

ANALYTICAL CHEMISTRY

Third Edition

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1

introduction

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 (the percent), per thousand, per million, or perhaps per billion of the sample. Other terms include 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, or corrosion resistance. The continuous analysis for mercaptans in the household gas supply assures the presence of an 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 used up or products appear. 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 1×10^{-6} to $1 \times 10^{-10}\%$. Recognition that the amounts of various minor elemental constituents in obsidian samples permit identification and location of their sources has enabled archeologists to trace prehistoric trade routes for tools and weapons 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 or the role of ancient languages in the education of scholars of classics.

Choice of Methods for an Analysis

The chemist or scientist who needs analytical data is frequently confronted with an array of methods which could be used to 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 detail are treated. Mastery of this material will permit students to perform many useful analyses and will provide them with the background from which they can develop the judgment necessary for the prudent choice of analytical methods.

2

a review of some elementary concepts

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 and Chapter 3 is to review the most important of these concepts.

The Chemical Composition of Solutions

Although both aqueous and organic solvents are widely used in chemical analysis, the former is more commonly encountered. Our discussion will therefore focus on the behavior of solutes in water; reactions in nonaqueous polar media will be considered only briefly.

ELECTROLYTES

Electrolytes are solutes that ionize in a solvent to produce an electrically conducting medium. *Strong electrolytes* are ionized completely—or nearly

TABLE 2-1
Classification of Electrolytes

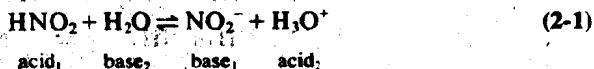
STRONG ELECTROLYTES	WEAK ELECTROLYTES
<ol style="list-style-type: none"> 1. The inorganic acids HNO_3, HClO_4, H_2SO_4,^a HCl, HI, HBr, HClO_3, HBrO_3 2. Alkali and alkaline-earth hydroxides 3. Most salts 	<ol style="list-style-type: none"> 1. Many inorganic acids such as H_2CO_3, H_3BO_3, H_3PO_4, H_2S, H_2SO_3 2. Most organic acids 3. Ammonia and most organic bases 4. Halides, cyanides, and thiocyanates of Zn, Cd, and Hg
<p>^a H_2SO_4 is completely dissociated into HSO_4^- and H_3O^+ ions and for this reason is classified as a strong electrolyte. However, it should be noted that the HSO_4^- ion is a weak electrolyte because it is only partially dissociated.</p>	

so—whereas *weak electrolytes* undergo partial ionization only. Table 2-1 summarizes the common strong and weak electrolytes in aqueous media.

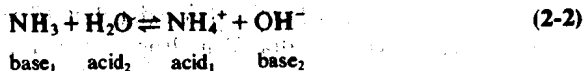
ACIDS AND BASES

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 acidic character of a substance 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:

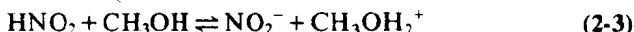


On the other hand, when ammonia is dissolved in water, the solvent provides a proton and is thus an acid:



Water is the classic example of an *amphiprotic* solvent because it exhibits both acidic and basic properties, depending on the solute. Other useful

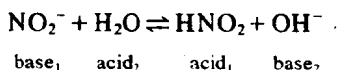
amphiprotic solvents include methyl alcohol, ethyl alcohol, and anhydrous acetic acid. When nitrous acid or ammonia is dissolved in one of these, reactions similar to those shown by Equations 2-1 and 2-2 occur. With methanol, for example, we may write



and

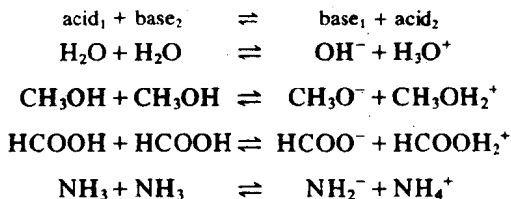


Conjugate Acids and Bases. After an acid has donated a proton, the species that remains is capable of accepting a proton to re-form the original acid. In Equation 2-1, for example, it is seen that nitrite ion is the product of the acidic action of nitrous acid; nitrite ion, however, can behave as a base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



Thus every Brønsted-Lowry acid 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, H_3O^+ , 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 H_3O_2^+ and H_7O_3^+ also exist, but they are significantly less stable than H_3O^+ . No unhydrated hydrogen ions appear to exist in aqueous solutions.

To emphasize the high stability of the singly hydrated proton many chemists use the notation H_3O^+ when writing equations for reactions in which the proton is a participant. As a matter of convenience others use H^+

to symbolize the proton, whatever its actual degree of hydration may be. This notation has the advantage of simplifying the writing of equations that require the proton for balance.

STRENGTHS OF ACIDS OR BASES

Figure 2-1 shows the reactions of a few common acids with water. The first entry, hydrochloric acid, is termed a *strong acid* because its reaction is sufficiently complete to leave essentially no HCl 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.

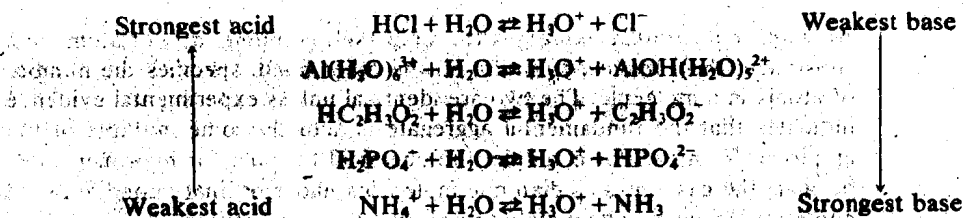
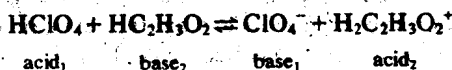


FIGURE 2-1 Relative strengths of some common weak acids and their conjugate bases.

The acids shown in Figure 2-1 become progressively weaker from the top to the bottom of the list. Thus, for the purposes of classification, hydrochloric acid is 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, NH_3 has a much stronger affinity for protons than any base above it in Figure 2-1.

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, only perchloric acid undergoes complete dissociation and remains a strong acid; the process can be expressed by the equation



Because they undergo only partial dissociation, hydrochloric and hydrobromic acids are weak acids in glacial acetic acid.

Units of Weight and Concentration

In the laboratory the mass of a substance is ordinarily determined in such metric units as the kilogram (kg), the gram (g), the milligram (mg), the microgram (μg), the nanogram (ng), or the picogram (pg).¹ For chemical calculations, however, it is more convenient 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 are employed in analytical work for this purpose. These terms are often shortened to the formula weight, the molecular weight, and the equivalent weight.

CHEMICAL FORMULAS, FORMULA WEIGHTS, AND MOLECULAR WEIGHTS

An *empirical formula* expresses the simplest combining ratio of atoms in a substance; the *chemical formula*, on the other hand, specifies the number of atoms in a molecule. The two are identical unless experimental evidence indicates that the fundamental aggregate is actually some multiple of the empirical formula. For example, the chemical formula for hydrogen is H_2 because the gas exists as diatomic molecules under ordinary conditions. In contrast, Ne serves adequately to describe the composition of neon, which is observed to be monatomic.

The entity expressed by the chemical formula may or may not actually exist. For example, no evidence has been found for the existence of sodium chloride molecules, as such, in the solid state or in an aqueous solution. Rather, this substance consists of sodium ions and chloride ions, no one of which can be shown to be in simple combination with any other single ion. Nevertheless, the formula NaCl is convenient for stoichiometric accounting and is therefore used. It is also necessary to note that the chemical formula is frequently that of the principal species only. Thus, for example, water in the liquid state contains small amounts of such entities as H_3O^+ , OH^- , H_2O_2 and undoubtedly others, in addition to H_2O . Here the chemical formula of H_2O is that for the predominant species and is perfectly satisfactory for chemical accounting; it is, however, only an approximation of the actual composition of the real substance.

The *gram formula weight* (gfw) is the summation of the atomic weights in grams for all the atoms in the chemical formula of a substance. Thus the gram formula weight for H_2 is 2.016 (2×1.008) g; for NaCl it is 58.44 ($35.45 + 22.99$) g. The definition for the gram formula weight carries with it no inference concerning the existence or nonexistence of the substance for which it has been calculated.

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

We shall employ the term *gram molecular weight* (gmw) rather than gram formula weight, to indicate that we are concerned with a real chemical species. Thus, the gram molecular weight of H_2 is also its gram formula weight, 2.016 g. It would be incorrect to assign a gram molecular weight to sodium chloride in the solid state (or in aqueous solution) because the *species* NaCl does not exist in these states. It is perfectly proper to assign gram molecular weights to Na^+ (22.99 g) and Cl^- (35.45 g) because these are real chemical entities (in the strict sense these should be called gram ionic weights rather than gram molecular weights, although this terminology is seldom encountered).

One molecular weight of a species contains 6.02×10^{23} particles of that species; this quantity is frequently referred to as the *mole*.² In a similar way the formula weight represents 6.02×10^{23} units of a substance, whether real or not, represented by the chemical formula.

EXAMPLE

A 25.0-g sample of H_2 contains

$$\frac{25.0 \text{ g}}{2.016 \text{ g/mole}} = 12.4 \text{ moles of } \text{H}_2$$

$$12.4 \text{ moles} \times \frac{6.02 \times 10^{23} \text{ molecules}}{\text{mole}} = 7.47 \times 10^{24} \text{ molecules } \text{H}_2$$

The same weight of NaCl contains

$$\frac{25.0 \text{ g}}{58.44 \text{ g/fw}} = 0.428 \text{ fw NaCl}$$

which corresponds to 0.428 mole Na^+ and 0.428 mole Cl^- .

Let us further distinguish between the formula weight and the molecular weight by considering exactly 1 fw of water which by definition weighs 18.015 g. Such a quantity contains slightly less than 1 mole of the species H_2O because of the existence of H_3O^+ , OH^- , H_2O_2 , and such other species as may be present.

Laboratory quantities are frequently more conveniently expressed in terms of *milliformula weights* (mfw) or *millimoles* (mmole); these

² In the International System (SI) of Units, proposed by the International Bureau of Weights and Measures, the only chemical unit for amount of substance is the *mole*. The mole is defined as the quantity of a material that contains as many elementary entities (these may be atoms, ions, electrons, ion-pairs, or molecules, but must be explicitly defined) as there are atoms of carbon in exactly 0.012 kg. of carbon-12 (that is, Avogadro's number). It seems probable that a shift to SI units will ultimately occur. It is equally important to have an understanding of the units upon which the present chemical literature is based, even though these may eventually disappear.