can change if there is a different concentration elsewhere in the flowing fluid and this different concentration is carried by advection to the fixed point of interest; this process corresponds to the term $V \cdot dC/dx$. The concentration can also change by Fickian transport if there is a spatially varying concentration gradient in the fluid; this process corresponds to the term $d/dx(D \cdot dC/dx)$. Changes in the concentration also can occur if a source or sink process, such as a chemical or biological reaction, is introducing or removing the compound of interest (r).

Equation [1-5] is pertinent to a one-dimensional system, such as a long, narrow tube full of water, where significant variations in concentration may be assumed to occur only along the length of the tube. In a three-dimensional situation, the advection–dispersion–reaction equation can be represented most succinctly using vector notation, where ∇ is the divergence operator:

$$\frac{dC}{dt} = -\vec{V} \cdot \boldsymbol{\nabla} C + \nabla \cdot D(\boldsymbol{\nabla} C) + r. \qquad [1\text{-}6]$$

Note that the transport terms (the second and third terms) in Eq. [1-6] are the three-dimensional counterparts of the corresponding terms in Eq. [1-5]. As in Eq. [1-4], D is assumed equal in all directions. In many cases, this assumption is an oversimplification; the value of D in the direction of flow can be very different than the value perpendicular to flow (i.e., D may be anisotropic). Furthermore, D may vary with location (i.e., be inhomogeneous), or vary with time. Often, a larger value of D may become applicable as the scale of the problem increases.

Although the forms of the mass conservation equation shown in Eqs. [1-5] and [1-6] may not appear to be directly applicable to large-scale environmental situations, they actually are very powerful tools. These equations can be integrated to yield mathematical solutions to chemical distributions in many physical systems. Given information on the inflow rates and chemical concentrations at the boundaries of a control volume, the chemical concentrations throughout the control volume may be determined by invoking solutions to Eqs. [1-5] and [1-6].

START

1.6 BASIC ENVIRONMENTAL CHEMISTRY

Now that the transport and storage terms of Eqs. [1-1a] and [1-1b] have been discussed, consider the source and sink terms. These correspond to the introduction or removal of a chemical due to either chemical reactions or transfer to another phase (e.g., volatilization of a chemical from water to air). Chemical reactions, which may occur spontaneously (abiotically) or be biologically mediated, result in the transformation of one chemical substance into another. Chemical substances can be uncharged atoms or molecules, ions (electrically charged atoms or aggregations of atoms), or free *radicals* (highly reactive atoms or aggregations of atoms having an unpaired valence electron). The degradation of pollutant chemicals is a subset of all possible chemical reactions occurring in the environment.

By definition, chemical reactions involve the formation or breakage of chemical bonds between atoms. Chemical bonds hold atoms together in a variety of ways. Bond types include *covalent bonds,* in which electrons are shared between atoms; *ionic bonds,* in which the bonding force arises from electric charges of opposite sign on adjacent atoms; and *hydrogen bonds,* in which the somewhat positively charged hydrogen at one end of a molecule loosely bonds with a somewhat negatively charged atom of another molecule. Other forces, such as *Van der Waals forces,* which cause weak mutual attractions between all molecules, can also contribute to bonding. A chemical bond may have characteristics of more than one idealized type of bonding. For further discussions on chemical reactions, the reader is referred to texts such as Petrucci (1989), Radel and Navidi (1990), and Shriver *et al.* (1994) for inorganic chemicals; and to Roberts and Caserio (1977), McMurry (1992), and Streitwieser *et al.* (1992) for organic chemicals.

1.6.1 CHEMICAL KINETICS VERSUS CHEMICAL EQUILIBRIUM

Chemical reactions may be described from the standpoint of either *kinetics* or *equilibrium.* Kinetics describes the *rate* at which a reaction takes place and is significant when comparing a particular reaction rate with the rate at which some other process occurs. For example, if a degradable chemical is discharged into a stream by an industrial outfall, the rate of degradation and the travel time to a downstream municipal water supply intake can be used to calculate the chemical concentration at the intake. The rates (kinetics) at which degradation and advection occur are the significant parameters.

Equilibrium, by contrast, describes the *final expected chemical composition* in a control volume. In chemical parlance, a control volume with its chemical contents is often referred to as a *system.* Equilibrium is relevant in the case of reactions that are rapid compared with other environmental processes of interest. For example, if potassium hydroxide (KOH) is added to municipal drinking water to decrease its acidity, the reaction of the potassium hydroxide and the acids present in the drinking water may be assumed to be instantaneous compared with the time it takes to transport water to customers. A consideration of equilibrium chemistry also is very useful to determine the expected final composition toward which a system is proceeding, even if at a particular time it has not yet reached equilibrium. The context of the environmental problem of concern usually makes it clear whether it is the equilibrium chemical composition of a system or the rate at which a system proceeds toward equilibrium that is of particular interest. In this section, chemical reactions are discussed in terms of equilibrium before kinetics is addressed.

1.6.2 FREE ENERGY

Regardless of the exact nature of the chemical bonds involved in a chemical reaction, a consideration of the *Gibbs free energy* of the chemical system provides information on both the direction in which a chemical reaction will proceed and the final equilibrium composition of the system. Gibbs free energy (G) is a function of both the *enthalpy,* which is the energy possessed by a mixture of chemicals in a system, and the *entropy,* or disorder, of the system. Gibbs free energy depends on the chemical composition, pressure, and temperature of the system and is quantitatively expressed as

$$G = H - TS, \tag{1-7}$$

where G is the Gibbs free energy, H is the enthalpy, S is the entropy, and T is the absolute temperature.

Enthalpy refers to the energy in a system. Enthalpy includes energy associated with all intramolecular forces (due to bonds and attractions within molecules) and intermolecular forces (due to bonds and attractions between molecules). Entropy refers to the degree of disorganization, or randomness, of a system. At the molecular level, the entropy of a chemical system at any given state (with the state defined on the basis of macroscopic quantities such as pressure, volume, and temperature) can be shown to be a measure of the probability that the molecules within the system will occur with a distribution that creates that particular state. At the macroscopic level, the incremental change in entropy associated with any given reversible process is equal to the heat energy entering the system divided by the absolute temperature of the system; thus, entropy is expressed in units of energy per Kelvin. A Kelvin (K) is a measurement of absolute temperature; degrees Celsius are converted to Kelvins by the equation K = °C + 273.15. For a more thorough discussion of entropy, the reader is referred to a text on chemical thermodynamics, such as that of Wall (1974).

It takes work to organize chemical molecules; an increase in the level of organization is reflected in a decrease in the entropy term (more organization, less uniformity). Conversely, a disorganized, more random system of molecules has an increased entropy (less organization, more uniformity). Reactions in a chemical system proceed toward a final composition that minimizes the Gibbs free energy of the system, by a combination of maximizing disorder and of minimizing enthalpy. For any reaction, the actual pathway taken, known as the *course of the reaction,* does not affect the final equilibrium state.

The change in Gibbs free energy (ΔG), which occurs as a system proceeds toward equilibrium, can be expressed as the sum of two terms. The first term is the *standard free energy change* (ΔG°), which is fixed for any given reaction. ΔG° can be calculated from the *stoichiometry* of the reaction (i.e., how many moles of one compound react with how many moles of another compound) and the standard free energies of the chemicals involved. The second term contains the *reaction quotient* (Q), which depends on the concentrations of chemicals present. The fact that ΔG can be expressed in terms of the concentrations of all chemicals present in a system makes it possible to determine in which direction a chemical reaction will proceed and to predict its final composition when it reaches equilibrium.

To get a better feel for Gibbs free energy, consider a reversible reaction occurring in water, where lowercase letters represent *stoichiometric coefficients* and uppercase letters represent four chemical compounds, A, B, C, and D:

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D} \qquad [1\text{-}8]$$

As this system proceeds toward equilibrium, the change in Gibbs free energy per additional mole reacting is

$$\Delta G = \Delta G^\circ + RT \ln Q, \qquad [1\text{-}9]$$

where ΔG° is the standard free energy change (and is a constant for a given reaction), R is the *gas constant,* T is the absolute temperature, and

$$Q = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{B}]^b[\mathrm{A}]^a}, \qquad [1\text{-}10]$$

with [A], [B], [C], and [D] referring to the *molar* concentrations of chemicals A, B, C, and D in water. Equivalent values of R are 0.0821 liter · atm/(mol · K), 8.31 J/(mol · K), and 1.99 cal/(mol · K), as shown in the Appendix.

If ΔG is negative, the reaction will proceed from left to right until ΔG becomes zero. (In mathematical terms, the only way for ΔG to become less negative is for $\ln Q$ to become less negative, which occurs as the product $[\mathrm{C}]^c[\mathrm{D}]^d$ in the numerator gets larger.) Conversely, if ΔG is positive, the reaction will proceed from right to left until ΔG becomes zero. For greater detail and derivations of these equations, the reader is referred to texts on chemical thermodynamics (Guggenheim, 1967; Wall, 1974; Denbigh, 1981; Castellan, 1983).

1.6.3 CHEMICAL EQUILIBRIUM

As previously mentioned, the Gibbs free energy of a chemical system is minimized at equilibrium. At equilibrium, the forward and reverse reactions of a chemical reaction, such as given in Eq. [1-8], are necessarily occurring at the same rate, and the change in Gibbs free energy is zero:

$$\Delta G = \Delta G^\circ + RT \ln Q = 0 \qquad \text{(at equilibrium).} \qquad [1\text{-}11a]$$

Therefore,

$$\Delta G^\circ = -RT \ln Q \qquad \text{(at equilibrium).} \qquad [1\text{-}11b]$$

For the moment, consider only reactions involving chemicals dissolved in water. The preceding equations can be combined with the definition of the reaction quotient, Eq. [1-10], to define an *equilibrium constant, K,* that applies to the *final expected* chemical composition of the system:

$$K = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{B}]^b[\mathrm{A}]^a} = e^{-\Delta G^\circ/RT}. \qquad [1\text{-}12]$$

Note that molar concentrations must be used in the expression for K and that K equals the reaction quotient Q *only* at equilibrium (Fig. 1-8). Equation [1-12], the expression of the equilibrium state of a reaction, is known as the *mass action law* and is a direct consequence of the minimization of Gibbs free

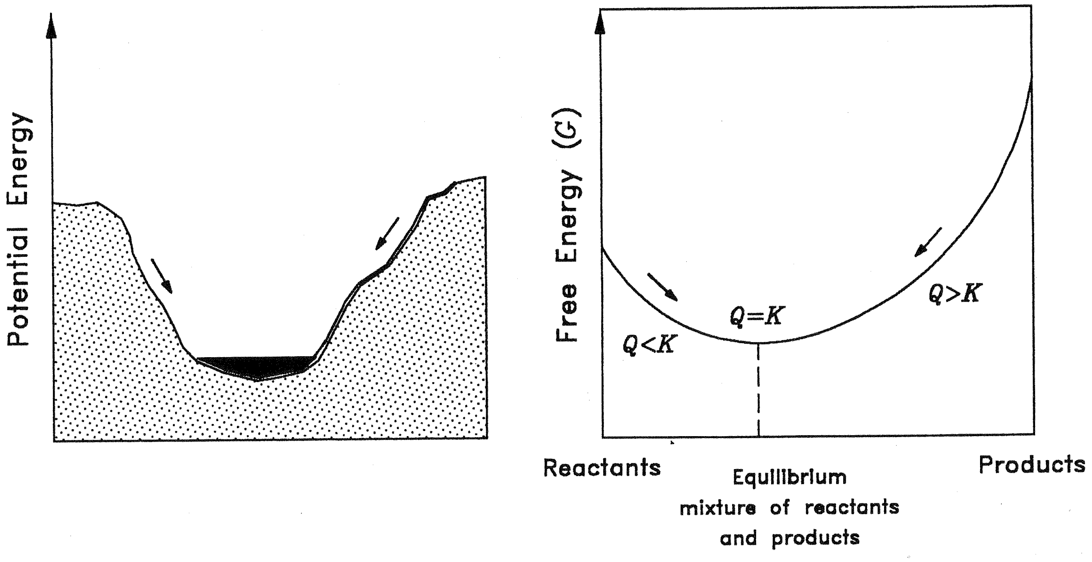


FIGURE 1-8 Free energy change in a chemical reaction. Analogous to water seeking its position of lowest gravitational energy on a hill slope, a chemical system will tend to move toward a composition having the lowest Gibbs free energy. Adapted from *Chemistry, 1st edition,* by S. Radel and M. Navidz. © 1990. Reprinted with permission of Brooks/Cole Publishing, a division of International Thomson Publishing. Fax 800-730-2215.

R= 8.3145 J/mol.K
L·atm

TABLE 1-1 Equilibrium Constants and Standard Free Energy Changes for Some Common Environmental Reactions[a]

					Approx. log K	ΔG° (kcal/mol)
		Acid–base reactions				
H_2CO_3* Carbonic acid	→	H^+ Hydrogen ion	+	HCO_3^- Bicarbonate ion	−6.3[b]	8.6
HCO_3^- Bicarbonate ion	→	H^+ Hydrogen ion	+	CO_3^{2-} Carbonate ion	−10.3[b]	14.1
CH_3COOH Acetic acid	→	H^+ Hydrogen ion	+	CH_3COO^- Acetate ion	−4.8[c]	6.5
$NH_3(g)$ Ammonia	→	NH_4^+ Ammonium ion	+	OH^- Hydroxide ion	−4.8[b]	6.5
		Precipitation–dissolution reactions				
$CaCO_3(s)$ Calcium carbonate (limestone)	→	Ca^{2+} Calcium ion	+	CO_3^{2-} Carbonate ion	−8.3[b]	11.6
$SiO_2(s)$ Quartz	+	$2H_2O$	→	H_4SiO_4 Silicic acid	−3.7[d]	5.0
$CaSO_4(s)$ Gypsum	→	Ca^{2+} Calcium ion	+	SO_4^{2-} Sulfate ion	−4.6[d]	6.3

[a] ΔG° values were calculated for a temperature of 25°C.
[b] Morel and Hering (1993).
[c] Weast (1990).
[d] Stumm and Morgan (1981).

energy. Table 1-1 presents standard free energy changes and equilibrium constants for some common environmental reactions.

EXAMPLE 1-4

Given the reaction between copper and hydroxide ions dissolved in water:

$$Cu^{2+} + OH^- \longrightarrow CuOH^+; \qquad \log K = 6.3,$$

what is the ratio of the Cu^{2+} (cupric) ion to the $CuOH^+$ ion in water if the hydroxide ion (OH^-) concentration is 10^{-4} mol/liter?

From mass action:

$$\frac{[\mathrm{CuOH^+}]}{[\mathrm{OH^-}][\mathrm{Cu^{2+}}]} = 10^{6.3}.$$

Given that $[\mathrm{OH^-}] = 10^{-4}$ mol/liter,

$$\frac{[\mathrm{CuOH^+}]}{[\mathrm{Cu^{2+}}]} = 10^{2.3}$$

or

$$\frac{[\mathrm{Cu^{2+}}]}{[\mathrm{CuOH^+}]} = 0.005.$$

Environmental reactions may involve not only chemicals dissolved in water but also chemicals in solid and gaseous forms. If a solid is part of a chemical reaction (i.e., if it is being formed or dissolved), its concentration is entered as one; if a gas is part of a reaction, its concentration is represented, by convention, as pressure, as discussed further in Section 1.8.1. Note that the letters (s) or (g) are often entered after a chemical formula to indicate solid or gas, respectively.

EXAMPLE 1-5

Limestone, $CaCO_3(s)$, is in equilibrium with water in which the carbonate ion, CO_3^{2-}, concentration is 10^{-5} *M*. What is the concentration of calcium ions, Ca^{2+}, in the water?

From Table 1-1, the relevant reaction and equilibrium constant can be obtained:

$$\frac{[\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}]}{[\mathrm{CaCO_3}]} = 10^{-8.3}$$

$$[\mathrm{Ca^{2+}}] = 10^{-8.3} \cdot \frac{[\mathrm{CaCO_3}]}{[\mathrm{CO_3{}^{2-}}]}$$

$$= 10^{-8.3} \cdot \frac{1}{10^{-5}}$$

$$[\mathrm{Ca^{2+}}] = 10^{-3.3}\ M.$$

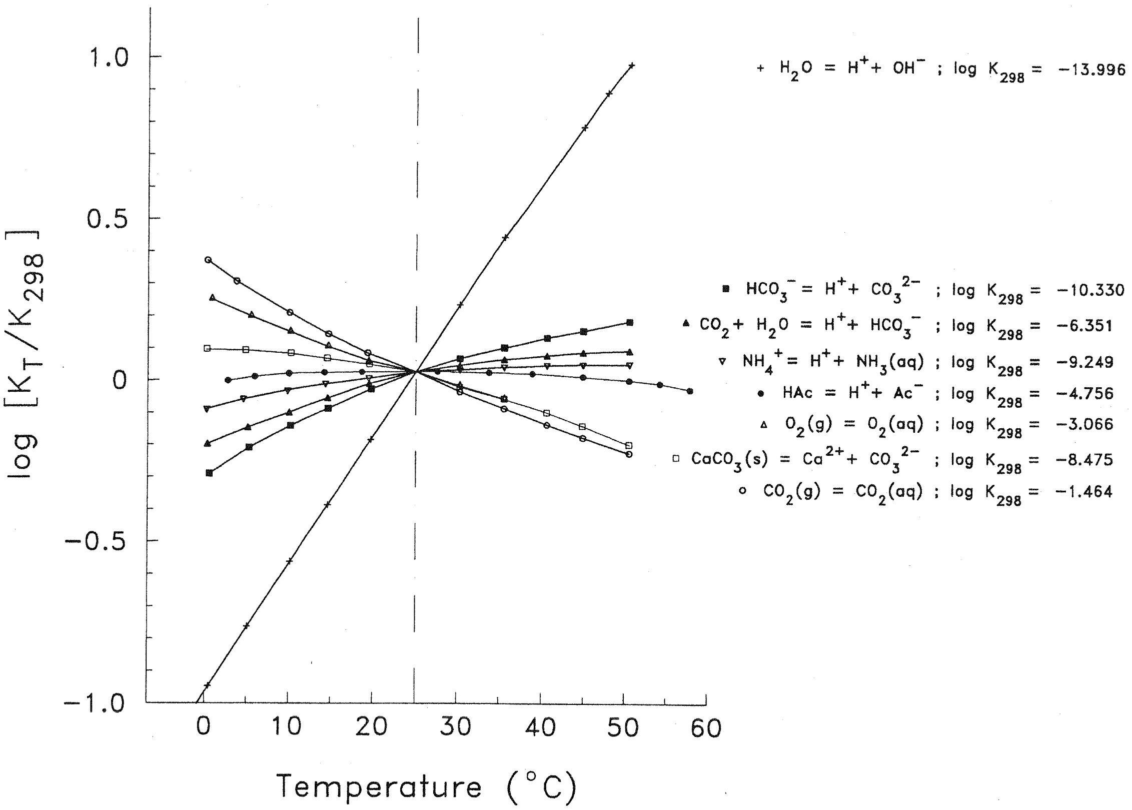


FIGURE 1-9 Temperature dependence of several common chemical reactions occurring in water. Although temperature may often be neglected in approximate calculations, for maximum accuracy, equilibrium constants must be corrected for the temperature of the chemical system of interest [adapted from *Principles and Applications of Aquatic Chemistry*, by F.M.M. Morel and J.G. Hering. Copyright © 1993, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.].

The equilibrium constant K varies somewhat with changes in environmental temperature and pressure, as indicated in Fig. 1-9 for several common environmental reactions. Equilibrium constants are known for a wide variety of reactions and form the basis (when combined with mass balance and electroneutrality equations as described later) for both manual and computerized techniques for determining the equilibrium composition of many complex mixtures of chemicals in surface waters and groundwater (Stumm and Morgan, 1996; Morel and Hering, 1993).

One of the most basic equilibrium reactions of environmental concern is the ionization of water (H_2O) to form hydrogen ions (H^+) and hydroxide ions (OH^-):

$$H_2O \rightleftharpoons H^+ + OH^-. \qquad [1\text{-}13]$$

As written, H_2O is a *reactant* and H^+ and OH^- are *products*. The equilibrium constant K for Eq. [1-13] can be written as

$$K = \frac{[H^+][OH^-]}{[H_2O]} = 1.8 \times 10^{-16} \text{ mol/liter.} \qquad [1\text{-}14]$$

It is conventional, however, to omit the concentration of water from mass action expressions and instead to absorb its value into a revised equilibrium constant. The concentration of water is 55.4 *M*; thus, Eq. [1-14] can be rewritten as

$$K_w = [H^+][OH^-] = 10^{-14} \text{ mol}^2/\text{liter}^2. \qquad [1\text{-}15]$$

This convention is valid for most environmental situations because the concentration of water is essentially constant at 55.4 *M*, negligibly affected by the mass of chemicals dissolved in it or by its self-ionization.

The acidity of a given water or chemical solution is determined by the concentration of hydrogen ions present. This concentration is usually expressed by the pH. For now, consider pH to be approximately equal to $-\log[H^+]$ (strictly speaking, pH is the negative $\log_{10}$ of the hydrogen ion *activity*, as described further in Section 1.6.5). The pH of most natural waters lies between 4 and 9, although both higher and lower values occur in some locations. Note that a pH of 7 means a water is neutral, because there are equal concentrations of hydrogen and hydroxide ions. Waters containing more hydrogen ions than hydroxide ions have a pH less than 7 and are *acidic;* waters containing fewer hydrogen than hydroxide ions are *basic* (or *alkaline*) with a pH greater than 7.

EXAMPLE 1-6

A barrel of hard cider is bought too early for a party. Bacteria in the barrel begin to convert the ethanol (C_2H_5OH) present (at approximately 6% by weight) to acetic acid (CH_3COOH) according to the following reaction:

$$O_2 + C_2H_5OH \longrightarrow CH_3COOH + H_2O.$$

By the time it is discovered that the hard cider is going bad, bacteria have converted approximately one-third of the ethanol. Assuming the pH is determined primarily by the acetic acid concentration, what is the pH of the cider at this time? The relevant reaction and equilibrium constant are

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-; \qquad K = 1.75 \times 10^{-5} \text{ mol/liter.}$$

First, estimate the molar concentration of ethanol that has been converted to acetic acid. If the density of cider is approximately that of water (1000 g/liter), the cider initially contains approximately 60 g/liter of ethanol. To convert one-third of that quantity, 20 g/liter, into a molar concentration, the molecular weight of ethanol needs to be calculated, using Table A-10 to obtain atomic weights:

$$2(12) + 6(1) + 1(16) = 46 \text{ g/mol}.$$

Therefore,

$$\frac{20 \text{ g}}{\text{liter}} \cdot \frac{1 \text{ mol}}{46 \text{ g}} = 0.43\ M.$$

Given that 1 mol of ethanol produces 1 mol of acetic acid, the cider will be a 0.43 *M* solution of acetic acid, once bacteria have converted one-third of the ethanol.

Second, estimate the pH due to the presence of acetic acid. The relevant mass action expression is

$$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.75 \times 10^{-5} \text{ mol/liter}.$$

Now make two simplifying assumptions: (1) all H^+ ions come from acetic acid, so $[H^+] = [CH_3COO^-]$ and (2) only a small amount of acetic acid actually reacts to form H^+. The first assumption is justifiable because the contribution of $[H^+]$ or $[OH^-]$ from the ionization of water is usually neglible when significant quantities (10^{-5} *M* or more) of acids or bases are added to water. The second assumption will be checked after $[CH_3COOH]$ is approximated by its initial concentration:

$$\frac{[H^+][H^+]}{0.43\ M} = 1.75 \times 10^{-5} \text{ mol/liter}$$

$$[H^+] = 2.8 \times 10^{-3}\ M$$

$$\text{pH} \approx -\log(2.8 \times 10^{-3}) = 2.6.$$

The concentration of H^+ is consistent with the second assumption; less than 1% of the acetic acid reacts to form H^+ and CH_3COO^-.

1.6.4 ELECTRONEUTRALITY

The principle of *electroneutrality* in aqueous chemical systems states that the sum of the concentrations of all positively charged ions (expressed in equivalents) equals the sum of the concentrations of all negatively charged ions, so that the overall charge of the solution is zero. (If this were not true, we would be constantly bombarded with electrical shocks!) When an equation based on the principle of electroneutrality is combined with equations provided by *conservation of mass,* and by the *mass action law,* Eq. [1-12], the equilibrium chemical composition of a system can be calculated.

EXAMPLE 1-7

A water sample is taken from a stream in Nevada receiving acid mine drainage. The stream passes through an area containing gypsum, $CaSO_4$. Laboratory analysis shows that the pH of the water is 4, the total concentration of sulfate (SO_4^{2-}) is 6×10^{-3} *M*, and the total concentration of chloride (Cl^-) is 3×10^{-4} *M*. (a) Assuming that the only other ionic species present is calcium (Ca^{2+}), what is the calcium concentration in the water? (b) Will the precipitation reaction,

$$Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_4(s); \qquad K = 10^{4.62},$$

occur further downstream (i.e., will a solid form)?

(a) The electroneutrality equation for this water is

$$2[Ca^{2+}] + [H^+] = 2[SO_4^{2-}] + [OH^-] + [Cl^-]$$

$$2[Ca^{2+}] = -10^{-4} + 2(6 \times 10^{-3}) + 10^{-10} + (3 \times 10^{-4})$$

$$[Ca^{2+}] = 6.1 \times 10^{-3}\ M.$$

(b) From mass action:

$$\frac{[CaSO_4]}{[Ca^{2+}][SO_4^{2-}]} = \frac{1}{(6.1 \times 10^{-3})(6 \times 10^{-3})} = 10^{4.4}.$$

Because the reaction quotient $10^{4.4}$ is less than the equilibrium constant $10^{4.62}$, the reaction will proceed to the right and a solid should form; the extent to which a solid actually forms may be limited by kinetic considerations.

1.6.5 ACTIVITY

Although the mass action equation, Eq. [1-12], is written in terms of *concentration,* in fact the quantities in the brackets should be *activities,* which may be thought of as "corrected" concentrations that take into account nonideal effects in aqueous systems. These nonideal effects arise from electrostatic forces between ions dissolved in the water, and they increase as the total concentration of dissolved ions, measured as *ionic strength,* increases,

$$I = \tfrac{1}{2} \sum (z_i)^2 S_i, \qquad [1\text{-}16]$$

where I is the ionic strength (mol/liter), z_i is the charge number on each ion, and S_i is the concentration of each ion (mol/liter).

Depending on the ionic strength, an activity for each ion can be calculated to account for nonideal effects,

def'n

$$\{x_i\} = \gamma_i [x_i], \qquad [1\text{-}17]$$

where $\{x_i\}$ is the activity of an ion (mol/liter), γ_i is the activity coefficient, and $[x_i]$ is the concentration of the ion in the water (mol/liter).

Table 1-2 provides the negative $\log_{10}$ of activity coefficients for varying ionic strengths and ion charges. At low ionic strength, less than about 0.001 *M*, γ becomes very close to one. For ions in natural waters, γ is generally less than or equal to one, and for approximate calculations in many fresh waters, ionic strength effects may be neglected. In saline waters, such as ocean water, activity coefficients usually need to be used. For dissolved gases, γ tends to be greater than one.

TABLE 1-2 $-\text{Log}_{10}$ of Activity Coefficients for Specific Charge Numbers and Ionic Strengths[a] Cu^{2+}

3+

Charges

z[b] I[c] (M)	1	2	3	4
	Ionic Strengths			
0.1	0.11	0.44	0.99	1.76
0.3	0.13	0.52	1.17	2.08
0.5	0.15	0.60	1.35	2.40
1.0	0.14	0.56	1.26	2.24
2.0	0.11	0.44	0.99	1.76
3.0	0.07	0.28	0.63	1.12

.25

.5

[a] Morel and Hering (1993).

[b] z, charge number on ion.

[c] I, ionic strength.

Interpolation

.3 - .1 = .2 ; .2(.75) = .15 ; .1 + .15 = .25

EXAMPLE 1-8

A water sample with a pH of 8 is found to contain 10^{-1} *M* chloride (Cl^-), 2×10^{-1} *M* sodium (Na^+), and 5×10^{-2} *M* sulfate (SO_4^{2-}). The cupric ion Cu^{2+} is detected at 10^{-7} *M*. If the behavior of copper in the water is of interest, what copper activity should be used in equilibrium expressions involving copper and other chemical species?

The ionic strength of the solution is

$$I = \tfrac{1}{2}\Big[(-1)^2[Cl^-] + (1)^2[Na^+] + (-2)^2[SO_4^{2-}] + (2)^2[Cu^{2+}] + (1)^2[H^+] + (-1)^2[OH^-]\Big]$$

$$I = \tfrac{1}{2}\Big[(-1)^2(10^{-1}\,M) + (1)^2(2 \times 10^{-1}\,M) + (-2)^2(5 \times 10^{-2}\,M) + (2)^2(10^{-7}\,M) + (1)^2(10^{-8}\,M) + (-1)^2(10^{-6}\,M)\Big]$$

$$I \approx 0.25\,M.$$

By using Table 1-2, the negative $\log_{10}$ of the activity coefficient for copper should be approximately 0.50 (interpolating between 0.44 and 0.52).

Therefore, the activity coefficient is 0.32, and the activity of copper is

$$\{Cu^{2+}\} = 0.32\,(10^{-7}\,M) = 3.2 \times 10^{-8}\,M.$$

Note that this is only a third of the activity that would exist in water of low ionic strength.

1.6.6 CHEMICAL KINETICS

Many environmental fate processes, such as the degradation of pollutant chemicals, are not usefully modeled as equilibrium chemistry problems because the *rate* of the reaction is more important to quantify than the final composition of the system. For example, even though it may be known that at equilibrium a certain chemical will be fully degraded, it is crucial to know whether degradation will take seconds, years, or perhaps centuries.

The rate at which a chemical reaction occurs may be limited by the frequency of collisions between the reacting atoms or molecules, as well as the likelihood that any particular collision will cause the reaction to proceed. Often several steps must occur in sequence to bring about a certain overall chemical process; the slowest is known as the *rate-limiting step*. Under other conditions, a molecule may react by itself without any collision to form another molecule. Under this condition, the number of molecules reacting in a time interval will simply be proportional to the number of molecules present. Then the rate at which the concentration of reacting molecules changes with time is described by *first-order kinetics,*

$$dC/dt = -k \cdot C, \qquad [1\text{-}18]$$

where C is the concentration of the *parent* compound [M/L^3], t is the time [T], and k is the rate constant [T^{-1}].

Such a chemical reaction, in which molecules are not colliding with other atoms or molecules, is called a *first-order reaction* because the rate at which chemical concentration changes at any instant in time is proportional to the concentration raised to the first power. Certain chemical processes, such as radioactive decay, are described by first-order kinetics. In the absence of any other sources of the chemical, first-order kinetics may lead to *exponential decay* or *first-order decay* of the chemical concentration (i.e., the concentration of the parent compound decreases exponentially with time):

$$C_t = C_0 e^{-kt}, \qquad [1\text{-}19]$$

where C_t is the concentration of the parent compound at some time t [M/L^3], C_0 is the initial concentration of the parent compound [M/L^3], k is the rate constant [T^{-1}], and t is the time [T].

Note that the integration of Eq. [1-18] leads to Eq. [1-19]. From Eq. [1-19] can be derived an expression, known as the *half-life* ($t_{1/2}$), which represents the amount of time it takes for the parent compound to decay to half its initial concentration:

$$\begin{aligned} \frac{C_t}{C_0} &= 0.5 = e^{-kt_{1/2}} \\ \ln(0.5) &= -kt_{1/2} \qquad [1\text{-}20] \\ t_{1/2} &= \frac{0.693}{k}. \end{aligned}$$

Note that half-lives convey exactly the same information as first-order decay rate constants, but may be more intuitive to some users. Half-lives for different decay processes may be easily compared to determine which decay mechanism is the most significant; they may also be compared with a transport time to determine whether a high or low chemical concentration will remain at a point downstream or downwind of a chemical source.

EXAMPLE 1-9

A sealed radioactive source used for physics demonstrations in 1940 contained 10 microcuries (μCi) of ^{60}Co (cobalt-60). Given a half-life of 1900 days for ^{60}Co, what would be the source strength in 1993?

The decay constant can be determined from the half-life using Eq. [1-20]:

$$k = \frac{0.693}{1900 \text{ days}} = 3.6 \times 10^{-4}/\text{day}.$$

Use Eq. [1-19] to calculate the concentration after 53 years:

$$C_t = 10e^{-(3.6\times10^{-4}/\text{day})(53 \text{ years})(365 \text{ days/year})}$$

$$C_t = 8.6 \times 10^{-3}\ \mu\text{Ci}.$$

Now consider the first type of reaction described in this section, in which more than one type of chemical molecule is involved. If two molecules A and B must collide to cause a reaction to occur, then the rates at which the concentrations of A and B decrease (in the absence of other sources) will be of the form:

$$dA/dt = -k \cdot A \cdot B \qquad [1\text{-}21a]$$

$$dB/dt = -k \cdot A \cdot B, \qquad [1\text{-}21b]$$

where A is the concentration of chemical A [M/L^3], B is the concentration of chemical B [M/L^3], k is the rate constant for the reaction [L^3/MT], and t is the time [T].

In this case, the rate at which a chemical disappears is proportional not only to its own concentration but also to the concentration of the other chemical with which it reacts. Increasing the concentration of either will increase the rate of reaction. Note that the units for the rate constant k are different from those used for the rate constant describing first-order kinetics in Eqs. [1-18] and [1-19]. Equations [1-21a] and [1-21b] are mathematically more complex than first-order kinetics. In some cases, however, the situation can be simplified because one of the chemicals involved in a reaction is approximately constant in concentration. For example, if a particular chemical is reacting with water, the concentration of water in an environmental water sample can be taken as nearly constant at 55.4 *M* (recall the treatment of water in Eqs. [1-13] through [1-15]). If a chemical is reacting with the hydrogen ion in a system where other chemical reactions keep the pH nearly constant, then the concentration of H^+ may be taken as constant. In such cases, it is convenient to multiply the rate constant k by the constant chemical concentration to obtain a new rate constant, k'. For example, if the concentration of chemical B is approximately constant, then the rate of reaction of chemical A could be described by

$$dA/dt = -k' \cdot A, \qquad [1\text{-}22]$$

where $k'[\mathrm{T}^{-1}]$ is the product of $k[\mathrm{L}^3/\mathrm{MT}]$ and $B[\mathrm{M/L}^3]$. As long as the concentration of one reacting chemical remains approximately constant, the simple mathematics of first-order kinetics—Eqs. [1-18] and [1-19]—can be used. This simplification is described as modeling the chemical reaction with *pseudo-first-order* kinetics.

Like equilibrium constants, rate constants also depend on environmental factors such as pressure and, especially, temperature. An increase in temperature usually gives rise to an increase in the chemical reaction rate, because molecules are moving faster and colliding more frequently with greater energy. If rate constants are known for two different temperatures, the rate constant for any other temperature can be calculated using the *Arrhenius rate law*,

$$k = A \cdot e^{-E_a/RT}, \qquad [1\text{-}23]$$

where k is the rate constant at a specific temperature, A is a constant (the *pre-exponential factor*), E_a is the Arrhenius activation energy, R is the universal gas constant, and T is the absolute temperature. When the rate constants for two different temperatures are available, the pre-exponential factor and Arrhenius activation energy can be estimated and then used to calculate the rate constant at a third temperature.

EXAMPLE 1-10

An ethylene *bis*-dithiocarbamate (EBDC) fungicide degrades in a storage tank to *N,N*-ethylene thiourea (ETU) at a rate of 0.046/day at 20°C; at 0°C, the reaction proceeds at a rate of 0.011/day. How fast will the reaction proceed at 15°C?

From Section 1.6.2, R is approximately 8.3 J/(mol · K). The two equations to be solved, based on the Arrhenius rate law in Eq. [1-23], are

$$0.046/\text{day} = A \cdot e^{-E_a/(8.3\ \text{J/mol}\cdot\text{K})(293\ \text{K})}$$

$$0.011/\text{day} = A \cdot e^{-E_a/(8.3\ \text{J/mol}\cdot\text{K})(273\ \text{K})}.$$

Solving for E_a,

$$E_a = 47.5\ \text{kJ/mol}.$$

Solving for A,

$$A = 0.046e^{(47{,}500)/(8.3)(293)} = 1.4 \times 10^7/\text{day}.$$

Therefore, at 15°C, the fungicide will degrade at a rate of

$$k = (1.4 \times 10^7/\text{day})(e^{-(47{,}500)/(8.3)(288)})$$

$$k = 0.033/\text{day}.$$

Note that rounding to an appropriate number of significant figures (two) is performed on the final result; for illustrative purposes, more figures are reported for the intermediate calculations. The next section discusses significant figures in greater detail.

END

CONTINUE
TO §2.4.1

1.7 ERROR IN MEASUREMENTS OF ENVIRONMENTAL QUANTITIES

The previous section discussed some of the basic concepts of environmental chemistry. Many of the chemical data required for the types of analyses presented in that section are based on experimental measurements made in the laboratory or the field. Any measurement of a chemical or physical quantity is always inaccurate to some degree because the exact, or *accurate,* value of a quantity can never be measured. The *error of observation* is the difference between the measured value of a quantity and the accurate value. Although the true value of the error of observation cannot be known, an estimate of the magnitude of the error is necessary to report meaningful uncertainty bounds for data. Uncertainty bounds allow a user to determine if the data are sufficiently accurate for a particular analysis. Sometimes the error of observation is negligible, but in other situations it is large enough to compromise an analysis or even render it completely meaningless.

Two types of errors of observation exist: systematic and random. The total error associated with a measurement is a function of the *systematic error,* commonly called *bias,* and the *random error.* Systematic errors in environmental measurements can be divided into three general categories: instrument errors (e.g., nonideal functioning of an instrument); interference from envi-

~~evaporates much faster from a slick (approximately 100 million times faster) than dissolved TCE volatilizes from a lake or river.~~

2.4 CHEMICAL AND BIOLOGICAL CHARACTERISTICS OF SURFACE WATERS

2.4.1 ACID–BASE CHEMISTRY

All natural waters contain dissolved chemicals, many present as inorganic *ions*. Common inorganic ions in natural waters are sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), ammonium (NH_4^+), sulfate (SO_4^{2-}), chloride (Cl^-), and nitrate (NO_3^-). Even pure water, containing no dissolved substances, ionizes to a certain extent to form hydrogen ions (H^+) and hydroxide ions (OH^-), as discussed in Section 1.6.3. The pH of most natural waters ranges from about 4 to 9; extreme environments, such as streams receiving acid mine drainage, may have a pH below 2, while some alkaline lakes may have a pH above 10.

pH often determines the suitability of a water body as a biological habitat or as a water supply, and also influences the chemical speciation of many dissolved compounds and the rates at which many pollutants degrade. As such, pH is often called a *master variable* in natural water chemistry, and the equilibrium of reactions that produce or consume H^+ is of special interest. *Acids* (such as the acetic acid of Example 1-6) ionize in water, producing H^+ and a negatively charged *anion*; *bases* produce OH^- and a positively charged *cation*. By definition, *strong acids* and *strong bases*, such as hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), and sodium hydroxide ($NaOH$), ionize completely in water under environmental conditions. Thus, if 1 mol of HNO_3 is put into water, 1 mol of H^+ and 1 mol of nitrate ion (NO_3^-) are formed. The contributions of H^+ from a mole of strong acid and OH^- from a mole of strong base cancel each other out; the H^+ and OH^- react to form H_2O. If strong acid is in excess of strong base, H^+ is formed in an amount equal to the difference. Thus, it is not necessary to use mass action expressions to determine how much H^+ or OH^- is produced in solution by a mixture of strong acids and bases; knowledge of the *difference* in their concentrations is sufficient. *Alkalinity* (Alk) is defined as the concentration of strong bases (C_B) minus the concentration of strong acids (C_A). Note that concentrations must be in equivalents per liter (Section 1.2):

$$\text{Alk} = C_B - C_A. \tag{2-41}$$

If the concentration of strong acids exceeds the concentration of strong bases, Alk is negative and in the absence of other bases is approximately equal to the negative of the H^+ concentration. For example, in a water containing only Alk of -10^{-4} equivalents per liter, $[H^+] = 10^{-4}\ M$. If Alk is positive, the concentration of OH^-, in the absence of other acids or bases, is approximately equal to Alk.

Inevitably, surface waters also contain dissolved carbon dioxide (CO_2), an acid that reacts in water to form three *carbonate system* species: $H_2CO_3^*$, HCO_3^-, and CO_3^{2-}. The predominant species in any given water depends on the pH of the water. In this book, the notation $H_2CO_3^*$ represents the sum of dissolved CO_2 and its reaction product with water, carbonic acid (H_2CO_3). $H_2CO_3^*$ is the dominant carbonate system species when the pH of a surface water is below approximately 6.3. $H_2CO_3^*$ ionizes to form bicarbonate ion (HCO_3^-), which is the most abundant of the three species when the pH is between approximately 6.3 and 10.3. Because the ionization of $H_2CO_3^*$ is incomplete over a large pH range, $H_2CO_3^*$ is called a *weak acid.* Bicarbonate is also a weak acid, which ionizes to form carbonate ion (CO_3^{2-}), the most abundant carbonate species above a pH of approximately 10.3. The relevant reaction equations and equilibrium constants are:

$$CO_2 + H_2O \rightleftarrows H_2CO_3^* \qquad (K_H = 10^{-1.5}\ \text{mol/(atm} \cdot \text{liter)}). \qquad [2\text{-}42]$$

$$H_2CO_3^* \rightleftarrows HCO_3^- + H^+ \qquad (K_{a1} \approx 10^{-6.3}\ \text{mol/liter}). \qquad [2\text{-}43]$$

$$HCO_3^- \leftrightarrows CO_3^{2-} + H^+ \qquad (K_{a2} \approx 10^{-10.3}\ \text{mol/liter}). \qquad [2\text{-}44]$$

EXAMPLE 2-9

A river has a pH of approximately 6. If the river water is in equilibrium with atmospheric carbon dioxide (which has a pressure, P_{CO_2}, of approximately $10^{-3.5}$ atm), what are the concentrations of carbonate system species in the water?

Because the river water is in equilibrium with atmospheric CO_2 and the pH is fixed by other acids and bases present in the water, Eq. [2-42] can be used to determine $[H_2CO_3^*]$:

$10^{-1.5}$

$$K_H = \frac{[H_2CO_3^*]}{P_{CO_2}} = \frac{10^{-1.5}\ \text{mol}}{\text{atm} \cdot \text{liter}}.$$

2.5

$5^{-1.5}$

Therefore,

$$[H_2CO_3^*] = 10^{-3.5}\ \text{atm} \cdot \frac{10^{-1.5}\ M}{\text{atm}}$$

$$= 10^{-5}\ M.$$

$[HCO_3^-]$ is then determined by using the mass action expression for the ionization of $[H_2CO_3^*]$ into $[H^+]$ and $[HCO_3^-]$, Eq. [2-43]:

$$K_{a1} = \frac{[HCO_3^-][H^+]}{[H_2CO_3^*]} = 10^{-6.3}.$$

$$[H^+] = \frac{Ka1[H_2CO_3]}{[HCO_3^-]}$$

Therefore,

$$[HCO_3^-] = \frac{(10^{-6.3})(10^{-5})}{10^{-6}} = 10^{-5.3}\ M.$$

By using Eq. [2-44],

$$K_{a2} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 10^{-10.3},$$

the carbonate ion concentration can be calculated as

$$[CO_3^{2-}] = \frac{ka_2[HCO_3^-]}{[H^+]}$$

$$[CO_3^{2-}] = \frac{(10^{-10.3})(10^{-5.3})}{(10^{-6})} = 10^{-9.6}\ M.$$

Recall that equilibrium constants are temperature dependent (see Section 1.6.3) and the values given previously are approximate. Although much of the CO_2 dissolved in surface waters originates from the atmosphere or from biological activity, some of it may also come from dissolution of underlying geologic formations, such as calcite, $CaCO_3$, and dolomite (Ca, Mg) · (CO_3).

Natural waters contain both carbonic acid and a mixture of strong acids and strong bases (i.e., alkalinity). Because weak acids such as $H_2CO_3^*$ and HCO_3^- ionize to a variable extent, calculation of the pH of such a mixture requires that mass conservation equations, the electroneutrality condition, and mass action equations for all weak acids be solved simultaneously.

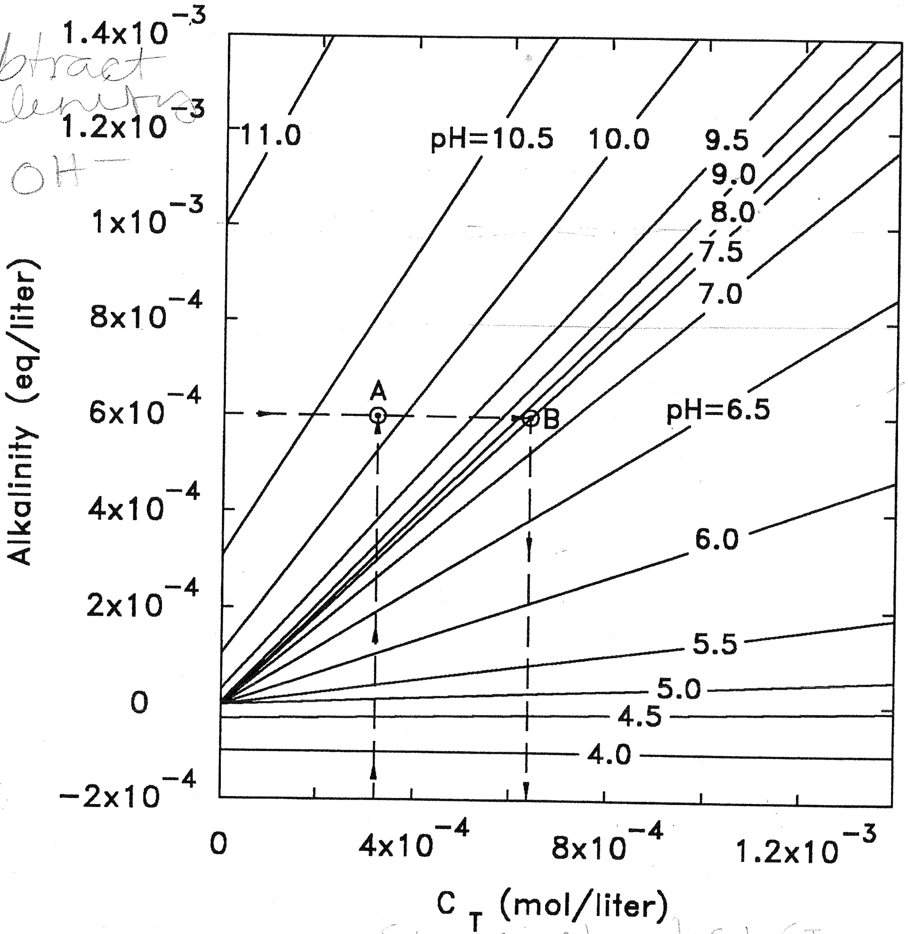
As an alternative to algebraic manipulation of these equations, graphic solutions, such as shown in Fig. 2-15, have been developed for determining the pH of water as a function of Alk and C_T, where C_T is the sum of the concentration of carbonic acid and the concentrations of the two anions produced when it ionizes (i.e., HCO_3^- and CO_3^{2-}).

Such a graph, also known as a *Deffeyes diagram*, may be derived from the electroneutrality equation, written with Alk in place of the difference between

$$C_T = HCO_3^- + CO_3^{2-} + H_2CO_3^*$$

$[H^+] = -Alk + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$

Add/Subtract alkalinity OH^-



Add/Sub CO_2

Expensive to test C_T

FIGURE 2-15 An alkalinity (Alk)–carbonate system plot, also called a *Deffeyes diagram*. In this figure, the relationship among Alk, C_T (the sum of all carbonate system species concentrations: $[H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$), and pH is shown. If any two of these quantities are known, the third may be immediately determined from the plot. For example, for a water in which Alk is 6×10^{-4} eq/liter, and C_T is 3.2×10^{-4} M, the pH is 10.2 (point A). If C_T is 6.4×10^{-4} M, the pH is 7.5 (point B) (see Example 2-10).

the strong base cation concentrations and the strong acid anion concentrations:

$$Alk + [H^+] - [OH^-] - [HCO_3^-] - 2[CO_3^{2-}] = 0 \qquad [2\text{-}45]$$

Eq. [2-45] may be rewritten as

$$Alk = \{-[H^+] + [OH^-]\} + \{[HCO_3^-] + 2[CO_3^{2-}]\} \qquad [2\text{-}46]$$

At any given pH, the first term on the right-hand side of Eq. [2-46] is a known constant (c_1), while the second term is equal to C_T multiplied by a second constant (c_2). Thus, the relationship between C_T and Alk at a given

Rain + $CaCO_3$ base carbonic acid

pH may be written as

$$\text{Alk} = c_1 + c_2 \cdot C_T \qquad [2\text{-}47]$$

The Deffeyes diagram of Fig. 2-15 is a family of such straight-line relationships, plotted for each of several pH values. Note that very similar graphs can be drawn in which P_{CO_2} is used in place of C_T; in this case, the carbonate species concentrations in the electroneutrality equation are equal to P_{CO_2} multiplied by a constant which is a function of pH.

The effects of additions of Alk or C_T to a water are easy to determine graphically using a Deffeyes diagram, as shown below in Example 2-10. For further detail on the acid–base chemistry of natural waters, the reader is referred to Stumm and Morgan (1996) or Morel and Hering (1993).

EXAMPLE 2-10

A lake water has an alkalinity of 6×10^{-4} eq/liter. In the early morning, a monitoring team measures the lake pH as part of an acid rain study and finds the pH to be 7.5.

(a) What is C_T in the lake water at this time?
(b) The survey team returns after lunch to recheck their data. By this time, algae and green plants have depleted the C_T of the lake to half of its morning value. What pH does the team find now?

The solution is based on the Alk–C_T graph (Deffeyes diagram) of Fig. 2-15.

In the early morning, C_T is found to be 6.4×10^{-4} M from the graph. [Follow the horizontal line from 6×10^{-4} on the Alk axis until it intersects pH 7.5 (point B); then follow the vertical line to the C_T axis.]

After lunch, C_T is approximately 3.2×10^{-4} M. Follow the vertical line up from the C_T axis until it intersects the horizontal line corresponding to the essentially unchanged Alk of 6×10^{-4} eq/liter (point A); the new pH is 10.2.

In addition to inorganic ions, surface waters contain *dissolved organic carbon* (DOC). A large fraction of DOC is made up of *humic* and *fulvic* acids, complex yellow-brown mixtures of organic chemicals originating primarily from decaying plant material. DOC also includes organic compounds leached or exuded from living organisms or released during cell *lysis* (rupture). DOC is measured as the total concentration of organically bound carbon, and ranges from less than 1 mg/liter to several tens of milligrams per liter in

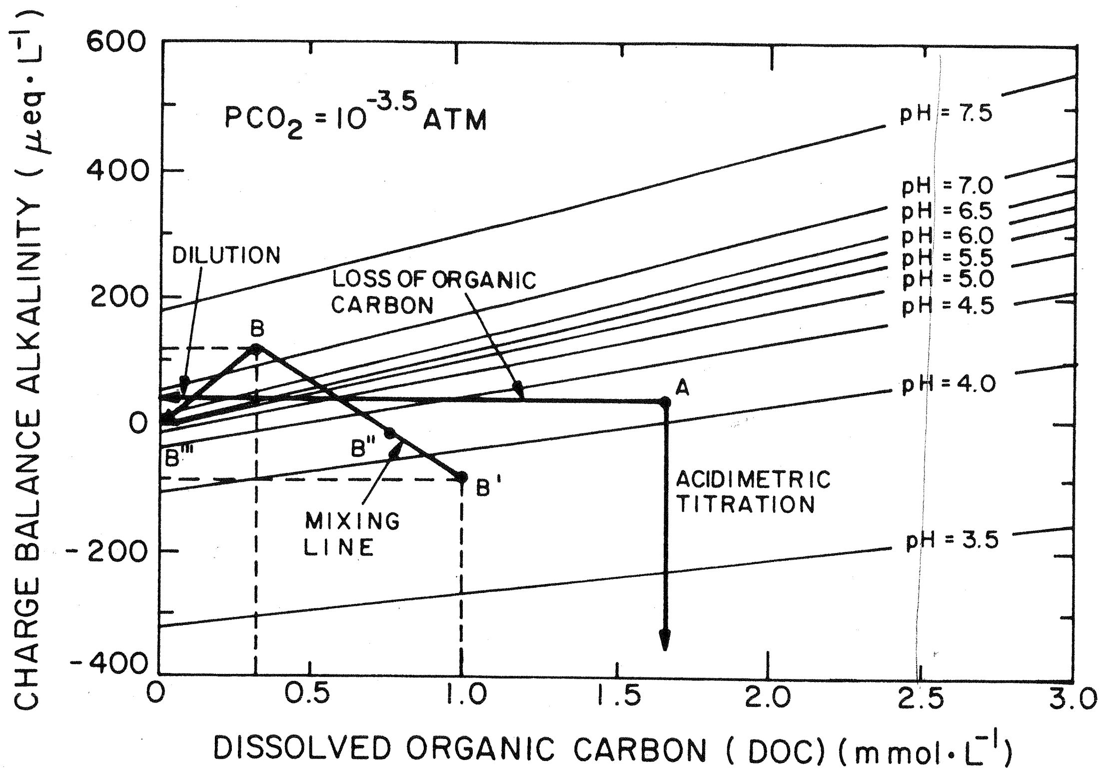


FIGURE 2-16 Plot of alkalinity (Alk) versus organic acid concentration over a range of pH values. This graph is analogous to the Deffeyes diagram of Fig. 2-15. Point A indicates that water having a DOC concentration of 1.7 mmol/liter (20 mg/liter) and an Alk of approximately 40 µeq/liter will have a pH of 4.2. Changes in pH resulting from decreasing Alk (as when adding strong acid) are shown along the vertical line pointing downward from point A, while the horizontal line extending to the left from the point shows the pH increase resulting from a decrease in DOC. The pH of a mix of two waters having compositions given by points B and B′ can be found along line BB′. If water of composition B is mixed with pure water (i.e., water with zero Alk and zero DOC), the resultant composition lies along the dilution line from B to the graph's origin. Note that this plot applies to a P_{CO_2} of $10^{-3.5}$ atm and an organic acid that ionizes according to one particular empirical model. Further details are given in Hemond (1990).

natural waters. *Dissolved organic material* (DOM) is sometimes measured and reported; DOC is about half of DOM, because organic carbon constitutes about half of most organic material in soils and sediments [58%; Lyman *et al.* (1990)]. DOC is significant as a source of organic carbon to bacteria, as an absorber of light and participant in photochemical reactions, as a natural acid, and as a *complexing agent* that binds with metal ions to form metal–organic *complexes*.

As their name implies, humic and fulvic acids have a significant impact on the pH of natural waters. The graphic approach described earlier for determining the pH of water as a function of Alk and C_T has been extended to include DOC effects, as shown in Fig. 2-16. The defining equation is again electroneutrality, with the inclusion of a term for organic acid anions. The full graphic relationship among pH, C_T (or P_{CO_2}), Alk, and DOC concentration must be represented as surfaces of constant pH in a three-dimensional graph whose axes are Alk, C_T (or P_{CO_2}), and DOC [Hemond, (1990)]. Fig. 2-16 is a slice of such a graph for water in equilibrium with the P_{CO_2} of the atmosphere.

END

2.4.2 AQUATIC ECOSYSTEMS

Surface waters are more than just physical entities; most surface waters teem with an incredible variety of living organisms. To better understand the behavior of pollutants in these waters, it is essential to understand the nature of the biota and their relationships to the physical and chemical processes occurring in the water bodies. To do this, surface waters must be considered as *ecosystems.* An ecosystem comprises a physical environment and the populations of organisms such as plants, animals, and bacteria (the biological community) that inhabit it. Biological communities and their physical environments interact in ways that are exceedingly complex; however, the fundamental principles driving ecosystems can be described in fairly general terms. Understanding the nature and functioning of aquatic ecosystems is crucial for two reasons: to understand chemical fate and transport, because biota transport and transform a great number of chemicals in the environment; and to recognize potential detrimental effects from pollutant chemicals on aquatic organisms themselves.

This section describes only the most general attributes of aquatic ecosystems. All ecosystems can be functionally characterized in terms of their *processing of energy* and their *cycling of mass* (e.g., carbon and nutrients). These functions, as well as the "life history" aspects of ecosystems, are discussed in the following subsections. [For a more complete discussion of ecosystems, the reader is referred to several texts, such as Odum (1971), Ricklefs (1990), or Curtis (1983)].

Energy Flow

All biota require energy to maintain themselves, to grow and reproduce, and to perform other activities. Therefore, there must be a constant flow of energy through an ecosystem. Sunlight is the source of this energy in nearly all ecosystems. Organisms use the light energy of the sun in the process of *photosynthesis* to form organic material from carbon dioxide and water; oxygen is released as a product. In a surface water ecosystem, organic material such as fallen leaves and insects can also be imported from other ecosystems; such *allochthonous* organic matter augments *autochthonous* organic matter, which is formed within the surface water ecosystem. In the presence of