phase liquid (NAPL, pronounced "napple"). An oil slick or a pool of industrial solvent floating on a water surface is an example of a NAPL. This section presents how to estimate the relative amounts of chemicals expected in different phases that are at equilibrium with one another.

In the discussion of chemical distribution among phases, it is assumed that chemicals are not transformed (i.e., no chemical bonds are formed or broken). For example, when liquid gasoline evaporates and enters the air in a partially empty gas tank, the bonds within individual molecules of the chemicals that compose gasoline are not being disrupted; the molecules are simply moving from a nonaqueous liquid phase to the gas phase without changing their identities. The *rate* at which this chemical movement occurs from one phase to another, relative to the timescale of interest, determines whether the problem is an equilibrium problem or a kinetics problem. Examples of both types abound in the environment; this section, however, refers only to the principles that govern *equilibrium.*

1.8.1 SOLUBILITY AND VAPOR PRESSURE

Aqueous solubility is a fundamental, chemical-specific property. It is defined as the concentration of a chemical dissolved in water when that water is both in contact and at equilibrium with the pure chemical. (For the moment, consider the chemical to be in either liquid or solid form; solubility of gases is discussed in Section 1.8.2.) Although aqueous solubility is temperature dependent, it does not vary greatly for a given chemical over the typical range of temperatures encountered in the environment.

As an example of solubility, pure liquid trichloroethene (C_2Cl_3H, commonly abbreviated TCE) dissolves into water until an aqueous concentration of approximately 1000 mg/liter is reached. See Table 1-3 for solubility values of several common chemicals.

Vapor pressure, another chemical-specific property, is defined as the *partial pressure* of a chemical in a gas phase that is in equilibrium with the pure liquid or solid chemical. For example, if at 20°C a bottle contains both air and pure liquid TCE, the partial pressure of TCE vapor in the air-filled neck of the bottle (the *headspace*) will be approximately 0.08 atm (61 mm Hg), which corresponds to 0.0033 mol/liter (440 mg/liter). The *ideal gas law* is used to convert the vapor pressure into the corresponding moles of vapor per unit volume:

$$\frac{n}{V} = \frac{P}{RT}, \qquad [1\text{-}29]$$

where P is the vapor pressure, V is the volume, n is the number of moles of the chemical, R is the gas constant, and T is the absolute temperature. Note

$C_g = \frac{n}{V} \frac{\text{mol}}{\text{L}} = \frac{P\ \text{atm}}{0.082\ [illegible]} = \frac{P\ [illegible]}{24.45\ [illegible]}$

TABLE 1-3 Some Properties of Various Chemicals

Chemical	Molecular weight (g/mol)[a]	Density (g/cm³)[a]	Solubility (mg/liter)[b]	Vapor pressure (atm)[b]	Henry's law constant (atm · m³/mol)[b]	Henry's law constant (dimensionless)[b]	log K_{ow}[c]	Comment
Acetic acid	60.05	1.05	∞					
Aroclor 1254	325.06[d]	1.50[d]	1.2×10^{-2}	1×10^{-7}	2.7×10^{-3}	1.2×10^{-1}	6.5[e]	Polychlorinate biphenyl mi (PCB)
Aroclor 1260	371.22[d]	1.57[d]	2.7×10^{-3}	5.3×10^{-8}	7.1×10^{-3}	3.0×10^{-1}	6.7[e]	Polychlorinate biphenyl mi (PCB)
Atrazine	215.68[d]		33[b]	4×10^{-10}[f]	3×10^{-9}[f]	1×10^{-7}[f]	2.68[b]	Herbicide
Benzene	78.11	0.88	1780	1.25×10^{-1}	5.5×10^{-3}	2.4×10^{-1}	2.13	Gasoline constituent
Benz[*a*]anthracene	228.29		2.5×10^{-4}[g]	6.3×10^{-9}[g]	5.75×10^{-6}[g]	2.4×10^{-4}[g]	5.91	Polycyclic aroı hydrocarboı (PAH)
Benzo(*a*)pyrene	252.32		4.9×10^{-5}[g]	2.3×10^{-10}[g]	1.20×10^{-6}[g]	4.9×10^{-5}[g]	6.50	PAH
Carbon tetrachloride	153.82	1.59	800	0.12	2.3×10^{-2}	9.7×10^{-1}	2.83[b]	
Chlorobenzene	112.56	1.11	472	1.6×10^{-2}	3.7×10^{-3}	1.65×10^{-1}	2.92	
Chloroform	119.38	1.48	8000	0.32	4.8×10^{-3}	2.0×10^{-1}	1.97[b]	
m-Cresol	108.14		2780[g]				1.96	
Cyclohexane	84.16	0.78	60[g]	0.13[g]	0.18[g]	7.3[g]	3.44	
1,1-Dichloroethane	98.96	1.18	4960[g]	3.0×10^{-1}[g]	6×10^{-3}[g]	2.4×10^{-1}[g]	1.79	
1,2-Dichloroethane	98.96	1.24	8426[g]	9.1×10^{-2}[g]	10^{-3}[g]	4.1×10^{-2}[g]	1.47	

(cont

TABLE 1-3 (*continued*)

Chemical	Molecular weight (g/mol)[a]	Density (g/cm³)[a]	Solubility (mg/liter)[b]	Vapor pressure (atm)[b]	Henry's law constant (atm · m³/mol)[b]	Henry's law constant (dimensionless)[b]	log K_{ow}[c]	Commen
cis-1,2-Dichloroethene	96.94	1.28	3500[h]	0.26[h]	3.4×10^{-3h}	0.25[h]	1.86[h]	
trans-1,2-Dichloroethene	96.94	1.26	6300[h]	0.45[h]	6.7×10^{-3h}	0.23[h]	2.06[h]	
Ethane	30.07		2.4×10^{-3g}	39.8[g]	4.9×10^{-1g}	20[g]		Gas
Ethanol	46.07	0.79	∞	7.8×10^{-2h}	6.3×10^{-6h}		−0.31[h]	Booze
Ethylbenzene	106.17	0.87	152	1.25×10^{-2}	8.7×10^{-3}	3.7×10^{-1}		
Lindane	290.9		7.3	1.2×10^{-8}	4.8×10^{-7}	2.2×10^{-5}		Pesticide
Methane	16.04				0.66[g]	27[g]		Natural gas
Methylene chloride	84.93	1.33	1.3×10^{4}	0.46	3×10^{-3}	1.3×10^{-1}	1.15	Also called dichlorome
Naphthalene	128.17	1.03	33	3×10^{-4}	1.15×10^{-3}	4.9×10^{-2}	3.36	PAH
Nitrogen	28.01							Atmospheric
n-Octane	114.23	0.70	0.72[g]	0.019[g]	2.95[g]	121[g]	4.00[b]	Alkane
Oxygen	32.00							Atmospheric
Pentachlorophenol	266.34	1.98	14	1.8×10^{-7}	3.4×10^{-6}	1.5×10^{-4}		
n-Pentane	72.15	0.63	40.6[g]	0.69[g]	1.23[g]	50.3[g]	3.62	
Perchloroethene	165.83	1.62	400	2×10^{-2}	8.3×10^{-3}	3.4×10^{-1}	2.88	Commonly us in dry clean tetrachloroe
Phenanthrene	178.23	0.98	6.2[g]	8.9×10^{-7g}	3.5×10^{-5g}	1.5×10^{-3g}	4.57	PAH
Styrene	104.15	0.91					2.95[b]	

(*cont*

TABLE 1-3 (*continued*)

Chemical	Molecular weight (g/mol)[a]	Density (g/cm³)[a]	Solubility (mg/liter)[b]	Vapor pressure (atm)[b]	Henry's law constant (atm · m³/mol)[b]	Henry's law constant (dimensionless)[b]	log K_{ow}[c]	Commen
Toluene	92.14	0.87	515	3.7×10^{-2}	6.6×10^{-3}	2.8×10^{-1}	2.69	A common so
1,1,1-Trichloroethane (TCA)	133.40	1.34	950	0.13	1.8×10^{-2}	7.7×10^{-1}	2.48	A common so
Trichloroethene (TCE)	131.39	1.46	1000	8×10^{-2}	1×10^{-2}	4.2×10^{-1}	2.42	A common so
o-Xylene	106.17	0.88	175	8.7×10^{-3}	5.1×10^{-3}	2.2×10^{-1}	3.12	1,2-Dimethyl benzene
Vinyl chloride	62.50	0.91	2790[g]	3.4	2.4	99	0.60	Degradation product of

[a] Values from Weast (1990), unless otherwise noted. Densities measured between 15.5 and 22°C, except for *o*-xylene at 10°C and phenanthrene at 4°C.
[b] Lyman *et al.* (1990). Solubility, vapor pressure, and Henry's law constants are for 20°C, unless otherwise noted.
[c] Schwarzenbach *et al.* (1993). Note that K_{ow} values are for 25°C.
[d] Values from Budavari (1989). Average number of chlorines per molecule for Aroclor 1254 and Aroclor 1260 is 4.96 and 6.30, respectively.
[e] Estimated from values in Anderson and Parker (1990).
[f] Riederer (1990).
[g] Schwarzenbach *et al.* (1993). Solubility, vapor pressure, and Henry's law constants are for 25°C.
[h] Howard (1990). Vapor pressure for *cis*-1,2-dichloroethene is for 35°C. Solubility and vapor pressure for *trans*-1,2-dichloroethene are for 25°C. Vapor pr for ethanol is for 25°C.

that the quotient, n/V, is the concentration of a chemical in the gas phase (typically expressed in moles per liter).

Vapor pressures are quite temperature dependent, and can vary appreciably over as little as 5 or 10°C. For example, the vapor pressure of trichloroethene increases by approximately 27% over less than 5°C: the vapor pressure at 25.50°C is approximately 9.546 kilopascals (kPa), compared with 7.506 kPa at 20.99°C (Boublík *et al.*, 1984). Therefore, it is extremely important to note the temperature at which a vapor pressure was measured or estimated. (See the Appendix for conversions between kilopascal and other units of pressure.) Over narrow temperature ranges, the *Antoine equation* is commonly used to predict vapor pressure of a liquid at a particular temperature,

$$\ln VP = \frac{-B}{T + C} + A, \qquad [1\text{-}30]$$

where VP is the vapor pressure of the chemical at a particular temperature, T is the absolute temperature (Kelvin) of interest, and A, B, and C are constants based on a regression equation fitted to vapor pressure data measured at many temperatures. In the CRC handbook (Weast, 1990), a very similar regression equation for log VP is provided; the third parameter C is not used. The CRC handbook contains tabulated values for A and B for both inorganic and organic chemicals. See Table 1-3 for vapor pressures of several common chemicals.

EXAMPLE 1-12

An automobile fuel tank has a filler pipe 2 ft in length with a diameter of 1.5 in. Estimate the amount of fuel lost (a) by molecular diffusion (if the gas cap is left off for a day) and (b) by advective "pumping" through a tank vent, when atmospheric pressure decreases from 30.0 to 29.5 in. Hg. Use an approximate diffusion coefficient of 0.1 cm²/sec. Assume the fuel is octane (C_8H_{18}, with a molecular weight of 114) having a vapor pressure of 0.015 atm at the ambient temperature of 70°F (21°C). The 70-liter tank is half full.

(a) Fick's first law can be used to estimate the rate of fuel loss by molecular diffusion. First, estimate the octane concentration in the tank headspace. Assume that the partial pressure of octane is equal to its vapor pressure inside the tank, because the air in the tank is in close contact with the fuel. Concentration of octane in the vapor phase is then given by the ideal gas law;

see Eq. [1-29]:

$$\frac{n}{V} = \frac{P}{RT} = \frac{0.015 \text{ atm}}{0.082 \text{ liter} \cdot \text{atm}/(\text{mol} \cdot \text{K}) \cdot (21 + 273)\text{K}} = 6.2 \times 10^{-4} M.$$

Given octane's molecular weight of 114, the preceding concentration corresponds to

$$6.2 \times 10^{-4} \frac{\text{mol}}{\text{liter}} \cdot 114 \frac{\text{g}}{\text{mol}} = 7.1 \times 10^{-2} \text{ g/liter},$$

or 7.1×10^{-5} g/cm^3.

The concentration gradient along the filler pipe can be estimated as

$$\frac{dC}{dx} = \frac{(7.1 \times 10^{-5} \text{ g/cm}^3 - 0 \text{ g/cm}^3)}{2 \text{ ft} \cdot 30.48 \text{ cm/ft}} = 1.2 \times 10^{-6} \frac{\text{g}}{\text{cm}^4}.$$

Fick's first law, Eq. [1-3], can then be used to estimate the flux density of octane:

$$J = -D \cdot \frac{dC}{dx} = 0.1 \frac{\text{cm}^2}{\text{sec}} \cdot 1.2 \times 10^{-6} \frac{\text{g}}{\text{cm}^4}$$

$$= 1.2 \times 10^{-7} \frac{\text{g}}{\text{cm}^2 \cdot \text{sec}}.$$

The rate of fuel loss is the flux density multiplied by the cross-sectional area:

$$1.2 \times 10^{-7} \frac{\text{g}}{\text{cm}^2 \cdot \text{sec}} \cdot \pi \cdot \left(\frac{1.5 \text{ in.}}{2} \cdot \frac{2.54 \text{ cm}}{\text{in.}}\right)^2 = 1.3 \times 10^{-6} \text{ g/sec}$$

$$= 0.11 \text{ g/day}.$$

(b) To estimate the amount of fuel lost by advective "pumping," consider that the amount of air leaving the tank can be estimated from the fact that the mass of air in the tank is proportional to pressure. Initially, air in the tank contains

$$35 \text{ liter} \cdot 7.1 \times 10^{-2} \text{ g/liter} = 2.5 \text{ g octane}.$$

When pressure drops from 30 to 29.5 in. Hg, the mass of air decreases to

$$\frac{29.5}{30} \cdot 100\% = 98.3\% \text{ of original mass}.$$

Therefore, approximately 1.7% of the air—and thus approximately 1.7% of the 2.5 g of octane in the air—leaves the tank:

$$1.7\% \cdot 2.5 \text{ g} = 0.041 \text{ g}.$$

Note that temperature changes, as well as atmospheric pressure changes, can cause fuel loss by pumping air into and out of the tank. Loss via pumping is proportional to the empty volume in the tank, and can be minimized by keeping the tank full. Loss via diffusion can be inhibited by putting the gas cap back on; diffusive loss is not greatly affected by the quantity of fuel in the tank. Note also that diffusive loss may be much greater than predicted if wind creates turbulence in the filler pipe, thereby increasing the Fickian transport coefficient.

1.8.2 HENRY'S LAW CONSTANTS

Now that solubility and vapor pressure have been defined, consider how a volatile chemical *partitions,* or distributes itself, between water and air phases at equilibrium. In general, a *partition coefficient* is the ratio of the concentrations of a chemical in two different phases, such as water and air, under equilibrium conditions. The *Henry's law constant, H* (or K_H), is a partition coefficient usually defined as the ratio of a chemical's concentration in air to its concentration in water at equilibrium. [Occasionally, a Henry's law constant is interpreted in an inverse fashion, as the ratio of a chemical's concentration in water to its concentration in air; see, e.g., Stumm and Morgan (1981, p. 179). Note that in that table, K_H is equivalent to $1/H$ as H is defined above.] Values of Henry's law constants are tabulated in a variety of sources (Lyman *et al.,* 1990; Howard, 1989, 1991; Mackay and Shiu, 1981; Hine and Mookerjee, 1975); Table 1-3 lists constants for some common environmental chemicals. When H is not tabulated directly, it can be estimated by dividing the vapor pressure of a chemical at a particular temperature by its aqueous solubility at that temperature. (Think about the simultaneous equilibrium among phases that would occur for a pure chemical in contact with both aqueous and gas phases.) Henry's law constants generally increase with increased temperature, primarily due to the significant temperature dependency of chemical vapor pressures; as previously mentioned, solubility is much less affected by the changes in temperature normally found in the environment.

Confusion about Henry's law constants often occurs because H can be expressed either in a dimensionless form or with units. The dimensionless form is obtained by using the same units for the chemical concentrations in both the air and the water phases, for example, (mol chemical/liter air) divided by (mol chemical/liter water). If the temperature at which H was measured or estimated is known, the dimensionless form can be readily converted to a form with units by using the ideal gas law—Eq. [1-21]—such that the molar air concentration is converted to units of partial pressure:

$$H = \frac{\text{mol chemical/liter air}}{\text{mol chemical/liter water}} \cdot \mathrm{R} \left(\frac{\text{liter air} \cdot \text{atm chemical}}{\text{mol chemical} \cdot \mathrm{K}} \right) \cdot \mathrm{T}\ (\mathrm{K}) \qquad [1\text{-}31]$$

$$= \frac{\text{atm chemical}}{\text{mol chemical/liter water}} = \frac{\text{atm} \cdot \text{liter}}{\text{mol}}.$$

Another common dimensional form of H has units of atm $\cdot$ m^3/mol. If the Henry's law constant has been measured or estimated at 25°C, it can be converted to a dimensionless form by multiplying by 40.9 mol/m^3 $\cdot$ atm:

$$H = \frac{\text{atm chemical}}{\text{mol/m}^3} \cdot \frac{40.9\ \text{mol/m}^3}{\text{atm}} = \text{dimensionless form of } H. \qquad [1\text{-}32]$$

Note that the value of 40.9 in Eq. [1-32] is obtained by multiplying the gas constant (0.0821 liter $\cdot$ atm/mol $\cdot$ K) by the absolute temperature (298 K) and by dividing by 1000 to convert liters into cubic meters. Similar factors can be readily derived for other temperatures.

EXAMPLE 1-13

Consider an unsaturated soil (i.e., a soil that contains both air and water in the pores between soil grains). Suppose the concentration of dissolved oxygen in soil water at equilibrium with soil air is 100 μmol/liter (μM). Given a Henry's law constant of 26 (dimensionless) for oxygen at 20°C, what is the corresponding oxygen concentration in soil air? What is the Henry's law constant in units of atm $\cdot$ m^3/mol at 20°C?

Given equilibrium between soil water and air, the oxygen concentration in soil air would be

100 μmol/liter (water) × 26 (Henry's law constant) = 2600 μmol/liter (air).

Use Eq. [1-22], with an additional conversion factor for liters to cubic meters, to convert the dimensionless Henry's law constant to a constant with units of atm $\cdot$ m^3/mol:

$$H = \frac{26\ \text{mol/liter (air)}}{1\ \text{mol/liter (water)}} \cdot RT \cdot 10^{-3}\text{m}^3\text{/liter}$$

$$H = \frac{26\ \text{mol/liter (air)}}{1\ \text{mol/liter (water)}} \cdot \frac{0.082\ \text{liter} \cdot \text{atm}}{\text{mol} \cdot \mathrm{K}} \cdot \frac{(20°\mathrm{C} + 273)\ \mathrm{K}}{1} \cdot \frac{1\ \text{m}^3}{1000\ \text{liter}}$$

$$H = \frac{0.63\ \text{atm} \cdot \text{m}^3}{\text{mol}}.$$

$\log K_H = 0.79$

1.8.3 CHEMICAL PARTITIONING TO SOLIDS

Chemical partitioning also occurs between water and solid phases and between air and solid phases, in a process most generally termed *sorption.* Types of sorption include *adsorption,* in which a chemical sticks to the two-dimensional surface of a solid, and *absorption,* in which a chemical diffuses into a three-dimensional solid. Chemical sorption in the environment is much more difficult to predict than is chemical partitioning between air and water, partly because the types of sorptive solid phases *(sorbents)* vary enormously, and partly because there are many different mechanisms by which sorption can occur. In this section, only partitioning between water and solid phases is considered.

Solids capable of sorbing chemicals *(sorbates)* include minerals, such as clays and metal oxides; natural organic material; and plastic, for example, polyvinyl chloride (PVC), commonly used in groundwater monitoring wells. The mechanisms by which sorption can occur include absorption into natural organic matter; adsorption to mineral surfaces via van der Waals, dipole–dipole, and other weak physical intermolecular forces; adsorption through electrostatic attractions to oppositely charged surface sites on the solids; and adsorption through covalent bonding to surface groups on the solids. The symbol K_p is frequently used to represent a solid–water partition coefficient; K_d, symbolizing a *distribution coefficient,* is an equivalent notation.

Use of a partition coefficient without reference to the conditions under which it was measured suggests that the coefficient is a constant. A constant coefficient implies a linear relationship between the amount of dissolved chemical and the amount sorbed. In actuality, the relationship between dissolved and sorbed chemical concentrations is often nonlinear and may be expressed as a *sorption isotherm.* (Use of the term isotherm indicates that sorption measurements are being made at a constant temperature.) Laboratory measurements of sorption sometimes fit a relationship known as the *Freundlich isotherm,*

$$C_{\text{sorb}} = K_f \cdot (C_w)^n, \qquad [1\text{-}33]$$

where C_{sorb} is the concentration of sorbed chemical [M/M], K_f is the Freundlich constant, C_w is the concentration of dissolved chemical [M/L^3], and n reflects nonlinearity—if n equals one, Eq. [1-33] reduces to a linear partition coefficient. If the value of n is less than one and the dissolved chemical concentration increases, the additional molecules sorb in a smaller proportion. If the value of n is greater than one, proportionally more sorption occurs if the dissolved concentration increases (Fig. 1-10).

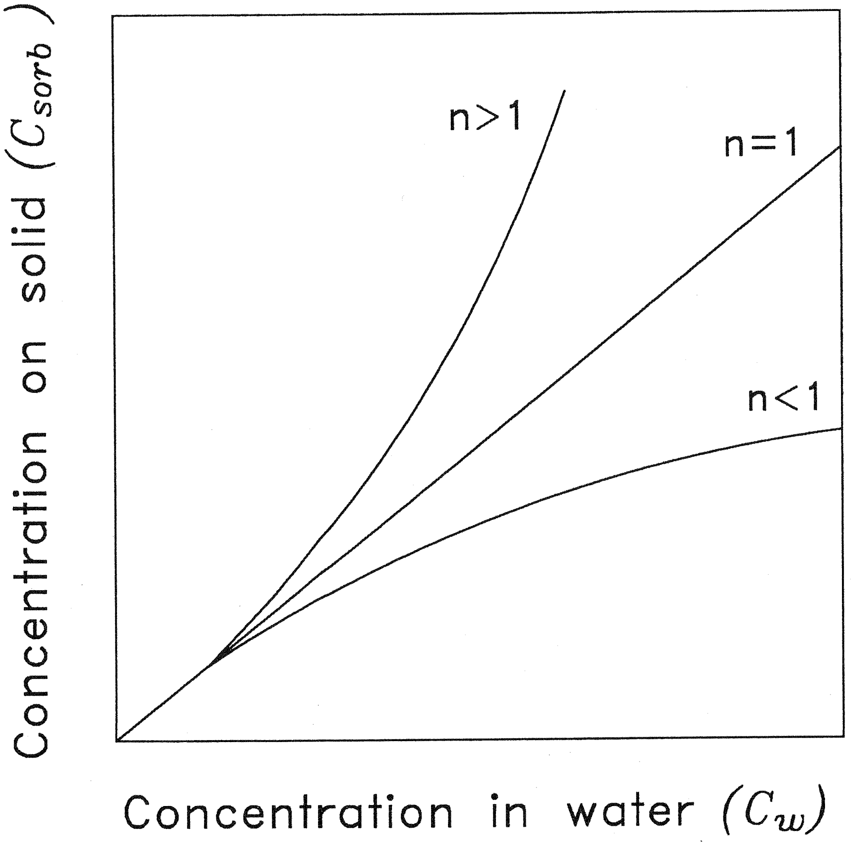

FIGURE 1-10 Freundlich isotherms having exponents less than, equal to, and greater than one. An exponent of one corresponds to a linear isotherm, in which case the relationship between the aqueous concentration of a chemical and the chemical's concentration on a solid phase at equilibrium with the water can be described by a single partition coefficient. If the exponent is less than one, the ratio of sorbed concentration to aqueous concentration decreases as the chemical concentration in the system increases. Such a decrease would happen, for example, if the solid contained a finite number of sites that became filled (saturated) at higher aqueous chemical concentrations. An exponent greater than one might occur if the sorbed chemical modified the solid phase to favor further sorption.

Unlike a Henry's law constant, whose value in a given environmental situation is predominantly dependent on only temperature, a solid–water partition coefficient can also be dependent on other factors, including water pH, type of solid, and ionic strength. For inorganic chemicals, it is not appropriate to apply a K_d value for a given pollutant in a particular environmental situation to the same chemical under other conditions. Furthermore, there is considerable uncertainty in predicting *a priori* a K_d value for inorganic chemicals, as well as for charged organic chemicals which sorb through chemical reactions with solid surfaces. For these types of chemicals, K_d often must be measured in the laboratory. However, for many neutral (uncharged)

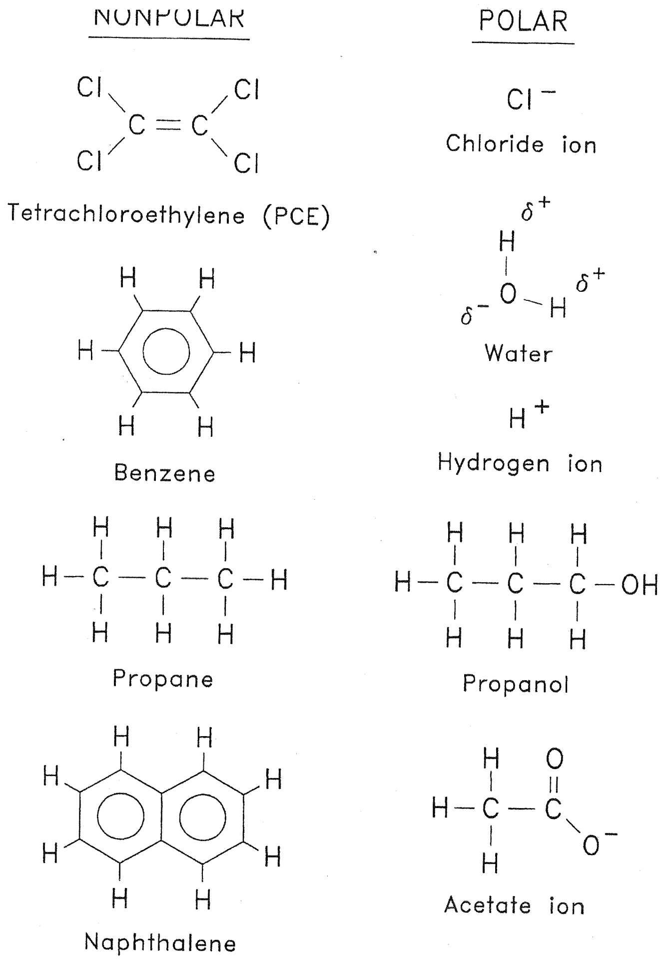

FIGURE 1-11 Some examples of polar and nonpolar chemical species. Note that unbalanced electrical charge, asymmetry, and presence of oxygen all tend to make chemicals more polar.

organic chemicals, a robust method for approximating K_d values exists. This method depends on both sorbate properties and sorbent properties (i.e., the concentration of natural organic matter in the solid), and assumes that absorption into natural organic matter is the primary sorption mechanism. The sorbate properties necessary for predicting K_d values are described below; the necessary sorbent properties and further estimation techniques are presented in Chapter 3.

Many neutral organic chemicals with low water solubility tend to absorb into natural organic matter because they are *nonpolar. Polarity* refers to the extent to which charge is unevenly distributed within a chemical molecule or substance (Fig. 1-11). Water itself is very polar, with an excess of negative charge associated with the oxygen atom and an equal excess of positive charge associated with the hydrogen atoms. Most natural minerals are also polar. Because of water's polarity, it readily dissolves other polar *(hydrophilic)* chemicals. However, the nonpolar (*hydrophobic*) chemicals tend to avoid the less favorable state (from a free energy point of view) of being dissolved in water by absorbing into natural organic matter.

The polarity of a chemical has a strong inverse correlation with the chemical's K_{ow}, the *octanol–water partition coefficient.* K_{ow} is the ratio of a chemical's concentration in octanol ($C_7H_{15}CH_2OH$) to its concentration in water at equilibrium. The concept of K_{ow} was developed by the pharmaceutical industry as a useful index of a drug's behavior in the body, because partitioning between water and octanol roughly mimics partitioning between water and body fat. In general, smaller molecules and more polar molecules dissolve more readily in water, have lower K_{ow} values, and have less tendency to sorb to solids. Larger molecules and less polar molecules are less soluble, have higher K_{ow} values, and are more likely to sorb to solids. K_{ow} is a very valuable index of the partitioning behavior of many organic compounds in the environment. Methods for using K_{ow} values in conjunction with sorbent parameters to predict K_d values are presented in Chapter 3.

K_{ow} has been measured and tabulated for many chemicals and also lends itself to estimation based on the chemical's structure (Lyman *et al.*, 1990; Howard, 1989–1991; Schwarzenbach *et al.*, 1993; Yalkowsky and Valvani, 1979; Syracuse Research Corporation's Environmental Fate Data Base; and Hansch and Leo, 1985). See Table 1-3 for K_{ow} values for some chemicals commonly found in the environment.

EXAMPLE 1-14

In a toxicity test, small fish are placed in aquaria containing various concentrations of toluene. For partitioning of toluene, these particular fish can be modeled as bags containing, by volume, 5% fatty tissue similar to octanol in its affinity for toluene, 3% air in a swim bladder, and 85% water. Treat the missing 7% as being nonsorptive for toluene. If equilibrium is assumed, what fractions of toluene in the fish will reside in fatty tissue and in the air bladder?

To solve this problem, first obtain the relevant partition coefficients, and then set up an expression in which all masses of toluene are written as functions of the volume of fish (V_{fish}) and the toluene concentration in the aquaria water (C_w). From Table 1-3, $H = 0.28$ and $\log K_{ow} = 2.69$ for toluene ($K_{ow} = 490$).

$$\text{Mass of toluene in water of fish} = (V_{fish})(0.85)C_w.$$

$$\text{Mass of toluene in swim bladder} = (V_{fish})(0.03)(H_{toluene} \cdot C_w).$$

$$\text{Mass of toluene in fatty tissue} = (V_{fish})(0.05)(K_{ow} \cdot C_w).$$

Then the fraction of toluene in fatty tissue can be written:

$$\frac{(V_{\text{fish}})(0.05)(K_{\text{ow}} \cdot C_{\text{w}})}{(V_{\text{fish}})(0.05)(K_{\text{ow}} \cdot C_{\text{w}}) + (V_{\text{fish}})(0.03)(H_{\text{toluene}} \cdot C_{\text{w}}) + (V_{\text{fish}})(0.85)C_{\text{w}}}$$

$$= \frac{0.05\ K_{\text{ow}}}{0.05\ K_{\text{ow}} + 0.03\ H_{\text{toluene}} + 0.85}$$

$$= \frac{0.05(490)}{0.05(490) + 0.03(0.28) + (0.85)}$$

$$= \frac{25}{25 + 0.008 + 0.85} = 97\%.$$

(Note that this is dimensionless—all units have cancelled out.) Similarly, only 0.03% is in the air bladder (and approximately 3% resides in the water fraction).

Although this model for an aquatic organism may seem very crude, such models are useful in many situations, as discussed further in Chapter 2.

1.8.4 EQUILIBRIUM PARTITIONING AMONG ALL PHASES: FUGACITY

From the preceding three sections, it is evident that the relative concentrations of a chemical in air, water, and soil phases at equilibrium can be predicted from a knowledge of the chemical's partition coefficients (i.e., vapor pressure, Henry's law constant, and distribution coefficient). Each of the chemical's partition coefficients describes a behavior that may also be thought of in terms of chemical potential; when equilibrium partitioning among phases is attained, the chemical potentials in all phases are equal. A convenient measure of chemical potential is *fugacity,* literally, the "tendency to flee." The fugacity of a chemical in a given phase is equal to the vapor pressure the chemical would have in a gas volume in equilibrium with the phase. The fugacity concept can provide a useful framework within which previously described partition coefficients may be used to compute the partitioning of chemicals among the phases of an ecosystem.

Fugacity has units of pressure, and can be related to the concentration of a chemical in a system through a *fugacity capacity constant,* commonly with units of (mol/atm · m^3). Thus the chemical concentration in a given phase is

$$C_i = Z_i \cdot f, \qquad [1\text{-}34]$$

where C_i is the chemical concentration in phase i [M/L^3], Z_i is the fugacity capacity [T^2/L^2], and f is the fugacity [M/LT^2]. At equilibrium, the fugacity for the entire system can be calculated as

$$f = \frac{M_{\text{tot}}}{\sum_i (Z_i \cdot V_i)}, \qquad [1\text{-}35]$$

where M_{tot} is the total moles of chemical in the system and V_i is the volume of phase i with which the chemical is associated [L^3].

In the air phase, under pressures normally found in the environment, fugacity equals the pressure exerted by the chemical's vapor. (At higher pressures, vapors do not exactly obey the ideal gas law, and a correction must be applied; this is small enough to ignore for practical purposes of fate and transport modeling in the environment.) By combining the ideal gas law (Eq. [1-29]) and Eq. [1-34], it is evident that the fugacity capacity for air is $1/RT$, for all chemicals:

$$P = \frac{n}{V} \cdot RT = f.$$

$$C_i = \frac{n}{V} \qquad [1\text{-}36]$$

$$\therefore Z_i = \frac{1}{RT}.$$

The fugacity capacity for other phases is a function of both the chemical's partition coefficient between that phase and water and the chemical's Henry's law constant. For water, the fugacity capacity is

$$Z_{\text{water}} = \frac{1}{H}, \qquad [1\text{-}37]$$

where H is the Henry's law constant [L^2/T^2].

For sediment, the fugacity capacity for a chemical can be expressed as

$$Z_{\text{sediment}} = \frac{\rho_s \cdot K_d}{H}, \qquad [1\text{-}38]$$

where ρ_s is the density of sediment [M/L^3] and K_d is the soil–water partition coefficient [L^3/M].

the fugacity capacity for a chemical can be described by

$$Z_{\text{fish}} = \frac{\rho_{\text{fish}} \cdot BCF}{H}, \qquad [1\text{-}39]$$

where ρ_{fish} is the density of fish [M/L^3] and BCF is the partition coefficient between fish and water (discussed in Chapter 2) [L^3/M].

Once the fugacity capacity for each phase has been calculated, the moles of chemical in each phase are given by

$$M_i = f \cdot V_i \cdot Z_i, \qquad [1\text{-}40]$$

where M_i is the moles of chemical in phase i.

Fugacity modeling does not allow any new calculations to be made that cannot already be made with the partition coefficients described in the previous three sections. However, a comparison of the fugacity capacity of a chemical in different phases permits a direct assessment of which phase will have the highest chemical concentration at equilibrium. For further details, the reader is referred to Mackay and Paterson (1981) and Schwarzenbach et al. (1993).

EXAMPLE 1-15

Consider a simplified ecosystem consisting of 10^{10} m^3 of air, 7×10^6 m^3 of water, and 3.5 m^3 of fish. Released into the water is 10 kg of methylene chloride. Predict the equilibrium partitioning of methylene chloride into each phase using the fugacity concept. Assume a BCF of 4.4 liter/kg, a fish density of 1 g/cm^3, and a temperature of 25°C.

First, gather the necessary data from Table 1-3: vapor pressure is 0.46 atm; H is 3×10^{-3} atm · m^3/mol; molecular weight is 84.93 g/mol.

Then convert the mass of methylene chloride into moles:

$$10 \text{ kg} \cdot \frac{1000 \text{ g}}{1 \text{ kg}} \cdot \frac{1 \text{ mol}}{84.93 \text{ g}} = 118 \text{ mol}.$$

Next, calculate the fugacity capacity for each phase. For the air phase, use Eq. [1-36]:

$$Z_{\text{air}} = \frac{1}{RT} = \frac{1}{0.0821 \text{ liter} \cdot \text{atm/(mol} \cdot \text{K)} \cdot 298 \text{ K}} \cdot \frac{1000 \text{ liter}}{1 \text{ m}^3}$$

$$Z_{\text{air}} = 40.9 \text{ mol/(atm} \cdot \text{m}^3).$$

For the water phase, use Eq. [1-37]:

$$Z_{\text{water}} = \frac{1}{3 \times 10^{-3}\ \text{atm} \cdot \text{m}^3/\text{mol}} = 333\ \text{mol}/(\text{atm} \cdot \text{m}^3).$$

For the fish phase, use Eq. [1-39]:

$$Z_{\text{fish}} = \frac{1000\ \text{g/m}^3 \cdot 4.4\ \text{liter/kg}}{3 \times 10^{-3}\ \text{atm} \cdot \text{m}^3/\text{mol}} \cdot \frac{1\ \text{kg}}{1000\ \text{g}} \cdot \frac{1\ \text{m}^3}{1000\ \text{liter}} = 1.5\ \text{mol}/(\text{atm} \cdot \text{m}^3).$$

Then calculate the fugacity for the entire system, from Eq. [1-35]:

$$f = \frac{118\ \text{mol}}{40.9 \cdot 10^{10} + 333 \cdot 7 \times 10^6 + 1.5 \cdot 3.5} = 2.9 \times 10^{-10}\ \text{atm}.$$

Finally, the moles of methylene chloride in each phase can be calculated from Eq. [1-40]:

$$M_{\text{air}} = 2.9 \times 10^{-10} \cdot 10^{10} \cdot 40.9 = 117\ \text{mol}$$

$$M_{\text{water}} = 2.9 \times 10^{-10} \cdot 7 \times 10^6 \cdot 333 = 0.7\ \text{mol}$$

$$M_{\text{fish}} = 2.9 \times 10^{-10} \cdot 3.5 \cdot 1.5 = 1.5 \times 10^{-9}\ \text{mol}.$$

Therefore, at equilibrium, the mass of methylene chloride will be overwhelmingly in the air as compared with the other two phases. However, the highest concentration of methylene chloride is in the water (1×10^{-7} mol/m^3), the phase with the highest fugacity capacity.

1.9 CONCLUSION

In this chapter the basic concepts of physical transport and environmental chemistry have been introduced. Next the three principal environmental media, surface waters, the subsurface environment, and the atmosphere, are examined in detail. In the following chapters, the physical, chemical, and biological structures of these media are discussed. By applying physical and chemical principles, one can interpret, explain, and make predictions about chemical behavior in each medium.

It should be kept in mind that an extensive body of literature exists, within which the basic concepts of this and the following chapters are further developed. The reader is encouraged to explore in greater detail the concepts presented in this book by consulting the literature; the references cited in each chapter provide a starting point.

by woody plants (trees and shrubs). *Bogs* and *fens* are typically northern wetlands; they may form deep deposits of *peat,* which is partially decomposed plant material. Bogs receive water predominantly from precipitation, whereas fens are partially recharged by more mineral-rich groundwater.

Chemical behavior in wetlands is strongly influenced by the organic content of the soil. Microbial decomposition of the organic matter in the soil (see Section 2.4.3) results in rapid oxygen consumption. Given that oxygen diffuses slowly through water-saturated soil relative to its transport through turbulent open water, wetland soils are usually strongly depleted in oxygen, and in many respects behave in a manner similar to bottom sediments (as discussed later). Wetland soils differ from bottom sediments, however, in that they are usually heavily vegetated and often are in contact with the atmosphere. The reader is referred to Mitsch and Gosselink (1993) for a more complete discussion of wetlands.

2.2.5 PARTICLES IN SURFACE WATERS

In the foregoing discussions it has been implicit that advection and the Fickian mixing processes of diffusion and dispersion are responsible for the transport of *dissolved* chemicals. It is not necessary, however, for a chemical to be dissolved to be transported by these fluid processes; chemicals that are adsorbed onto the surfaces of particles or absorbed into particles can also be readily transported by these processes.

Types of Particles

Particles can be of mineral or organic origin. Mineral particles are derived from geologic materials, such as bedrock or glacial outwash, by two primary methods: the flow of water, ice, and wind, which mechanically erodes rock and sediment; and the chemical weathering of rocks. Oxyhydroxide particles, such as those of iron [$Fe(OH)_3$] and manganese [$Mn(OH)_4$], and clay particles consisting of aluminosilicates, are quite common. The density of many mineral particles ranges between 2 and 3 g/cm^3 and is often approximated as 2.6 g/cm^3. Organic particles are derived from plant material, dead bacterial or algal cells, and decaying aquatic organisms. Organic particles usually have a density only slightly greater than that of water and contain a high fraction of organic carbon, which is an excellent sorbent for many pollutants. Anthropogenic sources of mineral and organic particles to surface waters include industrial effluent and sewage outfalls as well as emissions of fugitive dusts, which are initially released to the atmosphere but subsequently settle into lakes and streams.

No matter what their origin, particles affect the transport of pollutants that are sorbed. Most of the discussion about advection and dispersion of dissolved chemicals in surface waters can also be applied to chemicals sorbed to suspended particles, provided that the time required for particles to settle out of the water is much longer than the time required for advection or mixing.

Suspended Sediment Load

The transport of suspended sediment is most prominent in rivers and in streams, which have higher water velocities than those of most lakes. The concentration of suspended sediment varies widely from river to river. The suspended sediment load also varies with discharge, often increasing as discharge rises because the greater turbulence at high flow allows a greater load of sediment to be held in suspension. Of course, the higher sediment-carrying capacity of a stream at a higher flow rate will lead to an increased suspended sediment load only if a supply of additional sediment exists. The supply of suspended sediment can be increased during times of high discharge by erosion from the land surface and by the *resuspension* of particles that previously had settled to the bottom of the water body. Consequently, the total advective flux of river sediment, which is the product of discharge and concentration, typically increases at a faster rate than discharge, as shown in Fig. 2-10. For further information on the relationships among stream channel geometry, discharge, and sediment flux, the reader is referred to Leopold and Maddock (1953).

Bed Load

The bed load of a river consists of particles that spend the majority of the time on the river bottom, but are periodically *entrained* into the turbulent water flow and carried a short distance downstream before settling again. Bed load consists mostly of particles in the size category of 1 mm in diameter; particles with diameters less than 0.1 mm are likely to be classified as suspended material, while particles with diameters larger than 10 mm move little at average flows. Bed load at times of high flow, however, can include surprisingly large particles, including rocks many centimeters in diameter. It has been proposed that bed load is approximately proportional to the mechanical *power* (work per time) being dissipated in a river at high flows.

The movement of particles, both as suspended sediment and as bed load, is of great importance to the evolution of river channels. The *meandering* of rivers (see Fig. 2-1) is an example of the physical effects of particle transport (Henderson, 1966; Reid and Wood, 1976).

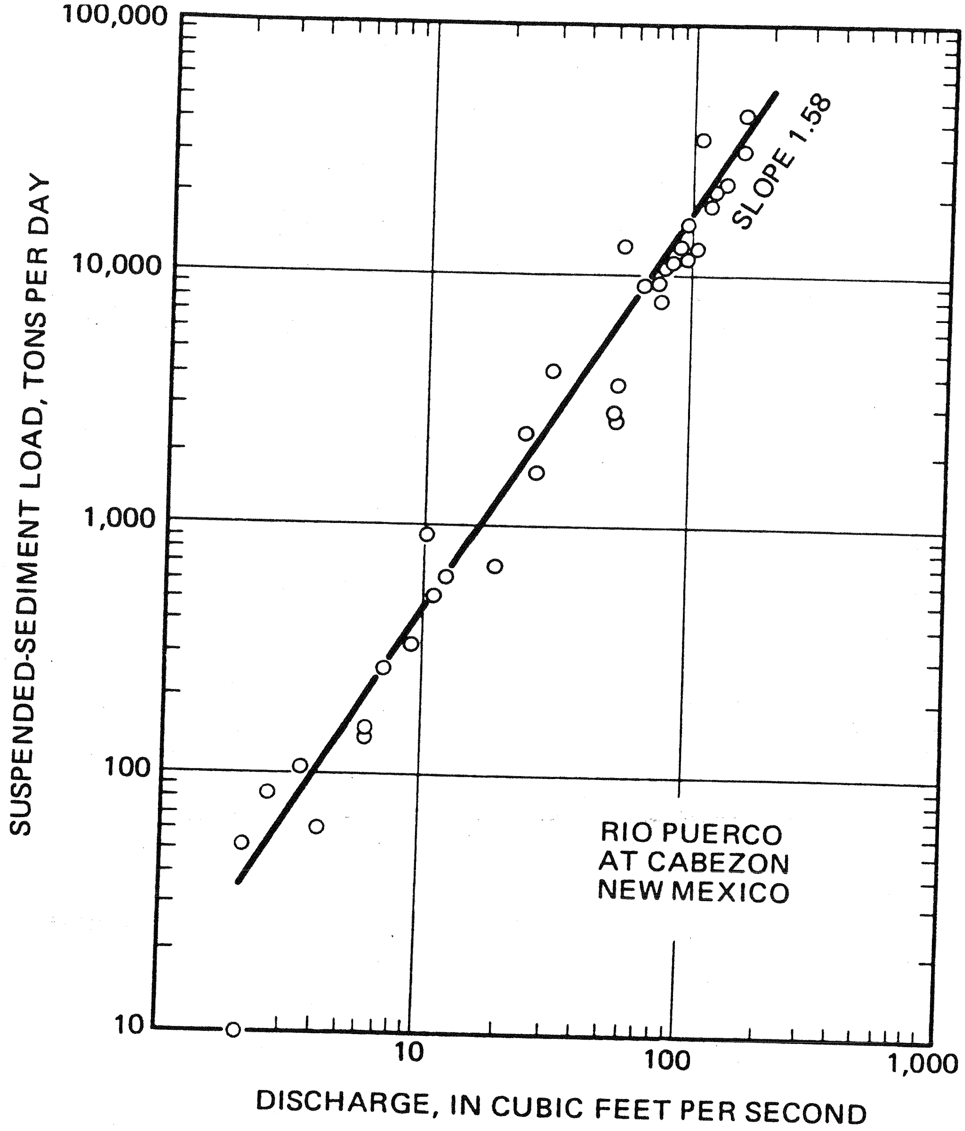

FIGURE 2-10 Suspended sediment load in the Rio Puerco, near Cabezon, New Mexico. Note the wide range of discharge (streamflow), which is typical of most rivers, and the even larger range of suspended sediment load (total flux of sediment), which varies over a factor of 1000. Sediment flux is the product of discharge and the concentration of suspended sediment in the river. Given that the slope of sediment flux versus discharge is greater than 1 (1.58), the suspended sediment concentration in the river must be increasing at higher flows [from *Ecology of Inland Waters and Estuaries, 2nd edition,* by G. K. Reid and R. D. Wood. © 1976. Reprinted with permission of Brooks/Cole Publishing, a division of International Thomson Publishing. Fax 800-730-2215.].

Particle Settling

Suspended particles in surface waters are eventually either transported out of the water body (e.g., carried to the ocean by a river) or deposited on the bottom of the water body by *settling.* Settling is especially important in relatively quiescent waters, such as lakes, which typically have a relatively short life span (as measured in geologic terms) because they tend to fill in with sediment. The average settling velocity of a particle can be approximated by *Stokes' law,* which estimates the settling velocity of a small sphere in a viscous fluid,

$$\omega_f = \frac{(2/9) \cdot g \cdot (\rho_s/\rho_f - 1) \cdot r^2}{\eta_f}, \qquad [2\text{-}20]$$

where ω_f is the settling velocity [L/T], g is the acceleration due to gravity [L/T^2], ρ_s is the density of the spherical particle [M/L^3], ρ_f is the density of the fluid [M/L^3], r is the radius of the particle [L], and η_f is the kinematic viscosity of the fluid [L^2/T]. *Kinematic viscosity* is the ratio of the dynamic viscosity of a fluid to the density of the fluid. Eq. [2-20] assumes that the particle is spherical, but is applicable to nonspherical particles if r is taken to be an empirical hydrodynamic radius.

Figure 2-11 presents data, including sizes and settling velocities, for many particles. Of particular note is the tremendous range of settling velocities among environmental particles. Given a finite settling velocity, it might seem that all particles in a surface water body should eventually settle out of the water. As particles settle toward the bottom, however, an upward concentration gradient is created, and upward Fickian transport begins to counteract the downward transport by settling. Even in very still water, particles have a diffusion coefficient, analogous to a molecular diffusion coefficient, that arises from their random *Brownian motion* (Fig. 2-11).

To illustrate particle diffusion, consider a tall water-filled volume in which particles have settled until a steady-state vertical concentration profile has been attained. Under this steady-state condition, the downward flux density of particles must equal the upward flux density of particles at every depth. The downward flux density can be expressed as

$$J_{\text{Stokes}} = C \cdot \omega_f, \qquad [2\text{-}21]$$

where J_{Stokes} is the downward flux density due to particle settling [M/L^{2}T], C is the particle concentration [M/L^3], and ω_f is the settling velocity [L/T]. The upward flux density is given by Fick's first law,

$$J_{\text{Fickian}} = D \cdot dC/dx, \qquad [2\text{-}22]$$

where J_{Fickian} is the upward flux density [M/L^{2}T], D is the particle diffusion coefficient [L^2/T], and x is the distance above the bottom of the water column [L]. Adding Eqs. [2-21] and [2-22] and equating their sum to zero gives

$$dC/dx = -(\omega_f/D) \cdot C = -(\text{constant}) \cdot C. \qquad [2\text{-}23]$$

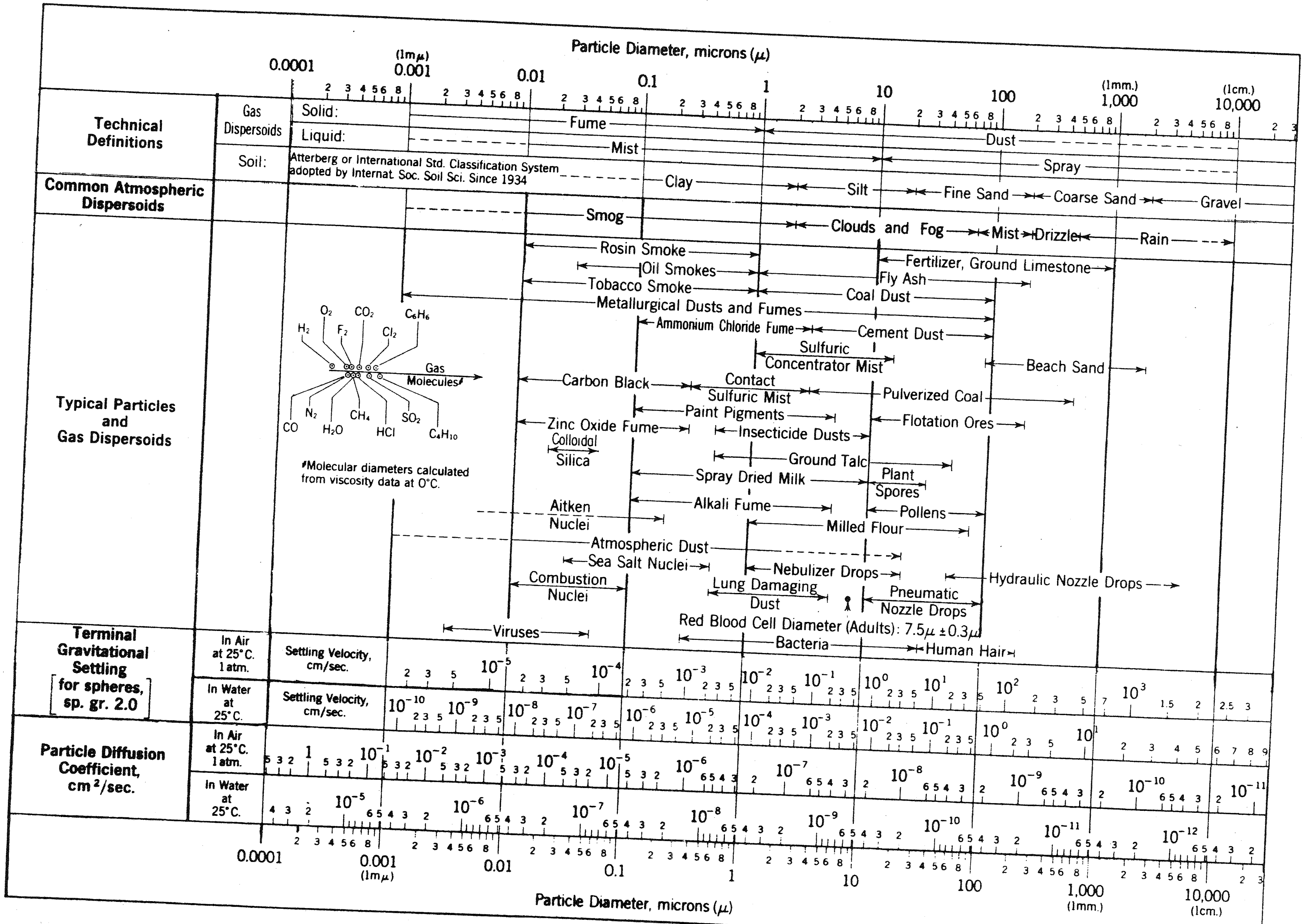

FIGURE 2-11 Some characteristics of environmental particles in both air and water. Note the enormous range of particle sizes, and the even larger range of settling velocities. Settling velocities and diffusion coefficients are calculated for spherical particles of density 2.0 g/cm³ (at the lower end of the density range for materials of mineral origin). In water, a particle of lesser density, such as a particle of organic material, whose density is commonly only slightly higher than the density of water, may settle much more slowly than shown here [adapted from Lapple (1961). Reprinted with permission of SRI International.].

The solution to the differential equation shown in Eq. [2-23] should be familiar through comparison with Eqs. [1-18] and [1-19],

$$C = C_0 \cdot e^{-(\text{constant}) \cdot x}, \qquad [2\text{-}24]$$

where C_0 is the concentration at the bottom of the water column, where x is zero. Note, however, that "decay" is occurring over depth, not time, so the "decay constant" has units of [1/L], not [1/T], as in Eqs. [1-18] and [1-19]. The vertical concentration profile of particles at steady state can therefore be written as

$$C = C_0 \cdot e^{-(\omega_f/D) \cdot x}. \qquad [2\text{-}25]$$

Thus, particle concentration in the water column follows an exponential decay upward from the bottom. If the decay constant, ω_f/D, is small enough, the particle concentration might be nearly uniform over a substantial distance above the bottom of the water column. This could occur for extremely small particles in quiescent waters, or for larger particles if D is much larger than the value inferred from Brownian motion. Because surface waters are rarely quiescent, D can become many orders of magnitude larger in the presence of even mild turbulence. Under these conditions, Fickian transport may be sufficient to keep particles several micrometers in diameter suspended in the water indefinitely.

EXAMPLE 2-3

Describe the steady-state distribution of 1-μm diameter clay particles and 0.01-μm diameter clay particles in still water. For each particle size, calculate the depth above the bottom of the water column at which the particle concentration is one-half the particle concentration at the bottom. Assume a kinematic viscosity of water of 0.013 cm²/sec at 50°F and a solid particle density of 2.6 g/cm³.

First, calculate the settling velocity of 1-μm diameter particles from Eq. [2-20]:

$$\omega_f = \frac{(2/9) \cdot 981 \text{ cm/sec}^2 \cdot ((2.6 \text{ g/cm}^3)/(1 \text{ g/cm}^3) - 1) \cdot (5 \times 10^{-5} \text{ cm})^2}{0.013 \text{ cm}^2\text{/sec}}$$

$$= 6.7 \times 10^{-5} \text{ cm/sec}.$$

Next, estimate the first-order decay constant. From Fig. 2-11, the particle diffusion coefficient in water for a 1-μm particle is approximately 5×10^{-9}

here [adapted from Lapple (1961). Reprinted with permission of SRI International.].

cm^2/sec:

$$\omega_f/D = \frac{6.7 \times 10^{-5}\ \text{cm/sec}}{5 \times 10^{-9}\ \text{cm}^2/\text{sec}} = 1.3 \times 10^4/\text{cm}.$$

Then use Eq. [2-25] to estimate the distance at which the concentration is halved:

$$\frac{1}{2} = e^{-(1.3\times 10^4/\text{cm})\cdot x}$$

$$x = 5 \times 10^{-5}\ \text{cm or } 0.5\ \mu\text{m}.$$

For a particle of 0.01-μm diameter, the diffusion coefficient in water from Fig. 2-11 is approximately 5×10^{-7} cm^2/sec. By repeating the preceding calculations, ω_f is approximately 6.7×10^{-9} cm/sec, the decay constant is approximately 0.013/cm, and therefore the distance at which the concentration is halved is approximately 50 cm.

Although small particles may remain separated from one another and travel long distances, small particles may also aggregate into larger particles. This process of flocculation creates particles that settle much faster than the original smaller particles, often leading to the deposition of the particles (and their sorbed pollutant loads) into bottom sediment, as will be discussed next. As previously mentioned, flocculation is a significant process in estuaries where the increasing salinity of water enhances the tendency of particles to stick to each other. Flocculation is also important in some wastewater treatment facilities, where chemicals such as polymers and ferric chloride ($FeCl_3$) are added to wastewater to enhance particle aggregation and settling.

EXAMPLE 2-4

A river of 2-m depth moving at an average velocity of 0.2 m/sec receives particles of 200-μm diameter from a storm drain emptying at the river surface. Assume that the particles are of mineral origin with a density of approximately 2.6 g/cm^3 and that the kinematic viscosity of water is 1.3×10^{-2} cm^2/sec (at 10°C). What is the minimum distance the particles will travel before settling to the river bottom?

First, use Eq. [2-20] to estimate the settling velocity:

$$\omega_f = \frac{(2/9)(981\ \text{cm/sec}^2)(2.6/1 - 1)(10^{-2}\ \text{cm})^2}{1.3 \times 10^{-2}\ \text{cm}^2/\text{sec}}$$

$$\omega_f = 2.7\ \text{cm/sec.}$$

The time required to settle 2 m to the river bottom can then be estimated as

$$\frac{200\ \text{cm}}{2.7\ \text{cm/sec}} = 75\ \text{sec.}$$

In 75 sec, the water will travel on average

$$75\ \text{sec} \cdot 0.2\ \text{m/sec} = 15\ \text{m.}$$

Therefore, the particles will travel at least 15 m before settling. They may travel further, depending on the degree of turbulence acting to keep material in suspension.

Bottom Sediment

Many chemicals in surface waters are sorbed onto suspended particles, which ultimately settle to the bottom of the water body. The settling of particles to the bottom of a water body is a mechanism for chemical removal from the water column. The magnitude of the settling flux of a chemical is equal to the product of the rate of sediment deposition and the chemical concentration associated with the settling particles.

Particle settling can represent a significant chemical flux, especially where flocculation or low turbulence promotes the settling process. Sometimes the sediment becomes a long-term repository for the chemical; alternatively, a chemical may be degraded within the sediments, or eventually be returned to the water by a variety of *remobilization* processes.

The chemical and biological conditions that develop in bottom sediment are similar to those that occur in wetlands. The physical presence of the sediment inhibits turbulent diffusion and thus inhibits the transport of dissolved oxygen into the *pore waters* (water between the solid particles) of the sediment. At the same time, the organic matter that composes a significant fraction of most bottom sediments promotes the growth of oxygen-consuming microorganisms. The usual result is that oxygen is consumed more rapidly than it can be replenished by the relatively slow process of molecular diffusion, and anoxic conditions result. Most animal life is inhibited, except for species that obtain oxygen from above the sediment [e.g., various worms that pump water through their burrows *(irrigation)* or extend gill structures above the bottom (good for bottom-feeding fish!)]. In addition, a whole suite of anaerobic microbial processes, some of which facilitate the remobilization of certain chemicals, occur. These processes are discussed further in Section 2.4.3; see also Berner (1980).

The Sedimentary Record

In a lake, as bottom sediment is deposited, it preserves a historical record of chemical and biological conditions in the lake basin. Remains of aquatic organisms, pollen from the adjoining land, and chemicals sorbed to sediment particles all reflect past conditions. The sediment record is sequential; in the absence of events that mix the sediment, deeper sediments are older. If it is possible to determine the date at which a particular layer of the sediment was deposited, the chemical and biological information contained in that layer can be assigned to a particular time in history.

An example of a sediment record from the Aberjona watershed in eastern Massachusetts is shown in Fig. 2-12. Figure 2-12a presents the arsenic concentration in bottom sediments of the Upper Mystic Lake as a function of depth below the sediment–water interface. These data reveal several features about the history of arsenic input into the Upper Mystic Lake from its watershed. The low concentrations of arsenic below approximately 80 cm show that natural, preindustrial levels of arsenic in this lake were low, as is typical of most unpolluted lakes. High concentrations around 60 cm indicate the release of large amounts of arsenic into the watershed, from the manufacture of sulfuric acid and arsenic-based pesticides. Although the arsenic concentrations are lower in sediments deposited during the period of decline of these industries (at depths of 50 to 40 cm), it is clear that arsenic pollution from the watershed continued long after active manufacturing stopped. Furthermore, there is a second major episode of arsenic release into the lake as indicated by the high concentration of arsenic at 30-cm depth; this episode probably occurred due to the disturbance associated with earthmoving at the former industrial sites where arsenic first was released.

Figure 2-12b shows the lead concentration as a function of depth in the same lake; in this instance the large industrial source revealed by the high concentrations near a 60-cm depth in the core is superimposed on another source that rises gradually until approximately a 20-cm depth, and then declines steadily. This other source is believed to be lead deposition from leaded gasoline, whose consumption increased steadily from its introduction in the 1930s until it was phased out in the United States during the 1970s and 1980s.

Thus, as shown in Fig. 2-12, the sedimentary record can reveal much about the magnitude and temporal sequence of chemical events occurring in a lake

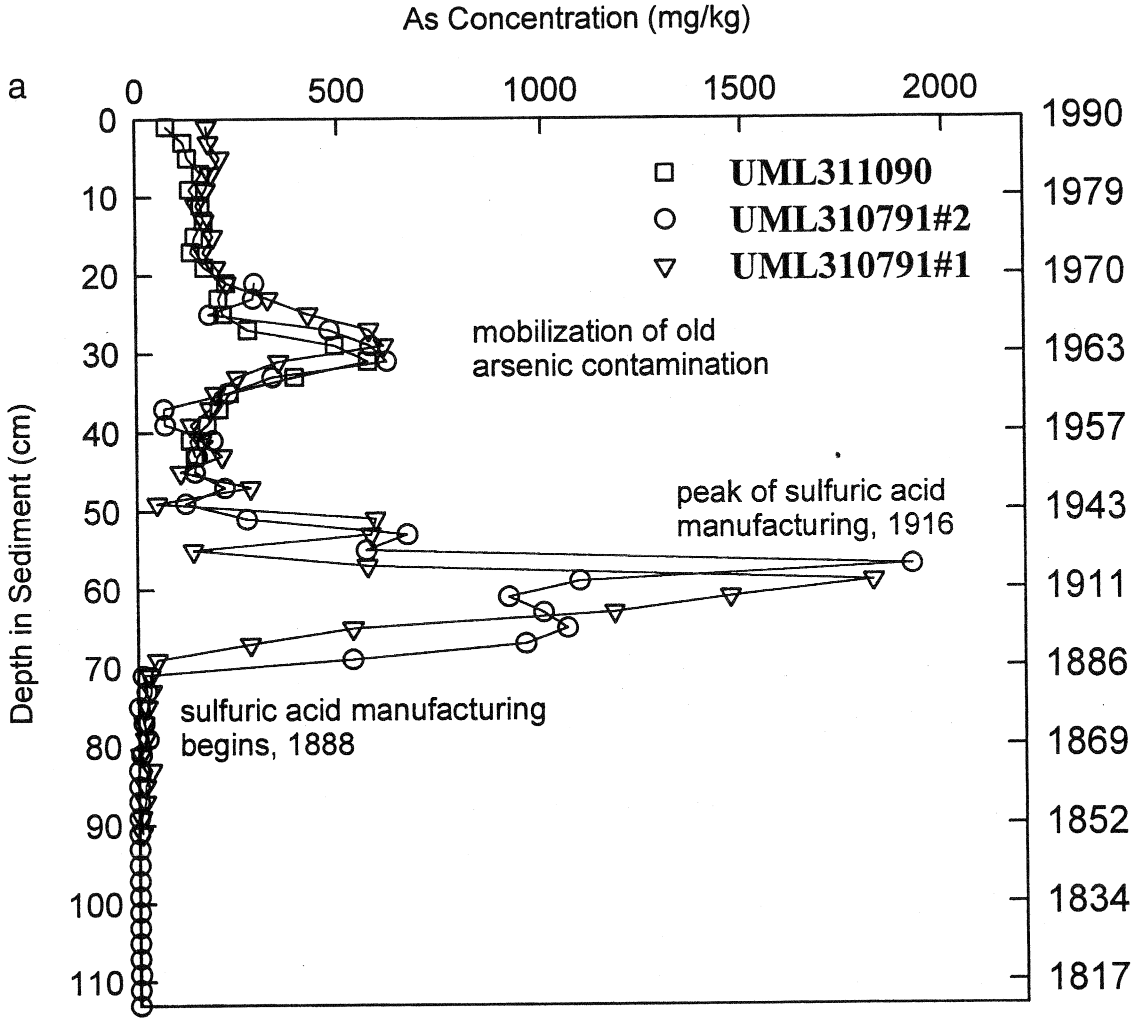

FIGURE 2-12 Arsenic and lead concentrations in bottom sediments of the Upper Mystic Lake on the Aberjona watershed in eastern Massachusetts. Figure 2-12a shows arsenic concentrations in three overlapping sediment cores, which all reflect the same high concentrations associated with particular events in the watershed. Figure 2-12b shows lead concentrations in two overlapping cores. These lead concentrations reflect both industrial activities in the watershed and regional lead deposition from the use of leaded gasoline [data from Spliethoff and Hemond (1996)] *(Figure continues)*.

and its watershed. Furthermore, it is often possible to assign actual dates to the watershed events recorded in the sediments. Among the several techniques used to date sediments (Lerman *et al.*, 1972), *lead-210 dating* is one of the most valuable. Lead-210 (^{210}Pb) dating is based on the relatively constant atmospheric deposition of this radionuclide onto surface waters, the subsequent sorption of ^{210}Pb by particles in the water, and ^{210}Pb deposition into the sediment by settling of those particles. Although several complicating factors must often be considered, the simplest case of constant annual ^{210}Pb deposition and no sediment mixing may be analyzed in a straightforward way. The ^{210}Pb concentration (as measured by its radioactivity) at any depth in the

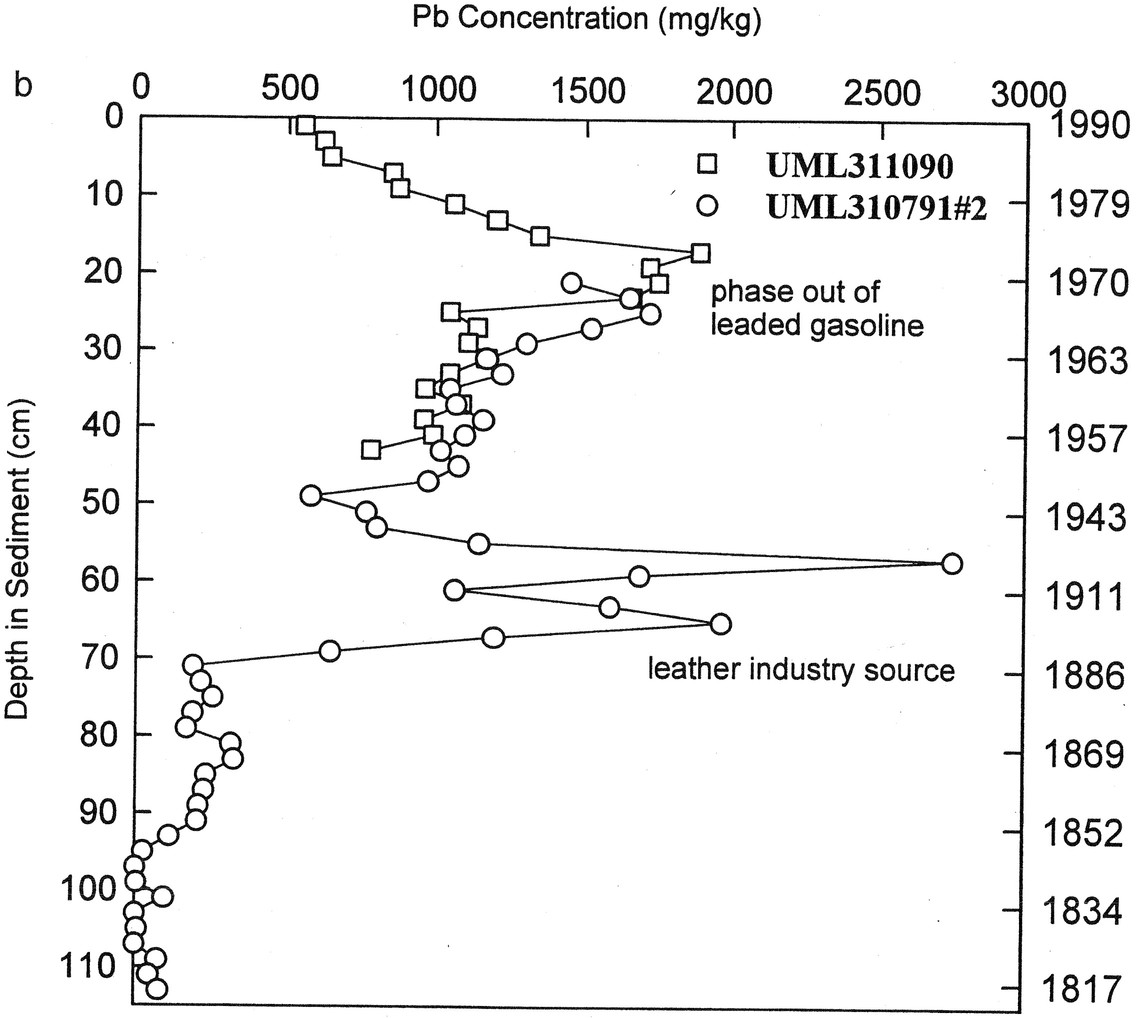

FIGURE 2-12 *(Continued)*

sediment is equal to its concentration in freshly deposited material multiplied by $\exp(-\lambda t)$, where λ is the radioactive decay constant for ^{210}Pb, which is approximately 0.03/year. (This first-order decay constant corresponds to a ^{210}Pb half-life of 22 years.) In this idealized case the age, t, of a layer of sediment at a depth d below the sediment–water interface is given by

$$t = \frac{-1}{\lambda} \cdot \ln\left(\frac{A_d}{A_0}\right), \qquad [2\text{-}26]$$

where A_0 is the ^{210}Pb activity (e.g., in becquerels per gram dry weight) at the sediment–water interface, and A_d is the activity at depth d. The amount of a nuclide that produces one nuclear disintegration event per second is 1 Bq (becquerel).