EXAMPLE 2-5

Sediment from a 10-cm depth in the bottom sediment of a lake has a ^{210}Pb activity of 2.5 disintegrations per minute (DPM). Sediment collected at the sediment–water interface has an activity of 4 DPM per gram. Assuming constant ^{210}Pb and sediment deposition rates, no sediment compression as the sediment ages, and no mixing or losses in the sediments, how rapidly does sediment accumulate in this lake?

Equation [2-26], the basic equation for radioactive decay, can be used:

$$t = \frac{-1}{0.03/\text{year}} \ln\left(\frac{2.5\ \text{DPM}}{4\ \text{DPM}}\right)$$

$$= 16\ \text{year}.$$

The sediment accumulation rate can then be estimated as

$$\frac{10\ \text{cm}}{16\ \text{year}} = 0.6\ \text{cm/year}.$$

2.3 AIR–WATER EXCHANGE

Thus far, the discussion of chemical removal from the water column has focused on incorporation of chemicals sorbed to particles into bottom sediment. However, chemicals dissolved in surface waters may also leave the water column and enter the atmosphere as gases or vapors. Conversely, chemicals present in the atmosphere may dissolve into a lake, river, or estuary. For volatile chemicals, which include most common industrial solvents and liquid fuels, the process of water-to-air exchange can be the most important mechanism of chemical removal from a surface water.

The concentration of a dissolved gas or vapor in a surface water *at equilibrium* with the atmosphere (C_{equil}) is determined by C_a, the concentration in air, and the Henry's law constant (H) of the chemical:

$$C_{\text{equil}} = C_a/H. \qquad [2\text{-}27]$$

If the concentration in water (C_w) is higher than C_{equil}, the chemical will volatilize from the water body into the atmosphere. The flux density is proportional to the product of the difference between the actual (C_w) and the equilibrium (C_{equil}) concentrations in the water:

$$J = -k_w(C_w - C_a/H), \qquad [2\text{-}28]$$

where J is the flux density [M/L^2T], k_w is the *gas exchange coefficient* [L/T], C_w is the chemical concentration in the water [M/L^3], C_a is the chemical concentration in the air [M/L^3], and H is the Henry's law constant (dimensionless). This gas exchange coefficient is sometimes called a *piston velocity* because in the special case where C_a is equal to zero in Eq. [2-28], the flux density J is equal to the flux that would result if a hypothetical piston were to move vertically through the water at speed k_w pushing the dissolved gas across the air–water interface. The magnitude of the piston velocity depends on the nature of the water flow and the air movement above the water. The flux density J is positive as defined in Eq. [2-28] if the flux is into the water. Note that C_a is an important term if the gas under consideration is a component of the atmosphere [e.g., nitrogen (N_2), oxygen (O_2), or carbon dioxide (CO_2)], but C_a is often essentially zero in the case of anthropogenic chemicals.

The most accurate determination of the gas exchange coefficient requires that careful field experiments be conducted. Although techniques for estimating k_w from measurable hydraulic attributes of a water body also exist, they are less accurate due to the state of incomplete understanding of the air–water gas exchange process and the fact that multiple factors may control the exchange rate for any particular chemical (Fig. 2-13). Two different models

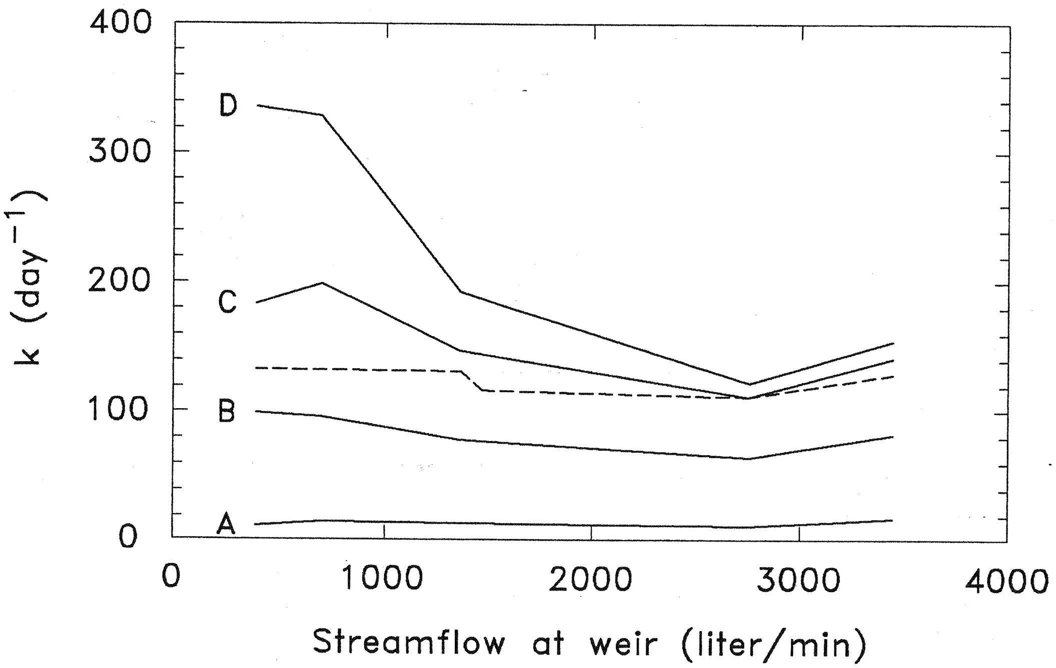

FIGURE 2-13 Air–water reaeration coefficients for oxygen in a reach of Walker Branch, a stream in Oak Ridge, Tennessee. Measured coefficients (dashed line) and calculated coefficients from several published predictive equations (solid lines) are shown. Until better predictive relationships are developed, highly accurate estimates of gas exchange appear to require experimental determination (data from Genereux and Hemond, 1992).

of the exchange process are currently in use: the *thin film model* and the *surface renewal model.* Each attempts to explain and predict the gas exchange coefficient on the basis of a different physical conceptualization of the microscale processes occurring at the air–water interface.

2.3.1 THIN FILM MODEL

The thin film (or *stagnant layer*) model is based on the assumption that a dissolved chemical has a uniform concentration throughout a surface water body, due to turbulent diffusion, except in a very thin layer at the water's surface. A similar assumption is made concerning the chemical concentration in overlying air. Within a few micrometers or millimeters of the water–air interface, it is assumed that the eddies responsible for turbulent diffusion are suppressed; therefore, chemical transport in this thin layer (or film) can only occur by molecular diffusion, which is considered to be the rate-limiting step of air–water exchange (Fig. 2-14) (Liss and Slater, 1974).

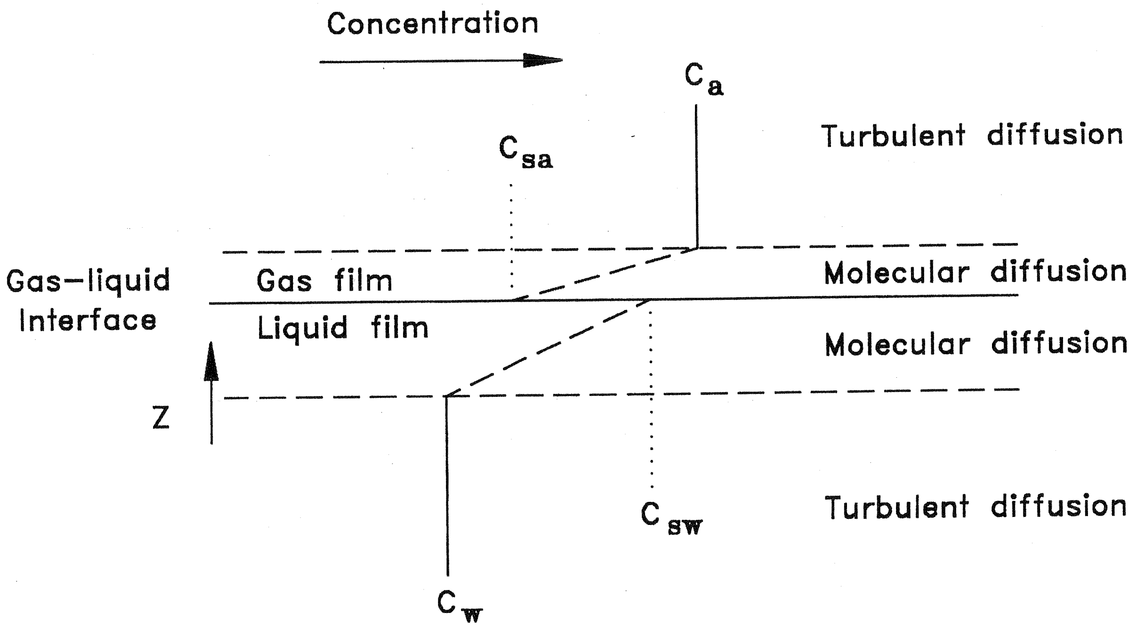

FIGURE 2-14 Schematic of the thin film model. All the resistance to gas exchange is assumed to lie in a thin stagnant (nonturbulent) layer of water and a similar stagnant layer of air. Within these films, transport occurs from higher to lower concentrations by molecular diffusion, governed by Fick's first law. Outside the films, in "bulk" air or water, Fickian transport coefficients are assumed to be much larger, due to turbulent diffusion; therefore, concentration gradients are negligible.

Water-Side Control

If the dimensionless Henry's law constant for a chemical, H, is much greater than 0.01—as is the case for a large number of solvents, fuels, and gases—resistance to gas exchange in the stagnant air layer immediately above the water can be neglected. The thin film model then describes the flux of a chemical into or out of the water by

$$J = -D_w(C_w - C_a/H)/\delta_w, \qquad [2\text{-}29]$$

where J is the flux density of the chemical [M/L^{2}T], D_w is the molecular diffusion coefficient for that chemical in water [L^2/T], C_w is the chemical concentration in the water [M/L^3], C_a is the chemical concentration in the air [M/L^3], H is the Henry's law constant (dimensionless), and δ_w is the thickness of the hypothetical thin boundary layer of water [L].

Under this theory, for water-side control, the gas exchange coefficient, k_w, is equal to the quotient D_w/δ_w. If the atmospheric concentration of a chemical is essentially zero, Eq. [2-29] simplifies to

$$J = \left(\frac{-D_w}{\delta_w}\right) C_w = -k_w C_w. \qquad [2\text{-}30]$$

It should be noted that film thickness cannot be measured directly; k_w, however, can be estimated, and δ_w can then be estimated from k_w and an independent knowledge of D_w. Typical values of δ_w are in the range of 20 to 200 μm.

Air-Side Control

If the dimensionless Henry's law constant for a chemical is much less than 0.01 [typically the case for polycyclic aromatic hydrocarbons (PAHs) and many pesticides], molecular diffusion through the stagnant boundary layer of air above the water surface becomes the most significant barrier to air–water gas exchange. In this situation the resistance due to the stagnant water film is considered to be negligible; thus, the concentration of chemical in the air at the water–air interface is given by the product $(C_w \cdot H)$. The flux density through the stagnant air film is then,

$$J = -(D_a/\delta_a) \cdot (C_w \cdot H - C_a)$$

or [2-31]

$$J = -(D_a \cdot H/\delta_a) \cdot (C_w - C_a/H),$$

where D_a is the molecular diffusion coefficient for the chemical in air [L^2/T] and δ_a is the thickness of the hypothetical stagnant air layer [L]. The quotient

D_a/δ_a may be considered to be an air-side gas exchange coefficient, k_a. Typical values of δ_a are on the order of 1 cm.

The General Situation

In the most general case, which must be invoked when the value of the dimensionless Henry's law constant is on the order of 0.01, both resistances contribute to limiting the gas exchange rate. In this case, the complete expression for flux density must be used:

$$J = -\left[\frac{1}{\delta_w/D_w + \delta_a/(D_a \cdot H)}\right]\left[C_w - \frac{C_a}{H}\right]. \qquad [2\text{-}32]$$

This equation is derived by setting the flux through the thin film in water, Eq. [2-29], equal to the flux through the stagnant air layer, Eq. [2-31]; the fluxes must be equal at steady state due to mass conservation.

Equation [2-32] reduces to Eq. [2-29] when δ_w/D_w is much greater than δ_a/D_aH, and to Eq. [2-31] when it is much less. Note that the molecular diffusion coefficient for molecules in air (D_a) is approximately 10^4 times greater than the corresponding molecular diffusion coefficient in water (D_w), whereas the air film thickness, δ_a, is generally much less than 10^4 times the water film thickness, δ_w.

Estimation of Gas Exchange Coefficients

A reasonably accurate gas exchange coefficient for a given chemical can be determined by introducing a tracer gas into the surface water body of interest and by observing the rate of loss of the tracer. In practice, such a tracer experiment is more feasible in a stream or river than in a lake or estuary. According to thin film theory, the ratio of the gas exchange coefficients of two volatile chemicals is equal to the ratio of their molecular diffusion coefficients in water; the ratio of molecular diffusion coefficients of two chemicals in turn is approximately equal to the inverse of the ratio of the square roots of their molecular weights. Thus, the measured gas exchange coefficient of a tracer gas (A) can be used to predict the gas exchange coefficient of another chemical (B):

$$\frac{k_A}{k_B} = \frac{D_A}{D_B} \approx \frac{\sqrt{\mathrm{MW}_B}}{\sqrt{\mathrm{MW}_A}}. \qquad [2\text{-}33]$$

In practice, a nontoxic, inexpensive, and easily measured substance such as propane (C_3H_8) is a convenient tracer; its measured gas exchange coeffi-

TABLE 2-5 **Empirical Equations for Gas Exchange in Surface Waters**

Equation	Reference	Line in Fig. 2-13
$K_{O_2} = 1.92 \cdot \left(\frac{V}{d}\right)^{0.85}$	Negelescu and Rojanski, 1969	A
$K_{O_2} = \frac{24.94 \cdot (1 + \sqrt{N}) \cdot u^*}{d}$	Thackston and Krenkel, 1969	B
$K_{O_2} = \frac{23.2\ V^{0.73}}{d^{1.75}}$	Owens *et al.*, 1964	C
$K_{O_2} = \frac{106\ V^{0.413} w^{0.273}}{d^{1.408}}$	Bennett and Rathbun, 1972	D

cient can be used to estimate gas exchange coefficients for many other volatile chemicals dissolved in a given surface water.

In the absence of tracer data, estimates of gas exchange coefficients in streams can be made from a number of empirical equations, which typically depend on a combination of the stream mean velocity and depth (V and d, respectively). Some equations contain other parameters, such as shear velocity, width, and *Froude number* (u^*, w, and N, respectively) of the stream. The Froude number is equal to ($V/\sqrt{gd}$), and is the ratio of stream velocity to the travel speed of a shallow-water surface wave. By convention, the empirical equations given for streams are usually for a *reaeration coefficient,* which is the gas exchange coefficient for oxygen divided by the average stream depth. Examples of empirical equations for reaeration coefficients are shown in Table 2-5.

Note that none of the equations in Table 2-5 include wind speed, because it is assumed that the turbulence generated within the stream due to velocity shear and turbulent diffusion primarily controls gas exchange. Unfortunately, the predictions of these equations are often not in good agreement with one another, and it is difficult to know which one is best in a given situation (see Fig. 2-13).

Gas exchange coefficients can also be estimated for lakes and estuaries using a variety of empirical equations, although the calculated values may differ from measured values by a factor of two or three in any given water body. Consistent with the assumption that turbulence is primarily driven by wind in such slowly flowing waters, the expressions typically have gas exchange coefficients as a function of wind speed. In the case of water-side control for slowly flowing waters, Schwarzenbach *et al.* (1993) suggest approximating k_w by

$$k_w(\text{cm/sec}) \approx 4 \times 10^{-4} + 4 \times 10^{-5} \cdot u_{10}^2, \qquad [2\text{-}34]$$

where u_{10} is the wind speed (in m/sec) measured 10 m above the water surface. Typical values of k_w range from 1 to 10 cm/hr. Note that Eq. [2-34] estimates k_w in units of cm/sec.

In the case of air-side control, Schwarzenbach *et al.* (1993) suggest approximating k_a by

$$k_a(\text{cm/sec}) \approx 0.3 + 0.2 \cdot u_{10}(\text{m/sec}). \qquad [2\text{-}35]$$

An even simpler formula for estimating k_a, which estimates k_a in units of centimeters per hour, is

$$k_a(\text{cm/hr}) \approx 1100 \cdot u(\text{m/sec}). \qquad [2\text{-}36]$$

There are other empirical equations relating gas exchange to wind speed, such as those given by O'Connor (1983) and Yu and Hamrick (1984).

EXAMPLE 2-6

The dissolved concentration of trichloroethylene (TCE, C_2Cl_3H) in a lake is 1 ppb. Given a dimensionless Henry's law constant, H, of 0.4, and a measured gas exchange coefficient of 3×10^{-3} cm/sec in water, for propane (C_3H_8), what is the flux density of TCE from the lake?

First, estimate the molecular weights of TCE and propane:

MW TCE:	131 g/mol
MW propane:	44 g/mol.

Assume C_a is essentially zero. Diffusion through air is not a bottleneck due to the fairly high H. D_w for TCE is approximately equal to D_w for propane multiplied by the inverse of the ratio of the square roots of the molecular weights, Eq. [2-33]:

$$\frac{D_{\text{TCE}}}{\delta_w} = 3 \times 10^{-3}\ \text{cm/sec} \cdot \frac{\sqrt{44}}{\sqrt{131}} = 1.7 \times 10^{-3}\ \text{cm/sec}.$$

Then use Eq. [2-30]:

$$J_{\text{TCE}} = (1.7 \times 10^{-3}\ \text{cm/sec}) \left(\frac{1\ \mu\text{g}}{\text{liter}}\right)\left(\frac{1\ \text{liter}}{1000\ \text{cm}^3}\right) = 1.7 \times 10^{-6}\ \frac{\mu\text{g}}{\text{cm}^2 \cdot \text{sec}}.$$

2.3.2 SURFACE RENEWAL MODEL

An alternative model of air–water gas exchange assumes that turbulent eddies in the water periodically bring small parcels of water to the surface, where they begin to equilibrate with the atmosphere. In this model, the average amount of time each water parcel spends at the surface determines the overall gas exchange rate. If parcels on average spend a long time at the surface, they may equilibrate with the atmosphere; after equilibrium is reached, no further chemical flux to the air occurs until the depleted parcel is replaced. If fresh parcels are more frequently brought to the surface, the average chemical flux across the interface is larger.

The surface renewal model, like the thin film model, yields a piston, or gas exchange, velocity that can be used to calculate chemical fluxes as previously described. In contrast with the thin film model, however, the surface renewal model predicts that the ratio of piston velocities for two different volatile chemicals depends on the *square root* of the ratio of their molecular diffusion coefficients (and thus approximately the *fourth root* of the inverse ratio of their molecular weights). Schwarzenbach *et al.* (1993) discuss molecular diffusion coefficients in more detail.

An explicit choice of an air–water exchange model must be made if gas exchange coefficients determined for one chemical (usually from a tracer experiment) are to be used to estimate gas exchange coefficients for another chemical. The existing literature is not adequate to make the choice of a model clear-cut. Commonly, the thin film model is considered to be more appropriate for relatively quiescent water bodies, such as lakes, while a surface renewal model is considered more appropriate for more highly turbulent surface waters, such as rivers. Usually, unavoidable experimental error, even in carefully conducted tracer experiments, prevents unequivocal endorsement of one model over the other. Often, field data on the gas exchange coefficients of two different chemicals are most consistent with a ratio of the chemical diffusion coefficients raised to some power between 0.5 and 1.0, suggesting that the actual mechanism of gas exchange contains some elements of each process and is more complex than either idealized model suggests (Genereux and Hemond, 1992).

EXAMPLE 2-7

Trichloroethylene has been spilled in a *river* so that the dissolved concentration is 1 ppb. Given a dimensionless Henry's law constant, H, of 0.4, and a piston velocity of 3×10^{-3} cm/sec in water for propane, what will be the flux density of TCE from the river?

MW TCE	131 g/mol
MW propane	44 g/mol.

Assuming C_a is essentially zero, diffusion through air is not a bottleneck due to the fairly high H, and D_w for TCE is approximately equal to D_w for propane multiplied by the square root of the inverse of the ratio of the square roots of the molecular weights:

$$\frac{D_{\text{TCE}}}{\delta_w} = 3 \times 10^{-3}\ \text{cm/sec} \cdot \sqrt{\frac{\sqrt{44}}{\sqrt{131}}} = 2.3 \times 10^{-3}\ \text{cm/sec}.$$

Then use Eq. [2-30]:

$$J = (2.3 \times 10^{-3}\ \text{cm/sec}) \left(\frac{1\ \mu\text{g}}{\text{liter}}\right)\left(\frac{1\ \text{liter}}{1000\ \text{cm}^3}\right) = 2.3 \times 10^{-6} \frac{\mu\text{g}}{\text{cm}^2 \cdot \text{sec}}.$$

Note that this flux is higher than that obtained in Example 2-6, but in practice the difference might be masked by experimental variability.

2.3.3 THE REAERATION COEFFICIENT

In the expressions for the gas exchange coefficient employed previously, it is evident that the air–water gas exchange flux density is proportional to the difference between a chemical concentration in the water (C_w) and the corresponding equilibrium concentration ($C_w \cdot H$) in air. Consequently, the difference between actual and equilibrium concentration in the water tends to decay exponentially, as expected for any first-order process. In many situations, exponential decay may provide a useful model of a volatile chemical concentration in a surface water. A classic example is *degassing* of a dissolved gas from a stream; if the gas is present at concentration C_0 upstream, atmospheric concentration of the gas is negligible, and flow is steady and uniform along the stream, then the gas concentration in the stream is given by

$$C = C_0 \cdot e^{-k_r \tau}, \qquad [2\text{-}37]$$

where C is the downstream concentration [M/L^3], C_0 is the upstream concentration [M/L^3], k_r is a coefficient characterizing the gas transfer process [T^{-1}], and τ is the travel time from upstream location to downstream location [T]. Note that the units of k_r are [T^{-1}]; k_r is equal to the gas exchange coefficient k[L/T] divided by average stream depth [L]. As previously mentioned, if oxygen (O_2) is the gas being transferred between air and water, then k_r is called the reaeration coefficient, an essential parameter in classical dissolved oxygen modeling in streams (see Section 2.5).

2.3.4 VOLATILIZATION FROM PURE PHASE LIQUIDS

A special situation in air–water gas exchange occurs when a liquid such as gasoline or a solvent forms a floating slick or a layer of *nonaqueous phase liquid* (NAPL) on a water surface or on the ground. Comparison of this situation with the thin film model suggests that chemical molecules from the slick can enter the atmosphere much more rapidly than if they were dissolved in water, because chemicals do not need to pass through a thin stagnant water layer to enter the atmosphere. If the slick is composed of a pure chemical compound, the only significant barrier to transport into the atmosphere is diffusion through a thin stagnant film of air. As is the case with water, this resistance to volatilization can be expressed as a gas exchange coefficient that depends on site-specific conditions, particularly wind speed. The situation is the same as previously described for air-side control, except that the concentration of vapor at the interface must be derived from the NAPL's vapor pressure, instead of being given by ($C_w \cdot H$). The temperature gradient in air above the liquid also has an effect; see the discussion of atmospheric stability in Section 4.2.

The concentration of the chemical at the base of the stagnant air layer, just above the surface of the NAPL, is determined from the vapor pressure of the chemical as

$$C_a = \frac{P}{RT}\,(\mathrm{MW}), \qquad [2\text{-}38]$$

where C_a is the chemical concentration in the air [M/L^3], P is the vapor pressure of the chemical [M/LT^2], R is the universal gas constant, T is absolute temperature, and MW is the molecular weight of the chemical (g/mol).

The rate of volatilization from a NAPL surface is then given by the following expression, as compared with Eq. [2-32]:

$$J = \frac{-D_a}{\delta_a} \cdot C_a. \qquad [2\text{-}39]$$

The quantity D_a/δ_a is the same as previously discussed, and can be estimated from empirical equations. This velocity is larger for chemicals having larger diffusion coefficients in air, and is smaller for larger slicks or pools, because vapor advected over a downwind point has the effect of decreasing the concentration gradient over that point. This effect is reflected in the following expression for the gas exchange coefficient (also called the *gas phase transfer velocity*) given by Thibodeaux (1979),

$$v = 0.029 v_w L^{-0.11} S_c^{-0.67}, \qquad [2\text{-}40]$$

where v (the gas phase transfer velocity) and v_w (wind speed at 10 m height) are in meters per hour, and L, the spill diameter, is in meters. The molecular diffusion coefficient is contained in the *Schmidt number* (S_c), which is the ratio of the kinematic viscosity [L^2/T] to the molecular diffusion coefficient [L^2/T] of the vapor and lies in the range of one to two for many common solvent vapors. However, because the gas phase transfer velocity is not strongly dependent on the slick diameter or the Schmidt number, the empirical equation for k_a previously presented in Eq. [2-36] may be used for approximate purposes with common solvents, modest pool sizes, and moderate wind speeds.

A layer of NAPL floating on water can also lose mass by dissolution into the water body. If the NAPL is denser than water (in which case it is abbreviated DNAPL, for dense NAPL), it will sink through the water body to the bottom sediments. Most halogenated solvents are denser than water (see Table 1-3) and therefore have greatly diminished volatilization rates from water bodies relative to loss rates for floating NAPLs.

EXAMPLE 2-8

Benzene is spilled onto a lake from an overturned tanker truck. Given a 3 m/sec wind speed at a 10-m height, what will be the flux density from the slick?

From Table 1-3, benzene vapor pressure is 0.12 atm at 20°C. Use Eq. [2-38] to calculate the concentration of benzene at the air–NAPL interface:

$$\frac{(0.12 \text{ atm})}{(293 \text{ K})\left(0.082 \dfrac{\text{atm} \cdot \text{liter}}{\text{mol} \cdot \text{K}}\right)} \cdot \frac{78 \text{ g}}{\text{mol}} = 0.4 \text{ g/liter}.$$

Then use Eqs. [2-36] and [2-39]:

$$J = \left(\frac{3300 \text{ cm}}{\text{hr}}\right)\left(\frac{0.4 \text{ g}}{\text{liter}}\right)\left(\frac{1 \text{ liter}}{1000 \text{ cm}^3}\right) = \frac{1.3 \text{ g}}{\text{cm}^2 \cdot \text{hr}} \quad \text{or} \quad \frac{360\ \mu\text{g}}{\text{cm}^2 \cdot \text{sec}}.$$

Compare this result with TCE volatilization shown in Examples 2-6 and 2-7. Although benzene and TCE have similar vapor pressures (Table 1-3), benzene 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):

$$\mathrm{Alk} = C_B - C_A. \qquad [2\text{-}41]$$