

CHAPTER 3 CHEMICAL EQUILIBRIUM

3.1. INTRODUCTION

In this chapter we will describe methods that will allow us to answer the questions "Will this reaction go?" and, if so, "How far can it proceed?." These are extremely important questions to pose prior to setting about the investigation of any chemical or biochemical system. If a reaction is impossible, there is absolutely no sense whatsoever in attempting to determine its rate, its mechanism, or its use in a water or waste treatment process. If, for example, you were to be approached by a salesman trying to sell you a chemical that would prevent carbon dioxide and nitrogen from combining with chloride to form dangerous hydrogen cyanide and hypochlorous acid during treatment of a particular wastewater, you could, by using techniques similar to those developed in this chapter, tell him that the reaction was not possible with or without the chemical and send him on his way. And you could do this conclusively without conducting a single experiment!

The techniques we will develop are based on the branch of science known as thermodynamics. The theoretical aspects of thermodynamics are extremely precise and orderly; its mathematical basis is complex. We, however, are only interested in what thermodynamics can do for us as a tool in solving problems of chemical equilibrium. We are in a situation similar to the automobile driver using a road map. Not many drivers thoroughly understand the principles of geometry and plane trigonometry that were used to draw the map. However, most know how to read a map and in doing so could manage reasonably well to get from Urbana to Berkeley.

3.2. THE DYNAMIC NATURE OF CHEMICAL EQUILIBRIUM

Let us examine the hypothetical, elementary, reversible reaction taking place at constant temperature,



The reactants A and B combine to form the products C and D. In this reaction, *a* moles of A combine with *b* moles of B to form *c* moles of C and *d* moles of D. If we were to introduce A and B into a suitable reaction

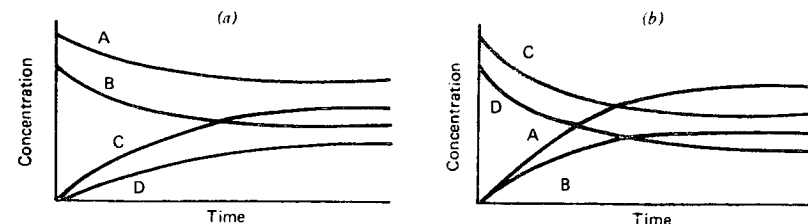


Fig. 3-1. Course of reaction between A, B, C, and D. (a) Initially only A and B are present; (b) initially only C and D are present.

vessel and at time intervals analyze the contents of the reaction vessel, we would obtain a concentration versus time profile such as in Fig. 3-1(a).

The concentrations of A and B decrease until they reach values that do not change with time, while the concentrations of C and D increase from zero to time-invariant values. If we were to add only the products of the reaction, C and D, to the reaction vessel under the same experimental conditions, we would observe a concentration-time change such as that depicted in Fig. 3-1(b). After a while A, B, C, and D concentrations all reach constant, time-invariant levels. If the ratio of the concentration of products to reactants, $[C]^c[D]^d/[A]^a[B]^b$ is the same as that attained in the previous experiment when A and B were initially present, we say that the reaction is at equilibrium and we call the concentrations of species present at that time equilibrium concentrations. The ratio is the so-called equilibrium constant, *K*.

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = K \quad (3-2)$$

The unit of concentration as indicated by [] is mole/liter, but other concentration units also can be used.¹ From this discussion we learn that the equilibrium state can be approached from both directions.

When we investigate the rate at which the equilibrium condition is approached, we can deduce that the equilibrium condition is a dynamic one, not a static situation. The interaction of reactants and products does not cease when equilibrium is reached. The forward and reverse reactions proceed at such a rate that the ratio of concentrations of products to reactants (as described by the equilibrium constant, Eq. 3-2), remains constant. Another way of stating this is that a chemical reaction is at equilibrium if its forward rate of reaction, *v_f*, is equal to the rate of the reverse reaction, *v_r*. For example, we have seen previously in Chapter 2

¹ Strictly speaking, the equilibrium constant is defined in terms of activity, or active concentrations, as discussed later in this chapter. Concentration, such as the molar concentration, often can be used as a good approximation of activity for species in dilute aqueous solutions.

that if the reaction in Eq. 3-1 is elementary, the forward rate of reaction, v_f , can be expressed by the rate law,

$$v_f = k_1[A]^a[B]^b \quad (3-3)$$

and the reverse rate by v_r ,

$$v_r = k_2[C]^c[D]^d \quad (3-4)$$

Initially, if only A and B are present, the forward rate of reaction will proceed at a finite rate while there will be no reverse reaction because no C and D are present. However, as soon as the reaction of A and B produces C and D, they will combine, and by the reverse reaction produce A and B. The reaction will proceed until the opposing reaction rates are equal, and

$$v_f = v_r \quad (3-5)$$

Therefore,

$$k_1[A]^a[B]^b = k_2[C]^c[D]^d \quad (3-6)$$

and

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{k_1}{k_2} = K \quad (3-7)$$

The equilibrium constant is thus the ratio of the rate constants of the forward and the reverse reactions—a fact that underscores the dynamic nature of equilibrium.²

3.3. THE THERMODYNAMIC BASIS OF CHEMICAL EQUILIBRIUM

A knowledge of the position of chemical equilibria is of the utmost importance to us in water chemistry. By knowing the position of chemical equilibria, we can determine whether it is possible for certain reactions between reactants at given concentrations to proceed. For example, we can provide answers to questions such as: Will calcium carbonate tend to precipitate or dissolve in this water? Can I possibly oxidize sulfide with nitrate? and so on. There are two general ways to answer questions like these. The first is to do an experiment and the second is to calculate the answer using previously determined equilibrium data. Although the first way may be more enjoyable to those who like puttering around in the laboratory, the second approach is far superior if time is of the essence.

To explore the various techniques that can be used to answer the

² If the chemical reaction is not elementary, derivation of K from rate constants is still possible but is more complex. See, e.g., T. S. Lee, in *Treatise on Analytical Chemistry*, I. M. Kolthoff, and P. J. Elving, eds., Part I, Vol. 1, Wiley-Interscience, New York, 1959.

question "Will this reaction go?" we must delve a little into the thermodynamic basis of equilibrium. Our treatment of thermodynamics will be brief; we will present only that which is useful and immediately applicable for our purpose. For a more comprehensive coverage of the topic, the student is referred to other texts (see Section 3-7).

Most of the reactions with which we are concerned in water chemistry take place in a closed system or can be analyzed as though they take place in a closed system. For thermodynamic purposes a closed system is one to which matter cannot be added or removed. Energy, however, may flow across its boundaries. Since, in addition to working with closed systems, we usually are interested in systems at constant temperature and pressure, we can make extensive use of the thermodynamic expression for free energy,

$$G = H - TS \quad (3-8)$$

where

G = Gibbs free energy, kcal

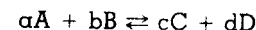
T = absolute temperature, °K

S = entropy, kcal/°K

H = enthalpy, kcal

The enthalpy is the total energy content of an element or compound. The free energy is that part of the total energy that is available to perform "useful work," that is, other than pressure-volume work. The entropy is a sort of internal manifestation of energy that can be visualized in several ways; for example, entropy is often defined as describing the degree of order or organization in a system. Highly structured materials (e.g., well-formed crystals) have low entropy while randomly arranged systems (e.g., a gas) have high entropy. The product TS is that part of the total energy which is not available for useful work.

For closed systems at constant pressure and constant temperature, the criterion for equilibrium is that the total free energy of the system (G_T) is a minimum. For example, consider the reversible reaction previously examined in Eq. 3-1,



If we were to add A and B to a reaction vessel and calculate the total free energy of the system as a function of extent of reaction as the reaction proceeded, we would find something like that depicted by the solid line at the left side of the diagram in Fig. 3-2. The total free energy, G_T , is the sum of the free energies of each of the reaction components. For example, if n_A , n_B , n_C and n_D represent the number of moles of A, B, C and D that are present and \bar{G}_A , \bar{G}_B , \bar{G}_C , and \bar{G}_D represent the free energy/mole of each substance, then

$$G_T = n_A\bar{G}_A + n_B\bar{G}_B + n_C\bar{G}_C + n_D\bar{G}_D$$

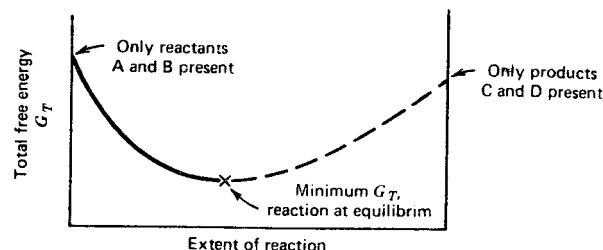


Fig. 3-2. Variation of Gibbs free energy for the chemical reaction $aA + bB \rightleftharpoons cC + dD$. Only reactants are present at the far left side of the diagram and only products at the far right side.

Conversely, if we were initially to add only C and D to the reaction vessel, calculation of the total free energy of the system as the reaction proceeded to form A and B would produce a curve of the form shown by the dashed line on the right-hand side of Fig. 3-2. In each case the reaction only proceeds spontaneously, or without any external help, as long as the value of G_T decreases. Because of this there exists, at a certain extent of reaction, a point where G_T is at a minimum. This point can be spontaneously reached from either the product or reactant side, and it is the equilibrium point of the system. Thus we may state that the equilibrium condition of a reaction is the point at which G_T is a minimum. Also, we may deduce that reaction in the direction that decreases G_T is spontaneous while reaction in the direction that increases G_T is not spontaneous or will not occur in a closed system.

It can be shown that as any reaction proceeds an incremental amount, the change in G_T is proportional to ΔG where

$$\Delta G = \left(\sum_i \nu_i \bar{G}_i \right)_{\text{products}} - \left(\sum_i \nu_i \bar{G}_i \right)_{\text{reactants}} \quad (3-9)$$

where ν_i is the stoichiometric coefficient (e.g., α , b , c , and d in Eq. 3-1) and \bar{G}_i is the free energy per mole.

We can therefore state that if,

1. ΔG is < 0 (i.e., ΔG is negative and thus G_T decreases as the reaction proceeds); the reaction may proceed spontaneously as written.
2. ΔG is > 0 (i.e., ΔG is positive and thus G_T would increase if the reaction were to proceed); the reaction cannot proceed spontaneously as written. Conversely, it may proceed spontaneously in the opposite direction to which it is written.

3. $\Delta G = 0$ (i.e., G_T is at a minimum); the reaction is at equilibrium and will not proceed spontaneously in either direction.

Values of ΔG for a reaction provide us with a powerful tool to predict whether or not reactions are possible. To calculate ΔG for the general reaction given by Eq. 3-1, we use the relationship

$$\Delta G = \Delta G^\circ + RT \ln \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b} \quad (3-10)$$

where

$$\Delta G^\circ = \left(\sum_i \nu_i \bar{G}_i^\circ \right)_{\text{products}} - \left(\sum_i \nu_i \bar{G}_i^\circ \right)_{\text{reactants}} \quad (3-11)$$

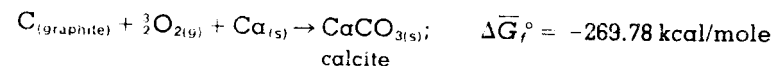
$\{ \}$ = activity, or active concentration (discussed later in this section)

\bar{G}_i° = free energy/mole of species i at 25°C and 1 atmosphere pressure

Equation 3-10 is developed in more detail later. The first step in determining ΔG is to determine \bar{G}_i° , the free energy per mole of each reactant and product at the standard state condition of 25°C and 1 atm total pressure. The term \bar{G}_i° is called the standard free energy per mole of species i .

At standard state every element is assigned, by convention, a free energy of zero per mole. Thus $H_{2(g)}$, $O_{2(g)}$, $C_{\text{graphite}(s)}$, and so forth, all are assigned free energy values of zero kcal/mole. Also, to establish a baseline for ionic substances in solution, H^+ at a concentration of 1 mole/liter in an ideal solution and at standard state conditions has been assigned a free energy of zero.

This convention is necessary because it is impossible to measure absolute values of free energy. However, we can measure changes in free energy. Thus, assigning a value of zero to elements at standard state allows us to measure the free energy change involved in forming compounds at standard state from their component elements at standard state. This free energy change is called the standard free energy of formation, $\Delta \bar{G}_f^\circ$. Table 3-1 presents a summary of $\Delta \bar{G}_f^\circ$ values for some substances commonly encountered in water chemistry; for example, we can determine that the formation of calcite ($CaCO_{3(s)}$) from carbon, calcium, and oxygen has the following free energy.



The minus sign indicates that free energy is released or given off. We can also deduce that to break down 1 mole of calcite into 1 mole of Ca metal, 1 mole of graphite, and $1\frac{1}{2}$ moles of oxygen would require the input of +269.78 kcal of free energy per mole.

TABLE 3-1 Thermodynamic Constants for Species of Importance in Water Chemistry.^a

Species	$\Delta \bar{H}_f^\circ$ kcal/mole	$\Delta \bar{G}_f^\circ$ kcal/mole
$\text{Ca}^{2+}_{(aq)}$	-129.77	-132.18
$\text{CaCO}_{3(s)}$, calcite	-288.45	-269.78
$\text{CaO}_{(s)}$	-151.9	-144.4
$\text{C}_{(s)}$, graphite	0	0
$\text{CO}_{2(g)}$	-94.05	-94.26
$\text{CO}_{2(aq)}$	-98.69	-92.31
$\text{CH}_{4(g)}$	-17.889	-12.140
$\text{H}_2\text{CO}^*_{3(aq)}$	-167.0	-149.00
$\text{HCO}^-_{3(aq)}$	-165.18	-140.31
$\text{CO}^{2-}_{3(aq)}$	-161.63	-126.22
CH_3COO^- , acetate	-116.84	-89.0
$\text{H}^+_{(aq)}$	0	0
$\text{H}_{2(g)}$	0	0
$\text{Fe}^{2+}_{(aq)}$	-21.0	-20.30
$\text{Fe}^{3+}_{(aq)}$	-11.4	-2.52
$\text{Fe}(\text{OH})_{3(s)}$	-197.0	-166.0
$\text{Mn}^{2+}_{(aq)}$	-53.3	-54.4
$\text{MnO}_{2(s)}$	-124.2	-111.1
$\text{Mg}^{2+}_{(aq)}$	-110.41	-108.99
$\text{Mg}(\text{OH})_{2(s)}$	-221.00	-199.27
$\text{NO}^-_{3(aq)}$	-49.372	-26.43
$\text{NH}_{3(g)}$	-11.04	-3.976
$\text{NH}_{3(aq)}$	-19.32	-6.37
$\text{NH}^+_{4(aq)}$	-31.74	-19.00
$\text{HNO}_{3(aq)}$	-49.372	-26.41
$\text{O}_{2(aq)}$	-3.9	3.93
$\text{O}_{2(g)}$	0	0
$\text{OH}^-_{(aq)}$	-54.957	-37.595
$\text{H}_2\text{O}_{(g)}$	-57.7979	-54.6357
$\text{H}_2\text{O}_{(l)}$	-68.3174	-56.690
$\text{SO}^{2-}_{4(aq)}$	-216.90	-177.34
$\text{HS}^-_{(aq)}$	-4.22	3.01
$\text{H}_2\text{S}_{(g)}$	-4.815	-7.892
$\text{H}_2\text{S}_{(aq)}$	-9.4	-6.54

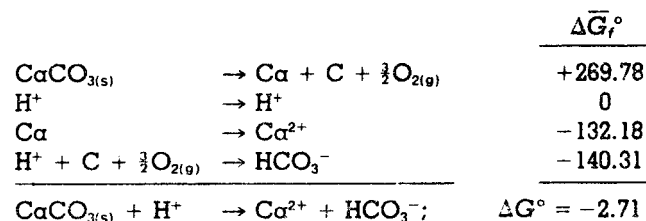
Source. Condensed from the listing of R. M. Garrels and C. L. Christ, *Solutions, Minerals, and Equilibria*, Harper & Row, New York, 1965; and *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Company, Cleveland, Ohio.

^a For a hypothetical ideal state of unit molality, which is approximately equal to that of unit molarity.

Now let us use this information to determine the free energy change associated with the reaction in which calcite dissolves in acid, H^+ , to form the calcium and bicarbonate ions.



Even though it does not occur physically, we can visualize this reaction as taking place by $\text{CaCO}_{3(s)}$ and H^+ reacting to form their component elements; these elements then recombine to form Ca^{2+} and HCO_3^- . Thus



This computation allows us to see two things. First, with respect to the dissolving of $\text{CaCO}_{3(s)}$ in acid, if we react 1 mole of H^+ with 1 mole of calcite to produce 1 mole of Ca^{2+} and 1 mole of HCO_3^- at 25°C, free energy is released because ΔG° is negative. Second, and more generally, we can see it is possible to determine the overall standard free energy change for the reaction as written, ΔG° , from the free energies of formation of reactants and products by using Eq. 3-11 with $\Delta \bar{G}_{f,i}^\circ$ being used in place of \bar{G}_i° . Thus

$$\Delta G^\circ = \left(\sum_i \nu_i \Delta \bar{G}_{f,i}^\circ \right)_{\text{products}} - \left(\sum_i \nu_i \Delta \bar{G}_{f,i}^\circ \right)_{\text{reactants}} \quad (3-13)$$

where ν_i is the stoichiometric coefficient of species i . Or for Eq. 3-12

$$\Delta G^\circ = \Delta \bar{G}_{f,\text{HCO}_3^-}^\circ + \Delta \bar{G}_{f,\text{Ca}^{2+}}^\circ - \Delta \bar{G}_{f,\text{H}^+}^\circ - \Delta \bar{G}_{f,\text{CaCO}_3}^\circ \quad (3-14)$$

Equation 3-13 has limited usefulness because it only refers to the situation when all reactants and products are at standard state. We are almost always interested in systems whose components are at other than standard state. We can relate the free energy of a single substance at a state other than standard to its free energy of formation at standard state by the expression

$$\bar{G}_i = \Delta \bar{G}_{f,i}^\circ + RT \ln \{i\} \quad (3-15)$$

where

\bar{G}_i = the free energy per mole of substance i in a state other than standard measured relative to our established datum
 $\{i\}$ = the active concentration, or activity, of species i

The value of the activity of a substance is dependent on the choice of standard state conditions—the conditions that result in unit activity—just as the value of $\Delta \bar{G}_r^\circ$ is dependent on the choice of standard state. Consistent with the choice of standard state conditions used to develop Table 3-1 and in most publications on aqueous chemistry, the following interpretation of activity is used throughout this book:

1. For ions and molecules in solution, $\{i\}$ is related to the molar concentration, $[i]$, by $\{i\} = \gamma_i[i]$ where γ_i = activity coefficient. As the solution becomes dilute (most cases of interest to us), γ_i approaches 1 and $\{i\}$ approaches $[i]$.
2. For the solvent in a solution, $\{i\} = \gamma_i X_i$ where X_i is the mole fraction. As the solution becomes more dilute, γ_i approaches 1. The activity generally is assumed to be 1 for the dilute solutions of concern to us.
3. For pure solids or liquids in equilibrium with a solution, $\{i\} = 1$.
4. For gases in equilibrium with a solution, $\{i\} = \gamma_i P_i$ where P_i is the partial pressure of the gas in atmospheres. As the total pressure decreases, γ_i approaches 1. When reactions take place at atmospheric pressure, the activity of a gas can be approximated closely by its partial pressure.
5. For mixtures of liquids, $\{i\} = X_i$ where X_i is the mole fraction.

Returning to our example of the dissolution of $\text{CaCO}_{3(s)}$ in acid, Eq. 3-12, and combining Eqs. 3-9 and 3-15, we can write

$$\Delta G = \Delta \bar{G}_{f, \text{HCO}_3^-}^\circ + RT \ln \{ \text{HCO}_3^- \} + \Delta \bar{G}_{f, \text{Ca}^{2+}}^\circ + RT \ln \{ \text{Ca}^{2+} \} \\ - \Delta \bar{G}_{f, \text{H}^+}^\circ - RT \ln \{ \text{H}^+ \} - \Delta \bar{G}_{f, \text{CaCO}_{3(s)}}^\circ - RT \ln \{ \text{CaCO}_{3(s)} \}$$

Collecting terms, we obtain

$$\Delta G = \Delta \bar{G}_{f, \text{HCO}_3^-}^\circ + \Delta \bar{G}_{f, \text{Ca}^{2+}}^\circ - \Delta \bar{G}_{f, \text{H}^+}^\circ - \Delta \bar{G}_{f, \text{CaCO}_{3(s)}}^\circ \\ + RT \ln \{ \text{HCO}_3^- \} + RT \ln \{ \text{Ca}^{2+} \} - RT \ln \{ \text{H}^+ \} - RT \ln \{ \text{CaCO}_{3(s)} \}$$

Since, from Eq. 3-13,

$$\Delta G^\circ = \Delta \bar{G}_{f, \text{HCO}_3^-}^\circ + \Delta \bar{G}_{f, \text{Ca}^{2+}}^\circ - \Delta \bar{G}_{f, \text{H}^+}^\circ - \Delta \bar{G}_{f, \text{CaCO}_{3(s)}}^\circ$$

we can state

$$\Delta G = \Delta G^\circ + RT \ln \frac{\{ \text{HCO}_3^- \} \{ \text{Ca}^{2+} \}}{\{ \text{H}^+ \} \{ \text{CaCO}_{3(s)} \}} \quad (3-16)$$

This is a specific form of Eq. 3-10 applied to the acid dissolution of

$\text{CaCO}_{3(s)}$ reaction. For dilute solutions, since the activity of pure solid is unity and assuming that the activity coefficients of the ionic component are equal to 1, we obtain

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{HCO}_3^-][\text{Ca}^{2+}]}{[\text{H}^+]} \quad (3-17)$$

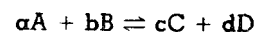
In examining Eqs. 3-16 and 3-17, and the general form of the equation, Eq. 3-10, we can see that the logarithmic term has a form that is reminiscent of the equilibrium constant for the reaction as written in Eq. 3-12. However, because the magnitude of the logarithmic term is not equal to the equilibrium constant except at equilibrium, we call this term the reaction quotient, Q , where

$$Q = \frac{\{ \text{HCO}_3^- \} \{ \text{Ca}^{2+} \}}{\{ \text{H}^+ \} \{ \text{CaCO}_{3(s)} \}} \quad (3-18)$$

or in dilute solution

$$Q = \frac{[\text{HCO}_3^-][\text{Ca}^{2+}]}{[\text{H}^+]}$$

More generally, for the reaction



$$Q = \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b} \quad (3-19)$$

or in dilute solution,

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Combining Eqs. 3-10 and 3-19 (or Eqs. 3-16 and 3-18), we can state,

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (3-20)$$

When the value of Q is identical to that of the equilibrium constant K , that is, the system is at equilibrium and $\Delta G = 0$, we can then write

$$0 = \Delta G^\circ + RT \ln K \quad (3-21)$$

or

$$\Delta G^\circ = -RT \ln K \quad (3-22)$$

Substituting Eq. 3-22 into Eq. 3-20, we obtain

$$\Delta G = -RT \ln K + RT \ln Q = RT \ln \frac{Q}{K} \quad (3-23)$$

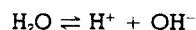
Equation 3-23 allows us to develop another set of criteria to determine whether reactions are possible or not because the ratio of Q/K will determine the sign of ΔG for a reaction.

1. If $Q/K > 1$, then ΔG is positive and the reaction is impossible as written.
2. If $Q/K = 1$, then $\Delta G = 0$ and the system is at equilibrium.
3. If $Q/K < 1$, then ΔG is negative and the reaction is spontaneous as written.

The use of the tables of free energy values and the determination of whether a reaction is at equilibrium is illustrated in the following examples.

Example 3-1

1. Determine the equilibrium constant for the reaction in which liquid H_2O dissociates to H^+ and OH^- at $25^\circ C$.



2. Is this reaction proceeding as written when $[H^+] = 10^{-6} M$ and $[OH^-] = 5 \times 10^{-8} M$?

Solution

1. From Table 3-1

	ΔG_f°
$H_2O_{(l)}$	-56.69
H^+	0
OH^-	-37.60

From Eq. 3-13, $\Delta G^\circ = (1)(0) + (1)(-37.60) - (1)(-56.69) = +19.09 \text{ kcal}$

$$\begin{aligned} \Delta G^\circ = 19.09 &= -RT \ln K \\ -19.09 &= \ln K = -32.24 \\ 1.987 \times 10^{-3} \times 298 & \end{aligned}$$

$$K = 9.96 \times 10^{-15} (\approx 1 \times 10^{-14})$$

Based on the selection of standard state conditions given previously in this section and neglecting ionic strength effects, K can be written as follows for dilute solutions,

$$K = [H^+][OH^-]$$

This equilibrium constant is usually given the special designation K_w .

2. From Eq. 3-20,

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln [H^+][OH^-] \\ \Delta G &= 19.09 + 2.3 \times 1.98 \times 10^{-3} \times 298 \times \log [(10^{-6})(5 \times 10^{-8})] \\ \Delta G &= +1.03 \end{aligned}$$

Because $\Delta G > 0$, the reaction is not spontaneous as written and can proceed spontaneously only in the opposite direction, that is, H^+ and OH^- are combining to form H_2O molecules.

We can solve this problem alternatively using

$$\begin{aligned} \Delta G &= RT \ln \frac{Q}{K} \\ Q &= [H^+][OH^-] = (10^{-6})(5 \times 10^{-8}) = 5 \times 10^{-14} \\ K &= 10^{-14} \end{aligned}$$

Since $Q/K > 1$, ΔG must be positive. Therefore, the reaction as written is not possible.

Example 3-2

Find the equilibrium constant for the reaction at $25^\circ C$,



in which ferrous iron is oxidized by molecular oxygen to ferric hydroxide in aqueous solution. Atmospheric oxygen is in equilibrium with the dissolved oxygen.

Give the form of the equilibrium constant making the assumption that activity coefficients have a value of 1.

Solution

From Table 3-1,

	ΔG_f° (kcal/mole)
Fe^{2+}	-20.3
$O_{2(g)}$	0
$H_2O_{(l)}$	-56.7
$Fe(OH)_{3(s)}$	-166.0
H^+	0

$$\Delta G^\circ = 4 \times 0 + 2(-166.0) - 2(-20.3) - \frac{1}{2}(0) - 5(-56.7)$$

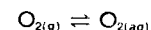
$$\Delta G^\circ = -7.9 = -RT \ln K$$

$$RT \ln K = 2.3 RT \log K = 1.364 \log K = 7.9$$

$$K = 6.2 \times 10^5 = 10^{5.8}$$

$$K = \frac{[H^+]^4 [Fe(OH)_{3(s)}]^2}{(X_{H_2O})^5 (P_{O_2})^{1/2} [Fe^{2+}]^2} = \frac{[H^+]^4}{(P_{O_2})^{1/2} [Fe^{2+}]^2}$$

It is important to note that we may only use gaseous oxygen as a reactant in this equation if it is in true equilibrium with the solution, that is, if the equilibrium

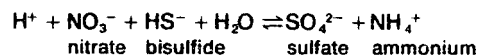


is satisfied. Otherwise we should use $O_{2(aq)}$ as a reactant and, correspondingly, the value of ΔG_f° for $O_{2(aq)}$.

We now have sufficient information to provide answers to the question posed earlier in the chapter about sulfide stability in the presence of nitrate.

Example 3-3

Is it possible at 25°C to oxidize sulfide in natural waters with nitrate? Typical concentrations that exist are 10^{-4} M of reacting species and pH 8 ($[H^+] = 10^{-8}$ M). Assume that ionic strength effects are negligible (these effects will be discussed later in this chapter). The reaction is



We must find out whether the reaction is spontaneous as written.

From Table 3-1,

	ΔG_f°
$H_2O_{(l)}$	-56.69
HS^-	+3.01
NO_3^-	-26.41
H^+	0
SO_4^{2-}	-177.34
NH_4^+	-19

From Eq. 3-13,

$$\Delta G^\circ = (-19 - 177.34) - (-26.41 + 3.01 - 56.69)$$

$$= -116.25$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$Q = \frac{[NH_4^+][SO_4^{2-}]}{[NO_3^-][HS^-][H^+]}$$

and since $[NH_4^+] = 10^{-4}$, $[SO_4^{2-}] = 10^{-4}$, $[NO_3^-] = 10^{-4}$, $[HS^-] = 10^{-4}$, and $[H^+] = 10^{-8}$,

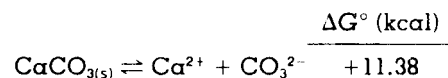
$$Q = \frac{(10^{-4})(10^{-4})}{(10^{-4})(10^{-4})(10^{-8})} = 10^8$$

Therefore,

$$\begin{aligned} \Delta G &= -116.25 + 1.987 \times 10^{-3} \times 298 \times 2.3 \log 10^8 \\ &= -116.25 + 10.9 = -105.35 \end{aligned}$$

Because ΔG is negative, the reaction will proceed spontaneously as written at the reactant concentrations indicated.

An important property of standard free energy changes, ΔG° , is that they are additive. For example, if in two reactions the product of one reaction serves as a reactant in the other, the ΔG° value for the combined reactions is the sum of the ΔG° values of the two reactions. In our previous example of the dissolution of $CaCO_3$ in acid, we wrote the equation $CaCO_{3(s)} + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$. In the strict chemical sense this overall reaction is a composite of



and



with a standard free energy change of $\Delta G^\circ = 11.38 - 14.09 = -2.71$ kcal. Whether the composite reaction is spontaneous depends upon the value of ΔG for that reaction, a function of ΔG° and Q . If ΔG for the composite reaction is negative (positive), it is not necessary that each of the individual reactions have a negative (positive) value of ΔG . Note further that it is the value of ΔG , not ΔG° , which controls the direction of a reaction.

3.4. ENTHALPY AND THE TEMPERATURE DEPENDENCE OF THE EQUILIBRIUM CONSTANT

The enthalpy change of a chemical reaction (ΔH) is the amount of heat that is released or taken up during the course of the reaction. If ΔH is negative, heat is evolved and the reaction is called exothermic; if ΔH is positive, heat is taken up and the reaction is called endothermic.

The term ΔH° is of most interest to us. For a reversible reaction in a closed system it is related to ΔG° by

$$\Delta H^\circ = \Delta G^\circ + T \Delta S^\circ \quad (3-24)$$

Similarly to ΔG° , ΔH° for a reaction can be calculated from

$$\Delta H^\circ = \left(\sum_i \nu_i \bar{H}_i^\circ \right)_{\text{products}} - \left(\sum_i \nu_i \bar{H}_i^\circ \right)_{\text{reactants}} \quad (3-25)$$

where

ν_i = the stoichiometric coefficient

\bar{H}_i° = the enthalpy of species i in kcal/mole at standard conditions of 25°C and 1 atm pressure

For the general reaction, $aA + bB \rightleftharpoons cC + dD$, ΔH° is equal to the amount of heat taken up or released when a moles of A and b moles of B , each in their standard states, are completely converted to c moles of C and d moles of D , each in their standard states.

Just as we could not determine the absolute value of \bar{G}_i° , we also cannot measure \bar{H}_i° . As with \bar{G}_i° , we circumvent this problem by assigning \bar{H}_i° a value of zero to all elements in their most stable form at 25°C and 1 atm pressure. In aqueous solution 1 mole/liter of the hydrogen ion, H^+ , in ideal solution ($\gamma = 1$) also is assigned an \bar{H}° value of zero. We can determine values of enthalpy of species based on these assignments and call these the enthalpy of formation, $\Delta \bar{H}_f^\circ$. Similarly to the computations for $\Delta \bar{G}_f^\circ$ values, we can compute the $\Delta \bar{H}_f^\circ$ values of various compounds from the assigned \bar{H}° values of their component elements. A selection of these $\Delta \bar{H}_f^\circ$ values is given in Table 3-1.

Standard enthalpy change values, ΔH° , for reactions are most commonly used in water chemistry to determine the effect of temperature on the position of equilibrium. A useful expression in this regard is due to Van't Hoff, which states that

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (3-26)$$

If we assume that, over a limited temperature range, ΔH° is not a function of temperature, integration of Eq. 3-26 yields

$$\ln \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3-27)$$

or

$$\ln K = -\frac{\Delta H^\circ}{RT} + \text{constant} \quad (3-28)$$

or

$$K = C' \exp \left(\frac{-\Delta H^\circ}{RT} \right) \quad (3-29)$$

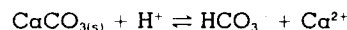
where C' is a constant. Application of the Van't Hoff relationship is illustrated in the following example.

Example 3-4

A municipal water supply enters a residence at 15°C and is heated to 60°C in the home water heater. If the water is just saturated with respect to $\text{CaCO}_3(\text{s})$ at 25°C, what will be the condition of the water (i.e., oversaturated or undersaturated) with respect to $\text{CaCO}_3(\text{s})$ (1) as it enters the residence and (2) as it leaves the water heater?

Solution

Let us tackle this problem using the equation



as the basis for our solution. We are told that at 25°C the concentrations of Ca^{2+} , HCO_3^- , and H^+ are such that the system is at equilibrium. First we will calculate the value of the equilibrium constant using the ΔG_f° value for this reaction of -2.71 kcal, which was calculated in Section 3-3, and then determine the value of the equilibrium constant at 15°C and at 60°C using ΔH_f° values from Table 3-1.

At 25°C,

	$\Delta \bar{H}_f^\circ$ kcal/mole
$\text{CaCO}_3(\text{s})$	-288.45
H^+	0
$\text{Ca}^{2+}(\text{aq})$	-129.77
$\text{HCO}_3^-(\text{aq})$	-165.18

Let K at 25°C = K_1 , then

$$\begin{aligned} -RT \ln K_1 &= -2.71 \\ \log K_1 &= 1.99 \\ K_1 &= 10^{+1.99} \end{aligned}$$

Calculate ΔH° from Eq. 3-25,

$$\begin{aligned} \Delta H^\circ &= \sum_i (\nu_i \Delta \bar{H}_{f,i}^\circ)_{\text{products}} - \sum_i (\nu_i \Delta \bar{H}_{f,i}^\circ)_{\text{reactants}} \\ \Delta H^\circ &= -129.77 - 165.18 - (-288.45 - 0) \\ \Delta H^\circ &= -6.5 \text{ kcal} \end{aligned}$$

Let $K_2 = K$ at 15°C (288°K), (T_2); and $K_3 = K$ at 60°C (333°K), (T_3). From Eq. 3-27,

$$\begin{aligned} \ln K_1 - \ln K_2 &= \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ -\ln K_2 + \ln 10^{+1.99} &= \frac{-6.5}{1.98 \times 10^{-3}} \left(\frac{1}{288} - \frac{1}{298} \right) \\ K_2 &= 10^{+2.15} \end{aligned}$$

Similarly, from Eq. 3-27,

$$\begin{aligned} \ln K_1 - \ln K_3 &= \frac{\Delta H^\circ}{R} \left(\frac{1}{T_3} - \frac{1}{T_1} \right) \\ -\ln K_3 + \ln 10^{+1.997} &= \frac{-6.5}{1.98 \times 10^{-3}} \left(\frac{1}{333} - \frac{1}{298} \right) \\ K_3 &= 10^{+1.48} \end{aligned}$$

At 15°C the equilibrium constant is greater, and at 60°C it is less, than that at 25°C. Thus the term

$$Q = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{H}^+]}$$

is greater than K at 60°C and less than K at 15°C. The water had a value of Q that met equilibrium conditions at 25°C and the value of this quantity will not change as temperature decreases. Therefore, if we may assume that $[\text{H}^+]$ remains constant, the water at 15°C contains less Ca^{2+} and HCO_3^- than allowed by equilibrium, that is, it is undersaturated. By similar reasoning, at 60°C the water is oversaturated with respect to $\text{CaCO}_3(\text{s})$, and $\text{CaCO}_3(\text{s})$ will be deposited within the heater. Note that these conclusions have some bearing on the life of home water heaters.

We see from the example that the equilibrium constant for $\text{CaCO}_3(\text{s}) + \text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^-$ at 15°C is approximately 1.5 times larger than at 25°C ; at 60°C it is less than $\frac{1}{3}$ as large as at 25°C . One could have sensed that K would decrease as the temperature increases from the value of ΔH° , which is negative. Since heat is produced as the reaction goes to the right, raising the temperature tends to drive the reaction to the left, thus decreasing the equilibrium constant. If we take heat away from the reaction by lowering the temperature, the equilibrium is shifted to the right and the equilibrium constant increases. This is an example of the general situation that for exothermic reactions, an increase in temperature will shift the equilibrium in the direction of less complete reaction; for endothermic reactions, an increase in temperature will shift the equilibrium in the direction of more complete reaction.

The ΔH° values for a series of consecutive reactions can be added, just as were ΔG° values, to yield an overall ΔH° value for the overall reaction.

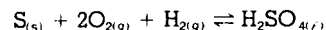
Example 3-5

Find the standard enthalpy of formation, ΔH° for $\text{H}_2\text{SO}_{4(l)}$ given the following reactions:

	ΔH° (kcal)
1. $\text{S}_{(s)} + \text{O}_{2(g)} \rightleftharpoons \text{SO}_{2(g)}$	-70.96
2. $\text{SO}_{2(g)} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_{3(g)}$	-23.5
3. $\text{SO}_{3(g)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{SO}_{4(l)}$	-31.14
4. $\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightleftharpoons \text{H}_2\text{O}_{(l)}$	-68.32

Solution

Adding reactions (1) through (4) and the ΔH° values, we obtain



where $\Delta H^\circ = -70.96 - 23.5 - 31.4 - 68.32 = -193.92$ kcal. Applying Eq. 3-25, we obtain

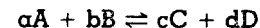
$$\Delta \bar{H}_f^\circ \text{ for } \text{H}_2\text{SO}_{4(l)} = -193.92 \text{ kcal}$$

3.5. NONIDEAL BEHAVIOR OF IONS AND MOLECULES IN SOLUTION

In very dilute aqueous solutions, ions behave independently of one another and it is valid to assume that activity coefficients of ions have values of unity. However, as the concentration of ions in solution increases, electrostatic interactions between the ions also increase and the activity of ions becomes somewhat less than their measured or analytical concentration. Thus, in the equation,

$$\{i\} = \gamma_i [i] \quad (3-30)$$

the activity coefficient, γ_i , becomes less than 1 and chemical equilibrium is affected. For example, for the general reaction,



it becomes necessary to write the equilibrium constant and reaction quotient in the form

$$Q \text{ or } K = \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b} = \frac{(\gamma_C[C])^c (\gamma_D[D])^d}{(\gamma_A[A])^a (\gamma_B[B])^b} \quad (3-31)$$

To calculate activity coefficients of ions in aqueous solution, we must employ the quantity ionic strength, μ , which was devised by Lewis and Randall³ to describe the intensity of the electric field in a solution:

$$\mu = \frac{1}{2} \sum_i (C_i Z_i^2) \quad (3-32)$$

where

C_i = concentration of ionic species, i

Z_i = charge of species i

Application of this equation is shown in the following two examples.

Example 3-6

Compute the ionic strength of a solution containing the following concentration of ions:

$$\begin{aligned} [\text{Ca}^{2+}] &= 10^{-4} M, & [\text{CO}_3^{2-}] &= 10^{-5} M, & [\text{HCO}_3^-] &= 10^{-3} M \\ [\text{SO}_4^{2-}] &= 10^{-4} M, & [\text{Na}^+] &= 1.02 \times 10^{-3} M \end{aligned}$$

Solution

$$\begin{aligned} \mu &= \frac{1}{2} ([10^{-4} \times 2^2] + [10^{-5} \times 2^2] + [10^{-3} \times 1^2] + [10^{-4} \times 2^2] + [1.02 \times 10^{-3} \times 1^2]) \\ \mu &= 1.43 \times 10^{-3} \end{aligned}$$

Example 3-7

Which of the following brines has the greater ionic strength?

1. Brine a: 5800 mg/liter NaCl.
2. Brine b: 3100 mg/liter MgSO_4 .

Solution

The atomic weights are Na, 23; Cl, 35.5; Mg, 24; S, 32; and O, 16.

For brine a,

$$\begin{aligned} [\text{Na}^+] &= \frac{5800 \text{ mg/liter}}{58,500 \text{ mg/mole}} = 0.099 M \\ [\text{Cl}^-] &= \frac{5800 \text{ mg/liter}}{58,500 \text{ mg/mole}} = 0.099 M \\ \mu &= \frac{1}{2} (0.099 \times 1^2 + 0.099 \times 1^2) = 0.099 = 0.1 \end{aligned}$$

³ G. N. Lewis and M. Randall, *J. Am. Chem. Soc.*, 43: 1111 (1921)

For brine b,

$$[\text{Mg}^{2+}] = \frac{3100 \text{ mg/liter}}{120,000 \text{ mg/mole}} = 0.026 \text{ M}$$

$$[\text{SO}_4^{2-}] = \frac{3100 \text{ mg/liter}}{120,000 \text{ mg/mole}} = 0.026 \text{ M}$$

$$\mu = \frac{1}{2}(0.026 \times 2^2 + 0.026 \times 2^2) = 0.104 \approx 0.1$$

They both have virtually the same ionic strength.

Rather than work through laborious calculations of ionic strength for more complex solutions than those given in the examples, it is usually precise enough for most purposes in water chemistry to use an approximation of ionic strength derived from a correlation with specific conductivity or TDS (total dissolved solids). The conductivity of a solution is a measure of the ability of a solution to conduct a current. It is a property attributable to the ions in solution. Electrical current is transported through solutions via the movement of ions, and conductivity increases as ion concentration increases. Figure 3-3 is a presentation of data given by Lind⁴ on the conductivity versus ionic strength of various surface and groundwaters. If the conductivity of a water sample is known, this figure can be used to provide a crude estimate of ionic strength.

Langelier presented the approximation,⁵

$$\mu = 2.5 \times 10^{-5} \times \text{TDS} \quad (3-33)$$

for several waters he examined. In this expression TDS is the total dissolved solids in mg/liter. Russell⁶ derived the following correlation between ionic strength and conductivity for 13 waters of widely varying composition,

$$\mu = 1.6 \times 10^{-5} \times \text{conductivity } (\mu\text{mho})$$

This is similar to the expression that can be derived from the data in Fig. 3-3.

Ionic strength appears in each of the various expressions used to calculate activity coefficients in aqueous solutions. The Debye-Hückel theory of interaction of ions in aqueous solution incorporates both the electrostatic interactions between ions and the thermal motion of the ions. The basic equation, called the Debye-Hückel limiting law, was

⁴ C. J. Lind, U.S. Geological Survey Professional Paper 700 D, 1970, pp. D272-D280.

⁵ W. F. Langelier, "The Analytical Control of Anti-Corrosion Water Treatment," *J. Am. Water Works Assoc.*, 28: 1500 (1936).

⁶ L. L. Russell, "Chemical Aspects of Groundwater Recharge with Wastewaters," Ph.D. Thesis, University of California, Berkeley, Dec. 1976.

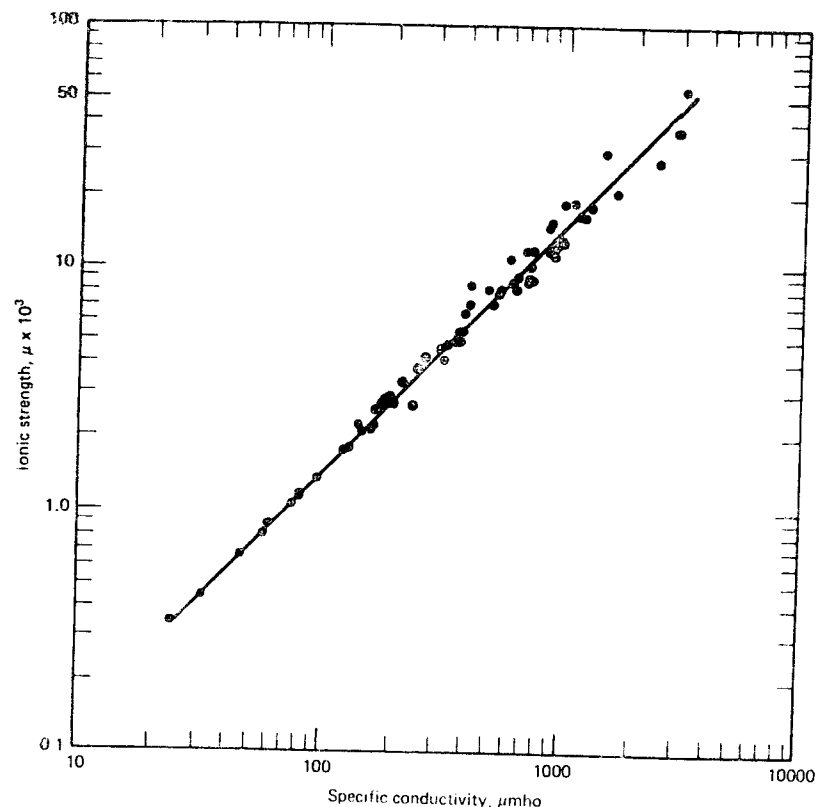


Fig. 3-3. Specific conductance as a means of estimating ionic strength. After C. J. Lind, U.S. Geological Survey Professional Paper 700D, pp. D272-D280, 1970.

developed for ionic strengths of less than approximately 5×10^{-3} and can be stated as

$$-\log \gamma_i = 0.5Z_i^2 \mu^{1/2} \quad (3-34)$$

An alternative equation, the extended Debye-Hückel approximation of the Debye-Hückel limiting law, which is applicable for ionic strength of less than approximately 0.1, is

$$-\log \gamma_i = \frac{AZ_i^2 \mu^{1/2}}{1 + Ba_i \mu^{1/2}} \quad (3-35)$$

where

$A = a$ constant that relates to the solvent:

for water at 25°C, $A = 0.509$

for water at 15°C, $A = 0.50$

for water at 0°C, $A = 0.488$

$B = a$ constant that relates to the solvent:

for water at 25°C, $B = 0.328 \times 10^8$

for water at 15°C, $B = 0.326 \times 10^8$

for water at 0°C, $B = 0.324 \times 10^8$

$a_i = a$ constant that relates to the diameter of the hydrated ion: for monovalent ions, for example, with the exception of H^+ , this is usually about 3 to 4×10^{-8}

Figure 3-4 shows the variations of activity coefficients as a function of ionic strength for some ions commonly found in water. These curves were calculated using Eq. 3-35.

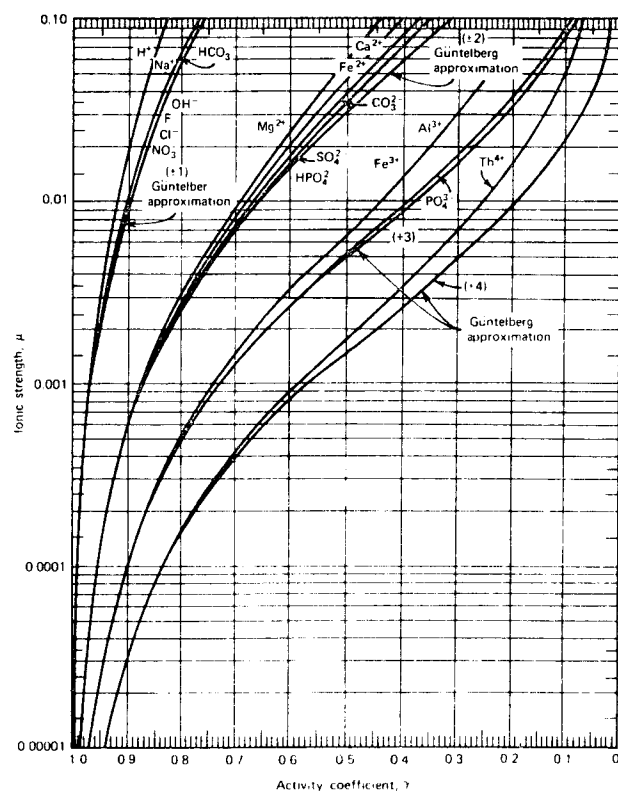


Fig. 3-4. Activity coefficients of aqueous ions based on the extended Debye-Hückel equation (Eq. 3-35) and the Guntelberg approximation (Eq. 3-36).

For monovalent ions at 15°C, Eq. 3-35 becomes

$$-\log \gamma_i = \frac{0.5Z_i^2\mu^{1/2}}{1 + (0.326 \times 10^8 \times 3 \times 10^{-8})\mu^{1/2}} = \frac{0.5Z_i^2\mu^{1/2}}{1 + \mu^{1/2}} \quad (3-36)$$

Equation 3-36 is also called the Guntelberg approximation of the Debye-Hückel theory and is also commonly used to calculate γ for ions of various charge at temperatures other than 15°C. It is also plotted in Fig. 3-4. There have been other extensions of the theory to make it apply at higher ionic strengths. There is, however, no satisfactory theory that provides a good estimate of the activity coefficient for ionic strengths of greater than about 0.5.

Because anions cannot be added to a solution without an equivalent number of cations (and vice versa), it is impossible to determine experimentally the activity coefficient of a single ion. Therefore, Eqs. 3-34, 3-35, and 3-36 cannot be verified directly. However, it is possible to define, and measure experimentally, a mean activity coefficient, γ_{\pm} , as,

$$\gamma_{\pm} = (\gamma_+ \gamma_-)^{1/2} \quad (3-37)$$

The Debye-Hückel and Guntelberg relationships can be extended to the mean activity coefficient thus:

$$-\log \gamma_{\pm} = 0.5 |Z_+ Z_-| \mu^{1/2} \quad (3-38)$$

$$-\log \gamma_{\pm} = \frac{0.5 |Z_+ Z_-| \mu^{1/2}}{1 + \mu^{1/2}} \quad (3-39)$$

where Eq. 3-38 is the Debye-Hückel limiting law, Eq. 3-39 is the Guntelberg approximation, and

Z_+ = charge of the positive ion

Z_- = charge of the negative ion

γ_{\pm} = mean of the two activity coefficients

Example 3-8

Find the ratio, at equilibrium, of the molar concentrations of carbonate to bicarbonate at 25°C in a solution with an ionic strength of 10^{-3} . Also find the pH. The equilibrium constant, $K_{a,2}$, for the reaction



is $10^{-10.3}$. $[H^+] = 10^{-10}$ moles/liter.

Solution

$$K = 10^{-10.3} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{\gamma_{H^+}[H^+]\gamma_{CO_3^{2-}}[CO_3^{2-}]}{\gamma_{HCO_3^-}[HCO_3^-]}$$

Using the Debye-Hückel limiting law,

$$-\log \gamma_{\text{H}^+} = -\log \gamma_{\text{HCO}_3^-} = 0.5 \times 1^2 (10^{-3})^{1/2} = 0.0158$$

$$\gamma_{\text{H}^+} = \gamma_{\text{HCO}_3^-} = 0.96$$

$$-\log \gamma_{\text{CO}_3^{2-}} = 0.5 \times 2^2 \times (10^{-3})^{1/2}$$

$$\gamma_{\text{CO}_3^{2-}} = 0.86$$

$$10^{-10.3} = \frac{(0.96)(10^{-10})(0.86)[\text{CO}_3^{2-}]}{(0.96)[\text{HCO}_3^-]}$$

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 0.58$$

If we had not taken activity coefficients into account the ratio $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$ would have been

$$10^{-10.3} = \frac{10^{-10}[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{10^{-10.3}}{10^{-10}} = 0.501$$

Also

$$\begin{aligned} \text{pH} &= -\log \{\text{H}^+\} = -\log(\gamma_{\text{H}^+} [\text{H}^+]) \\ &= -\log(0.96 \times 10^{-10}) = 10.02 \end{aligned}$$

The theory for predicting the activity coefficients of nonelectrolytes in aqueous solution is not as well developed as for electrolytes. An empirical equation of the form

$$\log \gamma = k_s \mu \quad (3.40)$$

is generally used to relate activity to ionic strength. The salting-out coefficient k_s must be experimentally determined. Because values of k_s generally fall in the range from 0.01 to 0.15, nonionic or molecular solutes have activity coefficients of approximately 1 for ionic strengths of less than 0.1.

For example, if $k_s = 0.132$ for oxygen in NaCl solution⁷ and

$$\log \gamma = 0.132 \times 0.05 = 0.0066$$

then

$$\gamma \cong 1.02$$

As the ionic strength increases, for example, in seawater ionic strength is approximately 0.7, Eq. 3.40 predicts that the activity coefficient of oxygen will be

$$\log \gamma = 0.132 \times 0.7 = 0.0924$$

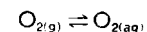
$$\gamma = 1.24$$

⁷ M. Randall and C. F. Failey, *Chem. Rev.*, 4: 285 (1927).

The activity coefficient is greater than one. We can visualize that this is indeed possible if we think of the condition of the water in seawater. Because there is so much salt present, there will be a significant quantity of the H_2O present as water of hydration associated with the ions present in the seawater. Oxygen dissolves less well in water which is bonded to ions so that a given total volume of water will dissolve a smaller concentration of oxygen at equilibrium if it contains much salt. If the oxygen dissolved in the seawater is in equilibrium with the atmosphere, the activity of oxygen in the water is controlled only by the partial pressure of oxygen in the atmosphere. It is not a function of salt content of the water. Therefore, if the dissolved oxygen activity is constant while the dissolved oxygen concentration decreases as the salt concentration increases, we see from the equation, $\{i\} = \gamma_i [i]$, that γ must be greater than 1. This phenomenon is illustrated by Example 3-9. The effect of decreasing the solubility of molecular species, such as dissolved oxygen, by increasing salt concentration is known as the "salting-out effect."

Example 3-9

Given that the equilibrium constant, Henry's constant, K_H , for the reaction



is 1.29×10^{-3} at 25°C and assuming a salting-out coefficient, k_s , of 0.132, determine the molar dissolved oxygen activity and concentration at 25°C for (1) distilled water, (2) the Sacramento River water (specific conductivity = $450 \mu\text{mho}$), and for (3) Pacific Ocean water (ionic strength = 0.7).

Solution

Dissolved oxygen in distilled water:

Since $\mu = 0$, $\{\text{O}_{2(aq)}\} = [\text{O}_{2(aq)}]$. Knowing P_{O_2} we can calculate $[\text{O}_{2(aq)}]$ from the equilibrium constant,

$$K = \frac{\{\text{O}_{2(aq)}\}}{P_{\text{O}_2}} = 1.29 \times 10^{-3}$$

In dry air the volume fraction of oxygen is 0.21. At 25°C the vapor pressure of water is 23.8 mm Hg. Given that X_{O_2} is the volume fraction of O_2 in dry air,

$$\begin{aligned} P_{\text{O}_2} &= \left(\frac{\text{atmospheric pressure (mmHg)} - \text{vapor pressure (mmHg)}}{760} \right) X_{\text{O}_2} \\ &= \left(\frac{760 - 23.8}{760} \right) (0.21) = 0.203 \end{aligned}$$

$$[\text{O}_{2(aq)}] = \{\text{O}_{2(aq)}\} = 1.29 \times 10^{-3} \times 0.203$$

$$= 2.62 \times 10^{-4} M \text{ (or } 8.4 \text{ mg/liter)}$$

The ionic strength estimate for Sacramento River water:

From Fig. 3.3 for a specific conductance of $460 \mu\text{mho}$, $\mu = 0.007$

Let us assume that the partial pressure of oxygen is the same over the Pacific Ocean as it is over the Sacramento River (a reasonable assumption). Because of this the dissolved oxygen activity will be the same in both solutions.

For Sacramento River water,

$$\begin{aligned}\mu &= 0.007 \quad \text{and} \quad k_s = 0.132 \\ \log \gamma &= 0.132 \times 0.007 \\ \gamma &= 1.002\end{aligned}$$

For Pacific Ocean water,

$$\begin{aligned}\mu &= 0.7 \quad \text{and} \quad k_s = 0.132 \\ \log \gamma &= 0.7 \times 0.132 \\ \gamma &= 1.24\end{aligned}$$

Now since

$$K = \frac{\{O_{2(aq)}\}}{P_{O_2}} = \frac{\gamma\{O_{2(aq)}\}}{P_{O_2}}$$

For Sacramento River water,

$$\begin{aligned}[O_{2(aq)}] &= \frac{2.62 \times 10^{-4}}{1.002} = 2.62 \times 10^{-4} M \\ &= 8.4 \text{ mg/liter}\end{aligned}$$

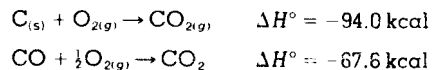
For Pacific Ocean water,

$$\begin{aligned}[O_{2(aq)}] &= \frac{2.62 \times 10^{-4}}{1.24} = 2.11 \times 10^{-4} M \\ &= 6.75 \text{ mg/liter}\end{aligned}$$

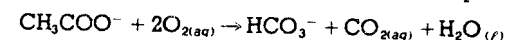
For both waters the activity of oxygen is the same at $2.62 \times 10^{-4} M$ or 8.4 mg/liter. It is significant to note that a dissolved oxygen test conducted on the two waters using the wet chemical method (Winkler method) will produce a result of 8.4 mg/liter for the river water and 6.75 mg/liter for the ocean water. The same analysis conducted using a membrane-covered, specific oxygen electrode will produce an identical reading in both solutions because it responds to activity rather than concentration. We might ask how a fish feels with respect to the dissolved oxygen content of these two waters. Does it care about dissolved oxygen activity or dissolved oxygen concentration? We leave the reader to ponder this question.

3.6. PROBLEMS

- The heat of combustion of a substance is defined as the enthalpy change that occurs when 1 mole of a substance reacts with elemental oxygen to form liquid water and gaseous CO_2 . Determine the heat available from the combustion of methane, $CH_{4(g)}$, at $25^\circ C$ and a constant pressure. Express the answer in terms of kcal/mole and kcal/g.
- Calculate the standard enthalpy of formation, $\Delta \bar{H}_f^\circ$, for $CO_{2(g)}$ using the following information:



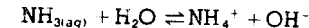
- An average man produces about 2500 kcal of heat a day through metabolic activity. If a man had a mass of 70 kg with the heat capacity of water (1 cal/g $^\circ C$), what would be the temperature rise in a day if no heat were lost? Man is actually an open system, and the main mechanism of heat loss is the evaporation of water. How much water would he need to evaporate in a day to maintain constant temperature? (ΔH° for vaporization at $37^\circ C$ is 575 cal/g.)
- An important reaction in muscular activity is the oxidation of lactic to pyruvic acid. Calculate ΔH° for the reaction given that the ΔH° of combustion (see Problem 1) is -279 kcal/mole for pyruvic acid and -326 kcal/mole for lactic acid (lactic acid = $CH_3CHOHCOOH$; pyruvic acid = $CH_3COCOOH$).
- Calculate the amount of energy available (that is, ΔG°) for all maintenance and synthesis of new bacterial cells when 1 mole of acetate ion undergoes aerobic oxidation by bacteria. The reaction can be represented as follows:



The bacteria function as a catalyst in the reaction but do not alter the amount of energy that can be obtained from the reaction.

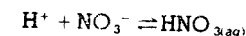
Note: Not all of the available energy is used for synthesis and maintenance. There is a certain amount of inefficiency involved.

- Ammonia, NH_3 , is a base and will readily accept a proton in accordance with the following reaction



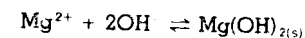
- Calculate the equilibrium constant, K , for this reaction at $25^\circ C$.
- If, at some time, $pH = 9.0$, $[NH_3] = 10^{-5} M$, and $[NH_4^+] = 10^{-6} M$, is the reaction at equilibrium? If not, in which direction is the reaction going?

- Assuming that the reaction



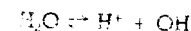
is at equilibrium in aqueous solution, what percent of C_{T,NO_3} (where $C_{T,NO_3} = ([NO_3^-] + [HNO_3])$) is present as HNO_3 at $pH = 1$? (Use standard free energy tables to make your calculations and assume that all activity coefficients have a value of 1.0.)

- $Mg(OH)_{2(s)}$ is precipitated according to the following reaction



How much Mg^{2+} , moles/liter, is present in solution at equilibrium when the pH is 10.0? (Neglect ionic strength effects.)

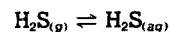
- (a) Find the equilibrium constant, K_w , at 25 and $40^\circ C$ for the following reaction,



- Is the reaction exothermic or endothermic?

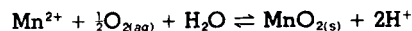
10. Calculate

- (a) Henry's constant,
- K_H
- , for
- H_2S
- . Note that
- $K_H = K$
- for the reaction,



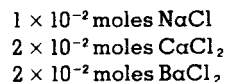
- (b) The partial pressure of
- $H_2S_{(g)}$
- overlying the water if the total soluble sulfide concentration,
- $C_{T,S} = [H_2S_{(aq)}] + [HS^-] + [S^{2-}]$
- , is
- $1 \times 10^{-3} M$
- and the solution pH is 8.5. Assume that the gas is in equilibrium with the water. (
- $K_{a,1} = 10^{-7}$
- and
- $K_{a,2} = 10^{-14}$
- for
- H_2S
- where
- $K_{a,1}$
- is the equilibrium constant for
- $H_2S_{(aq)} \rightleftharpoons HS^- + H^+$
- and
- $K_{a,2}$
- is the equilibrium constant for
- $HS^- \rightleftharpoons S^{2-} + H^+$
- .)

11. The reaction of divalent manganese with
- O_2
- in aqueous solutions is given as follows:

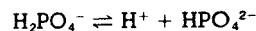


Delfino and Lee (*Environ. Sci. and Technol.*, December 1968) found that a lake water sample devoid of oxygen, pH = 8.5, originally contained 0.6 mg/liter of Mn^{2+} . The sample was aerated (atmospheric conditions) and after 10 days of saturation with atmospheric O_2 the Mn^{2+} concentration was 0.4 mg/liter.

- (a) Assuming that the pH remains constant during aeration, will the precipitate continue to form after the measurement on the tenth day?
- (b) What should the Mn^{2+} concentration be at equilibrium?
12. The following quantities of salts were added to a volume of water to make 1 liter of solution:



- (a) What is the ionic strength of the solution?
- (b) A small amount of phosphate salt is added to the same solution with negligible change in ionic strength. Given $K = 10^{-7.2}$ for the reaction



Calculate $[H^+][HPO_4^{2-}]/[H_2PO_4^-]$, called "K", using the Güntelberg approximation of the Debye-Hückel law.

- (c) Calculate the "salting-out" coefficient, k_s , for a nonelectrolyte in the same solution if its activity is $10^{-3} M$ and its concentration is $9.5 \times 10^{-4} M$.

13. Permanganate,
- MnO_4^-
- , decomposes in a solution that is in equilibrium with the atmosphere in accordance with the following reaction,



The equilibrium constant for this reaction is 10^{+68} .

- (a) If $[MnO_4^-] = 10^{-10} M$ and pH = 7, is the reaction at equilibrium or proceeding to the right or the left?
- (b) If the reaction is not at equilibrium for the conditions in part (a), calculate the pH at which the reaction will be at equilibrium if $[MnO_4^-] = 10^{-10} M$.

14. At 25°C, aqueous solutions of
- $CO_{2(aq)}$
- ,
- $NaHCO_3$
- , and
- HCl
- are mixed instantaneously so that the concentrations of
- $CO_{2(aq)}$
- ,
- HCO_3^-
- , and
- H^+
- are each
- $10^{-5} M$
- initially. In what direction does the following reaction proceed initially?

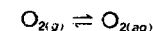


15. In order to cut costs at the lime softening plant, the operator decides to recalcinate the calcium carbonate sludge according to the reaction



The decision is made to store the sludge in a container open to the atmosphere prior to recalcination. Knowing that $P_{CO_2} = 10^{-3.5}$ atm, will any of the $CaCO_{3(s)}$ decompose according to the given reaction?

16. The reaction



has an equilibrium constant, K ($= K_H$, Henry's constant) $= 1.29 \times 10^{-3}$ at 25°C and $\Delta H^\circ = -3.9$ kcal.

- (a) Calculate the free energy of formation and the enthalpy of formation for the reactant and the product and compare to the values listed in Table 3-1.
- (b) Calculate the equilibrium constant at 50°C.
- (c) Given that the vapor pressure is as follows,

Temperature, °C	Vapor Pressure, mm Hg
25	23.8
50	92.5
100	760

and that dry air is 21 percent O_2 by volume, calculate the equilibrium concentration of O_2 in water at 25, 50, and 100°, for atmospheric pressure.

- (d) Given that 9.5 mg O_2 /liter is found in solution at 25°C, is the reaction at equilibrium? Why?

3.7. ADDITIONAL READING

Lewis, G. N., and M. Randall, *Thermodynamics*, revised by K. S. Pitzer and L. Brewer, 2nd ed., McGraw-Hill, 1961.

Moore, W. J., *Physical Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, N.J., 1972.