Chapter 2 Equilibrium Thermodynamics and Kinetics

Equilibrium thermodynamics *predicts the concentrations (or, more precisely, activities) of various species and phases if a reaction reaches equilibrium.* *Kinetics* tells us *how fast, or if, the reaction will reach equilibrium.* Thermodynamics is an elegant way to deal with problems of chemical equilibria, but it is important to note that kinetics will determine if these equilibrium conditions are actually attained. In the following sections we will consider these topics in the context of the typical conditions found in the surface and shallow subsurface environments.

THE LAWS OF THERMODYNAMICS

Thermodynamic principles are applied to systems. A *system* is *that portion of the universe we wish to study*, e.g., a beaker containing a solution, a room, the ocean, planet earth, the universe. The system can be *open* (*exchanging matter and energy with its surroundings*), *closed* (*not exchanging matter with its surroundings*), or *isolated* (*exchanges neither matter nor energy with its surroundings).* As an example, consider a beaker of water standing on a table. The system is open because it can exchange both heat with the surroundings and gases with the atmosphere. Now seal the top of the beaker. The result is a closed system because it cannot exchange matter (gases) with the atmosphere. If we place the beaker in a thermos bottle, it becomes an isolated system because it can exchange neither heat nor matter with its surroundings.

The properties of a system can be either intensive or extensive. *Intensive properties* are *independent of the magnitude of the system.* Examples are pressure and temperature. *Extensive properties* are *dependent on the magnitude of the system.* Examples are volume and mass.

A system can be described in terms of phases and components. A *phase* is defined as "*a uniform*, *homogeneous*, *physically distinct*, *and mechanically separable portion of a system*" (Nordstrom and Munoz, 1986, p. 67). *Components* are the *chemical constituents (species) needed to completely describe the chemical composition of every phase in a system.* The choice of components is determined by the physical-chemical conditions of the system. For example, consider the three-phase system solid water (ice)–liquid water–water vapor that would exist under normal surface conditions. The composition of each phase can be completely described by a single component—H_2O. Now consider the same system over a much wider range of temperatures so that a fourth phase, plasma, is found. In a plasma, the H_2O would break down into hydrogen and

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oxygen atoms. To completely describe the composition of this system we would need two components—H and O. The solid, liquid, and vapor phases of H_2O would be formed by combining the two components in the proportions $2H + O \rightarrow H_2O$.

First Law of Thermodynamics

The *first law of thermodynamics* deals with the conservation of energy. One statement of the law is that *energy can be neither created nor destroyed*, *it can only be changed from one form to another.* The concept of enthalpy (heat flow) arises from the first law.

The internal energy of a system is the sum of the kinetic and potential energies of its constituent atoms. Let us change the internal energy of this system by adding (or subtracting) heat and by doing mechanical work (on or by the system). We can write the following equation:

$$\Delta E = q - w \qquad\qquad (2–1)$$

where ΔE is the change in internal energy of the system, q is the heat added or removed from the system, and w is the work done on or by the system. By convention, heat added to a system is positive and work done by a system is positive. Thus, the internal energy of a system will increase if heat is added and will decrease if work is done by the system. For infinitesimal changes, equation 2–1 can be written

$$dE = dq - dw \qquad\qquad (2–2)$$

If the work done by or on a system causes a change in volume at constant pressure (pressure–volume work), then the equation for the change in internal energy can be written

$$\Delta E = q - P\,\Delta V \qquad\qquad (2–3)$$

For an infinitesimal change, equation 2–3 can be written

$$dE = dq - P\,dV \qquad\qquad (2–4)$$

Enthalpy is equal to the *heat flow when processes occur at constant pressure and the only work done is pressure–volume work.* This is the most likely situation in the natural surface environment. For an infinitesimal change, enthalpy can be written

$$dH = dE + P \, dV + V \, dP \qquad (2\text{--}5)$$

At constant *P, dP* = 0 and

$$dH = dE + P \, dV \qquad (2\text{--}6)$$

If we substitute for *dE* (equation 2–4), then *dH* equals *dq* at constant *P*.

$$dH = (dq - P \, dV) + P \, dV = dq \qquad (2\text{--}7)$$

Note that it is very difficult to determine absolute values for either internal energy (*E*) or enthalpy (*H*). Hence, these values are determined on a relative basis compared to standard conditions (see later). **Exothermic reactions** *release heat energy* (i.e., enthalpy is negative for the reaction), and **endothermic reactions** *use heat energy* (i.e., enthalpy is positive for the reaction).

    The **heat of formation** (sometimes called the *enthalpy* of formation or the *standard heat* of formation) is the *enthalpy change that occurs when a compound is formed from its elements at particular temperature and pressure* (the **standard state**). It is convenient to use 25°C and 1 bar as the temperature and pressure for the standard state. Hence, the standard state for a gas is the ideal gas at 1 bar and 25°C, for a liquid it is the pure liquid at 1 bar and 25°C, and for a solid it is a specified crystalline state at 1 bar and 25 °C. The heat of formation of the most stable form of an element is arbitrarily set equal to zero. For example, the heat of formation for La $_{metal}$ and N$_{2 \, (g)}$ equals zero. For dissolved ionic species, the heat of formation of H$^+$ is set equal to zero.

Second Law of Thermodynamics

The **second law of thermodynamics** deals with the concept of entropy. One statement of the law is that *for any spontaneous process*, *the process always proceeds in the direction of increasing disorder.* Another way of looking at this law is that during any spontaneous process there is a decrease in the amount of useable energy. As a simple example of the second law consider the burning of coal. In coal the atoms are ordered; i.e., they occur as complex organic molecules. During the combustion process these molecules are broken down, with the concomitant release of energy and the production of CO_2 and H_2O. The atoms are now in a much more disordered (dispersed) state. In order to produce more coal we need to recombine these atoms which requires energy—in fact, more energy than was released by the burning of the coal. Hence, there has been a

decrease in the amount of useable energy.

The second law has important practical and philosophical implications. During any process there is a decline in the amount of useable energy. This is an important concept in ecology in terms of the efficiency of ecosystems. As a rough rule of thumb, in biological systems about 90% of the energy is lost in going from one trophic level (nourishment level) to another. For example, for every 1000 calories of "grass energy" consumed by a cow, only 100 calories are converted to biomass. If the cow ends up as a steak, only 10% of the energy in the cow's biomass ends up as human biomass. Thus, vegetarians are more efficient users of primary biomass (green plants) than meat eaters. The second law of thermodynamics also predicts that at some point the universe will cease to function. A way of looking at this is to divide the universe into a high-temperature reservoir—the stars—and a low-temperature reservoir—the interstellar medium. As energy is lost from the stars to the interstellar medium, the temperature of the interstellar medium will rise. At some point, the temperatures of these reservoirs will become equal and energy transfers will cease. This has sometimes been referred to as the "heat death of the universe."

A mathematical statement of the second law is

$$\Delta S = \frac{q}{T}$$

$$(2–8)$$

where ΔS is the change in entropy and T is temperature in Kelvin (the absolute temperature scale). Rearranging equation 2–8 to give $q = T\Delta S$ and substituting into equation 2–1 gives

$$\Delta E = T\Delta S - w \quad (2–9)$$

Or, in differential form,

$$dE = T\, dS - dw \qquad (2–10)$$

If we consider only pressure–volume work, then equation 2–10 becomes

$$dE = T\, dS - P\, dV \,(2–11)$$

Substitution of equation 2–11 into equation 2–5 yields

$$dH = (T\, dS - P\, dV) + P\, dV + V\, dP = T\, dS + V\, dP \,(2–12)$$

EQUILIBRIUM THERMODYNAMICS

In the real world, systems can exist in several states: unstable, metastable, and stable. To illustrate these different states, consider a ball sitting at the top of a hill (Figure 2–1). In terms of gravitational energy, the lowest energy state is achieved when the ball is at the bottom of the hill. At the top the ball is unstable with respect to gravitational energy. The least disturbance will cause the ball to start rolling down the hill. Partway down the hill there is a small notch. If the ball does not have enough energy to roll up over the lip of the notch, it will be stuck at this position. Clearly, this is not the lowest possible energy state, which occurs at the bottom of the hill, and the ball is said to be in metastable equilibrium. However, it can remain indefinitely at this position if there isn't enough energy available to push it over the lip of the notch. This is an example of a kinetic impediment to the achievement of equilibrium, and we can regard the energy needed to push the ball out of the notch to be equivalent to the activation energy. Activation energy will be discussed in the latter part of this chapter. If sufficient energy is put into the system to push the ball out of the notch, it will roll to the bottom of the hill. At this position, the gravitational potential energy equals zero and the ball has achieved its equilibrium position in terms of gravitational energy. *In equilibrium thermodynamics it is this lowest energy state that is determined.*
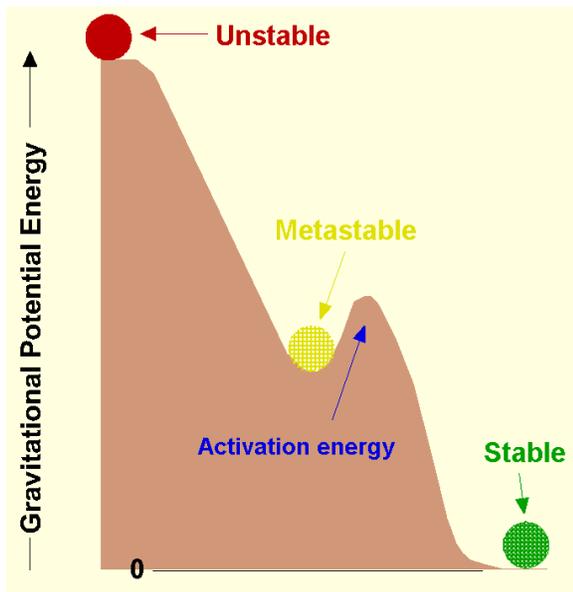
Figure 2–1 Illustration of the states of a system in terms of the gravitational energy of a ball.

Free Energy

A system at equilibrium is in a state of minimum energy. In chemical thermodynamics this energy is measured either as **Gibbs free energy** (when the reaction occurs at constant T and P) or **Helmholtz free energy** (when the reaction occurs at constant T and V). Here we will use Gibbs free energy, named for J. Willard Gibbs, a Yale University chemist.

For a system at constant T and P, Gibbs free energy can be written

$$G = H - TS \qquad (2\text{–}13)$$

where H is enthalpy (kJ mol^{-1}), S is entropy (J mol^{-1} K^{-1}), and T is temperature in K (Kelvin).

For changes that occur at constant T and P, the expression for Gibbs free energy becomes

$$\Delta G = \Delta H - T\Delta S \qquad (2\text{–}14)$$

If ΔG is (–), the process occurs spontaneously. If $\Delta G = 0$, the process is at equilibrium. If ΔG is (+), the reaction does not occur spontaneously. ***Note that chemical reactions are written from left to right.*** For example, consider the reaction

$$CaSO_{4\,anhydrite} \ \square \ \ Ca^{2+} + SO_4^{2-}$$

If the process occurs spontaneously, $CaSO_4$ will dissolve to form Ca^{2+} and SO_4^{2-} ions (i.e., the reaction is running from left to right). If the process is at equilibrium, the concentration of the various species remains constant. If the process does not occur spontaneously, the reaction would actually run from right to left. In the last case, if you rewrote the equation so that the ions were on the left side and the compound on the right side, the free energy would be negative.

We now write equation 2–14 as follows:

$$\Delta G_R^0 = \Delta H_R^0 - T\Delta S_R^0 \qquad (2\text{–}15)$$

where ΔG_R^0 is the free-energy change, ΔH_R^0 is the enthalpy change, and ΔS_R^0 is the entropy change for the reaction at standard conditions. The enthalpy and entropy changes are calculated, respectively, by subtracting the sum of the enthalpies or entropies of the reactants from the sum of

the enthalpies or entropies of the products. ***Neither equation 2–14 nor 2–15 can be used to find the*** ΔG_R^0 ***value for a single compound or species.***

Note: In the thermodynamic data table (Appendix II) the tabulated values for ΔG_t^0 and ΔH_t^0 are, respectively, the standard free energies and enthalpies of formation for the compounds from the elements in their standard state. S^0 is also tabulated in the thermodynamic data table. Free energy and enthalpy are in kJ mol^{-1} while entropy is in J mol^{-1} K^{-1}. When doing thermodynamic calculations be sure to convert either enthalpy to joules (1 kJ = 1000 J) or entropy to kilojoules (1 J = 1×10^{-3} kJ). Temperature is the absolute temperature in Kelvin. To convert centigrade temperatures to Kelvin, add 273.15 to the centigrade value. Failing to do this is one of the most common mistakes made by students on homework and exam problems. By international convention, the accepted units are SI units. In SI units, heat energy is expressed as joules. For years scientists and engineers used the calorie as the unit of heat measurement. Hence, many older tables of thermodynamic data tabulate heat energy in calories. The following conversion factor is used to convert calories to joules:

1 calorie = 4.184 joules

Chemical Potential

Chemical potential is defined as

$$\mu_i = \left(\frac{\Delta G}{\Delta n_i} \right)_{T,P} \qquad (2\text{–}16)$$

where μ_i is the chemical potential of a certain component in a system and Δn_i is the change in moles of that component in the system. For a system at equilibrium, μ_i is the same in all phases.

Activity and Fugacity

An important concept in dealing with chemical systems is ***activity*** (or ***fugacity,*** for a gas). This is the *apparent (or effective) concentration of a species* as opposed to the actual concentration. Activity and fugacity are a measure of the departure of a system from ideal behavior and need to be taken into account even when dealing with relatively dilute solutions. Activity (or fugacity) is

related to concentration through the *activity coefficient.*

$$\gamma_i = \frac{a_i}{m_i}$$

(2–17)

where γ_i is the activity coefficient, a_i is the activity, and m_i is the actual concentration. Rearranging equation 2–17 gives

$$a_i = \gamma_i m_i$$

(2–18)

A later section will deal with the calculation of the activity coefficient.

The Equilibrium Constant

We can write the chemical potential for component i as follows:

$$\mu_i = \mu_i^0 + RT \ln a_i$$

(2–19)

where μ_i^0 is the chemical potential of component i in its standard state and R is the gas constant (8.3143 J mol^{-1} K^{-1}). For solid solutions, solutions of two miscible liquids, and the solvent in aqueous solutions, the standard state is the pure substance at the same temperature and pressure.

Let us suppose we have a chemical reaction of the form

$$aA + bB \rightleftharpoons cC + dD$$

(2–20)

The uppercase letters represent the species and the lowercase letters represent the number of each species (each chemical entity). What follows is an exercise in letter manipulation, a common activity in the sciences and mathematics. To determine the change in free energy for the system, we subtract the free energies of the products (right side of the equation) from the free energy of the reactants (left side of the equation).

$$\Delta G_{reaction} = \Sigma \, \Delta G_{products} - \Delta G_{reactants}$$

(2–21)

From the definition of chemical potential (equation 2–16),

$$\Delta G = n_i \mu_i$$

(2–22)

and, on substitution, equation 2–21 becomes

$$\Delta G_R = c\mu_c + d\mu_d - a\mu_a - b\mu_b \qquad (2\text{–}23)$$

We substitute equation 2–19 for μ_i and write equation 2–23 as follows:

$$\Delta G_R = c\mu_C^0 + d\mu_D^0 - a\mu_A^0 - b\mu_B^0 + RT \ln\left(\frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}\right) \qquad (2\text{–}24)$$

The portion of equation 2–24 dealing with the chemical potentials in the standard state is equivalent to ΔG^0, and thus equation 2–24 reduces to

$$\Delta G_R = \Delta G_R^0 + RT \ln\left(\frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}\right) \qquad (2\text{–}25)$$

At equilibrium, $\Delta G_R = 0$ and equation 2–25 becomes

$$RT \ln\left(\frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}\right) = -\Delta G_R^0 \qquad (2\text{–}26)$$

Dividing both sides of equation 2–26 by R, T, and converting the natural log to an exponent, gives

$$K_{eq} = \left(\frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}\right) = \exp\left(\frac{-\Delta G_R^0}{RT}\right) \qquad (2\text{–}27)$$

For our last manipulation we will rearrange equation 2–27 to yield

$$\ln K_{eq} = \left(\frac{-\Delta G_R^0}{RT}\right) \qquad (2\text{–}28)$$

Note that in equation 2–28 we are calculating the natural log of K_{eq}. A natural log result can be converted to a base 10 log result by dividing by 2.30259, or by using the proper keystroke sequence on a calculator. If the reactions of interest are occurring at 25°C and 1 bar and the free energy is in kJ mol^{-1}, equation 2–28 can be written in base 10 log form as

$$\log K_{eq} = \frac{-\Delta G_R^0}{5.708} \qquad (2\text{–}29)$$

Equation 2–29 can only be used for reactions occurring at 25 °C and 1 bar. We have now completed our exercise in letter manipulation and everyone should feel very refreshed. The following example illustrates the calculation of an equilibrium constant.

A word about thermodynamic data. There are a number of data compilations in the literature. You may find that for any particular species the different compilations do not give the same value. Thermodynamic data are determined experimentally and are thus subject to error. In compiling a set of thermodynamic data, the compilers attempt to make the data internally consistent; i.e., calculations using the data set give reasonable and consistent answers. Where values have been determined by more than one laboratory, a judgment must be made by the compilers as to which values are more consistent with their data set. In addition, errors can creep into compilations, which can lead to some rather paradoxical answers. The user must be aware of these potential pitfalls. When using a water-chemistry computer model, you should take note of the thermodynamic database used by the model.

EXAMPLE 2–1 Calculate the solubility product for gypsum at 25°C. The solubility product is a special form of an equilibrium constant (i.e., it enables us to calculate the activity of the ions in solution at saturation).

The reaction is

$$CaSO_4 \cdot 2H_2O_{gypsum} \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O$$

The equilibrium equation is written

$$K_{eq} = \frac{[Ca^{2+}][SO_4^{2-}][H_2O]^2}{[CaSO_4 \cdot 2H_2O_{gypsum}]}$$

Note that the various species are enclosed in brackets. The convention is that enclosing the *species in brackets indicates activity*, while enclosing the *species in parentheses indicates concentrations.* $CaSO_4 \cdot 2H_2O$ is in its standard state (pure solid) and its activity equals 1. For a dilute solution, the activity of water also equals 1. The activity of water in cases other than dilute solutions is considered in a later section. For the dissolution of gypsum, the equilibrium equation

becomes

$$K_{eq} = \left[Ca^{2+} \right] \left[SO_4^{2-} \right] = K_{sp}$$

Selecting the appropriate free energies of formation (Appendix II, source 2) yields (remember, products – reactants)

$$\Delta G_R^0 = (-552.8) - (-744.0) + (2)(-237.14) - (-1797.36) = 26.28 \text{kJ mol}^{-1}$$

$$\log K_{sp} = \frac{-\Delta G_R^0}{5.708} = \frac{-26.28}{5.708} = -4.60, \quad K_{sp} = 10^{-4.60}$$

Henry's Law

This relationship is used in several ways. In solutions, it is used to describe the activity of a dilute component as a function of concentration. In this case, the relationship is written

$$a_i = h_i X_i \qquad\qquad (2\text{--}30)$$

where a_i is the activity of species i, h_i is the Henry's law proportionality constant, and X_i is the concentration of species i.

For gases, Henry's law relates the fugacity of the gas to its activity in solution. At total pressures of 1 bar or less and temperatures near surface temperatures, gases tend to obey the ideal gas law, and hence the fugacity of a gas equals its partial pressure. In this case, we write Henry's law as

$$C_i = K_H P_i \qquad\qquad (2\text{--}31)$$

Table 2–1 Henry's Law Constants for Gases at 1 Bar Total Pressure in Mol L^{-1} Bar^{-1}*

$T(°C)$	O_2	N_2	CO_2	H_2S	SO_2
0	2.18×10^{-3}	1.05×10^{-3}	7.64×10^{-2}	2.08×10^{-1}	3.56
5	1.91×10^{-3}	9.31×10^{-4}	6.35×10^{-2}	1.77×10^{-1}	3.01
10	1.70×10^{-3}	8.30×10^{-4}	5.33×10^{-2}	1.52×10^{-1}	2.53
15	1.52×10^{-3}	7.52×10^{-4}	4.55×10^{-2}	1.31×10^{-1}	2.11
20	1.38×10^{-3}	6.89×10^{-4}	3.92×10^{-2}	1.15×10^{-1}	1.76
25	1.26×10^{-3}	6.40×10^{-4}	3.39×10^{-2}	1.02×10^{-1}	1.46
30	1.16×10^{-3}	5.99×10^{-4}	2.97×10^{-2}	9.09×10^{-2}	1.21
35	1.09×10^{-3}	5.60×10^{-4}	2.64×10^{-2}	8.17×10^{-2}	1.00
40	1.03×10^{-3}	5.28×10^{-4}	2.36×10^{-2}	7.41×10^{-2}	0.837
50	9.32×10^{-4}	4.85×10^{-4}	1.95×10^{-2}	6.21×10^{-2}	—

*Data are from Pagenkopf (1978).

where C_i is the concentration of the gaseous species in solution, K_H is the Henry's law constant in mol L^{-1} bar^{-1}, and P_i is the partial pressure of gaseous species i. Henry's law constants vary as a function of temperature (Table 2–1). We will use Henry's law in later chapters to calculate the activity of various gases dissolved in water and the partial pressure of various volatile organic solvents.

EXAMPLE 2–2 Calculate the solubility of oxygen in water at 20°C.

At sea level—i.e., a total atmospheric pressure of 1 bar (in terms of the standard atmosphere, precisely 1.0135 bar)—the partial pressure of oxygen is 0.21 bar. At 20°C, the Henry's law constant for oxygen is 1.38×10^{-3} mol L^{-1} bar^{-1}.

$$O_{2\ (aq)} = K_H P_{O_2} = (1.38 \times 10^{-3}\ \text{mol L}^{-1}\ \text{bar}^{-1})(0.21\ \text{bar}) = 2.90 \times 10^{-4}\ \text{mol L}^{-1}$$

Converting to concentration in mg L^{-1} (equivalent to ppm in freshwater at temperatures near 25°C)

$$\text{Concentration} = (2.9 \times 10^{-4}\ \text{mol L}^{-1})(32.0\ \text{g O}_2\ \text{mol}^{-1})$$

$$= 9.28 \times 10^{-3}\ \text{g L}^{-1} = 9.28\ \text{mg L}^{-1}$$

Free Energies at Temperatures Other Than 25°C

So far we have considered reactions that take place at 25°C. Free energy does vary as a function of temperature. If the reaction of interest occurs at a temperature other than 25°C, the free-energy values must be corrected. Unfortunately, this is not a trivial issue. We will briefly consider the problem here. More detailed discussions can be found in Drever (1997), Langmuir (1997), and elsewhere.

If the deviations in temperature from 25°C are small (15° or less, i.e., from 10° to 40°C), we can make the assumption that ΔH_R^0 and ΔS_R^0 are constant. With reference to equation 2–15 and equation 2–28 we can write

$$\Delta G_R^0 = \Delta H_R^0 - T\Delta S_R^0 = -RT \ln K_{eq} \qquad (2\text{--}32)$$

Rearranging yields

$$\ln K_{eq} = \frac{-\Delta H_R^0}{RT} + \frac{\Delta S_R^0}{R} \qquad (2\text{--}33)$$

We can also write this equation in terms of the equilibrium constant and the standard enthalpy of the reaction (a form of the van't Hoff equation) as follows:

$$\ln K_t = \ln K_r + \frac{\Delta H_R^0}{R}\left(\frac{1}{T_r} - \frac{1}{T_r}\right) \qquad (2\text{--}34)$$

where K_t is the equilibrium constant at temperature t, K_r is the equilibrium constant at 25°C, T, is the temperature t, and T_r is 298.15 K (25°C). $R = 8.314 \times 10^{-3}\text{kJ mol}^{-1}\ \text{K}^{-1}$.

EXAMPLE 2–3 Calculate the solubility product for gypsum at 40°C using equation 2–34. From a previous example (2–1), the solubility product at 25°C is $K_{sp} = 10^{-4.60}$. Calculate ΔH_R^0 for the reaction.

Using the thermodynamic values from Appendix II, source 2,

$$\Delta H_R^0 = (-543.0) + (-909.34) + (2)(-285.83) - (-2022.92) = -1.08 \text{kJ mol}^{-1}$$

Substituting the appropriate values into equation 2–34 yields

$$\ln K_t = \ln(10^{-4.60}) + \frac{-1.08}{8.314 \times 10^{-3}} \left(\frac{1}{298.15} - \frac{1}{313.15} \right) = -10.61$$

Converting to base 10,

$$\log K_t = -4.61 \text{ or } K_t = 10^{-4.61}$$

The solubility of gypsum decreases slightly as temperature changes from 25°C to 40°C. For this particular reaction, the change is small (about 2.0%). However, for other reactions the change can be large (see the problem set).

For temperature departures of more than 15°C from standard conditions, the computation becomes more complex. The following equations are easily solved using a spreadsheet (or a computer program). The biggest problem is obtaining the appropriate thermodynamic data, particularly for the ionic species. For enthalpy, we can write the following equation:

$$\int_{H_{298}^0}^{H_T^0} dH = \int_{298}^{T} c_P dT \tag{2–35}$$

where T is the temperature of interest and c_P is the heat capacity. **Heat capacity** is defined as *the amount of heat energy required to raise the temperature of 1 gram of a substance 1°C.* There are two different heat capacities, one determined at constant volume (c_v) and the other determined at constant pressure (c_P). At constant volume, changes in heat energy only change the temperature of

the system. At constant pressure, changes in heat energy lead to changes in both temperature and volume (pressure–volume work). Thus, c_P is always larger than c_v. The heat capacity varies as a function of temperature. The relationship can be written as follows:

$$c_P = a + bT - \frac{c}{T^2}$$

(2–36)

and a, b, and c are experimentally determined constants. Particularly for ionic species, the requisite experiments have not been done. Thus, in many cases it is not possible to calculate c_P as a function of temperature. Substituting equation 2–36 into equation 2–35 and integrating yields

$$H_T^0 = H_{298}^0 + a(T - 298) + \frac{b}{2}(T^2 - 298^2) + c\left(\frac{1}{T} - \frac{1}{298}\right)$$

(2–37)

Similarly, for entropy,

$$S_T^0 = \int_{298}^T \frac{c_P}{T}\,dT + S_{298}^0 = \left[a\ln T + bT + \frac{c}{2T^2}\right]_{298}^T + S_{298}^0$$

(2–38)

which becomes, after inserting limits,

$$S_T^0 = \left[a\ln\left(\frac{T}{298}\right) + b(T - 298) + \frac{c}{2}\left(\frac{1}{T^2} - \frac{1}{298^2}\right)\right] + S_{298}^0$$

(2–39)

Substitution of equations 2–37 and 2–39 into equation 2–15 allows us to calculate Gibbs free energy as a function of temperature. In the context of environmental geochemistry, many processes of interest occur at or near standard (1 atm) pressure. For substantial departures from standard pressure, we would need to include a term to account for changes in free energy due to changes in pressure and volume. This is straightforward for solids, reasonably simple for liquids, but complicated in the case of gases (changes in volume are significant). A detailed account of the effect of pressure on free-energy calculations can be found in Langmuir (1997).

Le Châtelier's Principle

In the preceding sections we have developed several quantitative measures that can be used to determine what happens during equilibrium reactions. We can also make reasonable predictions

about the effect a perturbation will have on an equilibrium reaction using **Le Châtelier's principle**, which can be stated: *If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce the change.* We can consider three possibilities: changes in concentration, changes in pressure, and changes in temperature.

Changes in Concentration Consider the following reaction that we used in Example 2–1 :

$$CaSO_4 \cdot 2H_2O_{gypsum} \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O$$

We have already calculated the equilibrium constant for this reaction—i.e., $K_{eq} = 10^{-4.60}$ —and have noted that this is a solubility product. At equilibrium, the concentration of $Ca^{2+} = SO_4^{2-} = 10^{-2.30}$. Suppose we added 0.01 mol of Ca^{2+} ion to the solution. The solution would now be oversaturated and the reaction would go to the left until enough of the added Ca^{2+} ion had been removed for the reaction to return to equilibrium. If you do the calculation, you will find that when the reaction is once again at equilibrium there will be more Ca^{2+} than we started with (and less SO_4^{2-}), but the amount of Ca^{2+} will be less than that immediately after we added Ca^{2+} to the solution. In terms of changes in concentration, we can state Le Châtelier's principle as follows: If a product or reactant is added to a system at equilibrium, the reaction will go in the direction that decreases the amount of the added constituent. If a product or reactant is removed from a system at equilibrium, the reaction will go in the direction that increases the amount of the removed constituent.

Changes in Pressure There are three possibilities: (1) Add or remove a gaseous reactant or product, (2) add an inert gas (one not involved in the reaction), and (3) change the volume of the container. Case (1) is analogous to what happens when you change the concentration of a constituent. Consider the following reaction, a very familiar one in metamorphic petrology:

$$CaCO_{3 \text{ calcite}} + SiO_{2 \text{ quartz}} \rightleftharpoons CaSiO_{3 \text{ wollastonite}} + CO_{3 \text{ (g)}}$$
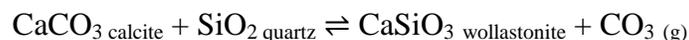
If we added CO_2 to the system, the reaction would move to the left in order to reduce the amount of CO_2. Case (2) has no effect on the system. At first glance this might not seem reasonable because an increase in pressure should favor the solid phases, which occupy a smaller volume. But note that the gas we are concerned with is CO_2, and only changes in the pressure of CO_2 would affect

the reaction. If there was a decrease in volume [Case (3)], the reaction would respond by reducing the number of gaseous molecules in the system. This is accomplished by converting some of the CO_2 into solid $CaCO_3$, which occupies a significantly smaller volume. An increase in volume would have the opposite effect.

Changes in Temperature Changes in temperature are different from the previous cases in that changes in temperature cause changes in the equilibrium constant. However, we can make predictions regarding the effect that changes in temperature will have on the equilibrium constant. With increasing temperature, reactions move in the direction that consumes heat energy. Returning to the reaction

$$CaSO_4 \cdot 2H_2O_{\text{gypsum}} \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O$$

in Example 2–3, we found that this reaction was exothermic because ΔH_R^0 for the reaction was negative. At first glance, this may appear counterintuitive. But if you write the equation used to determine ΔH_R^0, you will find that heat is a product. If ΔH_R^0 is positive, the reaction is endothermic (i.e., heat is a reactant). Because heat is consumed when the reaction moves to the left, with increasing temperature we would expect the reaction to move to the left and the concentrations of the products would decrease with respect to the concentration of the reactant. This would lead to a decrease in the equilibrium constant, as confirmed by the calculations in Example 2–3. If the reaction was endothermic, increasing temperature would cause the reaction to shift to the right, leading to an increase in the equilibrium constant.

CALCULATION OF ACTIVITY COEFFICIENTS

In an ideal solution, activity would equal concentration. It is often assumed that in very dilute solutions concentration does equal activity; i.e., the solution is behaving ideally. While this assumption may be justified in special cases, for most real solutions ideality is not achieved. This is particularly true for solutions that contain ionic species. The departure from ideal behavior is caused mainly by two factors:

1. Electrostatic interactions between charged ions.

2. The formation of hydration shells around ions.

The latter factor is easily understood in terms of the structure of the water molecule. Because the bond angle between the H atoms in H_2O is 104.5°, one side of the molecule has a slight positive charge and the other side a slight negative charge. The water molecule is said to be polar. Positive ions (cations) in solution will be surrounded by water molecules with their negative sides facing the cation, while negative ions (anions) will be surrounded by water molecules with their positive sides facing the anion. This tends to shield the cations and anions from each other. For uncharged species, which do not have electrostatic interactions, concentration equals activity in dilute solutions. In concentrated solutions, the uncharged species do show deviations from ideality, and an activity coefficient must be calculated for the uncharged species.

A variety of models (Debye–Hückel, Davies, Truesdell–Jones, Bronsted– Guggenheim– Scatchard specific ion interaction theory, and Pitzer) are used to calculate activity coefficients. Each is effective for a particular range of ionic strengths. Langmuir (1997) gives a detailed description of the different models and their effective concentration ranges. The first step in an activity coefficient calculation is to determine the ionic strength of the solution. The ***ionic strength*** of a solution is calculated as follows:

$$I = \frac{1}{2}\sum m_i z_i^2$$

(2–40)

where m_i = the moles per liter of ion i and z_i = the charge of ion i.

Debye–Hückel Model

The simplest form of the model assumes that (1) positive ions are surrounded by a cloud of negative ions and vice versa, (2) interactions between species are entirely electrostatic, (3) the ions can be considered to be point charges, and (4) ions around any particular ion follow a Boltzmann distribution. This simple form of the model fails at relatively low ionic strengths because it does not take into account the finite size of the ions. The more complex form of the model takes into account the size of the ions and is the preferred version of the Debye–Hückel equation,

$$\log \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}}$$

(2–41)

Table 2–2 Density of Water, Dielectric Constant, and Debye–Hückel and Truesdell–Jones Constants at 1 Bar Pressure*

Temperature (°C)	Density of water $(kg\ m^{-3})$	Dielectric constant	Debye–Hückel Constants	
			A	B
0	0.99984	87.8191	0.4912	0.3248
5	0.99977	85.8838	0.4942	0.3254
10	0.99970	83.9785	0.4976	0.3262
15	0.99896	82.1042	0.5012	0.3270
20	0.99821	80.2618	0.5052	0.3279
25	0.99693	78.4520	0.5094	0.3289
30	0.99565	76.6755	0.5138	0.3299
35	0.99394	74.9326	0.5185	0.3310
40	0.99222	73.2238	0.5235	0.3322
45	0.99013	71.5493	0.5287	0.3334
50	0.98803	69.9094	0.5342	0.3347
55	0.98562	68.3043	0.5399	0.3360
60	0.98320	66.7342	0.5459	0.3373

*Density of water from *CRC Handbook of Chemistry and Physics* (2000).

where A and B are constants depending only on T and P, and a_i is the hydrated radius of a particular ion.

At atmospheric pressure, $A = 1.824928 \times 10^6 \rho_0^{0.5} (\varepsilon T)^{-1.5}$ and $B = 50.3(\varepsilon T)^{-0.5}$, where ρ_0 is the density of water, ε is the dielectric constant of water, and T is in Kelvin. At any temperature T (in the range 0° to 100°C), the dielectric constant can be determined from the following relationship:

$$\varepsilon = 2727.586 + 0.6224107T - 466.9151 \ln T - 52000.87/T \tag{2–42}$$

where T is in Kelvin. At 25°C, $\rho_0 = 0.99693$, $\varepsilon = 78.4520$, A = 0.5094, and $B = 0.3289$. Values for the density of water, the dielectric constant of water, and the A and B Debye–Hückel constants at 1 bar, from 0° to 60°C, are tabulated in Table 2–2.

A **word of caution.** Compilations of the hydrated radii of ions (a_i) tend to use different units. If the radii are given directly in angstroms, then the value for B can be used as calculated (or as given in Table 2–2). If the radii are tabulated as 10^{-10} m or 10^{-8} cm, then B must be multiplied by 10^{10} or 10^8, respectively.

Truesdell–Jones Model

The Truesdell–Jones (Truesdell and Jones, 1974) and Davies (Davies, 1962) equations are extended versions of the Debye–Hückel equation. An additional term is added to the Debye–Hückel equation that takes into account the observation that in high-ionic-strength experimental systems the activity coefficients begin to increase with increasing ionic strength. The Truesdell–Jones equation is written

$$\log \gamma_i = \frac{-Az_i^2 \sqrt{I}}{1 + Ba_i \sqrt{I}} + bI \tag{2–43}$$

where a_i and b are determined from experimental data. Because the a_i values are determined experimentally—i.e., they are selected so that the calculated curves fit the observed data—these a_i values can only be used in the Truesdell–Jones equation (2–43). The A and B constants are the same in both the Truesdell–Jones and Debye–Hückel equations. Selected values for Debye–Hückel a_i and Truesdell–Jones a_i and b are given in Table 2–3.

Table 2–3 Parameters for the Debye–Hückel and Truesdell–Jones Equations at 1 Atm*

Ion	Debye–Hückel a_i(Å)	Truesdell–Jones a_i (Å)	Truesdell–Jones b (L mol^{-1})
H^+	9.0	4.78	0.24
Na^+	4.0	4.32	0.06
K^+	3.0	3.71	0.01
Mg^{2+}	8.0	5.46	0.22
Ca^{2+}	6.0	4.86	0.15
Sr^{2+}	5.0	5.48	0.11
Ba^{2+}	5.0	4.55	0.09
Mn^{2+}	6.0	7.04	0.22
Fe^{2+}	6.0	5.08	0.16
Co^{2+}	6.0	6.17	0.22
Ni^{2+}	6.0	5.51	0.22
Zn^{2+}	6.0	4.87	0.24
Cd^{2+}	5.0	5.80	0.10
Pb^{2+}	4.5	4.80	0.01
Al^{3+}	9.0	6.65	0.19
OH^-	3.5	10.65	0.21
F^-	3.5	3.46	0.08
Cl^-	3.0	3.71	0.01
HCO_3^-	4.0	5.4	0
CO_3^{2-}	4.5	5.4	0
SO_4^{2-}	4.0	5.31	–0.07

* Debye–Hückel radii from Kielland (1937). Truesdell–Jones parameters from Truesdell and Jones (1974) and Parkhurst (1990).

EXAMPLE 2–4 Given the following river water chemistry, calculate the activity coefficient for Ca^{2+} at 25°C using both the Debye–Hückel and Truesdell–Jones equations.

River Water Concentration (mg L^{-1})							
Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	SiO_2
14.7	3.7	7.2	1.4	8.3	11.5	53	10.4

Water–chemistry data are sometimes reported in ppm, which is a weight/weight measure. For example, 1 ppm = 1 mg kg^{-1}. This is approximately equivalent to 1 mg L^{-1}, but for very precise calculations the density of the water should be used to adjust ppm to mg kg^{-1}; i.e., multiply ppm by the density of the water. To calculate the ionic strength, we need to convert the weight of each ion to moles of each ion. 1 mg = 10^{-3} g. Divide the weight of each ion (in grams) by its gram-molecular weight. For example, $Ca^{2+} = 14.7 \times 10^{-3}$ g/40.08 = 3.67×10^{-4} mol L^{-1} and

$HCO_3^- = 53 \times 10^{-3}$ g / 61.02 = 8.69×10^{-4} mol L^{-1}. Converting all of the ions to mol L^{-1} and solving for I,

$$I = 0.5 \ \Sigma \ m_i z_i^2 = 0.5[(3.67 \times 10^{-4})(2)^2 + (1.52 \times 10^{-4})(2)^2 + (3.13 \times 10^{-4})(1)^2 + (3.58 \times 10^{-5})(1)^2$$
$$+ (2.34 \times 10^{-4})(1)^2 + (1.20 \times 10^{-4})(2)^2$$
$$+ (8.69 \times 10^{-4})(1)^2] = 2 \times 10^{-3} \ \text{mol charge L}^{-1}$$

Solving for the activity coefficient using the Debye–Hückel equation,

$$\log \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} = \frac{-(0.5094)(2)^2 \sqrt{2.0 \times 10^{-3}}}{1 + (0.3289)(6.0) \sqrt{2.0 \times 10^{-3}}} = 0.084$$
$$\gamma_i = 0.82$$

Table 2–4 Appropriate Ranges of Ionic Strengths for Activity-Coefficient Models

Model	Ionic strength (mol L^{-1})
Debye–Hückel	0 to 0.1
Davies	0 to 0.6
Truesdell–Jones	0 to 2
Specific ion interaction	0 to 4
Pitzer	0 to 6

*From Langmuir (1997).

Solving for the activity coefficient using the Truesdell–Jones equation,

$$\log \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} + bI$$

$$= \frac{-(0.5094)(2)^2 \sqrt{2.0 \times 10^{-3}}}{1 + (0.3289)(4.86)\sqrt{2.0 \times 10^{-3}}} + (0.15)(2.0 \times 10^{-3}) = -0.085$$

At concentrations typical of river water, both models yield essentially the same activity coefficient, and hence either model could be used to calculate the activity coefficients for river and lake waters with low ionic strength. The useable range of ionic strengths for each model is tabulated in Table 2–4.

Pitzer Model

For solutions of higher ionic strength, the Pitzer model would be most appropriate. The Pitzer model (Pitzer, 1973, 1979, 1980) takes into account binary interactions between two ions of the same or opposite sign and ternary interactions between three or more ions. This model is most effective for concentrated brines. The solutions are generally complex and best carried out by computer. Further details on the Pitzer model can be found in Langmuir (1997). Several of the commonly used water-chemistry computer codes (SOLMINEQ.88, PHRQPITZ, and PRHEEQC) use the Pitzer model.

Why Do We Care About Activity-Coefficient Models?

The preceding has not been an exhaustive discussion of activity coefficient calculations for ionic species, but it has drawn attention to the types of models and the limitations of the models. A number of computer codes have been developed to calculate speciation in natural waters. These different programs use different activity-coefficient models. The user should be aware of these differences. For example, it would be inappropriate to do speciation calculations for a brine using a computer code based on the Debye–Hückel model. The user should select a computer model appropriate for the system being considered. Table 2–4 summarizes the range of ionic strengths appropriate for each activity-coefficient model.

Calculation of Activity Coefficients for Uncharged Species

There are several activity-coefficient models for uncharged species. Plummer and MacKenzie

(1974) calculate the activity coefficient (γ) for an uncharged species as follows:

$$\gamma = 10^{0.11} \qquad (2\text{--}44)$$

where I is the ionic strength. The empirical Setchenow equation (Millero and Schreiber, 1982) calculates γ as follows:

$$\log \gamma_i = K_i I \qquad (2\text{--}45)$$

where K_i is a constant ranging in value from 0.02 to 0.23 at 25°C. For relatively dilute aqueous systems, such as rivers and lakes, which have ionic strengths on the order of 2×10^{-3}, and brackish waters with ionic strengths on the order of 2×10^{-2}, both equations give activity coefficients close to 1. For concentrated solutions, such as seawater, the activity coefficient is greater than 1. Seawater has an ionic strength of about 0.7, which, using the Plummer and MacKenzie (1974) model, yields an activity coefficient of 1.17. Values calculated from the Setchenow equation will vary as a function of the uncharged species. For example, the K_i value for $H_4SiO_{4\ (aq)}$ at 25°C is 0.080 (Marshall and Chen, 1982), giving a calculated activity of 1.14 for this uncharged species. An important point is that with increasing ionic strength, compounds that yield uncharged species on dissolution (such as quartz, which dissolves to form $H_4SiO_{4\ (aq)}$) become less soluble while ionic compounds (such as NaCl, which dissolves to form Na^+ and Cl^-) become more soluble (Figure 2–2). In very high ionic strength solutions (>1.0 mol L^{-1}), the activity coefficients for the ions will also start to increase and the preceding observation will no longer be true.
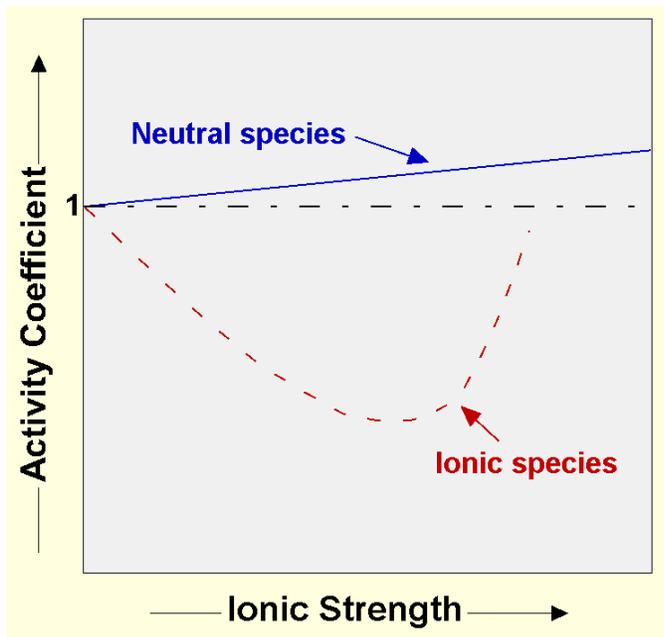
Figure 2-2 Schematic representation of the variation in activity coefficients versus the ionic strength of solutions.

Activity of Water

When water is a solvent, pure liquid water at infinite dilution is used as the standard state; i.e., the activity of $H_2O = 1$ at infinite dilution. The activity of water is related to the mole fraction of pure water, X_{H_2O} as follows:

$$\mu_{H_2O} = \mu_{H_2O}^0 + RT \ln X_{H_2O} \qquad (2\text{--}46)$$

In most cases, we are dealing with dilute solutions and we can set the activity of $H_2O = 1$. In more concentrated solutions, such as seawater, the activity will be slightly less than 1.

AQUEOUS COMPLEXES

An **aqueous complex** is a *dissolved species formed from two or more simpler species*, *each of which can exist in aqueous solution* (Drever, 1997, p. 34). In the context of equilibrium calculations, complexes are important because their formation can increase the solubility of various compounds. Consider the following reaction:

$$A^+ + B^- \rightleftharpoons AB_{(aq)} \qquad\qquad (2\text{--}47)$$

We can write an equilibrium equation for this reaction in the usual way. In this case, the equilibrium constant is called a stability constant because it is a measure of the stability of the aqueous complex.

$$K_{stab} = \frac{\left[AB_{(aq)}\right]}{[A^+][B^-]} \qquad\qquad (2\text{--}48)$$

The solubility of compounds whose ions form aqueous species is increased over that predicted from the solubility product for the compound. This is because some of the ions released during the dissolution process are taken up by the aqueous complex. For a solution at saturation, the concentration of the aqueous complex can be determined from

$$[AB_{(aq)}] = K_{stab} \cdot [A+][B^-] = K_{stab}\, K_{sp} \qquad\qquad (2\text{--}49)$$

Setting the activity of the solid equal to 1, $K_{sp} = [A^+][B^-]$. Since the aqueous complex is an uncharged species, at low to moderate ionic strengths the activity coefficient is 1, and concentration equals activity.

EXAMPLE 2–5 In pure water the solubility of gypsum is 10.2×10^{-3} mol L^{-1}. Calcium and sulfate ions in solution form an aqueous complex according to the following reaction:
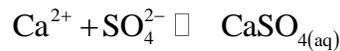
$$Ca^{2+} + SO_4^{2-} \ \Box \ \ CaSO_{4(aq)}$$

$$K_{stab} = \frac{\left[CaSO_{4(aq)}\right]}{[Ca^{2+}]\left[SO_4^{2-}\right]} = 10^{2.23}$$

$$\left[CaSO_{4(aq)}\right] = K_{stab}\left[Ca^{2+}\right]\left[SO_4^{2-}\right] = K_{stab} \cdot K_{sp(gypsum)}$$
$$= \left(10^{2.23}\right)\left(10^{-4.60}\right) = 10^{-2.37} = 4.3 \times 10^{-3}$$

The activity coefficient for an uncharged species is approximately 1. Therefore, the activity and concentration of the uncharged species is the same. Given that the concentration of CaSO$_{4\,(aq)}$ is 4.3×10^{-3} mol L^{-1}, the solubility of gypsum in pure water has increased from 10.2×10^{-3} mol L^{-1} to

14.5×10^{-3} mol L^{-1} an increase in solubility of approximately 40% due to the formation of the aqueous complex.

Some elements occur in solution predominantly as complexes rather than free ions. For these elements it is the properties of the complexes rather than the free ions that determine their behavior in natural systems. Certain metals become soluble when the opportunity arises to form a particular type of aqueous complex. For example, Fe^{3+} and Al^{3+} are generally immobile in the weathering environment. However, in the presence of oxalic acid ($H_2C_2O_4$) these ions can become mobile. Oxalic acid dissociates to form H^+ and COO^- (an oxalate ion). This ion can bond to a metal, forming a complex species. The anion is a ***ligand*** *(an anion or neutral molecule that can combine with a cation).* Given the abundance of dissolved organic matter in the natural environment, this type of aqueous complex can be important in the transport of iron and aluminum.

Ligands can be either monodentate (one pair of shared electrons in a complex) or multidentate (more than one pair of shared electrons in a complex). Inorganic ligands tend to form monodentate complexes, and organic ligands tend to form multidentate complexes. The maximum number of ligands that can bond to a single cation is a function of the relative size of the cation and ligand (see Chapter 7 for a discussion of coordination). In natural waters the number of potential ligands is usually too low for this maximum number to be achieved. Ligands that form multiple bonds with a cation and have a "cagelike" structure are referred to as *chelates.* The metal cation is strongly bonded in these types of structures and chelation is an important process for the removal of metals from the aqueous environment.

MEASUREMENT OF DISEQUILIBRIUM

We have now considered the thermodynamic basis of equilibrium calculations. A remaining question is, How do we measure how close a particular reaction is to equilibrium? Consider the dissolution of gypsum:

$$CaSO_4 \cdot 2H_2O_{\text{gypsum}} \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O$$

The solubility product for this reaction is written

$$K_{sp} = \left[Ca^{2+}\right]\left[SO_4^{2-}\right] = 10^{-4.60}$$

If the system is at equilibrium, the concentration of species in solution (*Activity Product* [AP] if both ions and uncharged species are involved; *Ion Activity Product* [IAP] if only charged species are involved) will equal the solubility product. In this example we are dealing with ions, so at equilibrium IAP = $10^{-4.60}$ (the K_{sp} for gypsum). If the IAP is less than $10^{-4.60}$, the solution is undersaturated with respect to gypsum; and if the IAP is greater than $10^{-4.60}$, the solution is supersaturated with respect to gypsum. Quantitatively, the approach to equilibrium can be expressed as AP (or IAP)/K_{sp}, which is 1 at equilibrium, or log [AP (or IAP)/K_{sp}], which is 0 at equilibrium.

EXAMPLE 2–6 In a particular solution [Ca^{2+}] = 10^{-3} mol L^{-1} and $\left[SO_4^{2-}\right]$. At 25°C, is the solution over-or undersaturated with respect to gypsum? Give a quantitative measure of the degree of over-or undersaturation.

$$\frac{IAP}{K_{sp}} = \frac{(10^{-3})(10^{-2})}{10^{-4.60}} = 10^{-0.40}$$

IAP/K_{sp} is less than 1 so the solution is undersaturated with respect to gypsum.

KINETICS

Equilibrium thermodynamics predicts the final state of the system. Kinetics tells us if the system will actually achieve this state within a reasonable time. In practice, the determination of rates of reaction is not a straightforward exercise. A number of factors affect these rates, and careful experimentation is required to understand the reaction mechanisms. Consider, for example, the dissolution of gypsum in water.

$$CaSO_4 \cdot 2H_2O_{gypsum} \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$
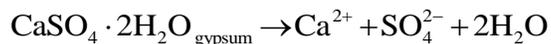
This reaction involves several steps. First, the ions need to be freed from the crystal structure, and then they need to be transported away from the crystal surface. The first step requires an energy input to break the bonds in the crystal structure, and the second step is diffusion controlled. The

importance of the second step may not be obvious, but consider what will happen if the Ca^{2+} and SO_4^{2-} ions are not removed from the immediate vicinity of the gypsum crystal. The concentration of the ions in solution will increase until the microenvironment surrounding the gypsum crystal becomes saturated with respect to gypsum. At this point the dissolution will stop. Whichever of these steps is the slowest will determine the rate at which the dissolution reaction proceeds. As another example, from metamorphic petrology, consider the apparently simple phase transition sillimanite $\rightleftharpoons$ kyanite. Sillimanite and kyanite are polymorphs of Al_2SiO_5, and the reaction suggests that sillimanite is directly converted to kyanite through the rearrangement of atoms in the crystal structure. Petrographic investigations, however, suggest that this is a much more complex reaction, in which the sillimanite first breaks down to form other minerals and is then reformed as kyanite. Hence, what appears to be a very simple reaction actually involves several steps. The slowest of these steps would determine the rate for the overall reaction.

Reactions are of two types: homogeneous and heterogeneous. **Homogeneous** reactions *only involve one phase (gas, liquid, or solid).* **Heterogeneous** reactions *involve two or more phases.* Consider the condensation of water vapor in the atmosphere. If the condensation process involves water vapor condensing directly from the vapor phase, the reaction is homogeneous (it occurs in the gas phase). If the water vapor condenses onto a particle, the reaction is heterogeneous (a gas and a solid are involved). Direct nucleation turns out to be difficult, and in the homogeneous system significant supersaturation is required before condensation actually occurs. On the other hand, the presence of particles facilitates nucleation and in the heterogeneous system condensation occurs close to saturation. Another example from everyday experience is the crystallization of "rock candy." In practice, this is done by heating water on a stove and dissolving copious amounts of sugar in the water. The water is then slowly cooled to room temperature, and the system is now significantly supersaturated with respect to sugar. A small sugar crystal is introduced into the water and serves as a site of nucleation. Rapid crystal growth occurs as the sugar in the supersaturated system precipitates onto the sugar crystal. Virtually all reactions of interest in nature are heterogeneous, but the best understood reactions in terms of kinetics are homogeneous, a not unusual situation in science.

Order of Reactions

For an elementary reaction, the *order* is defined by the number of individual atoms or molecules involved in the reaction. We can talk about order in terms of an individual species or in terms of the overall reaction. Consider the reaction $A + B \rightarrow AB$. The reaction is first order in terms of A and B and the overall reaction is second order. The reaction $A + 2B \rightarrow C$ is first order with respect to A and C, second order with respect to B, and third order overall. Differential and integrated equations follow for the different types of reactions. Also listed is the equation for the half-life ($t_{1/2}$) of each type of reaction—i.e., the time it will take for half of the reactant to be consumed in the reaction.

 Zeroth order. The reaction rate is independent of the concentration of the reactant (A).

$$\frac{dA}{dt} = -k, \quad A = A_0 - kt, \quad t_{1/2} = \frac{0.5A_0}{k} \tag{2–50}$$

 First order. The reaction rate is dependent on the concentration of the reactant, $A \rightarrow B$.

$$\frac{dA}{dt} = -kA, \quad \ln A = \ln A_0 - kt, \quad t_{1/2} = \frac{0.693}{k} \tag{2–51}$$

The first-order rate equations may look familiar since radioactive decay is a first-order reaction—$t_{1/2}$ in this case being the half-life of the radioactive parent.

 Second order. The reaction rate is dependent on the concentration of the reactant, $2A \rightarrow B$.

$$\frac{dA}{dt} = -kA^2, \quad \frac{1}{A} = \frac{1}{A_0} = kt, \quad t_{1/2} = -\frac{1}{kA_0} \tag{2–52}$$

 Note that the units for k depend on the order of the reaction. For example, zeroth-order reaction, mol cm^{-1} s^{-1}; first-order, s^{-1}, and second-order, cm^3 mol^{-1} s^{-1}. Higher-order reactions are possible, but in most geochemical systems of interest the reactions are second order or less. The order of a reaction can be determined by experiment. For example, if the reaction is zeroth order, an arithmetic plot of concentration versus time will yield a straight line. If the reaction is first order, an arithmetic plot of concentration versus time will yield a curved line, because for a first-order reaction the relationship between concentration and time is exponential. A log-log plot of the rate of the reaction versus concentration will yield a straight line whose slope defines the

order of the reaction (0 for zeroth order, 1 for first order, 2 for second order, etc.). The various reaction orders are shown graphically in Figure 2–3.
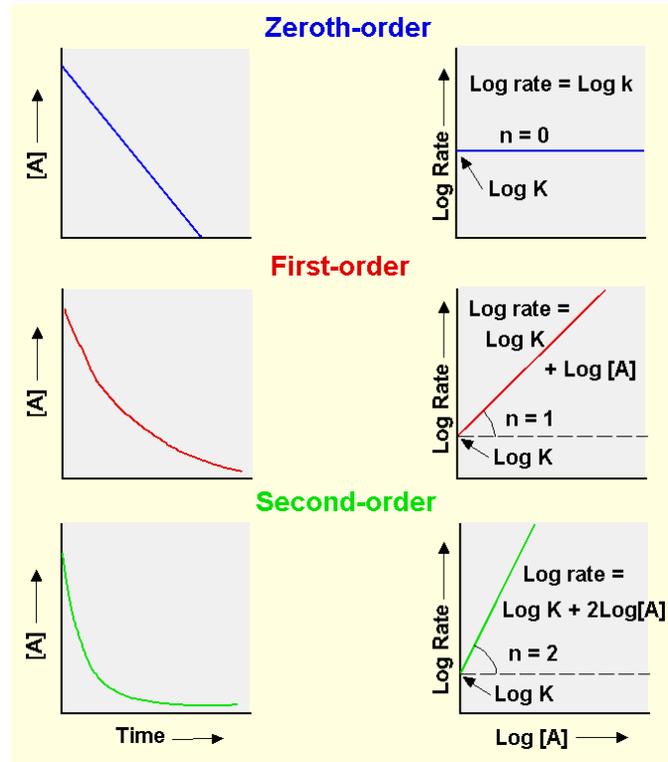
Figure 2–3 Graphical illustration of various reaction orders in terms of the variation in concentration of species A versus time and reaction rate versus concentration of species A. After Appelo and Postma (1996).

EXAMPLE 2–7 At pH > 4, the oxidation of Fe^{2+} in solution can be represented by the overall reaction

$$Fe^{2+} + \frac{1}{4}O_2 + \frac{5}{2}H_2O \rightarrow Fe(OH)_3 + 2H^+$$
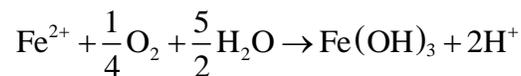
For this reaction, the empirical rate law (Langmuir, 1997) is

$$\frac{d(Fe(II))}{dt} = -k + \frac{(Fe^{2+})}{(H^+)^2}P_{O_2}$$

k_+ indicates that this is the rate constant in the forward direction. For this reaction, at 20°C, $k_+ = 1.2$

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$\times 10^{-11} \, mol^2 \, bar^{-1} \, d^{-1}$. Under atmospheric conditions, $P_{O_2} = 0.2$ bar. Given that Fe^{2+} in solution = $1 \times 10^{-3} \, mol \, L^{-1}$, calculate the reaction rate at $pH = 5$ and $pH = 7$.

At $pH = 5$,

$$Rate = -k_+ \frac{(Fe^{2+})}{(H^+)^2} P_{O_2} = -(1.2 \times 10^{-11}) \frac{(1 \times 10^{-3})}{(10^{-5})^2}(0.2) = -2.4 \times 10^{-5} \, mol \, L^{-1} \, d^{-1}$$

At $pH = 7$,

$$Rate = -k_+ \frac{(Fe^{2+})}{(H^+)^2} P_{O_2} = -(1.2 \times 10^{-11}) \frac{(1 \times 10^{-3})}{(10^{-7})^2}(0.2)$$
$$= -2.4 \times 10^{-1} \, mol \, L^{-1} \, d^{-1}$$

The reaction rate increases by 4 orders of magnitude in going from $pH = 5$ to $pH = 7$.
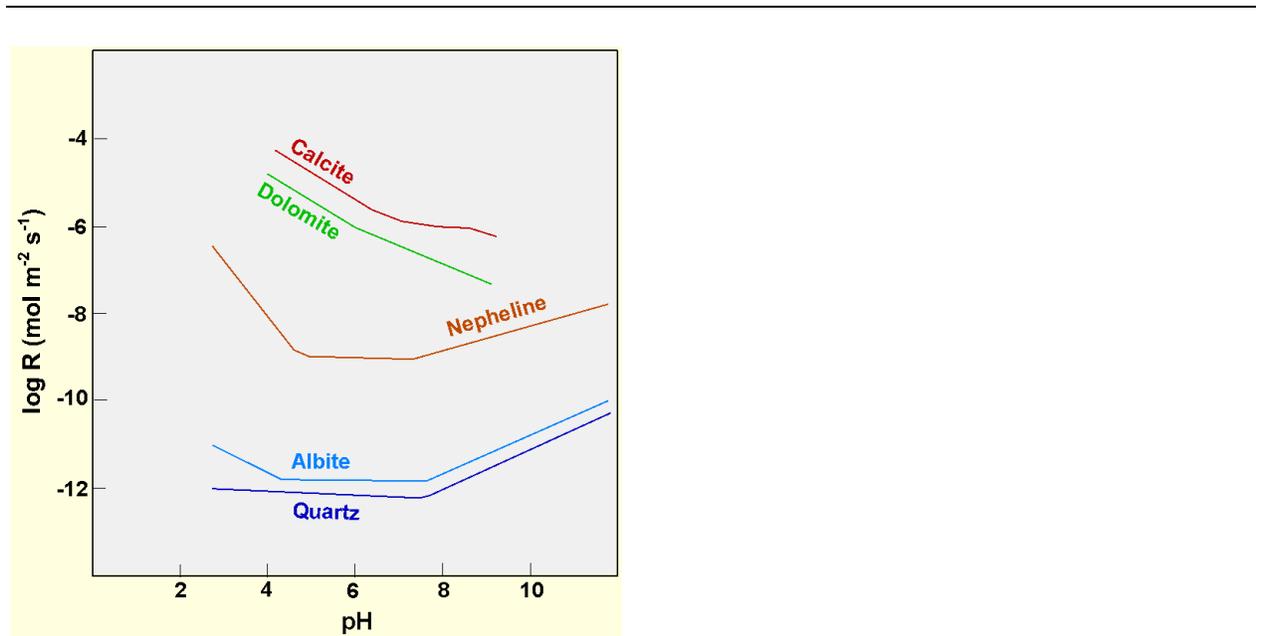
Figure 2–4 Dissolution rates ($mol \, m^{-2} \, s^{-1}$) for common minerals, carbonates, and silicates, as a function of pH. After Lerman (1990). From "Transport and kinetics in surficial processes" by A. Lerman in AQUATIC CHEMICAL KINETICS edited by W. Stumm, pp. 505–534. Copyright © 1990. This material is used by permission of John Wiley & Sons, Inc.
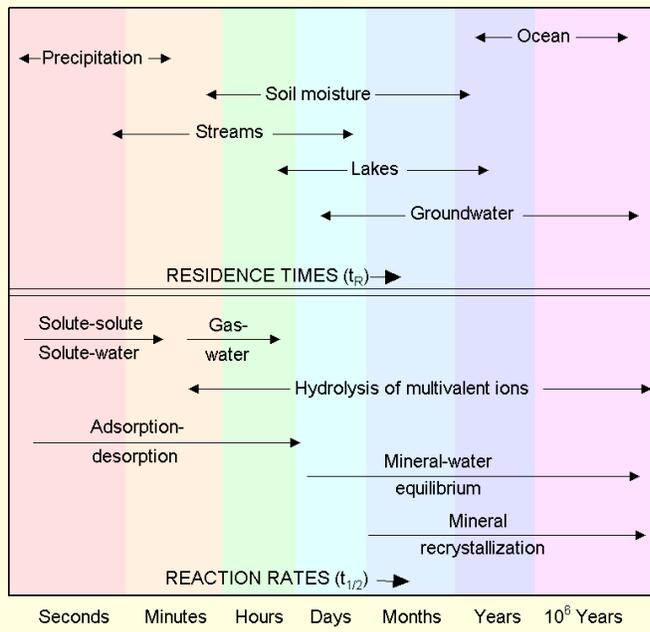
Figure 2–5 Comparison of half-lives of various reactions and residence times of water in different reservoirs. From Langmuir (1997).

Reaction rates have been determined experimentally for a number of important reactions. The results of some of these experiments are portrayed graphically in Figure 2–4. A more complete discussion of reaction rates and their calculation can be found in standard textbooks on water chemistry. Of particular interest for geoscientists is the text by Langmuir (1997), and the interested student should consult this text for further details regarding the calculation of reaction rates.

The half-life of a reaction is a useful concept in that it enables us to assess the significance of kinetics on the attainment of thermodynamic equilibrium. In Figure 2–5 the residence time of water in various reservoirs is compared to the reaction rate (measured as $t_{1/2}$) for a number of different types of chemical processes. If $t_{1/2}$ for a particular chemical process is less then the residence time, then it would be expected that this process would achieve equilibrium. For example, gas–water reactions are rapid ($t_{1/2}$ = hours to days) compared to the residence time of water in the groundwater and ocean reservoirs ($t_{1/2}$ = days to millions of years). Hence, we would expect that gas–water reactions would be in equilibrium in these reservoirs. Conversely, if $t_{1/2}$ was greater than the residence time, then it would be expected that the process would not achieve equilibrium. The reaction rates for mineral–water equilibria are long ($t_{1/2}$ = days to thousands of

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years) compared to the residence time for precipitation in the atmosphere $(t_{1/2}$ = seconds to hours). Hence, in atmospheric aerosols we would not expect solid particles and the liquid or vapor phase to be in equilibrium.

The Arrhenius Equation

*The **Arrhenius equation** relates the rate at which a reaction occurs to the temperature:*

$$k = A\exp\left(\frac{-E_a}{RT}\right) \qquad (2\text{--}53)$$

where A is a pre-exponential factor generally determined by experiment and relatively independent of temperature, E_a is the activation energy for the reaction, R is the ideal gas constant, and T is the temperature in Kelvin. Converting to base 10 logs gives

$$\log k = \log A - \frac{E_a}{2.303RT} \qquad (2\text{--}54)$$

Activation energies are determined by experiment. If a particular reaction follows the Arrhenius relationship, then a plot of log k versus $1/T$ yields a straight line with a slope of $-E_a/2.303R$. A rough rule of thumb is that the reaction rate doubles with every $10°C$ increase in temperature. Measured activation energies (in kJ mol^{-1}) vary from 8 to 500 depending on the process. Simple physical adsorption has low activation energies, and solid phase reactions (such as solid-state diffusion) have high activation energies.

EXAMPLE 2–8 One of the reactions in the carbonate system is

$$CaCO_{3\,calcite} + H_2CO_{3\,(aq)} \rightarrow Ca^{2+} + 2HCO_3^-$$
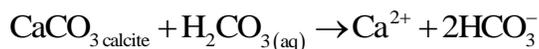
For this reaction, the rate constant at $25°C$ is 3.47×10^{-5} s^{-1} and log $k = -4.46$. Determine the value of the pre-exponential term A for this reaction and determine the rate constant for the reaction at $10°C$.

The activation energy for the reaction is 41.85 kJ mol^{-1}. First determine the preexponential factor by rearranging equation 2–54 to solve for log A.

$$\log A = \log k - \frac{E_a}{2.303RT} = -4.46 + \frac{41.85 \text{ kJ mol}^{-1}}{(2.303)(8.314 \times 10^{-3} \text{kJ mol}^{-1} \text{ K}^{-1})(298.15 \text{K})}$$

$$= -4.46 + 7.33 = 2.87$$

Calculate the reaction rate constant at 10°C using equation 2–54.

$$\log k = \log A - \frac{E_a}{2.303RT} = -2.87 - \frac{41.85 \text{ kJ mol}^{-1}}{(2.303)(8.314 \times 10^{-3} \text{kJ mol}^{-1} \text{ K}^{-1})(283.15 \text{K})}$$

$$= 2.87 - 7.72 = -4.85$$

and $k = 1.41 \times 10^{-5} \text{ s}^{-1}$. Changing the temperature from 25°C to 10°C leads to an approximately 2.5X decrease in the reaction rate.

Nucleation

There are two types of nucleation—homogeneous and heterogeneous. ***Homogeneous*** nucleation occurs when a *nucleus forms spontaneously in an oversaturated solution.*

Heterogeneous nucleation occurs when a *nucleus forms in contact with a, usually solid, surface*. Homogeneous nucleation requires a much greater degree of supersaturation than heterogeneous nucleation.

The free energy of formation of a nucleus consists of the energy gained from the formation of bonds and the energy required to create the surface. This can be written mathematically as

$$\Delta G_{\text{nuc}} = \Delta G_{\text{bulk}} + \Delta G_{\text{surf}} \qquad (2\text{–}55)$$

For an oversaturated solution, ΔG_{bulk} is always negative. For ΔG_{bulk}, we can write the following equation:

$$\Delta G_{\text{bulk}} = \frac{4\pi r^3}{3V} k_B T \ln \frac{a}{a_0} \qquad (2\text{–}56)$$

where $4\pi r^3/3V$ is the volume of a spherical nucleus, V is the *molecular* volume, k_B is the Boltzmann constant (1.3805×10^{-23} J K^{-1}), T is the temperature in Kelvin, a is actual activity, and a_0 is the activity for a saturated solution.

For ΔG_{surf}, we can write

$$\Delta G_{\text{surf}} = 4\pi r^2 \bar{\gamma} \qquad\qquad (2\text{--}57)$$

where $\bar{\gamma}$ is the interfacial energy. Interfacial energies vary over several orders of magnitude. For example, amorphous silica has a surface free energy of 46×10^{-3} J m^{-2} and goethite has a surface free energy of 1600×10^{-3} J m^{-2}. Combining equations 2–56 and 2–57 yields

$$\Delta G_{\text{nuc}} = \frac{4\pi r^3}{3V} k_B T \ln\frac{a}{a_0} + 4\pi r^2 \bar{\gamma} \qquad (2\text{--}58)$$

From equation 2–58 it is obvious that increasing the degree of oversaturation favors nucleation, as does increasing the radius of the particle. For any particular particle size and degree of oversaturation the ease of nucleation is a function of the interfacial energy; e.g., from the data just given it is much more difficult to nucleate goethite than amorphous silica. The rate at which nuclei form can be determined from the standard Arrhenius rate equation,

$$\text{Rate of nucleation} = \bar{A}\exp\left(\frac{-\Delta G^*}{k_B T}\right) \qquad (2\text{--}59)$$

where $\bar{A}$ is a factor related to the efficiency of collisions of ions or molecules, ΔG^* is the maximum energy barrier (see Figure 2–6), k_B is the Boltzmann constant, and T is the temperature in Kelvin.

Interfacial energies are different for nuclei formed via homogeneous reactions versus nuclei formed via heterogeneous reactions. A discussion of this difference can be found in standard water-chemistry books, such as Stumm and Morgan (1996).
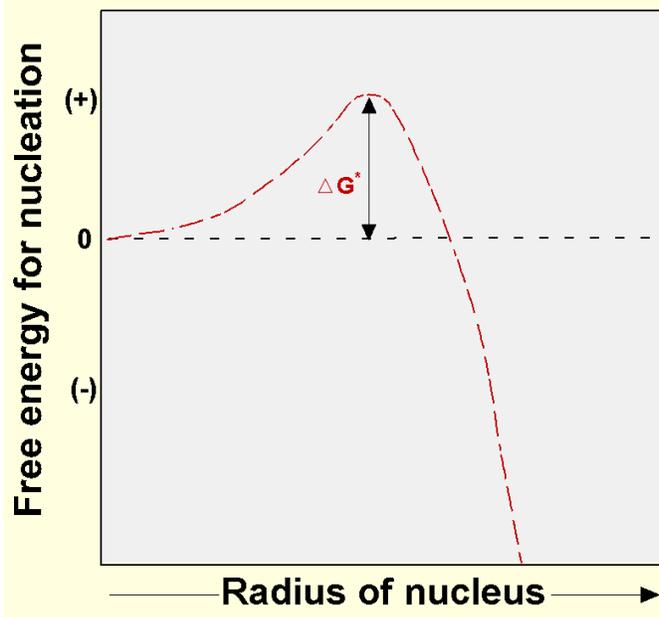
Figure 2–6 Variation of free energy of nucleation as a function of particle radius. The maximum free energy of formation corresponds to the maximum energy barrier. At greater particle radii the free energy of nucleation decreases and eventually becomes negative, and nucleation will proceed spontaneously. Modified from Drever (1997).

Dissolution and Growth

Once a nucleus has formed, the next question is, how fast will the particle grow? This is a function of several factors: (1) the rate at which the ions (or complex molecules) diffuse through the liquid to the surface of the growing particle and (2) the rate at which the ions or molecules are attached to the surface of the growing particle. One of these will be the rate-limiting step. In addition, during dissolution of a particle, there may be a reaction zone between the surface of the original grain and the solution. For example, feldspars break down by *incongruent dissolution* (the feldspar decomposes to a mineral of different composition and species that enter the solution). Thus, a feldspar grain may become coated with a rim of reaction product through which the ions must diffuse in order for the reaction to continue. As the thickness of this reaction rim increases, the diffusion of ions or molecules through the reaction zone may become the rate-limiting step (Figure 2–7).
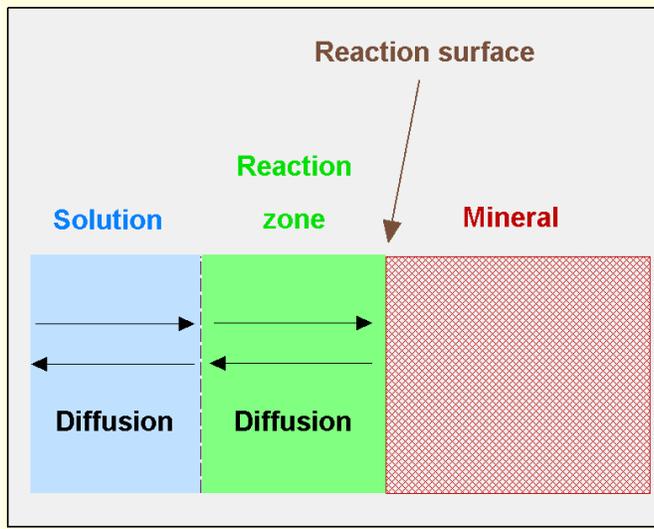
Figure 2–7 Schematic representation of a mineral reacting with a solution during dissolution. The rate-controlling step can be the diffusion of species through the solution, diffusion of species through the reaction zone, or the rate of the surface reaction. Given the slow rate of diffusion of species through the reaction zone, at some point the thickness of this zone will become sufficiently great that the diffusion of species through the reaction zone will become the rate controlling step. Modified from Drever (1997).

The topology of the mineral surface is also important in determining the rate at which both dissolution and particle growth occur. The mineral surface is usually not planar, but consists of *steps* and *kinks.* Atoms that form steps and kinks have higher energy, and dissolution or growth takes place at these locations. **Dislocations** occur *when one part of a crystal Structure is offset relative to another part.* The number and types of dislocations are important in determining the rate of dissolution or growth. **Inhibitors**, or **surface poisons**, are *foreign species adsorbed at points of high energy on the* crystal surface that may inhibit crystal growth or *dissolution.* For example, in seawater the concentration of phosphate ions affects the dissolution rate of calcite. It is believed that the phosphate ion acts as an inhibitor and is preferentially attached to sites of high energy on the crystal surface.

WATER-CHEMISTRY COMPUTER MODELS

The previous discussion of thermodynamics and kinetics has been far from exhaustive but was

intended to introduce the basic concepts used in the modeling of water chemistry. Because these calculations can be very laborious, a number of computer models have been developed to do these types of computations. These computer models can be divided into three basic types: speciation, mass transfer, and chemical mass transport. **Speciation models** *calculate the partitioning of elements between aqueous species and determine the degree of saturation with respect to mineral and gas phases.* The calculations that we considered in the section on equilibrium thermodynamics were of this type. The U.S. Geological Survey's WATEQ4F is an example of this type of model. **Mass transfer models** do the *same types of calculations as speciation models but in addition consider the effect of mass transfer processes (dissolution, precipitation, gas exchange, ion exchange, adsorption, etc*.). Examples of these types of models are PHREEQC and PHRQPITZ (U.S. Geological Survey). **Chemical mass transport models** include *speciation*, *mass transfer processes*, *and hydrodynamic advection and dispersion.* An example of this type of model is the U.S. Geological Survey's PHREEQM-2D.

The major sources of free computer models are the U.S. Environmental Protection Agency and the U.S. Geological Survey. These models can be accessed from the appropriate agency's web pages. The addresses listed here are current at the time of publication, but the various agencies do occasionally change their web addresses.

The site for the U.S. Environmental Protection Agency software is **http://www.epa.gov/epahome/models.htm.** The programs are developed and maintained by the Center for Exposure Assessment Modeling (CEAM). These are DOS-based programs, and a number of different types are available. The water-chemistry model is MINTEQA2, which can be used to calculate the equilibrium compositions of dilute solutions.

The site for the U.S. Geological Survey software is **http://water.usgs.gov/software.** Most of the programs can be run on UNIX or DOS platforms. Windows versions are available for some of the programs. One of the problems with USGS software is that it has not been very user-friendly. This problem has been addressed through the development of CHEMFORM, which serves as an interface for the various programs. Included in the program inventory are mass balance models (NETPATH), speciation models (WATEQ4F) and mass transfer models (PHREEQC, PHREEQCI, PHRQPITZ). Besides water-chemistry models, a number of other hydrological models are available at this site.

Another site of interest, not only in terms of water-chemistry models but also in terms of geochemical data and analysis in general, is the Geochemical Earth Reference Model (GERM). The address for GERM is **http://earthref.org/GERM/main.htm.** This site not only provides links to a number of water-chemistry models but also has tabulations of thermodynamic data, information on elemental abundances in various reservoirs, and a number of other useful tabulations. The site is under continual development and over time should become a major source of geochemical and environmental data. The Geochemical Society, **http://gs.wustl.edu,** also has links to sites that provide geochemical data. This site, presumably, will also expand with time and the number of linkages will increase.

Among the commercially available software, the most powerful and widely used is the Geochemist's Workbench (Bethke, 1996). This set of computer models was originally developed at the University of Illinois and consists of a number of modules that can be used to carry out calculations involving speciation, plotting of stability diagrams, reaction paths, and a variety of mass transfer processes.

Only a few of the models include kinetics, and a variety of activity-coefficient models are used. The user should consult the documentation that comes with each computer code to determine how that particular code does the computations. Particular attention should be paid to the activity-coefficient models (i.e., are they appropriate for the problem?) and the thermodynamic database. Further information on computer models can be found in Mangold and Tsang (1991), van der Heijde and Elnawawy (1993), and Langmuir (1997).

CASE STUDIES

The following three case studies show how water-chemistry computer models can be applied to environmental problems. The Case Study 2–1 considers the impact of acid mine drainage on the downstream quality of a watercourse. The author of the study used geochemical modeling to determine the chemical processes affecting the concentration of each species of interest. The author was also able to determine the first-order rate constant for the removal of iron from the stream. Such calculations are of interest because they tell us how far a particular contaminant will be transported by a river system.

In Case Study 2–2, the authors used several ionic species as tracers to determine the relative

percentage of leachate from a municipal landfill sited on an aquifer. One of the species was found to behave conservatively, and the other was found to show nonconservative behavior when there was a significant leachate component in the aquifer.

In Case Study 2–3, the author investigated the impact of acid deposition on ground-water quality and concluded that the system was not well buffered against acid additions. Increased acidity might result in the release of trace metals, tied up in clay minerals, to the groundwater system.

CASE STUDY 2–1

Geochemical Modeling of Coal Mine Drainage, Summit County, Ohio

A serious problem associated with coal mining is the generation of acid mine drainage (AMD). During mining, sulfur-bearing minerals, such as pyrite (FeS_2), are exposed to oxygen and water, leading to a series of oxidation and hydrolysis reactions that produce sulfuric acid. The resulting waters are strongly acidic (pH of 2 or less is possible) and have high concentrations of SO_4^{2-}, Fe^{2+}, Al^{3+}, and Mn^{2+}. Such waters are toxic to aquatic life and vegetation.

Foos (1997) investigated the downstream changes in the chemistry of coal mine drainage at Silver Creek Metropark, Summit County, Ohio. The first step was to construct a simple mixing model in which AMD and water discharged from Silver Creek lake were the end members. This model successfully predicted the concentrations of Cl^-, PO_4^{3-}, Ca^{2+}, Mg^{2+} and Na^+, indicating that these species behaved conservatively; i.e., they were not reacting with their surroundings. However, the model did not accurately predict the concentrations of HCO_3^-, SO_4^{2-}, Fe^{3+}, Mn^{2+}, and Si. The model underestimated the concentration of HCO_3^-, indicating that this species was being added to the system, and overestimated the concentrations of the other four species, indicating that they were being removed from the system. Sampling along the length of the discharge stream showed a downstream increase in HCO_3^- and a downstream decrease in the other four species. There was an excellent correlation between Fe^{2+} concentration and distance.

Saturation indices (SI) were calculated, using the water-chemistry program WATEQ4F, for solid phases that could play a role in controlling the concentrations of these species. The results are tabulated here. SI = log(IAP/K_{sp}) and the equilibrium constants were calculated for a temperature of 11.5°C, the temperature of the AMD discharge.

Phase	Formula	SI	Phase	Formula	SI
Hematite	Fe_2O_3	14.93	Quartz	SiO_2	0.53
Goethite	FeOOH	6.96	Chalcedony	SiO_2	0.06
Ferrihydrite	$Fe(OH)_3$	1.07	$SiO_{2 (aq)}$	SiO_2	−0.83
Pyrolusite	MnO_2	−14.27	Aragonite	$CaCO_3$	−2.09
Manganite	MnOOH	−6.44	Calcite	$CaCO_3$	−1.94
Rhodochrosite	$MnCO_3$	−1.17	Dolomite	$CaMg(CO_3)_2$	−4.61

The water was supersaturated with respect to all of the iron-containing phases, and further investigation revealed that about 80% of the iron was removed as ferrihydrite. Thus, precipitation of iron-containing phases was the cause of the decrease in Fe^{2+} in the downstream direction. The water was undersaturated with respect to all Mn-bearing phases, and it was concluded that Mn^{2+} was being removed by adsorption onto the surface of the iron hydroxides. The water was slightly oversaturated with respect to the Si-containing phases, so it is possible that precipitation of these phases was causing the downstream decrease in Si. The waters are undersaturated in terms of the carbonate-containing phases, and it was concluded that the downstream increase in HCO_3^- was due to the addition of organic carbon where the stream flowed from an area of mowed lawn into a wooded area of dense vegetation.

The author of the study was able to calculate a rate constant for the removal of Fe^{2+} assuming a steady-state model. The model is a first-order rate equation that can be written as follows:

$$V \cdot \frac{dC}{dx} - kC = 0$$

where V is the velocity of the stream, C is the concentration, and x is the distance. Solving this equation for k gives a rate constant of 2.9×10^{-4} s^{-1}.

Source: Foos (1997).

CASE STUDY 2–2

Leachate Geochemistry at a Municipal Landfill, Memphis, Tennessee

Mirecki and Parks (1994) investigated the impact of leachate from a municipal landfill on the Memphis aquifer. The landfill was sited in alluvium of Quaternary age and was believed to be isolated from the Tertiary-age Memphis aquifer. However, it was found that a discontinuity existed in the confining unit that allowed landfill leachate to enter the Memphis aquifer. Chloride (which is usually considered to be a conservative tracer), barium, boron, and strontium were investigated as possible tracers because they occurred in much higher concentrations in the alluvial aquifer downgradient from the landfill. The water-chemistry program PHREEQE was used to construct mixing curves for these four species using the mean concentrations of leachate-contaminated alluvial aquifer samples and the mean concentrations of uncontaminated Memphis aquifer samples as end members. Chloride and boron were ultimately not used as tracers because they did not seem to behave conservatively. Thus, the analysis focused on barium and strontium concentrations. The following table gives the calculated saturation indices (log[Ion Activity Product/K_{sp}]) for barite ($BaSO_4$), celestite ($SrSO_4$), and strontianite ($SrCO_3$) for different mixtures of the end members.

Mineral	100% contaminated alluvial aquifer water	40%	30%	20%	10%	5%	100% Memphis aquifer water
Barite	0.399	0.136	0.063	–0.031	–0.159	–0.246	–0.360
Celestite	–3.015	–3.287	–3.361	–3.454	–3.581	–3.665	–3.775
Strontianite	–4.355	–4.649	–4.726	–4.821	–4.947	–5.067	–5.140

These calculations indicate that strontium would behave conservatively and that only in mixtures that contained more than 28% water from the contaminated alluvial aquifer would barium behave nonconservatively. In this case, the concentration of barium in the mixture could be predicted from the model calculations. The barium tracer indicated that the leachate component in the Memphis aquifer ranged between 5% and 7%, while the strontium tracer suggested higher amounts of contamination that ranged between 10% and 37%. The authors suggested that the leachate probably flows away from the landfill as discrete pulses in response to precipitation events and that this may account for the variability observed in the chemical date.

Source: Mirecki and Parks (1994).

CASE STUDY 2–3

Ionic Composition and Mineral Equilibria of Acidic Groundwater on the West Coast of Sweden

Halland County, situated on the west coast of Sweden, has some of the most acidified soil and groundwater in the country. This is due to the transport of sulfur and nitrous oxides from Central Europe, leading to high deposition of acidic components. Sjöström (1993) investigated the groundwater chemistry of 14 shallow wells and 10 springs in Halland County. Most of the wells and springs are situated on glacial till or glaciofluvial sediments. The Halland County soils were found to consist of quartz, plagioclase, K-feldspar, amphibole, and chlorite-vermiculite. In the A_2 and B soil subhorizons, goethite, hematite, Ti-oxides, and, possibly, pyrite are common. The groundwaters are dominated by the following major ions: Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+, and K^+ but have an overall low ionic strength, presumably due to the short residence times for the ionic species. The water-chemistry model WATEQX was used to calculate the saturation indices (SI) for minerals that might regulate the water chemistry. The results of these calculations are given here for solid phases that were at least 50% over-or undersaturated in the spring and ground waters.

Mineral	Average SI	Mineral	Average SI
Silica gel	−0.75	Vermiculite	−17.46
SiO_2, amorphous	−1.03	Na,K,Mg−beidellite	1.74
Quartz	−0.67	Mg-montmorillonite	4.42
Albite	−4.04	Ca-montmorillonite	5.43
Anorthite	−6.44	Kaolinite	3.14
Sanidine	−1.05	Diaspore	2.98
K-mica	−0.44	Boehmite	1.27
Chlorite	−21.90	Jarosite	−15.89
Hydroxy-Al vermiculite	8.24		

The waters are significantly undersaturated in the mafic silicate minerals, feldspar, K-mica, and chlorite. The soils are dominated by quartz and feldspar, and because these minerals decompose slowly, the buffering capacity of the soils is limited. The waters are oversaturated with respect to a number of the clay minerals, and these could form in the soils as weathering products of the primary aluminosilicates. During increased acidification it is these clay minerals plus, possibly, oxides of A1 and Fe that will buffer the H^+ addition (see Chapter 3). These buffering reactions will tend to maintain the pH, but Al and Fe will be released to the groundwater and may, at high enough concentrations, pose a health risk.

Source: Sjöström (1993).
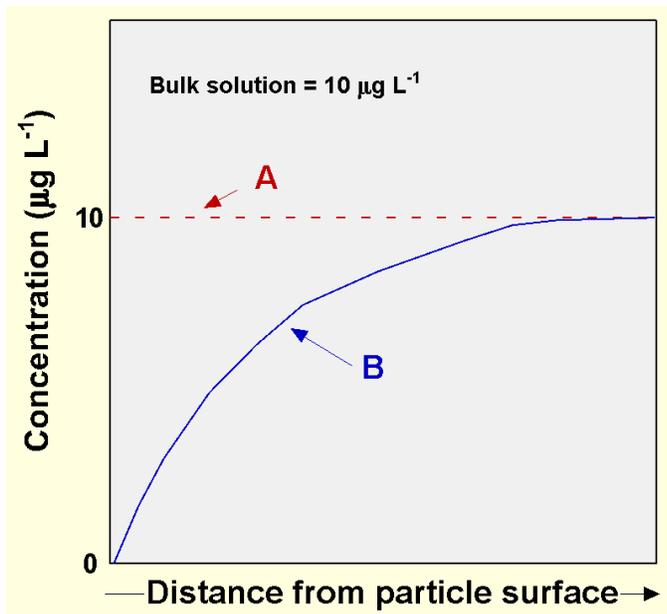
Figure 2–8 Variation in concentration as a function of distance from the surface of a growing particle.

QUESTIONS AND PROBLEMS

1. Why are herbivores more energy efficient than carnivores?

2. What are *intensive variables*? What are *extensive variables*?

3. Distinguish between *open*, *closed*, and *isolated* systems.

4. How can you tell if a reaction is *endothermic* or *exothermic*?

5. *Define* enthalpy *and* entropy.

6. What is the *standard state*?

7. *Define* heat capacity.

8. What is *Le Châtelier's principle* and how can it be used to predict changes in a reaction at equilibrium?

9. When you add HC1 to $CaCO_3$, the following reaction occurs:

$$CaCO_3 + 2HCl \rightarrow Ca^{2+} + 2Cl^- + H_2O + CO_2$$
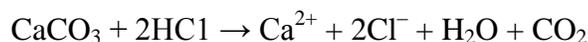
This reaction will proceed differently if it is in a closed container (sealed from the atmosphere) versus open to the atmosphere (for example, on a desktop). How will the reaction differ under these two conditions?

10. What factors are responsible for the nonideal behavior of ions in solution?

11. What is an *aqueous complex*?

12. NaCl dissolves in water to produce Na^+ and Cl^-. Salt is added to a beaker of water until no more salt will dissolve and salt crystals are observed in the beaker.

   a. How many phases are present in this system?

   b. How many components are needed to completely describe the system, and what are the components?

   c. What is the free energy of the system when it becomes saturated in NaCl—i.e., no more salt crystals dissolve in the solution?

13. What is the difference between activity and the measured concentrations of a species in solution?

14. Why and how does the formation of the aqueous complex $CaCO_{3\,(aq)}$ affect the solubility of calcite $(CaCO_3)$?

15. Distinguish between *homogeneous* and *heterogeneous* reactions.

16. Why is an understanding of the kinetics of reactions important in dealing with environmental problems?

17. How could you determine if a reaction was zeroth, first, or second order?

18. What is an *inhibitor*?

19. For the reaction Diamond $\rightarrow$ Graphite, $\Delta G_t^0 = -2.9\,kJ\,mol^{-1}$ at 25°C and 1 atm pressure. Thermodynamically, diamond should be the stable form of carbon at the earth's surface.

Why don't diamonds invert to graphite at the earth's surface?

20. The rate-determining step in the growth of a particle can be either the rate at which species are added to the surface of the growing particle or the rate at which species diffuse to the surface of the growing particle. Figure 2–8 schematically illustrates the variation in concentration of an ionic species in solution as a function of distance from the surface of a particle. For case A, what is the rate-controlling step, and why? For case B, what is the rate-controlling step, and why?

21. Refer to Case Study 2–2. What is meant by conservative behavior? Why did the authors conclude that barium would only behave conservatively in mixtures that contained less than 28% water from the contaminated aquifer while strontium would behave conservatively in all possible mixtures?

22. With reference to Case Study 2–3, what should happen to anorthite grains when acidified water passes through the soil horizon? Explain.

23. During chemical weathering, forsterite is dissolved by the carbonic acid in rainwater. The weathering reaction is as follows:
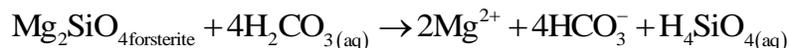
$$Mg_2SiO_{4\,forsterite} + 4H_2CO_{3\,(aq)} \rightarrow 2Mg^{2+} + 4HCO_3^- + H_4SiO_{4(aq)}$$

Use the thermodynamic data from Appendix II, source 2, for the following calculations.

a. Calculate the K_{eq} for this weathering reaction at 25°C.

b. If the reaction is at equilibrium, using Le Châtelier's principle, predict what would happen if Mg^{2+} ions were added to the solution.

c. Using Le Châtelier's principle, predict what would happen to the equilibrium constant if the reaction occurred at a higher temperature.

d. Calculate the K_{eq} for this reaction at 40°C. Does the solubility of forsterite increase or decrease with increasing temperature? How does this result compare with your prediction in part (c)?

24. a. Calculate the K_{sp} for magnesite ($MgCO_3$) at 25°C. Use the thermodynamic data from Appendix II, source 2, for this calculation.

b. What is the solubility of magnesite in pure water? How much difference does it make if it is assumed that activity equals concentration versus activity calculated from the Debye–Hückel equation? (*Note:* In order to answer the latter part of the question, you will have to calculate the final solubility by successive approximations. Use the original ion concentrations to determine the ionic strength, then determine the activity coefficients. Use the coefficients to recalculate the ion concentrations. Repeat this process until there is no change in the activity coefficients.)

c. Mg^{2+} and CO_3^- form the complex $MgCO_{3 \ (aq)}$. For this complex, $K_{stab} = 10^{2.98}$. How does the existence of this complex affect the solubility of magnesite? A numerical answer is required.

25. The Hubbard Brook watershed in the White Mountain National Forest in New Hampshire, USA, has been the site of a long-term study on the effect of natural and anthropogenic processes on aquatic ecosystems. Water collected from the brook has the following chemical composition (Likens et al., 1977):

Concentration (mg L^{-1})	
Ca^{2+}	1.7
Mg^{2+}	0.4
Na^+	0.9
K^+	0.3
Cl^-	0.55
SO_4^{2-}	6.3
HCO_3^-	0.9
SiO_2 (aq)	4.5
pH	4.9
TDS	19

Note that the pH for Hubbard Brook is much less than 5.7. This is a region in which acid rain is a problem, and the acid rain input is reflected in the water chemistry.

a. Calculate the concentrations of the ionic species in mol L^{-1}.

b. Calculate the total negative and positive charge. Do the charges balance; i.e., does the total positive charge equal the total negative charge?

c. Calculate the activity coefficients for Ca^{2+} and SO_4^{2-} at 25°C using the Debye–Hückel equation.

d. At 25°C, gypsum has the following solubility product, $K_{sp} = 10^{-4.60}$. Is Hubbard Brook saturated or undersaturated with respect to gypsum? Calculate the IAP and the saturation index.

26. The Rio Grande river at Laredo, Texas, has the following water chemistry (Livingstone, 1963):

Concentration (mg L^{-1})	
Ca^{2+}	109
Mg^{2+}	24
Na^+	117
K^+	6.7
Cl^-	171
SO_4^{2-}	238
HCO_3^-	183
SiO_2 (aq)	30
TDS	881

The Rio Grande water chemistry is very different from that of Hubbard Brook (problem 25). Hubbard Brook is located in a forested watershed in the northeastern United States, a region of temperate climate and moderate rainfall; the Rio Grande is on the U.S.–Mexico border, a warm region with low annual precipitation. The differences in climate are at least partly responsible for the differences in water chemistry. Use the thermodynamic data from Appendix II, source 2, for the following calculations.

a. Calculate the concentrations of the ionic species in mol L^{-1}

b. Calculate the solubility product (equilibrium constant) for gypsum given a water temperature of 30°C.

c. Calculate the activity coefficient for Ca^{2+} and SO_4^{2-} at 30°C using the Debye– Hückel equation.

d. By how much is the water supersaturated or undersaturated with respect to $CaSO_4 \cdot 2H_2O$? Your answer should include a numerical estimate.

27. Fluoride is sometimes found in high concentrations in ground and surface waters. Fluoride, in low concentrations, is often added to drinking water to minimize dental carries, but in higher concentrations fluoride can pose a health risk. The following table gives the composition of relatively fluoride-rich waters from three locations: groundwaters drawn from the Bongo granite, Ghana, groundwaters from Rajasthan, India, and surface waters from Lake Abiata, Ethiopia. Use the thermodynamic data from Appendix II, source 3, for the following calculations.

Ground and Surface Water Chemistry (mg L^{-1})			
Species	Bongo granites, Ghana[1]	Rajasthan, India[2]	Lake Abiata, Ethiopia[2]
Ca^{2+}	25.3	27.1	1.0
Mg^{2+}	11.5	19.1	0.9
Na^+	23.9	1101	4460
K^+	2.0	5.9	192
Cl^-	6.7	617	1911

Ground and Surface Water Chemistry (mg L^{-1})			
Species	Bongo granites, Ghana[1]	Rajasthan, India[2]	Lake Abiata, Ethiopia[2]
F$^-$	2.3	6.8	119
SO$_4^{2-}$	4.8	500	14.4
HCO$_3^-$	156	903	8420

[1]Apambire et al. (1997).

[2]Apello and Postma (1996).

a. Two minerals that may control the concentration of fluoride ion in solution are fluorite (CaF$_2$) and villiaumite (NaF). For each of the waters listed in the table, determine the saturation index at 25°C for these minerals. (*Note*: Activity is important and must be included in the calculations.) Would either of these minerals control the fluoride concentration of these waters?

b. What is a possible explanation for the very high concentrations of Na$^+$, Cl$^-$, F$^-$, and HCO$_3^-$ in the waters of Lake Abiata? The lake has a pH of 9.62.

28. Knauss et al. (2000) determined various thermodynamic quantities for the aqueous solubilities of two organic liquids of environmental interest, trichloroethene (TCE) and tetracholorethene (PCE). The thermodynamic data at 298 K are tabulated here. Note that the reaction is organic liquid → organic liquid dissolved in water.

	ΔG_{soln} (kJ mol^{-1})	ΔH_{soln} (kJ mol^{-1})	ΔS_{soln} (J mol^{-1} K^{-1})	$\Delta C_{p\ soln}$ (J mol^{-1} K^{-1})
TCE	11.282	−3.35	−49.07	385.2
PCE	15.80	−1.79	−59.00	354.6

a. Calculate the equilibrium constants for both reactions.

b. If 1 kg of each organic liquid was spilled into 1000 kg of water, calculate the concentration of each organic liquid dissolved in the water.

c. Using Le Châtelier's principle, predict what would happen to the solubility of each organic liquid in water with increasing temperature.

d. For each organic liquid calculate the equilibrium constant at 40°C. Were the predictions you made using Le Châtelier's principle, part (c), correct?

29. Asbestos minerals are considered to be a health hazard. The most common type of asbestos is chrysotile, and this mineral comprises about 95% of the asbestos in the United States. Small asbestos fibers can be taken into the lung, where they interact with the lining of the lung. This problem deals with the solubility of chrysotile asbestos in the lung. A later problem deals with the rate at which chrysotile fibers will break down in the lung. The dissolution reaction for chrysotile can be written
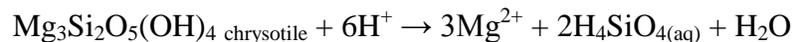
$$Mg_3Si_2O_5(OH)_{4\ chrysotile} + 6H^+ \rightarrow 3Mg^{2+} + 2H_4SiO_{4(aq)} + H_2O$$

Use the thermodynamic data from Appendix II, source 3, for the following calculations.

a. Calculate the equilibrium constant for this reaction at $T = 37°C$, the average temperature of the human body.

b. For fluid in lung tissues, pH = 4, $Mg^{2+} = 8.7 \times 10^{-4}$ mol L^{-1}, and $H_4SiO_{4(aq)} = 1.5 \times 10^{-6}$ mol L^{-1}. Assume activity equals concentration. Are the lung fluids under– or oversaturated with respect to chrysotile? Give a numerical answer.

c. Redo the calculation in part (b) given an ionic strength for the lung fluids of 0.12.

d. Based on these calculations, would you expect chrysotile to persist in the lungs? Explain your answer.

30. Knauss et al. (2000) determined Henry's law constants for TCE and PCE at various temperatures. Henry's law is often expressed as

$$H_c = \frac{\text{Concentration vapor}}{\text{Concentration liquid}}$$

which is the form of Henry's law used by Knauss et al. (2000).

	TCE		PCE	
T (K)	H_c (atm m^3 mol^{-1})	T (K)	H_c (atm m^3 mol^{-1})	
294	0.006942	295	0.017574	
323	0.025183	324	0.057607	
348	0.048869	348	0.121925	
372	0.067645	374	0.182980	
390	0.060473	397	0.189062	

a. 1×10^{-4} mol m^{-3} of TCE are dissolved in water at 294 K. Calculate the equilibrium vapor pressure.

b. 1×10^{-5} mol m^{-3} of PCE are dissolved in water at 324 K. Calculate the equilibrium vapor pressure.

31. At 25°C and pH = 5, the following dissolution rates have been obtained for quartz, microcline, albite, diopside, forsterite, and anorthite (data from Lasaga et al., 1994). These dissolution reactions are zeroth-order reactions.

Mineral	Formula	Density g cm^{-3}	Log rate mol m^{-2} s^{-1}
Quartz	SiO_2	2.65	−13.39
Microcline	$KAlSi_3O_8$	2.59	−12.50
Albite	$NaAlSi_3O_8$	2.62	−12.26
Diopside	$CaMgSi_2O_6$	3.22	−10.15
Forsterite	Mg_2SiO_4	3.22	−9.50
Anorthite	$CaAl_2Si_2O_8$	2.76	−8.55

Assuming a planar surface, calculate how long it will take to dissolve a 1-mm-thick layer from each of the minerals. Note that the dissolution rates are determined for a square meter of surface area, so you should do these calculations for 1 m^2 of surface area

retreating 1 mm. You will first need to calculate the total moles of each mineral in the volume to be removed. Then calculate the dissolution times, in years, for each mineral. Compare these dissolutions times to the preservation/loss of these minerals during weathering and transport. Is there a relationship between the dissolution times and the persistence of these minerals in the weathering environment?

32. Hume and Rimstidt (1992) investigated the dissolution of chrysotile in lung solutions. They found that the rate-controlling step is the release of Si to solution, and that the reaction is zeroth order. The experimentally determined rate constant is $k = 5.9 \times 10^{-10}$ mol m^{-2} s^{-1}. They modeled the breakdown of a fiber as if it were an infinitely long cylinder dissolving over its lateral surface. The resulting equation is

$$t = \frac{3}{4}\left(d / V_m k\right)$$

where t is the time in seconds, d is the diameter of the fiber in meters, V_m is the volume occupied by 1 mol of silica in chrysotile (5.4×10^{-5} m^3 mol^{-1}), and k is the rate constant. Calculate the dissolution time for a chrysotile fiber 1 μm in diameter.

33. Foos (1997) determined a first-order rate constant for the removal of Fe^{2+} from a stream (Case Study 2–1). Discharge from a point source adds Fe^{2+} to a river. Using the rate constant determined by Foos (1997) and a stream velocity of 0.5 m s^{-1}, calculate the transport distance required to achieve a 90% reduction in the amount of Fe^{2+} in solution. To do this problem you will first need to find the amount of time required to reduce the iron concentration by 90%.

34. The breakdown of pyrite (and marcasite) is important in determining the pH of waters draining from coal mines and spoils (acid mine drainage). Aqueous oxidation of pyrite by molecular oxygen can be represented by the following reaction:

$$FeS_{2\,pyrite} + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
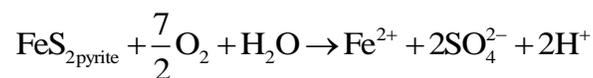
For this reaction, Williamson and Rimstidt (1994) determined the following rate constant:

$$r = 10^{-8.19} \frac{m_{DO}^{0.5}}{m_{H^+}^{0.11}}$$

where m_{DO} is the amount of dissolved oxygen, m_{H^+} is the hydrogen ion concentration, and r is the rate of pyrite destruction in mol m^{-2} s^{-1}. Assume the activation energy for this reaction is 60 kJ mol^{-1}. Spoils from a coal mine contain small pyrite cubes having an average specific surface area of 0.01 m^2 g^{-1}. Water percolating down through this spoils pile is saturated with respect to atmospheric oxygen ($10^{-3.6}$ mol L^{-1}). The water has a pH of 5.0. Assume that the breakdown of pyrite only occurs according to the preceding reaction.

a. Calculate the rate constant for the breakdown of pyrite in contact with the water percolating through the spoils pile.

b. Given that the reaction is pseudo zero order, calculate the time required ($t_{1/2}$) for oxidation of half the pyrite in the spoils pile. You will first need to calculate the number of moles in 1 g of pyrite, and then determine the moles per square meter of specific surface area. The result of this calculation is the value for A_0 in the rate equation.

c. If the reaction rate was determined at 20°C, calculate the reaction rate at 30°C.

35. Several studies have been done on the rate at which organic matter breaks down in the marine environment. Westerich and Berner (1984) identified three types of organic matter in marine sediments—highly reactive, less reactive, and nonreactive (didn't break down during the course of their experiments). The following equation summarizes the results of their experiments:

$$G_T(t) = G_{01}[\exp(-k_1 t)] + G_{02}[\exp(-k_2 t)] + G_{nr}$$

where G_T is the total organic carbon, G_{01} is the highly reactive fraction, G_{02} is the less reactive fraction, and G_{nr} is the nonreactive fraction. Different rate constants were determined for oxic and anoxic decay. Middelburg (1989) developed a different model that expressed the decay of organic matter in marine sediments in terms of a single first-order

rate equation in which k changes with time. The following equation relates the rate constant and its change with time:

$$\log k = -0.95 \log t - 0.81$$

and

$$G_{t1} = G_{t0} \exp 3.2(-t^{0.05})$$

where G_{t1} is the amount of organic carbon remaining at time t, G_{t0} is the amount of organic carbon initially present, and t is time.

For a number of years New York City has disposed of its sewage sludge in the New York Bight.

a. Using the model of Westerich and Berner (1984), calculate the amount of sludge remaining 1 year after deposition in the New York Bight. Assume that the sewage consists of 45% highly reactive organic carbon, 45% less reactive organic carbon, and 10% nonreactive organic carbon. For oxic decay, $k_1 = 18$ y^{-1} and $k_2 = 2.3$ y^{-1}.

b. Do the same calculation as in (a) using the model of Middelburg (1989).

c. Compare the two answers. Why are they different?

d. Using the equation of Middelburg (1989), calculate the length of time it will take for 50% and 99% of the organic matter to decompose. Are both of these answers realistic? You may want to read the original paper to get a better understanding of the model.

36. The dissolution of quartz in H_2O can be represented by the following reaction:

$$SiO_{2\ (s)} + 2H_2O \rightarrow H_4SiO_{4\ (aq)}$$

Rimstidt and Barnes (1980) determined the reaction rate for the dissolution of quartz as a function of temperature. Their data are listed in the following table:

Temperatures and Reaction Rates for the Dissolution of Quartz	
T (°C)	k (sec^{-1})
65	3.81×10^{-9}
105	8.15×10^{-9}
145	1.36×10^{-7}
170	7.68×10^{-8}
213	1.05×10^{-6}
265	1.85×10^{-6}
305	3.69×10^{-6}

a. Plot log k versus $1/T$. Note that temperature should be in Kelvin.

b. Using the graph, determine the activation energy for this reaction and the preexponential factor.

37. The bacterial reduction of organic matter in marine sediments has been investigated by Berner (1981a). The following data table, showing the variation in sulfate as a function of time, was derived from the experiments of Berner (1981a).

Dissolved Sulfate Versus Time for Marine Sediments	
SO_4^{2-} (mmol L^{-1})	Time (days)
20	0
15	5
10	10
5	15
0	20

a. Graph the data.

b. What is the order of the reaction?

c. Calculate the rate constant.

38. If you have read the book *Civil Action* or seen the movie, you may recall that trichloroethene (TCE) was one of the contaminants found in wells G and H. Much of the

court case dealt with the source of this contaminant. Knauss et al. (1999) determined the kinetic rate law for the aqueous oxidation of TCE in aerobic, pH neutral waters. The Arrhenius activation energy (E_a) for the reaction was determined to be 108.0 ± 4.5 kJ mol[1]. A series of experiments yielded the following concentration and rate data. Note that the data are given in log form.

Run	Log C_o (mol)	Log initial rate (mol kg^{-1} s^{-1})
TCE-35	−4.330	−9.748
TCE-39	−3.781	−9.724
TCE-41	−4.949	−10.300
TCE-42	−5.662	−11.261
TCE-43	−4.899	−10.195
TCE-51	−4.329	−9.741
TCE-53	−4.401	−9.770

a. Plot the data. Put Log C_o on the *x-axis* and Log rate on the *y-axis.* Fit a straight line through the data points. Note that these are real data and there is scatter. The straight line can be fit either by eye or by linear regression. Linear regression is the preferred method and is most easily done using a spreadsheet. The intercept of this line with the y-axis gives the rate constant for this reaction at 25°C. What is the value of the rate constant? What is the slope of the line?

b. Based on the slope of the line, what is the order of the reaction?

c. Using the rate constant from part (a), calculate the pre-exponential factor for the rate equation.

d. Calculate the rate of the reaction at 5°C. By how much does the reaction rate change in going from 25°C to 5°C?

e. Calculate the reaction half-life at 25°C and 5°C.

f. Assuming that the groundwater in the vicinity of wells G and H had a temperature of 5°C, what might you conclude about the transport time for TCE delivered to these wells,

i.e., would it be months or years? Explain your answer. In answering this question you need to consider how long TCE would persist in the groundwater under these conditions. If it has already degraded by the time the water reaches the well, it wouldn't be found in the well water.