Unsaturated Zone Hydrology for Scientists and Engineers

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Chemical Properties and Principles of Soil Water

INTRODUCTION

Natural waters are never pure, always containing some type of impurity in the form of solids or gases. The quantity of such impurities determines the usefulness of water for various purposes, whether for agricultural, industrial, recreational, or personal use. Thus, the chemical properties of water become as important as the physical properties and quantity. Whereas it is commonly assumed that physical processes within a soil-water system are the dominant influences affecting change and equilibrium, chemical processes in ground and soil water have been found to be the controlling influences (Freeze and Cherry 1979).

A detailed study of water chemistry is beyond the scope of this chapter; the reader is referred to Freeze and Cherry (1979) and Stumm and Morgan (1996) for a comprehensive study of such material. The purpose of this chapter is to present the reader with a basic background in the chemical properties and principles that control the behavior of dissolved constituents in ground and soil water.

5.1 ORGANIC COMPOUNDS AND CONSTITUENTS

As a general rule, most organic compounds are those that contain carbon, with oxygen and hydrogen as the main elemental components for their structure. Humic and fulvic acids make up a large component of organics found in soil systems (see chapter 3); although little is known about them, they are not of great concern as contaminants within the unsaturated zone, even though they may be a source of contamination by complexation of heavy metals. The greatest concern for contamination in the unsaturated zone is caused by man-made organic chemicals. Most of these are in the form of pesticides, volatile organic compounds (VOCs) such as solvents or petroleum products, or semivolatile organic compounds (SVOCs) such as creosote or phenolic compounds. Adsorption, volatilization, chemical degradation, and biological uptake and degradation are mechanisms that help prevent their transport through the unsaturated zone. Most organic compounds have very low solubility in water; however, the constraints offered by low solubility are often insufficient to prevent migration to groundwater. Because many are toxic at low concentrations they often enter the biosphere, causing environmental problems.

Understanding sorption, biodegradation, and transport of organic chemicals through the unsaturated zone is essential in predicting their fate and transport in the environment. Most pesticides and other organics undergo some type of biochemical degradation, it being

the dominant mechanism of organic chemical transformation in soils and aquifers. Some organic compounds are subject to microbial degradation but others are resistant; generally, the rate of biodegradation is limited by physical and chemical processes that lower solute concentrations. These include sorption, hydrodynamic dispersion, and factors such as temperature and water content that limit physiological activity of the microbial population in soils, or lower concentrations in the solution phase. Biodegradation is also limited by factors that hinder substrate uptake by microorganisms such as hydrophobicity, and intracellular or biochemical factors that limit utilization of the compound, that is, the presence of enzyme systems. The organics of greatest concern are refractory compounds; compounds not readily degraded by bacteria within the unsaturated zone nor easily removed in water-treatment (sewage) facilities. These compounds are often relatively soluble and nonvolatile. In-situ or on-site bioremediation that uses indigenous microorganisms is a current technology being applied in an attempt to increase biodegradation of such compounds.

Transport of Organic Constituents in the Unsaturated Zone

Organic particles within a soil usually vary in size, are widely dispersed, and are heterogeneously packed (see chapter 2). In addition, the unsaturated zone has both air and water within the pores and may contain cracks, root channels, and faunal tunnels. Consequently, concentration of chemicals in the unsaturated zone may vary locally because of preferential flow, aqueous phase chemical reactions, or phase transfer of the solute (i.e., to or from solid surfaces, or to or from the gas phase).

Examining adsorption–desorption (phase interaction between liquid phase and solid phase), the one-dimensional form of the advection–dispersion equation for homogeneous saturated porous media may be written as

$$-v \frac{\partial C_i}{\partial z} + D \frac{\partial^2 C_i}{\partial z^2} - \frac{\rho}{\phi} \frac{\partial S_i}{\partial t} = \frac{\partial C_i}{\partial t} \tag{5.1}$$

where the first, second, and third terms of the equation refer to advection, dispersion, and adsorption respectively; v is the linear velocity (length/time), D is the dispersion coefficient (length^2/time), C_i is the concentration of species i (mol/L), z is the distance along the direction of flow (in length units), S_i is the concentration of species i sorbed (mol/kg), ρ is the bulk density (kg/m^3), and ϕ is the porosity. For equations 5.1 to 5.5, the porosity, ϕ, is generally expressed in terms of water-filled porosity. As a result, θ is often substituted for ϕ; where θ is water filled porosity. The third term on the left side of equation 5.1 represents concentration change in solution caused by adsorption or desorption. This term can be expressed as

$$\frac{\rho}{\phi} \frac{\partial S_i}{\partial t} = \frac{\rho}{\phi} \frac{\partial S_i}{\partial C_i} \frac{\partial C_i}{\partial t} \tag{5.2}$$

where $(\partial S_i / \partial C_i)$ can be interpreted as the linear adsorption coefficient (K_{oc}), such that

$$\frac{\partial S_i}{\partial C_i} = K_{oc} \text{ (volume/kg)} \tag{5.3}$$

If the dispersion term of equation 5.1 is set to zero so that

$$D \frac{\partial^2 C_i}{\partial z^2} = 0 \tag{5.4}$$

then, the transport–adsorption equation can be rewritten as

$$-v \frac{\partial C_i}{\partial z} = \frac{\partial C_i}{\partial t} \left(1 + \frac{\rho}{\phi} K_{oc} \right) \tag{5.5}$$
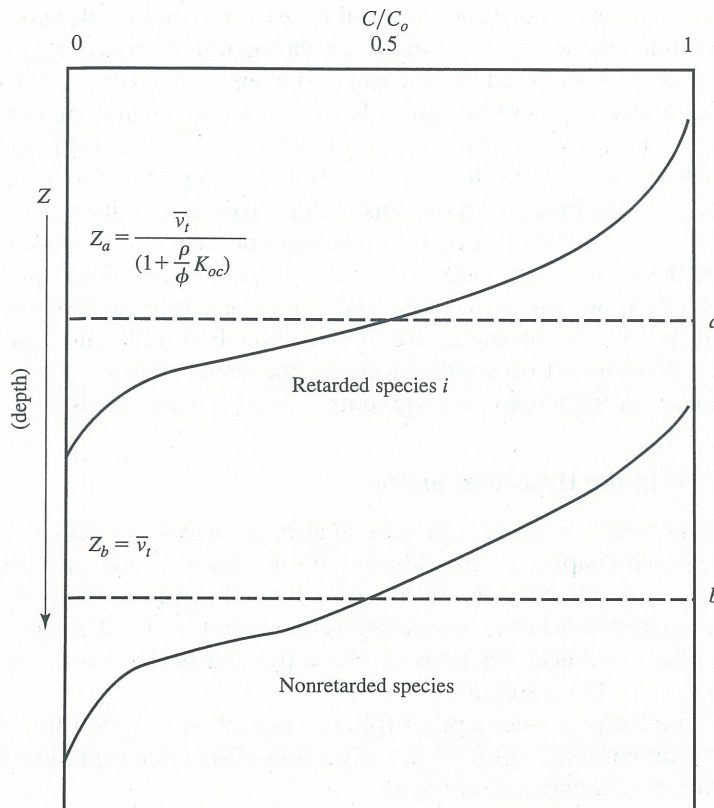
Figure 5.1   Advancing fronts of adsorbed and nonadsorbed solutes in a soil column represented by breakthrough curves where K_{oc} is the coefficient of adsorption, C is the measured concentration, C_o is the initial concentration, z is depth (subscripts a and b refer to depth of movement of retarded and nonretarded species), v is average velocity, t is time, ρ is bulk density, and ϕ is porosity

In the figure:

$$Z_a = \frac{\bar{v}_t}{\left(1 + \frac{\rho}{\phi} K_{oc}\right)}$$

Retarded species i

$$Z_b = \bar{v}_t$$

Nonretarded species

where the term in parenthesis is the retardation factor R. The retardation factor is written simply as the average linear velocity of groundwater v' over the average linear velocity of the retarded constituent v_i' (i.e., v'/v_i' or more simply, $1/R$). Generally, both velocities are measured where C/C_o is 0.5 in the concentration profile as in a breakthrough curve; see figure 5.1. The measured concentration during an experiment is C, while the initial concentration is represented as c_o. This is true only for soils; for water, we really do not have a C/C_o. In general, a conservative tracer is added along with a reactive tracer to determine v'. This is one of many models which have been proposed for investigating the transport of organics in the unsaturated zone since the 1970s. A majority of models have been written to predict biodegradation during transport through soil.

Coupled Processes

Because of the complexity involved, many models are written to include coupled processes. A coupled process is a combination of two or more of the basic flux laws (i.e., Newton's, Fourier's, or Fick's), which state that a nonuniform distribution of a state variable such as temperature produces a flux of the corresponding extensive quantity, such as heat. However, gradients of state variables corresponding to other extensive quantities, such as deformation flow, temperature flow, osmotic potential, and others can also contribute to the flux of an extensive quantity. Such phenomena are referred to as coupled processes or cross-effects. The governing differential equation that serves as the framework for most coupled-transport processes is described by

$$\left[\frac{\partial(\theta C_i)}{\partial t}\right] = [\nabla \cdot D\theta \nabla C_i] - [\nabla \cdot qC_i] - \left[\frac{\partial(\rho S_i)}{\partial t}\right] \pm \sum \Phi_i \qquad (5.6)$$

where C_i is the solution phase concentration of species i (M/L^3; L refers to length), S_i is the sorbed phase concentration of species i (M/M), t is time (T), ρ is bulk density (M/L^3), θ is the fractional volumetric water content (unitless), D is the local-scale hydrodynamic dispersion coefficient (L^2/T), q is Darcy's flux for water flow (L/T), ∇ is the Laplacian differential operator, and Φ_i is the rate(s) (M/L^{3}T) of gain or loss via various sources and sinks. A detailed discussion of coupled phenomena is beyond the scope of this text; the reader is referred to Bear and Bachmat (1991) for a complete and detailed mathematical discussion of the subject.

5.2   MASS ACTION AND GOVERNING EQUATIONS

Most chemical reactions that take place in soil water in the unsaturated zone are spontaneous, and usually proceed until a dynamic equilibrium is attained. At equilibrium, both forward and reverse reactions take place at the same rate, and concentrations then remain relatively constant over time. While this is a simple assumption to make when sampling soil-pore water, it is not necessarily true because the soil-pore water system is dynamic.

All chemical systems tend toward equilibrium. The relation that governs the relative proportions of each of these chemical reactions and their products is simple, usually written as

$$aA + bB \rightleftharpoons eE + fF \tag{5.7}$$

where a, b, e, and f are the number of moles present of each of the reactants A and B and products E and F, respectively. At constant temperature, the condition that is fulfilled at equilibrium is

$$\frac{[E]^e\,[F]^f}{[A]^a\,[B]^b} = K_c \tag{5.8}$$

where the quantities in brackets are the equilibrium molar concentrations and K_c is the thermodynamic equilibrium constant. This relation is known as the law of mass action and is very useful in the analysis of soil-water samples. The left side of equation 5.8 is termed the mass action expression. This term is constructed using the molar coefficients in the balanced equation as exponents for the appropriate concentration.

The important point to remember about the law of mass action is that there are no restrictions on the individual concentrations of any reactant or product. The only requirement for equilibrium is that when these concentrations are substituted into the mass action expression, the fraction is equal to K_c. It should be noted that a given reaction does not necessarily reach immediate equilibrium; this may take minutes, hours, even years, depending on the reactant and disturbance to the system. Additionally, any change in temperature, pressure, or both can shift the system toward a new equilibrium. If disturbances are constant, groundwater equilibrium essentially will never be reached, usually the case with soil-pore water.

When chemical reactions involve gases, the concentration of each of the reactants and the products are proportional to the partial pressures. The equilibrium expression or constant for these reactions, K_p, may be expressed similarly to that for reactions in water, except that they are written in terms of partial pressures rather than concentrations, in the form of

$$\frac{P^e E\, P^f F}{P^a A\, P^b B} = K_p \tag{5.9}$$

where P is the partial pressure (atm) and K_p is used to denote equilibrium constants derived from partial pressures, not concentrations. The rate law cannot be predicted for a chemical

reaction based on the balanced overall equation, but this does not affect the kinetic interpretation of the law of mass action. Without showing the mathematics of the proof (which can be found in any general inorganic chemistry text), one always arrives at the same requirement for equilibrium, regardless of the mechanism of the reactions.

When working with dynamic systems such as in the unsaturated zone, temperature and pressure are not always constant; they may vary at any time during the course of an experiment, especially during seasonal fluctuations in weather patterns. The basic relations which influence equilibrium due to temperature change are

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{5.10}$$

Integrating from initial temperature (T_1) to final temperature (T_2), we obtain

$$\ln \frac{K_2}{K_1} = \int_{T_1}^{T_2} \frac{\Delta H^\circ}{RT^2} \, dT \tag{5.11}$$

where ΔH° is change in enthalpy (kJ mol^{-1}), K_1 and K_2 are equilibrium constants at initial and final condition (unitless), R is the gas constant (8.314 J K^{-1} mol^{-1}), and T is temperature (Kelvin). If ΔH° is independent of temperature, we may write

$$\ln K = -\frac{\Delta H^\circ}{RT} + C \tag{5.12}$$

or

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \tag{5.13}$$

where C is a constant. When the heat capacity, C_p°, of a reaction is independent of temperature, then

$$\Delta H_2^\circ = \Delta H_1^\circ + \Delta C_p^\circ (T_2 - T_1) \tag{5.14}$$

By integrating equation 5.10 and combining with equation 5.14, we obtain

$$\ln \frac{K_2}{K_1} = \frac{\Delta H_1^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + \frac{\Delta C_p^\circ}{R} \left(\frac{T_1}{T_2} - 1 - \ln \frac{T_1}{T_2} \right) \tag{5.15}$$

or

$$\ln K = B - \frac{\Delta H_0}{RT} + \frac{\Delta C_p^\circ}{R} \ln T \tag{5.16}$$

where B and ΔH_0 are constants. When the heat capacity is a function of temperature and is given for each reactant and product in the form

$$C_p^\circ = a_i + b_i T + C_i T^2 \tag{5.17}$$

then the heat capacity can be mathematically expressed as

$$\frac{d \Delta H^\circ}{dT} = \Delta a + \Delta b T + \Delta c T^2 = \Delta C_p^\circ \tag{5.18}$$

which upon integration will yield

$$\ln K = B - \frac{\Delta H_0}{RT} + \frac{\Delta a}{R} \ln T + \frac{\Delta b}{2R} T + \frac{\Delta b}{6R} T^2 \tag{5.19}$$

where Δa is $\Sigma \, v_i a_i b_i$, ... , B and ΔH_0 are constants as before, and v_i is the stoichiometric coefficient, that is, the relative molar number. For example, one may be working with H_2SO_4; the molar number for H, S, and O would be 2, 1, and 4.

The basic relations which influence equilibrium due to pressure change are

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \overline{V_i} \tag{5.20}$$

and

$$\left(\frac{\partial \mu_i^0}{\partial P}\right)_T = \overline{V_i^0} \tag{5.21}$$

where V_i and V_i^0 are the partial molar volumes of i under actual conditions, as well as under defined standard-state conditions. The rate of change of molar volume with pressure (the standard partial molar compressibility, $\overline{k_i^0}$) is represented mathematically by

$$\overline{k_i^0} = -\left(\frac{\partial V_i^0}{\partial P}\right)_T \tag{5.22}$$

and

$$\Delta V = \sum v_i \overline{V_i}$$

$$\Delta V^0 = \sum v_i \overline{V_1^*} \tag{5.23}$$

where ΔV and ΔV^0 are the changes in volume of the reaction under actual and defined standard-state conditions. Also,

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V^0}{RT} \tag{5.24}$$

In this instance, K is the equilibrium constant. If ΔV^0 is pressure-independent, then

$$\ln \frac{K_p}{K_1} = -\frac{\Delta V^0 (P-1)}{RT} \tag{5.25}$$

If Δk^0 (where $\Delta k^0 = \sum v_i \overline{k_i^0}$) is pressure-independent, then

$$\ln \frac{K_p}{K_1} = -\frac{1}{RT}\left[\Delta V^0 (P-1) - \frac{1}{2}\Delta K^0 (P-1)^2\right] \tag{5.26}$$

However, if Δk^0 is a function of pressure, then

$$RT \ln \frac{K_p}{K_1} = -\Delta V^0 (P-1) + \Delta K^0 (B+1)(P-1) - (B+1)^2 \ln\left(\frac{B+P}{B+1}\right) \tag{5.27}$$

Here B is pressure-independent, but depends on temperature.

QUESTION 5.1

The heat capacity of N_2 can be represented by

$$C_p(N_2) = 26.984 + 5.91 \times 10^{-3}T + (-3.377 \times 10^{-7})T^2 \tag{5.28}$$

How much heat is required to heat a mole of N_2 from 300 K to 1000 K at constant pressure?

5.3   ACTIVITY COEFFICIENTS

Standard Methods

For a simple definition as applied to solutions, an activity coefficient, γ, having units of kg/mol, is a correction factor that compensates for non-ideal behavior. Ideal behavior for a solution is defined as a lack of interactions between the molecules of a liquid; that is, the

solution would behave as if any molecular interactions present had a negligible effect on the intensive properties of the solution, such as Gibbs' energy, entropy, enthalpy, or volume. However, due to the driving forces for mixing, et cetera, (ionic strength, electrostatic attraction, hydration shells, changes in entropy), very few solutions are ideal. Thus, the activity of an ion is related to its concentration and is adjusted for non-ideal behavior by an activity coefficient. Generally, if molality of a chemical is known, both equilibrium and solubility of a substance can be calculated. The chemical activity of a substance *must* be calculated before the law of mass action can be applied. The general theoretical expressions for calculation of the activity coefficient are the Debye-Hückel:

$$\log \gamma_i = -Az^2\sqrt{I} \tag{5.29}$$

Extended Debye-Hückel:

$$\log \gamma_i = -Az^2\frac{\sqrt{I}}{1 + a_i B\sqrt{I}} \tag{5.30}$$

the Güntelberg:

$$\log \gamma_i = -Az^2\frac{\sqrt{I}}{1 + \sqrt{I}} \tag{5.31}$$

and the Davies:

$$\log \gamma_i = -Az^2\left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I\right) \tag{5.32}$$

where I is the ionic strength equal to $\frac{1}{2}\Sigma\, m_i z_i^2$ (m is the molality of ith ion and z is the ion charge), $A = 1.82 \times 10^6(DT^{-3/2})$ (D is the dielectric constant), $B = 50.3(\varepsilon T)^{-1/2}$, and a is the effective diameter of the ion in angstroms. By calculation and at a pressure of one atmosphere, the values of A and B are 0.5085 and 0.3281 Å^{-1} in water at 25 °C. The range of solution ionic strength (M) for applicability is $< 10^{-2.3}$, $< 10^{-1}$, $< 10^{-1}$, and < 0.5 for the Debye-Hückel, extended Debye-Hückel, Güntelberg, and Davies' equations, respectively. It should be noted that the range given for Güntelberg is considered useful in solutions of several electrolytes, while the other equations are useful only for single-ion activities. The general relation between activity and molality may be written as $\alpha = \gamma m$, where α is the chemical activity (dimensionless), m is the molal concentration, and γ is the activity coefficient. Before $\log \gamma_i$ can be determined, I must be known or calculated. As a note of interest, the Debye-Hückel and its extension presented here are simplifications of the electrochemical equations described in chapter 3, for charged-clay particles.

Quantities that are important to the environmental scientist can be estimated from knowledge of the activity coefficients. Examples of these would include Henry's law constants, solubility limits, solution equilibria, and octanol–water partition coefficients. An often-used example of this shows that the octanol–water partition coefficient, K_{ow}, is proportional to the ratio of activity coefficients of a component α in water and octanol, described mathematically as

$$K_{ow} = 0.151\frac{(\gamma_w^\alpha)^\infty}{(\gamma_o^\alpha)^\infty} \tag{5.33}$$

where γ_w and γ_o are the infinite-dilution activity coefficients of component α in water and octanol, respectively. Octanol–water activity coefficients range in value from 0.4 to 10^7 and are dimensionless. For inorganic solutes in water at infinite dilution, the activity coefficient would be one and activity will equal molality. For a binary system (a mixture of two fluids in which interaction between ion pairs is not required), the basic equation that describes the activity coefficient is

$$G^M = RT(n_1 \ln x_1 + n_2 \ln x_2) + RT(n_1 \ln \gamma_1 + n_2 \ln \gamma_2) \tag{5.34}$$

where G^M is the energy of mixing, R is the gas constant, T is the temperature, n is the number of moles in compound 1 or 2 and x is the mole fraction, that is, $x_2 = n_2/(n_1 + n_2)$. The first term on the right-hand side of equation 5.34 is normally referred to as G^I (the Gibbs free energy of mixing for an ideal mixture), and the second term as G^E (the excess Gibbs free energy). The expression for G^E can be rewritten to obtain

$$\left(\frac{\partial G^E}{\partial n_1}\right) = RT \ln \gamma_1; \quad \left(\frac{\partial G^E}{\partial n_2}\right) = RT \ln \gamma_2 \tag{5.35}$$

Consequently, one may relate activity coefficients to composition in mole fraction.

In addition to the standard methods for calculating activity coefficients shown above, two other methods can be of value in calculations. The first is the infinite-dilution activity coefficient, described in the next section; the second is the UNIFAC (UNIQUAC Functional Group Activity Coefficients) method, which estimates the concentration dependence of γ_1 directly (see Nicolaides and Eckert 1978).

Infinite-Dilution Activity Coefficients

The infinite-dilution activity coefficient alone (see equation 5.36 and subsequent definition) can be used to estimate Henry's law constants, octanol-water partition coefficients, and solubility limits. It can also be used to estimate the parameters in any two-parameter equation, such as the van Laar equation, $g^E = [(Ax_1x_2)/\{x_1(A/B) + x_2\}]$ (Reid, Pravsnitz, and Sherwood 1977), which is used to estimate activity coefficients at any composition. The infinite-dilution method requires a knowledge of the molecular structure of the compounds involved, because it relates γ^∞ to the molecular structures of both solvent and solute molecules by using an equation that contains the number of carbon atoms (N) for the solute and solvent; if the solvent were water, with no carbon atoms, $N_2 = 0$. This equation may be written in the form

$$\log \gamma_1^\infty = A_{1,2} + B_2\frac{N_1}{N_2} + \frac{C_1}{N_1} + D(N_1 - N_2)^2 + \frac{F_2}{N_2} \tag{5.36}$$

$A_{1,2}$ is a coefficient dependent on the nature of the solute and solvent functional groups; B_2 is a coefficient dependent only on the nature of the solvent functional group; C_1 is a coefficient dependent only on the solute functional group; D is a coefficient independent of both solute and solvent functional groups; and F_2 is a coefficient essentially dependent on the nature of solvent functional groups.

If a secondary or tertiary alcohol is contained within a mixture, the C term is modified so that it becomes $C_1(1/N_1' + 1/N_1'')$ and $C_1(1/N_1' + 1/N_1'' + 1/N_1''')$ for secondary and tertiary alcohols, respectively. The "primed" Ns are the number of carbon atoms of the respective branches counted from polar groupings: such as 6 for benzene, 0 for water. A single value for C_1 will work for most primary alcohols with little loss of accuracy. The F_2 term can be similarly represented if alcohol is the solvent. Additional modifications are needed for acetals, cyclic hydrocarbons, and ketones; see Pierotti, Deal, and Derr 1959, and Reid, Pravsnitz, and Sherwood 1977. For example, a mixture of benzene and water would require a modification of equation 5.36, such that the second term on the right-hand side becomes $B_2(N_1 - 6)$, the third term becomes $C_1[1/(N_1 - 4)]$, and the remaining terms are eliminated (see Reid, Pravsnitz, and Sherwood 1977).

The basic steps to follow when calculating an infinite-dilution activity coefficient are: (1) draw the structure of the chemical involved; (2) obtain appropriate correlation constants (see table 5.1) and modify equation 5.36 if needed (see Reid, Pravsnitz, and Sherwood 1977); (3) substitute constants and modifications into equation 5.36; (4) if using an aromatic compound with water as the solvent, calculate $\log \gamma_1^\infty$ for the unsubstituted hydrocarbon, and substitute any corrections to $\log \gamma_1^\infty$; and (5) the antilog (corrected if necessary) of the $\log \gamma_1^\infty$ will yield γ_1^∞.

TABLE 5.1   Correlation Constants for Activity Coefficients at Infinite Dilution

Solute	Solvent	Temp. °C	$A_{1,2}$	B_2	C_1	D	F_2
n-primary alcohols	water	25	−0.995	0.622	0.558	0	0
		60	−0.755	0.583	0.460	0	0
		100	−0.420	0.517	0.230	0	0
Secondary alcohols	water	25	−1.220	0.622	0.170	0	0
		60	−1.023	0.583	0.252	0	0
		100	−0.870	0.517	0.400	0	0
Tertiary alcohols	water	25	−1.740	0.622	0.170	0	0
		60	−1.477	0.583	0.252	0	0
		100	−1.291	0.517	0.400	0	0
n-ketones	water	25	−1.475	0.622	0.500	0	0
		60	−1.040	0.583	0.330	0	0
		100	−0.621	0.517	0.200	0	0
n-nitriles	water	25	−0.587	0.622	0.760	0	0
		60	−0.368	0.583	0.413	0	0
		100	−0.095	0.517	0	0	0
n-alkylbenzenes	water	25	3.554	0.622	−0.466	0	0
Water	n-alcohols	25	0.760	0	0	0	−0.630
		60	0.680	0	0	0	−0.440
		100	0.617	0	0	0	−0.280
Water	Benzene	25	3.04	0	0	0	−3.14
Water	n-ketones	25	1.857	0	0	0	−1.019
		60	1.493	0	0	0	−0.730
		100	1.231	0	0	0	−0.557
Ketones	n-alcohols	25	−0.088	0.176	0.500	−0.00049	−0.630
		60	−0.035	0.138	0.330	−0.00057	−0.440
		100	−0.035	0.112	0.200	−0.00061	−0.280

Data from Pierotti, Deal, and Derr (1959) and Reid, Pravsnitz, and Sherwood (1977)

QUESTION 5.2

You have extracted a sample from a 2-m depth within the unsaturated zone using a suction lysimeter, in which the molal concentration of calcium is 0.00633. Calculate the activity coefficient γ_i and chemical activity α. Assume 25 °C, $I = 0.0281$, and $a_i = 6$ Å, that is, 6×10^{-8} cm.

QUESTION 5.3

At a chemical spill near an industrial complex, a colleague has extracted an unsaturated zone solution sample and determined it to be a mixture of benzene and water. What are the infinite-dilution activity coefficients for the system?

5.4   EQUILIBRIUM AND FREE ENERGY

When dealing with contaminant transport through the unsaturated zone, it is important to know whether the system in question is at equilibrium, or in the process of immediate change. When a system is at equilibrium, it cannot undergo a spontaneous change; in this state, any small change that may take place is said to be reversible. Any irreversible change at this point would result in an equilibrium shift, that is, the original equilibrium would be

displaced. The equilibrium of a system can be described by the entropy of a system. However, for the second law of thermodynamics at constant temperature and pressure, the Gibbs free energy, G, provides a more convenient measure of the thermodynamic property than the entropy. The Gibbs free energy of any chemical reaction represents the driving force of the reaction (the change in internal energy per unit mass), which also yields a measure of the system's ability to perform nonmechanical work.

The relation for the Gibbs free energy of a reaction (ΔG) for mixtures to the composition of the system is obtained by substituting the expression for the chemical potential, μ_i, (equal to $\partial G/\partial n_i$ at constant temperature and pressure) in terms of the species activity $\{i\}$

$$\mu_i = \mu_i^0 + RT \ln \{i\} \tag{5.37}$$

into the expression for ΔG (change in Gibbs energy of reaction)

$$\Delta G = \sum_i v_i \mu_i \tag{5.38}$$

Upon rearrangement, this yields

$$\Delta G = \Delta G^0 + RT \ln \prod_i \{i\}^{v_i} \tag{5.39}$$

ΔG^0 is the standard Gibbs free energy of the reaction. The term $\prod_i \{i\}^{v_i}$ is an algebraic short-hand for a continuation of products, also known as the reaction quotient, Q, and defined as

$$Q = \prod_i \{i\}^{v_i} = \frac{\{C\}^{v_C} \{D\}^{v_{D...}}}{\{A\}^{v_A} \{B\}^{v_{B...}}} \tag{5.40}$$

At equilibrium, $\Delta G = 0$ and the numerical value of Q is K, thus, $\Delta G^0 = -RT \ln K$. For most conditions this may be rewritten in the form

$$\Delta G^0 = RT \ln \frac{Q}{K} \tag{5.41}$$

where K is the equilibrium composition of the mixture. This is the primary relation in chemical thermodynamics of mixtures under most conditions. Thus, comparison of Q (actual composition) with K (equilibrium composition) yields a test for equilibrium conditions ($\Delta G = 0$). When comparing the standard Gibbs free energy of formation ΔG^0 at a standard-state pressure of $P^0 = 1$ bar with the value of the standard Gibbs energy of formation at $P^* = 1$ atm, it is important to know that

$$\Delta G^0 = \Delta G^* - \left[RT \ln \left(\frac{P^*}{P^0} \right) \right] \delta \tag{5.42}$$

$$\Delta G^0 = \Delta G^* - (0.109 \text{ J K}^{-1} \text{mol}^{-1}) T \delta$$

where δ is the net increase of moles of gas in the formation reaction of the substance from its elements. The standard Gibbs free energy of formation may therefore be calculated by

$$\Delta G^0 = \Delta H^0 - T \left[S^0 - \sum v_i S_i^0 (\text{element}) \right] \tag{5.43}$$

where $\sum v_i S_i^0$ (element) is the sum of the standard entropies of the elements in the formation reaction. The standard Gibbs free energies of formation, of elements in their reference states, are zero at all temperatures. Thus, for a chemical reaction to proceed spontaneously as written, there must be a net decrease in free energy; ΔG must be less than zero (negative). If $\Delta G > 0$, the reaction will proceed from right to left, when $\Delta G = 0$, the reaction is in equilibrium and will not proceed in either direction.

Occasionally, both liquid and gas samples in the unsaturated zone are difficult to obtain. In the absence of data therefore, the standard Gibbs free energy of formation of a substance may be estimated for the perfect gas state using the Benson group method (Benson 1978; Benson et al. 1969). The estimation of the standard enthalpy of formation ΔH^0 and entropy of mixing ΔS_{mix} is necessary for this procedure. Although not discussed here, the reader is free to peruse a standard physical chemistry text to refresh his or her memory on these principles.

QUESTION 5.4

As a scientist working for an environmental consulting firm, you have been assigned a project working on nitrogen dynamics in the unsaturated zone. To predict the movement of nitrates at your site and estimate the time at which the nitrate will reach ground water, the sophisticated model you are using requires the partial pressure of nitrous oxide (NO) in air. What is the equilibrium partial pressure of NO in air at 298 K using the following equation? Assume the value of $\Delta G = 77.77$ kJ mol^{-1}.

$$\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \leftrightharpoons NO(g) \tag{5.44}$$

QUESTION 5.5

Estimate the standard Gibbs energy of formation of n-pentane at 298.15 K. (In lieu of insubstantial data, one may substitute the Gibbs free energy of a closely related alcohol for this value.)

5.5   ELECTRONEUTRALITY

Equilibrium conditions between acids and bases can be described by various fundamental equations involving the law of mass action. The equations define both acidity constants and the ion product of water for a given reaction; additional equations are required to describe the concentration and the electroneutrality condition. The underlying principle of electroneutrality is that, on a large or macroscopic scale, an equal number of positive and negative charges usually exist, so that a neutral electric-charge condition exists in the solution. Perhaps the simplest example of this would be a mixture of salt and water

$$Na^+ + 2H^+ = Cl^- + O^{-2} \tag{5.45}$$

Thus, the positive charge for one species balances the negative charge of the other, to yield a condition of electroneutrality. This is more aptly expressed by

$$\sum z m_{cat} = \sum z m_{an} \tag{5.46}$$

where z is the valence of the species and m_{cat} and m_{an} represent the molality of the cation and anion species, respectively; this is the electroneutrality equation.

As a general rule, although the negative and positive charges balance out on a macroscopic scale, they will not necessarily balance on a microscopic scale that is more indicative of conditions in the unsaturated zone. For example, at low-water contents in the unsaturated zone, all charges on a particle's surface may not be satisfied through exchange with opposite charges in soil solution; complete wetting does not allow exchange to occur, or there may be occluded pockets where no exchange occurs due to lack of solution. Such conditions can cause a charge imbalance. The charge-balance error E_c, is a measure of the deviation from electroneutrality. This is normally expressed as

$$E_c = \frac{\sum z m_c - \sum z m_a}{\sum z m_c + \sum z m_a} \times 100 \tag{5.47}$$
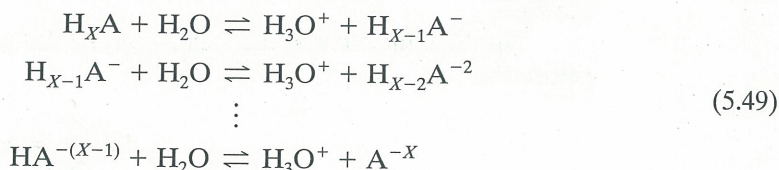
where all components have been described previously. Chemicals with no net charge, such as silicon, do not affect this relation. In certain cases a significant deviation from equality of cations and anions may occur. This is normally caused by laboratory errors in analysis, or because of high concentrations of species that may not have been included in the charge-balance calculation. Consequently, the charge balance is a good manifestation of the accuracy of data extracted from water-sample analyses. Normally, an $E_c < 5\%$ is an acceptable limit of error for many laboratory analyses, however, this is dependent on the protocol being followed and tolerance limits allowed. The charge balance applies just as well to surface-water or precipitation samples.

5.6   ACID DISSOCIATION

Chemical properties that determine acid–base interactions between a chemical and the soil matrix exert a major influence on partitioning between gaseous, solid, and solution components. The ionization of an organic acid or base can be markedly different from the corresponding neutral molecule in adsorption, bioconcentration, solubility, and toxicity characteristics. For organic chemicals that are weakly acidic, HA, the acid dissociation constant, K_a, is defined as the equilibrium constant for the reaction. For example,

$$HA + H_2O \rightarrow H_3O^+ + A^- \tag{5.48}$$
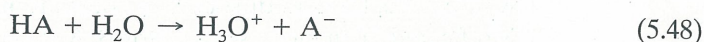
Polyprotic chemicals (chemicals that have more than one acidic proton) undergo a successive dissociation. Each dissociation has its own equilibrium constant, K. The dissociation is

$$H_X A + H_2O \rightleftharpoons H_3O^+ + H_{X-1}A^-$$
$$H_{X-1}A^- + H_2O \rightleftharpoons H_3O^+ + H_{X-2}A^{-2}$$
$$\vdots \tag{5.49}$$
$$HA^{-(X-1)} + H_2O \rightleftharpoons H_3O^+ + A^{-X}$$

As a result,

$$K_a = \frac{a_{H_3O} + a_{A^-}}{a_{HA} a_{H_2O}} \tag{5.50}$$

where a_i is the activity of species, i, in an aqueous solution. It is generally assumed that the solution is dilute enough that the activity of water is unaffected by the presence of solute(s). This is equivalent to choosing pure water at standard state, and is useful for concentrations < 0.1 M. Thus, the activity of water would be unity and equation 5.50 may be rewritten

$$K_a = \frac{(\gamma_{H_3O}[H_3O^+]) \, (\gamma_{A^-}[A^-])}{\gamma_{HA}[HA]} \tag{5.51}$$

where γ_i is the molar activity coefficient and the brackets are the molar concentration (mol L^{-1}) of species i. Further simplification of equation 5.51 can be obtained by assuming that all of the activity coefficients are unity and activities equal concentrations. Equation 5.51 then becomes

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{5.52}$$

If the ionic strength is maintained constant, it is convenient to use the apparent acid dissociation constant, K_{app}, that is expressed in terms of concentrations, such that

$$K_{app} = \frac{K_a \gamma_{HA}}{\gamma_A^-} = \frac{10^{-pH}[A^-]}{[HA]} \tag{5.53}$$

By taking the negative logarithm of both sides of equation 5.52, we get

$$-\log K_a = -\log [H^+] - \log \frac{[A^-]}{[HA]} \quad \text{also} \quad pK_a = pH - \log \frac{[A^-]}{[HA]} \quad (5.54)$$

where $pK_a = -\log K_a$. One may observe that the concentration of an organic acid in the dissociated $[A^-]$ and free $[HA]$ forms are equal when $pH = pK_a$. The ratio of A^- to HA will increase by an order of magnitude for each unit of pH above pK_a. The acid–base behavior of a weakly basic organic compound can be treated in much the same way when adding a base to water $[B + H_2O \rightarrow BH^+ + OH^-]$, so that the K_b of the base may be written as

$$K_b = \frac{\gamma_{HB} + \gamma_{OH^-}}{\gamma_B \gamma_{H_2O}} \quad (5.55)$$

The relation between the dissociation of an acid and a base can be mathematically described as

$$K_a = \frac{K_w}{K_b} \quad (5.56)$$

where K_w is the autodissociation constant of water. Consequently, a decrease in K_a for BH^+ is reflected in an increase in K_b for B. A stronger base automatically corresponds to a weaker conjugate acid. A uniform scale can be applied over the complete range of organic acid–base behavior in aqueous media by using the pK_a of the conjugate acid to measure the strength of the base.

The Hammett correlation can be used for aromatic acids to estimate K_a, and is expressed as

$$\log \frac{K_a^x}{K_a^o} = \sigma\rho \quad (5.57)$$

where the numerator is the acid dissociation constant of the substituted compound (x), the denominator is the dissociation constant of the parent compound (O), σ is the substituent constant and ρ is the reaction constant. The substituent constant is derived from the groups attached to the parent compound. For example, p-tert butyl benzoic acid has the tert butyl group $C(CH_3)_3$ attached to it, which is a hydrocarbon group: $\sigma = -0.197$. Other basic groups include carbonyl, nitrogen, halogens and alkyl halide, hydroxy and alkoxy, sulfur, phosphorus, and other miscellaneous groups. The correlation can be rewritten for problem-solving convenience such that

$$K_a^x = K_a^o 10^{\sigma\rho} \quad \text{also} \quad pK_a^x = pK_a^o - \sigma\rho \quad (5.58)$$

To estimate the dissociation of a substituted acid, one must select an appropriate parent compound with known K_a^o and ρ values; select substituent constant values, and calculate K_a^x or pK_a^x. The substituted acid will provide a suitable comparison to the compound in question, especially if you do not know the reaction constant for the compound being tested. Selecting such parameters from a similar, known compound may be prudent. For aliphatic systems, the Taft relation (Shorter 1972) can be used for estimating acid dissociation constants. Both of these methods are accomplished by applying a linear free energy relation (ΔF), which is an empirical correlation between the standard free energies of reaction $(\Delta F°)$ or activation $(\Delta F^\ddagger)$. One may remember that for an equilibrium process $\Delta G° = -RT \ln K$, and for a kinetic process $\Delta G^\ddagger$ is proportional to $-RT \ln K$. For greater insight on the process, the reader may wish to consult Wells (1968).

QUESTION 5.6

What is the dissociation constant (estimated) for 3-chloro-4-methoxyphenyl-phosphonic acid? Choose an appropriate parent compound, such as phenylphosphonic acid. Thus, $\rho = 0.755$, $pK_a^o = 1.83$, $K_a^o = 1.46 \times 10^{-2}$, and the substituent constant, σ, for 3-chloro-4-methoxy is 0.268.

5.7   HYDROLYSIS

The chemical transformation process in which an organic molecule, R—X, reacts with water to form a new carbon–oxygen bond is termed hydrolysis. When the new bond is formed, a C—X bond from the original organic molecule is detached. The reaction is typically written as

$$R{-}X \xrightarrow{\text{H}_2\text{O}} R{-}OH + X^- + H^+ \tag{5.59}$$

Hydrolysis is probably one of the most important reactions of organic compounds in aqueous solutions. It is a very significant environmental-fate process for organic chemicals. The process is similar to the transformation of nitrogen in that many reaction steps take place, thus changing the organic chemical from its original state. Some of the functional groups which can hydrolyze under environmental conditions are: amides, alkyl halides, amines, carbamates, carboxylic acid esters, nitriles, phosphonic acid esters, and sulfonic acid esters. During hydrolysis, a water or hydroxide ion (nucleophile) attacks a carbon atom, phosphorus atom, or other electrophile, which then displaces some groups such as chloride, phenoxide, and others. The displaced groups are called leaving groups.

Hydrolysis reactions usually fit within two unique patterns; these are termed S_N1 (substitution, nucleophilic, unimolecular) and S_N2 (substitution, nucleophilic, bimolecular). The S_N1 process (kinetic) is characterized by a rate independent of concentration and nucleophile nature; a rate enhancement by electron-donor substituents on the central atom; and the formation of racemic products from optically active material. The term optically active refers to the rotation of the plane of plane-polarized light when it passes through a solution. It is believed that the S_N1 pattern is a two-step process. The first step is the ionization of R—X which yields a planar carbonium ion and is the rate-determining step; the second step is a rapid nucleophilic attack on the product of the first step to form an R—OH group. This can be described by equations such that

$$R{-}X \xrightarrow{\text{slow}} R^+ + X^-$$
$$R^+ + \text{H}_2\text{O} \xrightarrow{\text{fast}} R{-}OH + H^+ \tag{5.60}$$
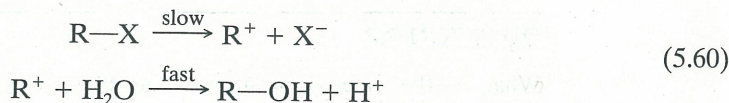
As a result, the limiting S_N1 process is favored by R— systems that form a stable carbonium ion (such as tributyl systems), by X— systems that are good leaving groups such as halide ions and sulfonate ions, and by high-dielectric-constant solvents, such as water.

For the S_N2 process, the rate is dependent on both the concentration and identity of the nucleophile and the optically active starting material. The process is essentially one step that can be described by

$$\text{H}_2\text{O} + R{-}X \rightarrow [\text{H}_2\text{O} \cdots R \cdots X] \rightarrow H^+ + R{-}OH + X^- \tag{5.61}$$
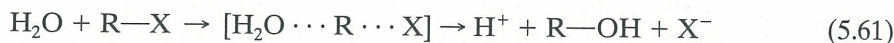
As may be seen, the S_N2 process involves a nucleophilic attack on the central atom at the side opposite the leaving groups. This limiting process is favored by R— systems with low steric hindrance and a low carbonium-ion stability (such as methyl and other alkyl (primary) systems), by X— systems that are poor leaving groups such as CH_3CH_2O—, and by organic solvents like acetone.

The rate of disappearance of R—X is proportional to the compound concentration, such that

$$\frac{-d[\text{R–X}]}{dt} = k_T[\text{R–X}] \tag{5.62}$$

where k_T is the hydrolysis rate constant. Thus, the hydrolysis of the organic chemical in water is first-order and implies that the hydrolysis half-life of R—X is independent of the R—X concentration. As a result, data obtained at one concentration (whether high or low) may be extrapolated to another concentration assuming pH and temperature are constant. The hydrolysis half-life may be determined from

$$t_{1/2} = \frac{0.693}{k_T} \tag{5.63}$$

The typical procedure for estimating the rate of hydrolysis for an organic chemical is to: **(1)** categorize the chemical in terms of functional groups; **(2)** determine if k_H (rate constant for specific acid–catalyzed hydrolysis) and/or k_{OH} (rate constant for specific base–catalyzed hydrolysis) in the groups which can be hydrolized are significant in a pH range of 5–8; **(3)** estimate k_H, k_{OH}, and/or k_o from correlations; **(4)** calculate k_T for the pH(s) of interest from

$$k_T = k_H[\text{H}^+] + k_o + k_{OH}[\text{OH}^-] \tag{5.64}$$

and **(5)** adjust for temperature, if not 25 °C. This is done by

$$\log k_{25\,°C} = \log k_{T_2} - 3830 \left(\frac{T_2 - 298}{298T_2} \right) \tag{5.65}$$

where T_2 is a temperature other than 25 °C for k_H, k_{OH}, and/or k_o. Also, T_2 is in K and an average of $\Delta H^‡$ or E_A value of 17.5 kcal mol^{-1} is also inherently assumed.

QUESTION 5.7

What is k_H and the estimated hydrolosis half-life for ethyl p-nitrobenzoate? (Assume $k_H^o = 10^{-7}\,\text{M}^{-1}\,\text{s}^{-7}$ for ethyl benzoate in water at 25 °C, $\rho = 0.11$ for ethyl benzoate hydrolysis, $\sigma = 0.778$ for a p-nitro substituent.)

QUESTION 5.8

What is the rate constant for the hydrolysis of methyl p-nitrobenzoate? (Assume $k_{OH}^0 = 7.2 \times 10^{-3}\,\text{M}^{-1}\,\text{s}^{-1}$, $\rho = 2.38$, and $\sigma = 0.778$.)


QUESTION 5.9

Estimate the rate constant for neutral hydrolysis, k_o, for p-methylbenzyl chloride. (Assume $k_o^0 = 6.2 \times 10^{-6}\,\text{s}^{-1}$, 25 °C, $\rho = -1.31$, and $\sigma = -0.17$.)

5.8   ION COMPLEXES AND DISSOLVED SPECIES

In soil-pore water and ground water, many ion complexes may form. These may be familiar from the study of ground water and saturated water flow. A typical example would be that of $CaSO_4^0$, which forms as a result of the presence of Ca^{2+} and SO_4^{2-} within soil-pore water. Other examples would be CO_3^{2-} complexes which may include $CaCO_3^0$, $MgCO_3^0$, or $NaCO_3^-$, depending on the constituents present.

Complexations of metal ions released to the unsaturated zone through agricultural and industrial activities is of primary concern to the unsaturated-zone hydrologist. Such complexation occurs between dissolved metal ions and mineral or organic hydroxyl groups exposed at soil surfaces. As an example, dissolved Cu^{2+} might react with such a group, designated S—OH according to the reaction

$$S\text{—}OH + Cu^{2+} \rightleftharpoons S\text{—}OCu^+ + H^+ \tag{5.66}$$
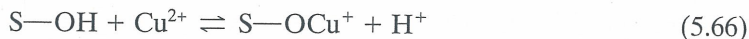
with a resulting equilibrium constant of (based on the law of mass action; Stumm and Morgan 1996)

$$K_{Cu} = \frac{(S\text{—}OCu^+)\,[H^+]}{(S\text{—}OH)\,[Cu^{2+}]} \tag{5.67}$$

Note that this reaction results in a surface-charge imbalance, with the surface having a net positive charge. A bidentate surface complex, as described by the reaction below,

$$2S\text{—}OH + Cu^{2+} = (S\text{—}O)_2Cu + 2H^+ \tag{5.68}$$
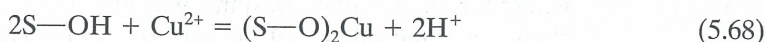
may occur simultaneously. This complex results in charge neutrality at the surface.

A good example of mineral surface hydroxyl groups is that of Fe(III) oxide; when acting as the central ion of a mineral surface, it results in the hydroxyl group $\equiv Fe\text{—}OH$, which acts as a Lewis acid and exchanges its structural OH against other ligands.

Because of the surface-charge imbalance created by the reaction given in equation 5.66, sorption of cations is affected by Coulombic forces that repel additional cations from the charged surface, and the equilibrium constant, K, must be corrected. This is accomplished by converting the law-of-mass-action equation first into a Langmuir-type equation, and then into a Frumpkin-type equation (Stumm and Morgan 1996) to correct for electrostatic effects. Consider again a reaction involving dissolved copper ions, such that

$$SH + Cu^{2+} \rightleftharpoons SCu^+ + H^+ \tag{5.69}$$

Then (by the law of mass action),

$$\frac{K_{Cu}}{[H^+]} = \frac{[SCu^+]}{[SH]\,[Cu^{2+}]} \tag{5.70}$$

and

$$[SH] + [SCu^+] + [S^-] = S_T \tag{5.71}$$

where S_T is the maximum concentration of surface sites, S represents the adsorption sites on the solid surface occupied by hydrogen ions, and SCu^+ represents the surface sites occupied by copper ions, and S^- are the sites where hydrogen ions have been removed through the process of mass action (i.e., exchange). The brackets, [ ], denote concentration, which for surface concentrations, may be expressed as moles/L solution, per kg solid; per m^2 of solid surface; or per mole of solid.

In most natural systems, either [SH] or [S^-] dominates, dependent on the nature of the surface and the pH. For surfaces dominated by iron and aluminum hydrous oxides, the concentration of SH_2^+ may be significant at low pH. Such sites are especially important in anion sorption; however, for most oxides in the normal pH range found in soils, [S^-] $<<$ [SH]. Consequently,

$$[SH] + [SCu^+] \approx S_T \tag{5.72}$$

S_T may be used to formulate a Langmuir type equation for

$$[SCu^+] = \frac{S_T K_{Cu}\,[H^+]\,[Cu^{2+}]}{1 + K_{Cu}\,[H^+]\,[Cu^{2+}]} \tag{5.73}$$

By definition, Γ_{Cu} is the surface concentration of copper which is $[SCu^+]$/mass of adsorbent and Γ_{max} is S_T/mass of adsorbent; consequently, one may write

$$\Gamma_{Cu} = \frac{\Gamma_{max}K_{Cu}[H^+][Cu^{2+}]}{1 + \frac{K_{Cu}}{[H^+]}[Cu^{2+}]} \quad (5.74)$$

Thus, K_{Cu} is now the surface (intrinsic) complex formation constant, and when divided by $[H^+]$ it is the adsorption constant for that $[H^+]$. This intrinsic equilibrium needs to be corrected for Coulombic effects, resulting in the apparent equilibrium constant, K_{ap}, as a Frumpkin-type equation

$$K_{ap} = K_{it} \exp\left(-\frac{\Delta_C F\psi}{RT}\right) \quad (5.75)$$

where F is the Faraday constant ($96,490$ C mol^{-1}), ψ is the surface potential (V), and Δ_C is the change in ionic valence of the surface species. For our example of the complexation of copper ions, the equation becomes

$$\frac{[SCu^+]}{[SH][Cu^{2+}]} = \frac{K_{Cu(ap)}}{[H^+]} = \frac{K_{Cu}}{[H^+]}\exp\left(-\frac{F\psi}{RT}\right) \quad (5.76)$$

The surface charge (ψ) cannot be measured experimentally. A potential candidate, the zeta potential (ζ) can be determined from electrophoretic measurements, but is smaller than ψ. However, ψ may be estimated from the surface charge of the medium, based on the constant capacitance model, $\psi = \sigma/C$, where σ is surface charge per unit area and C is surface capacity or capacitance per unit area. Surface charge is given (if $[SCu^+]$ is in units of moles/kg of absorbent,) by the equation $\sigma = F[SCu^+]/s$, where s is surface area of absorbent in m^2/kg. Surface capacity is given by the equation $C = \varepsilon\kappa/4\pi$ (Adamson 1990), where ε is permittivity of the fluid and κ is the Debye kappa, which is dependent on the concentration (as well as the valence) of ions in solution (see chapter 3). Thus, $\psi = (4\pi F[SCu^+])/s\varepsilon\kappa$. Substitution into equation 5.76 gives (if $[SCu^+]$ is written as θS_T)

$$\frac{[SCu^+]}{[SH][Cu^{2+}]} = \frac{K_{Cu(ap)}}{[H^+]} = \frac{K_{Cu}}{[H^+]}\exp\left(-\frac{4\pi F^2\theta S_T}{\varepsilon\kappa RT(s)}\right) \quad (5.77)$$

5.9 DIFFUSSION

Two types of diffusion are discussed in this text. The first type is the diffusion of solutions which will be discussed in brief here; the second type is the diffusion of particles (more accurately termed surface mobility). In the general process of diffusion that is commonly referred to as the molecular diffusion of solutions, ionic constituents are forced to move in the direction of a concentration gradient due to kinetic activity. Typically, the relative contribution of diffusion to transport is greatest in slow-flow conditions. Diffusion of a substance will continue to equilibrium (i.e., where no concentration gradients exist and there is no driving force). The transport of a molecule from one region to another involves work. The work of transporting a mole of solute from a zone where its chemical potential is $\mu(1)$ to a zone where its chemical potential is $\mu(2)$, is equal to $\mu(2) - \mu(1)$. Normally, the chemical potential of a substance in the vadose zone is a function of distance in the system; the work required to transfer a mole from x to $x + dx$ may be expressed as

$$d\mu = \mu(x + dx) - \mu(x) = [\mu(x) + (d\mu/dx)\,dx] - \mu(x)$$
$$= (d\mu/dx)\,dx \quad (5.78)$$

Because the work is equal to the negative of force × distance, the negative gradient of the chemical potential is also a force. For an ideal solution, $\mu = \mu^0 + RT \ln c$. Thus, the force is given by

$$F = \frac{d\mu}{dx} = -\frac{RT}{c}\frac{dc}{dx} \qquad (5.79)$$

where R is the gas constant, T is temperature in Kelvin, c is concentration, and dc/dx is the concentration gradient. The force opposing the diffusion of a molecule is the velocity, v, times the frictional coefficient, f. By setting these forces for a molecule equal to each other, one obtains

$$vc = -\frac{RT}{N_A f}\frac{dc}{dx}; \qquad fv = -\frac{RT}{N_A c}\frac{dc}{dx} \qquad (5.80)$$

where N_A is Avogadro's number. The relation expressed in these two equations corresponds to Fick's first law:

$$J = -D\frac{dc}{dx} \qquad (5.81)$$

where J is the flux written in terms of mass of solute per unit area per unit time $[M/L^2 T]$, D is the diffusion coefficient $[L^2/T]$, and c is the solute concentration $[M/L^3]$; dc/dx is the concentration gradient. There is a relation here with Fick's second law (the continuity equation) and electric mobility, which will be discussed in greater detail in chapter 11.

5.10 SOLUBILITY

Water solubility is one of the most important parameters affecting the fate and transport of organic chemicals in the environment. The greater the solubility of the chemical, the more rapidly it will be dispersed in the hydrologic cycle. Generally, the higher the compound's solubility, the lower the adsorption coefficient, thus, the more easily it is degraded by soil microorganisms. Also, compounds that are sorbed to the particle surface are more likely to be completely degraded because the residence time of the compound in the soil is longer. But the higher the solubility, generally the weaker the attachment of the compound to the particle, which makes it a readily usable form of energy for microbes. Solubility is essentially the maximum amount of a chemical that will dissolve in pure water at a specific temperature. If the organic chemical is a solid or liquid at the specified temperature, two phases will exist at equilibrium: a saturated aqueous solution, and a solid or liquid organic phase.

The concentration of an aqueous solution is normally expressed on a mass-per-mass basis (such as weight percent, g/kg, et cetera), or mass-per-volume basis (mg L^{-1}, et cetera). Most organic chemicals are soluble in water to a certain extent; solubility may range from extremely low concentration to 100,000 mg L^{-1} and higher. Thus, many orders of magnitude in variation may be involved, depending on the chemical being measured. Several methods may be used to determine the solubility coefficient, S, of a given chemical. These methods include regression equations which are based on fitting equations of a specified form to experimentally measured solubilities, addition of atomic fragments to the solution, and theoretical equations using estimated activity coefficients. Only the latter method allows calculation of solubility at any temperature. The other methods yield a suitable answer only if the data have been collected over a range of temperatures, preferably ranging from about 5–35 °C. No one method can be recommended as "best" for determination of S, due to the special problems that arise when estimating S for hydrophobic compounds, various methods may yield different values, and many organic compounds become more soluble as temperature increases.

Caution must be used when determining S; for example, the magnitude of the equilibrium constant is not a good indication of one chemical's solubility in water compared to that of another chemical. This is because, in the equilibrium relation, the activity of the molecule is raised to the power of the number of moles in the dissociation expression. Additionally, great differences in solubility between minerals are commonly found in groundwater and organic chemicals. As an example, gypsum has a solubility of 2200 mg L^{-1} in water, and is widely used to flocculate soils to enhance greater root growth and improve drainage without altering their pH. In comparison, the pesticides parathion, atrazine, and methoxychlor (an organochlorine), have solubilities of 24, 33, and 0.003 mg L^{-1}, respectively.

Factors affecting solubility of organic chemicals include temperature, salinity, dissolved organic matter, chemical of the organic compound, and pH. Solubility will either increase or decrease at higher temperatures depending on the nature of the chemical being measured. The presence of dissolved salts normally leads to moderate decreases in S. The general relation between salinity and solubility may be expressed as

$$\log \frac{S^0}{S_1} = K_S C_S \tag{5.82}$$

where S^0 is the molar solubility (mg/L) in pure water, S^1 is the molar solubility (mg/L) in salt solution, K_S is the salting parameter (generally ranging from ~ 0.04 to 0.4), and C_S is the molar salt concentration (M/L^3). The presence of dissolved organic material such as humic and fulvic acids may lead to an increase in solubility for many organic chemicals. In general, solubility of organic acids tends to increase with pH, but the solubility of organic bases tends to decrease.

Determination of solubility for a solid in a liquid solvent is different than the method previously discussed. Not only is solubility a function of temperature, but the heat of fusion of the solute also must be considered, since energy is required to overcome intermolecular forces of molecules within the solid as it dissolves. In this case, it is fairly typical for the chemical with the high heat of fusion to have a lower solubility. Assuming one knows the heat of fusion ΔH_f, the melting point, T_m (in Kelvin), and the activity coefficient γ_1 (as a function of composition), the solubility denoted as x_1 (in mole fraction) may be obtained from

$$\ln \gamma_1 x_1 = \frac{\Delta H_f}{RT}\left(\frac{T}{T_m} - 1\right) \tag{5.83}$$

where T is the system temperature (in kelvin) and R is the gas constant. Equation 5.83 neglects certain correction terms which are proportional to Δc_p (the specific heat difference between liquid and solid) because these data are likely unavailable. However, the uncertainties and errors associated with these omissions will likely be small. The solution of equation 5.83 for x_1 must be by trial-and-error because γ_1 is a function of x_1. The estimation procedure involves: **(1)** the estimation of γ_1 for various values of x_1 to obtain a plot; **(2)** calculating the value of the right-hand side of equation 5.83; and **(3)** using calculated and interpolated values of γ_1 (step 1) to determine $\ln \gamma_1 x_1$ that will match the value from step 2. If no value is found that matches the right-hand side, the two chemicals are completely miscible at the specific temperature. Set $\gamma_1 = 1$ as a first estimate of x_1.

QUESTION 5.10

Using the regression equation $\log S = -0.922 \log K_{ow} + 4.184$ (good for many pesticides), what is the solubility of atrazine?

QUESTION 5.11

What is an estimation of the mole fraction solubility of naphthalene in 1-butanol at 40 °C? Assume $T_m = 353.4$ K, $\Delta H_f = 4494$ cal mol^{-1}, $\gamma_1 = 3.85$ mole fraction, and $x_1 = 0.111$ mole fraction.

5.11   CHEMICAL SATURATION

To determine whether a solution is saturated, one must ascertain the free energy of dissolution; that is, whether or not the dissolution of the solid phase is negative, zero, or positive. As mentioned in section 5.4, the free energy of dissolution is given by $-\Delta G = RT \ln Q/K$. The extent of saturation may be expressed by a saturation index, S_{id}, which is expressed as

$$S_{id} = \frac{Q}{K_{eq}} \tag{5.84}$$

If S_{id} (the ratio of Q/K) is positive ($Q/K > 1$), the solution is oversaturated and precipitation will occur; if $Q/K < 1$, the solid will continue to dissolve; and if $Q/K = 1$, the solution is at equilibrium.

For reactions that involve a solid phase, one can compare Q (ion activity product: IAP; also expressed as the solubility product, K_{sp}) with K_{eq} and can thus define the state of saturation. An example of this would be

$$CaCO_3 \text{ (solid)} + H^+ = Ca^{2+} + HCO_3^-$$

we can then write ΔG or the saturation index, S_{id} as

$$-\Delta G = S_{id} = RT \ln \frac{[Ca^{2+}]_{act}[HCO_3^-]_{act}[H^+]_{eq}}{[H^+]_{act}[Ca^{2+}]_{eq}[HCO_3^-]_{eq}} = \frac{[Ca^{2+}]_a[HCO_3^-]_{act}}{[H^+]_{act}\,K_{eq}} \tag{5.85}$$

where the subscript *act* refers to actual activity and *eq* to activity at equilibrium. A simple test would be to compare either the actual concentration (or activity) of an individual reaction component such as H^+ with the concentration if it were in theoretical solubility equilibrium. Using this method, the state of saturation for calcite ($CaCO_3$) would be written in terms of $pH_{act} - pH_{eq}$. The resulting positive, negative, or zero value would have the same effect as discussed above: precipitation for a positive value; continued dissolution for a negative value; and equilibrium of solution for a zero value. Thus effectually, one may determine S_{id} by measuring the pH change upon addition of solid calcite.

5.12   OXIDATION AND REDOX REACTIONS

Oxidants and reductants are defined as electron, donors and electron acceptors. For purposes of our discussion, it should be remembered that an electron (e) has a negative charge and that there are no free electrons; thus, every oxidation reaction is accompanied by a reduction. The oxidation state of a species represents the hypothetical charge of the atom upon dissociation of the ion. The rules for assigning oxidation states can be found in any general college inorganic chemistry text; the student may wish to review these before proceeding further. Since every oxidation is accompanied by a subsequent reduction, there is always a balance of electrons. Using iron as an example, the oxidation state (written in half-reactions) is expressed as

$$4Fe^{2+} = 4Fe^{3+} + 4e$$

with the reduction state written as

$$O_2 + 4H^+ + 4e = 2H_2O$$

thus, the balanced, or redox, reaction is

$$O_2 + 4Fe^{2+} + 4H^+ = 4Fe^{3+} + 2H_2O$$
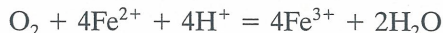
Most redox reactions that occur in ground water incur the use of oxygen. However, hydrogen is involved in many redox reactions as H^+, and other elements such as C, S, N, Mn, and Fe are involved in electron transfer. While surface water generally exhibits oxidizing conditions due to mixing with oxygen at its surface, water within soil pores often has reduced conditions because of decreasing oxygen content within the vadose zone. The oxygen that is present is normally consumed by biochemical and hydrochemical reactions.

As water content within the unsaturated zone increases, the availability of oxygen as an electron acceptor is severely restricted. This is particularly true in arid regions which have saline or sodic soils and low hydraulic conductivity. The increased wetting of a soil where seepage discharge is occurring and which contains decomposable organic matter, will cause an onset of anaerobic conditions because soil microorganisms that decompose the organic matter consume the available free oxygen in soil/ground water more rapidly than additional oxygen can diffuse from the land's surface into the wet soil. Typically, if microorganisms are respiring aerobically, the final electron sink is oxygen, which accepts electrons and converges with hydrogen to yield water. Thus, aerobic respiration involves the reduction of O_2 to water. If oxygen is deficient within the vadose zone, other substances can accept electrons and become reduced. Examples of this would be nitrate (NO_3^-) to nitrite (NO_2^-), sulfate to sulfide: $SO_4 + 8e + 10H^+ = H_2S + 4H_2O$; and H to H_2: $2H^+ + 2e = H_2$.

In the event of an oxygen deficiency in soil containing organic matter, the organic compounds present are no longer fully oxidized to carbon dioxide and water, but rather to intermediate products. These products are normally polycarboxylic acids, alcohols, simple fatty acids, et cetera. Further decomposition of these compounds will continue as methane and other hydrocarbons are produced in the soil. As a result, very wet and flooded soils may contain inorganic and organic compounds in reduced form.

The tendency of a solution to exchange electrons can be measured by its redox potential, E_h (measured in volts). The transfer of electrons is an electric current, and the more strongly reducing a substance, the lower its electric potential. As discussed earlier, the sign of the potential is positive in oxidizing reactions, and negative in reducing reactions. The standard potential, E^0, has been measured for many reactions at standard temperature and pressure. The total oxidation potential of a reaction is given by the Nernst equation, expressed as

$$E_h = E^0 + \frac{RT}{zF} \ln K_{eq} \qquad (5.86)$$

where F is the Faraday constant (96,790 C/mol), z is valence, and K_{eq} is the equilibrium constant; in some references, K_{eq} is also termed the solubility product of the mineral, K_{sp}. The oxidation potential can be measured quickly and easily with a standard specific-ion electrode meter. The E_h of a specific solution is the difference in voltage between a platinum electrode and a hydrogen reference electrode; however, for convenience a calomel reference electrode is usually used to obtain this difference. Since the voltage difference between a calomel and a hydrogen electrode is 0.248 V, $E_h = E$ measured + 0.248 V. The transfer of electrons in a solution usually induces a transfer of protons as well, thus the redox potential depends on solution pH. As a result, E_h in well-aerated solutions decreases linearly by 59 mV for each pH-unit rise in solution. This relation usually holds well for aerated soil.

Numerous reduction reactions can occur within the vadose zone when it becomes anaerobic; these reactions depend on the redox potential at which the compound of interest

is most strongly held. Compounds held at high redox potential, with their reactions going to completion before similar compounds held at a lower redox potential, can be important. The primary inorganic reactions (reductions) that occur in the unsaturated zone, when it becomes anaerobic, are: ferric hydroxide to ferrous ions; hydrogen ions to hydrogen gas; nitrate to nitrite; sulfate to sulfite to sulfide; and manganic salts or manganese dioxide to manganous ions. The reactions for both iron and manganese are reversible in the soil system. Once nitrate has been reduced to nitrite, it can easily be reduced further, and lost from the system as nitrous oxide gas. Likewise, sulfite is more easily reduced than sulfate. The reduction of sulfite to sulfide, in the absence of ferrous iron, can be lost as hydrogen sulfide gas. As a result, nitrate (always) and sulfate (sometimes) reductions are irreversible processes within the unsaturated zone.

The reduction of organic components within the unsaturated zone is much more complex than the reduction of inorganic compounds due to the wide sequence of reduction products normally involved. As the unsaturated zone first becomes very wet or flooded, decomposition will begin and a number of gases will be given off; typically, these will be nitrous oxide, hydrogen, and a range of low-molecular-weight hydrocarbons such as methane, ethane, ethylene (the latter having a marked effect on root growth), propane, and so on. However, production of these hydrocarbons will occur only in the initial stages of flooding and decreases rapidly until production ends within several days. Experimental results by Tindall, Petrusak, and McMahon (1995) comparing clay and sandy soils indicate that gases such as nitrous oxide are given off in larger quantities under mild reducing conditions than compared to stronger reducing conditions. Soils high in nitrate, or soils to which nitrate fertilizers have been added, maintain a redox potential of about +400 to +200 mV until all nitrate has been reduced and then the potential may fall rapidly; this may only take a few weeks (Couto, Sunzonowicz, and De O. Barcellos 1985). It is important to note that microorganisms are responsible for catalyzing most of the important redox reactions that occur within the unsaturated zone. Also, the microorganisms help to decompose the organic matter which may be present in the unsaturated zone.

In order to achieve reduction of inorganic constituents, other compounds must be oxidized; these other compounds are usually organic matter. The oxidation of organic matter is catalyzed by enzymes, soil bacteria, and other microorganisms deriving their energy by expediting the electron transfer. The dissolved oxygen in the unsaturated zone often decreases with depth, and the oxidation of even a small amount of organic matter can completely consume all of the oxygen present. Additionally, almost all of the reduction processes discussed regarding nitrate, sulfide, et cetera, consume oxygen and produce hydrogen gas, with little change in pH. In the root zone or near-surface area of the unsaturated zone, infiltrating water is in perpetual contact with organic matter, causing continual consumption of oxygen and production of carbon dioxide. The production of carbon dioxide will yield carbonate and bicarbonate.

5.13   MICROBIAL MEDIATION AND pH

Microorganisms act primarily as redox catalysts; they cannot carry out specific reactions that are not thermodynamically possible. Consequently, these organisms do not oxidize or reduce, they simply mediate electron transfer. For example, many species of bacteria found in soils are capable of reducing nitrates to nitrogenous gases (NO, N_2O, N_2), which are then released into the atmosphere. This dissimilatory reduction process is known as denitrification. The denitrifying bacteria that bring about these reactions are obligately aerobic, except for the ability to utilize nitrate in the absence of oxygen. Nitrate acts in lieu of oxygen as a terminal acceptor of electrons produced during anaerobic respiration. Denitrification is promoted by high soil-moisture conditions, neutral soil pH, high soil temperatures, a low oxygen-diffusion rate, the presence of organic matter, and nitrate. The amount of nitrogen

gas released from soils under normal aerobic conditions found within the upper horizon of the unsaturated zone can vary widely, 5–50% of applied nitrate (Mengel and Kirkby 1982). The release of nitrogen gases is generally lower on well-aerated sandy soils than in clay soils; however, physical parameters and soil characteristics can change this. Lower rates of release of nitrogen gases generally indicates a lack of efficient biological activity or mediation within the soil due to reduced water content, unavailable nutrient source for microorganisms, occluded pore spaces which reduce microbial activity, and other factors (Tindall, Petrusak, and McMahon 1995). As a result, denitrification must occur indirectly such as the reduction of nitrate to nitrite, with a subsequent reaction of nitrite with ammonium to produce nitrogen gas and water. The conversion of nitrate to nitrogen gas is nonreversible, thus NO_3^{-2}—N_2 cannot be used as a reliable redox indicator.

The dominant types of microorganisms present are dependent on environmental conditions. As with most living organisms, they compete with each other in all types of conditions. An example of this is the predominance of fungi rather than bacteria at lower pH. It is not that the fungi particularly thrive more; the fundamental reason is that there is less competition from bacteria at the lower pH. The environmental factors of temperature, pH, ionic strength, and oxygen concentration influence the rate of biologically mediated transformations and also dictate whether these processes operate within the time frame of interest.

The effect of pH on microbial activity is very important. For example, organic matter will frequently develop on the surface of strongly acid soils that result from the acidifying effects of fertilizers or rainfall (rainfall produces a weak carbonic acid whose pH can decrease with time). In the absence of microorganisms and soil fauna such as earthworms, organic debris accumulates on the surface layer; in the presence of these organisms, the organic matter is distributed throughout the upper horizon depending on adequate oxygen and other environmental parameters. There is substantial evidence that fresh organic matter initially decomposes more slowly in strongly acid soils (pH 3.0 to 4.0) than in soils with pH values greater than 5.0. This is due primarily to a reduced microbial population. The same is true of certain chemical transformations within the unsaturated zone. Evidence suggests that a general pH range of 5.5 to 8.0 is the best range for the occurrence of nitrogen transformations (Mengel and Kirkby 1982). Because nitrogen transformation processes are mediated by bacteria, this general range is the same as that at which there seems to be the greatest microbial activity. Hence, degradation, reduction, oxidation, and transformation processes can be severely limited by pH.

SUMMARY

In this chapter, we discussed how the chemical properties of water become as important as the physical properties and quantity. Also, though it is commonly assumed that physical processes within a soil–water system are the dominant influences affecting change and equilibrium, it has often been found that chemical processes in ground and soil water are the controlling influences (Freeze and Cherry 1979).

We discussed organic compounds, along with humic and fulvic acids, all of which make up a large component of organics found in soil systems (see chapter 3). Although little is known about these compounds, they are not of great concern as contaminants within the unsaturated zone, but may be a source of contamination by complexation of heavy metals. The greatest concern for contamination in the unsaturated zone comes from man-made organic chemicals in the form of pesticides, volatile organic compounds such as solvents or petroleum products, or semivolatile organic compounds such as creosote or phenolic compounds. We also explained mechanisms such as adsorption, biodegradation, and so on, which help prevent transport of organics through the unsaturated zone.

We covered spontaneous reactions that usually proceed until a dynamic equilibrium is attained, as well as the relation that governs the relative proportions of compounds of chemical reactions and their products. Because very few solutions in nature are ideal, we illustrated how the activity coefficient related to a compound's concentration is a correction factor which compensates for nonideal behavior. (Ideal behavior for a solution is defined as a lack of interactions between the molecules of a liquid; that is, the solution would behave as if any molecular interactions present had a negligible effect on the intensive properties—Gibbs energy, entropy, enthalpy, and volume—of the solution.)

We also explained how the equilibrium of a system can be described by the entropy of a system and that, for the second law of thermodynamics at constant temperature and pressure, the Gibbs free energy, G, provides a more convenient measure of the thermodynamic property than the entropy. Also, the Gibbs free energy of any chemical reaction represents the driving force of the reaction (the change in internal energy per unit mass), which yields a measure of the system's ability to perform nonmechanical work.

We described the law of mass action, which illustrates equilibrium conditions between acids and bases, as well as the underlying principle of electroneutrality, which shows that there is generally an equal number of positive and negative charges so that a neutral charge condition exists in a solution. We discussed how chemical properties that determine acid–base interactions between a chemical and the soil matrix exert a major influence on partitioning between gaseous, solid, and solution components; and how hydrolysis, one of the most important reactions of organic compounds in aqueous solutions, is the chemical transformation process in which an organic molecule, R—X, reacts with water to form a new carbon–oxygen bond.

This chapter described how ion complexes may form, depending on the constituents present, and that in the unsaturated zone, the focus is generally more on metal-ion complexes which may be the result of agriculture and industry, such as copper and iron-hydrous oxides.

Additionally, we explained diffusion and its relative contribution to transport, which is greatest in slow-flow conditions (diffusion of a substance will continue to equilibrium; that is, where no concentration gradients exist and there is no driving force). Following this, we described water solubility, which substantially affects the fate and transport of organic chemicals in the environment, and described how the greater the solubility of the chemical, the more rapidly it will be dispersed in the hydrologic cycle. We also discussed was solution saturation, where the extent of saturation is expressed by a saturation index, S_{id}; that discussion was followed by oxidation and redox reactions, each being defined as electron donors and electron acceptors. Finally, we ended the chapter with a discussion of microbial remediation and pH: how microorganisms act primarily as redox catalysts, which cannot carry out specific reactions that are not thermodynamically possible. (Thus, microorganisms do not oxidize or reduce, they mediate electron transfer.) Ultimately, this chapter serves as a precursor to the following chapters discussing various principles of water flow in soils.

ANSWERS TO QUESTIONS

5.1. Equation 5.30 is the same as 5.17. Heat, expressed as q, may be obtained by taking the integral

$$q = \int_{300}^{1000} (26.984 + 5.910 \times 10^{-3}T - 3.77 \times 10^{-7}T^2) \, dT$$

$$q = 26.984(1000 - 300) + \frac{1}{2}(5.910 \times 10^{-3})(1000^2 - 300^2)$$

$$- \frac{1}{3}(3.377 \times 10^{-7}(1000^3 - 300^3) = 21.468 \text{ kJ mol}^{-1}$$

5.2. At 25 °C, A = 0.5085 and B = 0.3281 Å^{-1}; thus, using equation 5.30 log γ_i = $-[0.5085(2)^2 \times (0.0281)^{1/2}]/[1 + (6)(0.3281)(0.0281)^{1/2}]$ = -0.2564 and taking the antilog = 0.554. As a result the chemical activity α = (0.554)(0.00633) = 0.00351.

5.3. By sketching the structure of benzene, N_1 = 6, and for the structure of water, N_2 = 0. However, the B_2 term is not infinite because of modification. The correlation coefficients for alkylbenzenes in water are $A_{1,2}$ = 3.554, B_2 = 0.622, and C_1 = -0.466 (see table 5.1). Equation 5.36 must be modified and now takes the form

$$\log \gamma_1^\infty = A_{1,2} + B_2 (N_1 - 6) + C_1 \left[\frac{1}{N_1 - 4} \right]$$

For the typical modifications and additional information on equation 5.36, the student is referred to Reid, Pravsnitz, and Sherwood (1977). Thus, log γ_1^∞ = 3.554 + 0.622(6 − 6) − 0.466[1/6 − 4] = 3.321. Taking the antilog, we obtain 2,094. Repeat this sequence to obtain the infinite dilution activity coefficient for water as the solute and benzene as the solvent using correlation coefficients of $A_{1,2}$ = 3.04 and F_2 = -3.14. (Note that equation 5.36 must be modified for these parameters also.) For this case, B_2 = C_1 = D = 0. Thus, log γ_2^∞ = 3.04 − 3.14/6 = 2.517; take antilog = 329. The student may wish to estimate the solubility of benzene in water and water in benzene, as well as determine the Henry's-law constant for benzene in water. For solubility, x_2 = 3.5 × 10^{-3} mole fraction, and for the Henry's-law constant, H = 0.126/26.1 = 4.7 × 10^{-3} atm m^3/mole.

5.4. First, solve equation 5.41 for K. Thus, K = exp ($-77,772/8.3144 \times 298$) = 2.33 × 10^{-14} = $[(P_{NO}/P^0)/(P_{N_2}/P^0)^{1/2}(P_{O_2}/P^0)^{1/2}]$ = $[(P_{NO}/P^0)/(0.80)^{1/2}(0.20)^{1/2}]$. Consequently, P_{NO} = 9.319 × 10^{-15} bar or 9.319 × 10^{-13} kPa. The partial pressure of NO in the denominator is ignored because it is very small.

5.5. Using equation 5.43 we obtain Δ = 147.25 − (298.15)[(354.4 − {5 × 5.74} − {6 × 130.68})/1000] = -10.6 kJ mol^{-1}. The experimental value for this formation is 8.3 kJ mol^{-1}. The equilibrium mole fraction is equal to the equilibrium pressure fraction. The equilibrium constant for the formation reaction is given by K_i = $O_i/P_{H_2}^6$ = exp ($\Delta G^0/RT$).

5.6. By substituting the given values into the top part of equation 5.58, we have K_a^x = (1.46 × 10^{-2})10$^{(0.268)(0.755)}$ = 2.33 × 10^{-2}. Note that this is about 300 percent higher than an experimentally measured value of 0.56 × 10^{-2}; consequently, one of the special purpose equations may yield better results in this case.

5.7. First, simplify the Hammett correlation, equation 5.58, such that log k = $\rho\sigma$ + log k_o. Thus, log k_H = (0.11)(0.778) − 7.0 = -6.92. Hence, k_H = 1.2 × 10^{-7} M^{-1} s^{-1}. Thus, k_T = (1.2 × 10^{-7} M^{-1} s^{-1})(10^{-6}) = 1.2 × 10^{-13} s^{-1}. Using equation 5.63, the hydrolysis half-life $t_{1/2}$ = 0.693/(1.2 × 10^{-13}) = 5.8 × 10^{12} s^{-1}.

5.8. Using a simplification of the Hammett correlation, as in question 5.7, log k_{OH} = $\rho\sigma$ + log k_{OH}^0, the log k_{OH} = (2.38)(0.778) + log(7.2 × 10^{-3}) = -0.29. Hence, k_{OH} = 5.1 × 10^{-1} M^{-1} s^{-1}. You may wish to compare this to the k_{OH} for water.

5.9. Again, using a simplification of the Hammett correlation, log k_o = $(-1.31)(-0.17)$ − 5.21 = -4.99. Thus, k_o = 10^{-5} s^{-1}. This is for 25 °C; the student may wish to recalculate the value for 30 °C using the correction factor given by equation 5.65. The literature value at this temperature is k_o = 2.97 × 10^{-3} s^{-1}. How close are you to this upon recalculation? You may wish to contemplate the reason(s) for any differences.

5.10. The log K_{ow} for atrazine is 2.68, thus log S = $-0.922(2.68)$ + 4.184; log S = 1.713 and S = 51.642 mg/L.

5.11. Using equation 5.83 we have 4494/[(1.987)(313.2)] × [(313.2/353.4) −1] = -0.8214 (no units).

ADDITIONAL QUESTIONS

5.12. A contaminant spill has occurred; it consists of a mixture of ethanol (1)-n-hexane (2). The structure of ethanol is CH_3CH_2OH and hexane is $CH_3(CH_2)_4CH_3$. What is the infinite-dilution activity coefficient? In this case, N_1 = 2 and N_2 = 6; this is a mixture of an alcohol in paraffin. Assume a temperature of 25 °C. Also, $A_{1,2}$ = 1.96, C_1 = 0.475, and D = -4.9 × 10^{-4}.

5.13. Estimate the infinite-dilution activity coefficient of aniline in water at 25 °C. Assume the correlation factor for NH_2 on a benzene ring is -1.35.

5.14. Estimate the dissociation constant for p-tert butyl ($C(CH_3)_3$) benzoic acid. Assume K_a^o for benzoic acid is 6.26×10^{-5}, $\rho = 1.0$, $\sigma = -0.197$.

5.15. Estimate the dissociation constant for 3,4-dimethylanaline. Assume $\rho = 2.77$, $pK_a^o = 4.60$ and $\sigma = -0.303$.

5.16. What is k_{OH} for diisobutyl phthalate? Assume 25 °C and $\log k_{T2} = -3.03^{-1}$.

5.17. Using the regression equation given in question 5.11, calculate s for DDT and Carbofuran. Assume $\log k_{ow}$ is 5.98 and 1.60, respectively.

5.18. What is the solubility of 1,4-diiodobenzene in water? Assume 25 °C, $T_m = 402.6$ K, $\Delta Hf = 5340$ cal/mol and $\gamma_1^{\infty} = 1.66 \times 10^6$.

5.19. Estimate the solubility of 4-chloro-1,3 dinitrobenzene in water. Assume 50 °C, $T_m = 328$ K, and $\gamma_1^{\infty} = 27{,}500$; also assume that the value for ΔHf is not available.

5.20. Using the regression equation given in question 5.11, estimate s for 2-isopropoxyphenyl-N-methylcarbamate (mw $= 209.2$ g/mole). Assume $t_m = 91$ °C and $\log k_{ow} = 1.55$.

5.21. To determine s for benzene and benzene derivatives (aromatics), the following equation has been found to work well:

$$\log 1/s = 0.996 \log k_{ow} - 0.339$$

Using this equation, estimate s for trichloroethylene and 1,2,4-tribromobenzene (spilled on a nearby landfill, say). Assume $\log k_{ow} = 2.42$ and 4.98 and $t_m = 25$ and 44, respectively.