*Fundamentals of*

# SEMI-MICRO

# QUALITATIVE  ANALYSIS

*By*

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## PREFACE

The normal text book of qualitative analysis follows the somewhat standard pattern: a lengthy section on equilibrium theory, the properties and analytical reactions of the cations and their separation and detection, a similar treatment for the anions, and a closing section on systematic analysis. The instruction in theory must, perforce, be spread over the duration of the course, whereas, in following the conventional order, the laboratory work plunges the student prematurely into all the complexities of cation groups I and II, long before he, on the one hand, has acquired necessary experimental experience and technique and, on the other hand, has gained a sufficient understanding of the underlying theory. To overcome these difficulties, a rearrangement of the course of instruction is presented in this book, based upon the author's successful experience over the past five years.

The course of instruction begins with the alkali metals and proceeds into a study of the alkaline earth elements, during which time the solubility product principle is introduced. This is followed by the laboratory study of the metals of cation group III, offering thus an appropriate introduction to oxidation theory with iron, manganese, and chromium as examples; amphoterism as illustrated by aluminum, chromium, and zinc; and the theory of complex ions as exhibited by nickel, cobalt, and zinc. By the time this phase of instruction is completed, the student is better conditioned both in theory and practice to understand and carry out the more difficult reactions, steps and procedures of groups I and II. Common-ion effect or buffering is incorporated here in the theory. Arsenic forms the transition from cation analysis to anion analysis. Remaining sections of theory are included in the chapters on anion study. For complete systematic analysis, anion procedures precede cation procedures.

The most important features of this book are (1) the introduction of the cations, in reverse order, before complete systematic analysis is undertaken and (2) the gradual introduction of selected portions of theory at appropriate intervals to accompany the ex-

perimental work. The author believes he has successfully integrated theory with practice. A schedule of laboratory and classroom assignments is suggested in the appendix to aid the teacher in planning his course based on this new arrangement.

Incorporated in the sections on theory are numerous illustrative calculations followed by problem sets, ten in all, each set comprising 20 problems, half with and half without answers. This provides ample material for instruction in chemical calculations, thus dispensing with the use of a separate problem book.

Portions of this book have been taken from the first and second editions of *Semi-Micro Qualitative Analysis* by Engelder, Dunkelberger, and Schiller.

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## CHAPTER I

## INTRODUCTION. REACTIONS AND EQUATIONS. APPARATUS AND TECHNIQUE. REAGENTS

Analytical chemistry deals with the methods and principles involved in determining the composition of matter. A qualitative analysis reveals what constituents are contained in a given material, and a quantitative analysis determines how much of each is present. Various chemical and physical methods and instruments are employed in the examination, utilizing the differences in the chemical and physical properties of the constituents as a means of identifying the constituents and determining the amount of each present. In qualitative chemical analysis the identification depends for the most part upon the chemical properties of the constituent; the methods therefore involve, in general, a separation of the constituents one from another by applying suitable chemical reactions, followed by the addition of appropriate reagents which give distinctive identifying tests. In the broadest sense qualitative analysis includes the identification of any substance—animal, vegetable or mineral—present either by itself or mixed with other substances.

Elementary qualitative analysis, moreover, deals almost exclusively with mixtures of relatively simple inorganic compounds. The only organic compounds considered are salts of several organic acids. In the qualitative analysis of such a mixture the procedure for the separation and identification of the metal constituents (cations) is carried out on one portion of the sample, whereas the acid radicals (anions) are detected by applying another scheme of separation and identification to another portion of the sample. It is therefore impossible to state what particular compounds are present in a mixture of compounds. To illustrate, if a sample, consisting of $K_2SO_4$, $NaNO_3$ and $CuCl_2$, is dissolved and analyzed, the analyst would detect in the cation analysis the presence of

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potassium, sodium and copper, and in the anion analysis the presence of sulfate, nitrate and chloride ions; analysis of a mixture of $KNO_3$, $NaCl$ and $CuSO_4$ however would lead to exactly the same result. Moreover, only a limited number of metal ions and of acid radicals is considered in elementary qualitative analysis.

Methods of qualitative analysis were devised early in the development of chemistry. These methods have undergone and are still undergoing modifications, as better methods of separation are devised and as newer and more sensitive tests are developed. As far as the scale of operations or the total amount of material handled is concerned, there are today three more or less distinct techniques. The first and oldest of these is the macro technique in which beakers, flasks, funnels and test tubes of the usual size are employed and where the volumes of solutions are relatively large, ranging from several milliliters up to 100 ml. or more. At the other extreme is the truly micro technique, with its highly specialized, diminutive apparatus; the microscope is employed as an important adjunct, and the volumes of test materials usually are not more than several cubic millimeters. Intermediate between these two is the special technique or mode of operation upon which the procedures in this book are based (the author has termed this technique "semi-micro"); it has borrowed methods and appliances from the other two techniques. It is partly macro and partly micro chemical.

Among the features which characterize and define this technique are: (1) the volumes of solutions and amounts of material are limited so that group precipitations, separations, washings and similar operations generally are confined to 1 or 2 ml. of solution; (2) identifying tests are made with drop portions of test substance and reagents, the reacting solutions being brought together in small test tubes or centrifuge tubes, on spot plates, glass slides or drop-reaction paper; and (3) "filtrations" are conducted ordinarily by centrifugation. The microscope is not employed in the methods described here.

There are no sharp boundaries among these three techniques, and obviously there is some overlapping. The technique is necessarily determined by the amount of material handled; this in turn depends upon the size of the sample, the weight of each constituent in the sample and the volume of the solution. The whole matter is governed, in practice, by the conditions which it is possible to establish in order to obtain a fairly sensitive positive test for the

presence of any given constituent. By the term "sensitivity" is meant the quantity of material which responds to the test reagent; if the quantity of test ion refers to its concentration, that is, the amount present in a given volume, the limit of sensitivity is reached when a more dilute solution fails to give the test. If the absolute quantity of test substance, usually expressed in weight, is referred to, the sensitivity of a reaction is expressed in terms of actual weight of the test ion. The unit of microchemical weight is 1 microgram (1 $\mu$g.) or 1 gamma (1 $\gamma$), that is, 0.001 milligram, or 0.000001 gram. Accordingly, on this definition of sensitivity, the limit of identification ranges from 1 milligram to much less than 0.1 microgram, depending on the technique employed. The sensitivity of a test depends, too, on the amounts of other substances present in the mixture when the test reagent is applied, for which the term "limiting proportions" is used.

In the field of qualitative analysis, during the past two decades, an enormous amount of work has been done, the object of which has been to find extremely sensitive reagents and specific reactions which would give tests for certain ions in the presence of other ions. The current chemical literature contains a wealth of published information on the results of such investigations. To Fritz Feigl in particular much credit is due for his contribution, *Qualitative Analyse mit Hilfe von Tüpfel reaktionen*,[1] which is the authoritative reference. Feigl gives an excellent discussion of a considerable number of specific and highly sensitive reactions conducted as spot and drop tests, less attention being given to systematic separations.

Learning the procedures and acquiring the skills necessary to separate and identify the constituents of a mixture is, of course, a primary aim in any course in qualitative analysis. But to an ever-increasing extent the course of instruction in qualitative analysis is being recognized as the most favorable place to present and review, to emphasize and apply many of the fundamental principles upon which not only it but also all of chemistry is based. This is as it should be, for it is only by the understanding, appreciation and application of such fundamental information that really intelligent progress can be made in scientific work.

Students frequently are concerned about the relative emphases placed upon the "theoretical" and the "practical" in their courses.

[1] Available in English translation from the third German edition, Nordemann Publishing Co., New York, 1939.

Unfortunately, the word "theory" frequently seems to connote something indefinite and uncertain, probably incorrect or at least inaccurate, and of no conceivable usefulness or importance: in short, an unnecessary burden imposed upon students by an unsympathetic instructor. "Practical," on the other hand, seems to imply something of real importance, something directly applicable to everyday life. Such a distinction is absurd. If we interpret "theoretical" broadly, as we should, to mean the explanatory discussion which makes it possible not only to correlate the results of actual experiments but also to predict or calculate the results of untried experiments, we can say with conviction that nothing is so practical as a good theory and few things are so inefficient as practical work unguided by theoretical information.

The fundamental laws of chemical change which underlie and control all chemical reactions are so amply illustrated and so frequently encountered in the laboratory work of qualitative analysis that the student should acquire a thorough grasp and understanding of the basic principles of chemistry. The two fundamental laws are (1) the Law of Definite Proportions (closely related to the Law of Combining Weights) and (2) the Law of Chemical Equilibrium. The former states that the weights of reacting components are proportional to the atomic or molecular weights of the elements concerned; its application enables one to calculate the proportions in which elements are united in compounds as well as to determine how much product is formed, or how much reagent is required in a (practically complete) chemical reaction. The Law of Chemical Equilibrium, on the other hand, controls in part the extent of a reaction and enables one to calculate the concentrations of reactants and products which are present when equilibrium is reached.

To comprehend fully and apply competently both laws to chemical reactions requires more time than reasonably can be alloted to the study of qualitative analysis alone. It has been customary therefore to direct the study, in the course of instruction of qualitative analysis, to the applications of the Law of Chemical Equilibrium and to reserve a more intensive study and application of direct proportion and combining weights for the course in quantitative analysis. Equilibrium theory therefore is emphasized in qualitative analysis; the student however should realize that reaction by direct proportion is nonetheless operative here and, further, that the equilibria attained in reactions that are carried

out quantitatively are even more important than when applied to the same reaction encountered in the qualitative procedures.

The study of chemical equilibria and their applications to the several different types of reactions constitutes the most important part of the theory of qualitative analysis. A theory or fundamental law can only be adequately understood and appreciated when it is reduced to a rigorous mathematical test—hence the numerous problems which accompany the sections on theory throughout this book. The student should not regard the weekly problem assignments as mere exercises in algebra; on the contrary, the correct solution of a problem is proof to him that he comprehends and can apply a certain principle. A fair knowledge of algebra and a working facility with exponents and logarithms are essential. A brief review of mathematical operations is given in the Appendix.
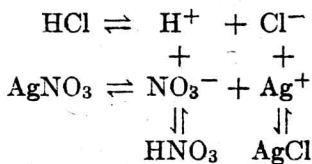
## REACTIONS AND EQUATIONS

The study of the reactions encountered in the procedures of qualitative analysis constitutes one of the most important parts of the student's work, since, naturally, the methods of separation and identification are based on suitably selected reactions. Reactions, to be of the greatest service in bringing about sharp separations and distinctive tests, must run practically to completion. In aqueous solutions most reactions are ionic and attain equilibria quickly.

**Ionic Nature of Reactions.** Since most of the reactions of qualitative analysis take place in aqueous solutions of ionized electrolytes, the actual chemical changes involved must be considered as taking place between ions and not between the non-ionized components of the solute. In other words, we are concerned almost entirely with ionic reactions, and the reactions therefore are represented as ionic and not molecular equations. An example will make this clear. Suppose we take a solution of $AgNO_3$ and add to it dilute HCl. A curdy white precipitate of AgCl will form at once. The same result can be obtained by mixing a solution of NaCl, $NH_4Cl$, $BaCl_2$ or other soluble chloride with the solution of any soluble silver salt. If the reaction were expressed as a molecular equation thus,

$$HCl + AgNO_3 \rightarrow \underline{AgCl} + HNO_3$$
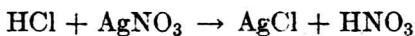
it would imply a reaction between molecules. But in aqueous solutions $AgNO_3$, HCl and NaCl are dissociated into their respective

ions. The complete scheme by which reactions of this kind can be represented is

$$
\begin{array}{ccccc}
\text{HCl} & \rightleftharpoons & \text{H}^+ & + & \text{Cl}^- \\
& & + & & + \\
\text{AgNO}_3 & \rightleftharpoons & \text{NO}_3^- & + & \text{Ag}^+ \\
& & \Updownarrow & & \Updownarrow \\
& & \text{HNO}_3 & & \underline{\text{AgCl}}
\end{array}
$$

This double decomposition reaction indicates that $Ag^+$ ions and $Cl^-$ ions are removed from the solution in the form of a slightly soluble precipitate of AgCl, leaving $H^+$ ions and $NO_3^-$ ions, equivalent to the appearance of $HNO_3$ in the solution. It is not accurate to say that $HNO_3$ is formed in this reaction; it merely happens that the ions constituting it are left after the other ions are removed. The formula of silver chloride is underscored to indicate that AgCl is only slightly soluble and therefore forms a precipitate, causing the reaction to go practically to completion toward the right. Only the $Ag^+$ ions and $Cl^-$ ions are concerned in the reaction; so, for simplicity, we express the change as a simple ionic equation:

$$Ag^+ + Cl^- \rightarrow \underline{AgCl}$$
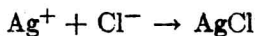
The student early must acquire this ionic point of view and consider all reactions, with but few exceptions, as taking place between the ions concerned.

**Classification of Ionic Reactions.** In general, it can be stated that an ionic reaction takes place and in most cases runs practically to completion whenever *ionic concentrations are decreased.* The concentrations of the reacting ions can be diminished in one of two general ways, namely (1) by ions uniting and (2) by ions transferring one or more electrons. These are the two important classes of reactions. In the first class are included several types, the reaction taking place because:

(*a*) A precipitate is formed, since in the formation of a solid ions are removed from solution.

(*b*) A complex ion is formed.

(*c*) A weakly ionized acid or base or, in rare cases, a weakly ionized salt is the product of the reaction. Neutralization reactions also come under this heading, since the fundamental reaction here is the union of $H^+$ and $OH^-$ to form water; and closely allied to this are the reactions in which an amphoteric form is altered. Included here are also the reactions of hydrolysis. We should

remember, further, that certain weakly ionized substances are gases, and therefore their liberation aids in the removal of ions from solution.

Reactions of the second class, namely, those in which electrons are transferred from one ion to another and thereby diminish the ionic concentrations of the initial reactants, are the important and frequently encountered oxidation–reduction reactions. Such reactions hereafter will be spoken of as *redox reactions*, the word "redox" being derived from the term "reduction–oxidation." The other class of reactions accordingly will be referred to as *non-redox reactions*.

The equilibrium relationships based on this classification of ionic reactions constitute the most important part of the study of the fundamental principles of qualitative analysis. This is discussed in greater detail in Chapter III.

**The Writing and Balancing of Chemical Equations.** The writing of equations and the ability to balance them correctly must be acquired before any intelligent progress can be made in the study of analytical chemistry. A chemical equation cannot be written and balanced unless the reactants and products are known. What takes place in a reaction must be discovered by experiment. The equation must represent what actually takes place.

If the formulas of the compounds or ions involved are known, it is usually a comparatively simple matter to balance the coefficients. A great many equations can be balanced by inspection. Where the actions are more complicated, writing the equations in steps and canceling out the components that are common to the two successive reactions usually will result in a correctly balanced final equation. Special consideration is given in a later section, Chapter IV, to oxidation–reduction or *redox* equations, which usually are the most difficult to balance.

Inasmuch as most of the reactions with which we are concerned are between ions, the equations representing such reactions are written as ionic equations. In this book the simple ionic form usually will be used, which shows only those ions and products which are mainly involved in the reactions. Sometimes reactions will be given in molecular form, whenever such chemical changes can be more clearly comprehended and the chemical relationships better shown; it must be understood, however, that the reaction is always ionic, even though for certain purposes or emphasis the reaction may be expressed in molecular form. The equations for

ionic reactions which lead to the formation of precipitates, of less ionized products, of complex ions and of amphoteric changes usually are easy to balance, the selection of the correct coefficients being ordinarily a matter of simple inspection.

In writing equations of this kind, only the essential ions and molecules which take part in the reaction should be put into the equation. Highly ionized substances, such as strong acids, alkalies and salts, in general should be stripped of their non-essential ions, whereas weakly ionized substances may be written in the molecular form. Among the weakly ionized substances are included $H_2S$, $HC_2H_3O_2$, $NH_4OH$ or $NH_3$, and $H_2O$. Precipitates and gases, of course, are formulated as molecules

**Conventions Used in Writing Equations.** The following rules are to be applied in the use of symbols or signs which appear in a chemical equation:

1. Whenever it is the purpose merely to indicate the direction or the tendency of the chemical change (sometimes even without an attempt to balance the equation) or to illustrate the methods of balancing the equation, a wavy arrow ($\rightsquigarrow$) is employed. See, for example, page 99.)

2. If a balanced equation for a practically complete reaction is expressed, the simple arrow ($\rightarrow$) is used.

3. When special attention is to be called to an equilibrium relationship, that is, to the reversibility of a reaction, the reversible sign (double arrows, $\rightleftharpoons$) is used.

4. A precipitate is indicated by underscoring the formula, and a gas or volatile compound by overscoring.

5. A small circle ($^\circ$) written above and to the right of the symbol indicates an element in the atomic, electrically neutral state.

### The Apparatus and Technique of Semi-Micro Analysis

The apparatus used and the technique followed in the semi-micro methods of qualitative analysis described in this book are so simple that no lengthy description is deemed necessary. The apparatus listed in the Appendix has been found ample for the work at hand. Except for the centrifuge, one of which can be shared by several students, each student's outfit consists of such relatively simple items as centrifuge tubes, test tubes, a spot plate, drop-reaction paper, glass slides, medicine droppers, and reagent vials for an individual set of reagents.

**Preparatory Laboratory Work.** The preliminary assignments in the laboratory, before the actual experiments and study of the reactions are begun, consist of two general parts: (1) preparation of certain pieces of apparatus and equipment and (2) assembly of the necessary reagents.

In connection with the first, check over the contents of the locker assigned you, and report and replace missing or damaged apparatus. Procure the non-returnable apparatus if this has not been supplied. Seal the piece of platinum wire in a short length of glass tubing. Draw out a medicine dropper to a thin capillary tube by heating in a hot flame; this will be your capillary pipet. Follow the instructions given by the laboratory instructor for the making of a wash bottle and other pieces of apparatus required.

Certain general instructions regarding the assembling of the reagent kit and preparation of a few reagents are given in the section on assembling of reagents.

**Semi-Micro Technique.** The technique employed in carrying out the methods described in this book is simple and so easily acquired that no special provision in the form of preliminary experimentation is made. The more important operations and manipulations are described in the following.

*Precipitation.* Precipitations are carried out by the following methods:

1. In a centrifuge tube. The precipitating agent is added to the solution in a centrifuge tube. The advantage of this procedure lies in the ease with which the precipitate may be observed after centrifuging and the facility with which a separation can be carried out.

2. On the spot plate. Here a drop of the solution to be tested is brought into contact with a drop of the precipitating agent in the cavity of a spot plate. This procedure is effective for detecting the formation of colored precipitates. Black spot plates sometimes are used for observing white precipitates.

3. On a glass slide. In this method a drop of the solution and one of the precipitant are placed side by side on a slide, and then the two are mixed by means of a stirring rod or a platinum wire. When heating is necessary, the drops are placed as near to one corner of the slide as possible and the heat from a burner cautiously applied.

*Filtration.* Since most of the precipitations in the semi-micro procedures are carried out in centrifuge tubes, the main filtration

operations are concerned with removing the supernatant liquids (centrifugate) from the precipitates. This is best accomplished by using a medicine dropper or capillary pipet. The bulb of the pipet first is compressed to expel all the air and then is carefully introduced into the centrifuge tube containing the liquid and precipitate. The tip of the pipet should be brought as close as possible to the precipitate, and then the bulb is gently released. If the operation is conducted successfully, the liquid drawn into the pipet should be clear and the precipitate undisturbed. In some cases where it is difficult to do this, a small plug of cotton may be placed in the tip of the pipet. This will filter out any particles of the precipitate.

If washing of the precipitate is required, a few drops of wash solution are added, the precipitate stirred with a platinum wire or thin glass rod, the mixture centrifuged and the centrifugate drawn off with a medicine dropper.

*Color Reactions.* These are carried out on drop-reaction paper. Such methods usually are more sensitive than those carried out on a spot plate or glass slide, owing to the concentration of the solution in the capillary pores of the paper.

With certain of these reactions, the colors are brought out or "developed" by allowing hydrochloric acid vapor or ammonia fumes to come into contact with the reaction mixture on the paper. This is done by holding the reaction paper in the fumes evolved either by heating a few drops of concentrated HCl or $NH_4OH$, as the case requires, in a crucible, or else by passing the paper over the mouth of the reagent bottle containing the concentrated acid or ammonia.

*Evaporation.* Evaporations are carried out by transferring the solution to a crucible and carefully heating. The heating may be conducted by placing the crucible in a water bath; this procedure lessens the danger of solution losses due to spattering. When the crucible is heated directly, care must be exercised to prevent superheating, in which case solution will be lost. The container should be kept moving continually while being heated.

*Cleanliness.* Absolute cleanliness is essential to successful use of semi-micro methods. All apparatus should be cleaned thoroughly with cleaning solution and then rinsed several times with distilled water. All pipets and stirring rods should be kept in a beaker of distilled water and should be rinsed before using. Immediately after any equipment has been used, it should be rinsed and then placed

in cleaning solution; the pipets should be rinsed several times with distilled water and then placed in a beaker containing distilled water.

Soap solution or sodium phosphate frequently are employed as the cleaning substance. Dichromate cleaning solution may be used in place of either of the other two. In order that this cleaner be sufficiently cool before the close of the laboratory period, it is imperative that its preparation be attended to immediately.

The dichromate cleaner is made as follows: Dissolve 50 grams of commercial $Na_2Cr_2O_7$ in 150 ml. of warm water. Cool and add slowly, with constant stirring, 230 ml. of commercial $H_2SO_4$. The mixing is best done in a large evaporating dish. When it is thoroughly cool, at the close of the laboratory period, transfer to a 500-ml. wide-mouthed bottle and use as required. This cleaning mixture can be used repeatedly as long as it remains red and thick.

Always rinse apparatus with distilled water immediately before use. Use distilled water sparingly.

**Assembling of the Reagents.** In the locker of your desk will be found a reagent rack and a considerable number of small (30-ml.) bottles and screw-cap vials (3-ml.) provided with dropping tubes, as well as small biological vials with corks. These are to contain your individual set of reagents. If these containers are not already labeled, labels will have to be prepared neatly and attached to the proper-sized bottle or vial.

In general, the 30-ml. bottles are to contain the reagents used in larger quantities such as the common acids and alkalies and the group precipitating reagents. These are as follows:

| | |
|---|---|
| conc. HCl | dil. HCl |
| conc. $HNO_3$ | dil. $HNO_3$ |
| conc. $H_2SO_4$ | dil. $H_2SO_4$ |
| conc. $NH_4OH$ | dil. $NH_4OH$ |
| 4 $M$ KOH | 4 $M$ NaOH |
| $(NH_4)_2CO_3$ | dil. $HC_2H_3O_2$ |
| $Ca(NO_3)_2$ | $Ba(NO_3)_2$ |
| $Zn(NO_3)_2$ | $AgNO_3$ |

Fill these bottles with the reagents designated from the stock supply except those for the dilute HCl, $HNO_3$, $H_2SO_4$ and $NH_4OH$. These four dilute reagents are to be prepared from the concentrated ones by dilution as follows:

Place 10 ml. of concentrated HCl in the "dilute HCl" bottle and add 20 ml. of distilled water, making approximately 30 ml. of the diluted reagent. This is a 1:2 solution.

Likewise, for the dilute $HNO_3$, dilute 10 ml. with about 20 ml. of water. This, too, is a 1:2 reagent.

In preparing the dilute $H_2SO_4$, place 25 ml. of distilled water in the 30-ml. bottle and slowly add 5 ml. of concentrated $H_2SO_4$. This is a 1:5 solution.

The dilute $NH_4OH$ is made by mixing 15 ml. of concentrated ammonia reagent with 15 ml. of distilled water (a 1:1 dilution).

The large number of liquid reagents listed in the appendix are used in smaller quantities and some only infrequently. A number of them are supplementary or used only in optional tests. Some are unstable and will be supplied as needed. Still others will be dispensed by the instructor or placed at the disposal of the student at convenient locations in the laboratory. The instructor will furnish a list of those which are to be supplied for the student's individual set. These are to be supplied from the stock bottles and placed in the screw-cap vials, and labels are to be provided.

Solid reagents, from a list provided by the instructor, are to be placed in the corked vials.

**Reagents Used in the Procedures of Analysis.** Examination of the reagent list in the Appendix indicates that both solid and liquid reagents are included. The reasons for supplying some of the reagents in solid form are that (1) certain of these substances are insoluble, (2) some give unstable solutions and are prepared when a fresh solution is called for, and (3) more intensified reactions are obtained in certain cases when the reagent is added in the solid form rather than as a solution. With regard to the liquid reagents, the following observations might profitably be made, thereby providing a broad perspective of their general nature and method of preparation. Note that:

1. Some of the reagents are pure organic liquids such as ether, alcohols, chloroform, whereas the majority are solutions.

2. Water is the usual solvent, although organic liquids are used in the preparation of a few reagents.

3. Inorganic as well as organic compounds constitute the solutes.

4. Most of the reagents have been prepared by dissolving the specified amount of the solute in 100 ml. of the solvent. These are called "empirical" solutions.

5. The "concentrated" acids, namely, HCl, $H_2SO_4$ and $HNO_3$, as well as $NH_4OH$, are designated by their specific gravity and percentage by weight. These designations are discussed further in the following section.

6. The reagent list indicates the purpose of the reagent when it is used as a final test reagent; when not so designated the reagents find their proper use throughout the procedures of analysis.

A general discussion of reagents including the various methods of designating their strength together with calculations based on their preparation and use follows.

## REAGENTS

In the laboratory work of qualitative analysis, the experimenter is engaged primarily and continuously in observing the effect of reagents on test substances of known and unknown composition. In fact, from the experimental side it may be said that experimental qualitative analysis consists very largely in the intelligent selection and proper use of reagents. At the outset, therefore, in the study of this subject, the student must become acquainted with the reagents to be employed and learn how to carry out the calculations involved in the preparation and use of a wide variety of reagents.

In general, reagents are added to the test substances for the following purposes:

1. As precipitating reagents.
2. As solvents for dissolving precipitates, residues and samples.
3. For acidifying, neutralizing or rendering a solution alkaline.
4. As oxidizing or reducing agents.

There are several methods or systems in common use for preparing and for designating the strength of reagent and other solutions. Three of these systems bear a close relationship to the molecular weight of the solute; they are the (1) molar, (2) molal and (3) normal systems.

**1. Molar Solutions.** A molar solution contains the molecular weight in grams of the solute in a liter of solution. This system is of extreme fundamental importance in the theory of qualitative analysis. Although only a few of the laboratory reagents are actually designated in terms of their molarity, the units of mass or concentration used in this system, namely, the gram mole and gram ion, form the basis of the mathematical treatment of all equilibrium relationships. Molar concentrations are introduced in the following chapter and are used subsequently in practically all calculations throughout this book.

**2. Molal Solutions.** A molal solution contains one gram-molecular weight of the solute in 1000 grams of the solvent. Molal