5.27 Calculate the number of components present in each of the following situations:

(**a**) Water, including autodissociation into H^+ and OH^- ions.

(**b**) Consider the following reaction in a closed container:

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

(**i**) All three gases were present initially in arbitrary amounts, but the temperature is too low for the reaction to occur.

(**ii**) Same as (**i**), but the temperature is raised sufficiently to allow for the equilibrium to be established.

(**iii**) Initially only NH_3 was present. The system is then allowed to reach equilibrium.

Additional Problems

5.28 Give the conditions under which each of the following equations may be applied.

(**a**) $dA \leq 0$ (for equilibrium and spontaneity)

(**b**) $dG \leq 0$ (for equilibrium and spontaneity)

(**c**) $\ln \frac{P_2}{P_1} = \frac{\Delta \overline{H}}{R} \frac{(T_2 - T_1)}{T_1 T_2}$

(**d**) $\Delta G = nRT \ln \frac{P_2}{P_1}$

5.29 When ammonium nitrate is dissolved in water, the solution becomes colder. What conclusion can you draw about $\Delta S°$ for the process?

5.30 Protein molecules are polypeptide chains made up of amino acids. In their physiologically functioning or native state, these chains fold in a unique manner such that the nonpolar groups of the amino acids are usually buried in the interior region of the proteins, where there is little or no contact with water. When a protein denatures, the chain unfolds so that these nonpolar groups are exposed to water. A useful estimate of the changes of the thermodynamic quantities as a result of denaturation is to consider the transfer of a hydrocarbon such as methane (a nonpolar substance) from an inert solvent (such as benzene or carbon tetrachloride) to the aqueous environment:

(**a**) $CH_4(\text{inert solvent}) \rightarrow CH_4(g)$

(**b**) $CH_4(g) \rightarrow CH_4(aq)$

If the values of $\Delta H°$ and $\Delta G°$ are approximately 2.0 kJ mol^{-1} and −14.5 kJ mol^{-1}, respectively, for (**a**) and −13.5 kJ mol^{-1} and 26.5 kJ mol^{-1}, respectively, for (**b**), then calculate the values of $\Delta H°$ and $\Delta G°$ for the transfer of 1 mole of CH_4 according to the equation

$$CH_4(\text{inert solvent}) \rightarrow CH_4(aq)$$

Comment on your results. Assume $T = 298$ K.

5.31 Find a rubber band that is about 0.5 cm wide. Quickly stretch the rubber band and then press it against your lips. You will feel a slight warming effect. Next, reverse the process. Stretch a rubber band and hold it in position for a few seconds. Then quickly release the tension and press the rubber band against your lips. This time you will feel a slight cooling effect. Use Equation 5.3 to present a thermodynamic analysis of this behavior.

5.32 A rubber band is stretched vertically by tying a weight to one end and attaching the other end to a ring stand. When heated with a hot-air blower, the rubber band shrinks slightly in length. Account for this observation.

5.33 Hydrogenation reactions are facilitated by the use of a transition metal catalyst, such as Ni or Pt. Predict the signs of $\Delta_r H$, $\Delta_r S$, and $\Delta_r G$ when hydrogen gas is adsorbed onto the surface of nickel metal.

5.34 A sample of supercooled water freezes at −10°C. What are the signs of ΔH, ΔS, and ΔG for this process? All the changes refer to the system.

5.35 The boiling point of benzene is 80.1°C. Estimate **(a)** its $\Delta_{\text{vap}}\overline{H}$ value and **(b)** its vapor pressure at 74°C. (*Hint:* Use Trouton's rule on p. 147.)

5.36 A chemist has synthesized a hydrocarbon compound (C_xH_y). Briefly describe what measurements are needed to determine the values of $\Delta_f\overline{H}°$, $\overline{S}°$, and $\Delta_f\overline{G}°$ of the compound.

5.37 Calculate ΔA and ΔG for the vaporization of 2.00 moles of water at 100°C and 1.00 atm. The molar volume of $H_2O(l)$ at 100°C is 0.0188 L mol^{-1}. Assume ideal gas behavior.

5.38 A person heated water in a cup in a microwave oven for tea. After removing the cup from the oven, she added a tea bag to the hot water. To her surprise, the water started to boil violently. Explain what happened.

5.39 Consider the reversible isothermal compression of 0.45 mole of helium gas from 0.50 atm and 22 L to 1.0 atm at 25°C. **(a)** Calculate the values of w, ΔU, ΔH, ΔS, and ΔG for the process. **(b)** Can you use the sign of ΔG to predict whether the process is spontaneous? Explain. **(c)** What is the maximum work that can be done for the compression process? Assume ideal-gas behavior.

5.40 The molar entropy of argon (Ar) is given by

$$\overline{S}° = (36.4 + 20.8 \ln T/\text{K})\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Calculate the change in Gibbs energy when 1.0 mole of Ar is heated at constant pressure from 20°C to 60°C. (*Hint:* Use the relation $\int \ln x\, dx = x \ln x - x$.)

5.41 Derive the thermodynamic equation of state:

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

Apply the equation to **(a)** an ideal gas and **(b)** a van der Waals gas. Comment on your results. (*Hint:* See Appendix 5.1 for thermodynamic relationships.)

CHAPTER 6

Nonelectrolyte Solutions

> *If a solution of iodine in benzene is cooled, the red color deepens, while if it is warmed, the color approaches the violet of iodine vapor, indicating that the solvation decreases with rising temperature, as would be expected.*
>
> —J. H. Hildebrand and C. A. Jenks*

The study of solutions is of great importance because many interesting and useful chemical and biological processes occur in liquid solutions. Generally, a solution is defined as a homogeneous mixture of two or more components that form a single phase. Most solutions are liquids, although gas solutions (e.g., air) and solid solutions (e.g., solder) also exist. This chapter is devoted to the thermodynamic study of ideal and nonideal solutions of nonelectrolytes—solutions that do not contain ionic species—and the colligative properties of these solutions.

6.1 Concentration Units

Any quantitative study of solutions requires that we know the amount of solute dissolved in a solvent or the concentration of the solution. Chemists employ several different concentration units, each one having advantages and limitations. The use of the solution generally determines how we express its concentration. In this section, we shall define four concentration units: percent by weight, mole fraction, molarity, and molality.

Percent by Weight

The percent by weight (also called percent by mass) of a solute in a solution is defined as

$$\begin{aligned}\text{percent by weight} &= \frac{\text{weight of solute}}{\text{weight of solute} + \text{weight of solvent}} \times 100\% \\ &= \frac{\text{weight of solute}}{\text{weight of solution}} \times 100\% \qquad (6.1)\end{aligned}$$

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* J. H. Hildebrand and C. A. Jenks, *J. Am. Chem. Soc.* **42**, 2180 (1920).

Mole Fraction (x)

The concept of mole fraction was introduced in Section 1.7. We define the mole fraction of a component i of a solution, x_i, as

$$x_i = \frac{\text{number of moles of component } i}{\text{number of moles of all components}}$$

$$= \frac{n_i}{\sum_i n_i} \tag{6.2}$$

The mole fraction has no units.

Molarity (M)

Molarity is defined as the number of moles of solute dissolved in 1 liter of solution, that is,

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{liters of solution}} \tag{6.3}$$

Thus, molarity has the units moles per liter (mol L^{-1}). By convention, we use square brackets [ ] to represent molarity.

Molality (m)

Molality is defined as the number of moles of solute dissolved in 1 kg (1000 g) of solvent, that is,

$$\text{molality} = \frac{\text{number of moles of solute}}{\text{mass of solvent in kg}} \tag{6.4}$$

Thus, molality has the units of moles per kg of solvent (mol kg^{-1}).

We shall now compare the usefulness of these four concentration terms. Percent by weight has the advantage that we do not need to know the molar mass of the solute. This unit is useful to biochemists, who frequently work with macromolecules either of unknown molar mass or of unknown purity. (A common unit for protein and DNA solutions is mg mL^{-1}, or mg per milliliter.) Furthermore, the percent by weight of a solute in a solution is independent of temperature, because it is defined in terms of weight. Mole fractions are useful for calculating partial pressures of gases (see Section 1.7) and in the study of vapor pressures of solutions (to be introduced later). Molarity is one of the most commonly employed concentration units. The advantage of using molarity is that it is generally easier to measure the volume of a solution using precisely calibrated volumetric flasks than to weigh the solvent. Its main drawback is that it is temperature dependent, because the volume of a solution usually increases with increasing temperature. Another drawback is that molarity does not tell us the amount of solvent present. Molality, on the other hand, is temperature independent because it is a ratio of the number of moles of solute to the weight of the solvent. For this reason, molality is the preferred concentration unit in studies that involve changes in temperature, as in some of the colligative properties of solutions (see Section 6.7).

6.2 Partial Molar Quantities

The extensive properties of a one-component system at a constant temperature and pressure depend only on the amount of the system present. For example, the volume of water depends on the quantity of water present. If the volume is expressed as a molar quantity, however, it is an intensive property. Thus, the molar volume of water at 1 atm and 298 K is 0.018 L mol^{-1}, no matter how little or how much water is present. For solutions, the criteria are different. A solution, by definition, contains at least two components. The extensive properties of a solution depend on temperature, pressure, and the composition of the solution. In discussing the properties of any solution, we cannot employ molar quantities; instead, we must use *partial molar quantities*. Perhaps the easiest partial molar quantity to understand is *partial molar volume*, described below.

Partial Molar Volume

The molar volumes of water and ethanol at 298 K are 0.018 L and 0.058 L, respectively. If we mix half a mole of each liquid, we might expect the combined volume to be the sum of 0.018 L/2 and 0.058 L/2, or 0.038 L. Instead, we find the volume to be only 0.036 L. The shrinkage of the volume is the result of unequal intermolecular interaction between unlike molecules. Because the forces of attraction between water and ethanol molecules are greater than those between water molecules and between ethanol molecules, the total volume is less than the sum of the individual volumes. If the intermolecular forces are weaker, then expansion will occur and the final volume will be greater than the sum of individual volumes. Only if the interactions between like and unlike molecules are the same will volume be additive. If the final volume is equal to the sum of the separate volumes, the solution is called an *ideal* solution. Figure 6.1 shows the total volume of a water–ethanol solution as a function of their mole fractions. In a real (nonideal) solution, the partial molar volume of each component is affected by the presence of the other components.

Financially, this shrinkage in volume has a detrimental effect on bartenders.

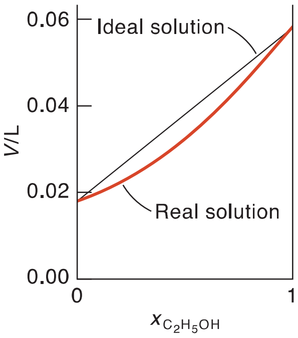


Figure 6.1
Total volume of a water–ethanol mixture as a function of the mole fraction of ethanol. At any concentration, the sum of the number of moles is 1. The straight line represents the variation of volume with mole fraction for an ideal solution. The curve represents the actual variation. Note that at $x_{C_2H_5OH} = 0$, the volume corresponds to that of the molar volume of water, and at $x_{C_2H_5OH} = 1$, V is the molar volume of ethanol.

At constant temperature and pressure, the volume of a solution is a function of the number of moles of different substances present; that is,

$$V = V(n_1, n_2, \ldots)$$

For a two-component system the total differential, dV, is given by

$$\begin{aligned} dV &= \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1} dn_2 \\ &= \overline{V}_1 dn_1 + \overline{V}_2 dn_2 \qquad (6.5) \end{aligned}$$

where $\overline{V}_1$ and $\overline{V}_2$ are the partial molar volumes of components 1 and 2. The partial molar volume $\overline{V}_1$, for example, tells us the rate of change in volume with number of moles of component 1, at constant T, P, and component 2. Alternatively, $\overline{V}_1$ can be viewed as the increase in volume resulting from the addition of 1 mole of component 1 to a very large volume of solution so that its concentration remains unchanged. The quantity $\overline{V}_2$ can be similarly interpreted. Equation 6.5 can be integrated to give

$$V = n_1\overline{V}_1 + n_2\overline{V}_2 \qquad (6.6)$$

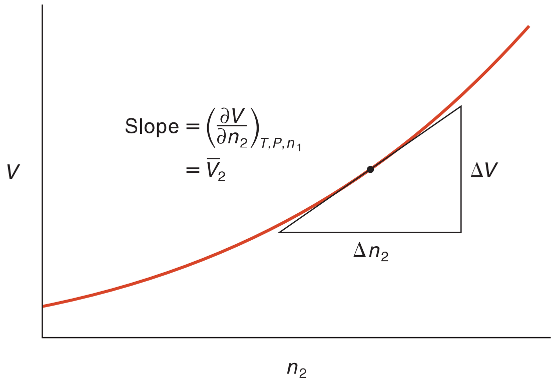


Figure 6.2
Determination of partial molar volume. The volume of a two-component solution is measured as a function of the number of moles, n_2, of component 2. The slope at a particular value n_2 gives the partial molar volume, $\overline{V}_2$, at that concentration while holding temperature, pressure, and number of moles of component 1 constant.

This equation enables us to calculate the volume of the solution by summing the products of the number of moles and the partial molar volume of each component (see Problem 6.55).

Figure 6.2 suggests a way of measuring partial molar volumes. Consider a solution composed of substances 1 and 2. To measure $\overline{V}_2$, we prepare a series of solutions at certain T and P, all of which contain a fixed number of moles of component 1 (i.e., n_1 is fixed) but different amounts of n_2. When we plot the measured volumes, V, of the solutions against n_2, the slope of the curve at a particular composition of 2 gives $\overline{V}_2$ for that composition. Once $\overline{V}_2$ has been measured, $\overline{V}_1$ at the same composition can be calculated using Equation 6.6:

$$\overline{V}_1 = \frac{V - n_2\overline{V}_2}{n_1}$$

Figure 6.3 shows the partial molar volumes of ethanol and water in an ethanol–water solution. Note that whenever the partial molar volume of one component rises, that of the other component falls. This relationship is a characteristic of *all* partial molar quantities.

Partial Molar Gibbs Energy

Partial molar quantities permit us to express the total extensive properties, such as volume, energy, enthalpy, and Gibbs energy, of a solution of any composition. The partial molar Gibbs energy of the ith component in solution $\overline{G}_i$ is given by

$$\overline{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \tag{6.7}$$

where n_j represents the number of moles of all other components present. Again we can think of $\overline{G}_i$ as the coefficient that gives the increase in the Gibbs energy of the

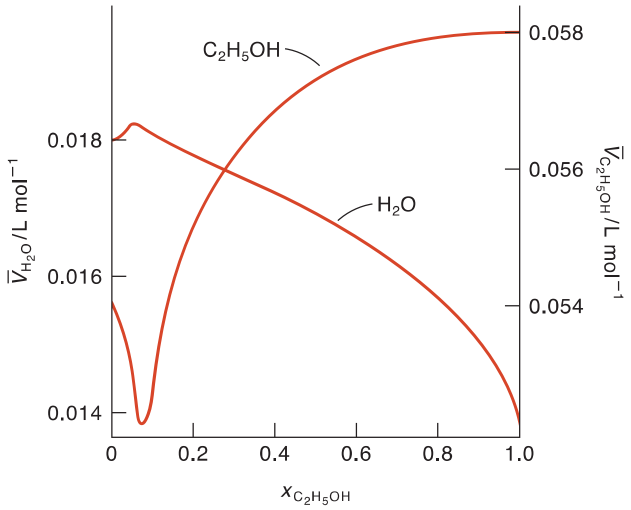


Figure 6.3
The partial molar volumes of water and ethanol as a function of the mole fraction of ethanol. Note the different scales for water (left) and ethanol (right).

solution upon the addition of 1 mole of component *i* at constant temperature and pressure to a large amount of solution of specified concentration. Partial molar Gibbs energy is also called the *chemical potential* (μ), so we can write

$$\overline{G}_i = \mu_i \tag{6.8}$$

The expression for the total Gibbs energy of a two-component solution is similar to Equation 6.6 for volumes:

$$G = n_1\mu_1 + n_2\mu_2 \tag{6.9}$$

The chemical potential provides a criterion for equilibrium and spontaneity for a multicomponent system, just as molar Gibbs energy does for a single-component system. Consider the transfer of dn_i moles of component *i* from some initial state A, where its chemical potential is μ_i^{A}, to some final state B, where its chemical potential is μ_i^{B}. For a process carried out at constant temperature and pressure, the change in the Gibbs energy, dG, is given by

$$\begin{aligned} dG &= \mu_i^{\mathrm{B}} dn_i - \mu_i^{\mathrm{A}} dn_i \\ &= (\mu_i^{\mathrm{B}} - \mu_i^{\mathrm{A}}) dn_i \end{aligned}$$

If $\mu_i^{\mathrm{B}} < \mu_i^{\mathrm{A}}$, $dG < 0$, and transfer of dn_i moles from A to B will be a spontaneous process; if $\mu_i^{\mathrm{B}} > \mu_i^{\mathrm{A}}$, $dG > 0$, and the process will be spontaneous from B to A. As we shall see later, the transfer can be from one phase to another or from one state of chemical combination to another. The transfer can be transport by diffusion, evaporation, sublimation, condensation, crystallization, solution formation, or chemical reaction. Regardless of the nature of the process, in each case the transfer proceeds from a higher μ_i value to a lower μ_i value. This characteristic explains the name *chemical potential*. In mechanics, the direction of spontaneous change always takes the system from a higher potential-energy state to a lower one. In thermodynamics, the situation is not quite so simple because we have to consider both energy and entropy factors. Nevertheless, we know that at constant temperature and pressure, the direction of a spontaneous change is always toward a decrease in the system's Gibbs energy. Thus, the role Gibbs energy plays in thermodynamics is analogous to that of potential energy in mechanics. This is the reason that molar Gibbs energy or, more commonly, partial molar Gibbs energy, is called the chemical potential.

6.3 Thermodynamics of Mixing

The formation of solutions is governed by the principles of thermodynamics. In this section, we shall discuss the changes in thermodynamic quantities that result from mixing. In particular, we shall focus on gases.

Equation 6.9 gives the dependence of the Gibbs energy of a system on its composition. The spontaneous mixing of gases is accompanied by a change in composition; consequently, the system's Gibbs energy decreases. In Section 5.4, we obtained an expression for the molar Gibbs energy of an ideal gas (Equation 5.18):

$$\overline{G} = \overline{G}^\circ + RT \ln \frac{P}{1\ \text{bar}}$$

In a mixture of ideal gases, the chemical potential of the ith component is given by

$$\mu_i = \mu_i^\circ + RT \ln \frac{P_i}{1\ \text{bar}} \tag{6.10}$$

where P_i is the partial pressure of component i in the mixture and μ_i° is the standard chemical potential of component i when its partial pressure is 1 bar. Now consider the mixing of n_1 moles of gas 1 at temperature T and pressure P with n_2 moles of gas 2 at the same T and P. Before mixing, the total Gibbs energy of the system is given by Equation 6.9, where chemical potentials are the same as molar Gibbs energies,

For simplicity, we omit the term "1 bar." Note that the resulting P values are dimensionless.

$$G = n_1\overline{G}_1 + n_2\overline{G}_2 = n_1\mu_1 + n_2\mu_2$$

$$G_{\text{initial}} = n_1(\mu_1^\circ + RT \ln P) + n_2(\mu_2^\circ + RT \ln P)$$

After mixing, the gases exert partial pressures P_1 and P_2, where $P_1 + P_2 = P$, and the Gibbs energy is*

$$G_{\text{final}} = n_1(\mu_1^\circ + RT \ln P_1) + n_2(\mu_2^\circ + RT \ln P_2)$$

---

* Note that $P_1 + P_2 = P$ only if there is no change in volume as a result of mixing; that is, $\Delta_{\text{mix}}V = 0$. This condition holds for ideal solutions.

The Gibbs energy of mixing, $\Delta_{\text{mix}}G$, is given by

$$\begin{aligned}\Delta_{\text{mix}}G &= G_{\text{final}} - G_{\text{initial}} \\ &= n_1RT\ln\frac{P_1}{P} + n_2RT\ln\frac{P_2}{P} \\ &= n_1RT\ln x_1 + n_2RT\ln x_2\end{aligned}$$

where $P_1 = x_1P$ and $P_2 = x_2P$, and x_1 and x_2 are the mole fractions of 1 and 2, respectively. (The standard chemical potential, $\mu°$, is the same in the pure state and in the mixture.) Further, from the relations

$$x_1 = \frac{n_1}{n_1 + n_2} = \frac{n_1}{n} \quad \text{and} \quad x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n}$$

where n is the total number of moles, we have

$$\Delta_{\text{mix}}G = nRT(x_1\ln x_1 + x_2\ln x_2) \tag{6.11}$$

Because both x_1 and x_2 are less than unity, $\ln x_1$ and $\ln x_2$ are negative quantities, and hence so is $\Delta_{\text{mix}}G$. This result is consistent with our expectation that the mixing of gases is a spontaneous process at constant T and P.

Now we can calculate other thermodynamic quantities of mixing. From Equation 5.10, we see that at constant pressure

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

Thus, the entropy of mixing is obtained by differentiating Equation 6.11 with respect to temperature at constant pressure:

$$\begin{aligned}\left(\frac{\partial \Delta_{\text{mix}}G}{\partial T}\right)_P &= nR(x_1\ln x_1 + x_2\ln x_2) \\ &= -\Delta_{\text{mix}}S\end{aligned}$$

or

$$\Delta_{\text{mix}}S = -nR(x_1\ln x_1 + x_2\ln x_2) \tag{6.12}$$

This result is equivalent to Equation 4.17. The minus sign in Equation 6.12 makes $\Delta_{\text{mix}}S$ a positive quantity, in accord with a spontaneous process. The enthalpy of mixing is given by rearranging Equation 5.3:

$$\begin{aligned}\Delta_{\text{mix}}H &= \Delta_{\text{mix}}G + T\Delta_{\text{mix}}S \\ &= 0\end{aligned}$$

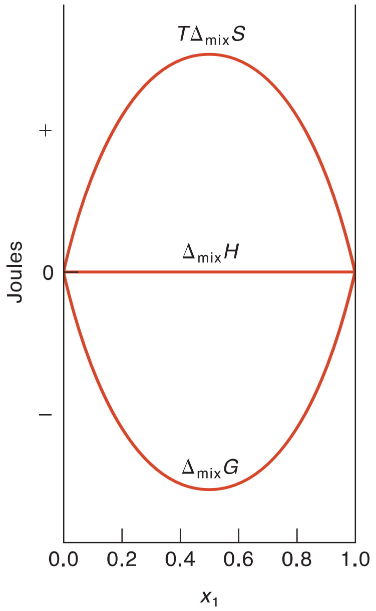


Figure 6.4
Plots of $T\Delta_{\text{mix}}S$, $\Delta_{\text{mix}}H$, and $\Delta_{\text{mix}}G$ as a function of composition x_1 for the mixing of two components to form an ideal solution.

This result is not surprising, because molecules of ideal gases do not interact with one another, so no heat is absorbed or produced as a result of mixing. Figure 6.4 shows the plots of $\Delta_{\text{mix}}G$, $T\Delta_{\text{mix}}S$, and $\Delta_{\text{mix}}H$ for a two-component system as a function of composition. Note that both the maximum (for $T\Delta_{\text{mix}}S$) and the minimum (for $\Delta_{\text{mix}}G$) occur at $x_1 = 0.5$. This result means that we achieve maximum disorder by mixing equimolar amounts of gases and that the Gibbs energy of mixing reaches a minimum at this point (see Problem 6.57).

Reversing the process for a two-component solution of equal mole fractions leads to an increase in Gibbs energy and a decrease in entropy of the system, so energy must be supplied to the system from the surroundings. Initially, at $x_1 \approx x_2$, the $\Delta_{\text{min}}G$ and $T\Delta_{\text{mix}}S$ curves are fairly flat (see Figure 6.4), and separation can be carried out easily. However, as the solution becomes progressively richer in one component, say 1, the curves become very steep. Then, a considerable amount of energy input is needed to separate component 2 from 1. This difficulty is encountered, for example, in the attempt to clean up a lake contaminated by small amounts of undesirable chemicals. The same consideration applies to the purification of compounds. Preparing most compounds in 95% purity is relatively easy, but much more effort is required to attain 99% or higher purity, which is needed, for example, for the silicon crystals used in solid-state electronics.

As another example, let us explore the possibility of mining gold from the oceans. Estimates are that there is approximately 4×10^{-12} g of gold/mL of seawater. This amount may not seem like much, but when we multiply it by the total volume of ocean water, 1.5×10^{21} L, we find the amount of gold present to be 6×10^{12} g or 7 million tons, which should satisfy anybody. Unfortunately, not only is the concentration of gold in seawater very low, but gold is also just one of some 60 different elements in the ocean. Separating one pure component initially present in a very low concentration in seawater (i.e., starting at the steep portions of the curves in Figure 6.4) would be a very formidable (and expensive) undertaking indeed.

EXAMPLE 6.1

Calculate the Gibbs energy and entropy of mixing 1.6 moles of argon at 1 atm and 25°C with 2.6 moles of nitrogen at 1 atm and 25°C. Assume ideal behavior.

ANSWER

The mole fractions of argon and neon are

$$x_{\mathrm{Ar}} = \frac{1.6}{1.6 + 2.6} = 0.38 \quad x_{\mathrm{N_2}} = \frac{2.6}{1.6 + 2.6} = 0.62$$

From Equation 6.11,

$$\begin{aligned}\Delta_{\mathrm{mix}} G &= nRT(x_1 \ln x_1 + x_2 \ln x_2)\\ &= (4.2\ \mathrm{mol})(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(298\ \mathrm{K})[(0.38) \ln 0.38 + (0.62) \ln 0.62]\\ &= -6.9\ \mathrm{kJ}\end{aligned}$$

Because $\Delta_{\mathrm{mix}} S = \Delta_{\mathrm{mix}} G/T$, we write

$$\begin{aligned}\Delta_{\mathrm{mix}} S &= -\frac{-6.9 \times 10^3\ \mathrm{J}}{298\ \mathrm{K}}\\ &= 23\ \mathrm{J\ K^{-1}}\end{aligned}$$

COMMENT

In this example, the gases are at the same temperature and pressure when they are mixed. If the initial pressures of the gases differ, then there will be two contributions to $\Delta_{\mathrm{mix}} G$: the mixing itself and the changes in pressure. Problem 6.58 illustrates this situation.

6.4 Binary Mixtures of Volatile Liquids

The results obtained in Section 6.3 for mixtures of gases also apply to ideal liquid solutions. For the study of solutions, we need to know how to express the chemical potential of each component. We shall consider a solution containing two volatile liquids, that is, liquids with easily measurable vapor pressures.

Let us start with a liquid in equilibrium with its vapor in a closed container. Because the system is at equilibrium, the chemical potentials of the liquid phase and the vapor phase must be the same, that is,

$$\mu^*(l) = \mu^*(g)$$

where the asterisk denotes a pure component. Further, from the expression for $\mu^*(g)$ for an ideal gas, we can write[†]

$$\mu^*(l) = \mu^*(g) = \mu^\circ(g) + RT \ln \frac{P^*}{1 \text{ bar}} \tag{6.13}$$

where $\mu^\circ(g)$ is the standard chemical potential at $P^* = 1$ bar. For a two-component solution at equilibrium with its vapor, the chemical potential of each component is still the same in the two phases. Thus, for component 1 we write

$$\mu_1(l) = \mu_1(g) = \mu_1^\circ(g) + RT \ln \frac{P_1}{1 \text{ bar}} \tag{6.14}$$

where P_1 is the partial pressure. Because $\mu^\circ(g) = \mu_1^\circ(g)$, we can combine the previous two equations to get

$$\begin{aligned}\mu_1(l) &= \mu_1^\circ(g) + RT \ln \frac{P_1}{1 \text{ bar}} \\ &= \mu_1^*(l) - RT \ln \frac{P_1^*}{1 \text{ bar}} + RT \ln \frac{P_1}{1 \text{ bar}} \\ &= \mu_1^*(l) + RT \ln \frac{P_1}{P_1^*}\end{aligned} \tag{6.15}$$

Thus, the chemical potential of component 1 in solution is expressed in terms of the chemical potential of the liquid in the pure state and the vapor pressures of the liquid in solution and in the pure state.

Raoult's Law

The French chemist François Marie Raoult (1830–1901) found that for some solutions, the ratio P_1/P_1^* in Equation 6.15 is equal to the mole fraction of component 1, that is,

$$\frac{P_1}{P_1^*} = x_1$$

or

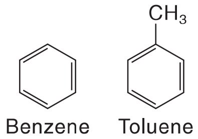
$$P_1 = x_1 P_1^* \tag{6.16}$$

Equation 6.16 is known as *Raoult's law*, which states that the vapor pressure of a component of a solution is equal to the product of its mole fraction and the vapor pressure of the pure liquid. Substituting Equation 6.16 into Equation 6.15, we obtain

$$\mu_1(l) = \mu_1^*(l) + RT \ln x_1 \tag{6.17}$$

[†] This equation follows from Equation 5.18. For a pure component, the chemical potential is equal to the molar Gibbs energy.

We see that in a pure liquid ($x_1 = 1$ and $\ln x_1 = 0$), $\mu_1(l) = \mu_1^*(l)$. Solutions that obey Raoult's law are called *ideal solutions*. An example of a nearly ideal solution is the benzene–toluene system. Figure 6.5 shows a plot of the vapor pressures versus the mole fraction of benzene.



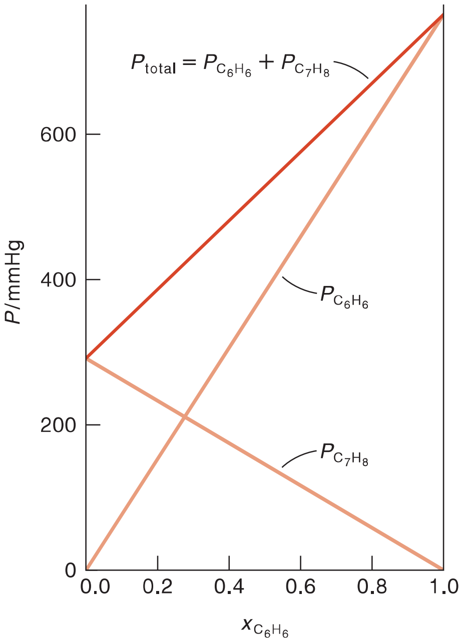


Figure 6.5
Total vapor pressure of the benzene–toluene mixture as a function of the benzene mole fraction at 80.1°C.

EXAMPLE 6.2

Liquids A and B form an ideal solution. At 45°C, the vapor pressures of pure A and pure B are 66 torr and 88 torr, respectively. Calculate the composition of the vapor in equilibrium with a solution containing 36 mole percent A at this temperature.

ANSWER

Because $x_A = 0.36$ and $x_B = 1 - 0.36 = 0.64$, we have, according to Raoult's law

$$P_A = x_A P_A^* = 0.36(66 \text{ torr}) = 23.8 \text{ torr}$$

$$P_B = x_B P_B^* = 0.64(88 \text{ torr}) = 56.3 \text{ torr}$$

The total vapor pressure, P_T, is given by

$$P_T = P_A + P_B = 23.8 \text{ torr} + 56.3 \text{ torr} = 80.1 \text{ torr}$$

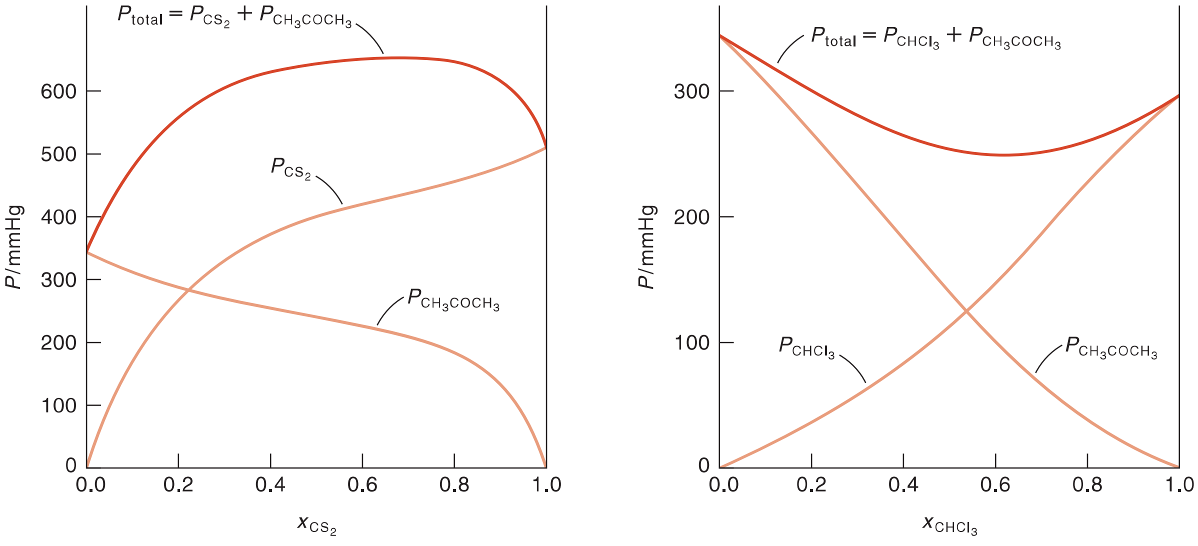
Finally, the mole fractions of A and B in the vapor phase, x_A^v and x_A^v, are given by

$$x_A^v = \frac{P_A}{P_T} = \frac{23.8 \text{ torr}}{80.1 \text{ torr}} = 0.30$$

and

$$x_B^v = \frac{P_B}{P_T} = \frac{56.3 \text{ torr}}{80.1 \text{ torr}} = 0.70$$

In an ideal solution, all intermolecular forces are equal, whether the molecules are alike or not. The benzene–toluene system approximates this requirement because benzene and toluene molecules have similar shapes and electronic structures. For an ideal solution, we have both $\Delta_{mix}H = 0$ and $\Delta_{mix}V = 0$. Most solutions do *not* behave ideally, however. Figure 6.6 shows the positive and negative deviations from Raoult's law. The positive deviation (Figure 6.6a) corresponds to the case in which the intermolecular forces between unlike molecules are weaker than those between like molecules, and



(a) **(b)**

Figure 6.6
Deviations from Raoult's law by nonideal solutions. (a) Positive deviation from Raoult's law: carbon disulfide–acetone system at 35.2°C. (b) Negative deviation: chloroform–acetone system at 25.2°C. (From Hildebrand, J. and R. Scott, *The Solubility of Nonelectrolytes* © 1950, Litton Educational Publishing. Reprinted by permission of Van Nostrand Reinhold Company.)

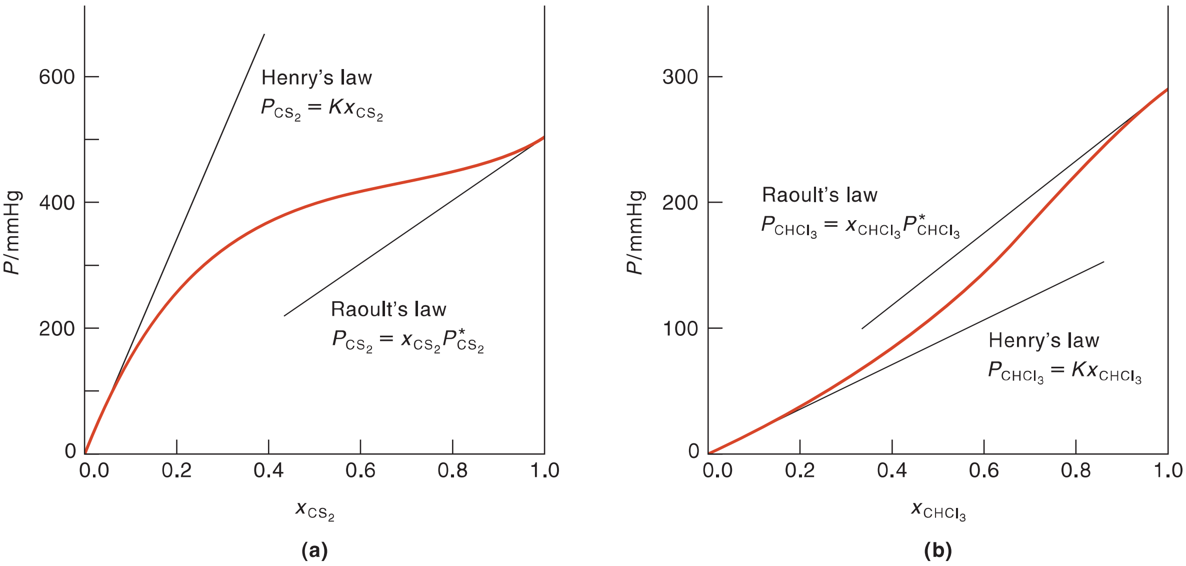


Figure 6.7
Diagrams showing regions over which Raoult's law and Henry's law are applicable for a two-component system (see Figure 6.6) The Henry's law constants can be obtained from the intercepts on the *y* (pressure) axis.

there is a greater tendency for these molecules to leave the solution than in the case of an ideal solution. Consequently, the vapor pressure of the solution is greater than the sum of the vapor pressures for an ideal solution. Just the opposite holds for a negative deviation from Raoult's law (Figure 6.6b). In this case, unlike molecules attract each other more strongly than they do their own kind, and the vapor pressure of the solution is less than the sum of the vapor pressures for an ideal solution.

Henry's Law

When one solution component is present in excess (this component is called the solvent), its vapor pressure is quite accurately described by Equation 6.16. The regions where Raoult's law is applicable are shown for the carbon disulfide–acetone system in Figure 6.7. In contrast, the vapor pressure of the component present in a small amount (this component is called the solute) does not vary with the composition of the solution, as predicted by Equation 6.16. Still, the vapor pressure of the solute varies with concentration in a linear manner:

There is no sharp distinction between solvent and solute. Where applicable, we shall call component 1 the solvent and component 2 the solute.

$$P_2 = Kx_2 \tag{6.18}$$

Equation 6.18 is known as *Henry's law* (after the English chemist William Henry, 1775–1836), where *K*, the Henry's law constant, has units of pressure. Henry's law relates the mole fraction of the solute to its partial (vapor) pressure. Alternatively, Henry's law can be expressed as

$$P_2 = K'm \tag{6.19}$$

Table 6.1
Henry's Law Constants for Some Gases in Water at 298 K

Gas	K/torr	K'/atm mol^{-1} kg H_2O
H_2	5.54×10^7	1311
He	1.12×10^8	2649
Ar	2.80×10^7	662
N_2	6.80×10^7	1610
O_2	3.27×10^7	773
CO_2	1.24×10^6	29.3
H_2S	4.27×10^5	10.1

where m is the molality of the solution and the constant K' now has the units atm mol^{-1} kg of the solvent. Table 6.1 lists the values of K and K' for several gases in water at 298 K.

Henry's law is normally associated with solutions of gases in liquids, although it is equally applicable to solutions containing nongaseous volatile solutes. It has great practical importance in chemical and biological systems and therefore merits further discussion. The effervescence observed when a soft drink or champagne bottle is opened is a nice demonstration of the decrease in gas—mostly CO_2—solubility as its partial pressure is lowered. The emboli (gas bubbles in the bloodstream) suffered by deep-sea divers who rise to the surface too rapidly also illustrate Henry's law. At a point some 40 m below the surface of seawater, the total pressure is about 6 atm. The solubility of nitrogen in the blood plasma is then about 0.8×6 atm$/1610$ atm mol^{-1} kg H_2O, or 3.0×10^{-3} mol (kg H_2O)$^{-1}$, which is six times the solubility at sea level. If the diver swims upward too rapidly, dissolved nitrogen gas will start boiling off. The mildest result is dizziness; the most serious, death.* Because helium is less soluble in the blood plasma than nitrogen is, it is the preferred gas for diluting oxygen gas for use in deep-sea diving tanks.

There are several types of deviations from Henry's law. First, as mentioned earlier, the law holds only for dilute solutions. Second, if the dissolved gas interacts chemically with the solvent, then the solubility can be greatly enhanced. Gases such as CO_2, H_2S, NH_3, and HCl all have high solubilities in water because they react with the solvent. The third type of deviation is illustrated by the dissolution of oxygen in blood. Normally, oxygen is only sparingly soluble in water (see Table 6.1), but its solubility increases dramatically if the solution contains hemoglobin or myoglobin.

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* For other interesting illustrations of Henry's law, see T. C. Loose, *J. Chem. Educ.* **48**, 154 (1971), W. J. Ebel, *J. Chem. Educ.* **50**, 559 (1973), and D. R. Kimbrough, *J. Chem. Educ.* **76**, 1509 (1999).

EXAMPLE 6.3

Calculate the molal solubility of carbon dioxide in water at 298 K and a CO_2 pressure of 3.3×10^{-4} atm, which corresponds to the partial pressure of CO_2 in air.

ANSWER

The mole fraction of solute (carbon dioxide) is given by Equation 6.18:

$$x_{CO_2} = \frac{P_{CO_2}}{K}$$

Because the number of moles of CO_2 dissolved in 1000 g of water is small, we can approximate the mole fraction as follows:

$$x_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} \approx \frac{n_{CO_2}}{n_{H_2O}}$$

so that

$$n_{CO_2} = \frac{P_{CO_2} n_{H_2O}}{K}$$

Finally, looking up the K value of CO_2 in Table 6.1 we write

$$\begin{aligned} n_{CO_2} &= (3.3 \times 10^{-4} \times 760)\ \text{torr} \times \frac{1000\ \text{g}}{18.01\ \text{g mol}^{-1}} \times \frac{1}{1.24 \times 10^6\ \text{torr}} \\ &= 1.12 \times 10^{-5}\ \text{mol} \end{aligned}$$

Because this is the number of moles of CO_2 in 1000 g or 1 kg of H_2O, the molality is 1.12×10^{-5} mol (kg H_2O)$^{-1}$.

Alternatively, we can use Equation 6.19 and proceed as follows:

$$\begin{aligned} m &= \frac{P_{CO_2}}{K'} \\ &= \frac{3.3 \times 10^{-4}\ \text{atm}}{29.3\ \text{atm mol}^{-1}\ \text{kg H}_2\text{O}} = 1.12 \times 10^{-5}\ \text{mol (kg H}_2\text{O)}^{-1} \end{aligned}$$

COMMENT

Carbon dioxide dissolved in water is converted to carbonic acid, which causes water that is exposed to air for a long period of time to become acidic.

6.5 Real Solutions

As pointed out in Section 6.4, most solutions do not behave ideally. One problem that immediately arises in dealing with nonideal solutions is how to write the chemical potentials for the solvent and solute components.

The Solvent Component

Let us look at the solvent component first. As we saw earlier, the chemical potential of the solvent in an ideal solution is given by (see Equation 6.17)

$$\mu_1(l) = \mu_1^*(l) + RT \ln x_1$$

where $x_1 = P_1/P_1^*$ and P_1^* is the equilibrium vapor pressure of pure component 1 at T. The standard state is the pure liquid and is attained when $x_1 = 1$. For a nonideal solution, we write

$$\mu_1(l) = \mu_1^*(l) + RT \ln a_1 \tag{6.20}$$

where a_1 is the *activity* of the solvent. Nonideality is the consequence of unequal intermolecular forces between solvent–solvent and solvent–solute molecules. Therefore, the extent of nonideality depends on the composition of solution, and the activity of the solvent plays the role of "effective" concentration. The solvent's activity can be expressed in terms of vapor pressure as

$$a_1 = \frac{P_1}{P_1^*} \tag{6.21}$$

Table 6.2
Activity of Water in Water–Urea Solutions at 273 K[a]

Molality of urea, m_2	Mole fraction of water, x_1	Vapor pressure of water, P_1/atm	Activity of water, a_1	Activity coefficient of water, γ_1
0	1.000	6.025×10^{-3}	1.000	1.000
1	0.982	5.933×10^{-3}	0.985	1.003
2	0.965	5.846×10^{-3}	0.970	1.005
4	0.933	5.672×10^{-3}	0.942	1.010
6	0.902	5.501×10^{-3}	0.913	1.012
10	0.847	5.163×10^{-3}	0.857	1.012

[a] Data from National Research Council. *International Critical Tables of Numerical Data: Physics, Chemistry, and Technology*, Vol. 3. © 1928, McGraw-Hill. Used by permission of McGraw-Hill. Note that the solute (urea) is nonvolatile.

where P_1 is the partial vapor pressure of component 1 over the (nonideal) solution. Activity is related to concentration (mole fraction) as follows:

$$a_1 = \gamma_1 x_1 \tag{6.22}$$

where γ_1 is the *activity coefficient*. Equation 6.20 can now be written as

$$\mu_1(l) = \mu_1^*(l) + RT \ln \gamma_1 + RT \ln x_1 \tag{6.23}$$

The value of γ_1 is a measure of the deviation from ideality. In the limiting case, where $x_1 \rightarrow 1$, $\gamma_1 \rightarrow 1$ and activity and the mole fraction are identical. This condition also holds for an ideal solution at all concentrations.

Equation 6.21 provides a way of obtaining the activity of the solvent. By measuring P_1 of the solvent vapor over a range of concentrations, we can calculate the value of a_1 at each concentration if P_1^* is known.[†] Table 6.2 shows the activity of water in various water–urea solutions.

The Solute Component

We now come to the solute. Ideal solutions in which both components obey Raoult's law over the entire concentration range are rare. In dilute, nonideal solutions in which there is no chemical interaction, the solvent obeys Raoult's law, and the solute obeys Henry's law.[‡] Such solutions are sometimes called "ideal dilute solutions." If the solution were ideal, the chemical potential of the solute is also given by Raoult's law

$$\begin{aligned} \mu_2(l) &= \mu_2^*(l) + RT \ln x_2 \\ &= \mu_2^*(l) + RT \ln \frac{P_2}{P_2^*} \end{aligned}$$

In an ideal dilute solution, Henry's law applies. That is $P_2 = Kx_2$, so that

$$\begin{aligned} \mu_2(l) &= \mu_2^*(l) + RT \ln \frac{K}{P_2^*} + RT \ln x_2 \\ &= \mu_2^\circ(l) + RT \ln x_2 \end{aligned} \tag{6.24}$$

where $\mu_2^\circ(l) = \mu_2^*(l) + RT \ln (K/P_2^*)$. Although Equation 6.24 seems to take the same form as Equation 6.17, there is an important difference, which lies in the choice of standard state. According to Equation 6.24, the standard state is defined as the pure solute, attained by setting $x_2 = 1$. Equation 6.24 holds only for dilute solutions, however. How can these two conditions be met simultaneously? The simple way out of this dilemma is to recognize that standard states are often hypothetical states, not physically realizable. Thus, the standard state of solute defined by Equation 6.24 is

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[†] To obtain the value of P_1, we must measure the total pressure, P, and also analyze the composition of the mixture. Then we can calculate partial pressure P_1 using Equation 1.6; that is, $P_1 = x_1^{\mathrm{v}} P$, where x_1^{v} is the mole fraction of the solvent in the vapor phase.

[‡] For ideal solutions, Raoult's law and Henry's law become identical; that is, $P_2 = Kx_2 = P_2^* x_2$.

the hypothetical pure component 2 with a vapor pressure equal to K (when $x_2 = 1$, $P_2 = K$). In a sense, this is an "infinite dilution state of unit mole fraction"; that is, it is infinitely dilute with respect to component 1, the solvent, with the solute at unit mole fraction. For nonideal solutions in general (beyond the dilute solution limit), Equation 6.24 is modified to

$$\mu_2(l) = \mu_2^\circ(l) + RT \ln a_2 \tag{6.25}$$

where a_2 is the activity of the solute. As in the case of the solvent component, we have $a_2 = \gamma_2 x_2$, where γ_2 is the activity coefficient of the solute. Here, we have $a_2 \to x_2$ or $\gamma_2 \to 1$ as $x_2 \to 0$. Henry's law is now given by

$$P_2 = K a_2 \tag{6.26}$$

Concentrations are usually expressed in molalities (or molarities) instead of mole fractions. In molality, Equation 6.24 takes the form

$$\mu_2(l) = \mu_2^\circ(l) + RT \ln \frac{m_2}{m^\circ} \tag{6.27}$$

where $m^\circ = 1$ mol kg^{-1} so that the ratio m_2/m° is dimensionless. Here, the standard state is defined as a state at unit molality but in which the solution is behaving ideally. Again, this standard state is a hypothetical state, not attainable in practice (Figure 6.8). For nonideal solutions, Equation 6.27 is rewritten as

$$\mu_2(l) = \mu_2^\circ(l) + RT \ln a_2 \tag{6.28}$$

where $a_2 = \gamma_2(m_2/m^\circ)$. In the limiting case of $m_2 \to 0$, we have $a_2 \to m_2/m^\circ$ or $\gamma_2 \to 1$ (see Figure 6.8b).

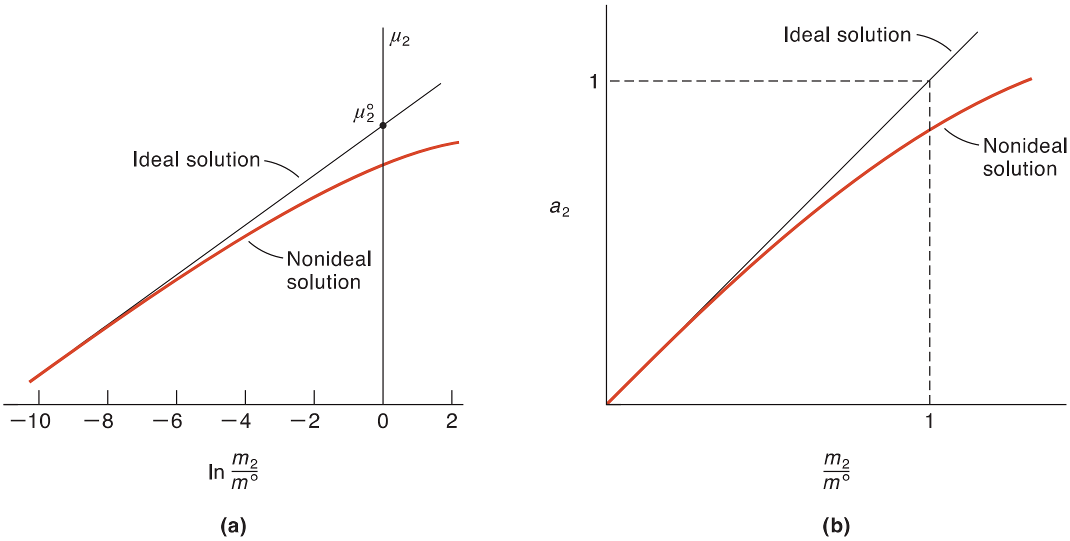


Figure 6.8
(a) Chemical potential of a solute plotted against the logarithm of molality for a nonideal solution. (b) Activity of a solute as a function of molality for a nonideal solution. The standard state is at $m_2/m^\circ = 1$.

Keep in mind that although Equations 6.24 and 6.27 were derived using Henry's law, they are applicable to any solute, whether or not it is volatile. These expressions are useful in discussing the colligative properties of solutions (see Section 6.7), and, as we shall see in Chapter 8, in deriving the equilibrium constant.

6.6 Phase Equilibria of Two-Component Systems

Before we study colligative properties, let us first apply the phase diagram and the Gibbs phase rule to the properties of solutions containing two components.

Distillation

The separation of two volatile liquid components is usually accomplished by fractional distillation, which has many applications in the laboratory and in industrial processes. To use this procedure, we must understand how pressure and temperature affect the vapor–liquid equilibrium of binary liquid mixtures.

Pressure–Composition Diagram. We begin by constructing phase diagrams that show the vapor pressure of a solution as a function of mole fraction and as a function of the composition of the vapor in equilibrium with the solution. Using the ideal benzene–toluene solution as an example, we can express the vapor pressures of both components in terms of Raoult's law:

$$P_\mathrm{b} = x_\mathrm{b}P_\mathrm{b}^* \quad \text{and} \quad P_\mathrm{t} = x_\mathrm{t}P_\mathrm{t}^*$$

where x_b and x_t are the mole fractions of benzene and toluene in solution, respectively, and the asterisk denotes a pure component. The total pressure, P, is given by

$$\begin{aligned} P &= P_\mathrm{b} + P_\mathrm{t} \\ &= x_\mathrm{b}P_\mathrm{b}^* + x_\mathrm{t}P_\mathrm{t}^* \\ &= x_\mathrm{b}P_\mathrm{b}^* + (1 - x_\mathrm{b})P_\mathrm{t}^* \\ &= P_\mathrm{t}^* + (P_\mathrm{b}^* - P_\mathrm{t}^*)x_\mathrm{b} \end{aligned} \tag{6.29}$$

Figure 6.9a shows a plot of P versus x_b, which is a straight line.

Next we want to express P in terms of x_b^v, which is the mole fraction of benzene in the vapor phase. According to Equation 1.6, the mole fraction of benzene in the vapor phase is given by

$$x_\mathrm{b}^\mathrm{v} = \frac{P_\mathrm{b}}{P} = \frac{x_\mathrm{b}P_\mathrm{b}^*}{P_\mathrm{t}^* + (P_\mathrm{b}^* - P_\mathrm{t}^*)x_\mathrm{b}}$$

This equation can be solved for x_b to obtain the following expression for the mole fraction of benzene in solution that corresponds to its mole fraction x_b^v in the vapor phase at equilibrium:

$$x_\mathrm{b} = \frac{x_\mathrm{b}^\mathrm{v}P_\mathrm{t}^*}{P_\mathrm{b}^* - (P_\mathrm{b}^* - P_\mathrm{t}^*)x_\mathrm{b}^\mathrm{v}} \tag{6.30}$$

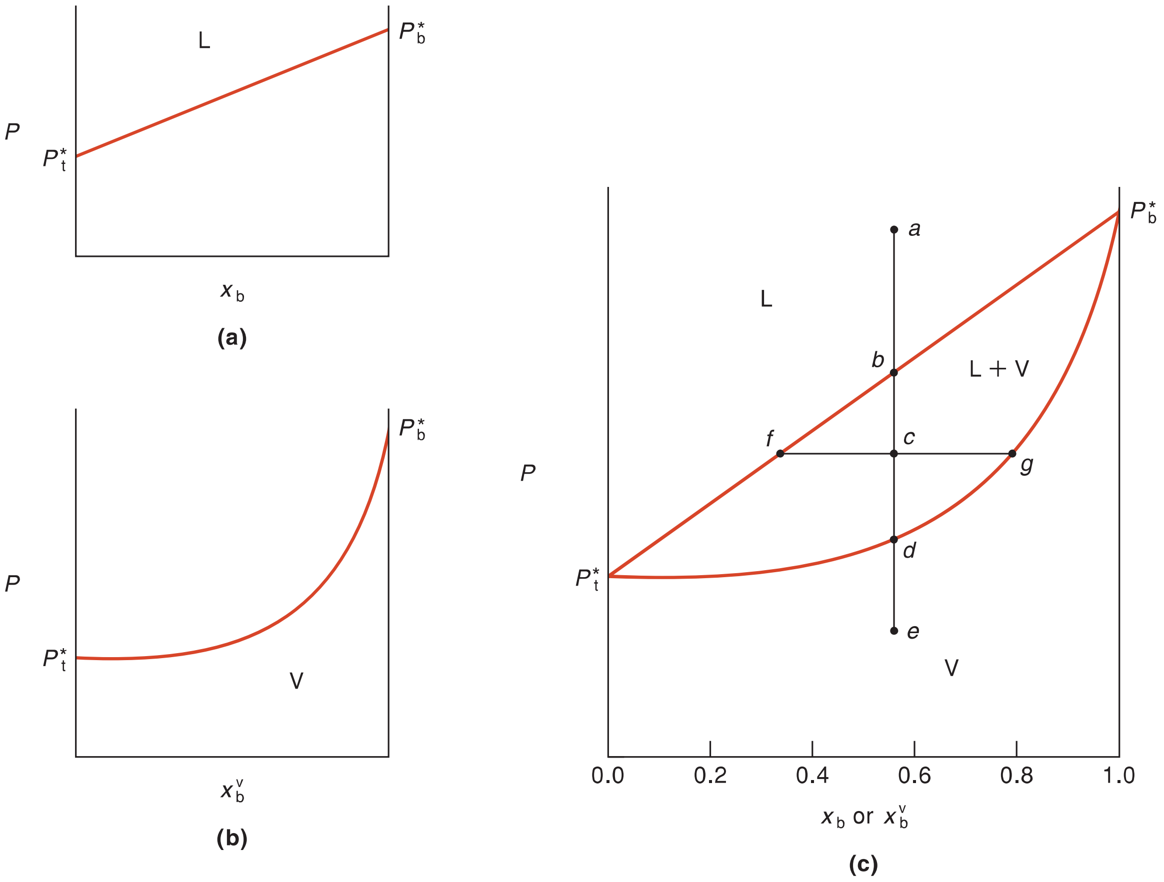


Figure 6.9

Pressure versus composition liquid (L)–vapor (V) phase diagram for the benzene–toluene solution at 23°C. (a) Plot of vapor pressure versus the mole fraction of a benzene in solution. (b) Plot of vapor pressure versus the mole fraction of benzene in the vapor phase. (c) Combined plots of (a) and (b). Above the straight line, the system is entirely in the liquid state; below the curve, the system is entirely in the vapor state; both liquid and vapor are present in the enclosed area. At point *c*, the liquid composition is $x_b = 0.30$ and the vapor composition is $x_b^v = 0.80$.

Again, referring to Equation 1.6 and Raoult's law,

$$P_b = x_b^v P = x_b P_b^*$$

and using Equation 6.30, we write

$$P = \frac{x_b P_b^*}{x_b^v} = \frac{P_b^* P_t^*}{P_b^* - (P_b^* - P_t^*)x_b^v} \qquad (6.31)$$

Figure 6.9b shows a plot of P versus x_b^v.

The combined plots of Equations 6.29 and 6.31 are shown in Figure 6.9c. Above the straight line, the system is in the liquid state. (This result is consistent with our expectation that at high pressures, liquid is the more stable phase.) Below the curve, that is, at low pressures, the system exists as a vapor. At a point between the two lines (i.e., a point in the enclosed area) both liquid and vapor are present.

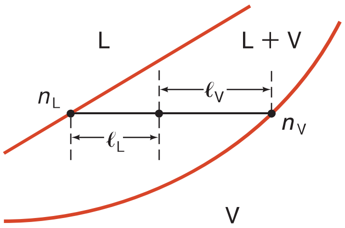


Figure 6.10
The lever rule gives the ratio of moles present in each phase of a two-phase system as $n_L\ell_L = n_V\ell_V$, where ℓ_L and ℓ_V are the distances from the point corresponding to the system's overall mole fraction to the endpoints of the tie line.

Now suppose we begin with the benzene–toluene system initially in the liquid phase at point *a* in Figure 6.9c. According to the Gibbs phase rule (see p. 196), we have a two-component, one-phase system, so that the degrees of freedom are

$$\begin{aligned} f &= c - p + 2 \\ &= 2 - 1 + 2 = 3 \end{aligned}$$

At constant temperature and a fixed mole fraction, we are left with one degree of freedom. Therefore, we can lower the pressure at constant composition and temperature (from point *a*) until point *b* is reached. At this point, the liquid can exist in equilibrium with its vapor. (This is the point at which the liquid just begins to vaporize.) Further decreasing the pressure takes us to point *c*. The horizontal "tie line" indicates that the composition (in mole fraction) of the liquid is *f* and that of the vapor is *g* at this point. The relative amounts of liquid and vapor present in equilibrium are given by the lever rule (Figure 6.10):

$$n_L\ell_L = n_V\ell_V \tag{6.32}$$

where n_L and n_V are the number of moles of liquid and vapor, respectively, and ℓ_L and ℓ_V are the distances defined in Figure 6.10. At point *c*, we have a two-component, two-phase system so that the total degrees of freedom are

$$\begin{aligned} f &= 2 - 2 + 2 \\ &= 2 \end{aligned}$$

At constant temperature, then, we have only one degree of freedom, so that if we select a particular pressure, the compositions of the liquid and vapor must be fixed (as shown by the tie line).

Figure 6.11 suggests a way to separate benzene from toluene at a fixed temperature. We can lower the pressure on a solution until it begins to vaporize (point *a*). At this point, the mole fractions are $x_b = 0.2$ and $x_t = 1 - 0.2 = 0.8$, respectively. The composition of the vapor in equilibrium with the solution (point *b*) has the following values: $x_b^v = 0.5$ and $x_t^v = 0.5$. Thus, the vapor phase is richer in benzene than is the liquid phase. Now, if we condense the vapor ($b \rightarrow c$) and re-evaporate the liquid ($c \rightarrow d$), the mole fraction of benzene will be even higher in the vapor phase. Repeating the process at constant temperature will eventually lead to a quantitative separation of benzene and toluene.

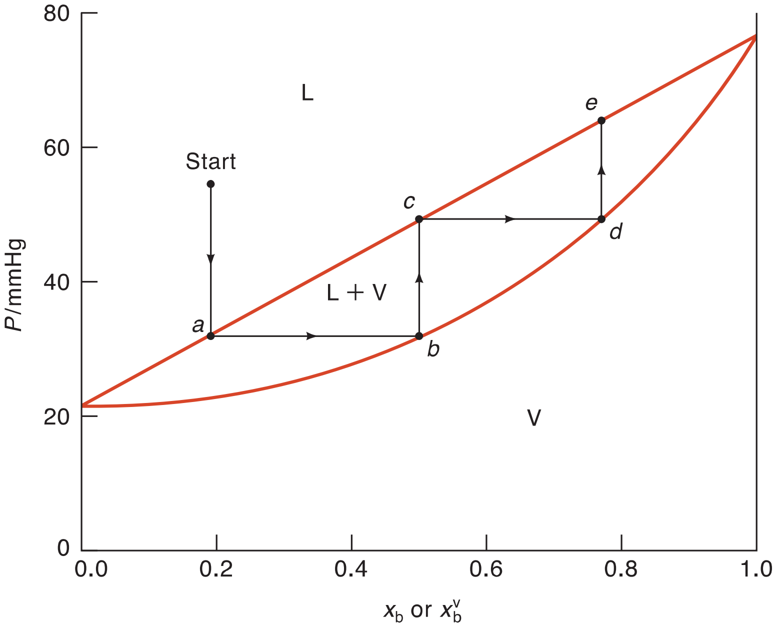


Figure 6.11
Pressure–composition diagram of the benzene–toluene system at 23°C.

Temperature–Composition Diagram. In practice, distillation is carried out more conveniently at constant pressure than at constant temperature; therefore, we need to examine the *temperature–composition* or *boiling-point diagram*. The relationship between temperature and composition is complex and is usually determined experimentally.

Referring again to the benzene–toluene system and comparing Figure 6.12 with Figure 6.9, we see that the liquid and vapor regions are inverted and that neither the liquid nor the vapor curve is a straight line. The more volatile component, benzene, has a higher vapor pressure and hence a lower boiling point. Figure 6.9 shows that at a constant temperature, liquid is the stable phase at high pressures. Similarly, Figure 6.12 tells us that at a constant pressure, the stable phase at low temperatures is also the liquid. During fractional distillation, the solution is heated until it starts to evaporate $(a \longrightarrow b)$. The vapor, which is richer in benzene, is condensed $(b \longrightarrow c)$ and then evaporated $(c \longrightarrow d)$. Repeating the process will eventually separate the two components completely. This procedure is called *fractional distillation*. Each vaporization and condensation step is called a *theoretical plate*.

In the laboratory, chemists use an apparatus like that shown in Figure 6.13 to separate volatile liquids. The round-bottomed flask containing the benzene–toluene solution is fitted with a long column packed with small glass beads. When the solution boils, the vapor condenses on the beads in the lower portion of the column, and the liquid falls back into the distilling flask. As time goes on, the beads gradually heat up, allowing the vapor to move upward slowly. In essence, the packing material gives the column many theoretical plates and causes the benzene–toluene mixture to be subjected continuously to numerous vaporization–condensation steps. At each step, the composition of the vapor in the column will be richer in the more volatile, or lower boiling-point, component (in this case, benzene). The vapor that rises to the top

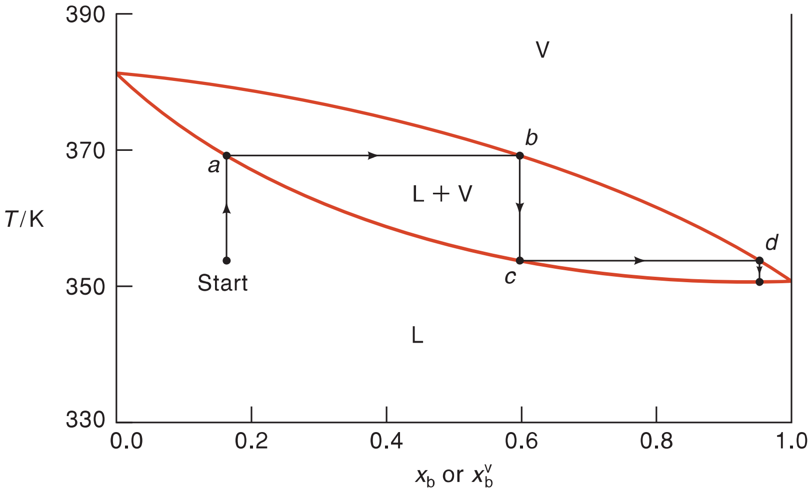


Figure 6.12
Temperature–composition diagram of the benzene–toluene system at 1 atm. The boiling points of benzene and toluene are 80.1°C and 110.6°C, respectively.

of the column is essentially pure benzene, which is then condensed and collected in a receiving flask. Petroleum refining employs a similar approach. Crude oil is a complex mixture of thousands of compounds. By heating and condensing the crude oil up a distillation column that may be 80 meters high and contain hundreds of theoretical plates, workers can separate fractions according to their boiling-point ranges.

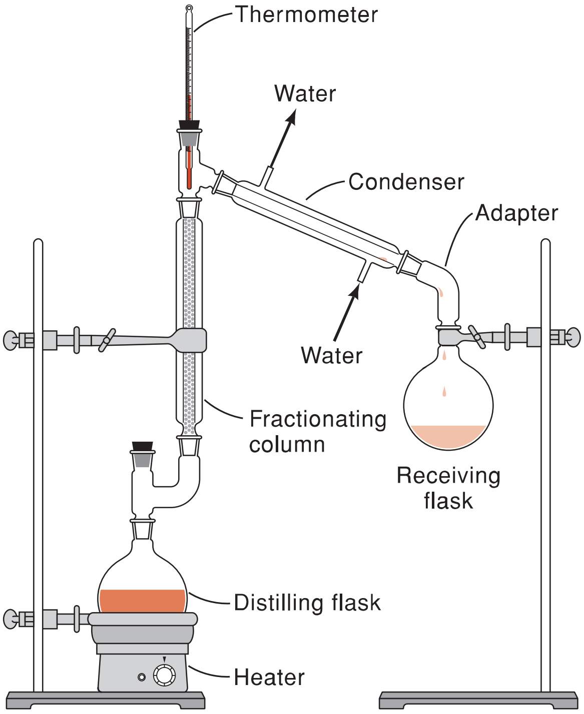
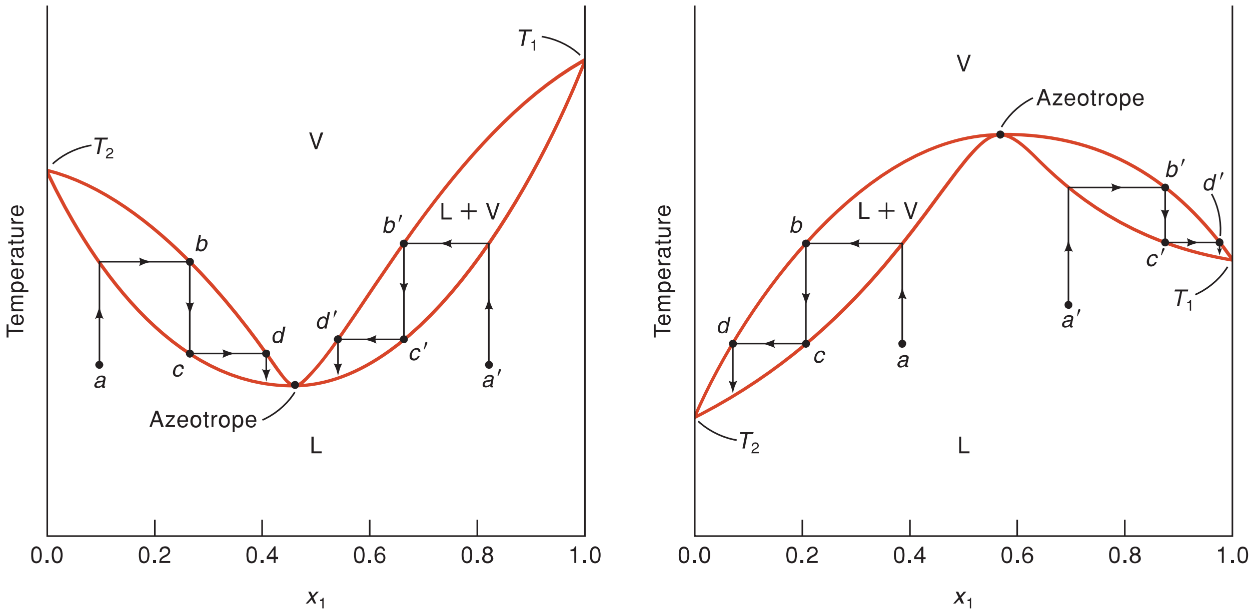


Figure 6.13
A laboratory setup for fractional distillation. The fractioning column contains many small glass beads, which act as theoretical plates for the condensation–evaporation steps.



(a) **(b)**

Figure 6.14
Azeotropes: (a) minimum boiling point, (b) maximum boiling point.

Azeotropes. Because most solutions are nonideal, their experimentally determined temperature–composition diagrams are more complicated than the one shown in Figure 6.12. If the system exhibits a positive deviation from Raoult's law, the curve will show a minimum boiling point. Conversely, a negative deviation from Raoult's law will result in a maximum boiling point (Figure 6.14). Examples of the former are acetone–carbon disulfide, ethanol–water, and *n*-propanol–water. Systems that show a maximum boiling point are less common; among the known examples are acetone–chloroform and hydrochloric acid–water. In every case, the mixture cannot be completely separated into pure components by simple fractional distillation.

Consider the following steps, shown in Figure 6.14a. The solution is heated at a certain composition denoted by point *a*. The condensed vapor ($b \longrightarrow c$) becomes richer in component 1, while the solution remaining in the pot becomes richer in component 2. Consequently, the point representing the composition of the solution in the pot on the liquid curve will move toward the left as the distillation proceeds and the boiling point rises. Boiling the solution, condensing the vapor, and again boiling the condensed vapor results in a distillate that has the same composition as the solution in the pot. Such a distillate is known as an *azeotrope* (from the Greek word meaning "to boil unchanged"). The boiling point of the solution remaining in the pot will eventually reach that of pure component 2 (i.e., T_2). Once the azeotrope distillate has been produced, further distillation will result in no further separation, and it will boil at a constant temperature. If we started at point *a*′ and went through the same evaporation–condensation steps, the vapor would become richer in component 2 until it formed the same azeotrope, while the boiling point of the solution would approach that of component 1. The maximum boiling point system (Figure 6.14b) can be similarly explained except that a pure component appears in the distillate, and the azeotrope appears in the pot.

Table 6.3
Variation of Boiling Point and Composition of the HCl-Water Azeotrope with Pressure[a]

P/torr	Composition (percent by weight HCl)	Boiling point/°C
760	20.222	108.584
700	20.360	106.424
500	20.916	97.578

[a] W. D. Bonner and R. E. Wallace, *J. Am. Chem. Soc.* **52**, 1747 (1930).

Although an azeotrope behaves in distillation as if it were a single component, that can easily be demonstrated not to be the case. As the data in Table 6.3 show, the composition of the azeotrope depends on the pressure.

Solid–Liquid Equilibria

If a liquid solution of two substances is cooled to a sufficiently low temperature, a solid will form. This temperature is the solution's freezing point, which depends on the composition of the solution. As we shall see in the next section, the freezing point of a solution is always lower than that of the solvent.

Let us consider a two-component system made of antimony (Sb) and lead (Pb). The solid–liquid phase diagram for this system is shown in Figure 6.15. This phase diagram is constructed by measuring the melting points of a series of solutions of

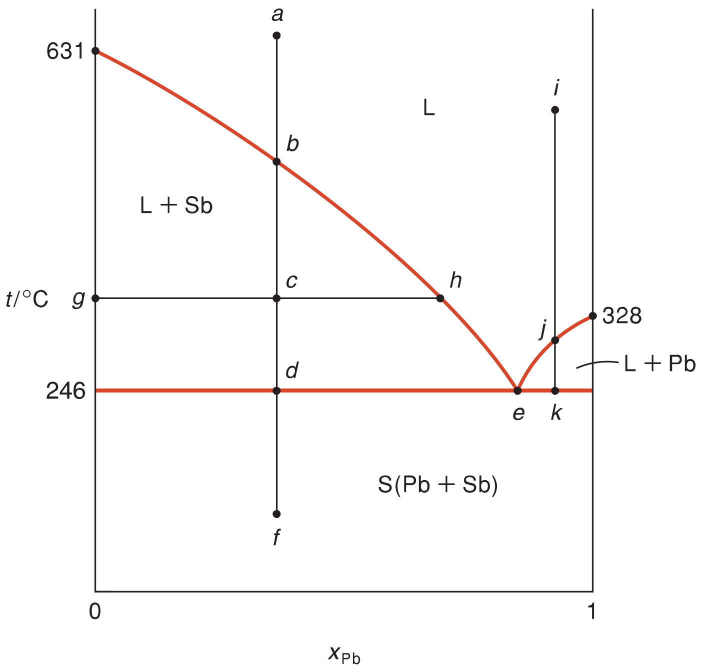


Figure 6.15
The solid–liquid phase diagram of the lead–antimony system. The eutectic point is at *e*.

different compositions at constant pressure. The asymmetric, V-shaped curve is the freezing point curve, above which the system is liquid. (The melting points of Pb and Sb are 328°C and 631°C, respectively.) Consider what happens when the solution at point *a* is cooled at constant pressure. When point *b* is reached, the solution begins to freeze, and the solid that separates from the solution is pure Sb. As the temperature is lowered further, more Sb freezes, and the solution becomes progressively richer in Pb. The composition of the solution at point *c*, for example, is given by drawing the tie line *gch*. As this point, the composition of the solution is given by the projection of the vertical line from point *h* onto the *x* axis. If we continue to lower the temperature of the solution, eventually we reach point *d*. At this temperature, the composition of the solution is given by point *e*.

Now suppose we start to cool the solution at point *i*. At point *j*, the solution begins to freeze, and solid Pb forms. On further cooling, eventually we reach point *k*. At this point, the composition of the solution is again given by point *e*; therefore, this is the point at which the liquid is in equilibrium with both solids. Point *e* is called the *eutectic point*. The eutectic point has the following significance: (1) It represents the lowest temperature at which a liquid solution can exist, and (2) at the eutectic point, the solid that separates from the solution has the *same* composition as the solution. In this respect, a solution that has eutectic composition behaves like a pure compound. Because the composition of a eutectic mixture depends on external pressure, however, we can readily distinguish its behavior from that of a pure liquid by studying the freezing phenomenon at different pressures.

The eutectic point is at 246°C.

At the eutectic point, we have two components (Pb and Sb) and three phases (solid Pb, solid Sb, and solution), so the degrees of freedom, *f*, is given by

$$\begin{aligned} f &= c - p + 2 \\ &= 2 - 3 + 2 \\ &= 1 \end{aligned}$$

This single degree of freedom, however, is used to specify the pressure. Consequently, at the eutectic point, neither the temperature nor the composition can vary.

A familiar eutectic mixture is the solder used in constructing electronic circuit boards. Solder is about 33% lead and 67% tin and melts at 183°C. (Tin melts at 232°C.)

6.7 Colligative Properties

General properties of solutions include vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure. These properties are commonly referred to as *colligative*, or *collective*, *properties* because they are bound together through their common origin. Colligative properties depend only on the number of solute molecules present, not on the size or molar mass of the molecules. To derive equations describing these phenomena, we shall make three important assumptions: (1) The solutions are ideal dilute, so that the solvent obeys Raoult's law; (2) the solutions are dilute; and (3) the solutions contain nonelectrolytes. As usual, we shall consider only a two-component system.

Vapor-Pressure Lowering

Consider a solution that contains a solvent 1 and a *nonvolatile* solute 2, such as a solution of sucrose in water. Because the solution is ideal dilute, Raoult's law applies:

$$P = x_1 P_1^*$$

Because $x_1 = 1 - x_2$, the equation above becomes

$$P_1 = (1 - x_2)P_1^*$$

Rearranging this equation gives

$$P_1^* - P_1 = \Delta P = x_2 P_1^* \qquad (6.33)$$

where ΔP, the decrease in vapor pressure from that of the pure solvent, is directly proportional to the mole fraction of the solute.

Why does the vapor pressure of a solution fall in the presence of a solute? We may be tempted to suggest that it does because of the modification of intermolecular forces. But this idea is not right because vapor-pressure lowering occurs even in ideal solutions, in which there is no difference between solute–solvent and solvent–solvent interactions. A more convincing explanation is provided by the entropy effect. When a solvent evaporates, the entropy of the universe increases because the entropy of any substance in the gaseous state is greater than that in the liquid state (at the same temperature). As we saw in Section 6.3, the solution process itself is accompanied by an increase in entropy. This result means that there is an extra degree of randomness, or disorder, in a solution that was not present in the pure solvent. Therefore, the evaporation of solvent from a solution will result in a *smaller* increase in entropy. Consequently, the solvent has less of a tendency to leave the solution, and the solution will have a lower vapor pressure than the pure solvent (see Problem 6.40).

Boiling-Point Elevation

The boiling point of a solution is the temperature at which its vapor pressure is equal to the external pressure. The previous discussion might lead you to expect that because the addition of a nonvolatile solute lowers the vapor pressure, it should also raise the boiling point of a solution. This effect is indeed the case.

For a solution containing a *nonvolatile* solute, the boiling-point elevation originates in the change in the chemical potential of the solvent due to the presence of the solute. From Equation 6.17, we can see that the chemical potential of the solvent in a solution is less than the chemical potential of the pure solvent by an amount equal to $RT \ln x_1$. How this change affects the boiling point of the solution can be seen from Figure 6.16. The solid lines refer to the pure solvent. Because the solute is nonvolatile, it does not vaporize; therefore, the curve for the vapor phase is the same as that for the pure vapor. On the other hand, because the liquid contains a solute, the chemical potential of the solvent decreases (see the dashed curve). The points where the curve for the vapor intersects the curves for the liquids (pure and solution) correspond to the boiling points of the pure solvent and the solution, respectively. We see that the boiling point of the solution (T_b') is higher than that of the pure solvent (T_b).

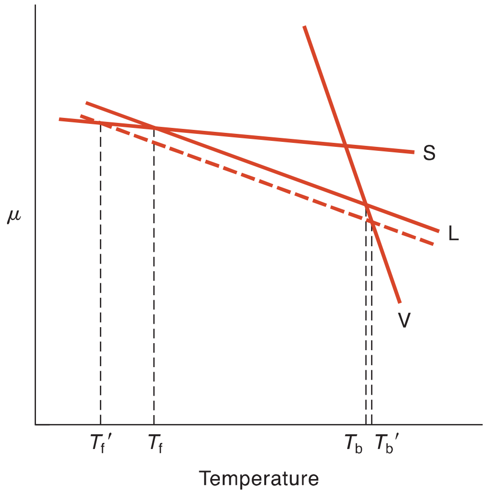


Figure 6.16
Plot of chemical potentials versus temperature to illustrate colligative properties. The dashed red line denotes the solution phase. T_b and T_b' are the boiling points of the solvent and the solution, and T_f and T_f' are the freezing points of the solvent and solution, respectively.

We now turn to a quantitative treatment of the boiling-point elevation phenomenon. At the boiling point, the solvent vapor is in equilibrium with the solvent in solution, so that

$$\mu_1(g) = \mu_1(l) = \mu_1^*(l) + RT \ln x_1$$

or

$$\Delta\mu_1 = \mu_1(g) - \mu_1^*(l) = RT \ln x_1 \tag{6.34}$$

where $\Delta\mu_1$ is the Gibbs energy change associated with the evaporation of 1 mole of solvent from the solution at temperature T, its boiling point. Thus, we can write $\Delta\mu_1 = \Delta_{\text{vap}}\overline{G}$. Dividing Equation 6.34 by T, we obtain

$$\frac{\Delta_{\text{vap}}\overline{G}}{T} = \frac{\mu_1(g) - \mu_1^*(l)}{T} = R \ln x_1$$

From the Gibbs–Helmholz equation (Equation 5.15), we write

$$\frac{d(\Delta G/T)}{dT} = -\frac{\Delta H}{T^2} \quad \text{(at constant } P\text{)}$$

or

$$\frac{d(\Delta_{\text{vap}}\overline{G}/T)}{dT} = \frac{-\Delta_{\text{vap}}\overline{H}}{T^2} = R\frac{d(\ln x_1)}{dT}$$

where $\Delta_{\text{vap}}\overline{H}$ is the molar enthalpy of vaporization of the solvent from the solution. Because the solution is dilute, $\Delta_{\text{vap}}\overline{H}$ is taken to be the same as the molar enthalpy of vaporization of the pure solvent. Rearranging the last equation gives

$$d \ln x_1 = \frac{-\Delta_{\text{vap}}\overline{H}}{RT^2} dT \tag{6.35}$$

To find the relationship between x_1 and T, we integrate Equation 6.35 between the limits T'_b and T_b, the boiling points of the solution and pure solvent, respectively. Because the mole fraction of the solvent is x_1 at T'_b and 1 at T_b, we write

$$\int_{\ln 1}^{\ln x_1} d\ln x_1 = \int_{T_\text{b}}^{T'_\text{b}} \frac{-\Delta_\text{vap}\overline{H}}{RT^2}\,dT$$

or

$$\begin{aligned}
\ln x_1 &= \frac{\Delta_\text{vap}\overline{H}}{R}\left(\frac{1}{T'_\text{b}} - \frac{1}{T_\text{b}}\right) \\
&= \frac{-\Delta_\text{vap}\overline{H}}{R}\left(\frac{T'_\text{b} - T_\text{b}}{T'_\text{b}T_\text{b}}\right) \\
&= \frac{-\Delta_\text{vap}\overline{H}}{R}\,\frac{\Delta T}{T_\text{b}^2} \qquad (6.36)
\end{aligned}$$

where $\Delta T = T'_\text{b} - T_\text{b}$. Two assumptions were used to obtain Equation 6.36, both of which are based on the fact that T'_b and T_b differ only by a small amount (a few degrees). First, we assumed $\Delta_\text{vap}\overline{H}$ to be temperature independent and second, $T'_\text{b} \approx T_\text{b}$, so that $T'_\text{b}T_\text{b} \approx T_\text{b}^2$.

Equation 6.36 gives the boiling-point elevation, ΔT, in terms of the concentration of the solvent (x_1). By custom, however, we express the concentration in terms of the amount of solute present, so we write

$$\ln x_1 = \ln(1 - x_2) = \frac{-\Delta_\text{vap}\overline{H}}{R}\,\frac{\Delta T}{T_\text{b}^2}$$

where*

$$\begin{aligned}
\ln(1 - x_2) &= -x_2 - \frac{x_2^2}{2} - \frac{x_2^3}{3}\cdots \\
&\approx -x_2 \quad (x_2 \ll 1)
\end{aligned}$$

We now have

$$\Delta T = \frac{RT_\text{b}^2}{\Delta_\text{vap}\overline{H}}x_2$$

To convert the mole fraction x_2 into a more practical concentration unit, such as molality (m_2), we write

$$x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} = \frac{n_2}{w_1/\mathcal{M}_1} \quad (n_1 \gg n_2)$$

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[*] This expansion is known as Maclaurin's series. You can verify this relationship by employing a small numerical value for x_2 (≤ 0.1).

where w_1 is the mass of the solvent in kg and $\mathscr{M}_1$ is the molar mass of the solvent in kg mol^{-1}, respectively. Because n_2/w_1 gives the molality of the solution, m_2, it follows that $x_2 = \mathscr{M}_1 m_2$ and thus

$$\Delta T = \frac{RT_b^2 \mathscr{M}_1}{\Delta_{vap}\overline{H}} m_2 \tag{6.37}$$

Note that all the quantities in the first term on the right of Equation 6.37 are constants for a given solvent, and so we have

$$K_b = \frac{RT_b^2 \mathscr{M}_1}{\Delta_{vap}\overline{H}} \tag{6.38}$$

where K_b is called the *molal boiling-point-elevation constant*. The units of K_b are K mol^{-1} kg. Finally,

$$\Delta T = K_b m_2 \tag{6.39}$$

The advantage of using molality, as mentioned in Section 6.1, is that it is independent of temperature and thus is suitable for boiling-point elevation studies.

Figure 6.17 shows the phase diagrams of pure water and an aqueous solution. Upon the addition of a nonvolatile solute, the vapor pressure of the solution decreases at every temperature. Consequently, the boiling point of the solution at 1 atm will be greater than 373.15 K.

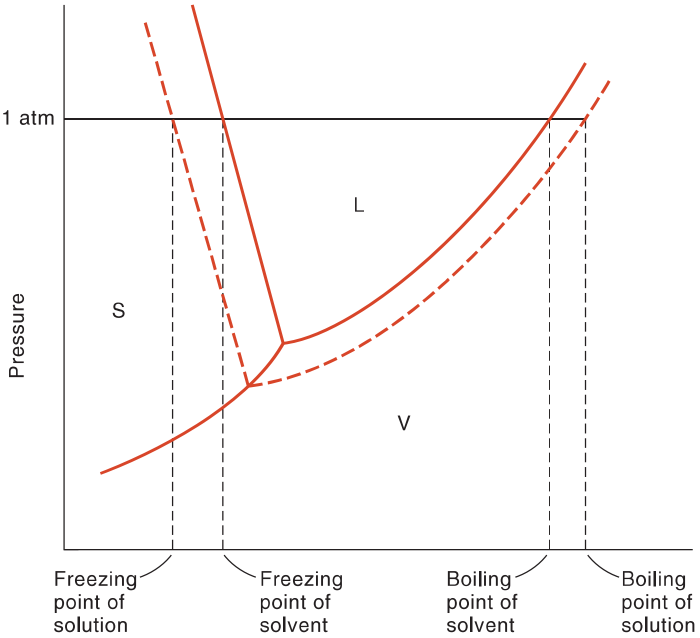

Figure 6.17
Phase diagrams of pure water (solid red lines) and of water in an aqueous solution containing a nonvolatile solid (dashed red lines). (Note that the axes are not drawn to scale.)

Freezing-Point Depression

A nonchemist may be forever unaware of the boiling-point-elevation phenomenon, but any casual observer living in a cold climate witnesses an illustration of freezing-point depression: ice on winter roads and sidewalks melts readily when sprinkled with salt.* This method of thawing depresses the freezing point of water.

The thermodynamic analysis of freezing-point depression is similar to that of boiling-point elevation. If we assume that when a solution freezes, the solid that separates from the solution contains only the solvent, then the curve for the chemical potential of the solid does not change (see Figure 6.16). Consequently, the solid curve for the solid and the dashed curve for the solvent in solution now intersect at a point (T_f') *below* the freezing point of the pure solvent (T_f). By following the same procedure as that for the boiling-point elevation, we can show that the drop in freezing point ΔT (i.e., $T_f - T_f'$, where T_f and T_f' are the freezing points of the pure solvent and solution, respectively) is

$$\Delta T = K_f m_2 \tag{6.40}$$

where K_f is the *molal freezing-point-depression constant* given by

$$K_f = \frac{RT_f^2 \mathcal{M}_1}{\Delta_{\text{fus}}\overline{H}} \tag{6.41}$$

where $\Delta_{\text{fus}}\overline{H}$ is the molar enthalpy of fusion of the solvent.

The freezing-point-depression phenomenon can also be understood by studying Figure 6.17. At 1 atm, the freezing point of solution lies at the intersection point of the dashed curve (between the solid and liquid phases) and the horizontal line at 1 atm. It is interesting that whereas the solute must be nonvolatile in the boiling-point-elevation case, no such restriction applies to lowering the freezing point. A proof of this statement is the use of ethanol (b.p. = 351.65 K) as an antifreeze.

Either Equation 6.39 or 6.40 can be used to determine the molar mass of a solute. In general, the freezing-point-depression experiment is much easier to carry out. It is commonly employed in measuring the molar mass of compounds. Table 6.4 lists the K_b and K_f values for several common solvents.

The freezing-point-depression phenomenon has many examples in everyday life and in biological systems. As mentioned above, salts, such as sodium chloride and calcium chloride, are used to melt ice on roads and sidewalks. The organic compound ethylene glycol [$CH_2(OH)CH_2(OH)$] is the common automobile antifreeze. It is also employed to de-ice airplanes. In recent years, there has been much interest in understanding how certain species of fish manage to survive in the ice-cold waters of the polar oceans. The freezing point of seawater is approximately −1.9°C, which is the temperature of seawater surrounding an iceberg. A depression in freezing point of 1.9 degrees corresponds to a concentration of one molal, which is much too high for proper physiological function; for example, it alters osmotic balance (see section below on Osmotic Pressure). Besides dissolved salts and other substances that can

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* The salt employed is usually sodium chloride, which attacks cement and is harmful to many plants. Also see "Freezing Ice Cream and Making Caramel Topping," J. O. Olson and L. H. Bowman, *J. Chem. Educ.* **53**, 49 (1976).

Table 6.4
Molal Boiling-Point-Elevation and Molal Freezing-Point-Depression Constants of Some Common Solvents

Solvent	K_b/K mol^{-1} kg	K_f/K mol^{-1} kg
H_2O	0.51	1.86
C_2H_5OH	1.22	1.99
C_6H_6	2.53	5.12
$CHCl_3$	3.63	4.68
CH_3COOH	2.93	3.90
CCl_4	5.03	29.8

lower the freezing point colligatively, a special class of proteins resides in the blood of polar fishes that has some kind of protective effect. These proteins contain both amino acid and sugar units and are called glycoprotetins. The concentration of glycoproteins in the fishes' blood is quite low (approximately 4×10^{-4} *m*), so their action cannot be explained by colligative properties. The belief is that the glycoproteins have the ability to adsorb onto the surface of each tiny ice crystal as soon as it begins to form, thus preventing it from growing to a size that would cause biological damage. Consequently, the freezing point of blood in these fishes is below −2°C.

EXAMPLE 6.4

For a solution of 45.20 g of sucrose ($C_{12}H_{22}O_{11}$) in 316.0 g of water, calculate (a) the boiling point, and (b) the freezing point.

ANSWER

(a) Boiling point: $K_b = 0.51$ K mol^{-1} kg, and the molality of the solution is given by

$$m_2 = \frac{(45.20\text{ g})(1000\text{ g/1 kg})}{(342.3\text{ g mol}^{-1})(316.0\text{ g})} = 0.418\text{ mol kg}^{-1}$$

From Equation 6.39

$$\begin{aligned}\Delta T &= K_b m_2\\ &= (0.51\text{ K mol}^{-1}\text{ kg})(0.418\text{ mol kg}^{-1})\\ &= 0.21\text{ K}\end{aligned}$$

Thus, the solution will boil at (373.15 + 0.21) K, or 373.36 K.

(b) Freezing point: From Equation 6.40,

$$\begin{aligned}\Delta T &= K_\mathrm{f} m_2\\ &= (1.86\ \mathrm{K\ mol^{-1}\ kg})(0.418\ \mathrm{mol\ kg^{-1}})\\ &= 0.78\ \mathrm{K}\end{aligned}$$

Thus, the solution will freeze at (273.15 − 0.78) K, or 272.37 K.

COMMENT

For aqueous solutions of equal concentrations, the depression in freezing point is always greater than the corresponding elevation in boiling point. The reason can be seen by comparing the following two expressions from Equations 6.38 and 6.41:

$$K_\mathrm{b} = \frac{RT_\mathrm{b}^2 \mathcal{M}_1}{\Delta_\mathrm{vap}\overline{H}} \qquad K_\mathrm{f} = \frac{RT_\mathrm{f}^2 \mathcal{M}_1}{\Delta_\mathrm{fus}\overline{H}}$$

Although $T_\mathrm{b} > T_\mathrm{f}$, $\Delta_\mathrm{vap}\overline{H}$ for water is 40.79 kJ mol^{-1}, whereas $\Delta_\mathrm{fus}\overline{H}$ is only 6.01 kJ mol^{-1}. The large value of $\Delta_\mathrm{vap}\overline{H}$ in the denominator is what causes K_b and hence ΔT to be smaller.

Osmotic Pressure

The phenomenon of *osmosis* is illustrated in Figure 6.18. The left compartment of the apparatus contains pure solvent; the right compartment contains a solution. The two compartments are separated by a *semipermeable membrane* (e.g., a cellophane membrane), one that permits the solvent molecules to pass through but does not permit the movement of solute molecules from right to left. Practically speaking, then, this system has two different phases. At equilibrium, the height of the solution in the tube on the right is greater than that of the pure solvent in the left tube by h. This excess hydrostatic pressure is called the *osmotic pressure*. We can now derive an expression for osmotic pressure as follows.

Let μ_1^L and μ_1^R be the chemical potential of the solvent in the left and right compartments, respectively. Initially, before equilibrium is established, we have

$$\begin{aligned}\mu_1^\mathrm{L} &= \mu_1^* + RT\ln x_1\\ &= \mu_1^* \qquad\qquad (x_1 = 1)\end{aligned}$$

and

$$\mu_1^\mathrm{R} = \mu_1^* + RT\ln x_1 \qquad (x_1 < 1)$$

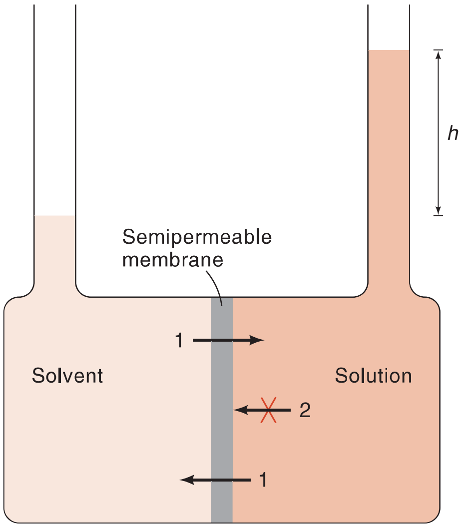

Figure 6.18
Apparatus demonstrating the osmotic pressure phenomenon. Here 1 represents the solvent and 2 the solute molecules.

Thus,

$$\mu_1^{\mathrm{L}} = \mu_1^* > \mu_1^{\mathrm{R}} = \mu_1^* + RT \ln x_1$$

Note that μ_1^{L} is the same as the standard chemical potential for the pure solvent, μ_1^*, and the inequality sign denotes that $RT \ln x_1$ is a negative quantity. Consequently, more solvent molecules, on the average, will move from left to right across the membrane. The process is spontaneous because the dilution of the solution in the right compartment by solvent leads to a decrease in the Gibbs energy and an increase in entropy. Equilibrium is finally reached when the flow of solvent is exactly balanced by the hydrostatic pressure difference in the two side tubes. This extra pressure increases the chemical potential of the solvent in solution, μ_1^{R}. From Equation 5.16, we know that

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

We can write a similar equation for the variation of the chemical potential with pressure at constant temperature. Thus, for the solvent component in the right compartment,

$$\left(\frac{\partial \mu_1^{\mathrm{R}}}{\partial P}\right)_T = \overline{V}_1 \tag{6.42}$$

where $\overline{V}_1$ is the partial molar volume of the solvent. For a dilute solution, $\overline{V}_1$ is approximately equal to $\overline{V}$, the molar volume of the pure solvent. The increase in the chemical potential of the solvent in the solution compartment ($\Delta\mu_1^{\mathrm{R}}$) when the pressure increases from P, the external atmospheric pressure, to $(P + \Pi)$ is given by

$$\Delta\mu_1^{\mathrm{R}} = \int_P^{P+\Pi} \overline{V}\, dP = \overline{V}\Pi$$

Note that $\overline{V}$ is treated as a constant because the volume of a liquid changes little with pressure. The Greek letter Π represents the osmotic pressure. The term *osmotic pressure of a solution* refers to the pressure that must be applied to the solution to increase the chemical potential of the solvent to the value of its pure liquid under atmospheric pressure.

At equilibrium, the following relations must hold:

$$\mu_1^{\mathrm{L}} = \mu_1^{\mathrm{R}} = \mu_1^* + RT\ln x_1 + \Pi\overline{V}$$

Because $\mu_1^{\mathrm{L}} = \mu_1^*$, we have

$$\Pi\overline{V} = -RT\ln x_1 \tag{6.43}$$

To relate Π to the concentration of the solute, we take the following steps. From the procedure employed for boiling-point elevation:

$$\begin{aligned} -\ln x_1 &= -\ln(1 - x_2) \\ &\approx x_2 \quad (x_2 \ll 1) \end{aligned}$$

Furthermore,

$$x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \quad (n_1 \gg n_2)$$

where n_1 and n_2 are the number of moles of solvent and solute, respectively. Equation 6.43 now becomes

$$\begin{aligned} \Pi\overline{V} &= RTx_2 \\ &= RT\left(\frac{n_2}{n_1}\right) \end{aligned} \tag{6.44}$$

Substituting $\overline{V} = V/n_1$ into Equation 6.44, we get

$$\Pi V = n_2RT \tag{6.45}$$

If V is in liters, then

$$\begin{aligned} \Pi &= \frac{n_2}{V}RT \\ &= MRT \end{aligned} \tag{6.46}$$

Equation 6.46 also applies to two similar solutions that have different concentrations.

where M is the molarity of the solution. Note that molarity is a convenient concentration unit here, because osmotic pressure measurements are normally made at constant temperature. Alternatively, we can rewrite Equation 6.46 as

$$\Pi = \frac{c_2}{\mathcal{M}_2}RT \tag{6.47}$$

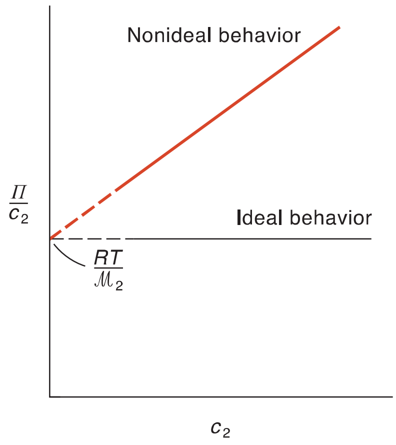

Figure 6.19
Determination of the molar mass of a solute by osmotic pressure measurements for an ideal and a nonideal solution. The intercept on the *y* axis (as $c_2 \rightarrow 0$) gives the correct value for the molar mass.

or

$$\frac{\Pi}{c_2} = \frac{RT}{\mathcal{M}_2} \tag{6.48}$$

where c_2 is the concentration of the solute in g L^{-1} of the solution and $\mathcal{M}_2$ is the molar mass of the solute. Equation 6.48 provides a way to determine molar masses of compounds from osmotic pressure measurements.

Equation 6.48 is derived by assuming ideal behavior, so it is desirable to measure Π at several different concentrations and extrapolate to zero concentration for molar mass determination (Figure 6.19). For a nonideal solution, the osmotic pressure at *any* concentration, c_2, is given by

Compare Equation 6.49 with Equation 1.10

$$\frac{\Pi}{c_2} = \frac{RT}{\mathcal{M}_2}(1 + Bc_2 + Cc_2^2 + Dc_2^3 + \cdots) \tag{6.49}$$

where B, C, and D are called the second, third, and fourth virial coefficients, respectively. The magnitude of the virial coefficients is such that $B \gg C \gg D$. In dilute solutions, we need be concerned only with the second virial coefficient. For an ideal solution, the second and higher virial coefficients are all equal to zero, so Equation 6.49 reduces to Equation 6.48.

Even though osmosis is a well-studied phenomenon, the mechanism involved is not always clearly understood. In some cases, a semipermeable membrane may act as a molecular sieve, allowing smaller solvent molecules to pass through while blocking larger solute molecules. In other cases, osmosis may be caused by the higher solubility of the solvent in the membrane than the solute. Each system must be studied individually. The previous discussion illustrates both the usefulness and limitation of thermodynamics. We have derived a convenient equation relating the molar mass of the solute to an experimentally measurable quantity—the osmotic pressure—simply in terms of the chemical potential difference. Because thermodynamics is not based on any specific model, however, Equation 6.47 tells us nothing about the mechanism of osmosis.

EXAMPLE 6.5

Consider the following arrangement, in which a solution containing 20 g of hemoglobin in 1 liter of the solution is placed in the right compartment, and pure water is placed in the left compartment (see Figure 6.18). At equilibrium, the height of the water in the right column is 77.8 mm in excess of the height of the solvent in the left column. What is the molar mass of hemoglobin? The temperature of the system is constant at 298 K.

ANSWER

To determine the molar mass of hemoglobin, we first need to calculate the osmotic pressure of the solution. We start by writing

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

$$= \frac{Ah\rho g}{A} = h\rho g$$

where A is the cross-sectional area of the tube, h the excess liquid height in the right column, ρ the density of the solution, and g the acceleration due to gravity. The parameters are

$$h = 0.0778 \text{ m}$$

$$\rho = 1 \times 10^3 \text{ kg m}^{-3}$$

$$g = 9.81 \text{ m s}^{-2}$$

(We have assumed that the density of the dilute solution is the same as that of water.) The osmotic pressure in pascals (N m^{-2}) is given by

$$\Pi = 0.0778 \text{ m} \times 1 \times 10^3 \text{ kg m}^{-3} \times 9.81 \text{ m s}^{-2}$$

$$= 763 \text{ kg m}^{-1}\text{ s}^{-2}$$

$$= 763 \text{ N m}^{-2}$$

From Equation 6.47,

$$\mathcal{M}_2 = \frac{c_2}{\Pi}RT$$

$$= \frac{(20 \text{ kg m}^{-3})(8.314 \text{ J K}^{-1}\text{ mol}^{-1})(298 \text{ K})}{763 \text{ N m}^{-2}} \times \frac{1 \text{ N m}}{1 \text{ J}}$$

$$= 65 \text{ kg mol}^{-1}$$

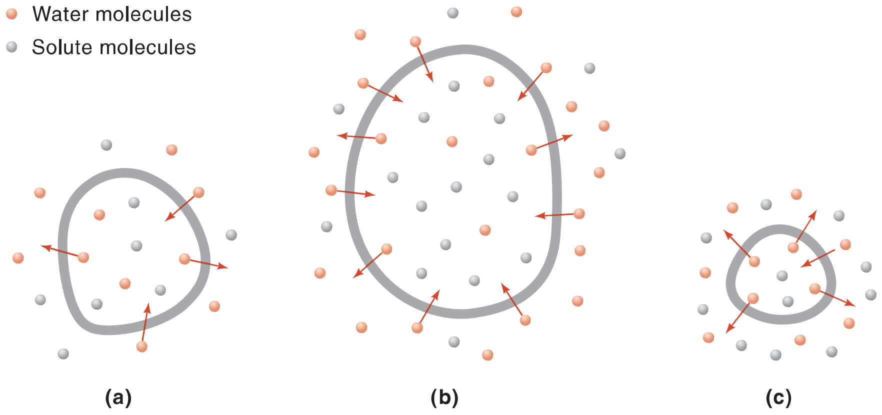

Figure 6.20
A cell in (a) an isotonic solution, (b) a hypotonic solution, and (c) a hypertonic solution. The cell remains unchanged in (a), swells in (b) , and shrinks in (c).

High-resolution mass spectrometry is now a common and convenient method for determining the molar mass of macromolecules.

Example 6.5 shows that osmotic pressure measurement is a more sensitive method to determine molar mass than the boiling-point-elevation and freezing-point-depression techniques, because 7.8 cm is an easily measurable height. On the other hand, the same solution will lead to an elevation in boiling point of approximately 1.6×10^{-4} °C and a depression in freezing point of 5.8×10^{-4} °C, which are too small to measure accurately. Most proteins are less soluble than hemoglobin. Nevertheless, their molar masses can often be determined by osmotic pressure measurements. A disadvantage of osmotic pressure measurements is that the time to reach equilibrium may be hours or days.

Many examples of the osmotic-pressure phenomenon are found in chemical and biological systems. If two solutions are of equal concentration, and hence have the same osmotic pressure, they are said to be *isotonic*. For two solutions of unequal osmotic pressures, the more concentrated solution is said to be *hypertonic*, and the less concentrated solution is said to be *hypotonic* (Figure 6.20). To study the contents of red blood cells, which are protected from the outside environment by a semipermeable membrane, biochemists employ a technique called *hemolysis*. They place the red blood cells in a hypotonic solution, which causes water to move into the cell. The cells swell and eventually burst, releasing hemoglobin and other protein molecules. When a cell is placed in a hypertonic solution, on the other hand, the intracellular water tends to move out of the cell by osmosis to the more concentrated, surrounding solution. This process, known as *crenation*, causes the cell to shrink and eventually cease functioning.

The mammalian kidney is a particularly effective osmotic device. Its main function is to remove metabolic waste products and other impurities from the bloodstream by osmosis to the more concentrated urine outside through a semipermeable membrane. Biologically important ions (such as Na^+ and Cl^-) lost in this manner are then actively pumped back into the blood through the same membrane. The loss of water through the kidney is controlled by the antidiuretic hormone (ADH), which is secreted into the blood by the hypothalamus and posterior pituitary gland. When little or no ADH is secreted, large amounts of water (perhaps 10 times normal) pass into the urine each day. On the other hand, when large quantities of ADH are present in the blood, the permeability of water through the membrane decreases so that the volume of urine formed may be as little as one-half the normal amount. Thus, the kidney–ADH combination controls the rate of loss of both water and other small waste molecules.

The chemical potential of water within the body fluids of freshwater fishes is lower than that in their environment, so they are able to draw in water by osmosis through their gill membranes. Surplus water is excreted as urine. An opposite process occurs for the marine teleost fishes. They lose body water to the more concentrated environment by osmosis across the gill membranes. To balance the loss, they drink seawater.

Osmotic pressure is also the major mechanism for water rising upward in plants. The leaves of trees constantly lose water to their surroundings, a process called *transpiration*, so the solute concentrations in leaf fluids increase. Water is then pushed up through the trunks and branches by osmotic pressure, which, to reach the tops of the tallest trees, can be as high as 10 to 15 atm.* Leaf movement is an interesting phenomenon that may also be related to osmotic pressure. The belief is that some processes can increase salt concentration in leaf cells in the presence of light. Osmotic pressure rises and cells become enlarged and turgid, causing the leaves to orient toward light.

Reverse Osmosis. A related phenomenon to osmosis is called *reverse osmosis*. If we apply pressure greater than the equilibrium osmotic pressure to the solution compartment shown in Figure 6.18, pure solvent will flow from the solution to the solvent compartment. This reversal of the osmotic process results in the unmixing of the solution components. An important application of reverse osmosis is the desalination of water. Several techniques discussed in this chapter are suitable, at least in principle, for obtaining pure water from the sea. For example, either distilling or freezing seawater would achieve the goal. However, these processes involve a phase change from liquid to vapor or liquid to solid and so would require considerable energy input to maintain. Reverse osmosis is more appealing, for it does not involve a phase change and is economically sound for large amounts of water.† Seawater, which is approximately 0.7 *M* in NaCl, has an estimated osmotic pressure of 30 atm. For a 50% recovery of pure water from the sea, an additional 60 atm would have to be applied on the seawater-side compartment to cause reverse osmosis. The success of large-scale desalination depends on the selection of a suitable membrane that is permeable to water but not to dissolved salts and that can withstand the high pressure over long periods of time.

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* *See* "Entropy Makes Water Run Uphill—in Trees," P. E. Steveson, *J. Chem. Educ.* **48**, 837 (1971).

† *See* "Desalination of Water by Reverse Osmosis," C. E. Hecht, *J. Chem. Educ.* **44**, 53 (1967).

Key Equations

$V = n_1\overline{V}_1 + n_2\overline{V}_2$	(Volume of a solution in terms of partial molar volumes)	(6.6)
$\overline{G}_i = \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$	(Definition of chemical potential)	(6.7)
$\Delta_{\text{mix}}G = nRT(x_1 \ln x_1 + x_2 \ln x_2)$	(Gibbs energy of mixing)	(6.11)
$\Delta_{\text{mix}}S = -nR(x_1 \ln x_1 + x_2 \ln x_2)$	(Entropy of mixing)	(6.12)
$P_1 = x_1P_1^*$	(Raoult's law)	(6.16)
$\mu_1(l) = \mu_1^*(l) + RT \ln x_1$	(Chemical potential of solvent in an ideal solution)	(6.17)
$P_2 = Kx_2$	(Henry's law)	(6.18)
$P_2 = K'm$	(Henry's law)	(6.19)
$a_1 = \frac{P_1}{P_1^*}$	(Activity of solvent)	(6.21)
$a_1 = \gamma_1x_1$	(Definition of activity coefficient)	(6.22)
$\mu_2(l) = \mu_2^\circ(l) + RT \ln a_2$	(Chemical potential of solute in a real solution)	(6.25)
$\mu_2(l) = \mu_2^\circ(l) + RT \ln \frac{m_2}{m^\circ}$	(Chemical potential of solute in an ideal solution)	(6.27)
$\Delta P = x_2P_1^*$	(Vapor-pressure lowering)	(6.33)
$\Delta T = K_{\text{b}}m_2$	(Boiling-point elevation)	(6.39)
$\Delta T = K_{\text{f}}m_2$	(Freezing-point depression)	(6.40)
$\Pi = MRT$	(Osmotic pressure)	(6.46)

Suggestions for Further Reading

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Problems

Concentration Units

6.1 How many grams of water must be added to 20.0 g of urea to prepare a 5.00% aqueous urea solution by weight?

6.2 What is the molarity of a 2.12 mol kg^{-1} aqueous sulfuric acid solution? The density of this solution is 1.30 g cm^{-3}.

6.3 Calculate the molality of a 1.50 M aqueous ethanol solution. The density of the solution is 0.980 g cm^{-3}.

6.4 The concentrated sulfuric acid we use in the laboratory is 98.0% sulfuric acid by weight. Calculate the molality and molarity of concentrated sulfuric acid if the density of the solution is 1.83 g cm^{-3}.

6.5 Convert a 0.25 mol kg^{-1} sucrose solution into percent by weight. The density of the solution is 1.2 g cm^{-3}.

6.6 For dilute aqueous solutions in which the density of the solution is roughly equal to that of the pure solvent, the molarity of the solution is equal to its molality. Show that this statement is correct for a 0.010 M aqueous urea $[(NH_2)_2CO]$ solution.

6.7 The blood sugar (glucose) level of a diabetic patient is approximately 0.140 g of glucose/100 mL of blood. Every time the patient ingests 40 g of glucose, her blood glucose level rises to approximately 0.240 g/100 mL of blood. Calculate the number of moles of glucose per milliliter of blood and the total number of moles and grams of glucose in the blood before and after consumption of glucose. (Assume that the total volume of blood in her body is 5.0 L.)

6.8 The strength of alcoholic beverages is usually described in terms of "proof," which is defined as twice the percentage by volume of ethanol. Calculate the number of grams of alcohol in 2 quarts of 75-proof gin. What is the molality of the gin? (The density of ethanol is 0.80 g cm^{-3} and 1 quart = 0.946 L.)

Thermodynamics of Mixing

6.9 Liquids A and B form a nonideal solution. Provide a molecular interpretation for each of the following situations: $\Delta_{\text{mix}}H > 0$, $\Delta_{\text{mix}}H < 0$, $\Delta_{\text{mix}}V > 0$, $\Delta_{\text{mix}}V < 0$.

6.10 Calculate the changes in entropy for the following processes: (**a**) mixing of 1 mole of nitrogen and 1 mole of oxygen, and (**b**) mixing of 2 moles of argon, 1 mole of helium, and 3 moles of hydrogen. Both (**a**) and (**b**) are carried out under conditions of constant temperature (298 K) and constant pressure. Assume ideal behavior.

6.11 At 25°C and 1 atm pressure, the absolute third-law entropies of methane and ethane are 186.19 J K^{-1} mol^{-1} and 229.49 J K^{-1} mol^{-1}, respectively, in the gas phase. Calculate the absolute third-law entropy of a "solution" containing 1 mole of each gas. Assume ideal behavior.

Henry's Law

6.12 Prove the statement that an alternative way to express Henry's law of gas solubility is to say that the volume of gas that dissolves in a fixed volume of solution is independent of pressure at a given temperature.

6.13 A miner working 900 ft below the surface had a soft drink beverage during the lunch break. To his surprise, the drink seemed very flat (i.e., not much effervescence was observed upon removing the cap). Shortly after lunch, he took the elevator up to the surface. During the trip up, he felt a great urge to belch. Explain.

6.14 The Henry's law constant of oxygen in water at 25°C is 773 atm $\mathrm{mol^{-1}}$ kg of water. Calculate the molality of oxygen in water under a partial pressure of 0.20 atm. Assuming that the solubility of oxygen in blood at 37°C is roughly the same as that in water at 25°C, comment on the prospect for our survival without hemoglobin molecules. (The total volume of blood in the human body is about 5 L.)

6.15 The solubility of N_2 in blood at 37°C and a partial pressure of 0.80 atm is 5.6×10^{-4} mol $\mathrm{L^{-1}}$. A deep-sea diver breathes compressed air with a partial pressure of N_2 equal to 4.0 atm. Assume that the total volume of blood in the body is 5.0 L. Calculate the amount of N_2 gas released (in liters) when the diver returns to the surface of water, where the partial pressure of N_2 is 0.80 atm.

Chemical Potential and Activity

6.16 Which of the following has a higher chemical potential? If neither, answer "same." (**a**) $H_2O(s)$ or $H_2O(l)$ at water's normal melting point, (**b**) $H_2O(s)$ at −5°C and 1 bar or $H_2O(l)$ at −5°C and 1 bar, (**c**) benzene at 25°C and 1 bar or benzene in a 0.1 *M* toluene solution in benzene at 25°C and 1 bar.

6.17 A solution of ethanol and *n*-propanol behaves ideally. Calculate the chemical potential of ethanol in solution relative to that of pure ethanol when its mole fraction is 0.40 at its boiling point (78.3°C).

6.18 Derive the Gibbs phase rule (Equation 5.23) in terms of chemical potentials.

6.19 The following data give the pressures for carbon disulfide–acetone solutions at 35.2°C. Calculate the activity coefficients of both components based on deviations from Raoult's law and Henry's law. (*Hint:* First determine Henry's law constants graphically.)

x_{CS_2}	0	0.20	0.45	0.67	0.83	1.00
P_{CS_2}/torr	0	272	390	438	465	512
$P_{C_3H_6O}$/torr	344	291	250	217	180	0

6.20 A solution is made up by dissolving 73 g of glucose ($C_6H_{12}O_6$; molar mass 180.2 g) in 966 g of water. Calculate the activity coefficient of glucose in this solution if the solution freezes at −0.66°C.

6.21 A certain dilute solution has an osmotic pressure of 12.2 atm at 20°C. Calculate the difference between the chemical potential of the solvent in the solution and that of pure water. Assume that the density is the same as that of water. (*Hint:* Express the chemical potential in terms of mole fraction, x_1, and rewrite the osmotic pressure equation as $\Pi V = n_2RT$, where n_2 is the number of moles of the solute and $V = 1$ L.)

6.22 At 45°C, the vapor pressure of water is 65.76 mmHg for a glucose solution in which the mole fraction of glucose is 0.080. Calculate the activity and activity coefficient of the water in the solution. The vapor pressure of pure water at 45°C is 71.88 mmHg.

6.23 Consider a binary liquid mixture of A and B, where A is volatile and B is nonvolatile. The composition of the solution in terms of mole fraction is $x_A = 0.045$ and $x_B = 0.955$. The vapor pressure of A from the mixture is 5.60 mmHg, and that of pure A is 196.4 mmHg at the same temperature. Calculate the activity coefficient of A at this concentration.

Colligative Properties

6.24 List the important assumptions in the derivation of Equation 6.39.

6.25 Liquids A (b.p. = T_A°) and B (b.p. = T_B°) form an ideal solution. Predict the range of boiling points of solutions formed by mixing different amounts of A and B.

6.26 A mixture of ethanol and *n*-propanol behaves ideally at 36.4°C. (**a**) Determine graphically the mole fraction of *n*-propanol in a mixture of ethanol and *n*-propanol that boils at 36.4°C and 72 mmHg. (**b**) What is the total vapor pressure over the mixture at 36.4°C when the mole fraction of *n*-propanol is 0.60? (**c**) Calculate the composition of the vapor in (**b**). (The equilibrium vapor pressures of ethanol and *n*-propanol at 36.4°C are 108 mmHg and 40.0 mmHg, respectively.)

6.27 Two beakers, 1 and 2, containing 50 mL of 0.10 *M* urea and 50 mL of 0.20 *M* urea, respectively, are placed under a tightly sealed bell jar at 298 K. Calculate the mole fraction of urea in the solutions at equilibrium. Assume ideal behavior. (*Hint:* Use Raoult's law and note that at equilibrium, the mole fraction of urea is the same in both solutions.)

6.28 At 298 K, the vapor pressure of pure water is 23.76 mmHg and that of seawater is 22.98 mmHg. Assuming that seawater contains only NaCl, estimate its concentration. (*Hint:* Sodium chloride is a strong electrolyte.)

6.29 Trees in cold climates may be subjected to temperatures as low as −60°C. Estimate the concentration of an aqueous solution in the body of the tree that would remain unfrozen at this temperature. Is this a reasonable concentration? Comment on your result.

6.30 Explain why jams and honey can each be stored under atmospheric conditions for long periods of time without spoilage.

6.31 Provide a molecular interpretation for the positive and negative deviations in the boiling-point curves and the formation of azeotropes.

6.32 The freezing-point-depression measurement of benzoic acid in acetone yields a molar mass of 122 g; the same measurement in benzene gives a value of 244 g. Account for this discrepancy. (*Hint:* Consider solvent–solute and solute–solute interactions.)

6.33 A common antifreeze for car radiators is ethylene glycol, $CH_2(OH)CH_2(OH)$. How many milliliters of this substance would you add to 6.5 L of water in the radiator if the coldest day in winter is −20°C? Would you keep this substance in the radiator in the summer to prevent the water from boiling? (The density and boiling point of ethylene glycol are 1.11 g cm^{-3} and 470 K, respectively.)

6.34 For intravenous injections, great care is taken to ensure that the concentration of solutions to be injected is comparable to that of blood plasma. Why?

6.35 The tallest trees known are the redwoods in California. Assuming the height of a redwood to be 105 m (about 350 ft), estimate the osmotic pressure required to push water up from the roots to the treetop.

6.36 A mixture of liquids A and B exhibits ideal behavior. At 84°C, the total vapor pressure of a solution containing 1.2 moles of A and 2.3 moles of B is 331 mmHg. Upon the addition of another mole of B to the solution, the vapor pressure increases to 347 mmHg. Calculate the vapor pressures of pure A and B at 84°C.

6.37 Fish breathe the dissolved air in water through their gills. Assuming the partial pressures of oxygen and nitrogen in air to be 0.20 atm and 0.80 atm, respectively, calculate the mole fractions of oxygen and nitrogen in water at 298 K. Comment on your results.

6.38 Liquids A (molar mass 100 g mol^{-1}) and B (molar mass 110 g mol^{-1}) form an ideal solution. At 55°C, A has a vapor pressure of 95 mmHg and B a vapor pressure of 42 mmHg. A solution is prepared by mixing equal weights of A and B. (**a**) Calculate the mole fraction of each component in the solution. (**b**) Calculate the partial pressures of A and B over the solution at 55°C. (**c**) Suppose that some of the vapor described in (**b**) is condensed to a liquid. Calculate the mole fraction of each component in this liquid and the vapor pressure of each component above this liquid at 55°C.

6.39 Lysozyme extracted from chicken egg white has a molar mass of 13,930 g mol^{-1}. Exactly 0.1 g of this protein is dissolved in 50 g of water at 298 K. Calculate the vapor pressure lowering, the depression in freezing point, the elevation of boiling point, and the osmotic pressure of this solution. The vapor pressure of pure water at 298 K is 23.76 mmHg.

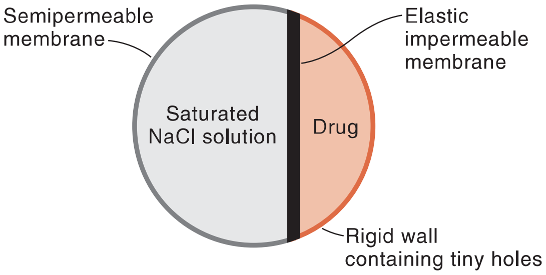
6.40 The following argument is frequently used to explain the fact that the vapor pressure of the solvent is lower over a solution than over the pure solvent and that lowering is proportional to the concentration. A dynamic equilibrium exists in both cases, so that the rate at which molecules of solvent evaporate from the liquid is always equal to that at which they condense. The rate of condensation is proportional to the partial pressure of the vapor, whereas that of evaporation is unimpaired in the pure solvent but is impaired by solute molecules in the surface of the solution. Hence the rate of escape is reduced in proportion to the concentration of the solute, and maintenance of equilibrium requires a corresponding lowering of the rate of condensation and therefore of the partial pressure of the vapor phase. Explain why this argument is incorrect. [*Source:* K. J. Mysels, *J. Chem. Educ.* **32**, 179 (1955).]

6.41 A compound weighing 0.458 g is dissolved in 30.0 g of acetic acid. The freezing point of the solution is found to be 1.50 K below that of the pure solvent. Calculate the molar mass of the compound.

6.42 Two aqueous urea solutions have osmotic pressures of 2.4 atm and 4.6 atm, respectively, at a certain temperature. What is the osmotic pressure of a solution prepared by mixing equal volumes of these two solutions at the same temperature?

6.43 A forensic chemist is given a white powder for analysis. She dissolves 0.50 g of the substance in 8.0 g of benzene. The solution freezes at 3.9°C. Can the chemist conclude that the compound is cocaine ($C_{17}H_{21}NO_4$)? What assumptions are made in the analysis? The freezing point of benzene is 5.5°C.

6.44 "Time-release" drugs have the advantage of releasing the drug to the body at a constant rate so that the drug concentration at any time is not high enough to have harmful side effects or so low as to be ineffective. A schematic diagram of a pill that works on this basis is shown below. Explain how it works.



6.45 A nonvolatile organic compound, Z, was used to make up two solutions. Solution A contains 5.00 g of Z dissolved in 100 g of water, and solution B contains 2.31 g of Z dissolved in 100 g of benzene. Solution A has a vapor pressure of 754.5 mmHg at the normal boiling point of water, and solution B has the same vapor pressure at the normal boiling point of benzene. Calculate the molar mass of Z in solutions A and B, and account for the difference.

6.46 Acetic acid is a polar molecule that can form hydrogen bonds with water molecules. Therefore, it has a high solubility in water. Yet acetic acid is also soluble in benzene (C_6H_6), a nonpolar solvent that lacks the ability to form hydrogen bonds. A solution of 3.8 g of CH_3COOH in 80 g C_6H_6 has a freezing point of 3.5°C. Calculate the molar mass of the solute, and suggest what its structure might be. (*Hint:* Acetic acid molecules can form hydrogen bonds among themselves.)

6.47 At 85°C, the vapor pressure of A is 566 torr and that of B is 250 torr. Calculate the composition of a mixture of A and B that boils at 85°C when the pressure is 0.60 atm. Also, calculate the composition of the vapor mixture. Assume ideal behavior.

6.48 Comment on whether each of the following statements is true or false, and briefly explain your answer: (**a**) If one component of a solution obeys Raoult's law, then the other component must also obey the same law. (**b**) Intermolecular forces are small in ideal solutions. (**c**) When 15.0 mL of an aqueous 3.0 *M* ethanol solution is mixed with 55.0 mL of an aqueous 3.0 *M* ethanol solution, the total volume is 70.0 mL.

6.49 Liquids A and B form an ideal solution at a certain temperature. The vapor pressures of pure A and B are 450 torr and 732 torr, respectively, at this temperature. (**a**) A sample of the solution's vapor is condensed. Given that the original solution contains 3.3 moles of A and 8.7 moles of B, calculate the composition of the condensate in mole fractions. (**b**) Suggest a method for measuring the partial pressures of A and B at equilibrium.

6.50 Nonideal solutions are the result of unequal intermolecular forces between components. Based on this knowledge, comment on whether a racemic mixture of a liquid compound would behave as an ideal solution.

6.51 Calculate the molal boiling-point elevation constant (K_b) for water. The molar enthalpy of vaporization of water is 40.79 kJ mol^{-1} at 100°C.

6.52 Explain the following phenomena. (**a**) A cucumber placed in concentrated brine (saltwater) shrivels into a pickle. (**b**) A carrot placed in fresh water swells in volume.

Additional Problems

6.53 Calculate the change in the Gibbs energy at 37°C when the human kidneys secrete 0.275 mole of urea per kilogram of water from blood plasma to urine if the molal concentrations of urea in blood plasma and urine are 0.005 mol kg^{-1} and 0.326 mol kg^{-1}, respectively.

6.54 (**a**) Which of the following expressions is incorrect as a representation of the partial molar volume of component A in a two-component solution? Why? How would you correct it?

$$\left(\frac{\partial V_m}{\partial n_A}\right)_{T,P,n_B} \qquad \left(\frac{\partial V_m}{\partial x_A}\right)_{T,P,x_B}$$

(**b**) Given that the molar volume of this mixture (V_m) of A and B is given by

$$V_m = [0.34 + 3.6x_Ax_B + 0.4x_B(1 - x_A)]\ \text{L mol}^{-1}$$

derive an expression for the partial molar volume for A and calculate its value at $x_A = 0.20$.

6.55 The partial molar volumes for a benzene–carbon tetrachloride solution at 25°C at a mole fraction of 0.5 are: $\overline{V}_b = 0.106$ L mol^{-1} and $\overline{V}_c = 0.100$ L mol^{-1}, respectively, where the subscripts b and c denote C_6H_6 and CCl_4. **(a)** What is the volume of a solution made up of one mole of each? **(b)** Given that the molar volumes are: $C_6H_6 = 0.089$ L mol^{-1} and $CCl_4 = 0.097$ L mol^{-1}, what is the change in volume on mixing 1 mole each of C_6H_6 and CCl_4? **(c)** What can you deduce about the nature of intermolecular forces between C_6H_6 and CCl_4?

6.56 The osmotic pressure of poly(methyl methacrylate) in toluene has been measured at a series of concentrations at 298 K. Determine graphically the molar mass of the polymer.

Π/atm	8.40×10^{-4}	1.72×10^{-3}	2.52×10^{-3}	3.23×10^{-3}	7.75×10^{-3}
c/g L^{-1}	8.10	12.31	15.00	18.17	28.05

6.57 Benzene and toluene form an ideal solution. Prove that to achieve the maximum entropy of mixing, the mole fraction of each component must be 0.5.

6.58 Suppose 2.6 moles of He at 0.80 atm and 25°C are mixed with 4.1 moles of Ne at 2.7 atm and 25°C. Calculate the Gibbs energy change for the process. Assume ideal behavior.

6.59 Two beakers are placed in a closed container. Beaker A initially contains 0.15 mole of naphthalene ($C_{10}H_8$) in 100 g of benzene (C_6H_6) and beaker B initially contains 31 g of an unknown compound dissolved in 100 g of benzene. At equilibrium, beaker A is found to have lost 7.0 g. Assuming ideal behavior, calculate the molar mass of the unknown compound. State any assumptions made.

6.60 As an after dinner party trick, the host brings out a glass of water with an ice cube floating on top and a thread. Then he asks the guests to remove the ice cube with the thread, but they are not allowed to tie a loop around the ice cube. Describe how the guests might accomplish this task.

6.61 A student carried out the following procedure to measure the pressure of carbon dioxide in a carbonated soft drink bottle. First, she weighed the bottle (853.5 g). Next, she carefully removed the cap to let the CO_2 gas escape. Finally, she measured the volume of the soft drink (452.4 mL). Given that the Henry's law constant for CO_2 in water at 25°C is 3.4×10^{-2} mol L^{-1} atm^{-1}, calculate the pressure of CO_2 in the original bottle. List the sources of errors.

6.62 **(a)** Derive the equation relating the molality (m) of a solution to its molarity (M)

$$m = \frac{M}{d - \frac{M\mathcal{M}}{1000}}$$

where d is the density of the solution (g/mL) and $\mathcal{M}$ is the molar mass of the solute (g/mol). (*Hint:* Start by expressing the solvent in kilograms in terms of the difference between the mass of the solution and the mass of the solute.) **(b)** Show that, for dilute aqueous solutions, m is approximately equal to M.

6.63 At 298 K, the osmotic pressure of a glucose solution is 10.50 atm. Calculate the freezing point of the solution. The density of the solution is 1.16 g/mL.

6.64 The mole fractions of dry air are approximately 21% O_2 and 79% N_2. Calculate the masses of these two gases dissolved in 1000 g of water at 25°C and 1 atm.

CHAPTER 7

Electrolyte Solutions

> *And when the rain has wet the kite and twine, so that it can conduct the electric fire freely, you will find it stream out plentifully from the key on the approach of your knuckle.*
>
> —Benjamin Franklin*

All biological and many chemical systems are aqueous solutions that contain various ions. The rates of many reactions are highly dependent on the type and concentration of ions present. It is important to have a clear understanding of the behavior of ions in solution.

An electrolyte is a substance that, when dissolved in a solvent (usually water), produces a solution that will conduct electricity. An electrolyte can be an acid, a base, or a salt. In this chapter, we shall consider ionic conductance, ionic dissociation, the thermodynamics of ions in solution, and the theory and colligative properties of electrolyte solutions.

7.1 Electrical Conduction in Solution

Some Basic Definitions

The ability of an electrolyte to conduct electricity provides us with a simple and direct means of studying ionic behavior in solution. We begin with a few basic definitions.

Ohm's Law. Ohm's law (after the German physicist George Simon Ohm, 1787–1854) states that the current (I) flowing through a particular medium is directly proportional to the voltage or the electrical potential difference (V) across the medium and indirectly proportional to the resistance (R) of the medium. Thus,

$$I = \frac{V}{R} \tag{7.1}$$

where I is in amperes (A), V in volts (V), and R in ohms (Ω).

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* Labaree. L. W., et al., Eds., *The Papers of Benjamin Franklin*, Yale University Press, New Haven, CT, 1961. Vol. 4, p.367. Used by permission.

Resistance (R). The *resistance* across a particular medium depends on the geometry of the medium; it is directly proportional to the length (l) and inversely proportional to the cross section area (A) of the medium. Thus,

$$R \propto \frac{l}{A}$$

$$= \rho \frac{l}{A} \tag{7.2}$$

where the proportionality constant ρ is called the *specific resistance*, or *resistivity*. Because the units of R are ohms (Ω), of l centimeters or meters, and of A square centimeters or square meters, the units of ρ are Ω cm or Ω m. Resistivity is a property characteristic of the material comprising the medium.

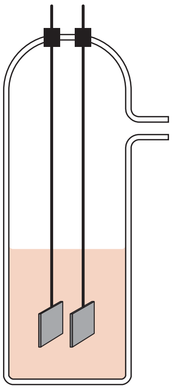


Figure 7.1
A conductance cell. The electrodes are made of platinum.

Conductance (C). *Conductance* is the reciprocal of resistance, that is,

$$C = \frac{1}{R} = \frac{1}{\rho}\frac{A}{l} = \kappa\frac{A}{l} \tag{7.3}$$

where κ is the *specific conductance*, or *conductivity* equal to $1/\rho$. The SI unit for conductance is siemens (S) (after the German physicist Werner von Siemens, 1816–1892), where $1\ \mathrm{S} = 1\ \Omega^{-1}$. Conductivity has the units $\Omega^{-1}\ \mathrm{cm}^{-1}$ or $\Omega^{-1}\ \mathrm{m}^{-1}$.

The historical unit of electric conductance was the mho ("ohm" backwards).

A typical conductance cell* is shown in Figure 7.1. The conductance is given by Equation 7.3. The ratio l/A, called the *cell constant*, is the same for all solutions. Here, A is the area of the electrodes and l the distance of separation between the electrodes. In practice, the cell constant is calibrated by measuring the conductance of a standard solution of potassium chloride with a known value of κ.

---

[*] It is customary to quote the conductance rather than the resistance of an electrolyte solution.

EXAMPLE 7.1

The conductance of a solution is $0.689\ \Omega^{-1}$. Calculate the specific conductance if the cell constant is $0.255\ \mathrm{cm}^{-1}$.

ANSWER

From Equation 7.3,

$$\kappa = C\frac{l}{A}$$

$$= 0.689\ \Omega^{-1} \times 0.255\ \mathrm{cm}^{-1}$$

$$= 0.176\ \Omega^{-1}\ \mathrm{cm}^{-1}$$

Although the specific conductance can be measured easily (from the known cell constant and the experimentally determined conductance), it is not the best value to use in studying the conduction process in electrolyte solutions. The specific conductances of solutions of different concentrations, for example, will differ simply because a given volume of the solutions will contain different numbers of ions. For this reason, expressing the conductance as a molar quantity is preferable. We define the *molar conductance* (Λ) as

$$\Lambda = \frac{\kappa}{c} \tag{7.4}$$

where c is the molar concentration of the solution. The SI units for Λ are $\Omega^{-1}\ \text{mol}^{-1}\ \text{m}^2$, although it is often more conveniently expressed as $\Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$.

EXAMPLE 7.2

The conductance of a cell containing an aqueous 0.0560 *M* KCl solution is 0.0239 Ω^{-1}. When the same cell is filled with an aqueous 0.0836 *M* NaCl solution, its conductance is 0.0285 Ω^{-1}. Given that the molar conductance of KCl is $1.345 \times 10^2\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$, calculate the molar conductance of the NaCl solution.

ANSWER

We need the cell constant. Our first step is to calculate the specific conductance of the KCl solution. From Equation 7.4,

$$\begin{aligned}\kappa &= \Lambda c\\ &= 1.345 \times 10^2\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2 \times \frac{0.0560\ \text{mol}}{1\ \text{L}} \times \frac{1\ \text{L}}{1000\ \text{cm}^3}\\ &= 7.53 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}\end{aligned}$$

Next, from Equation 7.3 we obtain the cell constant

$$\begin{aligned}\frac{l}{A} = \frac{\kappa}{C} &= \frac{7.53 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}}{0.0239\ \Omega^{-1}}\\ &= 0.315\ \text{cm}^{-1}\end{aligned}$$

The specific conductance of the NaCl solution is obtained by rearranging Equation 7.3:

$$\begin{aligned}\kappa &= \frac{l}{A}C\\ &= (0.315\ \text{cm}^{-1})(0.0285\ \Omega^{-1})\\ &= 8.98 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}\end{aligned}$$

Finally, the molar conductance of the NaCl solution is given by (see Equation 7.4)

$$\Lambda = \frac{\kappa}{c} = \frac{8.98 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}}{0.0836\ \text{mol L}^{-1}} \times \frac{1000\ \text{cm}^3}{1\ \text{L}}$$

$$= 1.07 \times 10^2\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$$

Strong electrolytes are substances that are completely dissociated into ions in solution.

Looking at Equation 7.4, we might expect Λ to be independent of the concentration of the solution. (κ is directly proportional to concentration, but κ/c should be constant for a given substance.) Careful measurements show that this is not the case, however. The German chemist Friedrich Wilhelm Georg Kohlrausch (1840–1910) discovered the following relationship between molar conductance and concentration for strong electrolytes at a particular temperature:

$$\Lambda = \Lambda_0 - B\sqrt{c} \tag{7.5}$$

where Λ_0 is the molar conductance at infinite dilution; that is, $\Lambda \to \Lambda_0$ as $c \to 0$, and B is a positive constant for a given electrolyte. Thus, Λ_0 can be readily obtained by plotting Λ versus $\sqrt{c}$ and extrapolating to zero concentration (Figure 7.2). This method is unsatisfactory for weak electrolytes because of the steepness of their curves at low concentrations (see plot for CH_3COOH).

Table 7.1 shows the values of Λ_0 for several electrolytes. An interesting pattern emerges when we examine the difference in Λ_0 for two electrolytes containing the same cation or anion. For example,

$$\Lambda_0^{\text{KCl}} - \Lambda_0^{\text{NaCl}} = 23.4\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$$

$$\Lambda_0^{\text{KNO}_3} - \Lambda_0^{\text{NaNO}_3} = 23.4\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$$

This same difference and similar observations led Kohlrausch to suggest that molar conductance at infinite dilution can be broken down into two contributions, one from the anion and the other from the cation:

$$\Lambda_0 = \nu_+\lambda_0^+ + \nu_-\lambda_0^- \tag{7.6}$$

where λ_0^+ and λ_0^- are the molar ionic conductances at infinite dilution, and ν_+ and ν_- are the number of cations and anions in the formula. Equation 7.6 is known as *Kohlrausch's law of independent migration*. It means that molar conductance at infinite dilution is made up of independent contributions from the cationic and anionic species. We can now see why the same value was obtained in the example above, because

Note that these are all 1:1 electrolytes, so $\nu_+ = \nu_- = 1$.

$$\Lambda_0^{\text{KCl}} - \Lambda_0^{\text{NaCl}} = \lambda_0^{\text{K}^+} + \lambda_0^{\text{Cl}^-} - \lambda_0^{\text{Na}^+} - \lambda_0^{\text{Cl}^-} = \lambda_0^{\text{K}^+} - \lambda_0^{\text{Na}^+}$$

and

$$\Lambda_0^{\text{KNO}_3} - \Lambda_0^{\text{NaNO}_3} = \lambda_0^{\text{K}^+} + \lambda_0^{\text{NO}_3^-} - \lambda_0^{\text{Na}^+} - \lambda_0^{\text{NO}_3^-} = \lambda_0^{\text{K}^+} - \lambda_0^{\text{Na}^+}$$

Table 7.2 lists the molar conductances of a number of ions.

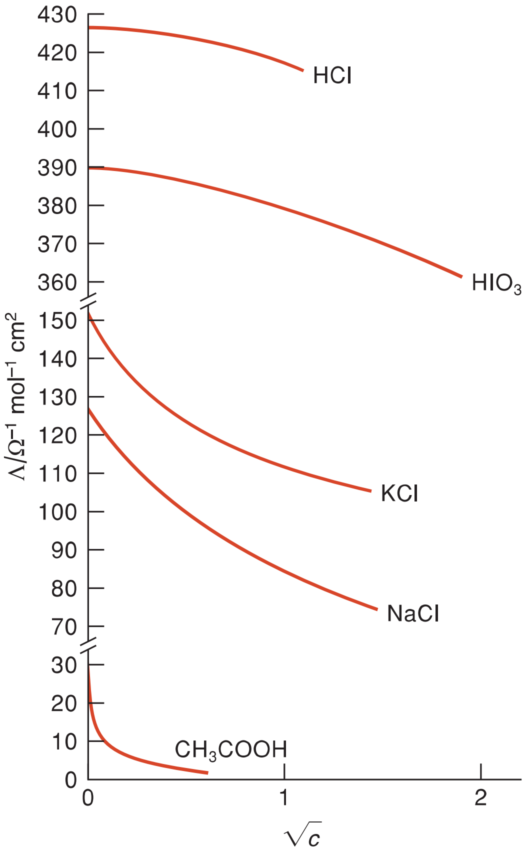


Figure 7.2
Plots of molar conductance versus the square root of concentration (mol L^{-1}) for several electrolytes.

Table 7.1
Molar Conductance at Infinite Dilution for Some Electrolytes in Water at 298 K[a]

Electrolyte	Λ_0/Ω^{-1} mol^{-1} cm^2
HCl	426.16
CH_3COOH	390.71
LiCl	115.03
NaCl	126.45
AgCl	137.20
KCl	149.85
$LiNO_3$	110.14
$NaNO_3$	121.56
KNO_3	144.96
$CuSO_4$	267.24
CH_3COONa	91.00

[a] To express Λ_0 as Ω^{-1} mol^{-1} m^2, multiply each number by 10^{-4}. Thus, Λ_0 for HCl is 426.16 Ω^{-1} mol^{-1} cm^2 or 4.2616×10^{-2} Ω^{-1} mol^{-1} m^2.

Table 7.2
Molar Ionic Conductance and Ionic Mobility of Some Common Ions at 298 K

Ion	λ_0[a] / Ω^{-1} mol^{-1} cm^2	Ionic mobility[b] / 10^{-4} cm^2 s^{-1} V^{-1}	Ionic radius/Å
H^+	349.81	36.3	
Li^+	38.68	4.01	0.60
Na^+	50.10	5.19	0.95
K^+	73.50	7.62	1.33
Rb^+	77.81	7.92	1.48
Cs^+	77.26	7.96	1.69
NH_4^+	73.5	7.62	
Mg^{2+}	106.1	5.50	0.65
Ca^{2+}	119.0	6.17	0.99
Ba^{2+}	127.3	6.59	1.35
Cu^{2+}	107.2	5.56	0.72
OH^-	198.3	20.50	
F^-	55.4	5.74	1.36
Cl^-	76.35	7.91	1.81
Br^-	78.14	8.10	1.95
I^-	76.88	7.95	2.16
NO_3^-	71.46	7.41	
HCO_3^-	44.50	4.61	
CH_3COO^-	40.90	4.24	
SO_4^{2-}	160.0	8.29	

[a] From Robinson, R. A., and R. H. Stokes, *Electrolyte Solutions*, Academic Press, New York, 1959. Used by permission.

[b] From Adamson, A. W. *A Textbook of Physical Chemistry*, Academic Press, New York, 1973. Used by permission.

Degree of Dissociation

At a certain concentration, an electrolyte may be only partially dissociated. At infinite dilution, any electrolyte, weak or strong, is completely dissociated. In 1887, the Swedish chemist Svante August Arrhenius (1859–1927) suggested that the *degree of dissociation* (α) of an electrolyte can be calculated by the simple relation

$$\alpha = \frac{\Lambda}{\Lambda_0} \tag{7.7}$$

where Λ is the molar conductance at a particular concentration to which α refers. Using Equation 7.7, the German chemist Wilhelm Ostwald (1853–1932) showed how one can measure the dissociation constant of an acid. Consider a weak acid HA of concentration c (mol L^{-1}). At equilibrium, we have

$$\begin{array}{ccccc} \mathrm{HA} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{A^-} \\ c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

where α is the fraction of HA dissociated. The dissociation constant, K_a, is given by

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

Using the expression for α in Equation 7.7, we obtain

$$K_a = \frac{c\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)} \tag{7.8}$$

Equation 7.8 can be rearranged to give

$$\frac{1}{\Lambda} = \frac{1}{K_a\Lambda_0^2}(\Lambda c) + \frac{1}{\Lambda_0} \tag{7.9}$$

Equation 7.9 is known as the *Ostwald dilution law*. Thus, the value of K_a can be obtained either directly from Equation 7.8 or more accurately from Equation 7.9 by plotting $1/\Lambda$ versus Λc (Figure 7.3). Note that Λ_0 must be known to apply Equation 7.8 alone.

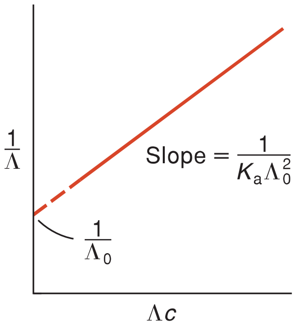


Figure 7.3 Graphical determination of K_a according to Equation 7.9.

EXAMPLE 7.3

The molar conductance of an aqueous acetic acid solution at concentration 0.10 M is 5.2 Ω^{-1} mol^{-1} cm^2 at 298 K. Calculate the dissociation constant of acetic acid.

ANSWER

From Table 7.1, Λ_0 = 390.71 Ω^{-1} mol^{-1} cm^2, and from Equation 7.8 we write

$$K_a = \frac{(0.10 \text{ mol L}^{-1})(5.2\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2)^2}{(390.71\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2)(390.71 - 5.2)\Omega^{-1}\text{ mol}^{-1}\text{ cm}^2}$$

$$= 1.8 \times 10^{-5} \text{ mol L}^{-1}$$

Ionic Mobility

The molar conductance of a solution depends on the ease of ionic movement. Ionic velocity is not a constant, however, because it depends on the strength of the electric field (E).* On the other hand, *ionic mobility* (u), defined as the ionic velocity per unit electric field, is a constant. Thus, the ionic mobility of a cation, u_+, is given by

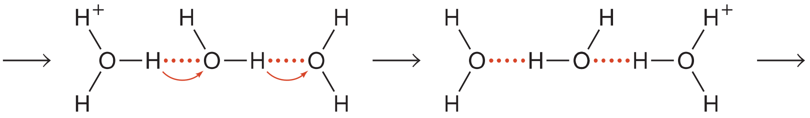
$$u_+ = \frac{v_+}{E} \tag{7.10}$$

where v_+ is the velocity of the cation moving in an electric field of strength E. Ionic mobility has the units (cm s^{-1})/V cm^{-1}, or cm^2 s^{-1} V^{-1}; it is related to the molar ionic conductance at infinite dilution as follows:

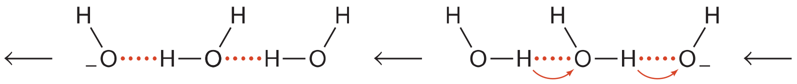
$$u_+ = \frac{\lambda_0^+}{F} \quad \text{and} \quad u_- = \frac{\lambda_0^-}{F} \tag{7.11}$$

where F is the Faraday constant (after the English chemist and physicist Michael Faraday, 1791–1867).†

Table 7.2 lists the ionic mobilities of various ions at 298 K. The ionic mobilities of H^+ and OH^- ions are much higher than those of other ions. These high values are due to hydrogen bonding. In water, the proton is hydrated, and its movement can be represented as follows:



Similarly, the movement of the hydroxide ion is



In each case, the ion can move along an extended hydrogen-bond network, resulting in very high mobility.

Ionic mobility is utilized in electrophoresis, a technique for purifying and identifying proteins and nucleic acids.

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* For example, if the potential drop between two electrodes separated by 2.0 cm in an electrolytic cell is 5.0 V, then the electric field is 5.0 V/2.0 cm. or 2.5 V cm^{-1}.

† The charge carried by 1 mole of electrons is called the faraday (F), given by 96,485 coulombs. In most calculations, we shall round off the quantity to 96,500 C mol^{-1}.

EXAMPLE 7.4

The mobility of a chloride ion in water at 25°C is 7.91×10^{-4} cm^2 s^{-1} V^{-1}. (a) Calculate the molar conductance of the ion at infinite dilution. (b) How long will it take for the ion to travel between two electrodes separated by 4.0 cm if the electric field is 20 V cm^{-1}?

ANSWER

From Equation 7.11,

$$\begin{aligned}\lambda_0^- &= Fu_- \\ &= (96500 \text{ C mol}^{-1})(7.91 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}) \\ &= 76.3 \text{ C s}^{-1} \text{ V}^{-1} \text{ mol}^{-1} \text{ cm}^2 \\ &= 76.3 \ \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2\end{aligned}$$

because 1 C s^{-1} = 1 A and A/V = Ω^{-1} (Ohm's law).

(b) First, we calculate the ionic velocity, given by Equation 7.10, for an anion

$$\begin{aligned}v_- &= Eu_- \\ &= (20 \text{ V cm}^{-1})(7.91 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}) \\ &= 1.58 \times 10^{-2} \text{ cm s}^{-1}\end{aligned}$$

Next, we write

$$\begin{aligned}\text{time} &= \frac{\text{distance}}{\text{velocity}} \\ &= \frac{4.0 \text{ cm}}{1.58 \times 10^{-2} \text{ cm s}^{-1}} \\ &= 2.5 \times 10^2 \text{ s} \\ &= 4.2 \text{ min}\end{aligned}$$

Applications of Conductance Measurements

Accurate conductance measurements are easy to make and have many applications. Two examples are described below.

Acid–Base Titration. As mentioned earlier, the conductances of H^+ and OH^- are considerably higher than those of other cations and anions. By plotting the conductance of a HCl solution as a function of NaOH solution added, we obtain a titration

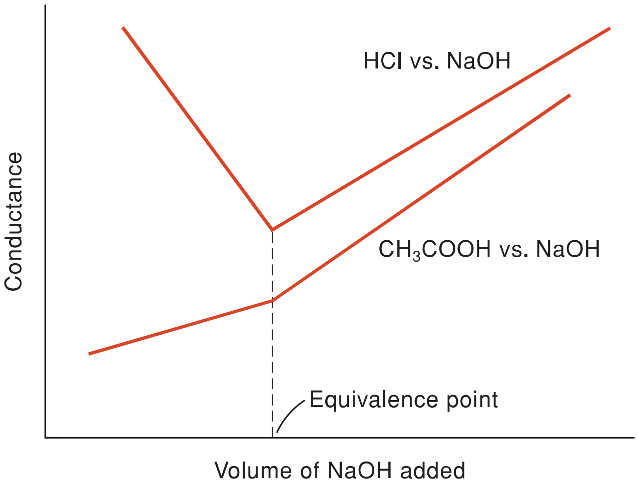

Figure 7.4
Acid–base titration monitored by conductance measurements. Note the difference between a strong acid–base titration (HCl vs. NaOH) and a weak acid–strong base titration (CH_3COOH vs. NaOH).

curve such as the one shown in Figure 7.4. Initially, the conductance of the solution falls, because H^+ ions are replaced by Na^+ ions, which have a lower ionic conductance. This trend continues until the equivalence point is reached. Beyond this point, the conductance begins to rise due to the excess of OH^- ions. If the acid is a weak electrolyte, such as acetic acid, the slope of the first part of the curve is much less steep—the conductance actually increases right from the beginning—and there is more uncertainty in determining the equivalence point.

Solubility Determination. We have seen how the dissociation constant of acetic acid can be obtained from conductance measurements. The same procedure can be applied to determine the solubility of a sparingly soluble salt. Suppose that we are interested in the molar solubility (mol L^{-1}) and the solubility product of AgCl (a 1:1 electrolyte) in water at 298 K. From Equation 7.4, we write

$$\Lambda = \frac{\kappa}{c} = \frac{\kappa}{S}$$

where S is the molar solubility in mol L^{-1}. Because AgCl is an insoluble salt, the concentration of the solution is low, so we can assume that $\Lambda \approx \Lambda_0$. Thus,

$$S = \frac{\kappa}{\Lambda} \approx \frac{\kappa}{\Lambda_0}$$

Experimentally, the specific conductance of a saturated AgCl solution is $1.86 \times 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$. Because water is a weak electrolyte, however, we must take out the contribution due to water itself (κ for water is $6.0 \times 10^{-8}\ \Omega^{-1}\ \text{cm}^{-1}$). Thus,

$$\kappa(\text{AgCl}) = (1.86 \times 10^{-6}) - (6.0 \times 10^{-8}) = 1.8 \times 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$$

According to Table 7.1, $\Lambda_0 = 137.2\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$ for AgCl. Finally, we have

$$S = \frac{\kappa}{\Lambda_0} = \frac{1.8 \times 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}}{137.2\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2} \times \frac{1000\ \text{cm}^3}{1\ \text{L}}$$

$$= 1.3 \times 10^{-5}\ \text{mol L}^{-1}$$

The solubility product, K_{sp}, for AgCl is given by

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (1.3 \times 10^{-5})(1.3 \times 10^{-5})$$

$$= 1.7 \times 10^{-10}$$

7.2 A Molecular View of the Solution Process

Why does NaCl dissolve in water and not in benzene? We know that NaCl is a stable compound in which the Na^+ and Cl^- ions are held by electrostatic forces in the crystal lattice. For NaCl to enter the aqueous environment, the strong attractive forces must somehow be overcome. The dissolution of NaCl in water presents two questions: How do the ions interact with water molecules, and how do they interact with one another?

Water is a good solvent for ionic compounds because it is a polar molecule and therefore can stabilize the ions through ion-dipole interaction that results in hydration. Generally, smaller ions can be hydrated more effectively than larger ions. A small ion contains a more concentrated charge, which leads to greater electrostatic interaction with the polar water molecules.* Figure 7.5 shows a schematic diagram of hydration. Because a different number of water molecules surrounds each type of ion, we speak of the *hydration number* of an ion. This number is directly proportional to the charge and inversely proportional to the size of the ion. Note that water in the "hydration sphere" and bulk water molecules have different properties,† which can be distinguished by spectroscopic techniques such as nuclear magnetic resonance. There is a dynamic equilibrium between the two types of molecules. Depending on the ion, the mean lifetime of a H_2O molecule in the hydration sphere can vary tremendously. For example, consider the mean lifetime of H_2O in the hydration sphere for the following ions: Br^-, 10^{-11} s; Na^+, 10^{-9} s; Cu^{2+}, 10^{-7} s; Fe^{2+}, 10^{-5} s; Al^{3+}, 7 s; and Cr^{3+}, 1.5×10^5 s, or 42 h.

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* According to electrostatic theory, the electric field at the surface of a charged sphere of radius r is proportional to ze/r^2, where z is the number of charges and e is the electronic charge.

† Water molecules in the hydration sphere of an ion do not exhibit individual translational motion. They move with the ion as a whole.

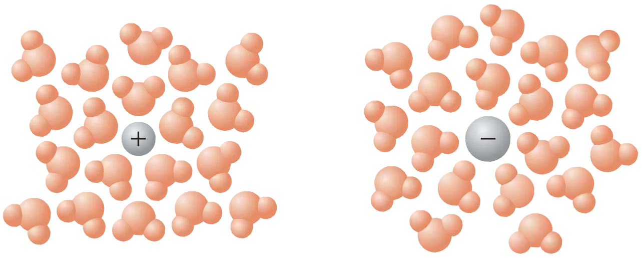

Figure 7.5
Hydration of a cation and an anion. In general, each cation and each anion has a specific number of water molecules associated with it in the hydration sphere.

The ion–dipole interaction (see Chapter 17) between dissolved ions and water molecules can affect several bulk properties of water. Small and/or multicharged ions such as Li^+, Na^+, Mg^{2+}, Al^{3+}, Er^{3+}, OH^-, and F^- are often called *structure-making ions*. The strong electric fields exerted by these ions can polarize water molecules, producing additional order beyond the first hydration layer. This interaction increases the solution's viscosity. On the other hand, large monovalent ions such as K^+, Rb^+, Cs^+, NH_4^+, Cl^-, NO_3^-, and ClO_4^- are *structure-breaking ions*. Because of their diffuse surface charges and hence weak electric fields, these ions are unable to polarize water molecules beyond the first layer of hydration. Consequently, the viscosities of solutions containing these ions are usually lower than that of pure water.

The effective radii of hydrated ions in solution can be appreciably greater than their crystal or ionic radii. For example, the radii of the hydrated Li^+, Na^+, and K^+ ions are estimated to be 3.66 Å, 2.80 Å, and 1.87 Å, respectively, although the ionic radii actually increase from Li^+ to K^+. We might expect the mobility of an ion to be inversely proportional to its hydrated radius. Table 7.2 nicely demonstrates the truth of this expectation. The high ionic mobility of the proton, which we would expect to be strongly hydrated because of its very small size, stems from the rapid movement of the H^+ ions via hydrogen bonds.

We now turn to the other question raised earlier: How do ions interact with one another? According to Coulomb's law (after the French physicist Charles Augustin de Coulomb, 1736–1806), the force (F) between Na^+ and Cl^- ions in a vacuum is given by

$$F = \frac{q_{\mathrm{Na}^+} q_{\mathrm{Cl}^-}}{4\pi\varepsilon_0 r^2} \tag{7.12}$$

where ε_0 is the *permittivity of the vacuum* ($8.854 \times 10^{-12}\ \mathrm{C^2\ N^{-1}\ m^{-2}}$), q_{Na^+} and q_{Cl^-} are the charges on the ions, and r is the distance of separation. The factor $4\pi\varepsilon_0$ is present as a result of using SI units. In the polar medium of water, as Figure 7.6 shows, the dipolar molecules align themselves with their positive ends facing the negative charge and the negative ends facing the positive charge. This arrangement reduces the effective charge at the positive and negative charge centers by a factor of $1/\varepsilon$, where ε is the *dielectric constant* of the medium (see Appendix 7.1 on p. 295). Therefore, in any medium other than a vacuum, Equation 7.12 takes the form

The dielectric constant of vacuum is 1.

$$F = \frac{q_{\mathrm{Na}^+} q_{\mathrm{Cl}^-}}{4\pi\varepsilon_0 \varepsilon r^2} \tag{7.13}$$

Table 7.3 lists the dielectric constants of several solvents. Keep in mind that ε always decreases with increasing temperature. For example, at 343 K, the dielectric constant

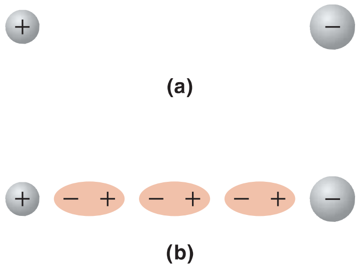

Figure 7.6
(a) Separation of a cation and an anion in a vacuum. (b) Separation of the same ions in water. The alignment of polar water molecules is exaggerated. Because of thermal motion, the polar molecules are only partially aligned. Nevertheless, this arrangement reduces the electric field and hence the attractive force between the ions.

Table 7.3
Dielectric Constants of Some Pure Liquids at 298 K

Liquid	Dielectric constant, ε[a]
H_2SO_4	101
H_2O	78.54
$(CH_3)_2SO$ (dimethylsulfoxide)	49
$C_3H_8O_3$ (glycerol)	42.5
CH_3NO_2 (nitromethane)	38.6
$HOCH_2CH_2OH$ (ethylene glycol)	37.7
CH_3CN (acetonitrile)	36.2
CH_3OH	32.6
C_2H_5OH	24.3
CH_3COCH_3 (dimethyl ether)	20.7
CH_3COOH	6.2
C_6H_6	4.6
$C_2H_5OC_2H_5$ (diethyl ether)	4.3
CS_2	2.6

[a] The dielectric constant is a dimensionless quantity.

of water is reduced to about 64. Water's large dielectric constant is what reduces the attractive force between the Na^+ and Cl^- ions and enables them to separate in solution.

The dielectric constant of a solvent also determines the "structure" of ions in solution. To maintain electrical neutrality in solution, an anion must be near a cation, and vice versa. Depending on the proximity of these two ions, we can think of them either as "free" ions or as "ion pairs." Each free ion is surrounded by at least one and perhaps several layers of water molecules. In an ion pair, the cation and anion are close to each other, and few or no solvent molecules are between them. Generally, free ions and ion pairs are thermodynamically distinguishable species that have quite different chemical reactivities. For dilute 1:1 aqueous electrolyte solutions, such as NaCl, ions are believed to be in the free-ion form. In higher-valence electrolytes, such as $CaCl_2$ and Na_2SO_4, the formation of ion pairs is indicated by conductance measurements, for a neutral ion pair cannot conduct electricity. Two opposing factors determine whether we have free ions or ion pairs in solution: the potential energy of attraction between the cation and anion, and the kinetic or thermal energy, of the order of k_BT, for individual ions.

We can now understand easily why NaCl does not dissolve in benzene. A nonpolar molecule, benzene does not solvate Na^+ and Cl^- ions effectively. In addition, its small dielectric constant means that the cations and anions will have little tendency to enter the solution as separate ions.

EXAMPLE 7.5

Calculate the force in newtons between a pair of Na^+ and Cl^- ions separated by exactly 1 nm (10 Å) in (a) a vacuum and (b) water at 25°C. The charges on the Na^+ and Cl^- ions are 1.602×10^{-19} C and -1.602×10^{-19} C, respectively.

ANSWER

From Equations 7.12 and 7.13 and Table 7.3, we proceed as follows.

(a)
$$\begin{aligned} F &= \frac{(1.602 \times 10^{-19}\ \text{C})(-1.602 \times 10^{-19}\ \text{C})}{4\pi(8.854 \times 10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2})(1)(1 \times 10^{-9}\ \text{m})^2} \\ &= -2.31 \times 10^{-10}\ \text{N} \end{aligned}$$

(b)
$$\begin{aligned} F &= \frac{(1.602 \times 10^{-19}\ \text{C})(-1.602 \times 10^{-19}\ \text{C})}{4\pi(8.854 \times 10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2})(78.54)(1 \times 10^{-9}\ \text{m})^2} \\ &= -2.94 \times 10^{-12}\ \text{N} \end{aligned}$$

COMMENT

As expected, the attractive force between the ions is reduced by a factor of about 80 from vacuum to the aqueous environment. The negative sign convention for F denotes attraction.

7.3 Thermodynamics of Ions in Solution

In this section, we shall briefly examine the thermodynamic parameters of the solution process involving ionic compounds and the thermodynamic functions of the formation of ions in aqueous solution.

The constant-pressure dissolution of NaCl can be represented by

$$\begin{tikzcd} & \mathrm{Na^+}(g) + \mathrm{Cl^-}(g) \arrow[dd, "2"] \\ \mathrm{NaCl}(s) \arrow[ur, "1"] \arrow[dr, "3"'] & \\ & \mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq) \end{tikzcd}$$

The enthalpy change for process 1 corresponds to the energy required to separate one mole of ions from the crystal lattice to an infinite distance. This energy is called the *lattice energy* (U_0). The enthalpy change for process 3 is the enthalpy of solution, $\Delta_{\text{soln}}\overline{H}^\circ$, which is the heat absorbed or released when NaCl dissolves in a large amount of water. The heat or enthalpy of hydration, $\Delta_{\text{hydr}}\overline{H}^\circ$, for process 2 is given by Hess's law:

$$\Delta_{\text{hydr}}\overline{H}^\circ = \Delta_{\text{soln}}\overline{H}^\circ - U_0$$

The quantity $\Delta_{\text{soln}}\overline{H}^\circ$ is experimentally measurable; the value of U_0 can be estimated if the structure of the lattice is known. For NaCl, we have $U_0 = 787\ \text{kJ mol}^{-1}$ and $\Delta_{\text{soln}}\overline{H}^\circ = 3.8\ \text{kJ mol}^{-1}$, so that

$$\Delta_{\text{hydr}}\overline{H}^\circ = 3.8 - 787 = -783\ \text{kJ mol}^{-1}$$

Thus, the hydration of Na^+ and Cl^- ions by water releases a large amount of heat.

The enthalpy of hydration obtained above comes from both ions together. We often want to know the value of individual ions. In reality, we cannot study them separately, but their values can be obtained as follows. The enthalpy of hydration for the process

$$H^+(g) \rightarrow H^+(aq)$$

has been reliably estimated by theoretical methods as $-1089\ \text{kJ mol}^{-1}$. Using this value as a starting point, we can calculate the $\Delta_{\text{hydr}}\overline{H}^\circ$ values for individual anions such as F^-, Cl^-, Br^-, and I^- (from data on HF, HCl, HBr, and HI), and in turn obtain $\Delta_{\text{hydr}}\overline{H}^\circ$ values for Li^+, Na^+, K^+, and other cations (from data on alkali metal halides). Table 7.4 lists the standard $\Delta_{\text{hydr}}\overline{H}^\circ$ values for a number of ions. All the $\Delta_{\text{hydr}}\overline{H}^\circ$ values are negative because the hydration of a gaseous ion is an exothermic process. Furthermore, there is a correlation between ionic charge/radius and hydration enthalpy. The values of $\Delta_{\text{hydr}}\overline{H}^\circ$ are larger (more negative) for smaller ions than for large ions of the same charge. A smaller ion has a more concentrated charge and can interact more strongly with water molecules. Ions bearing higher charges also have larger $\Delta_{\text{hydr}}\overline{H}^\circ$ values.

The other quantity of interest is the entropy of hydration, $\Delta_{\text{hydr}}\overline{S}^\circ$. The hydration process results in considerable ordering of water molecules around each ion, so that $\Delta_{\text{hydr}}\overline{S}^\circ$ also is a negative quantity. As Table 7.4 shows, the variation in standard $\Delta_{\text{hydr}}\overline{S}^\circ$ with ionic radius closely corresponds to that for $\Delta_{\text{hydr}}\overline{H}^\circ$. Finally, note that there are two contributions to the entropy of solution, $\Delta_{\text{soln}}\overline{S}^\circ$. The first is the hydration process, which results in a decrease in entropy. The other is the entropy gained when the solid breaks up into ions, which can move freely in solution. The sign of $\Delta_{\text{soln}}\overline{S}^\circ$ depends on the magnitudes of these opposing factors.

The entropy of hydration for $H^+(g)$ is estimated to be $-109\ \text{J K}^{-1}\ \text{mol}^{-1}$.

Enthalpy, Entropy, and Gibbs Energy of Formation of Ions in Solution

Because ions cannot be studied separately, we cannot measure the standard molar enthalpy of formation, $\Delta_f\overline{H}^\circ$, of an individual ion. To get around this problem, we arbitrarily assign a zero value to the formation of the hydrogen ion—that is, $\Delta_f\overline{H}^\circ[H^+(aq)] = 0$—and then evaluate the $\Delta_f\overline{H}^\circ$ values of other ions relative to this scale. Consider the following reaction:

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq) \quad \Delta_r H^\circ = -167.2\ \text{kJ mol}^{-1}$$

The standard enthalpy of the reaction, which is an experimentally measurable quantity, can be expressed as

$$\Delta_r H^\circ = \Delta_f\overline{H}^\circ[H^+(aq)] + \Delta_f\overline{H}^\circ[Cl^-(aq)] - (\tfrac{1}{2})(0) - (\tfrac{1}{2})(0)$$

Table 7.4
Thermodynamic Values for the Hydration of Gaseous Ions at 298 K

Ion	$\frac{-\Delta_{\text{hydr}}\overline{H}^\circ}{\text{kJ mol}^{-1}}$	$\frac{-\Delta_{\text{hydr}}\overline{S}^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$	Ionic radius/Å
H^+	1089	109	—
Li^+	520	119	0.60
Na^+	405	89	0.95
K^+	314	51	1.33
Ag^+	468	94	1.26
Mg^{2+}	1926	268	0.65
Ca^{2+}	1579	209	0.99
Ba^{2+}	1309	159	1.35
Mn^{2+}	1832	243	0.80
Fe^{2+}	1950	272	0.76
Cu^{2+}	2092	259	0.72
Fe^{3+}	4355	460	0.64
F^-	506	151	1.36
Cl^-	378	96	1.81
Br^-	348	80	1.95
I^-	308	60	2.16

so that

$$\Delta_r H^\circ = \Delta_f \overline{H}^\circ[\text{Cl}^-(aq)]$$

or

$$\Delta_f \overline{H}^\circ[\text{Cl}^-(aq)] = -167.2 \text{ kJ mol}^{-1}$$

Once the value of $\Delta_f \overline{H}^\circ[\text{Cl}^-(aq)]$ has been determined, we can measure the $\Delta_r H^\circ$ of the reaction

$$\text{Na}(s) + \tfrac{1}{2}\text{Cl}_2(g) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$$

from which we can determine the value of $\Delta_f \overline{H}^\circ[\text{Na}^+(aq)]$ and so on.

Table 7.5 lists the $\Delta_f \overline{H}^\circ$ values of some common cations and anions. Two points are worth noting about this table. First, for aqueous solutions, the standard state at

Table 7.5
Thermodynamic Data for Aqueous Ions at 1 bar and 298 K

Ion	$\Delta_f\overline{H}°$/kJ mol^{-1}	$\Delta_f\overline{G}°$/kJ mol^{-1}	$\overline{S}°$/J K^{-1} mol^{-1}
H^+	0	0	0
Li^+	−278.5	−293.8	14.23
Na^+	−239.7	−261.9	50.9
K^+	−252.4	−283.3	102.5
Mg^{2+}	−466.9	−454.8	−138.1
Ca^{2+}	−542.8	−553.6	−53.1
Fe^{2+}	−89.1	−78.9	−137.7
Zn^{2+}	−153.9	−147.2	−112.1
Fe^{3+}	−48.5	−4.7	−315.9
OH^-	−229.6	−157.3	−10.75
F^-	−329.1	−276.5	−13.8
Cl^-	−167.2	−131.2	56.5
Br^-	−121.6	−104.0	82.4
I^-	−55.2	−51.57	111.3
CO_3^{2-}	−677.1	−527.8	−56.9
NO_3^-	−206.6	−110.5	146.4
PO_4^{3-}	−1277.4	−1018.7	−221.8

298 K is a hypothetical state defined as the ideal solution of unit molality at 1 bar pressure, in which the activity of the solute (the ion) is unity. The ion thus has the properties it would possess in an infinitely dilute solution, in which interactions between the ions are negligible. Second, all the $\Delta_f\overline{H}°$ values are *relative* values based on the $\Delta_f\overline{H}°[H^+(aq)] = 0$ scale.

We can determine the standard molar Gibbs energy of formation of ions and standard molar entropy of ions at 298 K in a similar fashion, that is, by arbitrarily assigning zero values to $\Delta_f\overline{G}°[H^+(aq)]$ and $\overline{S}°[H^+(aq)]$. These values are also listed in Table 7.5. Because the entropy values of ions in aqueous solution are relative to that of the H^+ ion, they may be either positive or negative. For example, the entropy of $Ca^{2+}(aq)$ is −53.1 J K^{-1} mol^{-1}, and that of $NO_3^-(aq)$ is 146.4 J K^{-1} mol^{-1}. The magnitude and sign of these entropies are influenced by the extent to which they can order the water molecules around themselves in solution, compared with $H^+(aq)$. Small, highly charged ions have negative entropy values, whereas large, singly charged ions have positive entropy values.

EXAMPLE 7.6

Use the standard enthalpy of the reaction

$$\mathrm{Na}(s) + \tfrac{1}{2}\mathrm{Cl}_2(g) \rightarrow \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq) \qquad \Delta_r H^\circ = -406.9\ \mathrm{kJ\ mol^{-1}}$$

to calculate the value of $\Delta_f \overline{H}^\circ[\mathrm{Na}^+(aq)]$.

ANSWER

The standard enthalpy of reaction is given by

$$\Delta_r H^\circ = \Delta_f \overline{H}^\circ[\mathrm{Na}^+(aq)] + \Delta_f \overline{H}^\circ[\mathrm{Cl}^-(aq)] - (0) - (\tfrac{1}{2})(0)$$

$$-406.9\ \mathrm{kJ\ mol^{-1}} = \Delta_f \overline{H}^\circ[\mathrm{Na}^+(aq)] - 167.2\ \mathrm{kJ\ mol^{-1}}$$

so

$$\Delta_f \overline{H}^\circ[\mathrm{Na}^+(aq)] = -239.7\ \mathrm{kJ\ mol^{-1}}$$

7.4 Ionic Activity

Our next task is to learn to write chemical potentials of electrolytes in solution. First, we shall discuss ideal electrolyte solutions in which the concentrations are expressed on the molality scale.

For an ideal NaCl solution, the chemical potential, μ_{NaCl}, is given by

$$\mu_{\mathrm{NaCl}} = \mu_{\mathrm{Na^+}} + \mu_{\mathrm{Cl^-}} \tag{7.14}$$

Because cations and anions cannot be studied individually, $\mu_{\mathrm{Na^+}}$ and $\mu_{\mathrm{Cl^-}}$ are not measurable. Nevertheless, we can express the chemical potentials of the cation and anion as

Each m term is divided by m° [1 mol (kg H_2O)$^{-1}$], so the logarithmic term is dimensionless.

$$\mu_{\mathrm{Na^+}} = \mu^\circ_{\mathrm{Na^+}} + RT \ln m_{\mathrm{Na^+}}$$

$$\mu_{\mathrm{Cl^-}} = \mu^\circ_{\mathrm{Cl^-}} + RT \ln m_{\mathrm{Cl^-}}$$

where $\mu^\circ_{\mathrm{Na^+}}$ and $\mu^\circ_{\mathrm{Cl^-}}$ are the standard chemical potentials of the ions. Equation 7.14 can now be written as

$$\mu_{\mathrm{NaCl}} = \mu^\circ_{\mathrm{NaCl}} + RT \ln m_{\mathrm{Na^+}} m_{\mathrm{Cl^-}}$$

where

$$\mu^\circ_{\text{NaCl}} = \mu^\circ_{\text{Na}^+} + \mu^\circ_{\text{Cl}^-}$$

In general, a salt with the formula $\text{M}_{\nu_+}\text{X}_{\nu_-}$ dissociates as follows:

$$\text{M}_{\nu_+}\text{X}_{\nu_-} \rightleftharpoons \nu_+\text{M}^{z_+} + \nu_-\text{X}^{z_-}$$

where ν_+ and ν_- are the numbers of cations and anions per unit and z_+ and z_- are the numbers of charges on the cation and anion, respectively. For NaCl, $\nu_+ = \nu_- = 1$, $z_+ = +1$, $z_- = -1$. For CaCl_2, $\nu_+ = 1$, $\nu_- = 2$, $z_+ = +2$, and $z_- = -1$. The chemical potential is given by

$$\mu = \nu_+\mu_+ + \nu_-\mu_- \tag{7.15}$$

where

$$\mu_+ = \mu^\circ_+ + RT\ln m_+$$

Recall that each m term is divided by m°.

and

$$\mu_- = \mu^\circ_- + RT\ln m_-$$

The molalities of the cation and anion are related to the molality of the salt originally dissolved in solution, m, as follows:

$$m_+ = \nu_+ m \quad m_- = \nu_- m$$

Substituting the expressions for μ_+ and μ_- into Equation 7.15 yields

$$\mu = (\nu_+\mu^\circ_+ + \nu_-\mu^\circ_-) + RT\ln m_+^{\nu_+} m_-^{\nu_-} \tag{7.16}$$

We define *mean ionic molality* ($m_\pm$) as a geometric mean (see Appendix A) of the individual ionic molalities

$$m_\pm = (m_+^{\nu_+} m_-^{\nu_-})^{1/\nu} \tag{7.17}$$

where $\nu = \nu_+ + \nu_-$, and Equation 7.16 becomes

$$\mu = (\nu_+\mu^\circ_+ + \nu_-\mu^\circ_-) + \nu RT\ln m_\pm \tag{7.18}$$

Mean ionic molality can also be expressed in terms of the molality of the solution, m. Because $m_+ = \nu_+ m$ and $m_- = \nu_- m$, we have

$$\begin{aligned} m_\pm &= [(\nu_+ m)^{\nu_+}(\nu_- m)^{\nu_-}]^{1/\nu} \\ &= m[(\nu_+^{\nu_+})(\nu_-^{\nu_-})]^{1/\nu} \end{aligned} \tag{7.19}$$

EXAMPLE 7.7

Write the expression for the chemical potential of $Mg_3(PO_4)_2$ in terms of the molality of the solution.

ANSWER

For $Mg_3(PO_4)_2$, we have $v_+ = 3$, $v_- = 2$, and $v = 5$. The mean ionic molality is

$$m_\pm = (m_+^3 m_-^2)^{1/5}$$

and the chemical potential is given by

$$\mu_{Mg_3(PO_4)_2} = \mu^\circ_{Mg_3(PO_4)_2} + 5RT \ln m_\pm$$

From Equation 7.19,

$$\begin{aligned} m_\pm &= m(3^3 \times 2^2)^{1/5} \\ &= 2.55m \end{aligned}$$

so that

$$\mu_{Mg_3(PO_4)_2} = \mu^\circ_{Mg_3(PO_4)_2} + 5RT \ln 2.55m$$

Unlike nonelectrolyte solutions, most electrolyte solutions behave nonideally. The reason is as follows. The intermolecular forces between uncharged species generally depend on $1/r^7$, where r is the distance of separation; a 0.1-m nonelectrolyte solution is considered ideal for most practical purposes. But Coulomb's law has a $1/r^2$ dependence (Figure 7.7). This dependence means that even in quite dilute solutions (e.g., 0.05 m), the electrostatic forces exerted by ions on one another are enough to cause a deviation from ideal behavior. Thus, in the vast majority of cases, we must replace molality with activity. By analogy to the mean ionic molality, we define the *mean ionic activity* $(a_\pm)$ as

$$a_\pm = (a_+^{v_+} a_-^{v_-})^{1/v} \tag{7.20}$$

where a_+ and a_- are the activities of the cation and anion, respectively. The mean ionic activity and mean ionic molality are related by the *mean ionic activity coefficient*, $\gamma_\pm$; that is,

$$a_\pm = \gamma_\pm m_\pm \tag{7.21}$$

where

$$\gamma_\pm = (\gamma_+^{v_+} \gamma_-^{v_-})^{1/v} \tag{7.22}$$

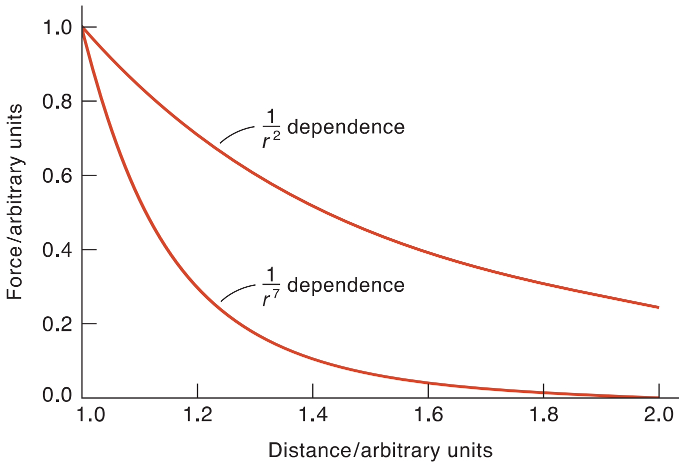

Figure 7.7
Comparison of dependence of attractive forces on distance, r: electrostatic forces ($1/r^2$) between ions and van der Waals forces ($1/r^7$) between molecules.

The chemical potential of a nonideal electrolyte solution is given by

$$\begin{aligned}\mu &= (\nu_+\mu_+^\circ + \nu_-\mu_-^\circ) + \nu RT \ln a_\pm \\ &= (\nu_+\mu_+^\circ + \nu_-\mu_-^\circ) + RT \ln a_\pm^\nu \\ &= (\nu_+\mu_+^\circ + \nu_-\mu_-^\circ) + RT \ln a \qquad (7.23)\end{aligned}$$

where the activity of the electrolyte, a, is related to its mean ionic activity by

$$a = a_\pm^\nu$$

Experimental values of $\gamma_\pm$ can be obtained from freezing-point depression and osmotic-pressure measurements* or electrochemical studies (see Chapter 9). Hence, the value of $a_\pm$ can be calculated from Equation 7.21. In the limiting case of infinite dilution ($m \to 0$), we have

$$\lim_{m \to 0} \gamma_\pm = 1$$

Figure 7.8 shows the plots of $\gamma_\pm$ versus m for several electrolytes. At very low concentrations, $\gamma_\pm$ approaches unity for all types of electrolytes. As the concentrations of electrolytes increase, deviations from ideality occur. The variation of $\gamma_\pm$ with concentration for dilute solutions can be explained by the Debye–Hückel theory, which is discussed next.

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* Interested readers should consult the standard physical chemistry texts listed in Chapter 1 for details of $\gamma_\pm$ measurements.

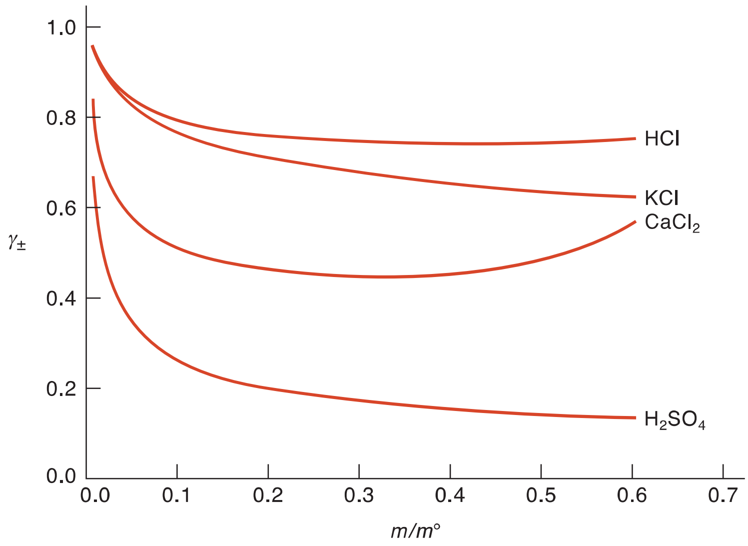

Figure 7.8
Plots of mean activity coefficient, $\gamma_\pm$ versus molality, m, for several electrolytes. At infinite dilution ($m \rightarrow 0$), the mean activity coefficient approaches unity.

EXAMPLE 7.8

Write expressions for the activities (a) of KCl, Na_2CrO_4, and $Al_2(SO_4)_3$ in terms of their molalities and mean ionic activity coefficients.

ANSWER

We need the relations $a = a_\pm^\nu = (\gamma_\pm m_\pm)^\nu$.

KCl: $\nu = 1 + 1 = 2;\ m_\pm = (m^2)^{1/2} = m$

Therefore, $a_{KCl} = m^2\gamma_\pm^2$

Na_2CrO_4: $\nu = 2 + 1 = 3;\ m_\pm = [(2m)^2(m)]^{1/3} = 4^{1/3}m$

Therefore, $a_{Na_2CrO_4} = 4m^3\gamma_\pm^3$

$Al_2(SO_4)_3$: $\nu = 2 + 3 = 5;\ m_\pm = [(2m)^2(3m)^3]^{1/5} = 108^{1/5}m$

Therefore, $a_{Al_2(SO_4)_3} = 108m^5\gamma_\pm^5$

7.5 Debye–Hückel Theory of Electrolytes

Our treatment of deviations from ideality by electrolyte solutions has been empirical: Using the ionic activities obtained from the activity coefficient and the known concentration, we calculate chemical potential, the equilibrium constant, and other properties. Missing in this approach is a physical interpretation of ionic behavior in solution. In 1923, Debye and the German chemist Erich Hückel (1896–1980) put forward a quantitative theory that has greatly advanced our knowledge of electrolyte solutions.

Based on a rather simple model, the Debye–Hückel theory enables us to calculate the value of $\gamma_\pm$ from the properties of the solution.

The mathematical details of Debye's and Hückel's treatment are too complex to present here. (Interested readers should consult the standard physical chemistry texts listed in Chapter 1.) Instead, we shall discuss the underlying assumptions and final results. Debye and Hückel began by assuming the following: (1) electrolytes are completely dissociated into ions in solution; (2) the solutions are dilute, with a concentration of 0.01 m or lower; and (3) on average, each ion is surrounded by ions of opposite charge, forming an *ionic atmosphere* (Figure 7.9a). Working from these assumptions, Debye and Hückel calculated the average electric potential at each ion caused by the presence of other ions in the ionic atmosphere. The Gibbs energy of the ions was then related to the activity coefficient of the individual ion. Because neither γ_+ nor γ_- could be measured directly, the final result is expressed in terms of the mean ionic activity coefficient of the electrolyte as follows:

$$\log \gamma_\pm = -0.509|z_+z_-|\sqrt{I} \tag{7.24}$$

where the | | signs denote the magnitude but not the sign of the product z_+z_-. Thus, for $CuSO_4$, we have $z_+ = 2$ and $z_- = -2$, but $|z_+z_-| = 4$. The quantity I, called the *ionic strength*, is defined as follows:

$$I = \tfrac{1}{2}\sum_i m_i z_i^2 \tag{7.25}$$

where m_i and z_i are the molality and the charge of the ith ion in the electrolyte, respectively. This quantity was first introduced by the American chemist Gilbert Newton Lewis (1875–1946), who noted that nonideality observed in electrolye solutions primarily stems from the *total* concentration of charges present rather than from the chemical nature of the individual ionic species. Equation 7.25 enables us to express the ionic concentrations for all types of electrolytes on a common basis so that we need not sort out the charges on the individual ions. Equation 7.24 is known as the *Debye–Hückel limiting law*. As written, it applies to an aqueous electrolyte solution at 298 K. Note that the right side of Equation 7.24 is dimensionless. Thus, the I term is assumed to be divided by $m°[1 \text{ mol (kg } H_2O)^{-1}]$.

The word "limiting" means that the law applies only to solutions in the limit of dilute concentrations.

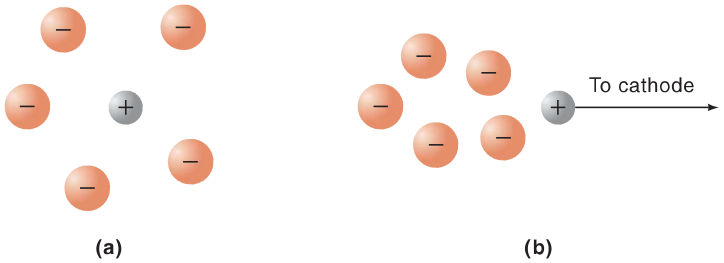

Figure 7.9
(a) Simplified presentation of an ionic atmosphere surrounding a cation in solution. (b) In a conductance measurement, the movement of a cation toward the cathode is retarded by the electric field exerted by the ionic atmosphere left behind.

EXAMPLE 7.9

Calculate the mean activity coefficient $(\gamma_\pm)$ of a 0.010 m aqueous solution of $CuSO_4$ at 298 K.

ANSWER

The ionic strength of the solution is given by Equation 7.25:

$$\begin{aligned} I &= \tfrac{1}{2}[(0.010\ m) \times 2^2 + (0.010\ m) \times (-2)^2] \\ &= 0.040\ m \end{aligned}$$

From Equation 7.26,

$$\begin{aligned} \log \gamma_\pm &= -0.509(2 \times 2)\sqrt{0.040} \\ &= -0.407 \end{aligned}$$

or

$$\gamma_\pm = 0.392$$

Experimentally, $\gamma_\pm$ is found to be 0.41 at the same concentration.

Two points are worth noting in applying Equation 7.24. First, in a solution containing several electrolytes, *all* the ions in solution contribute to the ionic strength, but z_+ and z_- refer only to the ionic charges of the particular electrolyte for which $\gamma_\pm$ is being calculated. Second, Equation 7.24 can be used to calculate the ionic activity coefficient of individual cations or anions. Thus, for the ith ion, we write

$$\log \gamma_i = -0.509 z_i^2 \sqrt{I} \qquad (7.26)$$

where z_i is the charge of the ion. The γ_+ and γ_- values calculated this way are related to $\gamma_\pm$ according to Equation 7.22.

Figure 7.10 shows calculated and measured values of log $\gamma_\pm$ at various ionic strengths. We can see Equation 7.24 holds quite well for dilute solutions but must be modified to account for the drastic deviations that occur at high concentrations of electrolytes. Several improvements and modifications have been applied to this equation for treating more concentrated solutions.

The generally good agreement between experimentally determined $\gamma_\pm$ values and those calculated using the Debye–Hückel theory provides strong support for the existence of an ionic atmosphere in solution. The model can be tested by taking a conductance measurement in a very strong electric field. In reality, ions do not move in a straight line toward the electrodes in a conductance cell but move along

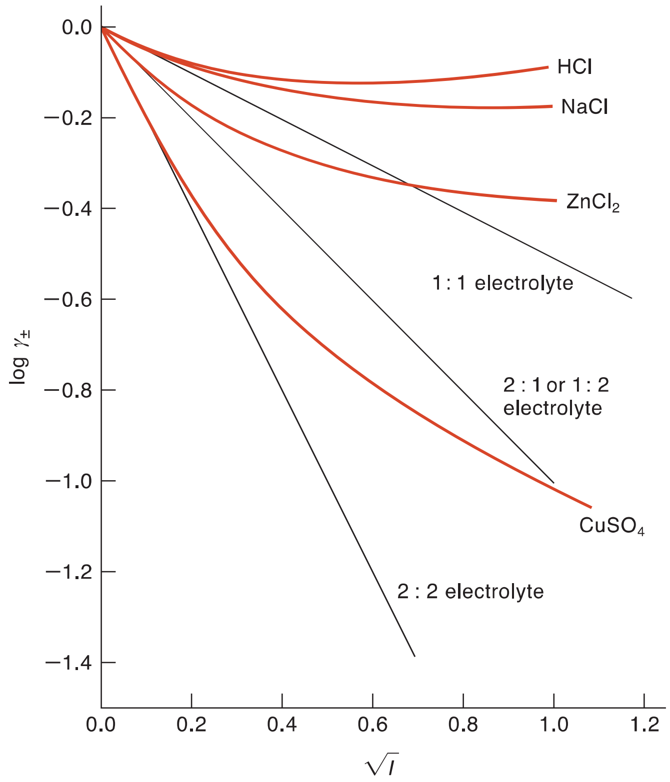

Figure 7.10
Plots of log $\gamma_\pm$ versus $\sqrt{I}$ for several electrolytes. The straight lines are those predicted by Equation 7.24.

a zigzag path. Microscopically, the solvent is not a continuous medium. Each ion actually "jumps" from one solvent hole to another, and as the ion moves across the solution, its ionic atmosphere is repeatedly being destroyed and formed again. The formation of an ionic atmosphere does not occur instantaneously but requires a finite amount of time, called the *relaxation time*, which is approximately 10^{-7} s in a 0.01-m solution. Under normal conditions of conductance measurement, the velocity of an ion is sufficiently slow so that the electrostatic force exerted by the atmosphere on the ion tends to retard its motion and hence to decrease the conductance (see Figure 7.9b). If the conductance measurement were carried out at a very strong electric field (approximately 2×10^5 V cm^{-1}), the ionic velocity would be approximately 10 cm s^{-1}. The radius of the ionic atmosphere in a 0.01-m solution is approximately 5 Å, or 5×10^{-8} cm, so that the time required for the ion to move out of the atmosphere is 5×10^{-8} cm/(10 cm s^{-1}), or 5×10^{-9} s, which is considerably shorter than the relaxation time. Consequently, the ion can move through the solution free of the retarding influence of the ionic atmosphere. The free movement leads to a marked increase in conductance. This phenomenon is called the *Wien effect*, after the German physicist Wilhelm Wien (1864–1928), who first performed the experiment in 1927. The Wien effect is one of the strongest pieces of evidence for the existence of an ionic atmosphere.

The Salting-In and Salting-Out Effects

The Debye–Hückel limiting law can be applied to study the solubility of proteins. The solubility of a protein in an aqueous solution depends on the temperature, pH, dielectric constant, ionic strength, and other characteristics of the medium. In this section, however, we shall focus on the influence of ionic strength.

Let us first investigate the effect of ionic strength on the solubility of an inorganic compound, AgCl. The solubility equilibrium is

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

The *thermodynamic* solubility product for the process, K_{sp}°, is given by

$$K_{\mathrm{sp}}^{\circ} = a_{\mathrm{Ag}^+} a_{\mathrm{Cl}^-}$$

The ionic activities are related to ionic concentrations as follows:

$$a_+ = \gamma_+ m_+ \quad \text{and} \quad a_- = \gamma_- m_-$$

so that

$$\begin{aligned} K_{\mathrm{sp}}^{\circ} &= \gamma_{\mathrm{Ag}^+} m_{\mathrm{Ag}^+} \gamma_{\mathrm{Cl}^-} m_{\mathrm{Cl}^-} \\ &= \gamma_{\mathrm{Ag}^+} \gamma_{\mathrm{Cl}^-} K_{\mathrm{sp}} \end{aligned}$$

where $K_{\mathrm{sp}} = m_{\mathrm{Ag}^+} m_{\mathrm{Cl}^-}$ is the *apparent* solubility product. The difference between the thermodynamic and apparent solubility products is as follows. As we can see, the apparent solubility product is expressed in molalities (or some other concentration unit). We can readily calculate this quantity if we know the amount of AgCl dissolved in a known amount of water to produce a saturated solution. Because of electrostatic forces, however, the dissolved ions are under the influence of their immediate neighbors. Consequently, the actual or effective number of ions is not the same as that calculated from the concentration of the solution. For example, if a cation forms a tight ion pair with an anion, then the actual number of species in solution, from a thermodynamic perspective, is one and not, as we would expect, two. This is the reason for replacing concentration with activity, which is the effective concentration. Thus, the thermodynamic solubility product represents the true value of the solubility product, which generally differs from the apparent solubility product. Because

$$\gamma_{\mathrm{Ag}^+} \gamma_{\mathrm{Cl}^-} = \gamma_{\pm}^2$$

we write

$$K_{\mathrm{sp}}^{\circ} = \gamma_{\pm}^2 K_{\mathrm{sp}}$$

Taking the logarithm of both sides and rearranging, we obtain

$$-\log \gamma_{\pm} = \log\left(\frac{K_{\mathrm{sp}}}{K_{\mathrm{sp}}^{\circ}}\right)^{1/2} = 0.509 |z_+ z_-| \sqrt{I}$$

The last equality in the above equation is the Debye–Hückel limiting law. The solubility product can be directly related to the molar solubility (S); for a 1:1 electrolyte,

$$(K_{\mathrm{sp}})^{1/2} = S \quad \text{and} \quad (K^{\circ}_{\mathrm{sp}})^{1/2} = S^{\circ}$$

where S and S° are the apparent and thermodynamic molar solubilities in mol $\mathrm{L^{-1}}$. Finally, we obtain the following equation relating the solubility of an electrolyte to the ionic strength of the solution:

$$\log \frac{S}{S^{\circ}} = 0.509|z_+z_-|\sqrt{I} \tag{7.27}$$

Note that the value of S° can be determined by plotting $\log S$ versus $\sqrt{I}$. The intercept on the $\log S$ axis ($I = 0$) gives $\log S^{\circ}$, and hence S°.

If AgCl is dissolved in water, its solubility (S) is 1.3×10^{-5} mol $\mathrm{L^{-1}}$. If it is dissolved in a KNO_3 solution, according to Equation 7.27, its solubility is greater because of the solution's increase in ionic strength. In a KNO_3 solution, the ionic strength is a sum of two concentrations, one from AgCl and the other from KNO_3. The increase in solubility, caused by the increase in ionic strength, is called the *salting-in effect*.

Equation 7.27 holds up only to a certain value of ionic strength. As the ionic strength of a solution increases further, it must be replaced by the following expression:

$$\log \frac{S}{S^{\circ}} = -K'I \tag{7.28}$$

where K' is a positive constant whose value depends on the nature of the solute and on the electrolyte present. The larger the solute molecule, the greater the value of K' is. Equation 7.28 tells us that the ratio of the solubilities in the region of high ionic strength actually decreases with I (note the negative sign). The decrease in solubility with increasing ionic strength of the solution is called the *salting-out effect*. This phenomenon can be explained in terms of hydration. Recall that hydration is the process that stabilizes ions in solution. At high salt concentrations, the availability of water molecules decreases, and so the solubility of ionic compounds also decreases. The salting-out effect is particularly noticeable with proteins, whose solubility in water is sensitive to ionic strength because of their large surface areas. Combining Equations 7.27 and 7.28, we have the approximate equation

$$\log \frac{S}{S^{\circ}} = 0.509|z_+z_-|\sqrt{I} - K'I \tag{7.29}$$

Equation 7.29 is applicable over a wider range of ionic strengths.

Figure 7.11 shows how the ionic strength of various inorganic salts affects the solubility of horse hemoglobin. As we can see, the protein exhibits a salting-in region at low ionic strengths.* As I increases, the curve goes through a maximum and eventually the slope becomes negative, indicating that the solubility decreases with increasing ionic strength. In this region, the second term in Equation 7.29 predominates. This trend is most pronounced for salts such as Na_2SO_4 and $(NH_4)_2SO_4$.

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* When I is less than unity, $\sqrt{I} > I$. Thus, at low ionic strengths, the first term in Equation 7.29 predominates.

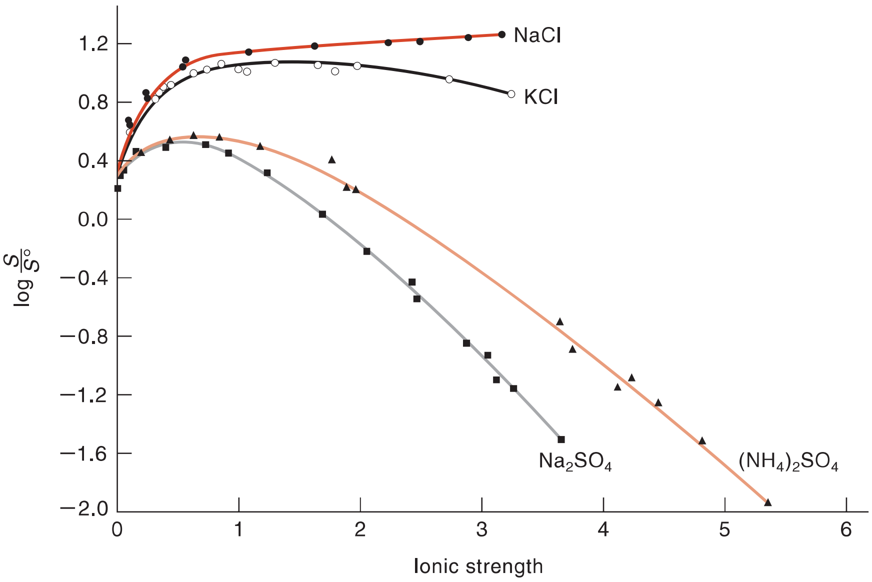

Figure 7.11

Plots of log($S/S°$) versus ionic strength for horse hemoglobin in the presence of various inorganic salts. Note that when $I = 0$, all the curves converge to the same point on the log($S/S°$) axis at zero and $S = S°$. [From Cohn, E., and J. Edsall, *Proteins, Amino Acids and Peptides*, © Litton Educational Publishing, 1943. Reprinted by permission of Van Nostrand Reinhold, New York.]

The practical value of the salting-out effect is that it enables us to precipitate proteins from solutions. In addition, the effect can also be used to purify proteins. Figure 7.12 shows the range of the salting-out phenomenon for several proteins in the presence of ammonium sulfate. Although the solubility of proteins is sensitive to the degree of hydration, the strength of binding of water molecules is not the same for all proteins. The relative solubility of different proteins at a particular ionic strength provides a means for selective precipitation. The point is that although higher ionic strengths are needed to salt out proteins, precipitation occurs over a small range of ionic strength, providing sharp separations.

7.6 Colligative Properties of Electrolyte Solutions

The colligative properties of an electrolyte solution are influenced by the number of ions present in solution. For example, we expect the aqueous freezing-point depression caused by a 0.01-m solution of NaCl to be twice that effected by a 0.01-m sucrose solution, assuming complete dissociation of the former. For incompletely dissociated salts, the relationship is more complicated, but understanding it provides us with another way to measure an electrolyte's degree of dissociation.

Let us define a factor i, called the van't Hoff factor (after the Dutch chemist Jacobus Hendricus van't Hoff, 1852–1911), as follows:

$$i = \frac{\text{actual number of particles in solution at equilibrium}}{\text{number of particles in solution before dissociation}} \tag{7.30}$$

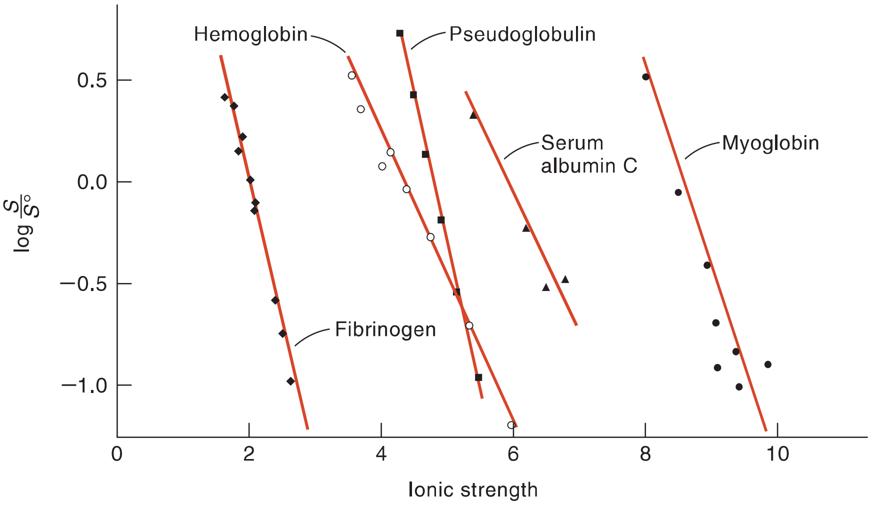

Figure 7.12
Plots of (*S*/*S*°) versus ionic strength for several proteins in aqueous ammonium sulfate, demonstrating the salting-out effect. [From Cohn, E. J., *Chem. Rev.* **19**, 241 (1936). Used by permission of Williams & Wilkins, Baltimore.]

If a solution contains N units of an electrolyte, and if α is the degree of dissociation,

$$\begin{array}{cccc} M_{\nu_+}X_{\nu_-} & \rightleftharpoons & \nu_+M^{z+} & + \quad \nu_-X^{z-} \\ N(1-\alpha) & & N\nu_+\alpha & N\nu_-\alpha \end{array}$$

there will be $N(1-\alpha)$ undissociated units and $(N\nu_+\alpha + N\nu_-\alpha)$, or $N\nu\alpha$ ions in solution at equilibrium, where $\nu = \nu_+ + \nu_-$. We can now write the van't Hoff factor as

$$i = \frac{N(1-\alpha) + N\nu\alpha}{N} = 1 - \alpha + \nu\alpha$$

and

$$\alpha = \frac{i-1}{\nu-1} \tag{7.31}$$

For strong electrolytes, i is approximately equal to the number of ions formed from each unit of the electrolyte; for example, $i \approx 2$ for NaCl and $CuSO_4$; $i \approx 3$ for K_2SO_4 and $BaCl_2$, and so on. The value of i decreases with increasing concentration of the solution, which is attributed to the formation of ion pairs.

The presence of ion pairs will also affect the colligative properties because it decreases the number of free particles in solution. In general, formation of ion pairs is most pronounced between highly charged cations and anions and in media of low dielectric constants. In an aqueous solution of $Ca(NO_3)_2$, for example, the Ca^{2+} and NO_3^- ions form ion pairs as follows:

$$Ca^{2+}(aq) + NO_3^-(aq) \rightleftharpoons Ca(NO_3)^+(aq)$$

The equilibrium constants for such ion pairing are not accurately known, however, thus making calculations of colligative properties of electrolyte solutions difficult. A recent study* showed that deviation from colligative properties for many electrolyte solutions is not the result of ion pair formation, but rather of hydration. In an electrolyte solution the cations and anions can tie up large numbers of water molecules in their hydration spheres, thus reducing the number of free water molecules in the bulk solvent. Deviations disappear when the correct number of water molecules in the hydration sphere is subtracted from the total water solvent molecules in calculating the concentrations (molality or molarity) of the solution.

EXAMPLE 7.10

The osmotic pressures of a 0.01 *m* solution of $CaCl_2$ and a 0.01 *m* sucrose solution at 298 K are 0.605 atm and 0.224 atm, respectively. Calculate the van't Hoff factor and the degree of dissociation for $CaCl_2$. Assume ideal behavior.

ANSWER

As far as osmotic pressure measurements are concerned, the main difference between calcium chloride and sucrose is that only $CaCl_2$ can dissociate into ions (Ca^{2+} and Cl^-). Otherwise, equal concentrations of $CaCl_2$ and sucrose solutions would have the same osmotic pressure. Because the osmotic pressure of a solution is directly proportional to the number of particles present, we can calculate the van't Hoff factor for the $CaCl_2$ solution as follows. From Equation 7.30,

$$i = \frac{0.605\ \text{atm}}{0.224\ \text{atm}} = 2.70$$

Because for $CaCl_2$, $\nu_+ = 1$, and $\nu_- = 2$, we have $\nu = 3$ and

$$\alpha = \frac{2.70 - 1}{3 - 1} = 0.85$$

Finally, we note that the equations used to determine the colligative properties of nonelectrolyte solutions (Equations 6.39, 6.40, and 6.46) must be modified for electrolyte solutions as follows:

$$\Delta T = K_b(im_2) \tag{7.32}$$

$$\Delta T = K_f(im_2) \tag{7.33}$$

$$\Pi = iMRT \tag{7.34}$$

Ideal behavior is assumed for the electrolyte solutions, so we use concentrations instead of activities.

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* A. A. Zavitsas, *J. Phys. Chem.* **105**, 7805 (2001).

The Donnan Effect

The Donnan effect (after the British chemist Frederick George Donnan, 1870–1956) has its starting point in the treatment of osmotic pressure. It describes the equilibrium distribution of small diffusible ions on the two sides of a membrane that is freely permeable to these ions but impermeable to macromolecular ions, in the presence of a macromolecular electrolyte on one side of the membrane.

Suppose that a cell is separated into two parts by a semipermeable membrane that allows the diffusion of water and small ions but not protein molecules. Let us consider the following three cases.

Case 1. The protein solution is placed in the left compartment; water is placed in the right compartment. We assume that the protein molecules are neutral species.* Let the concentration of the protein solution be c (mol L^{-1}) so that the osmotic pressure of the solution, according to Equation 6.46, is given by

$$\Pi_1 = cRT$$

Thus, from a measurement of the osmotic pressure, we can readily determine the molar mass of the protein molecule.

Case 2. In this case, the protein is the anion of the sodium salt, Na^+P^-, which we assume to be a strong electrolyte. Again, the protein solution of concentration c is placed in the left compartment, and pure water is in the right compartment. To maintain electrical neutrality, all of the Na^+ ions remain in the left compartment; the osmotic pressure of the solution now becomes

$$\Pi_2 = (c + c)RT = 2cRT$$

Because $\Pi_2 = 2\Pi_1$, it follows that the molar mass determined in this case will be only half of the true molar mass. (From Equation 6.47 we have $\mathscr{M}_2 = c_2RT/\Pi$, so that doubling Π would decrease the value of $\mathscr{M}_2$ by half.) In practice, the situation is actually much worse, because the protein ion may bear as many as 20 or 30 net negative (or positive) charges. In the early days of protein-molar-mass determination by osmotic pressure, disastrously poor results were obtained before the dissociation process was recognized and efforts made to correct for it (see Appendix 7.2 on p. 298).

Case 3. We start with an arrangement similar to that discussed in Case 2 and then add NaCl (of concentration b in mol L^{-1}) to the right compartment (Figure 7.13a). At equilibrium, a certain amount, x (mol L^{-1}), of Na^+ and Cl^- ions has diffused through the membrane from right to left, creating a final state shown in Figure 7.13b. Both sides of the membrane must be electrically neutral: in each compartment the number of cations equals the number of anions. The condition of equilibrium enables us to equate the chemical potentials of NaCl in the two compartments as follows (see Equation 7.23):

$$(\mu_{\text{NaCl}})^{\text{L}} = (\mu_{\text{NaCl}})^{\text{R}}$$

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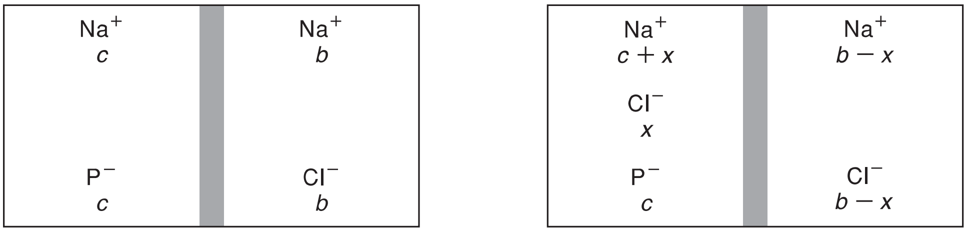
* Proteins are ampholytes, that is, they possess both acidic and basic properties. Depending on the pH of the medium, a protein can exist as an anion, a cation, or a neutral species.



(a) (b)

Figure 7.13
Schematic representation of the Donnan effect. (a) Before diffusion has begun. (b) At equilibrium. The membrane separating the left and right compartments is permeable to all but the P^- ions. The volumes in the two compartments are equal and assumed to remain constant.

or

$$(\mu^\circ + 2RT \ln a_\pm)^{\mathrm{L}}_{\mathrm{NaCl}} = (\mu^\circ + 2RT \ln a_\pm)^{\mathrm{R}}_{\mathrm{NaCl}}$$

Because μ°, the standard chemical potential, is the same on both sides, we obtain

$$(a_\pm)^{\mathrm{L}}_{\mathrm{NaCl}} = (a_\pm)^{\mathrm{R}}_{\mathrm{NaCl}}$$

From Equation 7.20,

$$(a_{\mathrm{Na^+}} a_{\mathrm{Cl^-}})^{\mathrm{L}} = (a_{\mathrm{Na^+}} a_{\mathrm{Cl^-}})^{\mathrm{R}}$$

If the solutions are dilute, then the ionic activities may be replaced by the corresponding concentrations, that is, $a_{\mathrm{Na^+}} = [\mathrm{Na^+}]$ and $a_{\mathrm{Cl^-}} = [\mathrm{Cl^-}]$. Hence,

$$([\mathrm{Na^+}][\mathrm{Cl^-}])^{\mathrm{L}} = ([\mathrm{Na^+}][\mathrm{Cl^-}])^{\mathrm{R}}$$

or

$$(c + x)x = (b - x)(b - x)$$

Table 7.6
The Donnan Effect and Osmotic Pressure

Initial concentration		Equilibrium concentration		
Left compartment	Right compartment	Left compartment		
$c = [\mathrm{Na^+}] = [\mathrm{P^-}]$	$b = [\mathrm{Na^+}] = [\mathrm{Cl^-}]$	$(c + x) = [\mathrm{Na^+}]$	$c = [\mathrm{P^-}]$	$x = [\mathrm{Cl^-}]$
0.1	0	0.1	0.1	0
0.1	0.01	0.1008	0.1	0.00083
0.1	0.1	0.1333	0.1	0.0333
0.1	1.0	0.576	0.1	0.476
0.1	10.0	5.075	0.1	4.975
$[\mathrm{P}] = 0.1$	0	0	$[\mathrm{P}] = 0.1$	0

Solving for x, we obtain

$$x = \frac{b^2}{c + 2b} \tag{7.35}$$

Equation 7.35 says that the amount of NaCl, x, that diffuses from right to left is inversely proportional to the concentration of the nondiffusible ion (P^-), c, in the left compartment. This unequal distribution of the diffusible ions (Na^+ and Cl^-) in the two compartments is the result of the Donnan effect.

In this case, then, the osmotic pressure of the protein solution is determined by the *difference* between the number of particles in the left compartment and the number in the right compartment. We write

$$\Pi_3 = [\underbrace{(c + c + x + x)}_{\text{left compartment}} - \underbrace{2(b - x)}_{\text{right compartment}}]RT = (2c + 4x - 2b)RT$$

From Equation 7.35,

$$\Pi_3 = \left(2c + \frac{4b^2}{c + 2b} - 2b\right)RT = \left(\frac{2c^2 + 2cb}{c + 2b}\right)RT$$

Two limiting cases may be applied to the equation above. If $b \ll c$, $\Pi_3 = 2cRT$, which gives the same result as Case 2. On the other hand, if $b \gg c$, $\Pi_3 = cRT$, which is identical to Case 1. The important conclusion we reach is that the presence of NaCl in the right compartment decreases the osmotic pressure of the protein solution compared to Case 2 and therefore minimizes the Donnan effect. When a very large amount of NaCl is present, the Donnan effect can be effectively eliminated. In general, we have $\Pi_1 \le \Pi_3 \le \Pi_2$. Because proteins are usually studied in buffer solutions that contain ionic species, the osmotic pressure measured will be less than in the case in which pure water is the solvent. Table 7.6 shows the Donnan effect for the NaCl example at several concentrations and the corresponding osmotic pressure at 298 K.

Equilibrium concentration		Percent NaCl transferred from right to left	Osmotic pressure/atm	Case
Right compartment				
$(b - x) = [Na^+]$	$(b - x) = [Cl^-]$			
0	0	0	4.90	2
0.00917	0.00917	8.3	4.48	3
0.0667	0.0667	33.3	3.26	3
0.524	0.524	47.6	2.56	3
5.025	5.025	49.75	2.46	3
0	0	0	2.45	1

Another way to eliminate the Donnan effect is to choose a pH at which the protein has no net charge, called the *isoelectric point*. At this pH, the distribution of any diffusible ion will always be equal in both compartments. This method is difficult to apply because most proteins are least soluble at their isoelectric points.

The discussion of the Donnan effect was simplified by assuming ideal behavior and no change in either the pH or the volume of the solution. In addition, for simplicity, we used a common diffusible ion, Na^+, in deriving Equation 7.35.

Understanding the Donnan effect is essential in studying the distribution of ions across the membranes of living organisms and membrane potentials (see Chapter 9).

Key Equations

$\Lambda = \dfrac{\kappa}{c}$	(Molar conductance)	(7.4)
$\Lambda_0 = \nu_+\lambda_0^+ + \nu_-\lambda_0^-$	(Kohlrausch's law of independent migration)	(7.6)
$\dfrac{1}{\Lambda} = \dfrac{1}{K_a\Lambda_0^2}(\Lambda c) + \dfrac{1}{\Lambda_0}$	(Ostwald dilution law)	(7.9)
$F = \dfrac{q_A q_B}{4\pi\varepsilon_0 r^2}$	(Coulomb's law)	(7.12)
$m_\pm = (m_+^{\nu_+} m_-^{\nu_-})^{1/\nu}$	(Mean ionic molality)	(7.17)
$a_\pm = (a_+^{\nu_+} a_-^{\nu_-})^{1/\nu}$	(Mean ionic activity)	(7.20)
$a_\pm = \gamma_\pm m_\pm$	(Definition of $\gamma_\pm$)	(7.21)
$\gamma_\pm = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/\nu}$	(Mean ionic activity coefficient)	(7.22)
$\log \gamma_\pm = -0.509\lvert z_+ z_-\rvert\sqrt{I}$	(Debye–Hückel limiting law)	(7.24)
$I = \frac{1}{2}\sum_i m_i z_i^2$	(Ionic strength)	(7.25)
$\log \dfrac{S}{S^\circ} = 0.509\lvert z_+ z_-\rvert\sqrt{I}$	(Salting-in effect)	(7.27)
$\log \dfrac{S}{S^\circ} = -K'I$	(Salting-out effect)	(7.28)

APPENDIX 7.1

Notes on Electrostatics

An electric charge (q_A) is said to produce an *electric field* (E) in the space around itself. This field exerts a force on any charge (q_B) within that space. According to Coulomb's law, the potential energy (V) between these two charges separated by distance r in a vacuum is given by

Potential energy V has units of energy Joule (J) or electron volt (eV); 1 eV = 1.602×10^{-19} J.

$$V = \frac{q_A q_B}{4\pi\varepsilon_0 r} \tag{1}$$

and the electrostatic force, F, between the charges is

$$F = \frac{q_A q_B}{4\pi\varepsilon_0 r^2} \tag{2}$$

where ε_0 is the permittivity of the vacuum (see p. 272). The electric field is the electrostatic force on a unit positive charge. Thus, the electric field at q_B due to q_A is F divided by q_B, or

$$E = \frac{q_A q_B}{4\pi\varepsilon_0 r^2 q_B} = \frac{q_A}{4\pi\varepsilon_0 r^2} \tag{3}$$

Note that E is a vector and is directed away from q_A toward q_B. Its units are V m^{-1} or V cm^{-1}.

Another important property of the electric field is its *electric potential*, ϕ, which is the potential energy of a unit positive charge in the electric field. Its units are J/C or V (1 J = 1 C × 1 V). A unit positive charge in an electric field E experiences a force equal in magnitude to E. When the charge is moved through a certain distance, dr, the potential energy change is equal to $qEdr$ or Edr because $q = 1$ C. Because the repulsive potential energy increases as the unit positive charge comes closer to the positive charge q_A that generates the electric field, the change in potential energy, $d\phi$, is $-Edr$. (The negative sign ensures that as dr decreases, $-Edr$ is a positive quantity, signifying the increase in repulsion between the two positive charges.) The electric potential at a certain point at a distance r from the charge q_A is the potential energy change that occurs in bringing the unit positive charge from infinity to distance r from the charge:

$$\phi = -\int_{r=\infty}^{r=r} Edr = -\int_{r=\infty}^{r=r} \frac{q_A}{4\pi\varepsilon_0 r^2} dr = \frac{q_A}{4\pi\varepsilon_0 r} \tag{4}$$

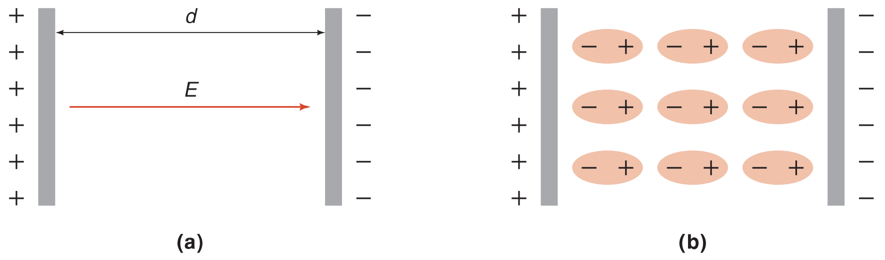


Figure 7.14
(a) The charge separation of a capacitor. The electric field, E, is directed from the positive plate to the negative plate, separated by distance d. With a vacuum between the plates, the dielectric constant is ε_0. (b) Orientation of the dipoles of a dielectric in a capacitor. The degree of orientation is exaggerated. The dielectric material decreases the electric field between the capacitor plates. The dielectric constant of the medium is ε.

Note that $\phi = 0$ at $r = \infty$. From Equation 4, we can define the electric potential difference between points 1 and 2 in an electric field as the work done in bringing a unit charge from 1 to 2; that is,

$$\Delta\phi = \phi_2 - \phi_1 \tag{5}$$

This difference is commonly referred to as the voltage between points 1 and 2.

Dielectric Constant (ε) and Capacitance (C)

When a nonconducting substance (called a *dielectric*) is placed between two flat, parallel metal plates with opposite charges that are equal in magnitude (called a *capacitor*), the substance becomes polarized. The reason is that the electric field of the plates either orients the permanent dipoles of the dielectric or induces dipole moments, as shown in Figure 7.14. The *dielectric constant* of the substance is defined as

$$\varepsilon = \frac{E_0}{E} \tag{6}$$

where E_0 and E are the electric fields in the space between the plates of the capacitor in the absence of a dielectric (a vacuum) and presence of a dielectric, respectively. Keep in mind that the orientation of the dipoles (or induced dipoles) reduces the electric field between the capacitor plates so that $E < E_0$ and $\varepsilon > 1$. For ions in aqueous solution, this decrease in electric field reduces the attraction between the cation and the anion (see Figure 7.6).

The *capacitance* (C) of a capacitor measures its ability to hold charges for a given electric potential difference between the plates; that is, it is given by the ratio of charge to potential difference. The capacitances of a capacitor, when the space between the plates is filled with a dielectric (C) and with a vacuum (C_0), are given respectively by

$$C = \frac{Q}{\Delta\phi} \tag{7}$$

and

$$C_0 = \frac{Q}{\Delta\phi_0} \tag{8}$$

Because $\Delta\phi = Ed$, where d is the distance between the plates, Equation 6 can also be written as

$$\varepsilon = \frac{(\Delta\phi_0/d)}{(\Delta\phi/d)} = \frac{(Q/C_0)}{(Q/C)} = \frac{C}{C_0} \tag{9}$$

Capacitance is an experimentally measurable quantity, so the dielectric constant of a substance can be determined. It has the unit farad (F), where 1 F = 1 C/V. Note that the ratio C/C_0 in Equation 9 makes ε a dimensionless quantity.

APPENDIX 7.2

The Donnan Effect Involving Proteins Bearing Multiple Charges

For a protein at a pH other than its isoelectric point, at which it will possess either a net positive or net negative charge, an additional factor must be considered; that is, the counterions needed to maintain charge neutrality. In the chapter, we considered the simple case where the protein bears only one negative charge. Here we deal with the situation in which a protein bears a number of negative charges (z). We assume that the protein, $Na_z^+P^{z-}$, is a strong electrolyte so that

$$Na_z^+P^{z-} \rightarrow zNa^+ + P^{z-}$$

Referring to Figure 7.13, we shall consider two cases.

Case 1

The protein solution is placed in the left compartment and water in the right compartment. The osmotic pressure of the solution (Π_1) is given by

$$\Pi_1 = (z + 1)cRT$$

where c is the concentration (molarity) of the protein solution. Because z is typically of the order of 30, using this arrangement to determine the molar mass of the protein yields a value that is only $\frac{1}{30}$ of the true value.

Case 2

Again the protein solution is placed in the left compartment, but a NaCl solution is placed in the right compartment. The requirement that the chemical potential of a component be the same throughout the system applies to the NaCl as well as to the water. To attain equilibrium. NaCl will move from the right to the left compartment. We can calculate the actual amount of NaCl that is transported. The initial molar concentration of $Na_z^+P^{z-}$ is c, and that of NaCl is b. At equilibrium, the concentrations are

$$[P^{z-}]^L = c \quad [Na^+]^L = (zc + x) \quad [Cl^-]^L = x$$

and

$$[Na^+]^R = (b - x) \quad [Cl^-]^R = (b - x)$$

where x is the amount of NaCl transported from right to left.

Because $(\mu_{NaCl})^L = (\mu_{NaCl})^R$ at equilibrium and for dilute solutions, we replace activities with concentrations so that

$$([Na^+][Cl^-])^L = ([Na^+][Cl^-])^R$$

or

$$(zc + x)(x) = (b - x)(b - x)$$

$$x = \frac{b^2}{zc + 2b}$$

The osmotic pressure (Π_2), which is proportional to the difference in solute concentration between the two sides, is now given by

$$\Pi_2 = [\underbrace{(c + zc + x + x)}_{\text{left compartment}} - \underbrace{(b - x + b - x)}_{\text{right compartment}}]RT$$

or

$$\Pi_2 = (c + zc - 2b + 4x)RT$$

Substituting for x, we obtain

$$\Pi_2 = \left(c + zc - 2b + \frac{4b^2}{zc + 2b}\right)RT$$

$$= \frac{zc^2 + 2cb + z^2c^2}{zc + 2b}RT \qquad (1)$$

Equation 1 was derived assuming no change in either the pH or the volume of the solutions. Two limiting cases follow.

If $b \ll zc$, (the salt concentration is much less than the protein concentration), then

$$\Pi_2 = \frac{zc^2 + z^2c^2}{zc}RT = (zc + c)RT$$

$$= (z + 1)cRT$$

$$= \Pi_1$$

If $b \gg z^2c$ (the salt concentration is much greater than the protein concentration),* then

$$\Pi_2 = \frac{2cb}{2b}RT = cRT \qquad (2)$$

In this limiting case, the osmotic pressure approaches that of the pure isoelectric protein. In effect, the added salt reduces (and at high enough salt concentrations, eliminates) the Donnan effect. Under these conditions, the molar mass determined by osmotic pressure measurement would correspond closely to the true value.

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* In practice, $c \le 1 \times 10^{-4}$ M, $z \le 30$, so that $z^2c \lesssim 0.1$ M. Thus, for this limiting case to hold, the concentration of the added salt should be about 1 M.

Suggestions for Further Reading

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Problems

Ionic Conductance

7.1 The resistance of a 0.010 *M* NaCl solution is 172 Ω. If the molar conductance of the solution is 153 Ω^{-1} mol^{-1} cm^2, what is the cell constant?

7.2 Using the cell described in Problem 7.1, a student determined the resistance of a 0.086 *M* KCl solution to be 20.4 Ω. Calculate the molar conductance of this solution.

7.3 The cell constant (l/A) of a conductance cell is 388.1 m^{-1}. At 25°C, the resistance of a 4.8×10^{-4} mol L^{-1} aqueous solution of sodium chloride is 6.4×10^4 Ω and that of a sample of water is 7.4×10^6 Ω. Calculate the molar conductance of the NaCl in solution at this concentration.

7.4 Given that the measurement of Λ_0 for weak electrolytes is generally difficult to obtain, how would you deduce the value of Λ_0 for CH_3COOH from the data listed in Table 7.1? (*Hint:* Consider CH_3COONa, HCl, and NaCl.)

7.5 A simple way to determine the salinity of water is to measure its conductivity and assume that the conductivity is entirely due to sodium chloride. In a particular experiment, the resistance of a sample solution is found to be 254 Ω. The resistance of a 0.050 *M* KCl solution measured in the same cell is 467 Ω. Estimate the concentration of NaCl in the solution. (*Hint:* First derive an equation relating R to Λ and c and then use Λ_0 values for Λ.)

7.6 A conductance cell consists of two electrodes, each with an area of 4.2×10^{-4} m^2, separated by 0.020 m. The resistance of the cell when filled with a 6.3×10^{-4} *M* KNO_3 solution is 26.7 Ω. What is the molar conductance of the solution?

7.7 Referring to Figure 7.4, explain why the slope of conductance versus volume of NaOH added rises right at the start if the acid employed in the titration is weak.

Solubility

7.8 Calculate the solubility of $BaSO_4$ (in g L^{-1}) in **(a)** water and **(b)** a 6.5×10^{-5} *M* $MgSO_4$ solution. The solubility product of $BaSO_4$ is 1.1×10^{-10}. Assume ideal behavior.

7.9 The thermodynamic solubility product of AgCl is 1.6×10^{-10}. What is $[Ag^+]$ in **(a)** a 0.020 *M* KNO_3 solution and **(b)** a 0.020 *M* KCl solution?

7.10 Referring to Problem 7.9, calculate the value of $\Delta G°$ for the process

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

to yield a saturated solution at 298 K. (*Hint:* Use the well-known equation $\Delta G° = -RT \ln K$.)

7.11 The apparent solubility products of CdS and CaF_2 at 25°C are 3.8×10^{-29} and 4.0×10^{-11}, respectively. Calculate the solubility (g/100 g of solution) of these compounds.

7.12 Oxalic acid, $(COOH)_2$, is a poisonous compound present in many plants and vegetables, including spinach. Calcium oxalate is only slightly soluble in water ($K_{sp} = 3.0 \times 10^{-9}$ at 25°C) and its ingestion can result in kidney stones. Calculate **(a)** the apparent and thermodynamic solubility of calcium oxalate in water, and **(b)** the concentrations of calcium and oxalate ions in a 0.010 *M* $Ca(NO_3)_2$ solution. Assume ideal behavior in **(b)**.

Ionic Activity

7.13 Express the mean activity, mean activity coefficient, and mean molality in terms of the individual ionic quantities (a_+, a_-, γ_+, γ_-, m_+, and m_-) for the following electrolytes: KI, $SrSO_4$, $CaCl_2$, Li_2CO_3, $K_3Fe(CN)_6$, and $K_4Fe(CN)_6$. [*Hint*: $Fe(CN)_6^{4-}$ is a complex ion.]

7.14 Calculate the ionic strength and the mean activity coefficient for the following solutions at 298 K: (**a**) 0.10 *m* NaCl, (**b**) 0.010 *m* $MgCl_2$, and (**c**) 0.10 *m* $K_4Fe(CN)_6$.

7.15 The mean activity coefficient of a 0.010 *m* H_2SO_4 solution is 0.544. What is its mean ionic activity?

7.16 A 0.20 *m* $Mg(NO_3)_2$ solution has a mean ionic activity coefficient of 0.13 at 25°C. Calculate the mean molality, the mean ionic activity, and the activity of the compound.

Debye–Hückel Limiting Law

7.17 The Debye–Hückel limiting law is more reliable for 1:1 electrolytes than for 2:2 electrolytes. Explain.

7.18 The size of the ionic atmosphere, called the Debye radius, is $1/\kappa$, where κ is given by

$$\kappa = \left(\frac{e^2 N_A}{\varepsilon_0 \varepsilon k_B T}\right)^{1/2} \sqrt{I}$$

where e is the electronic charge, N_A Avogadro's constant, ε_0 the permittivity of vacuum ($8.854 \times 10^{-12}\ C^2\ N^{-1}\ m^{-2}$), ε the dielectric constant of the solvent, k_B the Boltzmann constant, T the absolute temperature, and I the ionic strength (see the physical chemistry texts listed in Chapter 1). Calculate the Debye radius in a 0.010 *m* aqueous Na_2SO_4 solution at 25°C.

7.19 Explain why it is preferable to take the geometric mean rather than the arithmetic mean when defining mean activity, mean molality, and mean activity coefficient.

Colligative Properties

7.20 The freezing-point depression of a 0.010 *m* acetic acid solution is 0.0193 K. Calculate the degree of dissociation for acetic acid at this concentration.

7.21 A 0.010 *m* aqueous solution of the ionic compound $Co(NH_3)_5Cl_3$ has a freezing point depression of 0.0558 K. What can you conclude about its structure? Assume the compound is a strong electrolyte.

7.22 The osmotic pressure of blood plasma is approximately 7.5 atm at 37°C. Estimate the total concentration of dissolved species and the freezing point of blood plasma.

7.23 Calculate the ionic strength of a 0.0020 *m* aqueous solution of $MgCl_2$ at 298 K. Use the Debye–Hückel limiting law to estimate (**a**) the activity coefficients of the Mg^{2+} and Cl^- ions in this solution and (**b**) the mean ionic activity coefficients of these ions.

7.24 Referring to Figure 7.13, calculate the osmotic pressure for the following cases at 298 K: (**a**) The left compartment contains 200 g of hemoglobin in 1 liter of solution; the right compartment contains pure water. (**b**) The left compartment contains the same hemoglobin solution as in part (**a**), and the right compartment initially contains 6.0 g of NaCl in 1 liter of solution. Assume that the pH of the solution is such that the hemoglobin molecules are in the $Na^+\ Hb^-$ form. (The molar mass of hemoglobin is 65,000 g mol^{-1}.)

Additional Problems

7.25 From the following data, calculate the heat of solution for KI:

	NaCl	NaI	KCl	KI
Lattice energy/kJ mol^{-1}	787	700	716	643
Heat of solution/kJ mol^{-1}	3.8	−5.1	17.1	?

7.26 From the data in Table 7.2, determine Λ_0 for H_2O. Given that the specific conductance (κ) for water is $5.7 \times 10^{-8}\ \Omega^{-1}\ \text{cm}^{-1}$, calculate the ion product (K_w) of water at 298 K.

7.27 In this chapter (see Figures 7.2 and 7.11) and in Chapter 6 (see Π measurements in Figure 6.19), we extrapolated concentration-dependent values to zero solute concentration. Explain what these extrapolated values mean physically and why they differ from the value obtained for the pure solvent.

7.28 (**a**) The root cells of plants contain a solution that is hypertonic in relation to water in the soil. Thus, water can move into the roots by osmosis. Explain why salts (NaCl and $CaCl_2$) spread on roads to melt ice can be harmful to nearby trees. (**b**) Just before urine leaves the human body, the collecting ducts in the kidney (which contain the urine) pass through a fluid whose salt concentration is considerably greater than is found in the blood and tissues. Explain how this action helps conserve water in the body.

7.29 A very long pipe is capped at one end with a semipermeable membrane. How deep (in meters) must the pipe be immersed into the sea for fresh water to begin passing through the membrane? Assume seawater is at 20°C and treat it as a 0.70 M NaCl solution. The density of seawater is 1.03 g cm^{-3}.

7.30 (**a**) Using the Debye–Hückel limiting law, calculate the value of $\gamma_\pm$ for a 2.0×10^{-3} m Na_3PO_4 solution at 25°C. (**b**) Calculate the values of γ_+ and γ_- for the Na_3PO_4 solution, and show that they give the same value for $\gamma_\pm$ as that obtained in (**a**).

CHAPTER 8

Chemical Equilibrium

> *When a system is in chemical equilibrium, a change in one of the parameters of the equilibrium produces a shift in such a direction that, were no other factors involved in this shift, it would lead to a change of opposite sign in the parameter considered.*
>
> —Henri-Louis Le Châtelier

Turning from our discussion of nonelectrolyte and electrolyte solutions and physical equilibria in Chapters 6 and 7, we shall focus in this chapter on chemical equilibrium in gaseous and condensed phases. Equilibrium is a state in which there are no observable changes over time; at equilibrium, the concentrations of reactants and products in a chemical reaction remain constant. Much activity occurs at the molecular level, however, because reactant molecules continue to form product molecules while product molecules react to yield reactant molecules. This process is an example of dynamic equilibrium. The laws of thermodynamics help us predict equilibrium composition under different reaction conditions.

8.1 Chemical Equilibrium in Gaseous Systems

In this section, we shall derive an expression relating the Gibbs energy change for a reaction in the gas phase to the concentrations of the reacting species and temperature. We first consider the case in which all gases exhibit ideal behavior.

Ideal Gases

Examples of the simplest type of chemical equilibrium,

$$\mathrm{A}(g) \rightleftharpoons \mathrm{B}(g)$$

are cis–trans isomerization, racemization, and the cyclopropane-ring-opening reaction to form propene. The progress of the reaction can be monitored by the quantity ξ (Greek letter xi), called the *extent of reaction*. When an infinitesimal amount of A is converted to B, the change in A is $dn_\mathrm{A} = -d\xi$ and that in B is $dn_\mathrm{B} = +d\xi$ where dn denotes the change in number of moles. The change in Gibbs energy for this transformation at constant T and P is given by

$$\begin{aligned} dG &= \mu_\mathrm{A} dn_\mathrm{A} + \mu_\mathrm{B} dn_\mathrm{B} \\ &= -\mu_\mathrm{A} d\xi + \mu_\mathrm{B} d\xi \\ &= (\mu_\mathrm{B} - \mu_\mathrm{A}) d\xi \end{aligned} \tag{8.1}$$

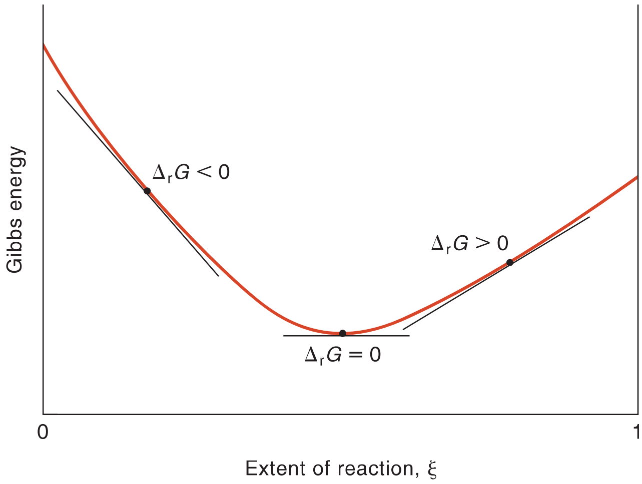

Figure 8.1
A plot of Gibbs energy versus extent of reaction. For a reacting system at equilibrium, the slope of the curve is zero.

where μ_A and μ_B are the chemical potentials of A and B, respectively. Equation 8.1 can be rearranged to give

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,\,P} = \mu_B - \mu_A \tag{8.2}$$

For simplicity, we use the units kJ mol^{-1} rather than kJ (mol reaction)$^{-1}$.

The quantity $(\partial G/\partial \xi)_{T,\,P}$ is represented by $\Delta_r G$, which is the change in Gibbs energy per mole of reaction; it has the units kJ mol^{-1}.

During the reaction, the chemical potentials vary with composition. The reaction proceeds in the direction of decreasing G, that is, $(\partial G/\partial \xi)_{T,\,P} < 0$. Therefore, the forward reaction (A → B) is spontaneous when $\mu_A > \mu_B$ whereas the reverse reaction (B → A) is spontaneous when $\mu_B > \mu_A$. At equilibrium, $\mu_A = \mu_B$ so that

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,\,P} = 0$$

Figure 8.1 shows a plot of Gibbs energy versus extent of reaction. At constant T and P, we have

$\Delta_r G < 0$	Forward reaction is spontaneous
$\Delta_r G > 0$	Reverse reaction is spontaneous
$\Delta_r G = 0$	Reacting system is at equilibrium

Let us now consider a more complicated case:

$$a\mathrm{A}(g) \rightleftharpoons b\mathrm{B}(g)$$

where a and b are stoichiometric coefficients. According to Equation 6.10, the chemical potential of the ith component in a mixture, assuming ideal behavior, is given by

$$\mu_i = \mu_i^\circ + RT \ln \frac{P_i}{P^\circ}$$

where P_i is the partial pressure of component i in the mixture, μ_i° is the standard chemical potential of component i, and $P^\circ = 1$ bar. Therefore, we can write

$$\mu_A = \mu_A^\circ + RT \ln \frac{P_A}{P^\circ} \tag{8.3a}$$

$$\mu_B = \mu_B^\circ + RT \ln \frac{P_B}{P^\circ} \tag{8.3b}$$

The Gibbs energy change for the reaction, $\Delta_r G$, can be expressed as

$$\Delta_r G = b\mu_B - a\mu_A \tag{8.4}$$

Substituting the expressions in Equation 8.3 into Equation 8.4, we get

$$\Delta_r G = b\mu_B^\circ - a\mu_A^\circ + bRT \ln \frac{P_B}{P^\circ} - aRT \ln \frac{P_A}{P^\circ} \tag{8.5}$$

The standard Gibbs energy change of the reaction, $\Delta_r G^\circ$, is just the difference between the standard Gibbs energies of products and reactants, that is,

$$\Delta_r G^\circ = b\mu_B^\circ - a\mu_A^\circ$$

Therefore, we can write Equation 8.5 as

$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{(P_B/P^\circ)^b}{(P_A/P^\circ)^a} \tag{8.6}$$

By definition, $\Delta_r G = 0$ at equilibrium, so Equation 8.6 becomes

$$0 = \Delta_r G^\circ + RT \ln \frac{(P_B/P^\circ)^b}{(P_A/P^\circ)^a}$$

$$0 = \Delta_r G^\circ + RT \ln K_P$$

or

$$\Delta_r G^\circ = -RT \ln K_P \tag{8.7}$$

K_P, the equilibrium constant (where the subscript P denotes that concentrations are expressed in pressures), is given by

$$K_P = \frac{(P_B/P^\circ)^b}{(P_A/P^\circ)^a} = \frac{P_B^b}{P_A^a}(P^\circ)^{a-b} \tag{8.8}$$

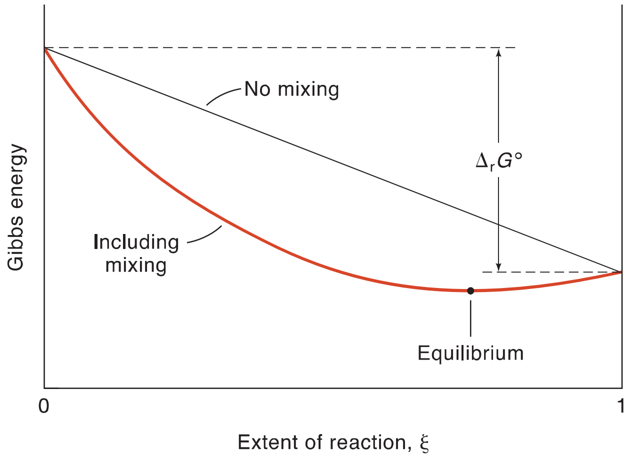

Figure 8.2
Total Gibbs energy versus extent of reaction for the $a\text{A}(g) \rightleftharpoons b\text{B}(g)$ reaction assuming $\Delta_r G° < 0$. At equilibrium, product is favored over reactant. Note that the equilibrium point, which is at the minimum of Gibbs energy, is a compromise between $\Delta_r G°$ and the Gibbs energy of mixing.

Equation 8.7 is one of the most important and useful equations in chemical thermodynamics. It relates the equilibrium constant, K_P, and the standard Gibbs energy change of the reaction, $\Delta_r G°$, in a remarkably simple fashion. Keep in mind that at a given temperature, $\Delta_r G°$ is a constant whose value depends only on the nature of the reactants and products and temperature. In our example, $\Delta_r G°$ is the standard Gibbs energy change when reactant A at 1 bar pressure and temperature T is converted to product B at 1 bar pressure and the same temperature per mole of reaction, as shown above. Figure 8.2 shows the Gibbs energy versus the extent of reaction for $\Delta_r G° < 0$. When there is no mixing of reactants with products, the Gibbs energy decreases linearly as the reaction progresses, and eventually the reactants will be completely converted to products. As Equation 6.11 shows, however, $\Delta_{\text{mix}} G$ is a negative quantity; therefore, the Gibbs energy for the actual path will be lower than that for the nonmixing case. Consequently, the equilibrium point, which is at the *minimum* of the Gibbs energy, is a compromise between these two opposing tendencies, that is, the conversion of reactants to products and the mixing of products with reactants.

Equation 8.7 tells us that if we know the value of $\Delta_r G°$, we can calculate the equilibrium constant K_P, and vice versa. The standard Gibbs energy of a reaction is just the difference between the standard Gibbs energies of formation ($\Delta_f \overline{G}°$) of the products and the reactants, discussed in Section 5.3. Thus, once we have defined a reaction, we can usually calculate the equilibrium constant from the $\Delta_f \overline{G}°$ values listed in Appendix B and Equation 8.7. Note that these values all refer to 298 K. Later in this chapter (Section 8.5), we shall learn how to calculate the value of K_P at another temperature if its value at 298 K is known.

Finally, note that the equilibrium constant is a function of temperature alone (because $\mu°$ depends only on temperature) and is dimensionless. This follows from the fact that in the expression for K_P, each pressure term is divided by its standard-state value of 1 bar, which cancels the pressure unit but does not alter P numerically.

EXAMPLE 8.1

From the thermodynamic data listed in Appendix B, calculate the equilibrium constant for this reaction at 298 K:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

ANSWER

The equilibrium constant for the equation is given by

$$K_P = \frac{(P_{NH_3}/P^\circ)^2}{(P_{N_2}/P^\circ)(P_{H_2}/P^\circ)^3}$$

To calculate the value of K_P, we need Equation 8.7 and the value of $\Delta_r G^\circ$. From Equation 5.12 and Appendix B, we have

$$\begin{aligned}\Delta_r G^\circ &= 2\Delta_f \overline{G}^\circ(NH_3) - \Delta_f \overline{G}^\circ(N_2) - 3\Delta_f \overline{G}^\circ(H_2)\\ &= (2)(-16.6\text{ kJ mol}^{-1}) - (0) - (3)(0)\\ &= -33.2\text{ kJ mol}^{-1}\end{aligned}$$

From Equation 8.7,

$$-33{,}200\text{ J mol}^{-1} = -(8.314\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})\ln K_P$$

$$\ln K_P = 13.4$$

or

$$K_P = 6.6 \times 10^5$$

COMMENT

Note that if the reaction were written as

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

the value of $\Delta_r G^\circ$ would be -16.6 kJ mol^{-1}, and the equilibrium constant would be calculated as follows:

$$K_P = \frac{(P_{NH_3}/P^\circ)}{(P_{N_2}/P^\circ)^{1/2}(P_{H_2}/P^\circ)^{3/2}} = 8.1 \times 10^2$$

Thus, whenever we multiply a balanced equation throughout by a factor n, we change the equilibrium constant K_P to K_P^n. Here $n = \frac{1}{2}$, so we have changed K_P to $K_P^{1/2}$.

A Closer Look at Equation 8.7

The change in standard Gibbs energy, $\Delta_r G°$, is generally not equal to zero. According to Equation 8.7, if $\Delta_r G°$ is negative, the equilibrium constant must be greater than unity; in fact, the more negative $\Delta_r G°$ is at a given temperature, the larger K_P is. The reverse holds true if $\Delta_r G°$ is a positive number. Here the equilibrium constant is less than unity. Of course, just because $\Delta_r G°$ is positive does not mean that no reaction will take place. For example, if $\Delta_r G° = 10$ kJ mol^{-1} and $T = 298$ K, then $K_P = 0.018$. While 0.018 is a small number compared to unity, an appreciable amount of products can still be obtained at equilibrium if we use large quantities of reactants for the reaction. There is also the special case in which $\Delta_r G° = 0$, which corresponds to a K_P of unity, meaning that the products and reactants are equally favored at equilibrium.

It is instructive to look at the factors that affect $\Delta_r G°$ and hence K_P. From Equation 5.3 we have

$$\Delta_r G° = \Delta_r H° - T\Delta_r S°$$

so the equilibrium constant at temperature T is governed by two terms: the change in enthalpy and temperature times the change in entropy. For many exothermic reactions ($\Delta_r H° < 0$) at room temperature and below, the first term on the right side of the above equation dominates. This means that K_P is greater than one, so products are favored over reactants. For an endothermic reaction ($\Delta_r H° > 0$), the equilibrium composition will favor products only if $\Delta_r S° > 0$ and the reaction is run at a high temperature. Consider the following reaction in which the A → B step is endothermic

$$\mathrm{A} \rightleftharpoons \mathrm{B}$$

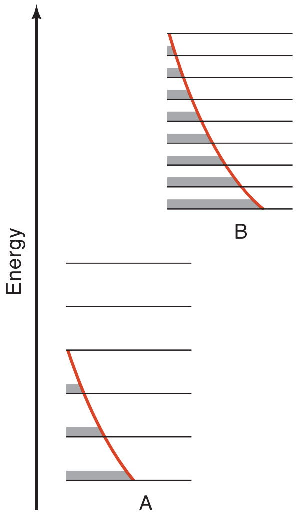

Figure 8.3
The occupancy of energy levels in B is greater than than in A. Consequently, there are more microstates in B and the entropy of B is greater than that of A. At equilibrium, B dominates even though the A → B reaction is endothermic.

As Figure 8.3 shows, the energy levels of A are below those of B, so the conversion of A to B is energetically unfavorable. This is, in fact, the nature of all endothermic reactions. But because the energy levels of B are more closely spaced together, the Boltzmann distribution law (see Equation 2.33) tells us that the population spread of the B molecules over the energy levels is greater than that of the A molecules. Consequently $\Delta_r S° > 0$ because the entropy of B is greater than that of A. At a sufficiently high temperature, then, the $T\Delta_r S°$ term will outweigh the $\Delta_r H°$ term in magnitude and $\Delta_r G°$ will be a negative quantity.

As an illustration of the relative importance of $\Delta_r H°$ versus $T\Delta_r S°$, let's consider the thermal decomposition of limestone or chalk ($CaCO_3$):

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{CaO}(s) + \mathrm{CO_2}(g) \qquad \Delta_r H° = 177.8 \text{ kJ mol}^{-1}$$

Using the data in Appendix B we can show that $\Delta_r S° = 160.5$ J K^{-1} mol^{-1}. At 298 K, we have

$$\begin{aligned}\Delta_r G° &= 177.8 \text{ kJ mol}^{-1} - (298 \text{ K})(160.5 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ &= 130.0 \text{ kJ mol}^{-1}\end{aligned}$$

Because $\Delta_r G°$ is a large positive quantity, we conclude that the reaction is not favored for product formation at 298 K. Indeed, the equilibrium pressure of CO_2 is so low at room temperature that it cannot be measured. In order to make $\Delta_r G°$ negative, we first have to find the temperature at which $\Delta_r G°$ is zero; that is,

$$0 = \Delta_r H° - T\Delta_r S°$$

or

$$
\begin{aligned}
T &= \frac{\Delta_r H^\circ}{\Delta_r S^\circ} \\
&= \frac{(177.8 \text{ kJ mol}^{-1})(1000 \text{ J/1 kJ})}{160.5 \text{ J K}^{-1} \text{ mol}^{-1}} \\
&= 1108 \text{ K or } 835^\circ\text{C}
\end{aligned}
$$

At a temperature higher than 835°C, $\Delta_r G^\circ$ becomes negative, indicating that the reaction now favors the formation of CaO and CO_2. For example, at 840°C, or 1113 K,

$$
\begin{aligned}
\Delta_r G^\circ &= \Delta_r H^\circ - T\Delta_r S^\circ \\
&= 177.8 \text{ kJ mol}^{-1} - (1113 \text{ K})(160.5 \text{ J K}^{-1} \text{ mol}^{-1})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \\
&= -0.8 \text{ kJ mol}^{-1}
\end{aligned}
$$

Two points are worth making about such a calculation. First, we used the $\Delta_r H^\circ$ and $\Delta_r S^\circ$ values at 25°C to calculate changes that occur at a much higher temperature. Because both $\Delta_r H^\circ$ and $\Delta_r S^\circ$ change with temperature, this approach will not give us an accurate value of $\Delta_r G^\circ$, but it is good enough for "ballpark" estimates. Second, we should not be misled into thinking that nothing happens below 835°C and that at 835°C $CaCO_3$ suddenly begins to decompose. Far from it. The fact that $\Delta_r G^\circ$ is a positive value at some temperature below 835°C does not mean that no CO_2 is produced, but rather that the pressure of the CO_2 gas formed at that temperature will be below 1 bar (its standard-state value). The significance of 835°C is that this is the temperature at which the equilibrium pressure of CO_2 reaches 1 bar. Above 835°C, the equilibrium pressure of CO_2 exceeds 1 bar.

A Comparison of $\Delta_r G^\circ$ with $\Delta_r G$

Suppose we start a gaseous reaction with all the reactants in their standard states (i.e., all at 1 bar). As soon as the reaction starts, the standard-state condition no longer exists for the reactants or the products because their pressures are different from 1 bar. Under conditions that are not standard state, we must use $\Delta_r G$ rather than $\Delta_r G^\circ$ to predict the direction of a reaction.

We can use the change in standard Gibbs energy ($\Delta_r G^\circ$) and Equation 8.6 to find $\Delta_r G$. The value of $\Delta_r G$ is determined by two terms: $\Delta_r G^\circ$ and a concentration dependent term. At a given temperature the value of $\Delta_r G^\circ$ is fixed, but we can change the value of $\Delta_r G$ by adjusting the partial pressures of the gases. Although the quotient composed of the pressures of reactants and products has the form of an equilibrium constant, it is *not* equal to the equilibrium constant unless P_A and P_B are the partial pressures at equilibrium. In general, we can rewrite Equation 8.6 as

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q \tag{8.9}$$

The sign of $\Delta_r G$ and not that of $\Delta_r G^\circ$ determines the direction of reaction spontaneity.

where Q is the *reaction quotient* and $Q \neq K_P$ unless $\Delta_r G = 0$. The usefulness of Equation 8.6 or Equation 8.9 is that it tells us the direction of a spontaneous change if the concentrations of the reacting species are known. If $\Delta_r G^\circ$ is a large positive or a large negative number (say, 50 kJ mol^{-1} or more), then the direction of the reaction (or the sign of $\Delta_r G$) is primarily determined by $\Delta_r G°$ alone, unless either the reactants or the products are present in a much larger amount so that the $RT \ln Q$ term in Equation 8.9 is comparable to $\Delta_r G°$ in magnitude but opposite in sign. If $\Delta_r G°$ is a small number, either positive or negative (say, 10 kJ mol^{-1} or less), then the reaction can go either way.*

---

* Alternatively, we can determine the direction of a reaction by comparing Q with K_P. From Equations 8.7 and 8.9 we can show that $\Delta_r G = RT \ln(Q/K_P)$. Therefore, if $Q < K_P$, $\Delta_r G$ is negative and the reaction will proceed in the forward direction (left to right). If $Q > K_P$, $\Delta_r G$ is positive. Here, the reaction will proceed in the reverse direction (right to left).

EXAMPLE 8.2

The equilibrium constant (K_P) for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

is 0.113 at 298 K, which corresponds to a standard Gibbs energy change of 5.40 kJ mol^{-1}. In a certain experiment, the initial pressures are $P_{NO_2} = 0.122$ bar and $P_{N_2O_4} = 0.453$ bar. Calculate $\Delta_r G$ for the reaction at these pressures and predict the direction of the net reaction.

ANSWER

To determine the direction of the net reaction, we need to calculate the Gibbs energy change under nonstandard-state conditions ($\Delta_r G$) using Equation 8.9 and the given $\Delta_r G°$ value. Note that the partial pressures are expressed as dimensionless quantities in the reaction quotient Q because each pressure is divided by its standard-state value of 1 bar.

$$\begin{aligned}\Delta_r G &= \Delta_r G° + RT \ln Q \\ &= \Delta_r G° + RT \ln \frac{P^2_{NO_2}}{P_{N_2O_4}} \\ &= 5.40 \times 10^3 \text{ J mol}^{-1} + (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \times \ln \frac{(0.122)^2}{0.453} \\ &= 5.40 \times 10^3 \text{ J mol}^{-1} - 8.46 \times 10^3 \text{ J mol}^{-1} \\ &= -3.06 \times 10^3 \text{ J mol}^{-1} = -3.06 \text{ kJ mol}^{-1}\end{aligned}$$

Because $\Delta_r G < 0$, the net reaction proceeds from left to right to reach equilibrium.

COMMENT

Note that although $\Delta_r G° > 0$, the reaction can be made initially to favor product formation by having a small concentration (pressure) of the product compared to that of the reactant.