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# **fundamentals of**

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# **analytical chemistry**

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fourth edition

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# introduction

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## 1

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Analytical chemistry deals with methods for the identification of one or more of the components in a sample of matter and the determination of the relative amounts of each. The identification process is called a *qualitative analysis* while the determination of amount is termed a *quantitative analysis*. This text is concerned largely with the latter.

A quantitative analysis provides numerical information concerning the quantity of some species (the *analyte*) in a measured amount of matter (the *sample*). The results of an analysis are expressed in such relative terms as parts of analyte per hundred (percent), per thousand, per million, or perhaps per billion of the sample. Also encountered are the weight (or volume) of analyte per unit volume of sample and the mole fraction.

Applications of chemical analyses are to be found everywhere in an industrialized society. For example, measurement of the parts per million of hydrocarbons, nitrogen oxides, and carbon monoxide in exhaust gases defines the effectiveness of automotive smog control devices. Determination of the concentration of ionized calcium in blood serum is important in the diagnosis of hyperparathyroidism in human patients. The nitrogen content of breakfast cereals and other foods can be directly related to their protein content and thus their nutritional qualities. Periodic quantitative analyses during the production of steel permit the manufacture of a product having a desired strength, hardness, ductility, and corrosion resistance. The continuous analysis for mercaptans in the household gas supply assures the presence of sufficient odorant to warn of dangerous leaks in the gas distribution system. The analysis of soils for nitrogen, phosphorus, potassium, and moisture throughout the growing season enables the farmer to tailor fertilization and irrigation schedules to meet plant needs efficiently and economically.

In addition to practical applications of the types just cited, quantitative analytical data are at the heart of research activity in chemistry, biochemistry, biology, geology, and the other sciences. Thus, for example, much of what is known of the

mechanisms by which chemical reactions occur has been learned through kinetic studies employing quantitative measurements of the rates at which reactants are consumed or products formed. Recognition that the conduction of nerve signals in animals and the contraction or relaxation of muscles involve the transport of sodium and potassium ions across membranes was the result of quantitative measurements for these ions on each side of such membranes. Studies concerned with the mechanisms by which gases are transported in blood have required methods for continuously monitoring the concentration of oxygen, carbon dioxide, and other species within a living organism. An understanding of the behavior of semiconductor devices has required the development of methods for the quantitative determination of impurities in pure silicon and germanium in the range of  $1 \times 10^{-6}$  to  $1 \times 10^{-10}\%$ . The amounts of minor elemental constituents serve to identify the source of obsidian samples, an observation that has enabled archeologists to trace prehistoric trade routes for tools and weapons that were fashioned from these materials.

For many investigators in chemistry and biochemistry, as well as some of the biological sciences, the acquisition of quantitative information represents a significant fraction of their experimental efforts. Analytical procedures, then, are among the important tools employed by such scientists in pursuit of their research goals. Both an understanding of the basis of the quantitative analytical process and the competence and confidence to perform analyses are therefore prerequisites for research in these fields. The role of analytical chemistry in the education of chemists and biochemists is analogous to the role of calculus and matrix algebra for aspiring theoretical physicists and to the role of ancient languages in the education of scholars of the classics.

## **1A PERFORMANCE OF QUANTITATIVE ANALYSES**

The results of a typical quantitative analysis are based upon two measurements (or sometimes two series of measurements), one of which is related to the quantity of sample taken and the second to the quantity of analyte in that sample. Examples of the quantities measured include mass, volume, light intensity, absorption of radiation, fluorescent intensity, and quantity of electricity. It is important to recognize, however, that these measurements are but a part of the typical quantitative analysis. Indeed, some of the preliminary steps are as important and often more difficult and time-consuming than the measurements themselves.

For the most part, the early chapters of this text are devoted to the final measurement steps; the other aspects of an analysis are not treated in detail until near the end of the book (Chapters 23 to 29). Thus, to lend perspective, it is useful at the outset to identify the several steps that make up the analytical process and to indicate their importance.

### **1A-1 SAMPLING**

To produce meaningful information, an analysis must be performed on a sample whose composition faithfully reflects that of the bulk of material from which it was taken. Where the bulk is large and inhomogeneous, great effort is required to procure a representative sample. Consider, for example, a railroad car containing 25 tons of silver ore. Buyer and seller must come to agreement regarding the value of

the shipment, based primarily upon its silver content. The ore itself is inherently heterogeneous, consisting of lumps of varying size and of varying silver content. The actual assay of this shipment will be performed upon a sample that weighs perhaps 1 g; its composition must be representative of the 25 tons (or approximately 22,700,000 g) of ore in the shipment. It is clear that the selection of a small sample for this analysis cannot be a simple one-step operation; in short, a systematic preliminary manipulation of the bulk of material will be required before it becomes possible to select 1 g and have any confidence that its composition is typical of the nearly 23,000,000 g from which it was taken.

Many sampling problems are not as formidable as the one just described. Nevertheless, the chemist needs the same assurance that the laboratory sample is representative of the whole before proceeding with the analysis.

#### 1A-2 PREPARATION OF THE LABORATORY SAMPLE FOR ANALYSIS

Most solid materials must be ground to reduce particle size and then thoroughly mixed to ensure homogeneity. In addition, removal of adsorbed moisture is often required for solid samples. Adsorption or desorption of water causes the percentage composition of a substance to depend upon the humidity of its surroundings at the time of the analysis. To avoid the problems arising from such variations, it is common practice to base the analysis on a dry sample.

#### 1A-3 MEASUREMENT OF THE SAMPLE

Quantitative analytical results are usually reported in relative terms; that is, in some way that expresses the quantity of the desired component present per unit weight or volume of sample. It is, therefore, necessary to know the weight or volume of the sample upon which the analysis is performed.

#### 1A-4 SOLUTION OF THE SAMPLE

Most, but certainly not all, analyses are performed on solutions of the sample. Ideally, the solvent should dissolve the entire sample (not just the analyte) rapidly and under sufficiently mild conditions that loss of the analyte cannot occur. Unfortunately, such solvents do not exist for many of the materials that are of interest to the scientist—a silicate mineral, a high-molecular-weight polymer, or a specimen of animal tissue, to mention a few. Conversion of the analyte in such materials into a soluble form can be a formidable and time-consuming task.

#### 1A-5 SEPARATION OF INTERFERING SUBSTANCES

Few, if any, chemical or physical properties of importance in analyses are unique to a single chemical species; instead, the reactions used and the properties measured are characteristic of a number of elements or compounds. This lack of truly specific reactions and properties adds greatly to the difficulties faced by the chemist when undertaking an analysis; it means that a scheme must be devised for isolating the species of interest from all others present in the original material that produce an effect upon the final measurement. Compounds or elements that prevent the direct measurement of the species being determined are called *interferences*; their separation prior to the final measurement constitutes an important step in most analyses. No hard and fast rules can be given for the elimination of interferences; this problem is often the most demanding aspect of the analysis.

### 1A-6 THE COMPLETION OF THE ANALYSIS

All preliminary steps in an analysis are undertaken to make the final measurement a true gauge of the quantity of the species being determined.

The chapters that follow contain descriptions of many types of final measurement, along with discussions of the chemical principles upon which such measurements are based.

### 1B CALIBRATION STANDARDS

All analytical methods are based upon the measurement of some physical quantity  $X$  that varies with the concentration  $C_A$  of the analyte. Ideally, the relationship between these two quantities is linear. That is,

$$C_A = kX$$

where  $k$  is a proportionality constant. With two exceptions, analytical methods require the empirical determination of  $k$  employing chemical standards for which  $C_A$  is known (the two exceptions are gravimetric and coulometric methods, which are discussed in Chapters 5 and 17, respectively). The process of determining  $k$  is an important step in most analyses and is termed *calibration*.

Smith and Parsons have listed desirable properties of chemical standards.<sup>1</sup> These include

1. *Stability*
  - a. The compound should not be **deliquescent**, **efflorescent**, or **hygroscopic**.
  - b. The compound should not undergo a **chemical change** upon drying.
  - c. The compound should be **easily weighable**.
  - d. Both the solution and the compound from which it is prepared should be stable in air and in solution.
2. *Purity*
  - a. The compound should be available to a purity of 99.5% or better.
3. *Solubility*
  - a. Since most analyses are performed on aqueous solutions, the compound should be readily soluble in water, common acids, or bases.
4. *Availability*
  - a. The compound should be readily available from common chemical suppliers.
  - b. The compound should not be unnecessarily costly.
5. *High Molecular Weight*
  - a. The compound should have as high a molecular weight as possible to permit accurate weighing.
6. *Toxicity*
  - a. The compound should have as low a toxicity as possible.

Few chemical compounds meet all of these criteria. The few that do are called *primary standards* and are discussed in detail in the several chapters on volumetric methods.

<sup>1</sup> B. W. Smith and M. L. Parsons, *J. Chem. Educ.*, **50**, 679 (1973).

A list of compounds suitable for preparation of solutions containing known concentrations of various common elements is provided in the end pages of this text.

### **1C CHOICE OF METHODS FOR AN ANALYSIS**

The chemist or scientist who needs analytical data is frequently confronted with an awesome array of methods that could provide the desired information. Such considerations as speed, convenience, accuracy, availability of equipment, number of analyses, amount of sample that can be sacrificed, and concentration range of the analyte must all be considered; the success or failure of an analysis is often critically dependent upon the proper selection of method. Because no generally applicable rules exist, the choice of method is a matter of judgment. Such decisions are difficult; the ability to make them comes only with experience.

This text presents many of the common unit operations associated with chemical analyses and includes a variety of methods for the final measurement of analytes. Both theory and practical details are treated. Mastery of this material will permit the reader to perform many useful analyses and, in addition, will provide the background from which the judgment needed for the prudent choice among analytical methods can be developed.

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**a review of some**

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**elementary concepts**

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**2**

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Most quantitative analytical measurements are performed on solutions of the sample. The study of analytical chemistry, therefore, makes use of solution concepts with which students should already be familiar. The purpose of this chapter is to review the most important of these concepts.

## **2A THE CHEMICAL COMPOSITION OF SOLUTIONS**

Both aqueous and organic solvents find widespread use in chemical analysis. Aqueous solvents, including solutions of the common inorganic acids and bases, are more widely used, however. Thus, our discussion will focus on the behavior of solutes in water; reactions in nonaqueous media will be considered in less detail.

### **2A-1 ELECTROLYTES**

Electrolytes are solutes which ionize in a solvent to produce an electrically conducting medium. *Strong electrolytes* ionize completely whereas *weak electrolytes* are only partially ionized in the solvent. Table 2-1 summarizes the common strong and weak electrolytes in aqueous media.

### **2A-2 ACIDS AND BASES**

For analytical chemists, the most useful acid-base concept is that proposed independently by Brønsted and Lowry in 1923. According to the Brønsted-Lowry view,

*an acid is any substance that is capable of donating a proton; a base is any substance that can accept a proton.*

It is important to recognize that the proton-donating character of an acid manifests itself only in the presence of a proton acceptor or base; similarly, basic behavior requires the presence of an acid. Many solvents act as proton acceptors or donors and thus induce acidic or basic behavior of the solutes dissolved in them. For example, when nitrous acid is dissolved in water, the solvent acts as a proton acceptor and thus behaves as a base:



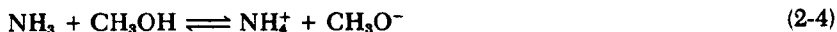
On the other hand, when ammonia is dissolved in water, the solvent provides a proton and is thus an acid:



Water is the classic example of an *amphiprotic* solvent because it exhibits both acidic and basic properties, depending on the solute. Other useful amphiprotic solvents include methyl alcohol, ethyl alcohol, and glacial acetic acid. When nitrous acid or ammonia is dissolved in one of these, reactions similar to those shown by Equations 2-1 and 2-2 occur. With methanol, for example, we may write



and

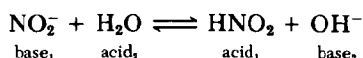


**Conjugate acids and bases.** After an acid has donated a proton, the species that remains is capable of accepting a proton to re-form the original acid. In Equation 2-1, for example, it is seen that nitrite ion is the product of the acidic action of nitrous acid; nitrite ion, however, can behave as a base and accept a proton from a suitable donor. Thus, when sodium nitrite is dissolved in water, nitrous acid is formed by the reaction

**Table 2-1 Classification of Electrolytes**

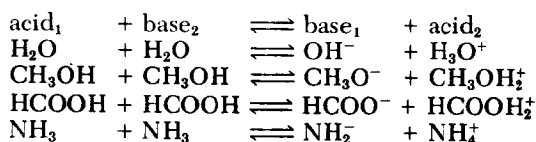
Strong Electrolytes	Weak Electrolytes
<ol style="list-style-type: none"> <li>1. The inorganic acids <math>\text{HNO}_3</math>, <math>\text{HClO}_4</math>, <math>\text{H}_2\text{SO}_4</math>,* <math>\text{HCl}</math>, <math>\text{HI}</math>, <math>\text{HBr}</math>, <math>\text{HClO}_3</math>, <math>\text{HBrO}_3</math></li> <li>2. Alkali and alkaline-earth hydroxides</li> <li>3. Most salts</li> </ol>	<ol style="list-style-type: none"> <li>1. Many inorganic acids such as <math>\text{H}_2\text{CO}_3</math>, <math>\text{H}_3\text{BO}_3</math>, <math>\text{H}_3\text{PO}_4</math>, <math>\text{H}_2\text{S}</math>, <math>\text{H}_2\text{SO}_3</math></li> <li>2. Most organic acids</li> <li>3. Ammonia and most organic bases</li> <li>4. Halides, cyanides, and thiocyanates of <math>\text{Hg}</math>, <math>\text{Zn}</math>, and <math>\text{Cd}</math></li> </ol>

\*  $\text{H}_2\text{SO}_4$  is completely dissociated into  $\text{HSO}_4^-$  and  $\text{H}_3\text{O}^+$  ions and for this reason is classified as a strong electrolyte. However, it should be noted that the  $\text{HSO}_4^-$  ion is a weak electrolyte, being only partially dissociated.



Every Brønsted-Lowry acid, then, is paired with a corresponding base called its *conjugate base*, and every Brønsted-Lowry base is paired with a *conjugate acid*. In Equation 2-1, nitrite ion is seen to be the conjugate base of nitrous acid; the hydronium ion,  $\text{H}_3\text{O}^+$ , is the conjugate acid of the base water. Note also (Equation 2-2) that reaction between the base ammonia and the acid water results in the formation of the conjugate acid ammonium ion and the conjugate base hydroxide ion, respectively.

**Autoprotolysis.** Amphiprotic solvents undergo self-ionization or *autoprotolysis* to form a pair of ionic species. Autoprotolysis is an acid-base reaction, as illustrated by the following equations:



The positive ion formed by the autoprotolysis of water is called the *hydronium* ion, the proton being covalently bonded to the parent molecule by one of the unshared electron pairs of the oxygen. Higher hydrates such as  $\text{H}_5\text{O}_2^+$  and  $\text{H}_9\text{O}_4^+$  also exist, but they are significantly less stable than  $\text{H}_3\text{O}^+$ . Essentially no unhydrated hydrogen ions appear to exist in aqueous solutions.<sup>1</sup>

To emphasize the extraordinary stability of the singly hydrated proton, many chemists use the notation  $\text{H}_3\text{O}^+$  when writing equations for reactions in which the proton is a participant. Others use  $\text{H}^+$  to symbolize the proton, whatever its actual degree of hydration may be, as a matter of convenience. This notation has the advantage of simplifying the writing of equations that require the proton for balance. We shall use both notations, as convenient, in various sections of the text.

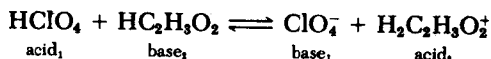
### 2A-3 STRENGTHS OF ACIDS OR BASES

Figure 2-1 shows the reactions of a few common acids with water. The first two entries are *strong acids* because their reaction with water is sufficiently complete to leave essentially no undissociated molecules, as such, in the solvent. The remaining acids are *weak acids*, which react incompletely to give solutions that contain significant quantities of both the parent acid and the conjugate base. Note that acids may be cationic, anionic, or electrically neutral.

The acids shown in Figure 2-1 become progressively weaker from the top to the bottom of the list. Thus, for the purpose of classification, perchloric and hydrochloric acid are completely dissociated; in contrast, only a few thousandths of a percent of the ammonium ions in an ammonium chloride solution are converted to ammonia molecules. It is also important to note that ammonium ion, the weakest acid, forms the strongest conjugate base of the group; that is,  $\text{NH}_3$  has a much stronger affinity for protons than any base above it in Figure 2-1.

<sup>1</sup> See: P. A. Giguère, *J. Chem. Educ.*, **56**, 571 (1979).

The extent of reaction between a solute acid (or base) and a solvent is critically dependent upon the tendency of the latter to donate or accept protons. Thus, for example, perchloric, hydrochloric, and hydrobromic acids are all classified as strong acids in water. If anhydrous acetic acid, a poorer proton acceptor than water, is used as *the solvent*, none of the acids undergoes complete dissociation and remains a strong acid; instead, equilibria such as the following develop:



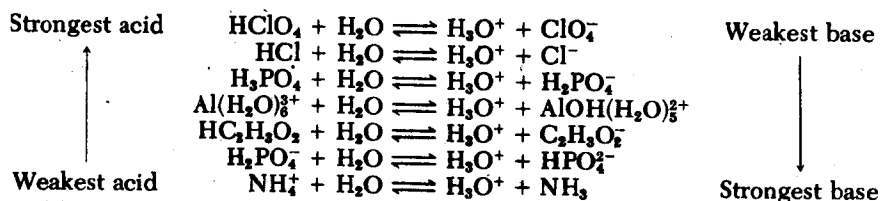
It is noteworthy that in this solvent, perchloric acid is a considerably stronger acid than either of the other two; the extent of its dissociation is 5000 times as great as that for hydrochloric acid, for example. Thus, glacial acetic acid serves as a *differentiating solvent* toward these acids in the sense that it reveals differences in the inherent acidities of the three compounds. On the other hand, water is termed a *leveling solvent* because the acidities of all acids that are strong are identical in this medium. Thus, no difference can be detected in the hydronium ion concentration of aqueous solutions containing hydrochloric and perchloric acids, provided their molar concentrations are the same.

## 2B UNITS OF WEIGHT AND CONCENTRATION

The mass of a substance is ordinarily determined in such metric units as the kilogram (kg), the gram (g), the milligram (mg), the microgram ( $\mu\text{g}$ ), the nanogram (ng), or the picogram (pg).<sup>2</sup> For chemical calculations, however, it is necessary to employ units that express the weight relationship or *stoichiometry* among reacting species in terms of small whole numbers. The gram formula weight, the gram molecular weight, and the gram equivalent weight serve this purpose in analytical work. These terms are often shortened to formula weight, molecular weight, and equivalent weight.

### 2B-1 EMPIRICAL FORMULAS, CHEMICAL FORMULAS, AND THE MOLE

An *empirical formula* expresses the simplest whole-number combining ratio for the atoms in a substance. The *chemical formula*, on the other hand, specifies the number of atoms in a molecule. An empirical formula may be shared by more than one substance. To illustrate,  $\text{CH}_2\text{O}$  is the empirical formula for formaldehyde,  $\text{CH}_2\text{O}$ , glyceraldehyde,  $\text{C}_3\text{H}_6\text{O}_3$ , and glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ . The empirical formula can



**Figure 2-1.** Relative strengths of some common weak acids and their conjugate bases.

<sup>2</sup> The relationship among these units is  $10^{-3} \text{ kg} = 1 \text{ g} = 10^3 \text{ mg} = 10^6 \mu\text{g} = 10^9 \text{ ng} = 10^{12} \text{ pg}$ .