The study of solutions is of great importance because most of the 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 (for example, air) and solid solutions (for example, solder) also exist. This chapter starts with the thermodynamic study of ideal and nonideal solutions of nonelectrolytes—solutions that do not contain ionic species—and the colligative properties of these solutions.

Because all biological and many chemical systems are aqueous solutions containing various ions, we shall also study the properties of electrolyte solutions. The stability of biomacromolecules and the rates of many biochemical reactions very much depend on the type and concentration of ions present. It is important to have a clear understanding of the behavior of ions in solution. Finally, we shall look briefly at biological membranes and membrane transport.

5.1 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

\[
\text{percent by weight} = \frac{\text{weight of solute}}{\text{weight of solute} + \text{weight of solvent}} \times 100\%
\]

\[= \frac{\text{weight of solute}}{\text{weight of solution}} \times 100\% \quad (5.1)\]
Mole Fraction ($x$)

The concept of mole fraction was introduced in Section 2.7. We define the mole fraction of a component $i$ of a solution, $x_i$, as

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

$$= \frac{n_i}{\sum n_i}$$ (5.2)

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,

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{L solution}}$$ (5.3)

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,

$$\text{molality} = \frac{\text{number of moles of solute}}{\text{weight of solvent in kg}}$$ (5.4)

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 2.7) 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 5.6).
5.2 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 the volumes be additive. If the final volume is equal to the sum of the separate volumes, the solution is called an ideal solution. Figure 5.1 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.

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

\[ dV = \left( \frac{\partial V}{\partial n_1} \right)_{T,P,n_2} \, dn_1 + \left( \frac{\partial V}{\partial n_2} \right)_{T,P,n_1} \, dn_2 \]

\[ dV = V_1 \, dn_1 + V_2 \, dn_2 \] (5.5)

where \( V_1 \) and \( V_2 \) are the partial molar volumes of components 1 and 2, respectively. The partial molar volume \( V_1 \), 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, \( V_1 \) 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 \( V_2 \) can be similarly interpreted. Equation 5.5 can be integrated to give

\[ V = n_1 V_1 + n_2 V_2 \] (5.6)

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

Figure 5.1
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 \( x_{\text{C}_2\text{H}_5\text{OH}} = 0 \), the volume corresponds to that of the molar volume of water, and at \( x_{\text{C}_2\text{H}_5\text{OH}} = 1 \), \( V \) is the molar volume of ethanol.
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 5.63).

Figure 5.2 suggests a way of measuring partial molar volumes. Consider a solution composed of substances 1 and 2. To measure \( \bar{V}_2 \), we prepare a series of solutions at certain \( T \) and \( P \), all of which contain a fixed number of moles of component 1 (that is, \( n_1 \) 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 \( \bar{V}_2 \) for that composition. Once \( \bar{V}_2 \) has been measured, \( \bar{V}_1 \) at the same composition can be calculated using Equation 5.6:

\[
\bar{V}_1 = \frac{V - n_2 \bar{V}_2}{n_1}
\]

Figure 5.3 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 \(i\)th component in solution \(G_i\) is given by

\[
G_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_j}
\]

where \(n_j\) represents the number of moles of all other components present. Again, we can think of \(G_i\) as the coefficient that gives the increase in the Gibbs energy of the 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 (\(\mu\)), so we can write

\[
\bar{G}_i = \mu_i
\]

The expression for the total Gibbs energy of a two-component solution is similar to Equation 5.6 for volumes:

\[
G = n_1\mu_1 + n_2\mu_2
\]

The Meaning of Chemical Potential

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 \(\mu_i^A\), to some final state B, where its chemical potential is \(\mu_i^B\). For a process carried out at constant temperature and pressure, the change in the Gibbs energy, \(dG\), is given by

\[
dG = \mu_i^A dn_i - \mu_i^B dn_i = (\mu_i^B - \mu_i^A)dn_i
\]

If \(\mu_i^B < \mu_i^A\), \(dG < 0\), and transfer of \(dn_i\) moles from A to B will be a spontaneous process; if \(\mu_i^B > \mu_i^A\), \(dG > 0\), 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 \(\mu_i\) value to a lower \(\mu_i\) 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.
5.3 The 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 5.9 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 4.8, we obtained an expression for the molar Gibbs energy of an ideal gas (Equation 4.34):

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

In a mixture of ideal gases, the chemical potential of the $i$th component is given by

$$\mu_i = \mu_i^o + RT \ln \frac{P_i}{1\text{ bar}}$$  \hspace{1cm} (5.10)

where $P_i$ is the partial pressure of component $i$ in the mixture and $\mu_i^o$ 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 5.9, where chemical potentials are the same as molar Gibbs energies,

$$G = n_1 \bar{G}_1 + n_2 \bar{G}_2$$

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

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

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

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

$$\Delta_{\text{mix}} G = G_{\text{final}} - G_{\text{initial}}$$

$$= n_1 RT \ln \frac{P_1}{P} + n_2 RT \ln \frac{P_2}{P}$$

$$= n_1 RT \ln x_1 + n_2 RT \ln x_2$$

where $P_1 = x_1 P$ and $P_2 = x_2 P$, and $x_1$ and $x_2$ are the mole fractions of 1 and 2, respectively. (The standard chemical potential, $\mu^o$, 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

*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.
\[ \Delta_{\text{mix}} G = nRT(x_1 \ln x_1 + x_2 \ln x_2) \] (5.11)

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 4.29, 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 5.11 with respect to temperature at constant pressure:

\[ \left( \frac{\partial \Delta_{\text{mix}} G}{\partial T} \right)_p = nR(x_1 \ln x_1 + x_2 \ln x_2) \]

\[ = -\Delta_{\text{mix}} S \]

or

\[ \Delta_{\text{mix}} S = -nR(x_1 \ln x_1 + x_2 \ln x_2) \] (5.12)

This result is equivalent to Equation 4.9. The minus sign in Equation 5.12 makes \( \Delta_{\text{mix}} S \) a positive quantity, in accord with a spontaneous process. The enthalpy of mixing is given by rearranging Equation 4.21:

\[ \Delta_{\text{mix}} H = \Delta_{\text{mix}} G + T\Delta_{\text{mix}} S \]

\[ = 0 \]

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 5.4 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 the maximum number of microstates by mixing equimolar amounts of gases and that the Gibbs energy of mixing reaches a minimum at this point (see Problem 5.65).

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 \( \Delta_{\text{mix}} G \) and \( T \Delta_{\text{mix}} S \) curves are fairly flat (see Figure 5.4), 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 \( 4 \times 10^{-12} \) 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, \( 1.5 \times 10^{21} \) L, we find the amount of gold present to be

![Figure 5.4](image-url)
$6 \times 10^{12}$ 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 (that is, starting at the steep portions of the curves in Figure 5.4) would be a very formidable (and expensive) undertaking indeed.

### Example 5.1

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

\[
x_{\text{Ar}} = \frac{1.6}{1.6 + 2.6} = 0.38 \quad x_{\text{N}_2} = \frac{2.6}{1.6 + 2.6} = 0.62
\]

From Equation 5.11,

\[
\Delta_{\text{mix}} G = (4.2 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K}) [(0.38) \ln 0.38 + (0.62) \ln 0.62]
\]

\[
= -6.9 \text{ kJ}
\]

Because $\Delta_{\text{mix}} S = -\frac{\Delta_{\text{mix}} G}{T}$, we write

\[
\Delta_{\text{mix}} S = -\frac{-6.9 \times 10^3 \text{ J}}{298 \text{ K}}
\]

\[
= 23 \text{ J K}^{-1}
\]

**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 $\Delta_{\text{mix}} G$: the mixing itself and the changes in pressure. Problem 5.66 illustrates this situation.

### 5.4 Binary Mixtures of Volatile Liquids

The results obtained in Section 5.3 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*  

\[ \mu^*(l) = \mu^*(g) = \mu^*(g) + RT \ln \frac{P^*}{1 \text{ bar}} \]  

(5.13)

where \( \mu^*(g) \) 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 have  

\[ \mu_1(l) = \mu_1(g) = \mu_1^*(g) + RT \ln \frac{P_1}{1 \text{ bar}} \]  

(5.14)

where \( P_1 \) is the partial pressure. Now the standard chemical potential of component 1 is the same in the pure state and in the solution; that is, \( \mu_1^*(g) = \mu_1^*(g) \) and \( \mu_1^*(g) = \mu_1^*(l) - RT \ln(P_1/1 \text{ bar}) \). Combining Equations 5.13 and 5.14 we get  

\[ \mu_1(l) = \mu_1^*(g) + RT \ln \frac{P_1}{1 \text{ bar}} \]

\[ = \mu_1^*(l) - RT \ln \frac{P_1}{1 \text{ bar}} + RT \ln \frac{P_1}{1 \text{ bar}} \]

\[ = \mu_1^*(l) + RT \ln \frac{P_1}{P_1} \]  

(5.15)

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 log of the ratio of the vapor pressures of the liquid in solution to that 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 5.15 is equal to the mole fraction of component 1; that is,  

\[ \frac{P_1}{P_1^*} = x_1 \]

or

\[ P_1 = x_1 P_1^* \]  

(5.16)

Equation 5.16 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 5.16 into Equation 5.15, we obtain  

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

(5.17)

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

* This equation follows from Equation 4.34. For a pure component, the chemical potential is equal to the molar Gibbs energy.
Example 5.2

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

\[
P_A = x_A P_A^0 = 0.36(66 \text{ torr}) = 23.8 \text{ torr}
\]

\[
P_B = x_B P_B^0 = 0.64(88 \text{ torr}) = 56.3 \text{ torr}
\]

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 \( x_B^V \), are given by

\[
x_A^V = \frac{23.8 \text{ torr}}{80.1 \text{ torr}} = 0.30
\]

and

\[
x_B^V = \frac{56.3 \text{ torr}}{80.1 \text{ torr}} = 0.70
\]
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 $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$. Most solutions do not behave ideally, however. Figure 5.6 shows the positive and negative deviations from Raoult’s law. The positive deviation (Figure 5.6a) corresponds to the case in which the intermolecular forces between unlike molecules are weaker than those between like molecules, and 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 5.6b). 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 5.16. The regions where Raoult’s law is applicable are shown for the carbon disulfide–acetone system in Figure 5.7. 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 5.16. Still, the vapor pressure of the solute varies with concentration in a linear manner:

$$P_2 = Kx_2$$  \hspace{1cm} (5.18)

Equation 5.18 is known as Henry’s law (after the English chemist William Henry, 1775–1836), where $K$, the Henry’s law constant, is in atm or torr. Henry’s law relates
the mole fraction of the solute to its partial (vapor) pressure. Alternatively, Henry’s law can be expressed as

\[ P_2 = K' m \quad (5.19) \]

where \( m \) is the molality of the solution and the constant \( K' \) now has the units atm mol\(^{-1}\) kg of the solvent. Table 5.1 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

<table>
<thead>
<tr>
<th>Gas</th>
<th>( K/\text{torr} )</th>
<th>( K'/\text{atm} \cdot \text{mol}^{-1} \cdot \text{kg H}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>( 5.54 \times 10^7 )</td>
<td>1311</td>
</tr>
<tr>
<td>He</td>
<td>( 1.12 \times 10^8 )</td>
<td>2649</td>
</tr>
<tr>
<td>Ar</td>
<td>( 2.80 \times 10^7 )</td>
<td>662</td>
</tr>
<tr>
<td>N(_2)</td>
<td>( 6.80 \times 10^7 )</td>
<td>1610</td>
</tr>
<tr>
<td>O(_2)</td>
<td>( 3.27 \times 10^7 )</td>
<td>773</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>( 1.24 \times 10^6 )</td>
<td>29.3</td>
</tr>
<tr>
<td>H(_2)S</td>
<td>( 4.27 \times 10^5 )</td>
<td>10.1</td>
</tr>
</tbody>
</table>

Figure 5.7
Diagrams showing regions over which Raoult’s law and Henry’s law are applicable for a two-component system (see Figure 5.6). Part (a) shows positive deviation and part (b) shows negative deviation. In each case the Henry’s law constants can be obtained from the intercepts on the \( y \) (pressure) axis.
point some 40 m below the surface of seawater, the total pressure is about 6 atm. The
solubility of N\textsubscript{2} in the blood plasma is 0.8 \times 6 \text{ atm}/1610 \text{ atm mol}^{-1} \text{ kg H}_2\text{O}, or
3.0 \times 10^{-3} \text{ mol (kg H}_2\text{O)}^{-1}—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 ear-
lier, 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\textsubscript{2}, H\textsubscript{2}S, NH\textsubscript{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 5.1), but its
solubility increases dramatically if the solution contains hemoglobin or myoglobin.
The nature of oxygen binding to the heme group in these molecules will be discussed
further in later chapters.

### Example 5.3

Calculate the molal solubility of carbon dioxide in water at 298 K and a CO\textsubscript{2} pressure
of 3.3 \times 10^{-4} \text{ atm}, which corresponds to the partial pressure of CO\textsubscript{2} in air.

**Answer**

We use Equation 5.19 and the data in Table 5.1:

\[
m = \frac{P_{\text{CO}_2}}{K^7} = \frac{3.3 \times 10^{-4} \text{ atm}}{29.3 \text{ atm mol}^{-1} \text{ kg H}_2\text{O}} = 1.12 \times 10^{-5} \text{ mol (kg H}_2\text{O)}^{-1}
\]

**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.

### 5.5 Real Solutions

As pointed out in Section 5.4, most solutions do not behave ideally. One problem
that immediately arises in dealing with nonideal solutions is how to write the chemi-
cal 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 5.17)

\[
\mu_1(l) = \mu_1^0(l) + RT \ln x_1
\]
where \( x_1 = \frac{P_1}{P^*_1} \) 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

\[
\mu_1(l) = \mu^*_1(l) + RT \ln a_1
\]  

(5.20)

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

\[
a_1 = \frac{P_1}{P^*_1}
\]  

(5.21)

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

\[
a_1 = \gamma_1 x_1
\]  

(5.22)

where \( \gamma_1 \) is the activity coefficient. Equation 5.20 can now be written as

\[
\mu_1(l) = \mu^*_1(l) + RT \ln \gamma_1 + RT \ln x_1
\]  

(5.23)

The value of \( \gamma_1 \) 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 5.21 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.*

---

**Example 5.4**

The vapor pressure of water in a 6.00 m urea solution is \( 5.501 \times 10^{-3} \) atm at 273 K. Calculate the activity and activity coefficient of water. The vapor pressure of pure water is \( 6.025 \times 10^{-3} \) atm at this temperature.

**A N S W E R**

To calculate the activity of water we use Equation 5.21:

\[
a_1 = \frac{5.501 \times 10^{-3} \text{ atm}}{6.025 \times 10^{-3} \text{ atm}} = 0.913
\]

To calculate the activity coefficient, we must first determine the mole fraction of water in the solution. Because the number of moles of water in 1 kg of the solvent is \( (1000 \text{ g}/18.02 \text{ g mol}^{-1}) \) or 55.50 mol, we have
\[ x_1 = \frac{m_1}{m_1 + m_2} = \frac{55.50}{55.50 + 6.00} = 0.902 \]

Finally, from Equation 5.22,

\[ \gamma_1 = \frac{a_1}{x_1} = \frac{0.913}{0.902} = 1.012 \]

**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. If a nonideal solution is dilute, and there is no chemical interaction, then 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:

\[ m_2(l) = m_2^*(l) + RT \ln x_2 \]

In an ideal dilute solution, Henry’s law applies. This is, \( P_2 = Kx_2 \), so that

\[ m_2(l) = \mu_2^*(l) + RT \ln \frac{P}{P_2^*} + RT \ln x_2 \]

where \( \mu_2^*(l) = \mu_2^*(l) + RT \ln \left( \frac{K}{P_2^*} \right) \). Although Equation 5.24 seems to take the same form as Equation 5.17, there is an important difference, which lies in the choice of standard state. According to Equation 5.24, the standard state is defined as the pure solute, attained by setting \( x_2 = 1 \). Equation 5.24 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 the solute defined by Equation 5.24 is 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 5.24 is modified to

\[ m_2(l) = \mu_2^*(l) + RT \ln a_2 \]

\[ \mu_2(l) = \mu_2^*(l) + RT \ln x_2 \] (5.24)

\[ \mu_2(l) = \mu_2^*(l) + RT \ln a_2 \] (5.25)

* For ideal solutions, Raoult’s law and Henry’s law become identical; that is, \( P_2 = Kx_2 = P_2^*x_2 \).
where \( a_2 \) is the activity of the solute. As in the case of the solvent component, we have \( a_2 = g_2 x_2 \), where \( g_2 \) is the activity coefficient of the solute. Here, we have \( a_2 \rightarrow x_2 \) or \( g_2 \rightarrow 1 \) as \( x_2 \rightarrow 0 \). Henry’s law is now given by

\[
P_2 = K a_2
\]  

(5.26)

Concentrations are usually expressed in molalities (or molarities) instead of mole fractions. In molality, Equation 5.24 takes the form

\[
\mu_2(l) = \mu_2^0(l) + RT \ln \frac{m_2}{m'}
\]  

(5.27)

where \( m' = 1 \text{ mol kg}^{-1} \) 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 5.8). For nonideal solutions, Equation 5.27 is rewritten as

\[
\mu_2(l) = \mu_2^0(l) + RT \ln a_2
\]  

(5.28)

where \( a_2 = g_2 (m_2/m') \). In the limiting case of \( m_2 \rightarrow 0 \), we have \( a_2 \rightarrow m_2/m' \) or \( g_2 \rightarrow 1 \) (see Figure 5.8b).

Keep in mind that although Equations 5.24 and 5.27 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 5.6), and, as we shall see in Chapter 6, in deriving the equilibrium constant.

### 5.6 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 two important assumptions: (1) The solutions are ideal dilute, so that the solvent obeys Raoult’s law and (2) 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:

$$P_1 = x_1 P_1^*$$

Because \( x_1 = 1 - x_2 \), the equation above becomes

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

Rearranging this equation gives

$$P_1^* - P_1 = \Delta P = x_2 P_1^*$$

(5.29)

where \( \Delta P \), 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? It is tempting to suggest that it is because of the modification of intermolecular forces. But this cannot be so, 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 5.3, the solution process itself is accompanied by an increase in entropy. Because the solution has a greater entropy than the pure solvent, it therefore has a smaller driving force for evaporation. In other words, evaporation from a solution will result in a smaller increase in entropy than the case for a pure solvent. 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.

**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 5.17, 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 5.9. 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 \( T_{0b} \) is higher than that of the pure solvent \( T_b \).

We now turn to a quantitative treatment of the boiling-point-elevation phenom-
enon. 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

\[
\Delta \mu_1 = \mu_1(g) - \mu_1^*(l) = RT \ln x_1 \tag{5.30}
\]

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
\( \Delta \mu_1 = \Delta_{\text{vap}} \mathcal{G} \). Dividing Equation 5.30 by \( T \), we obtain

\[
\frac{\Delta \mathcal{G}_{\text{vap}}}{T} = \frac{\mu_1(g) - \mu_1^*(l)}{T} = R \ln x_1
\]

From the Gibbs–Helmholz equation (Equation 4.31), we write

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

or

\[
\frac{d(\Delta \mathcal{G}_{\text{vap}}/T)}{dT} = -\frac{\Delta_{\text{vap}} \mathcal{H}}{T^2} = R \frac{d(\ln x_1)}{dT}
\]

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

\[
d \ln x_1 = \frac{-\Delta_{\text{vap}} \mathcal{H}}{RT^2} dT \tag{5.31}
\]
To find the relationship between $x_1$ and $T$, we integrate Equation 5.31 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

$$
\int_{\ln 1}^{\ln x_1} d\ln x_1 = \int_{T'_b}^{T_b} \frac{-\Delta v_p \Pi}{RT^2} dT
$$

or

$$
\ln x_1 = \frac{\Delta v_p \Pi}{R} \left( \frac{1}{T'_b} - \frac{1}{T_b} \right)
$$

$$
= \frac{-\Delta v_p \Pi}{R} \left( \frac{T_b' - T_b}{T_b T_b'} \right)
$$

$$
= \frac{-\Delta v_p \Pi}{R} \frac{\Delta T}{T_b^2}
$$

(5.32)

where $\Delta T = T'_b - T_b$. Two assumptions were used to obtain Equation 5.32, 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 $\Delta v_p \Pi$ to be temperature independent and second, $T'_b \approx T_b$, so that $T'_b T_b \approx T_b^2$.

Equation 5.32 gives the elevation of boiling point, $\Delta T$, 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

$$
\ln x_1 = \ln(1 - x_2) = \frac{-\Delta v_p \Pi}{R} \frac{\Delta T}{T_b^2}
$$

where*

$$
\ln(1 - x_2) = -x_2 - \frac{x_2^2}{2} - \frac{x_2^3}{3} \cdots
$$

$$
= -x_2 \quad (x_2 \ll 1)
$$

We now have

$$
\Delta T = \frac{RT_b^2}{\Delta v_p \Pi} x_2
$$

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

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

where $w_1$ is the mass of the solvent in kg and $\mathcal{M}_1$ 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 $x_2 = m_1 m_2$ and thus

$$
\Delta T = \frac{RT_b^2 \mathcal{M}_1}{\Delta v_p \Pi} m_2
$$

(5.33)

* This series expansion is known as Maclaurin’s theorem. You can verify this relationship by employing a small numerical value for $x_2$ ($\leq 0.2$).
Note that all the quantities in the first term on the right of Equation 5.33 are constants for a given solvent, and so we have

\[ K_b = \frac{RT_b^2 \Delta H_i}{\Delta v_p H} \]  

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

\[ \Delta T = K_b m_2 \]  

The advantage of using molality, as mentioned in Section 5.1, is that it is independent of temperature and thus is suitable for boiling-point-elevation studies.

Figure 5.10 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.

**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

---

* 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, \textit{J. Chem. Educ.} \textbf{53}, 49 (1976).
potential of the solid does not change (see Figure 5.9). 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 exactly the same procedure as that for the boiling-point elevation, we can show that the drop in freezing point \( \Delta T \) (that is, \( T_f - T_f' \), where \( T_f \) and \( T_f' \) are the freezing points of the pure solvent and solution, respectively) is

\[
\Delta T = K_f m_2
\]  

(5.36)

where \( K_f \) is the molal freezing-point-depression constant given by

\[
K_f = \frac{RT_f^2 \Delta \mu}{\Delta_{\text{fus}} H}
\]  

(5.37)

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

The freezing-point-depression phenomenon can also be understood by studying Figure 5.10. 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.

Both Equations 5.35 and 5.36 can be used to determine the molar mass of a solute. In general, the freezing-point-depression experiment is much easier to carry out. Table 5.2 lists the \( K_b \) and \( K_f \) values for several common solvents.

---

**Example 5.5**

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: \( K_b = 0.51 \text{ K mol}^{-1} \text{ kg} \), 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 5.35,
\[ \Delta T = (0.51 \text{ K mol}^{-1} \text{ kg})(0.418 \text{ mol kg}^{-1}) \]
\[ = 0.21 \text{ K} \]
Thus, the solution will boil at \((373.15 + 0.21) \text{ K}\), or 373.36 K.

(b) Freezing point: From Equation 5.36,
\[ \Delta T = (1.86 \text{ K mol}^{-1} \text{ kg})(0.418 \text{ mol kg}^{-1}) \]
\[ = 0.78 \text{ K} \]
Thus, the solution will freeze at \((273.15 - 0.78) \text{ K}\), 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 5.34 and 5.37:

\[ K_b = \frac{RT_b^2 \Delta H}{\Delta v_{ap} H} \quad K_f = \frac{RT_f^2 \Delta H}{\Delta f_{us} H} \]

Although \( T_b > T_f \), \( \Delta v_{ap} H \) for water is 40.79 kJ mol\(^{-1}\), whereas \( \Delta f_{us} H \) is only 6.01 kJ mol\(^{-1}\). The large value of \( \Delta v_{ap} H \) in the denominator is what causes \( K_b \) and hence \( \Delta T \) to be smaller.

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 \([\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})]\) 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 \(-1.9 \text{^\circ C}\), 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 the section below on Osmotic Pressure). Besides dissolved salts and other substances that can 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 glycoproteins. The concentration of glycoproteins in the fishes’ blood is quite low (approximately \(4 \times 10^{-4} \text{ mol} \)), 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 \(-2 \text{^\circ C}\).

**Osmotic Pressure**

The phenomenon of *osmosis* is illustrated in Figure 5.11. The left compartment of the apparatus contains pure solvent; the right compartment contains a solution. The two compartments are separated by a *semipermeable membrane* (for example, 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 $\mu_L^1$ and $\mu_R^1$ be the chemical potential of the solvent in the left and right compartments, respectively. Initially, before equilibrium is established, we have

$$\mu_L^1 = \mu_1^* + RT \ln x_1 = \mu_1^* \quad (x_1 = 1)$$

and

$$\mu_R^1 = \mu_1^* + RT \ln x_1 \quad (x_1 < 1)$$

Thus,

$$\mu_L^1 = \mu_1^* > \mu_R^1 = \mu_1^* + RT \ln x_1$$

Note that $\mu_L^1$ is the same as the standard chemical potential for the pure solvent, $\mu_1^*$, 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, $\mu_R^1$. From Equation 4.32, 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,
\[
\left( \frac{\partial \mu_1^R}{\partial P} \right)_T = V_1
\]

where \( V_1 \) is the partial molar volume of the solvent. For a dilute solution, \( V_1 \) is approximately equal to \( V \), the molar volume of the pure solvent. The increase in the chemical potential of the solvent in the solution compartment (\( \Delta \mu_1^R \)) when the pressure increases from \( P \), the external atmospheric pressure, to \( (P + \pi) \) is given by

\[
\Delta \mu_1^R = \int_P^{P+\pi} V \, dP = V \pi
\]

Note that \( V \) is treated as a constant because the volume of a liquid changes little with pressure. The Greek letter \( \pi \) 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:

\[
\mu_1^L = \mu_1^R = \mu_1^* + RT \ln x_1 + \pi V
\]

Because \( \mu_1^L = \mu_1^* \), we have

\[
\pi V = -RT \ln x_1
\]

To relate \( \pi \) to the concentration of the solute, we take the following steps. From the procedure employed for boiling-point elevation (p. 144):

\[
-\ln x_1 = -\ln (1 - x_2) = x_2 \quad (x_2 \ll 1)
\]

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 5.39 now becomes

\[
\pi V = RT x_2
\]

\[
= RT \left( \frac{n_2}{n_1} \right)
\]

Substituting \( \bar{V} = V/n_1 \) into Equation 5.40, we get

\[
\pi \bar{V} = n_2 RT
\]

If \( V \) is in liters, then

\[
\pi = \frac{n_2}{V} RT
\]

\[
\pi = MRT
\]
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 5.42 as

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

or

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

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 in g mol$^{-1}$. Equation 5.44 provides a way to determine molar masses of compounds from osmotic pressure measurements.

Equation 5.44 is derived by assuming ideal behavior, so it is desirable to measure $\pi$ at several different concentrations and extrapolate to zero concentration for molar mass determination (Figure 5.12). For a nonideal solution, the osmotic pressure at any concentration, $c_2$, is given by

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

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 5.45 reduces to Equation 5.44.

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 5.44 tells us nothing about the mechanism of osmosis.
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 5.11). At equilibrium, the height of the water in the right column is 77.8 mm in excess of the height of the solution 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

\[
\text{pressure} = \frac{\text{force}}{\text{area}}
\]

\[
\text{pressure} = \frac{Ah\rho g}{A} = \frac{h\rho g}{A}
\]

where \(A\) is the area of the cross section of the tube, \(h\) the excess liquid height in the right column, \(\rho\) the density of the solution, and \(g\) the acceleration due to gravity. The constants are

\[
\begin{align*}
    h &= 0.0778 \text{ m} \\
    g &= 9.81 \text{ m s}^{-2} \\
    \rho &= 1 \times 10^3 \text{ kg m}^{-3}
\end{align*}
\]

(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

\[
\pi = \frac{0.0778 \text{ m} \times 1 \times 10^3 \text{ kg m}^{-3} \times 9.81 \text{ m s}^{-2}}{763 \text{ kg m}^{-1} \text{ s}^{-2}} = 763 \text{ N m}^{-2}
\]

From Equation 5.44,

\[
\mathcal{M}_2 = \frac{c_2}{\pi} RT
\]

Using the conversion factors 1 g = 1 \times 10^{-3} kg and 1 L = 1 \times 10^{-3} m\(^3\), we have

\[
\mathcal{M}_2 = \frac{(20 \text{ kg m}^{-3})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{763 \text{ N m}^{-2}} = 65 \text{ kg mol}^{-1}
\]

Example 5.6 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 \times 10^{-4} \text{C} and a depression in freezing point of 5.8 \times 10^{-4} \text{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. In
Chapter 16, we shall discuss other useful techniques for determining the molar mass of macromolecules.

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 5.13). 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 to the 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 (see Section 5.10). 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 Crenation helps to prolong the shelf life of jams when exposed to air.
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 5.11, 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.

### 5.7 Electrolyte Solutions

Having studied the general properties of nonelectrolyte solutions, we now turn our attention to electrolyte solutions. 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.

**A Molecular View of the Electrolyte 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 together by electrostatic

---

forces in the crystal lattice. In order 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 5.14 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 H₂O molecule in the hydration sphere can vary tremendously. For example, consider the mean lifetime of H₂O in the hydration sphere for the following ions: Br⁻, 10⁻¹¹ s; Na⁺, 10⁻⁹ s; Cu²⁺, 10⁻⁷ s; Fe³⁺, 10⁻⁵ s; Al³⁺, 7 s; and Cr³⁺, 1.5 × 10⁵ s, or 42 h.

The ion–dipole interaction (see Chapter 13) between dissolved ions and water molecules can affect several bulk properties of water. Small and/or multicharged ions such as Li⁺, Na⁺, Mg²⁺, Al³⁺, Er³⁺, 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⁺, NH₄⁺, Cl⁻, NO₃⁻, and ClO₄⁻ 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 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

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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/r², 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.
The force \( F \) between \( \text{Na}^+ \) and \( \text{Cl}^- \) ions in a vacuum is given by

\[
F = \frac{q_{\text{Na}^+} q_{\text{Cl}^-}}{4 \pi \varepsilon_0 r^2}
\]  

(5.46)

where \( \varepsilon_0 \) is the permittivity of the vacuum \( (8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}) \), \( q_{\text{Na}^+} \) and \( q_{\text{Cl}^-} \) 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 so that \( F \) is expressed in newtons. In the polar medium of water, as Figure 5.15 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 \( \varepsilon \) is the dielectric constant of the medium (see Appendix 5.1 on p. 182). Therefore, in any medium other than a vacuum, Equation 5.46 takes the form

\[
F = \frac{q_{\text{Na}^+} q_{\text{Cl}^-}}{4 \pi \varepsilon_0 \varepsilon r^2}
\]  

(5.47)

Table 5.3 lists the dielectric constants of several solvents. Keep in mind that \( \varepsilon \) always decreases with increasing temperature. For example, at 343 K, the dielectric constant of water is reduced to about 64. It is the large dielectric constant of water that reduces the attractive force between the \( \text{Na}^+ \) and \( \text{Cl}^- \) ions and allows 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

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Dielectric Constant, ( \varepsilon^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{SO}_4 )</td>
<td>101</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>78.54</td>
</tr>
<tr>
<td>( \text{(CH}_3)_2\text{SO} )</td>
<td>49</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{O}_3 ) (glycerol)</td>
<td>42.5</td>
</tr>
<tr>
<td>( \text{CH}_3\text{NO}_2 ) (nitromethane)</td>
<td>38.6</td>
</tr>
<tr>
<td>( \text{HOCH}_2\text{CH}_2\text{OH} ) (ethylene glycol)</td>
<td>37.7</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CN} ) (acetonitrile)</td>
<td>36.2</td>
</tr>
<tr>
<td>( \text{CH}_3\text{OH} )</td>
<td>32.6</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{OH} )</td>
<td>24.3</td>
</tr>
<tr>
<td>( \text{CH}_3\text{COCH}_3 )</td>
<td>20.7</td>
</tr>
<tr>
<td>( \text{CH}_3\text{COOH} )</td>
<td>6.2</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_6 )</td>
<td>4.6</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{O}_2\text{H}_3 )</td>
<td>4.3</td>
</tr>
<tr>
<td>( \text{CS}_2 )</td>
<td>2.6</td>
</tr>
</tbody>
</table>

*The dielectric constant is a dimensionless quantity.*
NaCl, ions are believed to be in the free-ion form. In higher-valence electrolytes, such as CaCl\textsubscript{2} and Na\textsubscript{2}SO\textsubscript{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 $k_B T$, for individual ions.

We can now understand easily why NaCl does not dissolve in benzene. A nonpolar molecule, benzene does not solvate Na\textsuperscript{+} and Cl\textsuperscript{-} 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 5.7**

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

**A N S W E R**

From Equations 5.46 and 5.47 and Table 5.3, we proceed as follows:

(a) 

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

(b) 

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

**C O M M E N T**

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.

**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

$$\text{NaCl(s)} \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$$

The enthalpy change for process 1 corresponds to the energy required to separate the 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, $\Delta_{\text{solv}}H$, which is the heat absorbed or released when NaCl dissolves in a large amount of
water. The heat of hydration, $\Delta_{\text{hydr}} H$, for process 2 is given by Hess’s law:

$$\Delta_{\text{hydr}} H = \Delta_{\text{solv}} H - U_0$$

The quantity $\Delta_{\text{solv}} H$ 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 $\Delta_{\text{solv}} H = 3.8 \text{ kJ mol}^{-1}$, so that

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

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 hydration enthalpy for the process

$$\text{H}^+(g) \rightarrow \text{H}^+(aq)$$

has been reliably estimated by theoretical methods as 1089 kJ mol$^{-1}$. Using this value as a starting point, we can calculate the $\Delta_{\text{hydr}} H$ values for individual anions such as $\text{F}^-$, $\text{Cl}^-$, $\text{Br}^-$, and $\text{I}^-$ (from data on HF, HCl, HBr, and HI), and in turn obtain $\Delta_{\text{hydr}} H$ values for Li$^+$, Na$^+$, K$^+$, and other cations (from data on alkali metal halides). Table 5.4 lists the standard $\Delta_{\text{hydr}} H$ values for a number of ions. All the $\Delta_{\text{hydr}} H$ values are negative because the hydration of a gaseous ion is an exothermic process. Furthermore, there is a rough correlation between ionic charge/radius and hydration enthalpy. The values of $\Delta_{\text{hydr}} H$ 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 $\Delta_{\text{hydr}} H$ values.

Table 5.4

<table>
<thead>
<tr>
<th>Ion</th>
<th>$-\Delta_{\text{hydr}} H^\circ$ (kJ mol$^{-1}$)</th>
<th>$-\Delta_{\text{hydr}} S^\circ$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>Ionic Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>1089*</td>
<td>132*</td>
<td>—</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>520</td>
<td>119</td>
<td>0.60</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>405</td>
<td>89</td>
<td>0.95</td>
</tr>
<tr>
<td>K$^+$</td>
<td>314</td>
<td>51</td>
<td>1.33</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>468</td>
<td>94</td>
<td>1.26</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>1926</td>
<td>268</td>
<td>0.65</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>1579</td>
<td>209</td>
<td>0.99</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>1309</td>
<td>159</td>
<td>1.35</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>1832</td>
<td>243</td>
<td>0.80</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>1950</td>
<td>272</td>
<td>0.76</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>2092</td>
<td>239</td>
<td>0.72</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>4355</td>
<td>460</td>
<td>0.64</td>
</tr>
<tr>
<td>F$^-$</td>
<td>506</td>
<td>151</td>
<td>1.36</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>378</td>
<td>96</td>
<td>1.81</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>348</td>
<td>80</td>
<td>1.95</td>
</tr>
<tr>
<td>I$^-$</td>
<td>308</td>
<td>60</td>
<td>2.16</td>
</tr>
</tbody>
</table>

*a* This is a theoretical estimate.
The other quantity of interest is the entropy of hydration, \( \Delta_{\text{hydr}}S \). The hydration process results in considerable ordering of water molecules around each ion, which reduces various molecular motions and hence the number of microstates so that \( \Delta_{\text{hydr}}S \) also is a negative quantity. As Table 5.4 shows, the variation in standard \( \Delta_{\text{hydr}}S \) with ionic radius closely corresponds to that for \( \Delta_{\text{hydr}}H \). Finally, note that there are two contributions to the entropy of solution, \( \Delta_{\text{soln}}S \). 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 \( \Delta_{\text{soln}}S \) depends on the magnitudes of these opposing factors.

**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, \( \Delta_f H^o \), of an individual ion. To get around this problem, we arbitrarily assign a zero value to the formation of the hydrogen ion—that is, \( \Delta_f H^o [H^+(aq)] = 0 \)—and then evaluate the \( \Delta_f H^o \) values of other ions relative to this scale. Consider the following reaction:

\[
\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq) \quad \Delta_r H^o = -167.2 \text{ kJ mol}^{-1}
\]

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

\[
\Delta_r H^o = \Delta_f H^o[H^+(aq)] + \Delta_f H^o[Cl^-(aq)] - (\frac{1}{2})(0) - (\frac{1}{2})(0)
\]

so that

\[
\Delta_r H^o = \Delta_f H^o[Cl^-(aq)]
\]

or

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

Once the value of \( \Delta_f H^o[Cl^-(aq)] \) has been determined, we can measure the \( \Delta_r H^o \) of the reaction

\[
Na(s) + \frac{1}{2}Cl_2(g) \rightarrow Na^+(aq) + Cl^-(aq)
\]

from which we can determine the value of \( \Delta_f H^o[Na^+(aq)] \) and so on.

Table 5.5 lists the \( \Delta_f H^o \) values of some common cations and anions. Two points are worth noting about this table. First, for aqueous solutions, the standard state at 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 \( \Delta_f H^o \) values are relative values based on the \( \Delta_f H^o[H^+(aq)] = 0 \) 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 \( \Delta_f G^o[H^+(aq)] \) and \( \Delta S^o[H^+(aq)] \). These values are also listed in Table 5.5. 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 \(-55.23 \text{ J K}^{-1} \text{ mol}^{-1}\), and that of \( NO_3^-(aq) \) is \(146.4 \text{ J K}^{-1} \text{ mol}^{-1}\). 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 5.8

Use the standard enthalpy of the reaction

\[
\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) \quad \Delta_r H^\circ = -406.9 \text{ kJ mol}^{-1}
\]

to calculate the value of \(\Delta_r H^\circ[\text{Na}^+(aq)]\), given that \(\Delta_r H^\circ[\text{Cl}^-(aq)] = -167.2 \text{ kJ mol}^{-1}\).

**Answer**

The standard enthalpy of reaction is given by

\[
\Delta_r H^\circ = \Delta_r H^\circ[\text{Na}^+(aq)] + \Delta_r H^\circ[\text{Cl}^-(aq)] - (0) - \left(\frac{1}{2}\right)(0)
\]

\[-406.9 \text{ kJ mol}^{-1} = \Delta_r H^\circ[\text{Na}^+(aq)] - 167.2 \text{ kJ mol}^{-1}\]

so

\[
\Delta_r H^\circ[\text{Na}^+(aq)] = -239.7 \text{ kJ mol}^{-1}
\]

### 5.8 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, $\mu_{\text{NaCl}}$, is given by

$$\mu_{\text{NaCl}} = \mu_{\text{Na}^+} + \mu_{\text{Cl}^-}$$  \hspace{1cm} (5.48)

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

$$\mu_{\text{Na}^+} = \mu_{\text{Na}^+}^0 + RT \ln m_{\text{Na}^+}$$

$$\mu_{\text{Cl}^-} = \mu_{\text{Cl}^-}^0 + RT \ln m_{\text{Cl}^-}$$

where $\mu_{\text{Na}^+}^0$ and $\mu_{\text{Cl}^-}^0$ are the standard chemical potentials of the ions. Equation 5.48 can now be written as

$$\mu_{\text{NaCl}} = \mu_{\text{NaCl}}^0 + RT \ln m_{\text{Na}^+}m_{\text{Cl}^-}$$

where

$$\mu_{\text{NaCl}}^0 = \mu_{\text{Na}^+}^0 + \mu_{\text{Cl}^-}^0$$

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

$$\text{M}_{n+}\text{X}_{n-} \rightleftharpoons n+ \text{M}^z+ + n- \text{X}^z-$$

where $v_+$ and $v_-$ 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, $v_+ = v_- = 1$, $z_+ = +1$, and $z_- = -1$. For CaCl$_2$, $v_+ = 1$, $v_- = 2$, $z_+ = +2$, and $z_- = -1$. The chemical potential is given by

$$\mu = v_+\mu_+ + v_-\mu_-$$  \hspace{1cm} (5.49)

where

$$\mu_+ = \mu_{\text{Na}^+}^0 + RT \ln m_+$$

and

$$\mu_- = \mu_{\text{Cl}^-}^0 + RT \ln m_-$$

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

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

Substituting the expressions for $\mu_+$ and $\mu_-$ into Equation 5.49 yields

$$\mu = (v_+\mu_+^0 + v_-\mu_-^0) + RT \ln m_+^{v_+}m_-^{v_-}$$  \hspace{1cm} (5.50)

We define mean ionic molality ($m_\pm$) as a geometric mean (see Appendix 1) of the individual ionic molalities

$$m_\pm = (m_+^{v_+}m_-^{v_-})^{1/v}$$  \hspace{1cm} (5.51)
where $v = v_+ + v_-$, and Equation 5.50 becomes

$$\mu = (v_+ \mu_+^c + v_- \mu_-^c) + vRT \ln m_\pm$$

(5.52)

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

$$m_\pm = [(v_+ m)^{v_+} (v_- m)^{v_-}]^{1/v}$$

$$= m [(v_+^v)(v_-^v)]^{1/v}$$

(5.53)

**Example 5.9**

Write the expression for the chemical potential of $\text{Mg}_3(\text{PO}_4)_2$ in terms of the molality of the solution.

**Answer**

For $\text{Mg}_3(\text{PO}_4)_2$, 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

$$\mu_{\text{Mg}_3(\text{PO}_4)_2} = \mu_{\text{Mg}_3(\text{PO}_4)_2}^c + 5RT \ln m_\pm$$

From Equation 5.51,

$$m_\pm = m(3^3 \times 2^2)^{1/5}$$

$$= 2.55 m$$

so that

$$\mu_{\text{Mg}_3(\text{PO}_4)_2} = \mu_{\text{Mg}_3(\text{PO}_4)_2}^c + 5RT \ln 2.55 m$$

Unlike nonelectrolyte solutions, most electrolyte solutions behave nonideally. The reason is as follows. The intermolecular forces between uncharged species generally depend on $1/r^2$, 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 5.16). This dependence means that even in quite dilute solutions (for example, 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

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

(5.54)

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,

$$a_\pm = \gamma_\pm m_\pm$$

(5.55)
The chemical potential of a nonideal electrolyte solution is given by

\[
\mu = (v_+\mu_+^* + v_-\mu_-^*) + vRT\ln a_\pm \\
= (v_+\mu_+^* + v_-\mu_-^*) + RT\ln a_\pm^* \\
= (v_+\mu_+^* + v_-\mu_-^*) + RT\ln a
\]

(5.57)

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

\[
a = a_\pm^*
\]

Experimental values of \(\gamma_\pm\) can be obtained from freezing-point-depression and osmotic-pressure measurements* or electrochemical studies (see Chapter 7). Hence, the value of \(a_\pm\) can be calculated from Equation 5.55. In the limiting case of infinite dilution \((m \to 0)\), we have

\[
\lim_{m\to 0} \gamma_\pm = 1
\]

Figure 5.17 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, to be discussed next.

* Interested readers should consult the standard physical chemistry texts listed in Chapter 1 (p. 6) for details of \(\gamma_\pm\) measurements.
Example 5.10

Write expressions for the activities \( a \) of KCl, Na\(_2\)CrO\(_4\), and Al\(_2\)(SO\(_4\))\(_3\) in terms of their molalities and mean ionic activity coefficients.

**Answer**

We need the relations \( a = a^r_\pm = (\gamma_\pm m_\pm)^r \).

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

Therefore, \( a_{\text{KCl}} = m^2 \gamma_\pm^2 \)

Na\(_2\)CrO\(_4\): \( n = 2 + 1 = 3; m_\pm = [(2m)^2(m)]^{1/3} = 4^{1/3}m \)

Therefore, \( a_{\text{Na}_2\text{CrO}_4} = 4m^{1/3} \gamma_\pm^3 \)

Al\(_2\)(SO\(_4\))\(_3\): \( n = 2 + 3 = 5; m_\pm = [(2m)^2(3m)^3]^{1/5} = 108^{1/5}m \)

Therefore, \( a_{\text{Al}_2\text{(SO}_4)_3} = 108m^{1/5} \gamma_\pm^5 \)

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 Walter Karl Hückel (1895–1980) 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 \(0.01 \text{ m}\) or lower; and (3) on average, each ion is surrounded by ions of opposite charge, forming an ionic atmosphere (Figure 5.18a). 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 \(g_+\) nor \(g_-/C_0\) could be measured directly, the final result is expressed in terms of the mean ionic activity coefficient of the electrolyte as follows:

\[
\log \frac{g}{C_0} = \frac{1}{2} \frac{|z_+z_-|}{\sqrt{I}}
\]  

(5.58)

where the \(| |\) signs denote the magnitude but not the signs 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:

\[
I = \frac{1}{2} \sum_i m_i z_i^2
\]

(5.59)

where \(m_i\) and \(z_i\) are the molality and the charge of the \(i\)th 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 electrolyte solutions primarily stems from the total concentration of charges present rather than from the chemical nature of the individual ionic species. Equation 5.59 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. Because most studies are carried out in water at 298 K (that is, \(e = 78.54\), and \(T = 298\) K), Equation 5.58 becomes

\[
\log \gamma_\pm = -0.509 |z_+z_-| \sqrt{I}
\]

(5.60)

This equation is known as the Debye–Hückel limiting law, as is Equation 5.58.
Example 5.11

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 5.59:

\[
I = \frac{1}{2} [ (0.010 \ m) \times 2^2 + (0.010 \ m) \times (-2)^2 ] = 0.040 \ m
\]

From Equation 5.60,

\[
\log \gamma_\pm = -0.509 (2 \times 2) \sqrt{0.040} = -0.407
\]

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 5.60. 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 5.60 can be used to calculate the ionic activity coefficient of individual cations or anions. Thus, for the \( i \)th ion, we write

\[
\log \gamma_i = -0.509 z_i^2 \sqrt{I}
\]

where \( z_i \) is the charge of the ion. The \( \gamma_+ \) and \( \gamma_- \) values calculated this way are related to \( \gamma_\pm \) according to Equation 5.56.

Figure 5.19 shows calculated and measured values of \( \log \gamma_\pm \) at various ionic strengths. We can see Equation 5.60 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 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 5.18b).
If the conductance measurement were carried out at a very strong electric field (approximately $2 \times 10^5$ 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 $5 \times 10^{-8}$ cm, so that the time required for the ion to move out of the atmosphere is $5 \times 10^{-8}$ cm/10 cm s$^{-1}$, or $5 \times 10^{-9}$ 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

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+ (aq) + \text{Cl}^- (aq)$$
The thermodynamic solubility product for the process, $K_{sp}^{\circ}$, is given by

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

The ionic activities are related to ionic concentrations as follows:

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

so that

$$K_{sp}^{\circ} = \gamma_{Ag^+} m_{Ag^+} \gamma_{Cl^-} m_{Cl^-}$$

$$= \gamma_{Ag^+} \gamma_{Cl^-} K_{sp}$$

where $K_{sp} = m_{Ag^+} m_{Cl^-}$ 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

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

we write

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

Taking the logarithm of both sides and rearranging, we obtain

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

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

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

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

$$\log \frac{S}{S^\circ} = 0.509 |z_+ z_-| \sqrt{I} \quad (5.62)$$

Note that the value of $S^\circ$ 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 $S^\circ$.
If AgCl is dissolved in pure water, its solubility \( S \) is \( 1.3 \times 10^{-5} \) mol L\(^{-1}\). If it is dissolved in a KNO\(_3\) solution, according to Equation 5.62, 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 5.62 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:

\[
\log \frac{S}{S^0} = -K'I
\] (5.63)

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 5.63 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 5.62 and 5.63, we have the approximate equation

\[
\log \frac{S}{S^0} = 0.509|z_+z_-|\sqrt{I} - K'I
\] (5.64)

Equation 5.64 is applicable over a wider range of ionic strengths.

Figure 5.20 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 5.64 predominates. This trend is most pronounced for salts such as \( \text{Na}_2\text{SO}_4 \) and \( (\text{NH}_4)_2\text{SO}_4 \).

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 5.21 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.

### 5.9 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. With incompletely dissociated salts or in situations in which ion-pair formation occurs, the relationship is more complicated. 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:

\[
\frac{\text{actual number of particles in solution at equilibrium}}{\text{number of particles in solution before dissociation}} = i
\]

\[ (5.65) \]

* When \( I \) is less than unity, \( \sqrt{I} > I \). Thus, at low ionic strengths, the first term in Equation 5.64 predominates.
If a solution contains $N$ units of a weak electrolyte and if $\alpha$ is the degree of dissociation,

$$M_nX_n \rightleftharpoons v_+M^{z+} + v_-X^{z-}$$

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

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

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

and

$$\alpha = \frac{i - 1}{v - 1} \quad (5.66)$$

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$_2$SO$_4$ 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:

$$\text{Ca}^{2+}(aq) + \text{NO}_3^-(aq) \rightleftharpoons \text{Ca(NO}_3^+)^{+}(aq)$$

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 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 5.12**

The osmotic pressures of a 0.01 $m$ solution of a monoprotic acid HA and a 0.01 $m$ sucrose solution at 298 K are 0.306 atm and 0.224 atm, respectively. Calculate the van’t Hoff factor and the degree of dissociation for HA. Assume ideal behavior and no ion pair formation.

**Answer**

As far as osmotic pressure measurements are concerned, the main difference between HA and sucrose is that only HA can dissociate into ions (H$^+$ and A$^-$). Otherwise, equal
concentrations of HA 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, the ratio of the osmotic pressure for HA (with dissociation) to that of sucrose (no dissociation) must therefore be equal to the van’t Hoff factor; that is,

\[
i = \frac{0.306 \text{ atm}}{0.224 \text{ atm}} = 1.37
\]

For HA, \(\nu_+ = 1\) and \(\nu_- = 1\), so \(\nu = 2\). From Equation 5.66,

\[
z = \frac{1.37 - 1}{2 - 1} = 0.37
\]

The acid is 37% dissociated. Finally, the equations used to determine the colligative properties of non-electrolyte solutions (Equations 5.35, 5.36, and 5.43) must be modified for electrolyte solutions as follows:

\[
\Delta T = K_b(\imath m_2) \quad \text{(5.67)}
\]

\[
\Delta T = K_i(\imath m_2) \quad \text{(5.68)}
\]

\[
\pi = \frac{RT(\imath c_2)}{\mu_2} \quad \text{(5.69)}
\]

We assume ideal behavior and no ion pair formation.

### 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 uneven distribution at equilibrium 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 two cases.

**Case 1.** The protein solution is placed in the left compartment and water is placed in the right compartment. Proteins are ampholytes—that is, they possess both acidic and basic properties. Depending on the pH of the medium, a protein (P) can exist as an anion, a cation, or a neutral species. Let us assume that in this situation the protein is an anion bearing \(z\)-charges and \(\text{Na}^+\) is the counterion. In solution it dissociates as follows:

\[
\text{Na}_z^+\text{P}^{z-} \rightarrow z\text{Na}^+ + \text{P}^{z-}
\]

The osmotic pressure of the solution \((\pi_1)\), which depends on the number of particles present, is given by

\[
\pi_1 = (z + 1)cRT \quad \text{(5.70)}
\]
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 \(\frac{1}{31}\) 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 (Figure 5.22). 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, some of the 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\(^+\) P\(^-\) is \(c\), and that of NaCl is \(b\). At equilibrium, the concentrations are

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

and

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

where L and R denote the left and right compartment, respectively, and \(x\) is the amount of NaCl transported from right to left.

At equilibrium \((\mu_{NaCl})^L = (\mu_{NaCl})^R\) so that

\[
(\mu^e + RT \ln a_\pm)_{NaCl}^L = (\mu^e + RT \ln a_\pm)_{NaCl}^R
\]

Because \(\mu^e\), the standard chemical potential, is the same on both sides, we obtain

\[
(a_\pm)_{NaCl}^L = (a_\pm)_{NaCl}^R
\]

From Equation 5.54,

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

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

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

or

\[
(zc + x)(x) = (b - x)(b - x)
\]

**Figure 5.22**
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.
Solving for \( x \), we obtain

\[
x = \frac{b^2}{ze + 2b}
\]  

(5.71)

The osmotic pressure \( (\pi_2) \), which is proportional to the difference in solute concentration between the two sides, is now given by

\[
\pi_2 = [(c + ze + x + x) - (b - x + b - x)]RT
\]

left compartment right compartment

or

\[
\pi_2 = (c + ze - 2b + 4x)RT
\]

Substituting for \( x \) (Equation 5.71), we obtain

\[
\pi_2 = \left( c + ze - 2b + \frac{4b^2}{ze + 2b} \right)RT = \frac{ze^2 + 2cb + z^2c^2}{ze + 2b}RT
\]

(5.72)

Equation (5.72) was derived assuming no change in either the pH or the volume of the solutions. Two limiting cases follow.

Case 1. If \( b \ll ze \) (the salt concentration is much less than the protein concentration), then

\[
\pi_2 = \frac{ze^2 + z^2c^2}{ze}RT = (ze + c)RT = (z + 1)cRT = \pi_1
\]

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

\[
\pi_2 = \frac{2cb}{2b}RT = cRT
\]

In this limiting case, the osmotic pressure approaches that of the solution in which the protein bears no net charge. 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.

An alternative approach to eliminate the Donnan effect is to choose a pH at which the protein has no net charge, called the isoelectric point (see Chapter 8). At this pH, the distribution of any type of diffusible ions will always be the same in both compartments. This method is difficult in practice because most proteins are least soluble at their isoelectric points.

\(^*\) In practice, \( c \leq 1 \times 10^{-4} M, z \leq 30 \), so that \( z^2c \approx 0.1 M \). Thus, in order for this limiting case to hold, the concentration of the added salt should be about \( 1 M \).
We have simplified the discussion of the Donnan effect by assuming no change in either pH or volume of the solution. Also, for the sake of simplicity, we have used a common singly charged ion, Na\textsuperscript{+}. Equations for more complicated situations can be derived using the same principles. The Donnan effect is essential to understanding the distribution of ions across the membranes of living organisms. A particularly important case is the distribution of bicarbonate and chloride ions between plasma and red blood cells, discussed in Section 8.8. In other cases, such as the nerve cells, the Donnan effect cannot be easily applied because of the active transport phenomenon in which ions are transported across the membrane against a concentration gradient (see p. 178).

5.10 Biological Membranes

In this section we shall consider the structure and function of biological membranes. In particular, we shall concentrate on the transport of ions across these membranes.

Cell membranes are composed of two kinds of molecules: lipids and proteins. Lipids, such as fats and waxes, are insoluble in water but soluble in many organic solvents. There are three types of membrane lipids: phospholipids, cholesterol, and glycolipids. We shall consider only the phospholipids here. One of the most common phospholipids found in cellular membranes is phosphatidic acid, shown in Figure 5.23. Membrane lipids are unique in that one end of the molecule contains a polar group that is hydrophilic (“water-loving”), and the other end is a long hydrocarbon chain that is hydrophobic (“water-fearing”). The lipids form a bilayer (about 60 Å in thickness), arranged so their polar groups constitute the top and bottom surfaces of the membrane and the nonpolar groups are buried in the interior region, which has a dielectric constant of about 3.

Figure 5.24 shows a widely accepted model of cell membrane structure called the fluid mosaic model. Protein molecules may lie at or near the inner or outer membrane surface, or they may partially or totally penetrate the membrane. The extent of interaction between the proteins and the lipids depends on the types of intermolecular forces and thermodynamic considerations. Generally, cell membranes have

![Figure 5.23](image-url)

(a) Structure of phosphatidic acid (a phospholipid). (b) Simplified phosphatidic acid structure.
great physical strength and high electrical insulating properties. They are not rigid structures, however. On the contrary, many membrane proteins and lipids are constantly in motion (Figure 5.25). Fluorescence probes have shown that membrane proteins can normally diffuse laterally a distance of about several hundred angstroms in 1 minute. The phospholipid molecules, because of their smaller size, can diffuse much more quickly.

Membrane proteins have multiple functions: to act as receptors, to act as enzymes (for example, in the synthesis of important molecules, such as adenosine triphosphate (ATP) at the mitochondrial membrane, or in the initiation of photosynthesis at the chloroplast membrane), and to act as carriers for ions and other molecules across the membrane.

Figure 5.24
The fluid mosaic model of cell membrane structure. The large bodies are protein molecules that are embedded to varying degrees in the lipid bilayer. [From S. J. Singer and G. L. Nicolson, Science 175, 723 (1972). Copyright 1972 by the American Association for the Advancement of Science.]

Figure 5.25
Lateral diffusion (a) of lipids is much more rapid than flip-flop diffusion (b). Membrane proteins can only undergo lateral diffusion.
Membrane Transport

One of the key functions of cell membranes is to act as a permeability barrier. In general, membranes selectively control the passage of substances from one region to another; for example, they permit nutrients to enter the interior of the cell and expel waste products from metabolism to the outside. Membrane transport, the movement of substances across membranes, relies on membrane permeability and membrane transport mechanisms.

Cell membranes are freely permeable to water, carbon dioxide, and oxygen, but much less so to ions, polar molecules, and other substances. Generally speaking, small molecules pass through the membrane more readily than larger ones and most membranes are impermeable to large molecules, such as proteins. Because the interior region of the lipid bilayer is hydrophobic, we would expect the membrane to be more permeable to uncharged species and nonpolar molecules than to ions and polar molecules. This is indeed the case, although water is a conspicuous exception. The membrane permeability of ions in general is very low. Their movement across the membrane must therefore be aided by special mechanisms to be discussed shortly.

In order for many essential biological processes to take place, the ionic and molecular composition of the internal aqueous phase of the cell must be appreciably different from its external environment. For example, the concentration of potassium ions is some 35 times higher in erythrocytes (red blood cells) than in the extracellular blood plasma. The reverse is true for sodium ions—the extracellular sodium ion concentration is about 15 times that of the intracellular fluid. We would expect that, given enough time, the concentrations of the same types of ions would eventually become equal in the intra- and extracellular fluids. That this is not the case means that processes other than normal diffusion must be sustaining the differences in ionic concentrations. We shall briefly consider the three types of membrane transport mechanisms.

Simple Diffusion. A number of substances pass through the membrane by simple diffusion; that is, they pass from one region to another containing a lower concentration of the substance. There may be discrete pores (thought to be formed by the membrane-bound proteins) in the membrane structure through which small molecules pass, thereby circumventing the hydrophobic lipid bilayer. This mechanism not only accounts for the rapid rate at which oxygen and carbon dioxide move through the membrane, but also explains why polar molecules such as water penetrate the membrane with ease. The pores can be envisioned as protein-lined channels that penetrate the lipid bilayer. Because of the fluidity of the membrane structure, these pores are continually being destroyed and created. The rate of molecular movement across the membrane is directly proportional to the concentration gradient across the membrane. It is known that there are water-specific membrane-channel proteins, called aquaporins, that allow the passage of water molecules at a high rate (about $10^9$ molecules per second), which is essential for maintaining osmotic balance in cells. Computer simulation shows that water molecules diffuse through the channel in a highly cooperative fashion via hydrogen bonds with one another and with the atoms on the protein backbone that forms the channel wall. Ions (for example, $\text{H}_3\text{O}^+$) cannot pass through because they are repelled by the local electrostatic fields along the channel.

Facilitated Diffusion. Facilitated diffusion also involves the movement of molecules from a region of higher concentration to one having a lower concentration, but it differs from simple diffusion in that it is a carrier-assisted transport process. In facilitated diffusion, the substance to be transported is complexed with a carrier...
molecule (Figure 5.26). The carrier molecule is free to move back and forth across the membrane. At the outer face of the membrane (that is, the surface in contact with extracellular fluid), the carrier can bind to the substance, and the resulting complex diffuses across the membrane from a high- to a low-concentration region, where it dissociates into the carrier and the free substance. Each carrier has one or more specific binding sites for the substance it transports. After releasing its cargo, the carrier molecule diffuses back to the other side of the membrane and the process is repeated. Facilitated diffusion continues as long as there is a concentration gradient across the membrane for the transported substance. A different example of facilitated diffusion is the transport of glucose molecules into the erythrocyte. Glucose by itself is quite insoluble in the lipid bilayer, so the rate of simple diffusion of these molecules would be too slow to sustain metabolic processes. Instead, glucose enters the erythrocyte through a protein complex called glucose permease, which forms a hydrophilic path through the hydrophobic center of the membrane.

As mentioned, membrane transport by simple diffusion and facilitated diffusion are spontaneous processes. Consider the transfer of 1 mole of a solute X from a higher concentration region ($\alpha$) to a lower one ($\beta$). From Equation 5.27 we write the chemical potential of X as

$$\mu_X = \mu_X^\circ + RT \ln[X]$$

where $\mu_X^\circ$ is the standard chemical potential and we have used concentration instead of activity. The change in Gibbs energy in terms of the difference in chemical potentials is

$$\Delta G = (\mu_X)_\beta - (\mu_X)_\alpha = RT \ln[X]_\beta - RT \ln[X]_\alpha$$

$$= RT \ln \frac{[X]_\beta}{[X]_\alpha}$$

(Note that $\mu_X^\circ$ is a constant and therefore cancels in the subtraction.) Because $[X]_\beta < [X]_\alpha$, $\Delta G < 0$ and the process will continue until the concentrations in the two regions become equal and $\Delta G = 0$.

**Active Transport.** Unlike simple diffusion and facilitated diffusion, active transport involves the movement of substances across the membrane against a concentration gradient. Thermodynamics tells us that this is a nonspontaneous process; therefore, energy must be supplied from an external source in order for active transport to
occur. Earlier we mentioned the unequal concentrations of K$^+$ and Na$^+$ ions in the intra- and extracellular fluids. Maintaining these differences in ionic concentration requires active transport. Normal diffusion processes transport Na$^+$ ions from the exterior to the interior of the cell and move K$^+$ ions in the opposite direction. At the same time, Na$^+$ ions are constantly “pumped” out of the cell while K$^+$ ions are pumped in. The word pump is used to describe the movement of ions against concentration gradients. A steady state is reached when the flow of the ions of one type in one direction by active transport is balanced by the “leaking” (that is, diffusion) of the ions of the same type in the opposite direction.

The mechanism of active transport is fairly well understood. We know, for example, that the active transport of Na$^+$ and the active transport of K$^+$ ions across the membrane are linked together. Thus, the active transport system is often referred to as the sodium–potassium pump. As in facilitated diffusion, a carrier molecule is needed for active transport. Furthermore, the molecule must be such that an energy supply can be directly coupled to it. This carrier molecule is an enzyme called sodium–potassium ATPase (adenosinetriphosphatase). The energy provider is adenosine triphosphate (ATP), which hydrolyzes to adenosine diphosphate (ADP) and inorganic phosphate:

$$\text{ATP}^4\text{H}_2\text{O} \rightarrow \text{ADP}^3\text{HPO}_4^2^- + \text{H}^+ \quad \Delta_r G^\circ \approx -30 \text{ kJ mol}^{-1}$$

This spontaneous process (note the large decrease in the standard Gibbs energy) is coupled to sodium–potassium ATPase to drive the energetically unfavorable process of moving ions against a concentration gradient (Figure 5.27).

**Figure 5.27**
The Na$^+$–K$^+$ ATPase is primarily responsible for setting and maintaining the intracellular concentrations of Na$^+$ and K$^+$ ions, which it does by moving 3 Na$^+$ ions out of the cell for every 2 K$^+$ ions it moves in. Consequently, a potential is also established across the membrane.

We can estimate the increase in Gibbs energy for the process of transporting against a concentration gradient as follows. Suppose that 1 mole of a certain compound X is transported from the interior of the cell, where its concentration is $1.0 \times 10^{-4} \text{ M}$, to the outside, where its concentration is $1.0 \times 10^{-3} \text{ M}$. Because transport occurs against a concentration gradient, we have the following inequality in chemical potentials:

$$(\mu_X)_{ex} > (\mu_X)_{in}$$
where \( \text{in} \) and \( \text{ex} \) denote interior and exterior, respectively. At \( 37^\circ \text{C} \), the change in Gibbs energy for this process is given by

\[
\Delta G = (\mu_X)_{\text{ex}} - (\mu_X)_{\text{in}} = RT \ln \frac{[X]_{\text{ex}}}{[X]_{\text{in}}}
\]

\[
= (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(310 \text{ K}) \ln \frac{1.0 \times 10^{-3} \text{ M}}{1.0 \times 10^{-4} \text{ M}}
\]

\[
= 5.9 \text{ kJ mol}^{-1}
\]

If the substance transported carries a charge—for example, \( X^{\pm} \), where \( X \) denotes the ion and \( z^+ \) its charge—there is an additional effect, namely, the electrical potential established by the unequal concentrations of the ions across the membrane. Consequently, the Gibbs energy change is given by

\[
\Delta G = RT \ln \frac{[X^{\pm}]_{\text{ex}}}{[X^{\pm}]_{\text{in}}} + zF\Delta V
\]

(5.73)

where \( F \) is the faraday constant \((96,500 \text{ C mol}^{-1})\) and \( \Delta V \) is the difference in electrical potential (in volts) across the membrane. Consider the case in which \( \text{Na}^+ \) ions are being carried from the inside of the cell to the outside. To obtain an estimate for \( \Delta G \), let us use the following typical data: \( [\text{Na}^+]_{\text{ex}}/[\text{Na}^+]_{\text{in}} = 10 \), \( \Delta V = 80 \text{ mV} \) or \( 8.0 \times 10^{-2} \text{ V} \), and \( T = 37^\circ \text{C} \) or 310 K. Thus,

\[
\Delta G = (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(310 \text{ K}) \ln 10 + (1)(96,500 \text{ C mol}^{-1})(8.0 \times 10^{-2} \text{ V})
\]

\[
= 13.7 \text{ kJ mol}^{-1}
\]

where 1 J = 1 C \( \times \) 1 V. In this case the active transport becomes more nonspontaneous by the positive electrical potential due to the \( \text{Na}^+ \) ions. As mentioned earlier, this nonspontaneous process is made possible by the hydrolysis of ATP.

In recent years, a great deal of effort has been devoted to understand the structure and function of ion channels—the protein-based gatekeepers governing the cellular influx and outflow of ions. Much of the knowledge gained has come from the X-ray studies of the membrane-bound proteins that form these channels. Consider, for example, the potassium channels. In animals, these channels govern nerve cell signaling, heart beating rhythm, and the release of insulin. Experiments show that the channels are formed by a complex made up of four protein subunits. One of the early mysteries about these channels was how they can favor the larger \( \text{K}^+ \) ions (ionic radius: 1.33 Å) over the smaller \( \text{Na}^+ \) ions (ionic radius: 0.98 Å) in a ratio of about 1000 to 1. When an ion enters such a channel, it is stripped of its hydrated sphere that normally surrounds it when dissolved in water. The size of \( \text{K}^+ \) ions fits nicely inside the oxygen rich tunnel structure. The oxygen atoms (from the amino acids) take the place of water molecules in the favorable ion–dipole interaction that exists in the hydration shell. The \( \text{Na}^+ \) ions, on the other hand, are too small for this interaction and generally remain outside the channel. Another area of intense study is the mechanism of \textit{gating} of ion channels. Depending on the chemical and/or physical environment, some channels can open and close very quickly, on the order of microseconds. Certain channels open only in response to changes in voltage differences across the surrounding cell membranes. These so-called voltage-gated ion channels are of particular significance in nerve conduction (see Section 7.6).

Finally, we note that the ionic permeability across cell membranes can be altered by the naturally occurring antibiotics such as valinomycin and nonactin. These mol-
Molecules have a macrocyclic structure, with a cavity in the center and a hydrophobic exterior (Figure 5.28). They can form complexes with alkali metal ions (usually in a 1:1 ratio). Because of their external hydrophobic nature, the antibiotic–metal complexes can pass through cell membranes. Moreover, the complex formation is quite specific for individual ions, which must be of the appropriate size to fit into the cavity. For example, the formation constant for the valinomycin–K\(^{+}\) complex is about 1000 times greater than that of the valinomycin–Na\(^{+}\) complex. The increase in K\(^{+}\) ion permeability disturbs the delicate intra- and extracellular concentration balance, and can kill the targeted bacterial cells. Gramicidin A, another type of natural antibiotic, can dimerize to form a transmembrane pore that is permeable to monovalent ions (Figure 5.29).

Compounds such as valinomycin and crown ethers that can affect metal ion transport are called ionophores, or ion carriers.
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

\[
V = \frac{q_A q_B}{4\pi\varepsilon_0 r}
\]

and the electrostatic force, \(F\), between the charges is

\[
F = \frac{q_A q_B}{4\pi\varepsilon_0 r^2}
\]

where \(\varepsilon_0\) is the permittivity of the vacuum (see p. 156). The electric field is the electrostatic force on a unit positive charge. Thus, the electric field at \(q_B\) due to \(q_A\) is

\[
E = \frac{q_A q_B}{4\pi\varepsilon_0 r^2} = \frac{q_A}{4\pi\varepsilon_0 r^2}
\]

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

Another important property of the electric field is its electric potential, \(\phi\), which is the potential energy of a unit positive charge in the electric field. Its units are \(\text{J C}^{-1}\) or \(\text{V}\). 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 \(qE dr\) or \(E dr\) because \(q = 1\ \text{C}\). 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 \(-E dr\). (The negative sign ensures that as \(dr\) decreases, \(-E dr\) 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:

\[
\phi = -\int_{r=\infty}^{r=r} E \, dr = -\int_{r=\infty}^{r=r} \frac{q_A}{4\pi\varepsilon_0 r^2} \, dr = \frac{q_A}{4\pi\varepsilon_0} \left[1 - \frac{1}{r}ight]
\]

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

$$\Delta \phi = \phi_2 - \phi_1$$  \hspace{1cm} (5)

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

**Dielectric Constant ($\varepsilon$) 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 5.30. The *dielectric constant* of the substance is defined as

$$\varepsilon = \frac{E_0}{E}$$  \hspace{1cm} (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 5.15).

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 is filled with a dielectric ($C$) and when there is a vacuum ($C_0$) between the plates are given by

$$C = \frac{Q}{\Delta \phi}$$  \hspace{1cm} (7)

and

$$C_0 = \frac{Q}{\Delta \phi_0}$$  \hspace{1cm} (8)

![Figure 5.30](image-url)

(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 $\varepsilon_0$. (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.
Because $\Delta \phi = Ed$, where $d$ is the distance between the plates, Equation 6 can also be written as

$$\varepsilon = \frac{(\Delta \phi_0/d)}{(\Delta \phi/d)} = \frac{(Q/C_0)}{(Q/C)} = \frac{C}{C_0}$$  \hspace{1cm} (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/1 V. Note that the ratio $C/C_0$ in Equation 9 makes $\varepsilon$ a dimensionless quantity.

**Membrane Capacitance**

As stated in the chapter, ions can cross the membrane lipid bilayer only through ion channels. The unequal concentrations of ions in the cytoplasm and extracellular fluid produce a charge displacement, as shown in Figure 5.31. Because ions cannot cross the lipid bilayer due to the bilayer’s hydrophobic nature, they accumulate on the two surfaces of the membrane. The membrane thus stores electric charges in the same way charges are stored by a capacitor in an electric circuit.

Based on a lipid-layer thickness of about 5 nm and a dielectric constant of 3, which is roughly that of an 18-carbon fatty acid, the membrane capacitance has been calculated to be about 1 microfarad (1 $\mu$F) per square centimeter. This result is in good agreement with the experimentally determined value.


Suggestions for Further Reading

Books

Articles
Nonelectrolyte and Electrolyte Solutions

Phase Equilibria

Colligative Properties
Problems

Concentration Units

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

5.2 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\(^{-3}\).

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

5.4 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\(^{-3}\).

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

5.6 For dilute aqueous solutions in which the density of the solution is roughly equal to that of the pure solvent, the molality of the solution is equal to its molality. Show that this statement is correct for a 0.010 M aqueous urea \([\text{NH}_2\text{CO}]\) solution.

5.7 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.)

5.8 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\(^{-3}\); 1 quart = 0.946 L.)

Thermodynamics of Mixing

5.9 Liquids A and B form a nonideal solution. Provide a molecular interpretation for each of the following situations: \(\Delta_{\text{mix}}H > 0\), \(\Delta_{\text{mix}}H < 0\), \(\Delta_{\text{mix}}V > 0\), \(\Delta_{\text{mix}}V < 0\).
5.10 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.

5.11 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.

Chemical Potential

5.12 Which of the following has a higher chemical potential? If neither, answer “same.” (a) H₂O(s) or H₂O(l) at water’s normal melting point, (b) H₂O(s) at −5°C and 1 bar or H₂O(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.

5.13 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).

5.14 Write the phase equilibrium conditions for a liquid solution of methanol and water in equilibrium with its vapor.

Henry’s Law

5.15 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.

5.16 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 (that is, 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.

5.17 The Henry’s law constant of oxygen in water at 25°C is 773 atm 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.)

5.18 The solubility of N₂ in blood at 37°C and a partial pressure of 0.80 atm is 5.6 × 10⁻⁴ mol L⁻¹. A deep-sea diver breathes compressed air with a partial pressure of N₂ equal to 4.0 atm. Assume that the total volume of blood in the body is 5.0 L. Calculate the amount of N₂ gas released (in liters) when the diver returns to the surface of water, where the partial pressure of N₂ is 0.80 atm.

Colligative Properties

5.19 List the important assumptions in the derivation of Equation 5.35.

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

5.21 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.)

5.22 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.)

5.23 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.)

5.24 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.

5.25 Explain why jams can be stored under atmospheric conditions for long periods of time without spoilage.

5.26 Provide a molecular interpretation for the positive and negative deviations in the boiling-point curves.

5.27 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 242 g. Account for this discrepancy. (Hint: Consider solvent–solute and solute–solute interactions.)

5.28 A common antifreeze for car radiators is ethylene glycol, CH₂(OH)CH₂(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.)

5.29 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?
5.30 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.

5.31 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.

5.32 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.

5.33 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.

5.34 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.

5.35 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).]

5.36 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.

5.37 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?

5.38 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 (C₁₇H₂₁NO₄)? What assumptions are made in the analysis? The freezing point of benzene is 5.5°C.

5.39 “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.

5.40 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.

5.41 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 (C₆H₆), a nonpolar solvent that lacks the ability to form hydrogen bonds. A solution of 3.8 g of CH₃COOH in 80 g C₆H₆ 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.)

5.42 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.

5.43 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 solu-
tion is mixed with 55.0 mL of an aqueous 3.0 M ethanol solution, the total volume is 70.0 mL.

5.44 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.

5.45 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.

5.46 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.

5.47 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.

5.48 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.)

<table>
<thead>
<tr>
<th>$x_{CS_2}$</th>
<th>0</th>
<th>0.20</th>
<th>0.45</th>
<th>0.67</th>
<th>0.83</th>
<th>1.00</th>
</tr>
</thead>
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<td>$P_{CS_2}$/torr</td>
<td>344</td>
<td>291</td>
<td>250</td>
<td>217</td>
<td>180</td>
<td>0</td>
</tr>
<tr>
<td>$P_{C,H_2,O}$/torr</td>
<td>0</td>
<td>272</td>
<td>390</td>
<td>438</td>
<td>465</td>
<td>512</td>
</tr>
</tbody>
</table>

5.49 A solution is made up by dissolving 73 g of glucose (C$_4$H$_{12}$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.

5.50 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.)

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

5.52 Consider a binary liquid mixture 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.

**Ionic Activity and Debye–Hückel Limiting Law**

5.53 Express the mean activity, mean activity coefficient, and mean molality in terms of the individual ionic quantities ($a_+, a_-, \gamma_+, \gamma_-, m_+, m_-$, and $m$) for the following electrolytes: KI, SrSO$_4$, CaCl$_2$, Li$_2$CO$_3$, K$_3$Fe(CN)$_6$, and K$_4$Fe(CN)$_6$.

5.54 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$_4$Fe(CN)$_6$.

5.55 The mean activity coefficient of a 0.010 m H$_2$SO$_4$ solution is 0.544. What is its mean ionic activity?

5.56 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.

5.57 The Debye–Hückel limiting law is more reliable for 1:1 electrolytes than for 2:2 electrolytes. Explain.

5.58 In theory, the size of the ionic atmosphere is 1/k, called the Debye radius, and $k$ is given by

$$k = \left( \frac{e^2 N_A}{\epsilon_0 k_B T} \right)^{1/2} \sqrt{I}$$

where $e$ is the electronic charge, $N_A$ Avogadro’s constant, $\epsilon_0$ the permittivity of vacuum ($8.854 \times 10^{-12}$ C$^2$ N$^{-1}$ m$^{-2}$), $\epsilon$ 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$_2$SO$_4$ solution at 25°C.

5.59 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.

5.60 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.

**Additional Problems**

5.61 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 concentrations of urea in blood plasma and urine are 0.005 mol kg$^{-1}$ and 0.326 mol kg$^{-1}$, respectively.

5.62 (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?

$$\left( \frac{\partial V_m}{\partial n_A} \right)_{T, P, n_B} = \left( \frac{\partial V_m}{\partial X_A} \right)_{T, P, n_B}$$
(b) Given that the molar volume of this mixture \( (V_m) \) 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 at \( x_A = 0.20 \).

5.63 The partial molar volumes for a benzene–carbon tetrachloride solution at 25°C at a mole fraction of 0.5 are \( V_b = 0.106 \text{ L mol}^{-1} \) and \( V_c = 0.100 \text{ L mol}^{-1} \), respectively, where the subscripts b and c denote \( \text{C}_6\text{H}_6 \) and \( \text{CCl}_4 \). (a) What is the volume of a solution made up of one mole of each? (b) Given that the molar volumes are \( \text{C}_6\text{H}_6 = 0.089 \text{ L mol}^{-1} \) and \( \text{CCl}_4 = 0.097 \text{ L mol}^{-1} \), what is the change in volume on mixing 1 mole each of \( \text{C}_6\text{H}_6 \) and \( \text{CCl}_4 \)? (c) What can you deduce about the nature of intermolecular forces between \( \text{C}_6\text{H}_6 \) and \( \text{CCl}_4 \)?

5.64 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.

| \( \pi/\text{atm} \) | \( 8.40 \times 10^{-4} \) | \( 1.72 \times 10^{-3} \) | \( 2.52 \times 10^{-3} \) |
| \( c/\text{g} \cdot \text{L}^{-1} \) | 8.10 | 12.31 | 15.00 |

\[
\pi/\text{atm} = 3.23 \times 10^{-3} + 7.75 \times 10^{-3}c/\text{g} \cdot \text{L}^{-1}
\]

5.65 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.

5.66 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.

5.67 Two beakers are placed in a closed container. Beaker A initially contains 0.15 mole of naphthalene \( (\text{C}_9\text{H}_8) \) in 100 g of benzene \( (\text{C}_6\text{H}_6) \) 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.

5.68 From the following data, calculate the heat of solution for KI:

| \( \text{NaCl} \) | \( \text{NaI} \) | \( \text{KCl} \) | \( \text{KI} \) |
| Lattice energy/\( \text{kJ} \cdot \text{mol}^{-1} \) | 787 | 700 | 716 | 643 |
| Heat of solution/\( \text{kJ} \cdot \text{mol}^{-1} \) | 3.8 | -5.1 | 17.1 | ? |

5.69 The concentrations of \( \text{K}^+ \) and \( \text{Na}^+ \) ions in the intracellular fluid of a nerve cell are approximately 400 mM and 50 mM, respectively, but in the extracellular fluid the \( \text{K}^+ \) and \( \text{Na}^+ \) concentrations are 20 mM and 440 mM, respectively. Given that the electric potential inside the cell is \(-70 \text{ mV} \) relative to the outside, calculate the Gibbs energy change for the transfer of 1 mole of each type of ion against the concentration gradient at 37°C.

5.70 In this chapter (see Figures 5.12, 5.17, and 5.19), 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.

5.71 (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 CaCl₂) 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.

5.72 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.

5.73 (a) Using the Debye–Hückel limiting law, calculate the value of \( \gamma_\pm \) for a 2.0 × 10⁻³ m Na₃PO₄ solution at 25°C. (b) Calculate the values of \( \gamma_+ \) and \( \gamma_- \) for the Na₃PO₄ solution, and show that they give the same value for \( \gamma_\pm \) as that obtained in (a).

5.74 Calculate the solubility of BaSO₄ (in g L⁻¹) in (a) water and (b) a 6.5 × 10⁻⁵ M MgSO₄ solution. The solubility product of BaSO₄ is 1.1 × 10⁻¹⁰. Assume ideal behavior.

5.75 The thermodynamic solubility product of AgCl is 1.6 × 10⁻¹⁰. What is [Ag⁺] in (a) a 0.020 M KNO₃ solution and (b) a 0.020 M KCl solution?

5.76 Oxalic acid, \((\text{COOH})₂\), is a poisonous compound present in many plants and vegetables, including spinach. Calcium oxalate is only slightly soluble in water \( (K_{sp} = 3.0 \times 10⁻⁹ \text{ at 25°C}) \) 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(NO₃)₂ solution. Assume ideal behavior in (b).

5.77 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.

5.78 A 0.010 m aqueous solution of the ionic compound Co(NH₃)₅Cl₃ has a freezing-point depression of 0.0558 K. What can you conclude about its structure? Assume the compound is a strong electrolyte.

5.79 The osmotic pressure of blood plasma is approximately 7.5 atm at 37°C. Estimate the total concentra-
tion of dissolved species and the freezing point of blood plasma.

5.80 Referring to Figure 5.22, 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); 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.)

5.81 The antibiotic Gramicidin A can transport Na⁺ ions into a certain cell at the rate of 5.0 × 10⁷ Na⁺ ions channel⁻¹ s⁻¹. Calculate the time in seconds to transport enough Na⁺ ions to increase its concentration by 8.0 × 10⁻³ M in a cell whose intracellular volume is 2.0 × 10⁻¹⁰ mL.

5.82 The concentration of glucose inside a cell is 0.12 mM and that outside a cell is 12.3 mM. Calculate the Gibbs energy change for the transport of 3 moles of glucose into the cell at 37°C.

5.83 Referring to Figure 5.22, suppose we have a protein solution (Na₃P) in the left compartment at 0.0010 M concentration. Calculate the osmotic pressure of the solution if the concentration of the NaCl solution in the right compartment is at 0 M, 0.10 M, 2.0 M, and 10 M. The temperature is at 298 K.

5.84 Use Equations 5.34 and 5.37 to calculate $K_b$ and $K_f$ for water shown in Table 5.2.

5.85 Describe how you would experimentally distinguish between two types of cells containing and lacking aquaporins for transporting water.