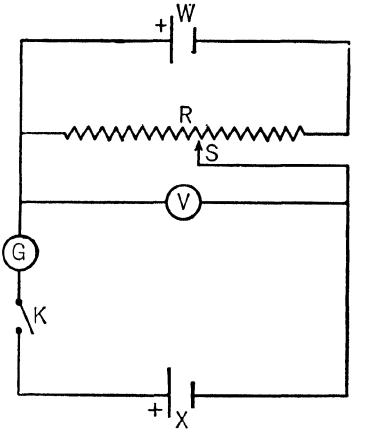


FIG. 35. Potentiometer circuit used for electrometric titrations.

Electrodes. A hydrogen and calomel electrode are shown in Fig. 36. To prepare the hydrogen electrode for use clean it in nitric acid, rinse well, immerse in a 1–5 per cent solution of platinic chloride, and electrolyze with 2–4 volts potential until a coat of platinum black is deposited. The electrode should be the cathode in this electrolysis, and a similar platinum electrode should be used as the anode. Rinse the plated electrode in distilled water, electrolyze for 1 minute in dilute sulfuric acid solution (using the plated electrode as cathode), and keep in distilled water until needed. To prepare the calomel electrode, triturate

calomel with mercury in a mortar in order to reduce any mercuric chloride present. Put the paste of mercury and calomel into the electrode vessel, and fill the vessel with a solution of 1 *M* potassium chloride which has been saturated with calomel.

Acid–base Titrations. Assemble the apparatus as shown in Fig. 36. Place in the beaker a measured volume of the acid to be titrated and

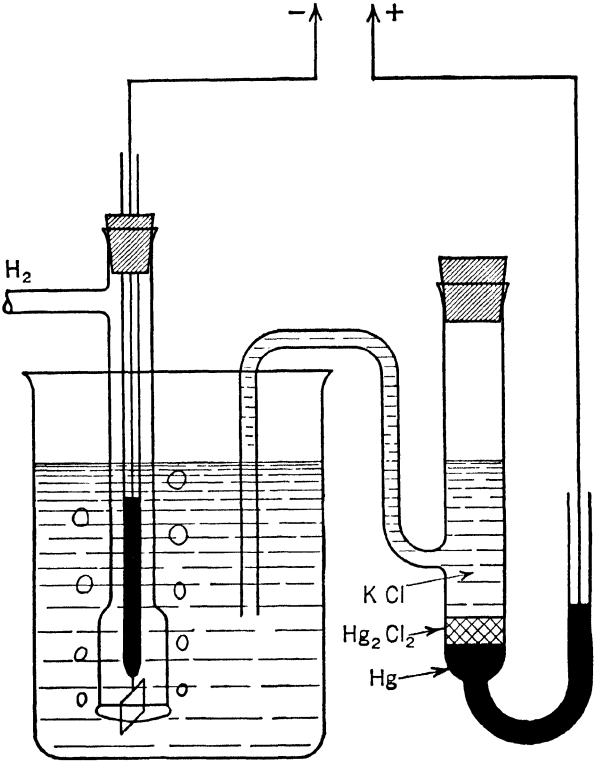


FIG. 36. Hydrogen and calomel electrode assembly for electrometric titration.

add water until the solution covers the mouth of the hydrogen bell. Pass a stream of hydrogen [3] through the bell at such a rate that there is a steady stream of bubbles of gas escaping through the solution. Run a little potassium chloride from the calomel electrode vessel, so as to obtain a junction of fresh solution. Connect the two electrodes to a

[3] Use compressed hydrogen, from a tank, if it is available. The gas should be purified by passage through a wash bottle filled with alkaline pyrogallol, which removes oxygen. If compressed hydrogen is not available, prepare the gas from arsenic-free zinc and hydrochloric acid, in a Kipp generator. Gas prepared in this manner should be purified by passage through successive wash bottles containing solutions of potassium permanganate and sodium hydroxide.

potentiometer. (The mercury is the + electrode.) Measure the emf. Titrate with standard sodium hydroxide solution, measuring the emf after each addition of base. Only a few measurements need be made until the stoichiometric point is approached, but in the vicinity of this point the emf should be measured after the addition of each drop of reagent.[4] Continue the titration 5–10 ml beyond the stoichiometric point, or until the addition of base causes little change in emf. Calculate the *p*H for each reading. Plot the results, as shown in Chapter 9.

Titration with Quinhydrone Electrode. Arrange the apparatus as shown in Fig. 36, except that the hydrogen electrode is replaced by a polished platinum electrode and no hydrogen gas is passed through the solution. Connect this electrode to the + terminal of the potentiometer, and the calomel half-cell to the − terminal. Place in the beaker a measured volume of acid, add a few crystals of quinhydrone, and proceed with the titration as in the previous exercise. In the quinhydrone titration the emf decreases. When it reaches zero, reverse the polarity of the electrodes, and continue the titration, recording all emf readings after reversal as negative values. Calculate *p*H values from the emf values obtained. Plot the titration curve.

Oxidation–reduction Titration. Arrange the apparatus just as in the quinhydrone titration. Place in the beaker a measured volume of ferrous sulfate solution and add 10–15 ml sulfuric acid. Titrate with permanganate or ceric sulfate solution. Plot emf as ordinate *vs.* volume of reagent added as abscissa. The end point of the titration is recognized by the abrupt break in the curve.

References

I. M. Kolthoff and N. H. Furman, *Potentiometric Titrations*, 2d Ed., Wiley, 1931.
W. M. Clark, *The Determination of Hydrogen Ion*, 3d Ed., Williams and Wilkins, 1928.
J. H. Hillebrand, *J. Am. Chem. Soc.*, **35**, 847 (1913).
Malcolm Dole, *Principles of Experimental and Theoretical Electrochemistry*, McGraw-Hill, 1935; *The Glass Electrode*, Wiley, 1941.
D. A. MacInnes, *The Principles of Electrochemistry*, Reinhold Publishing Corp., 1939.
I. M. Kolthoff and H. A. Laitinen, *p*H *and Electrotitrations*, Wiley, 1941.

QUESTIONS

1. Replot the titration data given in Chapter 9 for HCl against NaOH, with emf values on the *y*-axis for titration:

[4] Add methyl orange indicator in the titration of the first sample, so that the approach of the stoichiometric point may be easily recognized.

(*a*) With a hydrogen and normal calomel electrode.

(*b*) With a quinhydrone and normal calomel electrode.

(*c*) With the glass electrode with saturated calomel electrodes and a buffer of *p*H 7.

2. Why is not the quinhydrone electrode suitable for measuring the *p*H of a strongly basic solution?

3. Under what *p*H conditions and concentrations of other ions does the glass electrode operate most satisfactorily?

4. Why must an electronic voltmeter be used with a glass electrode of the conventional type?

5. Draw in some detail the cell which could be used for the determination of Fe^{++} by electrometric titration with $K_2Cr_2O_7$.

6. Describe a method for the determination of E° for the following oxidation–reduction systems:

(*a*) Ferrous–ferric.

(*b*) Quinone–hydroquinone.

(*c*) Ceric sulfate–cerous sulfate.

(*d*) An oxidation–reduction indicator.

List the sources of error which might affect each of the measurements.

7. How do you explain the fact that the stoichiometric emf found for ceric–ferrous titrations varies with the acid medium employed?

8. Ferric ion forms a complex with chloride ion. If HCl is added to an equimolar mixture of ferric and ferrous ions, how will the half-cell emf be changed?

9. Which titration will have the larger emf change at the stoichiometric point, silver ion with chloride ion or silver ion with iodide ion?

10. From the data cited in Question 1 (*a*), calculate the rate of change of emf with volume ($\Delta E/\Delta V$) for the volumes used in obtaining the various points in the titration curve. Plot $\Delta E/\Delta V$ as ordinate against V as abscissa. What advantage does this curve have in the accurate location of the stoichiometric volume in an electrometric titration?

PROBLEMS

1. What is the emf at the stoichiometric point for the silver chloride titration if it is made by means of the cell,

$$Hg, Hg_2Cl_2, KCl\ (1\ M) \parallel KNO_3 \parallel Ag^+, Ag$$

2. Derive equations for *p*H in terms of emf for the cells:

(*a*) Ag, AgCl, KCl (0.1 *M*) + H^+ (*x M*), Q + H_2Q, Pt

(*b*) Ag, AgCl, HCl (0.1 *M*) || H^+ (*x M*), H_2, Pt

3. If 50 ml 0.1 *M* silver nitrate solution is titrated by 0.1 *M* potassium iodide solution, compute the emf when the following quantities of iodide have been added: 0, 10, 40, 49, 49.9, 50.0, 50.1, 51, 60 ml. Plot the titration curve, with emf on the *y*-axis. Use the cell of problem 1.

4. What is the emf of each of the following cells:

(*a*) Normal calomel electrode || sodium acetate (0.1 *M*), hydrogen electrode.

(*b*) Normal calomel electrode || boric acid (0.03 *M*), quinhydrone electrode.

(*c*) Normal calomel electrode || $AgNO_3$(0.01 *M*) + NH_4OH(1 *M*), Ag.

(*d*) Pt, H_2(740 mm), KOH (0.001 *M*) || saturated calomel cell.

(*e*) Decinormal calomel cell || NH_4Cl (0.1 *M*), Q + H_2Q, Pt.

5. In an electrometric titration 50 ml 0.1 *M* ferrous sulfate solution is titrated with 0.1 *M* ceric sulfate solution. Compute the emf when 10, 20, 40, 49, 50, 51, 60 ml of ceric sulfate has been added (*a*) with a normal calomel reference electrode, and (*b*) with a hydrogen reference electrode. Plot the results obtained in (*b*), and compare with the curve given for this titration in sulfuric acid solution.

6. If *p*H is determined by a hydrogen electrode combined with a normal calomel electrode, what is the error in the *p*H value when the voltmeter used is in error by 2 mv?

7. What is the *p*H when the emf of a quinhydrone-saturated calomel cell is zero?

8. The voltage of the cell:

$$\text{Decinormal calomel cell} \parallel CH_3NH_3Cl\ (0.1\ M),\ Q + H_2Q,\ Pt$$

is 0.02 volt. Find the *p*H of the methyl ammonium chloride solution and the ionization constant of the base.

9. (*a*) Find the *p*H of a buffer solution in which the saturated calomel quinhydrone cell combination shows a voltage of 0.150 volt.

(*b*) How many grams of NaAc must be added to 250 ml of 0.15 *M* HAc to produce the buffer of this problem?

10. Develop an equation for the glass electrode when the internal reference electrode is Ag, AgCl, Cl^- (0.1 *M*) and the buffer in the electrode has a *p*H of 7.02.

11. Develop an equation for the glass electrode when the internal reference electrode is a Pt, $Q + H_2Q$ electrode which dips in a potassium acid phthalate solution of *p*H 4.

CHAPTER

25

Use of Analytical Literature. Standard Samples

It is not the objective of a beginning course in quantitative analysis to illustrate all the known analytical methods. As explained in Chapter 1, the student analyst should in the beginning course master the fundamental technique common to all methods. When this experience is attained, new methods may be quickly mastered without extensive training in all their details since they involve no technique which differs radically from the more common operations. It is extremely important, however, that the well-trained analyst know how to use the literature of analytical chemistry, so that when a new problem is presented he may avail himself of the published data concerning that problem.

PERIODICALS

A systematic method of attack should be employed for an analytical problem. First of all, the standard reference books peculiar to the type of analysis should be consulted. Not all methods are published in books. When a satisfactory treatment is not found in the reference books, the analyst should consult the current literature of the field. Several periodicals are devoted primarily to analytical chemistry; in addition, many analytical methods are published in the more general periodicals, such as the *Journal of the American Chemical Society*. The most commonly available periodicals on analytical chemistry are the following: *The Analyst* (London), *Annales de chimie analytique et de chimie appliquée et Revue de chimie analytique réunies* (Paris), *Zeitschrift für analytische Chemie* (Munich), *Journal of the Association of Official Agricultural Chemists*, and *Analytical Chemistry*, formerly *Industrial and Engineering Chemistry, Analytical Edition*. The last named is the

most widely available in the United States. Although of recent origin, this periodical, which is published by the American Chemical Society, is already the repository of much valuable current literature.

Few laboratories have access to the entire list of analytical publications, and, furthermore, a complete survey of all the publications would require a prohibitive amount of time. In order to simplify the use of literature various scientific societies publish brief reviews or abstracts of the current literature. The most readily available of these is *Chemical Abstracts*, published by the American Chemical Society. This periodical gives, semi-monthly, an abstract of all papers which have appeared in many fields. One entire section is devoted to the literature of analytical chemistry; the coverage is so complete that failure to find an analytical method in the *Abstracts* is almost certain proof that no publications have been made in the field. Each volume is concluded with a subject and an author index, and in addition a decennial index is published for each of the periods 1907–16, 1917–26, 1927–36 and 1937–46. These indexes greatly simplify the labor involved in finding an analytical method, since through one volume the entire literature for a 10-year period may be traced.

When a method cannot be found in reference books, the next step is to consult *Chemical Abstracts*. If it is thought that the subject matter sought will be found in recent publications, it is advisable to begin the search with the last complete volume by consulting the subject index. Although the index system is very excellent, it may happen that the desired article may not appear under the first subject which is consulted, and it is always advisable to continue the search by looking for other subjects under which work might be classified. If any volume consulted yields a reference, this article should be read before continuing the search, since it will often be found that a published article will give a complete bibliography of previous work. After the possibilities of the latest volume are exhausted, the search is continued through past volumes until the most recent decennial index is reached; thereafter the decennial index is used. It is seldom necessary to carry a search to publications prior to 1907, the time of beginning of *Chemical Abstracts*, since most of the methods published prior to that time will be found in the standard reference works. Should it be desired to seek publications prior to 1907 either *Chemisches Zentralblatt* (1830 to date) or *Journal of the Chemical Society* (1871–1925) may be consulted. Other publications are listed in the reference books cited below.

The reference system employed by *Chemical Abstracts* is simple. In the annual index the name of the subject is followed by a list of subheadings which usually enable the reader to determine whether a reference

relates to the particular aspect of the subject in which he is interested. The subheading is followed by a page reference which bears a small superscript number or letter [1] giving the position of the reference on the page. For this purpose the page is divided into ninths. The indexing may be illustrated by a sample notation from a page chosen at random. Under the heading "balances" there is a subheading, as follows:

Balances
analytical, with damping device, 2979[4]

The reference is located four-ninths of the distance from the top to the bottom of page 2979. In the decennial index the same reference is listed, but it now includes also the volume number:

Balances
analytical, with damping device, **18**:2979[4]

After the reference is obtained from the index, the abstract is read in order to determine whether the article contains the material sought. Should the abstract show the article to be of use, the periodical which contains the original article should then be investigated; often this is not available, but the abstract may be sufficiently complete to provide the desired information.

The number of journals abstracted is very large, and not all the abbreviations used for the names will be familiar to the average reader. *A Guide to the Literature of Chemistry* gives a complete list of periodicals, together with the official abbreviations, the name and address of the publisher, and the dates of publication for each one. A similar list, completely up to date, is given in the December 20, 1946, issue of *Chemical Abstracts*.

A recent publication of great value to the analyst is the Fifteen Year Collective Index for Volumes 1 to 15, *Industrial and Engineering Chemistry, Analytical Edition*. It covers the period 1929–1943.

References

E. J. Crane and A. M. Patterson, *A Guide to the Literature of Chemistry*, Wiley, 1927.
M. G. Mellon, *Chemical Publications*, McGraw-Hill, 1928.
B. A. Soule, *Library Guide for the Chemist*, McGraw-Hill, 1938.

[1] In 1947 *Chemical Abstracts* started to use superscript letters; before that time it used superscript numbers.

REFERENCE BOOKS

In the following list of reference books only the more recent publications in English are included. Textbooks are not listed, nor are the various books which deal chiefly with the theory of analysis, but attention is directed to those works which summarize a wide variety of methods or deal with widespread applications of particular methods. The list is not complete, but it will serve as a guide for ready location of desired analytical methods. The books which deal chiefly with methods other than gravimetric and volumetric analyses are listed elsewhere, in connection with the discussion of special methods.

A. H. ALLEN, *Commercial Organic Analysis*, 10 vols., Blakiston, 1923–33.

J. ALTIERI, *Gas Analysis and Testing of Gaseous Materials*, American Gas Association, 1945.

AMERICAN SOCIETY FOR TESTING MATERIALS, *Methods of Chemical Analysis*, Philadelphia, 1942.

R. E. DOOLITTLE, *et al.*, *Official and Tentative Methods of Analysis*, Association of Official Agricultural Chemists, Washington, 1940. This is the standard work for methods of analysis of all agricultural materials.

N. H. FURMAN, *Scott's Standard Methods of Chemical Analysis*, Van Nostrand, 1939.

M. GIBB, *Optical Methods of Chemical Analysis*, McGraw-Hill, 1942.

R. C. GRIFFIN, *Technical Methods of Analysis*, McGraw-Hill, 1927.

W. F. HILLEBRAND and G. E. F. LUNDELL, *Applied Inorganic Analysis*, Wiley, 1929. See also HILLEBRAND, Analysis of Silicate and Carbonate Rocks, *U. S. Geol. Survey Bull.* 700, 1919.

G. S. JAMIESON, *Volumetric Iodate Methods*, Chemical Catalog Co., 1926.

C. M. JOHNSON, *Rapid Methods for the Chemical Analysis of Special Steels*, Wiley, 1930.

I. M. KOLTHOFF and V. A. STENGER, *Volumetric Analysis*, Vol. I, Interscience, 1942; Vol. II, 1947.

A. E. LEACH and A. L. WINTON, *Food Inspection and Analysis*, Wiley, 1924.

N. W. LORD and D. J. DEMOREST, *Metallurgical Analysis*, McGraw-Hill, 1924.

A. H. LOW, A. J. MEINING, and W. P. SCHODER, *Technical Methods of Ore Analysis for Chemists and Colleges*, Wiley, 1939.

G. E. F. LUNDELL and J. I. HOFFMAN, *Outlines of Methods of Chemical Analysis*, Wiley, 1938.

G. E. F. LUNDELL, J. I. HOFFMAN, and H. A. BRIGHT, *Chemical Analysis of Iron and Steel*, Wiley, 1932.

G. LUNGE and C. A. KEANE, *Technical Methods of Chemical Analysis*, 3 vols., Van Nostrand, 1924–31.

E. G. MAHIN and R. H. CARR, *Quantitative Agricultural Analysis*, McGraw-Hill, 1923.

R. B. MOORE, *et al.*, Analytical Methods for Certain Metals, Including Cerium, Thorium, Molybdenum, Tungsten, Radium, Uranium, Vanadium, Titanium, and Zirconium, *Bur. Mines Bull.* 212.

R. E. Oesper, *Newer Methods of Volumetric Analysis*, Van Nostrand, 1938.
F. C. Phillips, *Methods for the Chemical Analysis of Ores, Iron and Steel*, Chemical Publishing Co., 1920.
American Public Health Association, *Standard Methods for the Examination of Water and Sewage*, New York, 1946.
F. D. Snell and F. M. Biffen, *Commercial Methods of Analysis*, McGraw-Hill, 1944.
E. P. Treadwell and W. P. Hall, *Analytical Chemistry*, Vol. II, 9th Ed., Wiley, 1942.
H. S. Washington, *Manual of the Chemical Analysis of Rocks*, Wiley, 1930.
H. W. Wiley, *Principles and Practice of Agricultural Analysis*, Chemical Publishing Co., 1926.
H. H. Willard and H. Diehl, *Advanced Quantitative Analysis*, Van Nostrand, 1943.
A. G. Woodman, *Food Analysis*, McGraw-Hill, 1931.

STANDARD ANALYZED SAMPLES

It has repeatedly been emphasized that many of the analytical methods are subject to determinate errors which may greatly affect the accuracy of the analysis. In general, as the complexity of the sample is increased, the probability of such determinate errors is also increased. One of the valuable methods for the elimination of determinate errors is to conduct an analysis of a known sample along with the analysis of the unknown material and to compare the results for the known and the unknown. The National Bureau of Standards has prepared a large number of analyzed samples which may be used as controls or for standardization of solutions for volumetric analyses. With these samples are furnished certificates of analysis. A typical certificate is shown in Table 38. It may be noted that the analysts are listed and that the analytical methods employed are indicated, where the methods are of unusual type. From such a composite analysis there is obtained not only a very accurate analysis for the sample, but also a clue as to the deviations that may be expected. If an analyst wishes to make a phosphorus determination on a steel of similar composition to the sample described in Table 38, he may use a portion of this sample for a control, carrying it through all the operations to which the unknown is subjected. If the results for Analyzed Sample 106 agree with the published analysis there is every reason to trust the accuracy of the unknown analysis obtained under similar conditions.

A partial list of the standard samples issued by the National Bureau of Standards is given in Table 39. At the end of this table are shown some chemicals which may be used for primary standards.

Full information concerning the standard samples is contained in Supplement to the National Bureau of Standards Circular C 398, which can be obtained free of charge on application to the National Bureau of Standards, Washington, D. C.

TABLE 38

TYPICAL CERTIFICATE OF ANALYSES FURNISHED WITH THE STANDARD SAMPLES ISSUED BY THE NATIONAL BUREAU OF STANDARDS

DEPARTMENT OF COMMERCE

Bureau of Standards
Certificate of Analyses
OF
STANDARD SAMPLE No. 106
CHROMIUM-MOLYBDENUM-ALUMINUM STEEL

ANALYST	C	Mn		P		S		Si			Cr		Mo		Al		
	CARBON 1. Direct Combustion	MANGANESE 1. Gravimetric (Ppt SO_4, $KMnO_4$ after removing Cl)	2. Persulphate Arsenite	PHOSPHORUS 1. Alkali-Molybdate[a]	2. Gravimetric (Weighed as $Mg_2P_2O_7$ after removal of arsenic)	SULPHUR 1. Gravimetric (Direct oxidation and final precipitation in reduced solution)	2. Evolution with HCl (± I) Zn-Iodine (Theoretical sulphur titres)	SILICON Sulphuric acid dehydration	COPPER H_2S-CuSCuO	NICKEL Weighed as nickel dimethyl-glyoxime	CHROMIUM $FeSO_4$-$KMnO_4$ titration	VANADIUM	MOLYBDENUM 1. Gravimetric	2. Colorimetric	ALUMINUM	ARSENIC	NITROGEN
1	0 339	0. 480		0 022	0. 020	0 018	0 019	0 253	0 145	0 130	1 29[c]	0 008[c]	0 164[d]	0 161	1. 06[e]	0 010	0. 009
2	.345	.483		.019	.019	.020		245[f]	.147[g]	.125	1 28		.166[h]	.165	1. 08		
3	337	.491[i]	0. 493	022	.022	.021	022	245[f]	.143[g]		1 28	.006[j]	.164[i]	.156	1. 06[m]	.008	
4	.342							246			1 28			.163	1. 05[n]		
5	.347[o]		.470	.020	.021[p]	.018	.020	252	.150[q]		1 29[o]		.159[r]	.156	1. 07[s]		
6	342	481[t]		.021	.022	021	020	255	135[q]	.125	1 29			.171	1 06		
7	345		.482	.021[u]		017[v]	016[v]	246	134[q]		1 30		.165[w]		1. 08[x]		
8	345		.49	.021[y]		021	.022[z]	257		.14	1 30[c]		.16[t]	.16	1 05[x]		
9	346	.491[a]		022		020	020[z]	244[f]	147[a]		1 30[c]	.008[a]	.174[t]		1. 05		
10	344			.018		019		26	149	127	1 28	01[a]	.159[b]		1 07[a]		
11	341		475[a]	.021		017		250	133[c]		1 28		.170[b]		1. 06[a]		
Averages	343	.485	482	.021	.020	.019	020	250	142	.129	1 29	.008	.165	.162	1 06	.009	.009
General averages	.343	.484		.020		.019		250	142	.129	1 29	.008	.164		1 06†	.009	.009

† Includes 0.017 percent of Al present as Al_2O_3

[a] Precipitated at 40°C., washed with 1 percent KNO_3 and titrated with alkali standardized by the use of the Bureau of Standards standard acid potassium phthalate and the 23 1 ratio

[b] Value obtained by standardization of titrating solution against sodium oxalate through $KMnO_4$ and Na_2SO_3

[c] Electrometric titration

[d] Precipitated with α benzoinoxime and weighed as MoO_3 B S Jour Research, vol 9 (RP453), p 1, July 1932

[e] Iron removed with ether and cupferron, chromium oxidized with $HClO_4$ and aluminum precipitated twice with NH_4OH, ignited to the oxide and corrected for Fe_2O_3, Cr_2O_3, and SiO_2.

[f] HCl dehydration

[g] Finished by electrolysis.

[h] Precipitated with H_2S molybdenum sulphide ignited to MoO_3 and corrected for impurities

[i] Bismuthate-arsenite

[j] $HClO_4$ dehydration

[k] Spectrographic method

[l] Weighed as $PbMoO_4$

[m] Aluminum precipitated with NH_4OH after removing interfering elements with ether, H_2S, and the mercury cathode

[n] Iron separated with cupferron chromium oxidized with $HClO_4$ and aluminum precipitated twice with NH_4OH

[o] CO_2 absorbed in $Ba(OH)_2$ and titrated with C_6H_5OH

[p] Ignited and weighed as P_2O_5 $24MoO_3$.

[q] $HClO_4$ oxidation

[r] Titrating solution standardized on standard steel

[s] $BaSO_4$ precipitated in $FeCl_3$ solution.

[t] H_2S absorbed in $CdCl_2$ solution

[u] Iron separated with NaOH, molybdenum reduced in Jones reductor and titrated with $KMnO_4$

[v] Iron and chromium separated with ether and NaOH, and aluminum precipitated twice with NH_4OH

[w] Most of the iron removed with ether, chromium and aluminum separated with Na_2CO_3 and Na_2O_2 and aluminum precipitated in the filtrate as hydroxide by carefully neutralizing with HCl.

[x] Oxidized with lead peroxide.

[y] KCN titration.

[z] Aluminum separated from most of the iron and chromium by hydrolysis in an ammonium sulphite sulphurous acid solution. Precipitate dissolved, the acid solution treated with $NaOH$-Na_2O_2, filtered, and aluminum precipitated with NH_4OH.

*LIST OF ANALYSTS

1. Ferrous Laboratory, Bureau of Standards, H. A. Bright in charge; analysis by R. M Fowler and J. C. Redmond.
2. Booth, Garrett, and Blair, Philadelphia, Pa.
3. M. S Argues, W. B Schers, and C. L. Platt, A. O. Smith Corporation, Milwaukee, Wis.
4. R. J. Price, The Electro Metallurgical Co., New York, N.Y.
5. L. H. James, Reo Motor Car Co., Lansing, Mich.
6. E J Richards and W. H Bolger, R. W. Hunt Co., Chicago, Ill
7. W F Lantz, Bethlehem Steel Co., Bethlehem, Pa.
8. C H. McCollam, The Timken Steel & Tube Co., Canton, Ohio
9. J A Wiley, The Midvale Co., Philadelphia, Pa.
10. W T. Hartley, The Ludlum Steel Co. Dunkirk, N.Y.
11. C M Johnson, The Crucible Steel Co. of America, Park Works, Pittsburgh, Pa.

Washington, D.C.
April 19, 1933

LYMAN J BRIGGS
Director

TABLE 39

STANDARD SAMPLES ISSUED BY THE NATIONAL BUREAU OF STANDARDS [2]

Sample Number	*Name*	*Constituents Determined or Intended Use*
		Steels
8g	Bessemer, 0.1 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo, Sn, N)
9d	Bessemer, 0.2 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo, N)
10e	Bessemer, 0.4 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, N, Mo, As)
22c	Bessemer, 0.6 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo, Al, N)
15d	B. O. H., 0.1 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo)
11e	B. O. H., 0.2 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo, N)
12e	B. O. H., 0.4 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo)
13d	B. O. H., 0.6 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo)
14c	B. O. H., 0.8 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo, Al)
16c	B. O. H., 1.0 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo)
19d	A. O. H., 0.2 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo, N)
20d	A. O. H., 0.4 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo)
21c	A. O. H., 0.6 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo, As)
34a	A. O. H., 0.8 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo, As)
35a	A. O. H., 1.0 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo, As, Al)
51a	Electric furnace, 1.2 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo, Sn)
65c	Basic electric	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo, Sn)
100	Medium manganese	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Mo)
105	High sulfur	C
30d	Chrome–vanadium	C, Mn, P, S, Si, Cr, V, (Cu, Ni, Mo)
32c	Chrome–nickel	C, Mn, P, S, Si, Cr, Ni, (Cu, V, Mo, N)
33c	Nickel	C, Mn, P, S, Si, Ni, (Cu, Cr, V, Mo, Sn, Al, N)
50b	Chrome–tungsten–vanadium	C, Mn, P, S, Si, W, Cr, V, (Cu, Mo, Sn, Ni, As)
72c	Chrome–molybdenum	C, Mn, P, S, Si, Cr, Mo
73a	Stainless	C, Mn, P, S, Si, Cr, (Cu, Ni, V, W, N, Mo)
101b	18 Cr, 9 Ni	C, Mn, P, S, Si, Cr, Ni, (Cu, V, N, Mo, Co, Sn)
106a	Cr–Mo–Al (nitralloy "G")	C, Mn, P, S, Si, Cr, Mo, Al, (Cu, Ni, V)
111a	Ni–Mo–Cr (SAE 4620)	C, Mn, P, S, Si, Cr, Ni, Mo, (Cu, V, N)
		Irons
4g	Cast iron	C, Mn, P, S, Si, Ti, (Cu, Ni, Cr, Mo, V)
5i	Cast iron	C, Mn, P, S, Si, Ti, (Cu, Ni, Cr, V)
6e	Cast iron	C, Mn, P, S, Si, Ti, (Cu, Ni, Cr, V, Mo)
7d	Cast iron	C, Mn, P, S, Si, Ti, (Cu, Ni, Cr, V, Mo)
55b	Ingot iron	C, Mn, P, S, Si, Cu, (Ni, Cr, N, Al, Co, Sn, V, Mo)
82	Nickel–chromium cast iron	C, Mn, P, S, Si, Cr, Ni, (Ti, Cu, V, Mo, As)
107	Nickel–molybdenum cast iron	C, Mn, P, S, Si, Ni, Mo, Cr, (V, Cu, Ti, W, As)
115	Nickel–chromium–copper cast iron	C, Mn, P, S, Si, Ni, Cr, Cu, (V, Mo, Co, As)

[2] A partial listing from the *Supplement to N. B. S. Circular C398* issued December 11, 1946.

TABLE 39 (*Continued*)

STANDARD SAMPLES ISSUED BY THE NATIONAL BUREAU OF STANDARDS

Sample Number	*Name*	*Constituents Determined or Intended Use*
	Steel-making Alloys	
57	Refined silicon	Complete analysis
58	Ferrosilicon (75% silicon)	
59	Ferrosilicon (50% silicon)	
61a	Ferrovanadium (high carbon)	
64a	Ferrochromium (high carbon)	
66a	Spiegeleisen	
67	Manganese metal	
68a	Ferromanganese	
75	Ferrotungsten	
90	Ferrophosphorus	Phosphorus
71	Calcium molybdate	Mo, Fe, Ti
116a	Ferrotitanium (low carbon)	Ti, C, Si, Cr, V, Al
	Non-ferrous Alloys	
86b	Aluminum-base casting alloy	Complete analysis
53b	Bearing metal, lead base	
54b	Bearing metal, tin base	
63a	Bearing metal, phosphor-bronze	
37d	Brass, sheet	
52b	Bronze, cast	
62b	Bronze, manganese	
94a	Zinc-base, die-casting alloy	
	Ores	
69	Bauxite	Complete analysis
26	Iron ore, Crescent	Al_2O_3, CaO, MgO
29a	Iron ore, Magnetite	Complete analysis
28	Iron ore, Norrie	Mn (low)
27b	Iron ore, Sibley	SiO_2, P, Fe
25b	Manganese ore	Manganese, available oxygen
56a	Phosphate rock (Tennessee)	P_2O_5, Fe_2O_3, Al_2O_3, etc.
120	Phosphate Rock (Florida)	P_2O_5, Fe_2O_3, Al_2O_3, etc.
	Ceramic Materials	
104	Burned magnesite	Complete analysis
76	Burned refractory (40% Al_2O_3)	
77	Burned refractory (60% Al_2O_3)	
78	Burned refractory (70% Al_2O_3)	
103	Chrome refractory	Cr_2O_3, SiO_2, Al_2O_3, FeO, CaO, MgO

TABLE 39 (*Continued*)

STANDARD SAMPLES ISSUED BY THE NATIONAL BUREAU OF STANDARDS

Sample Number	*Name*	*Constituents Determined or Intended Use*
	Ceramic Materials (*Continued*)	
97	Clay, flint	Complete analysis
98	Clay, plastic	
70	Feldspar, potash	
99	Feldspar, soda	
79	Fluorspar	
1a	Limestone, argillaceous	
88	Limestone, dolomitic	
92	Glass, low boron	B_2O_3
93	Glass, high boron	Complete analysis
89	Glass, lead-barium	
91	Glass, opal	
80	Glass, soda-lime	
81	Glass sand	Fe_2O_3, Al_2O_3, TiO_2, ZrO_2, CaO, MgO
102	Silica brick	Complete analysis
112	Silicon carbide	
	Fineness Standards	
114e	Cement (turbidimetric standard)	
	Melting-point Standards	
44d	Aluminum	659.7°C
45b	Copper	1083.2°C
49b	Lead	327.40°C
42d	Tin	231.90°C
43e	Zinc	419.50°C
	Thermoelectric Standards	
118	Alumel	Emf *vs.* temperature
119	Chromel P	Emf *vs.* temperature
	Chemicals	
84c	Acid potassium phthalate	Acidimetric value
39f	Benzoic acid	Acidimetric and calorimetric values
40c	Sodium oxalate	Oxidimetric value
83a	Arsenic trioxide	Oxidimetric value
17	Sucrose (cane-sugar)	Calorimetric and saccharimetric values
41	Dextrose (glucose)	Reducing value

APPENDIX I

MATHEMATICAL OPERATIONS

USE OF EXPONENTIALS

Operations which involve very large or very small numbers may often be simplified by writing the number involved in a "semi-exponential" form, as a power of 10. This permits placing the decimal point at the most convenient position. For example, the number 606,000,000,000,000,000,000,000, which expresses the number of molecules in a mole, is conveniently written as

$$6.06 \times 10^{23}$$

In this form the exponent of 10 indicates the number of places the decimal point must be shifted to write out the number in full. In the above number the decimal point must be shifted 23 places to the *right* in order to write the number in the conventional notation. A negative exponent for 10 indicates the number of places which the decimal point must be shifted to the left.

Examples:

$$(a)\ 12{,}345 = 1.2345 \times 10^4 = 12.345 \times 10^3$$
$$= 123.45 \times 10^2, \text{ etc.}$$
$$(b)\ 0.000018 = 18 \times 10^{-6} = 1.8 \times 10^{-5}, \text{ etc.}$$

The following rules govern the common operations which are performed with exponential numbers:

1. To multiply exponentials of the same base, add the exponents algebraically. Multiplication of the non-exponential numbers present is performed in the usual manner.

Examples:

$$(a)\ 10^1 \times 10^2 = 10 \times 100 = 1000 = 10^{1+2} = 10^3$$
$$(b)\quad 6 \times 10^3 \times 2 \times 10^2 \times 3 \times 10^{-7} =$$
$$6 \times 2 \times 3 \times 10^{3+2-7} = 36 \times 10^{-2} = 0.36$$

2. To divide exponentially, subtract the exponents algebraically.

Examples:

$$(a)\ \frac{1}{10^{-3}} = 1 \times 10^3 = 1000$$

$$(b)\ \frac{6 \times 10^3 \times 2 \times 10^{-5}}{3 \times 10^{-8}} = \frac{6 \times 2}{3} \times 10^{3-5-(-8)}$$
$$= 4 \times 10^{+3-5+8}$$
$$= 4 \times 10^6$$

3. To raise an exponential to a power, multiply the exponent by the desired power.

Examples:

$$(a)\ (10^2)^2 = (100)^2 = 10000 = 10^4$$

or

$$(b)\ (3 \times 10^{-5})^2 = (3)^2 \times (10^{-5})^2 = 9 \times 10^{-10}$$

4. To extract a root, divide the exponent by the desired root. If the exponent is not divisible by the root to give a whole number it is convenient to rewrite the number so as to obtain an exponent which is evenly divisible.

Examples:

$$(a)\ \sqrt{10^2} = 10^{2/2} = 10^1 = 10$$

$$(b)\ \sqrt{10^3} = \sqrt{10 \times 10^2} = \sqrt{10} \times \sqrt{10^2}$$
$$= 3.17 \times 10^1 = 31.7$$

$$(c)\ \sqrt[3]{8 \times 10^6} = \sqrt[3]{8} \times \sqrt[3]{10^6}$$
$$= 2 \times 10^2$$

$$(d)\ \sqrt[3]{8 \times 10^5} = \sqrt[3]{800 \times 10^3} = \sqrt[3]{800} \times \sqrt{10^3}$$
$$= 9.28 \times 10^1$$

$$(e)\ \sqrt[3]{8 \times 10^{-4}} = \sqrt[3]{800 \times 10^{-6}} = 9.28 \times 10^{-2}$$

USE OF LOGARITHMS

The logarithm (log) of a number is the power to which the base 10 must be raised to give the desired number. Conversely, the antilog of a logarithm is the number whose logarithm has the given value. That is,

$\log 10 = 1$	antilog $1 = 10$ or $10^1 = 10$
$\log 100 = 2$	antilog $2 = 100$ or $10^2 = 100$

Every logarithm has two parts, a characteristic and a mantissa. The characteristic is the integral number preceding the decimal point; the mantissa is the fractional portion of the logarithm.

$$\log 200 = 2.30103 \text{ or } 10^{2.30103} = 200$$

In this log the number 2 is the characteristic and the number .30103 is the mantissa.

1. Finding a logarithm. Look up the mantissa in a log table, interpolating if necessary. Directions for this operation are given in section IV, Appendix. Determine the characteristic as follows: Write the number in an exponential form by placing the decimal point after the first digit, and multiplying by the proper power of 10. The exponent of 10 is the characteristic of the log.

Examples:

$$(a)\ \log 2 = 0.30103 \text{ (from log table)}$$

$$(b)\ \log 20 = \log (2 \times 10^1) = \log 2 + \log 10^1$$
$$= 0.30103 + 1 = 1.30103$$

$$(c)\ \log 0.002 = \log (2 \times 10^{-3}) = \log 2 + \log 10^{-3}$$
$$= 0.30103 + (-3) = \bar{3}.30103 = 7.30103 - 10 \text{ etc.}$$

2. Negative mantissas. Log tables give only positive values of the mantissa. If an

operation provides a negative logarithm, this must be transformed into a logarithm with a positive mantissa before the antilog can be determined.

Example:

$$\log .002 = \bar{3}.30103$$

This number has a negative characteristic but a positive mantissa. It can be expressed as a negative logarithm by algebraically adding the two parts.

$$\bar{3}.30103 = -3 + 0.30103 = -2.69897$$

Example: Find antilog -2.69897.

Here the mantissa is negative. Rewriting to provide a positive mantissa gives $\bar{3}.30103$, the antilog of which is $10^{.30103} \times 10^{-3}$.

3. Raising a number to a given power. To raise a number to a power, find the log, multiply the log by the desired power, and find the antilog.

Example: (*a*) Find $(2 \times 10^4)^2$

$$\begin{aligned} \log\ (2 \times 10^4) &= 4.30103 \\ 2 \times 4.30103 &= 8.60206 \\ \text{antilog } 8.60206 &= \text{antilog } 8 + \text{antilog } 0.60206 \\ &= 10^8 \times 4 \end{aligned}$$

(*b*) Find $(0.002)^3$

$$\begin{aligned} \log 0.002 &= \bar{3}.30103 = -2.69897 \\ 3 \times -(2.69897) &= -8.09691 \\ -8.09691 &= \bar{9}.90309 \\ \text{antilog } \bar{9}.90309 &= \text{antilog } 0.90309 \times 10^{-9} \\ &= 8 \times 10^{-9} \end{aligned}$$

Optionally, the operation may be performed as follows:

$$\begin{aligned} \log 0.002 &= 0.30103 - 3 \\ 3 \times \log 0.002 &= 3 \times (0.30103 - 3) = 0.90309 - 9 \end{aligned}$$

4. Extraction of a root. To extract a root, divide the log of a number by the desired root and determine the antilog of the resulting number.

Example: Find $\sqrt[3]{0.02}$

$$\begin{aligned} \sqrt[3]{0.02} &= \sqrt[3]{20 \times 10^{-3}} = \sqrt[3]{20} \times \sqrt[3]{10^{-3}} \\ &= \sqrt[3]{20} \times 10^{-1} \\ \log 20 &= 1.30103 \\ \frac{1.30103}{3} &= 0.43367 \\ \text{antilog } 0.43367 &= 2.714 \\ \text{Therefore } \sqrt[3]{0.02} &= 2.714 \times 10^{-1} = 0.2714 \end{aligned}$$

Quadratic Equations

The roots of the equation $aX^2 + bX + c = 0$ are given by the formula:

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Example: (*a*) Find the roots of $3X^2 + 8X + 2 = 0$.

$$X = \frac{-8 \pm \sqrt{64 - 24}}{6} = \frac{-8 \pm \sqrt{40}}{6} = \frac{-8 \pm 6.3}{6} = \frac{-8 + 6.3}{6} \text{ or } \frac{-8 - 6.3}{6}$$

(*b*) Solve the following equation:

$$\frac{X^2}{0.1-X} = 10^{-6}$$

Rearranging:

$$X^2 = 10^{-7} - 10^{-6}X$$
$$X^2 + 10^{-6}X - 10^{-7} = 0$$

Application of the formula gives:

$$X = \frac{-10^{-6} \pm \sqrt{10^{-12} + 4 \times 10^{-7}}}{2}$$

This expression can be simplified by neglecting 10^{-12} (or 0.000000000001) with respect to 4×10^{-7} (or 0.0000004), an approximation which is justifiable, since the error introduced is very small.

$$X = \frac{-10^{-6} \pm \sqrt{40 \times 10^{-8}}}{2} = \frac{-10^{-6} \pm 6.3 \times 10^{-4}}{2}$$

In a chemical problem in which X represents the concentration of some ion, only the positive value has any significance. That is,

$$X = \frac{-10^{-6} + 6.3 \times 10^{-4}}{2} = \frac{-1 \times 10^{-6} + 630 \times 10^{-6}}{2}$$
$$= \frac{629 \times 10^{-6}}{2} = 315 \times 10^{-6} = 3.15 \times 10^{-4}$$

An approximate solution of a quadratic equation may often be obtained by neglecting some small term which is added to or subtracted from a larger number. For example, the equation

$$\frac{X^2}{0.1-X} = 10^{-6}$$

becomes $\frac{X^2}{0.1} = 10^{-6}$ when the X term in the denominator is neglected, or

$$X^2 = 10^{-7} = 10 \times 10^{-8}$$
$$X = 3.16 \times 10^{-4}$$

This answer does not deviate greatly from the answer obtained by exact solution of the equation. For most of the quadratic equations encountered in calculations pertaining to chemical equilibrium, the approximate solution is perfectly valid since the equilibrium constants are not in general known to a precision greater than 10–100 per cent. A term cannot be neglected in all equations, however, since it may cause serious error. For example, in the equation

$$\frac{X^2}{0.1 - X} = 0.1$$

neglecting X leads to a solution

$X = 0.1$, which is absurd.

As a rule, if the solution after neglecting a term X leads to a value for X which is appreciable in comparison with the term from which it has been subtracted or to which it has been added, the approximate solution is not valid.

APPENDIX II

EQUILIBRIUM CONSTANTS *

TABLE 1

IONIZATION CONSTANTS FOR WEAK ACIDS

Acid	Equilibrium	Ionization Constant (at Room Temperature)	
Acetic	$CH_3COOH = H^+ + CH_3COO^-$	1.8×10^{-5}	$10^{-4.7}$
Arsenic	$H_3AsO_4 = H^+ + H_2AsO_4^-$	4.5×10^{-3}	$10^{-2.3}$
Arsenious	$H_3AsO_3 = H^+ + H_2AsO_3^-$	2.1×10^{-8}	$10^{-7.7}$
Benzoic	$C_6H_5COOH = H^+ + C_6H_5COO^-$	6.6×10^{-5}	$10^{-4.2}$
Boric	$HBO_2 = H^+ + BO_2^-$	1.1×10^{-9}	$10^{-9.0}$
Carbonic	$H_2CO_3 = H^+ + HCO_3^-$	3×10^{-7}	$10^{-6.5}$
	$HCO_3^- = H^+ + CO_3^=$	7×10^{-11}	$10^{-10.2}$
Formic	$HCOOH = H^+ + HCOO^-$	2.1×10^{-4}	$10^{-3.7}$
Hydrocyanic	$HCN = H^+ + CN^-$	2.1×10^{-9}	$10^{-8.7}$
Hydrofluoric	$HF = H^+ + F^-$	6.9×10^{-4}	$10^{-3.2}$
Hydrogen peroxide	$H_2O_2 = H^+ + HO_2^-$	5×10^{-12}	$10^{-11.3}$
Hydrogen sulfide	$H_2S = H^+ + HS^-$	9×10^{-8}	$10^{-7.0}$
	$HS^- = H^+ + S^=$	1.2×10^{-15}	$10^{-14.9}$
Nitrous	$HNO_2 = H^+ + NO_2^-$	4.6×10^{-4}	$10^{-3.3}$
Oxalic	$H_2C_2O_4 = H^+ + HC_2O_4^-$	3.8×10^{-2}	$10^{-1.4}$
	$HC_2O_4^- = H^+ + C_2O_4^=$	5×10^{-5}	$10^{-4.3}$
Phenol	$C_6H_5OH = H^+ + C_6H_5O^-$	1.0×10^{-10}	10^{-10}
Phosphoric	$H_3PO_4 = H^+ + H_2PO_4^-$	7.5×10^{-3}	$10^{-2.1}$
	$H_2PO_4^- = H^+ + HPO_4^=$	6.3×10^{-8}	$10^{-7.2}$
	$HPO_4^= = H^+ + PO_4^{\equiv}$	3.6×10^{-13}	$10^{-12.4}$
Phthalic †	$C_8H_4O_4H_2 = H^+ + C_8H_4O_4H^-$	1.3×10^{-3}	$10^{-2.89}$
	$C_8H_4O_4H^- = H^+ + C_8H_4O_4^=$	3.9×10^{-6}	$10^{-5.41}$
Propionic.....	$C_2H_5COOH = H^+ + C_2H_5COO^-$	1.4×10^{-5}	$10^{-4.9}$
Sulfurous	$H_2SO_3 = H^+ + HSO_3^-$	1.7×10^{-2}	$10^{-1.8}$
	$HSO_3^- = H^+ + SO_3^=$	5×10^{-6}	$10^{-5.3}$
Tartaric	$C_4H_4O_6H_2 = H^+ + C_4H_4O_6H^-$	1.1×10^{-3}	10^{-3}
	$C_4H_4O_6H^- = H^+ + C_4H_4O_6^=$	6.9×10^{-5}	$10^{-4.2}$
Zinc hydroxide	$H_2ZnO_2 = H^+ + HZnO_2^-$	2×10^{-16}	$10^{-15.7}$

* Selected by permission from the values given by T. R. Hogness and W. C. Johnson, *Qualitative Analysis and Chemical Equilibrium*, Henry Holt, 3d edition, 1947. Many of the constants are given to two significant figures. For solution of the problems given in this text the constants may be rounded to only one significant figure, since calculations based upon the law of chemical equilibrium are only approximations when concentrations are substituted for activities.

† Taken from N. A. Lange, *Handbook of Chemistry*, Handbook Publishers, Inc., 6th edition, 1946.

TABLE 2

IONIZATION CONSTANTS OF WEAK BASES

Base	Equilibrium	Ionization Constant (at Room Temperature)	
Ammonium hydroxide	$NH_4OH = NH_4^+ + OH^-$	1.8×10^{-5}	$10^{-4.7}$
Methyl ammonium hydroxide	$CH_3NH_3OH = CH_3NH_3^+ + OH^-$	5×10^{-4}	$10^{-3.3}$
Dimethyl ammonium hydroxide	$(CH_3)_2NH_2OH = (CH_3)_2NH_2^+ + OH^-$	7.4×10^{-4}	$10^{-3.1}$
Trimethyl ammonium hydroxide	$(CH_3)_3NHOH = (CH_3)_3NH^+ + OH^-$	7.4×10^{-5}	$10^{-4.1}$
Ethyl ammonium hydroxide	$C_2H_5NH_3OH = C_2H_5NH_3^+ + OH^-$	5.6×10^{-4}	$10^{-3.3}$
Phenyl ammonium hydroxide	$C_6H_5NH_3OH = C_6H_5NH_3^+ + OH^-$	4.6×10^{-10}	$10^{-9.3}$
Hydrazine hydroxide	$H_2N{\cdot}NH_3OH = H_2N{\cdot}NH_3^+ + OH^-$	3×10^{-6}	$10^{-5.5}$

TABLE 3

SOLUBILITY-PRODUCT CONSTANTS AT ROOM TEMPERATURE

Substance	Equilibrium	Solubility-product Constant	
Acetates			
Silver acetate	$CH_3COOAg = Ag^+ + CH_3COO^-$	4×10^{-3}	$10^{-2.4}$
Bromates			
Silver bromate	$AgBrO_3 = Ag^+ + BrO_3^-$	6×10^{-5}	$10^{-4.2}$
Bromides			
Mercurous bromide	$Hg_2Br_2 = Hg_2^{++} + 2Br^-$	4×10^{-23}	$10^{-22.4}$
Silver bromide	$AgBr = Ag^+ + Br^-$	7.7×10^{-13}	$10^{-12.1}$
Carbonates			
Barium carbonate	$BaCO_3 = Ba^{++} + CO_3^=$	8.1×10^{-9}	$10^{-8.1}$
Calcium carbonate	$CaCO_3 = Ca^{++} + CO_3^=$	8.7×10^{-9}	$10^{-8.1}$
Lead carbonate	$PbCO_3 = Pb^{++} + CO_3^=$	4.0×10^{-14}	$10^{-13.4}$
Magnesium carbonate	$MgCO_3 = Mg^{++} + CO_3^=$	4.0×10^{-5}	$10^{-4.4}$
Silver carbonate	$Ag_2CO_3 = 2Ag^+ + CO_3^=$	6.2×10^{-12}	$10^{-11.2}$
Strontium carbonate	$SrCO_3 = Sr^{++} + CO_3^=$	1.6×10^{-9}	$10^{-8.8}$
Chlorides			
Mercurous chloride	$Hg_2Cl_2 = Hg_2^{++} + 2Cl^-$	1.5×10^{-18}	$10^{-17.8}$
Silver chloride	$AgCl = Ag^+ + Cl^-$	1.0×10^{-10}	10^{-10}
Chromates			
Barium chromate	$BaCrO_4 = Ba^{++} + CrO_4^=$	2.4×10^{-10}	$10^{-9.6}$
Lead chromate	$PbCrO_4 = Pb^{++} + CrO_4^=$	2.0×10^{-14}	$10^{-13.7}$
Silver chromate	$Ag_2CrO_4 = 2Ag^+ + CrO_4^=$	9.0×10^{-12}	10^{-11}
Cyanides			
Silver cyanide	$AgCN = Ag^+ + CN^-$	2.2×10^{-12}	$10^{-11.7}$
Dichromates			
Silver dichromate	$Ag_2Cr_2O_7 = 2Ag^+ + Cr_2O_7^=$	2.0×10^{-7}	$10^{-6.7}$
Fluorides			
Barium fluoride	$BaF_2 = Ba^{++} + 2F^-$	1.7×10^{-6}	$10^{-5.8}$
Calcium fluoride	$CaF_2 = Ca^{++} + 2F^-$	4.0×10^{-11}	$10^{-10.4}$
Lead fluoride	$PbF_2 = Pb^{++} + 2F^-$	3.7×10^{-8}	$10^{-7.4}$
Magnesium fluoride	$MgF_2 = Mg^{++} + 2F^-$	6.4×10^{-9}	$10^{-8.2}$
Strontium fluoride	$SrF_2 = Sr^{++} + 2F^-$	2.8×10^{-9}	$10^{-8.6}$
Hydroxides			
Copper hydroxide	$Cu(OH)_2 = Cu^{++} + 2OH^-$	6×10^{-20}	$10^{-19.2}$
Ferric hydroxide	$Fe(OH)_3 = Fe^{+++} + 3OH^-$	1.5×10^{-36}	$10^{-35.8}$
Ferrous hydroxide	$Fe(OH)_2 = Fe^{++} + 2OH^-$	2×10^{-14}	$10^{-13.7}$
Lead hydroxide	$Pb(OH)_2 = Pb^{++} + 2OH^-$	2.5×10^{-16}	$10^{-15.6}$
Magnesium hydroxide	$Mg(OH)_2 = Mg^{++} + 2OH^-$	1.5×10^{-11}	$10^{-10.8}$
Manganese hydroxide	$Mn(OH)_2 = Mn^{++} + 2OH^-$	4.5×10^{-14}	$10^{-13.3}$
Zinc hydroxide	$Zn(OH)_2 = Zn^{++} + 2OH^-$	2.0×10^{-14}	$10^{-13.7}$
	$Zn(OH)_2 = H^+ + HZnO_2^-$	5×10^{-17}	$10^{-16.3}$

TABLE 3 (*Continued*)

SOLUBILITY-PRODUCT CONSTANTS AT ROOM TEMPERATURE

Substance	Equilibrium	Solubility-product Constant	
Iodates			
Barium iodate	$Ba(IO_3)_2 = Ba^{++} + 2IO_3^-$	6.5×10^{-10}	$10^{-9.2}$
Calcium iodate	$Ca(IO_3)_2 = Ca^{++} + 2IO_3^-$	6.5×10^{-7}	$10^{-6.2}$
Cupric iodate	$Cu(IO_3)_2 = Cu^{++} + 2IO_3^-$	1.4×10^{-7}	$10^{-6.9}$
Lead iodate	$Pb(IO_3)_2 = Pb^{++} + 2IO_3^-$	2.6×10^{-13}	$10^{-12.6}$
Silver iodate	$AgIO_3 = Ag^+ + IO_3^-$	1.0×10^{-8}	10^{-8}
Iodides			
Lead iodide	$PbI_2 = Pb^{++} + 2I^-$	1.4×10^{-8}	$10^{-7.9}$
Mercurous iodide	$Hg_2I_2 = Hg_2^{++} + 2I^-$	4×10^{-29}	$10^{-28.4}$
Silver iodide	$AgI = Ag^+ + I^-$	1.5×10^{-16}	$10^{-15.8}$
Thallous iodide	$TlI = Tl^+ + I^-$	2.5×10^{-8}	$10^{-7.6}$
Oxalates			
Barium oxalate	$BaC_2O_4 = Ba^{++} + C_2O_4^=$	1.5×10^{-7}	$10^{-6.8}$
Cadmium oxalate	$CdC_2O_4 = Cd^{++} + C_2O_4^=$	1.5×10^{-8}	$10^{-7.8}$
Calcium oxalate	$CaC_2O_4 = Ca^{++} + C_2O_4^=$	2.6×10^{-9}	$10^{-8.6}$
Cupric oxalate	$CuC_2O_4 = Cu^{++} + C_2O_4^=$	2.9×10^{-8}	$10^{-7.5}$
Ferrous oxalate	$FeC_2O_4 = Fe^{++} + C_2O_4^=$	2.1×10^{-7}	$10^{-6.7}$
Lead oxalate	$PbC_2O_4 = Pb^{++} + C_2O_4^=$	2.8×10^{-11}	$10^{-10.6}$
Magnesium oxalate	$MgC_2O_4 = Mg^{++} + C_2O_4^=$	8.8×10^{-5}	$10^{-4.1}$
Strontium oxalate	$SrC_2O_4 = Sr^{++} + C_2O_4^=$	5.8×10^{-8}	$10^{-7.2}$
Zinc oxalate	$ZnC_2O_4 = Zn^{++} + C_2O_4^=$	1.5×10^{-9}	$10^{-8.8}$
Sulfates			
Barium sulfate	$BaSO_4 = Ba^{++} + SO_4^=$	1.1×10^{-10}	10^{-10}
Calcium sulfate	$CaSO_4 = Ca^{++} + SO_4^=$	6.1×10^{-5}	$10^{-4.2}$
Lead sulfate	$PbSO_4 = Pb^{++} + SO_4^=$	1.1×10^{-8}	10^{-8}
Strontium sulfate	$SrSO_4 = Sr^{++} + SO_4^=$	2.9×10^{-7}	$10^{-6.5}$
Sulfides			
Cadmium sulfide	$CdS = Cd^{++} + S^=$	1.0×10^{-28}	10^{-28}
Cobalt sulfide	$CoS = Co^{++} + S^=$	1.0×10^{-27}	10^{-27}
Cupric sulfide	$CuS = Cu^{++} + S^=$	3.5×10^{-38}	$10^{-37.5}$
Ferrous sulfide	$FeS = Fe^{++} + S^=$	3.7×10^{-19}	$10^{-18.4}$
Lead sulfide	$PbS = Pb^{++} + S^=$	7.0×10^{-30}	$10^{-29.2}$
Manganous sulfide	$MnS = Mn^{++} + S^=$	1.4×10^{-15}	$10^{-14.9}$
Mercuric sulfide	$HgS = Hg^{++} + S^=$	1×10^{-50}	10^{-50}
Nickelous sulfide	$NiS = Ni^{++} + S^=$	1.4×10^{-24}	$10^{-23.9}$
Silver sulfide	$Ag_2S = 2Ag^+ + S^=$	4×10^{-52}	$10^{-51.4}$
Thallous sulfide	$Tl_2S = 2Tl^+ + S^=$	6.4×10^{-23}	$10^{-22.2}$
Zinc sulfide	$ZnS = Zn^{++} + S^=$	1.2×10^{-23}	$10^{-22.9}$
Thiocyanates			
Silver thiocyanate	$AgCNS = Ag^+ + CNS^-$	1.2×10^{-12}	$10^{-11.9}$

TABLE 4

DISSOCIATION CONSTANTS OF COMPLEX IONS

Equilibrium	Dissociation Constant	
$Cd(NH_3)_4^{++} = Cd^{++} + 4NH_3$	1×10^{-7}	10^{-7}
$Ag(NH_3)_2^{+} = Ag^{+} + 2NH_3$	6.8×10^{-8}	$10^{-7.2}$
$Zn(NH_3)_4^{++} = Zn^{++} + 4NH_3$	2.6×10^{-10}	$10^{-9.6}$
$HgBr_4^{=} = Hg^{++} + 4Br^{-}$	2.2×10^{-22}	$10^{-21.7}$
$HgCl_3^{-} = Hg^{++} + 3Cl^{-}$	6.0×10^{-17}	$10^{-16.2}$
$Cd(CN)_4^{=} = Cd^{++} + 4CN^{-}$	1.4×10^{-17}	$10^{-16.9}$
$Cu(CN)_3^{=} = Cu^{+} + 3CN^{-}$	5.0×10^{-28}	$10^{-27.3}$
$Hg(CN)_4^{=} = Hg^{++} + 4CN^{-}$	4×10^{-42}	$10^{-41.4}$
$Ag(CN)_2^{-} = Ag^{+} + 2CN^{-}$	8×10^{-23}	$10^{-22.1}$
$HgI_4^{=} = Hg^{++} + 4I^{-}$	5.0×10^{-32}	$10^{-31.3}$
$Hg(CNS)_4^{=} = Hg^{++} + 4CNS^{-}$	1.0×10^{-22}	10^{-22}

APPENDIX III

PREPARATION OF INDICATOR SOLUTIONS

Bromcresol green. Dissolve 0.1 g bromcresol green in 7.2 ml 0.02 *N* NaOH, and dilute to 250 ml.

Bromphenol blue. Dissolve 0.1 g bromphenol blue in 7.5 ml 0.02 *N* NaOH, and dilute to 250 ml.

Bromthymol blue. Dissolve 0.1 g bromthymol blue in 8.0 ml 0.02 *N* NaOH, and dilute to 250 ml.

Dichlorofluorescein. Dissolve 0.1 g dichlorofluorescein in 100 ml 70 per cent alcohol, or dissolve 0.1 g sodium dichlorofluoresceinate in 100 ml water.

Diphenylamine sulfonate. Dissolve 0.32 g barium diphenylamine sulfonate in 100 ml water, and add 0.5 g sodium sulfate. Filter to remove barium sulfate precipitate.

Ferric alum. Dissolve 28 g ferric alum crystals in 80 ml hot water. Cool, filter, and dilute to 100 ml with 6 *N* nitric acid.

Ferroin. See phenanthroline–ferrous ion indicator.

Methyl orange. Dissolve 0.1 g methyl orange in 100 ml water.

Methyl red. Dissolve 0.1 g methyl red in 18.6 ml 0.02 *N* NaOH, and dilute to 250 ml.

Methyl red–bromcresol green mixed indicator. Mix 2 parts methyl red solution with 3 parts bromcresol green solution.

Modified methyl orange. Dissolve 0.75 g xylene cyanole FF and 1.5 g methyl orange in 1 l. water.

Phenanthroline–ferrous ion. (Ferroin). Dissolve 0.5 g phenanthroline monohydrate in 100 ml 0.025 *M* ferrous sulfate solution.

Phenolphthalein. Dissolve 0.1 to 0.5 g (depending on strength desired) phenolphthalein in 50 ml alcohol, and add 50 ml water.

Prop. Parts	N	0	1	2	3	4	5	6	7	8	9
	150	17 609	638	667	696	725	754	782	811	840	869
	51	17 898	926	955	984	*013	*041	*070	*099	*127	*156
29 28	52	18 184	213	241	270	298	327	355	384	412	441
1 2.9 2.8	53	469	498	526	554	583	611	639	667	696	724
2 5.8 5.6											
3 8.7 8.4	54	18 752	780	808	837	865	893	921	949	977	*005
4 11.6 11.2	55	19 033	061	089	117	145	173	201	229	257	285
5 14.5 14.0	56	312	340	368	396	424	451	479	507	535	562
6 17.4 16.8											
7 20.3 19.6	57	590	618	645	673	700	728	756	783	811	838
8 23.2 22.4	58	19 866	893	921	948	976	*003	*030	*058	*085	*112
9 26.1 25.2	59	20 140	167	194	222	249	276	303	330	358	385
	160	412	439	466	493	520	548	575	602	629	656
	61	683	710	737	763	790	817	844	871	898	925
27 26	62	20 952	978	*005	*032	*059	*085	*112	*139	*165	*192
1 2.7 2.6	63	21 219	245	272	299	325	352	378	405	431	458
2 5.4 5.2											
3 8.1 7.8	64	484	511	537	564	590	617	643	669	696	722
4 10.8 10.4	65	21 748	775	801	827	854	880	906	932	958	985
5 13.5 13.0	66	22 011	037	063	089	115	141	167	194	220	246
6 16.2 15.6											
7 18.9 18.2	67	272	298	324	350	376	401	427	453	479	505
8 21.6 20.8	68	531	557	583	608	634	660	686	712	737	763
9 24.3 23.4	69	22 789	814	840	866	891	917	943	968	994	*019
	170	23 045	070	096	121	147	172	198	223	249	274
	71	300	325	350	376	401	426	452	477	502	528
25	72	553	578	603	629	654	679	704	729	754	779
1 2.5	73	23 805	830	855	880	905	930	955	980	*005	*030
2 5.0											
3 7.5	74	24 055	080	105	130	155	180	204	229	254	279
4 10.0	75	304	329	353	378	403	428	452	477	502	527
5 12.5	76	551	576	601	625	650	674	699	724	748	773
6 15.0											
7 17.5	77	24 797	822	846	871	895	920	944	969	993	*018
8 20.0	78	25 042	066	091	115	139	164	188	212	237	261
9 22.5	79	285	310	334	358	382	406	431	455	479	503
	180	527	551	575	600	624	648	672	696	720	744
	81	25 768	792	816	840	864	888	912	935	959	983
24 23	82	26 007	031	055	079	102	126	150	174	198	221
1 2.4 2.3	83	245	269	293	316	340	364	387	411	435	458
2 4.8 4.6											
3 7.2 6.9	84	482	505	529	553	576	600	623	647	670	694
4 9.6 9.2	85	717	741	764	788	811	834	858	881	905	928
5 12.0 11.5	86	26 951	975	998	*021	*045	*068	*091	*114	*138	*161
6 14.4 13.8											
7 16.8 16.1	87	27 184	207	231	254	277	300	323	346	370	393
8 19.2 18.4	88	416	439	462	485	508	531	554	577	600	623
9 21.6 20.7	89	646	669	692	715	738	761	784	807	830	852
	190	27 875	898	921	944	967	989	*012	*035	*058	*081
	91	28 103	126	149	171	194	217	240	262	285	307
22 21	92	330	353	375	398	421	443	466	488	511	533
1 2.2 2.1	93	556	578	601	623	646	668	691	713	735	758
2 4.4 4.2											
3 6.6 6.3	94	28 780	803	825	847	870	892	914	937	959	981
4 8.8 8.4	95	29 003	026	048	070	092	115	137	159	181	203
5 11.0 10.5	96	226	248	270	292	314	336	358	380	403	425
6 13.2 12.6											
7 15.4 14.7	97	447	469	491	513	535	557	579	601	623	645
8 17.6 16.8	98	667	688	710	732	754	776	798	820	842	863
9 19.8 18.9	99	29 885	907	929	951	973	994	*016	*038	*060	*081
	200	30 103	125	146	168	190	211	233	255	276	298
Prop. Parts	**N**	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
200	30 103	125	146	168	190	211	233	255	276	298	
01	320	341	363	384	406	428	449	471	492	514	
02	535	557	578	600	621	643	664	685	707	728	22 21
03	750	771	792	814	835	856	878	899	920	942	1 2.2 2.1
											2 4.4 4.2
04	30 963	984	*006	*027	*048	*069	*091	*112	*133	*154	3 6.6 6.3
05	31 175	197	218	239	260	281	302	323	345	366	4 8.8 8.4
06	387	408	429	450	471	492	513	534	555	576	5 11.0 10.5
											6 13.2 12.6
07	597	618	639	660	681	702	723	744	765	785	7 15.4 14.7
08	31 806	827	848	869	890	911	931	952	973	994	8 17.6 16.8
09	32 015	035	056	077	098	118	139	160	181	201	9 19.8 18.9
210	222	243	263	284	305	325	346	366	387	408	
11	428	449	469	490	510	531	552	572	593	613	
12	634	654	675	695	715	736	756	777	797	818	20
13	32 838	858	879	899	919	940	960	980	*001	*021	1 2
											2 4
14	33 041	062	082	102	122	143	163	183	203	224	3 6
15	244	264	284	304	325	345	365	385	405	425	4 8
16	445	465	486	506	526	546	566	586	606	626	5 10
											6 12
17	646	666	686	706	726	746	766	786	806	826	7 14
18	33 846	866	885	905	925	945	965	985	*005	*025	8 16
19	34 044	064	084	104	124	143	163	183	203	223	9 18
220	242	262	282	301	321	341	361	380	400	420	
21	439	459	479	498	518	537	557	577	596	616	
22	635	655	674	694	713	733	753	772	792	811	19
23	34 830	850	869	889	908	928	947	967	986	*005	1 1.9
											2 3.8
24	35 025	044	064	083	102	122	141	160	180	199	3 5.7
25	218	238	257	276	295	315	334	353	372	392	4 7.6
26	411	430	449	468	488	507	526	545	564	583	5 9.5
											6 11.4
27	603	622	641	660	679	698	717	736	755	774	7 13.3
28	793	813	832	851	870	889	908	927	946	965	8 15.2
29	35 984	*003	*021	*040	*059	*078	*097	*116	*135	*154	9 17.1
230	36 173	192	211	229	248	267	286	305	324	342	
31	361	380	399	418	436	455	474	493	511	530	
32	549	568	586	605	624	642	661	680	698	717	18
33	736	754	773	791	810	829	847	866	884	903	1 1.8
											2 3.6
34	36 922	940	959	977	996	*014	*033	*051	*070	*088	3 5.4
35	37 107	125	144	162	181	199	218	236	254	273	4 7.2
36	291	310	328	346	365	383	401	420	438	457	5 9.0
											6 10.8
37	475	493	511	530	548	566	585	603	621	639	7 12.6
38	658	676	694	712	731	749	767	785	803	822	8 14.4
39	37 840	858	876	894	912	931	949	967	985	*003	9 16.2
240	38 021	039	057	075	093	112	130	148	166	184	
41	202	220	238	256	274	292	310	328	346	364	
42	382	399	417	435	453	471	489	507	525	543	17
43	561	578	596	614	632	650	668	686	703	721	1 1.7
											2 3.4
44	739	757	775	792	810	828	846	863	881	899	3 5.1
45	38 917	934	952	970	987	*005	*023	*041	*058	*076	4 6.8
46	39 094	111	129	146	164	182	199	217	235	252	5 8.5
											6 10.2
47	270	287	305	322	340	358	375	393	410	428	7 11.9
48	445	463	480	498	515	533	550	568	585	602	8 13.6
49	620	637	655	672	690	707	724	742	759	777	9 15.3
250	39 794	811	829	846	863	881	898	915	933	950	
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**Prop. Parts**

Prop. Parts	N	0	1	2	3	4	5	6	7	8	9
	250	39 794	811	829	846	863	881	898	915	933	950
	51	39 967	985	*002	*019	*037	*054	*071	*088	*106	*123
18	52	40 140	157	175	192	209	226	243	261	278	295
1 1.8	53	312	329	346	364	381	398	415	432	449	466
2 3.6											
3 5.4	54	483	500	518	535	552	569	586	603	620	637
4 7.2	55	654	671	688	705	722	739	756	773	790	807
5 9.0	56	824	841	858	875	892	909	926	943	960	976
6 10.8											
7 12.6	57	40 993	*010	*027	*044	*061	*078	*095	*111	*128	*145
8 14.4	58	41 162	179	196	212	229	246	263	280	296	313
9 16.2	59	330	347	363	380	397	414	430	447	464	481
	260	497	514	531	547	564	581	597	614	631	647
	61	664	681	697	714	731	747	764	780	797	814
17	62	830	847	863	880	896	913	929	946	963	979
1 1.7	63	41 996	*012	*029	*045	*062	*078	*095	*111	*127	*144
2 3.4											
3 5.1	64	42 160	177	193	210	226	243	259	275	292	308
4 6.8	65	325	341	357	374	390	406	423	439	455	472
5 8.5	66	488	504	521	537	553	570	586	602	619	635
6 10.2											
7 11.9	67	651	667	684	700	716	732	749	765	781	797
8 13.6	68	813	830	846	862	878	894	911	927	943	959
9 15.3	69	42 975	991	*008	*024	*040	*056	*072	*088	*104	*120
	270	43 136	152	169	185	201	217	233	249	265	281
	71	297	313	329	345	361	377	393	409	425	441
16	72	457	473	489	505	521	537	553	569	584	600
1 1.6	73	616	632	648	664	680	696	712	727	743	759
2 3.2											
3 4.8	74	775	791	807	823	838	854	870	886	902	917
4 6.4	75	43 933	949	965	981	996	*012	*028	*044	*059	*075
5 8.0	76	44 091	107	122	138	154	170	185	201	217	232
6 9.6											
7 11.2	77	248	264	279	295	311	326	342	358	373	389
8 12.8	78	404	420	436	451	467	483	498	514	529	545
9 14.4	79	560	576	592	607	623	638	654	669	685	700
	280	716	731	747	762	778	793	809	824	840	855
	81	44 871	886	902	917	932	948	963	979	994	*010
15	82	45 025	040	056	071	086	102	117	133	148	163
1 1.5	83	179	194	209	225	240	255	271	286	301	317
2 3.0											
3 4.5	84	332	347	362	378	393	408	423	439	454	469
4 6.0	85	484	500	515	530	545	561	576	591	606	621
5 7.5	86	637	652	667	682	697	712	728	743	758	773
6 9.0											
7 10.5	87	788	803	818	834	849	864	879	894	909	924
8 12.0	88	45 939	954	969	984	*000	*015	*030	*045	*060	*075
9 13.5	89	46 090	105	120	135	150	165	180	195	210	225
	290	240	255	270	285	300	315	330	345	359	374
	91	389	404	419	434	449	464	479	494	509	523
14	92	538	553	568	583	598	613	627	642	657	672
1 1.4	93	687	702	716	731	746	761	776	790	805	820
2 2.8											
3 4.2	94	835	850	864	879	894	909	923	938	953	967
4 5.6	95	46 982	997	*012	*026	*041	*056	*070	*085	*100	*114
5 7.0	96	47 129	144	159	173	188	202	217	232	246	261
6 8.4											
7 9.8	97	276	290	305	319	334	349	363	378	392	407
8 11.2	98	422	436	451	465	480	494	509	524	538	553
9 12.6	99	567	582	596	611	625	640	654	669	683	698
	300	47 712	727	741	756	770	784	799	813	828	842
Prop. Parts	**N**	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
300	47 712	727	741	756	770	784	799	813	828	842	
01	47 857	871	885	900	914	929	943	958	972	986	
02	48 001	015	029	044	058	073	087	101	116	130	
03	144	159	173	187	202	216	230	244	259	273	**15**
04	287	302	316	330	344	359	373	387	401	416	**1** 1.5
05	430	444	458	473	487	501	515	530	544	558	**2** 3.0
06	572	586	601	615	629	643	657	671	686	700	**3** 4.5
07	714	728	742	756	770	785	799	813	827	841	**4** 6.0
08	855	869	883	897	911	926	940	954	968	982	**5** 7.5
09	48 996	*010	*024	*038	*052	*066	*080	*094	*108	*122	**6** 9.0
310	49 136	150	164	178	192	206	220	234	248	262	**7** 10.5
11	276	290	304	318	332	346	360	374	388	402	**8** 12.0
12	415	429	443	457	471	485	499	513	527	541	**9** 13.5
13	554	568	582	596	610	624	638	651	665	679	
14	693	707	721	734	748	762	776	790	803	817	
15	831	845	859	872	886	900	914	927	941	955	
16	49 969	982	996	*010	*024	*037	*051	*065	*079	*092	**14**
17	50 106	120	133	147	161	174	188	202	215	229	**1** 1.4
18	243	256	270	284	297	311	325	338	352	365	**2** 2.8
19	379	393	406	420	433	447	461	474	488	501	**3** 4.2
320	515	529	542	556	569	583	596	610	623	637	**4** 5.6
21	651	664	678	691	705	718	732	745	759	772	**5** 7.0
22	786	799	813	826	840	853	866	880	893	907	**6** 8.4
23	50 920	934	947	961	974	987	*001	*014	*028	*041	**7** 9.8
24	51 055	068	081	095	108	121	135	148	162	175	**8** 11.2
25	188	202	215	228	242	255	268	282	295	308	**9** 12.6
26	322	335	348	362	375	388	402	415	428	441	
27	455	468	481	495	508	521	534	548	561	574	
28	587	601	614	627	640	654	667	680	693	706	
29	720	733	746	759	772	786	799	812	825	838	**13**
330	851	865	878	891	904	917	930	943	957	970	**1** 1.3
31	51 983	996	*009	*022	*035	*048	*061	*075	*088	*101	**2** 2.6
32	52 114	127	140	153	166	179	192	205	218	231	**3** 3.9
33	244	257	270	284	297	310	323	336	349	362	**4** 5.2
34	375	388	401	414	427	440	453	466	479	492	**5** 6.5
35	504	517	530	543	556	569	582	595	608	621	**6** 7.8
36	634	647	660	673	686	699	711	724	737	750	**7** 9.1
37	763	776	789	802	815	827	840	853	866	879	**8** 10.4
38	52 892	905	917	930	943	956	969	982	994	*007	**9** 11.7
39	53 020	033	046	058	071	084	097	110	122	135	
340	148	161	173	186	199	212	224	237	250	263	
41	275	288	301	314	326	339	352	364	377	390	**12**
42	403	415	428	441	453	466	479	491	504	517	**1** 1.2
43	529	542	555	567	580	593	605	618	631	643	**2** 2.4
44	656	668	681	694	706	719	732	744	757	769	**3** 3.6
45	782	794	807	820	832	845	857	870	882	895	**4** 4.8
46	53 908	920	933	945	958	970	983	995	*008	*020	**5** 6.0
47	54 033	045	058	070	083	095	108	120	133	145	**6** 7.2
48	158	170	183	195	208	220	233	245	258	270	**7** 8.4
49	283	295	307	320	332	345	357	370	382	394	**8** 9.6
350	54 407	419	432	444	456	469	481	494	506	518	**9** 10.8
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**Prop. Parts**

Prop. Parts	N	0	1	2	3	4	5	6	7	8	9
	350	54 407	419	432	444	456	469	481	494	506	518
	51	531	543	555	568	580	593	605	617	630	642
	52	654	667	679	691	704	716	728	741	753	765
	53	777	790	802	814	827	839	851	864	876	888
13											
1 1.3	54	54 900	913	925	937	949	962	974	986	998	*011
2 2.6	55	55 023	035	047	060	072	084	096	108	121	133
3 3.9	56	145	157	169	182	194	206	218	230	242	255
4 5.2											
5 6.5	57	267	279	291	303	315	328	340	352	364	376
6 7.8	58	388	400	413	425	437	449	461	473	485	497
7 9.1	59	509	522	534	546	558	570	582	594	606	618
8 10.4											
9 11.7	**360**	630	642	654	666	678	691	703	715	727	739
	61	751	763	775	787	799	811	823	835	847	859
	62	871	883	895	907	919	931	943	955	967	979
	63	55 991	*003	*015	*027	*038	*050	*062	*074	*086	*098
	64	56 110	122	134	146	158	170	182	194	205	217
	65	229	241	253	265	277	289	301	312	324	336
	66	348	360	372	384	396	407	419	431	443	455
12											
1 1.2	67	467	478	490	502	514	526	538	549	561	573
2 2.4	68	585	597	608	620	632	644	656	667	679	691
3 3.6	69	703	714	726	738	750	761	773	785	797	808
4 4.8											
5 6.0	**370**	820	832	844	855	867	879	891	902	914	926
6 7.2											
7 8.4	71	56 937	949	961	972	984	996	*008	*019	*031	*043
8 9.6	72	57 054	066	078	089	101	113	124	136	148	159
9 10.8	73	171	183	194	206	217	229	241	252	264	276
	74	287	299	310	322	334	345	357	368	380	392
	75	403	415	426	438	449	461	473	484	496	507
	76	519	530	542	553	565	576	588	600	611	623
	77	634	646	657	669	680	692	703	715	726	738
	78	749	761	772	784	795	807	818	830	841	852
	79	864	875	887	898	910	921	933	944	955	967
11											
1 1.1											
2 2.2	**380**	57 978	990	*001	*013	*024	*035	*047	*058	*070	*081
3 3.3											
4 4.4	81	58 092	104	115	127	138	149	161	172	184	195
5 5.5	82	206	218	229	240	252	263	274	286	297	309
6 6.6	83	320	331	343	354	365	377	388	399	410	422
7 7.7											
8 8.8	84	433	444	456	467	478	490	501	512	524	535
9 9.9	85	546	557	569	580	591	602	614	625	636	647
	86	659	670	681	692	704	715	726	737	749	760
	87	771	782	794	805	816	827	838	850	861	872
	88	883	894	906	917	928	939	950	961	973	984
	89	58 995	*006	*017	*028	*040	*051	*062	*073	*084	*095
	390	59 106	118	129	140	151	162	173	184	195	207
10											
1 1.0	91	218	229	240	251	262	273	284	295	306	318
2 2.0	92	329	340	351	362	373	384	395	406	417	428
3 3.0	93	439	450	461	472	483	494	506	517	528	539
4 4.0											
5 5.0	94	550	561	572	583	594	605	616	627	638	649
6 6.0	95	660	671	682	693	704	715	726	737	748	759
7 7.0	96	770	780	791	802	813	824	835	846	857	868
8 8.0											
9 9.0	97	879	890	901	912	923	934	945	956	966	977
	98	59 988	999	*010	*021	*032	*043	*054	*065	*076	*086
	99	60 097	108	119	130	141	152	163	173	184	195
	400	60 206	217	228	239	249	260	271	282	293	304
Prop. Parts	N	0	1	2	3	4	5	6	7	8	9

N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
400	60 206	217	228	239	249	260	271	282	293	304	
01	314	325	336	347	358	369	379	390	401	412	
02	423	433	444	455	466	477	487	498	509	520	
03	531	541	552	563	574	584	595	606	617	627	
04	638	649	660	670	681	692	703	713	724	735	
05	746	756	767	778	788	799	810	821	831	842	
06	853	863	874	885	895	906	917	927	938	949	
07	60 959	970	981	991	*002	*013	*023	*034	*045	*055	**11**
08	61 066	077	087	098	109	119	130	140	151	162	**1** 1.1
09	172	183	194	204	215	225	236	247	257	268	**2** 2.2 **3** 3.3 **4** 4.4
410	278	289	300	310	321	331	342	352	363	374	**5** 5.5 **6** 6.6
11	384	395	405	416	426	437	448	458	469	479	**7** 7.7
12	490	500	511	521	532	542	553	563	574	584	**8** 8.8
13	595	606	616	627	637	648	658	669	679	690	**9** 9.9
14	700	711	721	731	742	752	763	773	784	794	
15	805	815	826	836	847	857	868	878	888	899	
16	61 909	920	930	941	951	962	972	982	993	*003	
17	62 014	024	034	045	055	066	076	086	097	107	
18	118	128	138	149	159	170	180	190	201	211	
19	221	232	242	252	263	273	284	294	304	315	
420	325	335	346	356	366	377	387	397	408	418	
21	428	439	449	459	469	480	490	500	511	521	
22	531	542	552	562	572	583	593	603	613	624	**10**
23	634	644	655	665	675	685	696	706	716	726	**1** 1.0
24	737	747	757	767	778	788	798	808	818	829	**2** 2.0 **3** 3.0
25	839	849	859	870	880	890	900	910	921	931	**4** 4.0
26	62 941	951	961	972	982	992	*002	*012	*022	*033	**5** 5.0 **6** 6.0
27	63 043	053	063	073	083	094	104	114	124	134	**7** 7.0
28	144	155	165	175	185	195	205	215	225	236	**8** 8.0
29	246	256	266	276	286	296	306	317	327	337	**9** 9.0
430	347	357	367	377	387	397	407	417	428	438	
31	448	458	468	478	488	498	508	518	528	538	
32	548	558	568	579	589	599	609	619	629	639	
33	649	659	669	679	689	699	709	719	729	739	
34	749	759	769	779	789	799	809	819	829	839	
35	849	859	869	879	889	899	909	919	929	939	
36	63 949	959	969	979	988	998	*008	*018	*028	*038	
37	64 048	058	068	078	088	098	108	118	128	137	
38	147	157	167	177	187	197	207	217	227	237	**9**
39	246	256	266	276	286	296	306	316	326	335	**1** 0.9 **2** 1.8 **3** 2.7
440	345	355	365	375	385	395	404	414	424	434	**4** 3.6 **5** 4.5 **6** 5.4
41	444	454	464	473	483	493	503	513	523	532	**7** 6.3
42	542	552	562	572	582	591	601	611	621	631	**8** 7.2
43	640	650	660	670	680	689	699	709	719	729	**9** 8.1
44	738	748	758	768	777	787	797	807	816	826	
45	836	846	856	865	875	885	895	904	914	924	
46	64 933	943	953	963	972	982	992	*002	*011	*021	
47	65 031	040	050	060	070	079	089	099	108	118	
48	128	137	147	157	167	176	186	196	205	215	
49	225	234	244	254	263	273	283	292	302	312	
450	65 321	331	341	350	360	369	379	389	398	408	
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**Prop. Parts**

Prop. Parts	N	0	1	2	3	4	5	6	7	8	9
	450	65 321	331	341	350	360	369	379	389	398	408
	51	418	427	437	447	456	466	475	485	495	504
	52	514	523	533	543	552	562	571	581	591	600
	53	610	619	629	639	648	658	667	677	686	696
	54	706	715	725	734	744	753	763	772	782	792
	55	801	811	820	830	839	849	858	868	877	887
	56	896	906	916	925	935	944	954	963	973	982
10											
1 1.0	57	65 992	*001	*011	*020	*030	*039	*049	*058	*068	*077
2 2.0	58	66 087	096	106	115	124	134	143	153	162	172
3 3.0	59	181	191	200	210	219	229	238	247	257	266
4 4.0											
5 5.0	**460**	276	285	295	304	314	323	332	342	351	361
6 6.0											
7 7.0	61	370	380	389	398	408	417	427	436	445	455
8 8.0	62	464	474	483	492	502	511	521	530	539	549
9 9.0	63	558	567	577	586	596	605	614	624	633	642
	64	652	661	671	680	689	699	708	717	727	736
	65	745	755	764	773	783	792	801	811	820	829
	66	839	848	857	867	876	885	894	904	913	922
	67	66 932	941	950	960	969	978	987	997	*006	*015
	68	67 025	034	043	052	062	071	080	089	099	108
	69	117	127	136	145	154	164	173	182	191	201
	470	210	219	228	237	247	256	265	274	284	293
	71	302	311	321	330	339	348	357	367	376	385
9	72	394	403	413	422	431	440	449	459	468	477
1 0.9	73	486	495	504	514	523	532	541	550	560	569
2 1.8											
3 2.7	74	578	587	596	605	614	624	633	642	651	660
4 3.6	75	669	679	688	697	706	715	724	733	742	752
5 4.5	76	761	770	779	788	797	806	815	825	834	843
6 5.4											
7 6.3	77	852	861	870	879	888	897	906	916	925	934
8 7.2	78	67 943	952	961	970	979	988	997	*006	*015	*024
9 8.1	79	68 034	043	052	061	070	079	088	097	106	115
	480	124	133	142	151	160	169	178	187	196	205
	81	215	224	233	242	251	260	269	278	287	296
	82	305	314	323	332	341	350	359	368	377	386
	83	395	404	413	422	431	440	449	458	467	476
	84	485	494	502	511	520	529	538	547	556	565
	85	574	583	592	601	610	619	628	637	646	655
	86	664	673	681	690	699	708	717	726	735	744
	87	753	762	771	780	789	797	806	815	824	833
8	88	842	851	860	869	878	886	895	904	913	922
1 0.8	89	68 931	940	949	958	966	975	984	993	*002	*011
2 1.6											
3 2.4	**490**	69 020	028	037	046	055	064	073	082	090	099
4 3.2											
5 4.0	91	108	117	126	135	144	152	161	170	179	188
6 4.8	92	197	205	214	223	232	241	249	258	267	276
7 5.6	93	285	294	302	311	320	329	338	346	355	364
8 6.4											
9 7.2	94	373	381	390	399	408	417	425	434	443	452
	95	461	469	478	487	496	504	513	522	531	539
	96	548	557	566	574	583	592	601	609	618	627
	97	636	644	653	662	671	679	688	697	705	714
	98	723	732	740	749	758	767	775	784	793	801
	99	810	819	827	836	845	854	862	871	880	888
	500	69 897	906	914	923	932	940	949	958	966	975
Prop. Parts	N	0	1	2	3	4	5	6	7	8	9

N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
500	69 897	906	914	923	932	940	949	958	966	975	
01	69 984	992	*001	*010	*018	*027	*036	*044	*053	*062	
02	70 070	079	088	096	105	114	122	131	140	148	
03	157	165	174	183	191	200	209	217	226	234	
04	243	252	260	269	278	286	295	303	312	321	
05	329	338	346	355	364	372	381	389	398	406	
06	415	424	432	441	449	458	467	475	484	492	
07	501	509	518	526	535	544	552	561	569	578	9 | 1 0.9
08	586	595	603	612	621	629	638	646	655	663	2 1.8
09	672	680	689	697	706	714	723	731	740	749	3 2.7
510	757	766	774	783	791	800	808	817	825	834	4 3.6 5 4.5 6 5.4
11	842	851	859	868	876	885	893	902	910	919	7 6.3
12	70 927	935	944	952	961	969	978	986	995	*003	8 7.2
13	71 012	020	029	037	046	054	063	071	079	088	9 8.1
14	096	105	113	122	130	139	147	155	164	172	
15	181	189	198	206	214	223	231	240	248	257	
16	265	273	282	290	299	307	315	324	332	341	
17	349	357	366	374	383	391	399	408	416	425	
18	433	441	450	458	466	475	483	492	500	508	
19	517	525	533	542	550	559	567	575	584	592	
520	600	609	617	625	634	642	650	659	667	675	
21	684	692	700	709	717	725	734	742	750	759	
22	767	775	784	792	800	809	817	825	834	842	8 | 1 0.8
23	850	858	867	875	883	892	900	908	917	925	2 1.6
24	71 933	941	950	958	966	975	983	991	999	*008	3 2.4
25	72 016	024	032	041	049	057	066	074	082	090	4 3.2
26	099	107	115	123	132	140	148	156	165	173	5 4.0 6 4.8
27	181	189	198	206	214	222	230	239	247	255	7 5.6
28	263	272	280	288	296	304	313	321	329	337	8 6.4
29	346	354	362	370	378	387	395	403	411	419	9 7.2
530	428	436	444	452	460	469	477	485	493	501	
31	509	518	526	534	542	550	558	567	575	583	
32	591	599	607	616	624	632	640	648	656	665	
33	673	681	689	697	705	713	722	730	738	746	
34	754	762	770	779	787	795	803	811	819	827	
35	835	843	852	860	868	876	884	892	900	908	
36	916	925	933	941	949	957	965	973	981	989	
37	72 997	*006	*014	*022	*030	*038	*046	*054	*062	*070	
38	73 078	086	094	102	111	119	127	135	143	151	7 | 1 0.7
39	159	167	175	183	191	199	207	215	223	231	2 1.4
540	239	247	255	263	272	280	288	296	304	312	3 2.1 4 2.8
41	320	328	336	344	352	360	368	376	384	392	5 3.5
42	400	408	416	424	432	440	448	456	464	472	6 4.2
43	480	488	496	504	512	520	528	536	544	552	7 4.9 8 5.6
44	560	568	576	584	592	600	608	616	624	632	9 6.3
45	640	648	656	664	672	679	687	695	703	711	
46	719	727	735	743	751	759	767	775	783	791	
47	799	807	815	823	830	838	846	854	862	870	
48	878	886	894	902	910	918	926	933	941	949	
49	73 957	965	973	981	989	997	*005	*013	*020	*028	
550	74 036	044	052	060	068	076	084	092	099	107	
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**Prop. Parts**

Prop. Parts	N	0	1	2	3	4	5	6	7	8	9
	550	74 036	044	052	060	068	076	084	092	099	107
	51	115	123	131	139	147	155	162	170	178	186
	52	194	202	210	218	225	233	241	249	257	265
	53	273	280	288	296	304	312	320	327	335	343
	54	351	359	367	374	382	390	398	406	414	421
	55	429	437	445	453	461	468	476	484	492	500
	56	507	515	523	531	539	547	554	562	570	578
	57	586	593	601	609	617	624	632	640	648	656
	58	663	671	679	687	695	702	710	718	726	733
	59	741	749	757	764	772	780	788	796	803	811
	560	819	827	834	842	850	858	865	873	881	889
	61	896	904	912	920	927	935	943	950	958	966
8	62	74 974	981	989	997	*005	*012	*020	*028	*035	*043
1 0.8	63	75 051	059	066	074	082	089	097	105	113	120
2 1.6											
3 2.4	64	128	136	143	151	159	166	174	182	189	197
4 3.2	65	205	213	220	228	236	243	251	259	266	274
5 4.0	66	282	289	297	305	312	320	328	335	343	351
6 4.8											
7 5.6	67	358	366	374	381	389	397	404	412	420	427
8 6.4	68	435	442	450	458	465	473	481	488	496	504
9 7.2	69	511	519	526	534	542	549	557	565	572	580
	570	587	595	603	610	618	626	633	641	648	656
	71	664	671	679	686	694	702	709	717	724	732
	72	740	747	755	762	770	778	785	793	800	808
	73	815	823	831	838	846	853	861	868	876	884
	74	891	899	906	914	921	929	937	944	952	959
	75	75 967	974	982	989	997	*005	*012	*020	*027	*035
	76	76 042	050	057	065	072	080	087	095	103	110
	77	118	125	133	140	148	155	163	170	178	185
	78	193	200	208	215	223	230	238	245	253	260
	79	268	275	283	290	298	305	313	320	328	335
	580	343	350	358	365	373	380	388	395	403	410
	81	418	425	433	440	448	455	462	470	477	485
7	82	492	500	507	515	522	530	537	545	552	559
1 0.7	83	567	574	582	589	597	604	612	619	626	634
2 1.4											
3 2.1	84	641	649	656	664	671	678	686	693	701	708
4 2.8	85	716	723	730	738	745	753	760	768	775	782
5 3.5	86	790	797	805	812	819	827	834	842	849	856
6 4.2											
7 4.9	87	864	871	879	886	893	901	908	916	923	930
8 5.6	88	76 938	945	953	960	967	975	982	989	997	*004
9 6.3	89	77 012	019	026	034	041	048	056	063	070	078
	590	085	093	100	107	115	122	129	137	144	151
	91	159	166	173	181	188	195	203	210	217	225
	92	232	240	247	254	262	269	276	283	291	298
	93	305	313	320	327	335	342	349	357	364	371
	94	379	386	393	401	408	415	422	430	437	444
	95	452	459	466	474	481	488	495	503	510	517
	96	525	532	539	546	554	561	568	576	583	590
	97	597	605	612	619	627	634	641	648	656	663
	98	670	677	685	692	699	706	714	721	728	735
	99	743	750	757	764	772	779	786	793	801	808
	600	77 815	822	830	837	844	851	859	866	873	880
Prop. Parts	N	0	1	2	3	4	5	6	7	8	9

N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
600	77 815	822	830	837	844	851	859	866	873	880	
01	887	895	902	909	916	924	931	938	945	952	
02	77 960	967	974	981	988	996	*003	*010	*017	*025	
03	78 032	039	046	053	061	068	075	082	089	097	
04	104	111	118	125	132	140	147	154	161	168	
05	176	183	190	197	204	211	219	226	233	240	
06	247	254	262	269	276	283	290	297	305	312	
07	319	326	333	340	347	355	362	369	376	383	8 | 1 0.8 | 2 1.6 | 3 2.4 | 4 3.2 | 5 4.0 | 6 4.8 | 7 5.6 | 8 6.4 | 9 7.2
08	390	398	405	412	419	426	433	440	447	455	
09	462	469	476	483	490	497	504	512	519	526	
610	533	540	547	554	561	569	576	583	590	597	
11	604	611	618	625	633	640	647	654	661	668	
12	675	682	689	696	704	711	718	725	732	739	
13	746	753	760	767	774	781	789	796	803	810	
14	817	824	831	838	845	852	859	866	873	880	
15	888	895	902	909	916	923	930	937	944	951	
16	78 958	965	972	979	986	993	*000	*007	*014	*021	
17	79 029	036	043	050	057	064	071	078	085	092	
18	099	106	113	120	127	134	141	148	155	162	
19	169	176	183	190	197	204	211	218	225	232	
620	239	246	253	260	267	274	281	288	295	302	
21	309	316	323	330	337	344	351	358	365	372	
22	379	386	393	400	407	414	421	428	435	442	
23	449	456	463	470	477	484	491	498	505	511	7 | 1 0.7 | 2 1.4 | 3 2.1 | 4 2.8 | 5 3.5 | 6 4.2 | 7 4.9 | 8 5.6 | 9 6.3
24	518	525	532	539	546	553	560	567	574	581	
25	588	595	602	609	616	623	630	637	644	650	
26	657	664	671	678	685	692	699	706	713	720	
27	727	734	741	748	754	761	768	775	782	789	
28	796	803	810	817	824	831	837	844	851	858	
29	865	872	879	886	893	900	906	913	920	927	
630	79 934	941	948	955	962	969	975	982	989	996	
31	80 003	010	017	024	030	037	044	051	058	065	
32	072	079	085	092	099	106	113	120	127	134	
33	140	147	154	161	168	175	182	188	195	202	
34	209	216	223	229	236	243	250	257	264	271	
35	277	284	291	298	305	312	318	325	332	339	
36	346	353	359	366	373	380	387	393	400	407	
37	414	421	428	434	441	448	455	462	468	475	
38	482	489	496	502	509	516	523	530	536	543	6 | 1 0.6 | 2 1.2 | 3 1.8 | 4 2.4 | 5 3.0 | 6 3.6 | 7 4.2 | 8 4.8 | 9 5.4
39	550	557	564	570	577	584	591	598	604	611	
640	618	625	632	638	645	652	659	665	672	679	
41	686	693	699	706	713	720	726	733	740	747	
42	754	760	767	774	781	787	794	801	808	814	
43	821	828	835	841	848	855	862	868	875	882	
44	889	895	902	909	916	922	929	936	943	949	
45	80 956	963	969	976	983	990	996	*003	*010	*017	
46	81 023	030	037	043	050	057	064	070	077	084	
47	090	097	104	111	117	124	131	137	144	151	
48	158	164	171	178	184	191	198	204	211	218	
49	224	231	238	245	251	258	265	271	278	285	
650	81 291	298	305	311	318	325	331	338	345	351	
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**Prop. Parts**

Prop. Parts	N	0	1	2	3	4	5	6	7	8	9
	650	81 291	298	305	311	318	325	331	338	345	351
	51	358	365	371	378	385	391	398	405	411	418
	52	425	431	438	445	451	458	465	471	478	485
	53	491	498	505	511	518	525	531	538	544	551
	54	558	564	571	578	584	591	598	604	611	617
	55	624	631	637	644	651	657	664	671	677	684
	56	690	697	704	710	717	723	730	737	743	750
	57	757	763	770	776	783	790	796	803	809	816
	58	823	829	836	842	849	856	862	869	875	882
	59	889	895	902	908	915	921	928	935	941	948
	660	81 954	961	968	974	981	987	994	*000	*007	*014
	61	82 020	027	033	040	046	053	060	066	073	079
	62	086	092	099	105	112	119	125	132	138	145
7	63	151	158	164	171	178	184	191	197	204	210
1 0.7	64	217	223	230	236	243	249	256	263	269	276
2 1.4	65	282	289	295	302	308	315	321	328	334	341
3 2.1	66	347	354	360	367	373	380	387	393	400	406
4 2.8	67	413	419	426	432	439	445	452	458	465	471
5 3.5	68	478	484	491	497	504	510	517	523	530	536
6 4.2	69	543	549	556	562	569	575	582	588	595	601
7 4.9	**670**	607	614	620	627	633	640	646	653	659	666
8 5.6	71	672	679	685	692	698	705	711	718	724	730
9 6.3	72	737	743	750	756	763	769	776	782	789	795
	73	802	808	814	821	827	834	840	847	853	860
	74	866	872	879	885	892	898	905	911	918	924
	75	930	937	943	950	956	963	969	975	982	988
	76	82 995	*001	*008	*014	*020	*027	*033	*040	*046	*052
	77	83 059	065	072	078	085	091	097	104	110	117
	78	123	129	136	142	149	155	161	168	174	181
	79	187	193	200	206	213	219	225	232	238	245
	680	251	257	264	270	276	283	289	296	302	308
	81	315	321	327	334	340	347	353	359	366	372
6	82	378	385	391	398	404	410	417	423	429	436
1 0.6	83	442	448	455	461	467	474	480	487	493	499
2 1.2	84	506	512	518	525	531	537	544	550	556	563
3 1.8	85	569	575	582	588	594	601	607	613	620	626
4 2.4	86	632	639	645	651	658	664	670	677	683	689
5 3.0	87	696	702	708	715	721	727	734	740	746	753
6 3.6	88	759	765	771	778	784	790	797	803	809	816
7 4.2	89	822	828	835	841	847	853	860	866	872	879
8 4.8	**690**	885	891	897	904	910	916	923	929	935	942
9 5.4	91	83 948	954	960	967	973	979	985	992	998	*004
	92	84 011	017	023	029	036	042	048	055	061	067
	93	073	080	086	092	098	105	111	117	123	130
	94	136	142	148	155	161	167	173	180	186	192
	95	198	205	211	217	223	230	236	242	248	255
	96	261	267	273	280	286	292	298	305	311	317
	97	323	330	336	342	348	354	361	367	373	379
	98	386	392	398	404	410	417	423	429	435	442
	99	448	454	460	466	473	479	485	491	497	504
	700	84 510	516	522	528	535	541	547	553	559	566
Prop. Parts	**N**	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
700	84 510	516	522	528	535	541	547	553	559	566	
01	572	578	584	590	597	603	609	615	621	628	
02	634	640	646	652	658	665	671	677	683	689	
03	696	702	708	714	720	726	733	739	745	751	
04	757	763	770	776	782	788	794	800	807	813	
05	819	825	831	837	844	850	856	862	868	874	
06	880	887	893	899	905	911	917	924	930	936	
07	84 942	948	954	960	967	973	979	985	991	997	7 | 1 0.7 2 1.4 3 2.1 4 2.8 5 3.5 6 4.2 7 4.9 8 5.6 9 6.3
08	85 003	009	016	022	028	034	040	046	052	058	
09	065	071	077	083	089	095	101	107	114	120	
710	126	132	138	144	150	156	163	169	175	181	
11	187	193	199	205	211	217	224	230	236	242	
12	248	254	260	266	272	278	285	291	297	303	
13	309	315	321	327	333	339	345	352	358	364	
14	370	376	382	388	394	400	406	412	418	425	
15	431	437	443	449	455	461	467	473	479	485	
16	491	497	503	509	516	522	528	534	540	546	
17	552	558	564	570	576	582	588	594	600	606	
18	612	618	625	631	637	643	649	655	661	667	
19	673	679	685	691	697	703	709	715	721	727	
720	733	739	745	751	757	763	769	775	781	788	
21	794	800	806	812	818	824	830	836	842	848	
22	854	860	866	872	878	884	890	896	902	908	6 | 1 0.6 2 1.2 3 1.8 4 2.4 5 3.0 6 3.6 7 4.2 8 4.8 9 5.4
23	914	920	926	932	938	944	950	956	962	968	
24	85 974	980	986	992	998	*004	*010	*016	*022	*028	
25	86 034	040	046	052	058	064	070	076	082	088	
26	094	100	106	112	118	124	130	136	141	147	
27	153	159	165	171	177	183	189	195	201	207	
28	213	219	225	231	237	243	249	255	261	267	
29	273	279	285	291	297	303	308	314	320	326	
730	332	338	344	350	356	362	368	374	380	386	
31	392	398	404	410	415	421	427	433	439	445	
32	451	457	463	469	475	481	487	493	499	504	
33	510	516	522	528	534	540	546	552	558	564	
34	570	576	581	587	593	599	605	611	617	623	
35	629	635	641	646	652	658	664	670	676	682	
36	688	694	700	705	711	717	723	729	735	741	
37	747	753	759	764	770	776	782	788	794	800	
38	806	812	817	823	829	835	841	847	853	859	5 | 1 0.5 2 1.0 3 1.5 4 2.0 5 2.5 6 3.0 7 3.5 8 4.0 9 4.5
39	864	870	876	882	888	894	900	906	911	917	
740	923	929	935	941	947	953	958	964	970	976	
41	86 982	988	994	999	*005	*011	*017	*023	*029	*035	
42	87 040	046	052	058	064	070	075	081	087	093	
43	099	105	111	116	122	128	134	140	146	151	
44	157	163	169	175	181	186	192	198	204	210	
45	216	221	227	233	239	245	251	256	262	268	
46	274	280	286	291	297	303	309	315	320	326	
47	332	338	344	349	355	361	367	373	379	384	
48	390	396	402	408	413	419	425	431	437	442	
49	448	454	460	466	471	477	483	489	495	500	
750	87 506	512	518	523	529	535	541	547	552	558	
N	0	1	2	3	4	5	6	7	8	9	Prop. Parts

Prop. Parts	N	0	1	2	3	4	5	6	7	8	9
	750	87 506	512	518	523	529	535	541	547	552	558
	51	564	570	576	581	587	593	599	604	610	616
	52	622	628	633	639	645	651	656	662	668	674
	53	679	685	691	697	703	708	714	720	726	731
	54	737	743	749	754	760	766	772	777	783	789
	55	795	800	806	812	818	823	829	835	841	846
	56	852	858	864	869	875	881	887	892	898	904
	57	910	915	921	927	933	938	944	950	955	961
	58	87 967	973	978	984	990	996	*001	*007	*013	*018
	59	88 024	030	036	041	047	053	058	064	070	076
	760	081	087	093	098	104	110	116	121	127	133
	61	138	144	150	156	161	167	173	178	184	190
	62	195	201	207	213	218	224	230	235	241	247
6	63	252	258	264	270	275	281	287	292	298	304
1 0.6	64	309	315	321	326	332	338	343	349	355	360
2 1.2	65	366	372	377	383	389	395	400	406	412	417
3 1.8	66	423	429	434	440	446	451	457	463	468	474
4 2.4	67	480	485	491	497	502	508	513	519	525	530
5 3.0	68	536	542	547	553	559	564	570	576	581	587
6 3.6	69	593	598	604	610	615	621	627	632	638	643
7 4.2	**770**	649	655	660	666	672	677	683	689	694	700
8 4.8	71	705	711	717	722	728	734	739	745	750	756
9 5.4	72	762	767	773	779	784	790	795	801	807	812
	73	818	824	829	835	840	846	852	857	863	868
	74	874	880	885	891	897	902	908	913	919	925
	75	930	936	941	947	953	958	964	969	975	981
	76	88 986	992	997	*003	*009	*014	*020	*025	*031	*037
	77	89 042	048	053	059	064	070	076	081	087	092
	78	098	104	109	115	120	126	131	137	143	148
	79	154	159	165	170	176	182	187	193	198	204
	780	209	215	221	226	232	237	243	248	254	260
	81	265	271	276	282	287	293	298	304	310	315
	82	321	326	332	337	343	348	354	360	365	371
5	83	376	382	387	393	398	404	409	415	421	426
1 0.5	84	432	437	443	448	454	459	465	470	476	481
2 1.0	85	487	492	498	504	509	515	520	526	531	537
3 1.5	86	542	548	553	559	564	570	575	581	586	592
4 2.0	87	597	603	609	614	620	625	631	636	642	647
5 2.5	88	653	658	664	669	675	680	686	691	697	702
6 3.0	89	708	713	719	724	730	735	741	746	752	757
7 3.5	**790**	763	768	774	779	785	790	796	801	807	812
8 4.0	91	818	823	829	834	840	845	851	856	862	867
9 4.5	92	873	878	883	889	894	900	905	911	916	922
	93	927	933	938	944	949	955	960	966	971	977
	94	89 982	988	993	998	*004	*009	*015	*020	*026	*031
	95	90 037	042	048	053	059	064	069	075	080	086
	96	091	097	102	108	113	119	124	129	135	140
	97	146	151	157	162	168	173	179	184	189	195
	98	200	206	211	217	222	227	233	238	244	249
	99	255	260	266	271	276	282	287	293	298	304
	800	90 309	314	320	325	331	336	342	347	352	358
Prop. Parts	**N**	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

N	0	1	2	3	4	5	6	7	8	9
800	90 309	314	320	325	331	336	342	347	352	358
01	363	369	374	380	385	390	396	401	407	412
02	417	423	428	434	439	445	450	455	461	466
03	472	477	482	488	493	499	504	509	515	520
04	526	531	536	542	547	553	558	563	569	574
05	580	585	590	596	601	607	612	617	623	628
06	634	639	644	650	655	660	666	671	677	682
07	687	693	698	703	709	714	720	725	730	736
08	741	747	752	757	763	768	773	779	784	789
09	795	800	806	811	816	822	827	832	838	843
810	849	854	859	865	870	875	881	886	891	897
11	902	907	913	918	924	929	934	940	945	950
12	90 956	961	966	972	977	982	988	993	998	*004
13	91 009	014	020	025	030	036	041	046	052	057
14	062	068	073	078	084	089	094	100	105	110
15	116	121	126	132	137	142	148	153	158	164
16	169	174	180	185	190	196	201	206	212	217
17	222	228	233	238	243	249	254	259	265	270
18	275	281	286	291	297	302	307	312	318	323
19	328	334	339	344	350	355	360	365	371	376
820	381	387	392	397	403	408	413	418	424	429
21	434	440	445	450	455	461	466	471	477	482
22	487	492	498	503	508	514	519	524	529	535
23	540	545	551	556	561	566	572	577	582	587
24	593	598	603	609	614	619	624	630	635	640
25	645	651	656	661	666	672	677	682	687	693
26	698	703	709	714	719	724	730	735	740	745
27	751	756	761	766	772	777	782	787	793	798
28	803	808	814	819	824	829	834	840	845	850
29	855	861	866	871	876	882	887	892	897	903
830	908	913	918	924	929	934	939	944	950	955
31	91 960	965	971	976	981	986	991	997	*002	*007
32	92 012	018	023	028	033	038	044	049	054	059
33	065	070	075	080	085	091	096	101	106	111
34	117	122	127	132	137	143	148	153	158	163
35	169	174	179	184	189	195	200	205	210	215
36	221	226	231	236	241	247	252	257	262	267
37	273	278	283	288	293	298	304	309	314	319
38	324	330	335	340	345	350	355	361	366	371
39	376	381	387	392	397	402	407	412	418	423
840	428	433	438	443	449	454	459	464	469	474
41	480	485	490	495	500	505	511	516	521	526
42	531	536	542	547	552	557	562	567	572	578
43	583	588	593	598	603	609	614	619	624	629
44	634	639	645	650	655	660	665	670	675	681
45	686	691	696	701	706	711	716	722	727	732
46	737	742	747	752	758	763	768	773	778	783
47	788	793	799	804	809	814	819	824	829	834
48	840	845	850	855	860	865	870	875	881	886
49	891	896	901	906	911	916	921	927	932	937
850	92 942	947	952	957	962	967	973	978	983	988
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

Prop. Parts	
	6
1	0.6
2	1.2
3	1.8
4	2.4
5	3.0
6	3.6
7	4.2
8	4.8
9	5.4

Prop. Parts	
	5
1	0.5
2	1.0
3	1.5
4	2.0
5	2.5
6	3.0
7	3.5
8	4.0
9	4.5

Prop. Parts

Prop. Parts	N	0	1	2	3	4	5	6	7	8	9
	850	92 942	947	952	957	962	967	973	978	983	988
	51	92 993	998	*003	*008	*013	*018	*024	*029	*034	*039
	52	93 044	049	054	059	064	069	075	080	085	090
	53	095	100	105	110	115	120	125	131	136	141
	54	146	151	156	161	166	171	176	181	186	192
	55	197	202	207	212	217	222	227	232	237	242
	56	247	252	258	263	268	273	278	283	288	293
6 |	57	298	303	308	313	318	323	328	334	339	344
1 0.6	58	349	354	359	364	369	374	379	384	389	394
2 1.2	59	399	404	409	414	420	425	430	435	440	445
3 1.8											
4 2.4	**860**	450	455	460	465	470	475	480	485	490	495
5 3.0											
6 3.6	61	500	505	510	515	520	526	531	536	541	546
7 4.2	62	551	556	561	566	571	576	581	586	591	596
8 4.8	63	601	606	611	616	621	626	631	636	641	646
9 5.4	64	651	656	661	666	671	676	682	687	692	697
	65	702	707	712	717	722	727	732	737	742	747
	66	752	757	762	767	772	777	782	787	792	797
	67	802	807	812	817	822	827	832	837	842	847
	68	852	857	862	867	872	877	882	887	892	897
	69	902	907	912	917	922	927	932	937	942	947
	870	93 952	957	962	967	972	977	982	987	992	997
	71	94 002	007	012	017	022	027	032	037	042	047
	72	052	057	062	067	072	077	082	086	091	096
5 |	73	101	106	111	116	121	126	131	136	141	146
1 0.5	74	151	156	161	166	171	176	181	186	191	196
2 1.0	75	201	206	211	216	221	226	231	236	240	245
3 1.5	76	250	255	260	265	270	275	280	285	290	295
4 2.0	77	300	305	310	315	320	325	330	335	340	345
5 2.5	78	349	354	359	364	369	374	379	384	389	394
6 3.0	79	399	404	409	414	419	424	429	433	438	443
7 3.5											
8 4.0	**880**	448	453	458	463	468	473	478	483	488	493
9 4.5	81	498	503	507	512	517	522	527	532	537	542
	82	547	552	557	562	567	571	576	581	586	591
	83	596	601	606	611	616	621	626	630	635	640
	84	645	650	655	660	665	670	675	680	685	689
	85	694	699	704	709	714	719	724	729	734	738
	86	743	748	753	758	763	768	773	778	783	787
	87	792	797	802	807	812	817	822	827	832	836
	88	841	846	851	856	861	866	871	876	880	885
4 |	89	890	895	900	905	910	915	919	924	929	934
1 0.4											
2 0.8	**890**	939	944	949	954	959	963	968	973	978	983
3 1.2											
4 1.6	91	94 988	993	998	*002	*007	*012	*017	*022	*027	*032
5 2.0	92	95 036	041	046	051	056	061	066	071	075	080
6 2.4	93	085	090	095	100	105	109	114	119	124	129
7 2.8	94	134	139	143	148	153	158	163	168	173	177
8 3.2	95	182	187	192	197	202	207	211	216	221	226
9 3.6	96	231	236	240	245	250	255	260	265	270	274
	97	279	284	289	294	299	303	308	313	318	323
	98	328	332	337	342	347	352	357	361	366	371
	99	376	381	386	390	395	400	405	410	415	419
	900	95 424	429	434	439	444	448	453	458	463	468
Prop. Parts	N	0	1	2	3	4	5	6	7	8	9

N	0	1	2	3	4	5	6	7	8	9	Prop. Parts
900	95 424	429	434	439	444	448	453	458	463	468	
01	472	477	482	487	492	497	501	506	511	516	
02	521	525	530	535	540	545	550	554	559	564	
03	569	574	578	583	588	593	598	602	607	612	
04	617	622	626	631	636	641	646	650	655	660	
05	665	670	674	679	684	689	694	698	703	708	
06	713	718	722	727	732	737	742	746	751	756	
07	761	766	770	775	780	785	789	794	799	804	
08	809	813	818	823	828	832	837	842	847	852	
09	856	861	866	871	875	880	885	890	895	899	
910	904	909	914	918	923	928	933	938	942	947	
11	952	957	961	966	971	976	980	985	990	995	
12	95 999	*004	*009	*014	*019	*023	*028	*033	*038	*042	5
13	96 047	052	057	061	066	071	076	080	085	090	1 0.5
14	095	099	104	109	114	118	123	128	133	137	2 1.0 3 1.5
15	142	147	152	156	161	166	171	175	180	185	4 2.0
16	190	194	199	204	209	213	218	223	227	232	5 2.5 6 3.0
17	237	242	246	251	256	261	265	270	275	280	7 3.5
18	284	289	294	298	303	308	313	317	322	327	8 4.0
19	332	336	341	346	350	355	360	365	369	374	9 4.5
920	379	384	388	393	398	402	407	412	417	421	
21	426	431	435	440	445	450	454	459	464	468	
22	473	478	483	487	492	497	501	506	511	515	
23	520	525	530	534	539	544	548	553	558	562	
24	567	572	577	581	586	591	595	600	605	609	
25	614	619	624	628	633	638	642	647	652	656	
26	661	666	670	675	680	685	689	694	699	703	
27	708	713	717	722	727	731	736	741	745	750	
28	755	759	764	769	774	778	783	788	792	797	
29	802	806	811	816	820	825	830	834	839	844	
930	848	853	858	862	867	872	876	881	886	890	
31	895	900	904	909	914	918	923	928	932	937	4
32	942	946	951	956	960	965	970	974	979	984	1 0.4
33	96 988	993	997	*002	*007	*011	*016	*021	*025	*030	2 0.8 3 1.2
34	97 035	039	044	049	053	058	063	067	072	077	4 1.6
35	081	086	090	095	100	104	109	114	118	123	5 2.0
36	128	132	137	142	146	151	155	160	165	169	6 2.4 7 2.8
37	174	179	183	188	192	197	202	206	211	216	8 3.2
38	220	225	230	234	239	243	248	253	257	262	9 3.6
39	267	271	276	280	285	290	294	299	304	308	
940	313	317	322	327	331	336	340	345	350	354	
41	359	364	368	373	377	382	387	391	396	400	
42	405	410	414	419	424	428	433	437	442	447	
43	451	456	460	465	470	474	479	483	488	493	
44	497	502	506	511	516	520	525	529	534	539	
45	543	548	552	557	562	566	571	575	580	585	
46	589	594	598	603	607	612	617	621	626	630	
47	635	640	644	649	653	658	663	667	672	676	
48	681	685	690	695	699	704	708	713	717	722	
49	727	731	736	740	745	749	754	759	763	768	
950	97 772	777	782	786	791	795	800	804	809	813	
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**Prop. Parts**

Prop. Parts	N	0	1	2	3	4	5	6	7	8	9
	950	97 772	777	782	786	791	795	800	804	809	813
	51	818	823	827	832	836	841	845	850	855	859
	52	864	868	873	877	882	886	891	896	900	905
	53	909	914	918	923	928	932	937	941	946	950
	54	97 955	959	964	968	973	978	982	987	991	996
	55	98 000	005	009	014	019	023	028	032	037	041
	56	046	050	055	059	064	068	073	078	082	087
	57	091	096	100	105	109	114	118	123	127	132
	58	137	141	146	150	155	159	164	168	173	177
	59	182	186	191	195	200	204	209	214	218	223
	960	227	232	236	241	245	250	254	259	263	268
	61	272	277	281	286	290	295	299	304	308	313
5	62	318	322	327	331	336	340	345	349	354	358
1 0.5	63	363	367	372	376	381	385	390	394	399	403
2 1.0											
3 1.5	64	408	412	417	421	426	430	435	439	444	448
4 2.0	65	453	457	462	466	471	475	480	484	489	493
5 2.5	66	498	502	507	511	516	520	525	529	534	538
6 3.0											
7 3.5	67	543	547	552	556	561	565	570	574	579	583
8 4.0	68	588	592	597	601	605	610	614	619	623	628
9 4.5	69	632	637	641	646	650	655	659	664	668	673
	970	677	682	686	691	695	700	704	709	713	717
	71	722	726	731	735	740	744	749	753	758	762
	72	767	771	776	780	784	789	793	798	802	807
	73	811	816	820	825	829	834	838	843	847	851
	74	856	860	865	869	874	878	883	887	892	896
	75	900	905	909	914	918	923	927	932	936	941
	76	945	949	954	958	963	967	972	976	981	985
	77	98 989	994	998	*003	*007	*012	*016	*021	*025	*029
	78	99 034	038	043	047	052	056	061	065	069	074
	79	078	083	087	092	096	100	105	109	114	118
	980	123	127	131	136	140	145	149	154	158	162
	81	167	171	176	180	185	189	193	198	202	207
4	82	211	216	220	224	229	233	238	242	247	251
1 0.4	83	255	260	264	269	273	277	282	286	291	295
2 0.8											
3 1.2	84	300	304	308	313	317	322	326	330	335	339
4 1.6	85	344	348	352	357	361	366	370	374	379	383
5 2.0	86	388	392	396	401	405	410	414	419	423	427
6 2.4											
7 2.8	87	432	436	441	445	449	454	458	463	467	471
8 3.2	88	476	480	484	489	493	498	502	506	511	515
9 3.6	89	520	524	528	533	537	542	546	550	555	559
	990	564	568	572	577	581	585	590	594	599	603
	91	607	612	616	621	625	629	634	638	642	647
	92	651	656	660	664	669	673	677	682	686	691
	93	695	699	704	708	712	717	721	726	730	734
	94	739	743	747	752	756	760	765	769	774	778
	95	782	787	791	795	800	804	808	813	817	822
	96	826	830	835	839	843	848	852	856	861	865
	97	870	874	878	883	887	891	896	900	904	909
	98	913	917	922	926	930	935	939	944	948	952
	99	99 957	961	965	970	974	978	983	987	991	996
	1000	00 000	004	009	013	017	022	026	030	035	039
Prop. Parts	**N**	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

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