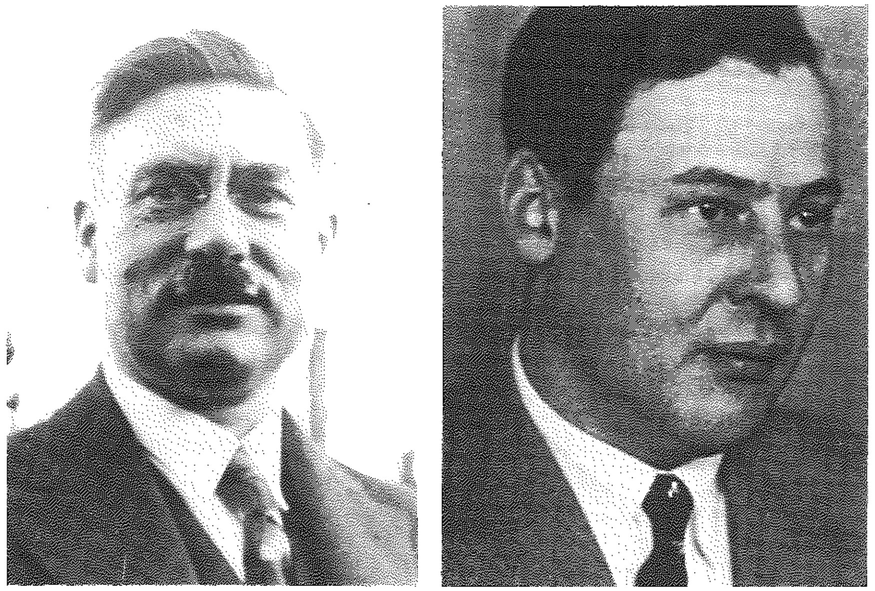


Peter Debye (left) was born in Maastricht, the Netherlands, on March 24, 1884 and died in 1966. Debye was originally trained as an electrical engineer but turned his attention to physics, receiving his Ph.D. from the University of Munich in 1908. After holding positions in Switzerland, the Netherlands, and Germany, he moved to the University of Berlin in the early 1930s. Although he had been assured that he would be able retain his Dutch citizenship, Debye found that he would be unable to continue his work in Berlin unless he became a German citizen. He refused and left Germany in 1939 for Cornell University, where he remained for the rest of his life, becoming an American citizen in 1946. Debye was awarded the Nobel Prize for chemistry in 1936 "for his contributions to our knowledge of molecular structure through his investigations on dipole moments and on the diffraction of X rays and electrons in gases." **Erich Hückel** (right) was born in Göttingen, Germany, on August 19, 1896 and died in 1980. He received his Ph.D. in physics from the University of Göttingen in 1921. He later worked with Peter Debye in Zurich, and together they developed a theory for the thermodynamic properties of solutions of strong electrolytes that is now known as the Debye–Hückel theory. Hückel also developed Hückel molecular orbital theory, which we learned in Chapter 10 applies to conjugated and aromatic molecules. Hückel was appointed professor of theoretical physics at the University of Marburg in 1937, where he remained until his retirement.

CHAPTER 25

Solutions II: Solid–Liquid Solutions

In the previous chapter, we studied binary solutions, such as ethanol/water solutions, in which the two components were miscible in all proportions. In such solutions, either component can be treated as a solvent. In this chapter, we will study solutions in which one of the components is present at much smaller concentrations than the other, so that the terms "solute" and "solvent" are meaningful. We will introduce a solute standard state based upon Henry's law such that the activity of the solute becomes equal to its concentration as its concentration goes to zero. In the first few sections, we will study solutions of nonelectrolytes, and then solutions of electrolytes. Unlike for solutions of nonelectrolytes, we will be able to present exact expressions for the activities and activity coefficients in dilute solutions of electrolytes. In Sections 25–3 and 25–4, we will discuss the colligative properties of solutions, such as osmotic pressure, as well as the depression of the freezing point and elevation of the boiling point of a solvent by the addition of solute.

25–1. We Use a Raoult's Law Standard State for the Solvent and a Henry's Law Standard State for the Solute for Solutions of Solids Dissolved in Liquids

In Section 24–8, we considered solutions in which one of the components is only sparingly soluble in the other. In cases such as these, we use the terms *solute* for the sparingly soluble component and *solvent* for the component in excess. We customarily denote solvent quantities by a subscript 1 and solute quantities by a subscript 2. The activities we defined for the solvent and solute are such that $a_1 \to x_1$ as $x_1 \to 1$ and $a_2 \to x_2$ as $x_2 \to 0$. Recall that a_1 is defined with respect to a Raoult's law standard state (Equation 24.39)

$$a_1 = \frac{P_1}{P_1^*} \qquad \text{(Raoult's law standard state)} \qquad (25.1)$$

and that a_2 is defined with respect to a Henry's law standard state (Equation 24.43)

$$a_{2x} = \frac{P_2}{k_{\mathrm{H},x}} \qquad \text{(Henry's law standard state)} \tag{25.2}$$

where the subscript x emphasizes that a_{2x} and $k_{\mathrm{H},x}$ are based on a mole fraction scale ($P_2 = k_{\mathrm{H},x}x_2$). Even if the solute does not have a measurable vapor pressure, defining the activity by Equation 25.2 is nevertheless convenient because the ratio is still meaningful; even though P_2 and $k_{\mathrm{H},2}$ may be exceedingly small, the ratio $P_2/k_{\mathrm{H},2}$ is finite.

Although we have defined the activities of the solvent and solute in terms of mole fractions, the use of mole fractions to express the concentration of a solute in a dilute solution is not numerically convenient. A more convenient unit is *molality* (m), which is defined as the number of moles of solute per 1000 grams of solvent. In an equation, we have

$$m = \frac{n_2}{1000 \text{ g solvent}} \tag{25.3}$$

where n_2 is the number of moles of solute (subscript 2). Note that the units of molality are $\mathrm{mol\cdot kg^{-1}}$. We say that a solution containing 2.00 moles of NaCl in 1.00 kg of water is 2.00 molal, or that it is a $2.00 \mathrm{\ mol\cdot kg^{-1}}$ NaCl(aq) solution. The relation between the mole fraction of solute (x_2) and molality (m) is

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{m}{\dfrac{1000 \mathrm{\ g\cdot kg^{-1}}}{M_1} + m} \tag{25.4}$$

where M_1 is the molar mass ($\mathrm{g\cdot mol^{-1}}$) of the solvent. The term $1000 \mathrm{\ g\cdot kg^{-1}}/M_1$ is the number of moles of solvent (n_1) in 1000 g of solvent and m, by definition, is the number of moles of solute in 1000 g of solvent. In the case of water, $1000 \mathrm{\ g\cdot kg^{-1}}/M_1$ is equal to $55.506 \mathrm{\ mol\cdot kg^{-1}}$, so Equation 25.4 becomes

$$x_2 = \frac{m}{55.506 \mathrm{\ mol\cdot kg^{-1}} + m} \tag{25.5}$$

Note that x_2 and m are directly proportional to each other if $m \ll 55.506 \mathrm{\ mol\cdot kg^{-1}}$, which is the case for dilute solutions.

EXAMPLE 25–1

Calculate the mole fraction of a $0.200 \mathrm{\ mol\cdot kg^{-1}}$ $C_{12}H_{22}O_{11}$(aq) solution.

SOLUTION: The solution contains 0.200 moles of sucrose per 1000.0 g of water. The mole fraction of sucrose is

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{0.200 \text{ mol}}{\dfrac{1000.0 \text{ g}}{18.02 \mathrm{\ g\cdot mol^{-1}}} + 0.200 \text{ mol}} = 0.000359$$

We define the solute activity in terms of molality by requiring that

$$a_{2m} \longrightarrow m \quad \text{as} \quad m \longrightarrow 0 \tag{25.6}$$

where the subscript m emphasizes that a_{2m} is based on a molality scale. We can express Henry's law in terms of the molality rather than the mole fraction by $P_2 = k_{\mathrm{H},m}m$, where once again the subscript m emphasizes that $k_{\mathrm{H},m}$ is based on a molality scale. In terms of $k_{\mathrm{H},m}$, the activity of the solute is defined by

$$a_{2m} = \frac{P_2}{k_{\mathrm{H},m}} \tag{25.7}$$

Another common concentration unit is *molarity* (c), which is the number of moles of solute per 1000 mL of solution. In an equation,

$$c = \frac{n_2}{1000 \text{ mL solution}} \tag{25.8}$$

Note that molarity has units of $\mathrm{mol\cdot L^{-1}}$. We say that a solution containing 2.00 moles of NaCl in 1.00 liter of solution is a 2.00-molar solution, or that it is a $2.00 \mathrm{\ mol\cdot L^{-1}}$ NaCl(aq) solution.

We define the solute activity in terms of molarity by requiring that

$$a_{2c} \longrightarrow c \quad \text{as} \quad c \longrightarrow 0 \tag{25.9}$$

where the subscript c emphasizes that a_{2c} is based on a molarity scale. We can express Henry's law in terms of the molarity rather than the mole fraction of solute by $P_2 = k_{\mathrm{H},c}c$, where once again the subscript c emphasizes that $k_{\mathrm{H},c}$ is based on a molarity scale. In terms of $k_{\mathrm{H},c}$, the activity of the solute is defined by

$$a_{2c} = \frac{P_2}{k_{\mathrm{H},c}} \tag{25.10}$$

Converting from molarity to molality is easy if we know the density of the solution, which is available for many solutions in handbooks. For example, the density of a $2.450 \mathrm{\ mol\cdot L^{-1}}$ aqueous sucrose solution at 20°C is $1.3103 \mathrm{\ g\cdot mL^{-1}}$. Thus, there are 838.6 g of sucrose in 1000 mL of solution, which has a total mass of 1310.3 g. Of these 1310.3 g, 838.6 g are due to sucrose, so 1310.3 g − 838.6 g = 471.7 g are due to water. The molality then is given by

$$m = \frac{2.450 \text{ mol sucrose}}{471.7 \text{ g } H_2O} \times \frac{1000 \text{ g } H_2O}{\text{kg } H_2O} = 5.194 \mathrm{\ mol\cdot kg^{-1}}$$

EXAMPLE 25–2

The density (in $\mathrm{g\cdot mL^{-1}}$) of an aqueous sucrose solution can be expressed as

$$\begin{aligned} \rho/\mathrm{g\cdot mL^{-1}} &= 0.9982 + (0.1160 \mathrm{\ kg\cdot mol^{-1}})m - (0.0156 \mathrm{\ kg^2\cdot mol^{-2}})m^2 \\ &\quad + (0.0011 \mathrm{\ kg^3\cdot mol^{-3}})m^3 \qquad 0 \le m \le 6 \mathrm{\ mol\cdot kg^{-1}} \end{aligned}$$

Calculate the molarity of a 2.00-molal aqueous sucrose solution.

SOLUTION: A 2.00-molal aqueous sucrose solution contains 2.00 moles (684.6 g) of sucrose per 1000 g of H_2O, or 2.00 moles of sucrose in 1684.6 g of solution. The density of the solution is given by

$$\begin{aligned}\rho/\mathrm{g\cdot mL^{-1}} &= 0.9982 + (0.1160\ \mathrm{kg\cdot mol^{-1}})(2.00\ \mathrm{mol\cdot kg^{-1}})\\ &\quad - (0.0156\ \mathrm{kg^2\cdot mol^{-2}})(4.00\ \mathrm{mol^2\cdot kg^{-2}})\\ &\quad + (0.0011\ \mathrm{kg^3\cdot mol^{-3}})(8.00\ \mathrm{mol^3\cdot kg^{-3}})\\ &= 1.177\end{aligned}$$

so the volume of the solution is

$$V = \frac{\text{mass}}{\text{density}} = \frac{1684.6\ \mathrm{g}}{1.177\ \mathrm{g\cdot mL^{-1}}} = 1432\ \mathrm{mL}$$

Therefore, the molarity of the solution is

$$c = \frac{2.00\ \text{mol sucrose}}{1.432\ \mathrm{L}} = 1.40\ \mathrm{mol\cdot L^{-1}}$$

Problem 25–5 asks you to derive a general relation between c and m.

EXAMPLE 25–3

Given the density (ρ) of the solution in $\mathrm{g\cdot mL^{-1}}$, derive a general relation between x_2 and c.

SOLUTION: Consider exactly a one liter sample of the solution. In this case, $c = n_2$, the number of moles of solute in the one-liter sample. The mass of the solution is given by

$$\text{mass of the solution per liter} = (1000\ \mathrm{mL\cdot L^{-1}})\rho$$

so the mass of the solvent is

$$\begin{aligned}\text{mass of the solvent per liter} &= \text{mass of the solution} - \text{mass of the solute}\\ &= (1000\ \mathrm{mL\cdot L^{-1}})\rho - cM_2\end{aligned}$$

where M_2 is the molar mass ($\mathrm{g\cdot mol^{-1}}$) of the solute. Therefore, n_1, the number of moles of solvent, is

$$n_1 = \frac{(1000\ \mathrm{mL\cdot L^{-1}})\rho - cM_2}{M_1}$$

so

$$\begin{aligned}x_2 = \frac{n_2}{n_1+n_2} &= \frac{c}{\dfrac{(1000\ \mathrm{mL\cdot L^{-1}})\rho - cM_2}{M_1} + c}\\ &= \frac{cM_1}{(1000\ \mathrm{mL\cdot L^{-1}})\rho + c(M_1 - M_2)}\end{aligned} \tag{25.11}$$

Table 25.1 summarizes the equations for the activities we have defined for the various concentration scales. In each case, the activity coefficient γ is defined by dividing the activity by the appropriate concentration. Thus, for example, $\gamma_m = a_{2m}/m$. Problem 25–12 asks you to derive a relation between the various solute activity coefficients in Table 25.1.

25–2. The Activity of a Nonvolatile Solute Can Be Obtained from the Vapor Pressure of the Solvent

The equations for the solute activities in Table 25.1 are applicable to nonvolatile as well as volatile solutes. The vapor pressure of a nonvolatile solute is so low, however, that these equations are not practical to use. Fortunately, the Gibbs–Duhem equation provides us with a way to determine the activity of a nonvolatile solute from a measurement of the activity of the solvent. We will illustrate this procedure using an

TABLE 25.1

A summary of the equations for the activities used for the various concentration scales for dilute solutions.

Solvent—Raoult's law standard state		
$a_1 = \dfrac{P_1}{P_1^*}$	$a_1 \to x_1$ as $x_1 \to 1$	
$\gamma_1 = \dfrac{a_1}{x_1}$	$P_1 \to P_1^* x_1$ as $x_1 \to 1$	(Raoult's law)
Solute—Henry's law standard state		
Mole fraction scale		
$a_{2x} = \dfrac{P_2}{k_{\mathrm{H},x}}$	$a_{2x} \to x_2$ as $x_2 \to 0$	
$\gamma_{2x} = \dfrac{a_{2x}}{x_2}$	$P_2 \to k_{\mathrm{H},x} x_2$ as $x_2 \to 0$	(Henry's law)
Molality scale		
$a_{2m} = \dfrac{P_2}{k_{\mathrm{H},m}}$	$a_{2m} \to m$ as $m \to 0$	
$\gamma_{2m} = \dfrac{a_{2m}}{m}$	$P_2 \to k_{\mathrm{H},m} m$ as $m \to 0$	(Henry's law)
Molarity scale		
$a_{2c} = \dfrac{P_2}{k_{\mathrm{H},c}}$	$a_{2c} \to c$ as $c \to 0$	
$\gamma_{2c} = \dfrac{a_{2c}}{c}$	$P_2 \to k_{\mathrm{H},c} c$ as $c \to 0$	(Henry's law)

aqueous solution of sucrose. According to a Raoult's law standard state, the activity of the water is given by P_1/P_1^*. Now let's consider a dilute solution, in which case $a_1 = x_1$. We now want to relate a_1 to the molality of the solute, m. For a dilute solution, $m \ll 55.506\ \text{mol}\cdot\text{kg}^{-1}$, so we can neglect m compared with $55.506\ \text{mol}\cdot\text{kg}^{-1}$ in the denominator of Equation 25.5 and write

$$x_2 \approx \frac{m}{55.506\ \text{mol}\cdot\text{kg}^{-1}}$$

Therefore, for small concentrations,

$$\ln a_1 = \ln x_1 = \ln(1 - x_2) \approx -x_2 \approx -\frac{m}{55.506\ \text{mol}\cdot\text{kg}^{-1}} \qquad (25.12)$$

where we have used the fact that $\ln(1 - x_2) \approx -x_2$ for small values of x_2.

Table 25.2 and Figure 25.1 give experimental data for the vapor pressure of water in equilibrium with an aqueous sucrose solution at 25°C as a function of molality and mole fraction, respectively. The equilibrium vapor pressure of pure water at 25°C is 23.756 torr, so $a_1 = P_1/P_1^* = P_1/23.756$ is given in the third column of Table 25.2.

Equation 25.12 relates a_1 to the molality m for only a dilute solution. For example, Table 25.2 shows that $a_1 = 0.93276$ at 3.00 molal, whereas Equation 25.12 gives $\ln a_1 = -0.054048$, or $a_1 = 0.9474$. To account for this discrepancy, we now define a quantity ϕ, called the *osmotic coefficient*, by

$$\ln a_1 = -\frac{m\phi}{55.506\ \text{mol}\cdot\text{kg}^{-1}} \qquad (25.13)$$

Note that $\phi = 1$ if the solution behaves as an ideal dilute solution. Thus, the deviation of ϕ from unity is a measure of the nonideality of the solution.

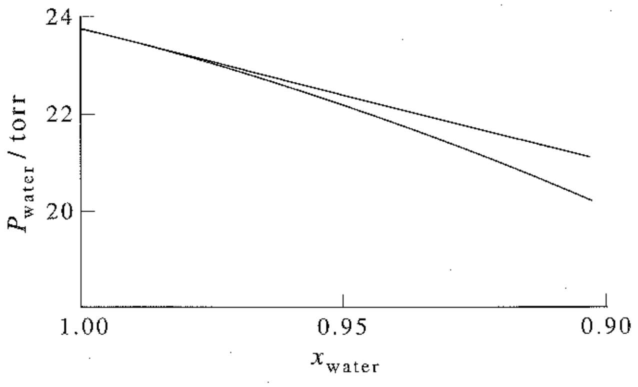


FIGURE 25.1
The vapor pressure of water in equilibrium with an aqueous sucrose solution at 25°C plotted against the mole fraction of water. Note that Raoult's law (the straight line in the figure) holds from $x_{\text{water}} = 1.00$ to about 0.97, but that deviations occur at lower values of x_{water}.

TABLE 25.2
The vapor pressure of water (P_1) in equilibrium with an aqueous sucrose solution at 25°C as a function of molality (m). Additional data are the activity of the water (a_1), the osmotic coefficient (ϕ), and the activity coefficient (γ_{2m}) of the sucrose.

$m/\text{mol}\cdot\text{kg}^{-1}$	P_1/torr	a_1	ϕ	γ_{2m}	$\ln \gamma_{2m}$
0.00	23.756	1.00000	1.0000	1.000	0.0000
0.10	23.713	0.99819	1.0056	1.017	0.0169
0.20	23.669	0.99634	1.0176	1.034	0.0334
0.30	23.625	0.99448	1.0241	1.051	0.0497
0.40	23.580	0.99258	1.0335	1.068	0.0658
0.50	23.534	0.99067	1.0406	1.085	0.0816
0.60	23.488	0.98872	1.0494	1.105	0.0998
0.70	23.441	0.98672	1.0601	1.125	0.1178
0.80	23.393	0.98472	1.0683	1.144	0.1345
0.90	23.344	0.98267	1.0782	1.165	0.1527
1.00	23.295	0.98059	1.0880	1.185	0.1723
1.20	23.194	0.97634	1.1075	1.233	0.2095
1.40	23.089	0.97193	1.1288	1.283	0.2492
1.60	22.982	0.96740	1.1498	1.335	0.2889
1.80	22.872	0.96280	1.1690	1.387	0.3271
2.00	22.760	0.95807	1.1888	1.442	0.3660
2.50	22.466	0.94569	1.2398	1.590	0.4637
3.00	22.159	0.93276	1.2879	1.751	0.5602
3.50	21.840	0.91933	1.3339	1.924	0.6544
4.00	21.515	0.90567	1.3749	2.101	0.7424
4.50	21.183	0.89170	1.4139	2.310	0.8372
5.00	20.848	0.87760	1.4494	2.481	0.9087
5.50	20.511	0.86340	1.4823	2.680	0.9858
6.00	20.176	0.84930	1.5111	3.878	1.3553

EXAMPLE 25–4
Using the data in Table 25.2, calculate the value of ϕ at $1.00\ \text{mol}\cdot\text{kg}^{-1}$.

SOLUTION: We simply use Equation 25.13 and find that

$$\phi = -\frac{(55.506\ \text{mol}\cdot\text{kg}^{-1})\ln(0.98059)}{1.00\ \text{mol}\cdot\text{kg}^{-1}} = 1.0880$$

in agreement with the entry in Table 25.2.

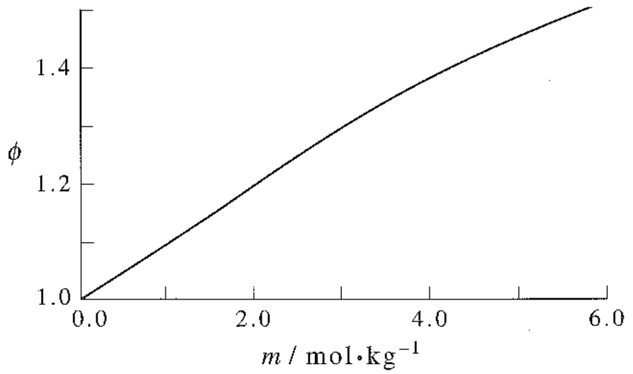


FIGURE 25.2
The osmotic coefficient (ϕ) of an aqueous sucrose solution at 25°C plotted against the molality (m). The magnitutde of the deviation of the value of ϕ from unity is a measure of the nonideality of the solution.

Figure 25.2 shows ϕ for an aqueous sucrose solution at 25°C plotted against m. Note that the solution becomes increasingly nonideal as m increases.

The fifth column in Table 25.2 gives the activity coefficient of the sucrose calculated from the activity of the water, or from the osmotic coefficient, by means of the Gibbs–Duhem equation,

$$n_1 d\ln a_1 + n_2 d\ln a_2 = 0$$

In terms of molality, m, $n_1 = 55.506$ mol and $n_2 = m$, so the Gibbs–Duhem equation becomes

$$(55.506\ \text{mol}\cdot\text{kg}^{-1})d\ln a_1 + m\,d\ln a_2 = 0 \qquad (25.14)$$

Using Equation 25.13, we see that $(55.506\ \text{mol}\cdot\text{kg}^{-1})d\ln a_1 = -d(m\phi)$. If we substitute this result and $a_{2m} = \gamma_{2m} m$ (Table 25.1) into Equation 25.14, we obtain

$$d(m\phi) = m\,d\ln(\gamma_{2m} m)$$

or

$$m\,d\phi + \phi\,dm = m(d\ln\gamma_{2m} + d\ln m)$$

We can rewrite this equation as

$$d\ln\gamma_{2m} = d\phi + \frac{\phi - 1}{m}dm$$

We now integrate from $m = 0$ (where $\gamma_{2m} = \phi = 1$) to arbitrary m to get

$$\ln\gamma_{2m} = \phi - 1 + \int_0^m \left(\frac{\phi - 1}{m'}\right)dm' \qquad (25.15)$$

Equation 25.15 allows us to calculate the activity coefficient of the solute from the data on the vapor pressure of the solvent. The vapor pressure of the solvent gives us the activity of the solvent from Equation 25.1; then the osmotic coefficient ϕ is calculated from Equation 25.13, and $\ln\gamma_{2m}$ is determined from Equation 25.15.

The data for ϕ in Table 25.2 can be fit with a polynomial in the molality. If we choose (arbitrarily) a 5th-degree polynomial, we find that (Problem 25–18)

$$\begin{aligned}\phi = {} & 1.00000 + (0.07349\ \text{kg}\cdot\text{mol}^{-1})m + (0.019783\ \text{kg}^2\cdot\text{mol}^{-2})m^2 \\ & - (0.005688\ \text{kg}^3\cdot\text{mol}^{-3})m^3 + (6.036\times10^{-4}\ \text{kg}^4\cdot\text{mol}^{-4})m^4 \\ & - (2.517\times10^{-5}\ \text{kg}^5\cdot\text{mol}^{-5})m^5 \qquad 0 \le m \le 6\ \text{mol}\cdot\text{kg}^{-1}\end{aligned}$$

We can substitute this expression into Equation 25.15 to obtain $\ln\gamma_{2m}$.

EXAMPLE 25–5
Use the above polynomial fit for ϕ and Equation 25.15 to calculate the value of γ_{2m} for a 1.00-molal aqueous sucrose solution.

SOLUTION: First, we need to evaluate the integral in Equation 25.15 (neglecting to write the units in the coefficients of the powers of m):

$$\begin{aligned}\int_0^1 \left(\frac{\phi - 1}{m}\right)dm &= \int_0^1 [0.07349 + 0.019783m - 0.005688m^2 \\ &\qquad + 6.036\times10^{-4}m^3 - 2.517\times10^{-5}m^4]dm \\ &= 0.07349 + \frac{0.019783}{2} - \frac{0.005688}{3} \\ &\qquad + \frac{6.036\times10^{-4}}{4} - \frac{2.517\times10^{-5}}{5} \\ &= 0.08163\end{aligned}$$

so

$$\begin{aligned}\ln\gamma_{2m} &= \phi - 1 + \int_0^1 \left(\frac{\phi - 1}{m}\right)dm \\ &= 0.08816 + 0.08163 = 0.1698\end{aligned}$$

or $\gamma_{2m} = 1.185$, in agreement with the entry in Table 25.2.

The values of $\ln\gamma_{2m}$ and γ_{2m} given in Table 25.2 have been calculated using the procedure in Example 25–5. Figure 25.3 shows $\ln\gamma_{2m}$ plotted against m for an aqueous sucrose solution at 25°C.

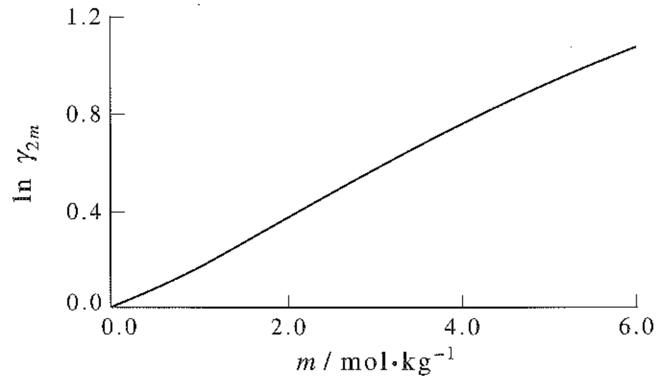


FIGURE 25.3
The logarithm of the activity coefficient (ln γ_{2m}) of sucrose in an aqueous sucrose solution at 25°C plotted against the molality (m).

25–3. Colligative Properties Are Solution Properties That Depend Only Upon the Number Density of Solute Particles

A number of solution properties, called *colligative properties*, depend, at least in dilute solution, upon only the number of solute particles, and not upon their kind. Colligative properties include the lowering of the vapor pressure of a solvent by the addition of a solute, the elevation of the boiling point of a solution by a nonvolatile solute, the depression of the freezing point of a solution by a solute, and osmotic pressure. We will discuss only freezing-point depression and osmotic pressure.

At the freezing point of a solution, solid solvent is in equilibrium with the solvent in solution. The thermodynamic condition of this equilibrium is that

$$\mu_1^{\mathrm{s}}(T_{\mathrm{fus}}) = \mu_1^{\mathrm{sln}}(T_{\mathrm{fus}})$$

where as usual the subscript 1 denotes solvent and T_{fus} is the freezing point of the solution. We use Equation 24.35 for μ_1 to obtain

$$\mu_1^{\mathrm{s}} = \mu_1^* + RT\ln a_1 = \mu_1^{\mathrm{l}} + RT\ln a_1$$

We have written μ_1^{l} for μ_1^* simply to compare it with μ_1^{s}. Solving for $\ln a_1$, we get

$$\ln a_1 = \frac{\mu_1^{\mathrm{s}} - \mu_1^{\mathrm{l}}}{RT} \tag{25.16}$$

Now differentiate with respect to temperature and use the Gibbs–Helmholtz equation (Example 24–1),

$$\left[\frac{\partial(\mu_1/T)}{\partial T}\right]_{P,x_1} = -\frac{\overline{H}_1}{T^2}$$

to obtain

$$\left(\frac{\partial \ln a_1}{\partial T}\right)_{P,x_1} = \frac{\overline{H}_1^{\mathrm{l}} - \overline{H}_1^{\mathrm{s}}}{RT^2} = \frac{\Delta_{\mathrm{fus}}\overline{H}}{RT^2} \tag{25.17}$$

where we have used the fact that $\overline{H}_1^{\mathrm{l}} - \overline{H}_1^{\mathrm{s}} = \Delta_{\mathrm{fus}}\overline{H}$ for the pure solvent. If we integrate Equation 25.17 from pure solvent, where $a_1 = 1$, $T = T_{\mathrm{fus}}^*$, to a solution with arbitrary values of a_1 and T_{fus}, we obtain

$$\ln a_1 = \int_{T_{\mathrm{fus}}^*}^{T_{\mathrm{fus}}} \frac{\Delta_{\mathrm{fus}}\overline{H}}{RT^2}\,dT \tag{25.18}$$

Equation 25.18 can be used to determine the activity of the solvent in a solution (Problem 25–20).

You may have calculated freezing-point depressions in general chemistry using the formula

$$\Delta T_{\mathrm{fus}} = K_{\mathrm{f}}m \tag{25.19}$$

where K_{f} is a constant, called the *freezing-point depression constant*, whose value depends upon the solvent. We can derive Equation 25.19 from Equation 25.18 by making a few approximations appropriate to dilute solutions. If the solution is sufficiently dilute, then $\ln a_1 = \ln x_1 = \ln(1 - x_2) \approx -x_2$, and if we assume that $\Delta_{\mathrm{fus}}\overline{H}$ is independent of temperature over the temperature range $(T_{\mathrm{fus}}, T_{\mathrm{fus}}^*)$, we obtain

$$\begin{aligned} -x_2 &= \frac{\Delta_{\mathrm{fus}}\overline{H}}{R}\int_{T_{\mathrm{fus}}^*}^{T_{\mathrm{fus}}} \frac{dT}{T^2} = \frac{\Delta_{\mathrm{fus}}\overline{H}}{R}\left(\frac{1}{T_{\mathrm{fus}}^*} - \frac{1}{T_{\mathrm{fus}}}\right) \\ &= \frac{\Delta_{\mathrm{fus}}\overline{H}}{R}\left(\frac{T_{\mathrm{fus}} - T_{\mathrm{fus}}^*}{T_{\mathrm{fus}}T_{\mathrm{fus}}^*}\right) \end{aligned} \tag{25.20}$$

Because x_2 and $\Delta_{\mathrm{fus}}\overline{H}$ are positive quantities, we see immediately that $T_{\mathrm{fus}} - T_{\mathrm{fus}}^* < 0$, or that $T_{\mathrm{fus}} < T_{\mathrm{fus}}^*$. Thus, we find that the addition of a solute will lower the freezing point of a solution. We can express x_2 in terms of molality by using Equation 25.4,

$$x_2 = \frac{m}{\dfrac{1000\ \mathrm{g\cdot kg^{-1}}}{M_1} + m} \approx \frac{M_1 m}{1000\ \mathrm{g\cdot kg^{-1}}} \tag{25.21}$$

for small values of m (dilute solution). Furthermore, because $T_{\mathrm{fus}}^* - T_{\mathrm{fus}}$ is usually only a few degrees (dilute solution once again), we can replace T_{fus} in the denominator of Equation 25.20 by T_{fus}^* to a good approximation to get finally (Problem 25–23)

$$\Delta T_{\mathrm{fus}} = T_{\mathrm{fus}}^* - T_{\mathrm{fus}} = K_{\mathrm{f}}m \tag{25.22}$$

where

$$K_f = \frac{M_1}{1000\ \text{g}\cdot\text{kg}^{-1}}\,\frac{R(T^*_{\text{fus}})^2}{\Delta_{\text{fus}}\overline{H}} \tag{25.23}$$

We can calculate the value of K_f for water.

$$\begin{aligned} K_f &= \left(\frac{18.02\ \text{g}\cdot\text{mol}^{-1}}{1000\ \text{g}\cdot\text{kg}^{-1}}\right)\frac{(8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(273.2\ \text{K})^2}{6.01\ \text{kJ}\cdot\text{mol}^{-1}} \\ &= 1.86\ \text{K}\cdot\text{kg}\cdot\text{mol}^{-1} \end{aligned}$$

Equation 25.22 tells us that the freezing point of a 0.20-molal solution of sucrose in water is $-(1.86\ \text{K}\cdot\text{kg}\cdot\text{mol}^{-1})(0.20\ \text{mol}\cdot\text{kg}^{-1}) = -0.37\ \text{K}$.

EXAMPLE 25–6

Calculate the value of K_f for cyclohexane, whose freezing point is 279.6 K and molar enthalpy of fusion is $2.68\ \text{kJ}\cdot\text{mol}^{-1}$.

SOLUTION: We use Equation 25-23 with $M_1 = 84.16\ \text{g}\cdot\text{mol}^{-1}$ and the above values of T^*_{fus} and $\Delta_{\text{fus}}\overline{H}$.

$$\begin{aligned} K_f &= \left(\frac{84.16\ \text{g}\cdot\text{mol}^{-1}}{1000\ \text{g}\cdot\text{kg}^{-1}}\right)\frac{(8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(279.6\ \text{K})^2}{2680\ \text{J}\cdot\text{mol}^{-1}} \\ &= 20.4\ \text{K}\cdot\text{kg}\cdot\text{mol}^{-1} \end{aligned}$$

Thus, the freezing point of a 0.20-molal solution of hexane in cyclohexane is 4.1 K lower than the freezing point of pure cyclohexane, or $T_{\text{fus}} = 275.5\ \text{K}$.

We can derive an expression for the boiling-point elevation of a solution containing a nonvolatile solute. The analog of Equation 25.22 is (Problem 25–25)

$$\Delta T_{\text{vap}} = T_{\text{vap}} - T^*_{\text{vap}} = K_b m \tag{25.24}$$

where the *boiling-point elevation constant* is given by

$$K_b = \frac{M_1}{1000\ \text{g}\cdot\text{kg}^{-1}}\,\frac{R(T^*_{\text{vap}})^2}{\Delta_{\text{vap}}\overline{H}} \tag{25.25}$$

The value of K_b for water is only $0.512\ \text{K}\cdot\text{kg}\cdot\text{mol}^{-1}$, so the boiling point elevation is a rather small effect for aqueous solutions.

25–4. Osmotic Pressure Can Be Used to Determine the Molecular Masses of Polymers

Figure 25.4 illustrates the development of osmotic pressure. In the initial state, we have pure water on the left and an aqueous sucrose solution on the right. The two liquids are separated by a membrane containing pores that allow water molecules but not solute molecules to pass through. Such a membrane is called a *semipermeable membrane*. (Many biological cells are surrounded by membranes semipermeable to water.) The levels of the two liquids in Figure 25.4 are initially the same, but water will pass through the semipermeable membrane until the chemical potentials of the water on the two sides of the membrane are equal. This process results in the situation shown in the equilibrium state, where the two liquid levels are no longer equal. The hydrostatic pressure head that is built up is called *osmotic pressure*.

Because the water is free to pass through the semipermeable membrane, the chemical potential of the water must be the same on the two sides of the membrane at equilibrium. In other words, the chemical potential of the pure water at a pressure P must equal the chemical potential of the water in the solution at a pressure $P + \Pi$ and an activity a_1. In an equation,

$$\begin{aligned} \mu_1^*(T, P) &= \mu_1^{\text{sln}}(T, P + \Pi, a_1) \\ &= \mu_1^*(T, P + \Pi) + RT \ln a_1 \end{aligned} \tag{25.26}$$

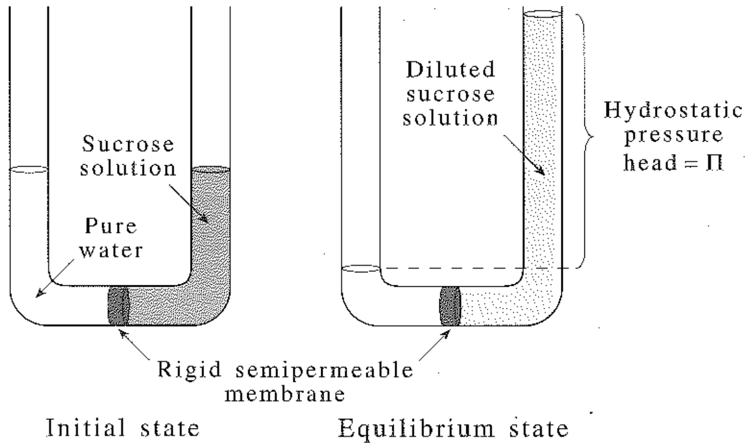


FIGURE 25.4
Passage of water through a rigid, semipermeable membrane separating pure water from an aqueous sucrose solution. The water passes through the membrane until the chemical potential of the water in the aqueous sucrose solution equals that of the pure water. The chemical potential of water in the sucrose solution increases as the hydrostatic pressure above the solution increases.

where $a_1 = P_1/P_1^*$. We can rewrite Equation 25.26. as

$$\mu_1^*(T, P + \Pi) - \mu_1^*(T, P) + RT \ln a_1 = 0 \tag{25.27}$$

The first two terms in Equation 25.27 are the difference in the chemical potential of the pure solvent at two different pressures. Equation 23.8

$$\left(\frac{\partial \mu_1^*}{\partial P}\right)_T = \overline{V}_1^* \tag{23.8}$$

where $\overline{V}_1^*$ is the molar volume of the pure solvent, tells us how the chemical potential varies with pressure. We can use Equation 23.8 to evaluate $\mu_1^*(T, P + \Pi) - \mu_1^*(T, P)$ by integrating both sides from P to $P + \Pi$ to get

$$\mu_1^*(T, P + \Pi) - \mu_1^*(T, P) = \int_P^{P+\Pi} \left(\frac{\partial \mu_1^*}{\partial P'}\right)_T dP' = \int_P^{P+\Pi} \overline{V}_1^* dP' \tag{25.28}$$

If we substitute Equation 25.28 into Equation 25.27, we obtain

$$\int_P^{P+\Pi} \overline{V}^* dP' + RT \ln a_1 = 0 \tag{25.29}$$

Assuming $\overline{V}_1^*$ does not vary with applied pressure, we can write Equation 25.29 as

$$\Pi \overline{V}_1^* + RT \ln a_1 = 0 \tag{25.30}$$

Furthermore, if the solution is dilute, then $a_1 \approx x_1 = 1 - x_2$, with x_2 small. Therefore, we can write $\ln a_1$ as $\ln(1 - x_2) \approx -x_2$, so that Equation 25.30 becomes

$$\Pi \overline{V}_1^* = RTx_2$$

Furthermore, because x_2 is small, $n_2 \ll n_1$ and

$$x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}$$

Substitute this into the above equation to get

$$\Pi = \frac{n_2 RT}{n_1 \overline{V}_1^*} \approx \frac{n_2 RT}{V}$$

where we have replaced $n_1 \overline{V}_1^*$ by the total volume of the solution, V (dilute solution). The above equation is usually written as

$$\Pi = cRT \tag{25.31}$$

where c is the molarity, n_2/V, of the solution. Equation 25.31 is called the van't Hoff equation for osmotic pressure. Using this equation, we calculate the osmotic pressure of a 0.100-molar aqueous solution of sucrose at 20°C to be

$$\begin{aligned}\Pi &= (0.100 \text{ mol}\cdot\text{L}^{-1})(0.08206 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(293.2 \text{ K}) \\ &= 2.40 \text{ atm}\end{aligned}$$

Thus, we see that osmotic pressure is a large effect. Because of this, osmotic pressure can be used to determine molecular masses of solutes, particularly solutes with large molecular masses such as polymers and proteins.

EXAMPLE 25–7

It is found that 2.20 g of a certain polymer dissolved in enough water to make 300 mL of solution has an osmotic pressure of 7.45 torr at 20°C. Determine the molecular mass of the polymer.

SOLUTION: The molarity of the solution is given by

$$\begin{aligned}c = \frac{\Pi}{RT} &= \frac{7.45 \text{ torr}/760 \text{ torr}\cdot\text{atm}^{-1}}{(0.08206 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(293.2 \text{ K})} \\ &= 4.07 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}\end{aligned}$$

Therefore, there are 4.07×10^{-4} moles of polymer per liter of solution, or $(0.300)(4.07 \times 10^{-4}) = 1.22 \times 10^{-4}$ moles per 300 mL of solution. Thus, we find that 1.22×10^{-4} moles corresponds to 2.20 g, or that the molecular mass is 18,000.

If a pressure in excess of 26 atm is applied to seawater at 15°C, the chemical potential of the water in the seawater will exceed that of pure water. Consequently, pure water can be obtained from seawater by using a rigid semipermeable membrane and an applied pressure in excess of the osmotic pressure of 26 atm. This process is known as *reverse osmosis*. Reverse osmosis units are commercially available and are used to obtain fresh water from salt water using a variety of semipermeable membranes, the most common of which is cellulose acetate.

25–5. Solutions of Electrolytes Are Nonideal at Relatively Low Concentrations

When sodium chloride dissolves in water, the solution contains sodium ions and chloride ions and essentially no undissociated sodium chloride. The ions interact with each other through a coulombic potential, which varies as $1/r$. We should compare this interaction with the one between neutral solute molecules (nonelectrolytes) such as sucrose, where the interaction varies as something like $1/r^6$. Thus, the interaction between ions in solution is effective over a much greater distance than the interaction between neutral solute particles, so solutions of electrolytes deviate from ideal behavior more strongly and at lower concentrations than do solutions of nonelectrolytes. Figure 25.5 shows $\ln \gamma_{2m}$ for sucrose, sodium chloride, and calcium chloride plotted versus molality. Note that $CaCl_2(aq)$ appears to behave more nonideally than NaCl(aq), which in turn behaves more nonideally than sucrose. The charge of $+2$ on the calcium ion leads to a stronger coulombic interaction and hence a stronger deviation from ideality than for NaCl. At $0.100\ \mathrm{mol \cdot kg^{-1}}$, the activity coefficient of sucrose is 0.998, whereas that of $CaCl_2(aq)$ is 0.518 and that of NaCl(aq) is 0.778.

Before we discuss the determination of activity coefficients for electrolytes, we must first introduce notation needed to describe the thermodynamic properties of solutions of electrolytes. Consider the general salt $C_{\nu_+}A_{\nu_-}$, which dissociates into ν_+ cations and ν_- anions per formula unit as in

$$C_{\nu_+}A_{\nu_-}(s) \xrightarrow{H_2O(l)} \nu_+C^{z_+}(aq) + \nu_-A^{z_-}(aq)$$

where $\nu_+z_+ + \nu_-z_- = 0$ by electroneutrality. For example, $\nu_+ = 1$ and $\nu_- = 2$ for $CaCl_2$ and $\nu_+ = 2$ and $\nu_- = 1$ for Na_2SO_4. Therefore, $CaCl_2$ is called a 1–2 electrolyte and Na_2SO_4 is called a 2–1 electrolyte. We write the chemical potential of the salt in terms of the chemical potentials of its constituent ions according to

$$\mu_2 = \nu_+\mu_+ + \nu_-\mu_- \tag{25.32}$$

where

$$\mu_2 = \mu_2^\circ + RT \ln a_2 \tag{25.33}$$

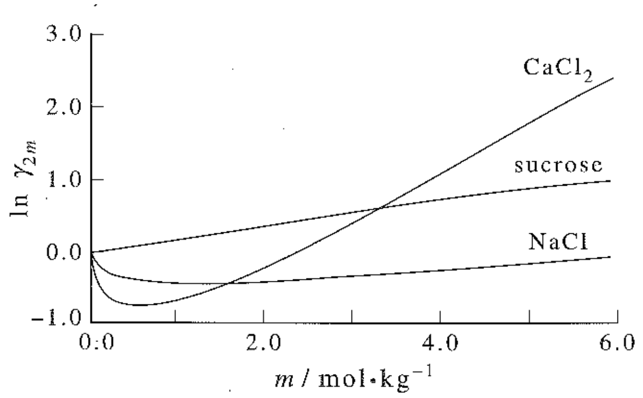


FIGURE 25.5
The logarithm of the activity coefficient ($\ln \gamma_{2m}$) of aqueous solutions of sucrose, sodium chloride, and calcium chloride plotted against molality (m) at 25°C. Note that the electrolyte solutions deviate from ideality ($\ln \gamma_{2m} = 0$) much more strongly than does sucrose at small concentrations.

and

$$\begin{aligned} \mu_+ &= \mu_+^\circ + RT \ln a_+ \\ \mu_- &= \mu_-^\circ + RT \ln a_- \end{aligned} \tag{25.34}$$

The superscript zeros here represent the chosen standard state, which we can leave unspecified at this point but is usually taken to be the solute or Henry's law standard state. If we substitute Equations 25.34 into Equation 25.32 and equate the result to Equation 25.33, we obtain

$$\nu_+ \ln a_+ + \nu_- \ln a_- = \ln a_2$$

where we have used the relation $\mu_2^\circ = \nu_+\mu_+^\circ + \nu_-\mu_-^\circ$ in analogy with Equation 25.32. We can rewrite the above equation as

$$a_2 = a_+^{\nu_+} a_-^{\nu_-} \tag{25.35}$$

For many of the formulas that occur in the thermodynamics of solutions of electrolytes, it is convenient to define a quantity $a_\pm$, called the *mean ionic activity*, by

$$a_2 = a_\pm^{\nu} = a_+^{\nu_+} a_-^{\nu_-} \tag{25.36}$$

where $\nu = \nu_+ + \nu_-$. Note that $a_\pm$ is raised to the same power as the sum of the exponents in the last term in Equation 25.36, For example, we write

$$a_{NaCl} = a_\pm^2 = a_+a_-$$

and

$$a_{CaCl_2} = a_\pm^3 = a_+a_-^2$$

Even though we cannot determine activities of single ions, we can still *define* single-ion activity coefficients by

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

where m_+ and m_- are the molalities of the individual ions, which are given by $m_+ = \nu_+m$ and $m_- = \nu_-m$. If we substitute these expressions for a_+ and a_- into Equation 25.36, we get

$$a_2 = a_\pm^{\nu} = (m_+^{\nu_+} m_-^{\nu_-})(\gamma_+^{\nu_+} \gamma_-^{\nu_-}) \tag{25.37}$$

In analogy with the definition of the *mean ionic activity* $a_\pm$ in Equation 25.36, we define a mean ionic molality $m_\pm$ by

$$m_\pm^{\nu} = m_+^{\nu_+} m_-^{\nu_-} \tag{25.38}$$

and a *mean ionic activity coefficient* $\gamma_{\pm}$ by

$$\gamma_{\pm}^{\nu} = \gamma_{+}^{\nu_+}\gamma_{-}^{\nu_-} \tag{25.39}$$

Again, notice that the sum of the exponents on both sides of Equations 25.38 and 25.39 are the same. Given these definitions, we can now write Equation 25.37 as

$$a_2 = a_{\pm}^{\nu} = m_{\pm}^{\nu}\gamma_{\pm}^{\nu} \tag{25.40}$$

EXAMPLE 25–8

Write out Equation 25.40 explicitly for $CaCl_2$.

SOLUTION: In this case, $\nu_+ = 1$ and $\nu_- = 2$. Furthermore, according to the equation

$$CaCl_2(s) \xrightarrow{H_2O(l)} Ca^{2+}(aq) + 2\,Cl^-(aq)$$

we see that $m_+ = m$ and $m_- = 2m$. Thus,

$$a_2 = a_{\pm}^3 = (m)(2m)^2\gamma_{\pm}^3 = 4m^3\gamma_{\pm}^3$$

The relations between a_2, m, and $\gamma_{\pm}$ for other types of electrolytes are given in Table 25.3.

TABLE 25.3

The relations between the activity of a strong electrolyte, its molality, and its mean ionic activity coefficient for various types of strong electrolytes.

Type	
1–1	
KCl(aq)	$a_2 = a_+a_- = a_{\pm}^2 = m_{\pm}^2\gamma_{\pm}^2 = (m_+)(m_-)\gamma_{\pm}^2 = m^2\gamma_{\pm}^2$
1–2	
$CaCl_2$(aq)	$a_2 = a_+a_-^2 = a_{\pm}^3 = m_{\pm}^3\gamma_{\pm}^3 = (m_+)(m_-)^2\gamma_{\pm}^3 = (m)(2m)^2\gamma_{\pm}^3 = 4m^3\gamma_{\pm}^3$
1–3	
$LaCl_3$(aq)	$a_2 = a_+a_-^3 = a_{\pm}^4 = m_{\pm}^4\gamma_{\pm}^4 = (m_+)(m_-)^3\gamma_{\pm}^4 = (m)(3m)^3\gamma_{\pm}^4 = 27m^4\gamma_{\pm}^4$
2–1	
Na_2SO_4(aq)	$a_2 = a_+^2a_- = a_{\pm}^3 = (m_+)^2(m_-)\gamma_{\pm}^3 = (2m)^2(m)\gamma_{\pm}^3 = 4m^3\gamma_{\pm}^3$
2–2	
$ZnSO_4$(aq)	$a_2 = a_+a_- = a_{\pm}^2 = m_{\pm}^2\gamma_{\pm}^2 = (m_+)(m_-)\gamma_{\pm}^2 = m^2\gamma_{\pm}^2$
3–1	
$Na_3Fe(CN)_6$(aq)	$a_2 = a_+^3a_- = a_{\pm}^4 = m_{\pm}^4\gamma_{\pm}^4 = (m_+)^3(m_-)\gamma_{\pm}^4 = (3m)^3(m)\gamma_{\pm}^4 = 27m^4\gamma_{\pm}^4$

Mean ionic activity coefficients can be determined experimentally by the same methods used for the activity coefficients of nonelectrolytes. We will illustrate their determination from the measurement of the vapor pressure of the solvent as we did for an aqueous sucrose solution in Section 25–2. In analogy with Equation 25.13, we define an osmotic coefficient for aqueous electrolyte solutions by

$$\ln a_1 = -\frac{\nu m\phi}{55.506\ \mathrm{mol\cdot kg^{-1}}} \tag{25.41}$$

Notice that this equation differs from Equation 25.13 by the inclusion of a factor of ν here. Equation 25.41 reduces to Equation 25.13 for nonelectrolyte solutions because $\nu = 1$ in that case. Problem 25–34 asks you to show that with this factor of ν, $\phi \to 1$ as $m \to 0$ for solutions of electrolytes or nonelectrolytes. Starting with Equation 25.41 and the Gibbs–Duhem equation, you can derive the analog of Equation 25.15 straightforwardly:

$$\ln\gamma_{\pm} = \phi - 1 + \int_0^m \left(\frac{\phi - 1}{m'}\right) dm' \tag{25.42}$$

Table 25.4 gives the vapor pressure of an aqueous solution of NaCl as a function of molality. Also included in the table are activities of the water (calculated from

TABLE 25.4

The vapor pressure (P_{H_2O}), activity of the water (a_w), osmotic coefficient (ϕ), and logarithm of the mean ionic activity coefficient ($\ln\gamma_{\pm}$) of the NaCl in an aqueous solution of NaCl at 25°C as a function of molality (m).

$m/\mathrm{mol\cdot kg^{-1}}$	P_{H_2O}/torr	a_w	ϕ	$\ln\gamma_{\pm}$
0.000	23.76	1.0000	1.0000	0.0000
0.200	23.60	0.9934	0.9245	−0.3079
0.400	23.44	0.9868	0.9205	−0.3685
0.600	23.29	0.9802	0.9227	−0.3977
0.800	23.13	0.9736	0.9285	−0.4143
1.000	22.97	0.9669	0.9353	−0.4234
1.400	22.64	0.9532	0.9502	−0.4267
1.800	22.30	0.9389	0.9721	−0.4166
2.200	21.96	0.9242	0.9944	−0.3972
2.600	21.59	0.9089	1.0196	−0.3709
3.000	21.22	0.8932	1.0449	−0.3396
3.400	20.83	0.8769	1.0723	−0.3046
3.800	20.43	0.8600	1.1015	−0.2666
4.400	19.81	0.8339	1.1457	−0.2053
5.000	19.17	0.8068	1.1916	−0.1389

$a_1 = P_1/P_1^*$), osmotic coefficients (calculated from Equation 25.41), and mean ionic activity coefficients (calculated from Equation 25.42).

For sucrose in Section 25–2, we curve fit ϕ to a polynomial in m and then used that polynomial to calculate the value of γ_{2m}. As we will see in Section 25–6, the osmotic coefficient of electrolytes is better described by an expression of the form (a polynomial in $m^{1/2}$)

$$\phi = 1 + am^{1/2} + bm + cm^{3/2} + \cdots$$

The osmotic coefficient data for sodium chloride given in Table 25.4 can be fit by

$$\begin{aligned}\phi = 1 &- (0.3920\ \mathrm{kg^{1/2}\cdot mol^{-1/2}})m^{1/2} + (0.7780\ \mathrm{kg\cdot mol^{-1}})m \\ &- (0.8374\ \mathrm{kg^{3/2}\cdot mol^{-3/2}})m^{3/2} + (0.5326\ \mathrm{kg^{2}\cdot mol^{-2}})m^{2} \\ &- (0.1673\ \mathrm{kg^{5/2}\cdot mol^{-5/2}})m^{5/2} + (0.0206\ \mathrm{kg^{3}\cdot mol^{-3}})m^{3} \\ &\qquad 0 \le m \le 5.0\ \mathrm{mol\cdot kg^{-1}} \qquad (25.43)\end{aligned}$$

This expression for ϕ along with Equation 25.42 were used to calculate the values of $\ln\gamma_\pm$ given in Table 25.4.

EXAMPLE 25–9

Verify the entry for $\ln\gamma_\pm$ at 1.00 molal in Table 25.4.

SOLUTION: We first write (neglecting the units in the coefficients of the powers of m in Equation 25.43)

$$\begin{aligned}\int_0^m \left(\frac{\phi-1}{m'}\right)dm' &= -(0.3920)(2m^{1/2}) + 0.7780m - (0.8374)\frac{2m^{3/2}}{3} \\ &+ (0.5326)\frac{m^2}{2} - (0.1673)\frac{2m^{5/2}}{5} + (0.0206)\frac{m^3}{3}\end{aligned}$$

and add this result to $\phi - 1$ to obtain

$$\begin{aligned}\ln\gamma_\pm &= -(0.3920)(3m^{1/2}) + (0.7780)(2m) - (0.8374)\frac{5m^{3/2}}{3} \\ &+ (0.5326)\frac{3m^2}{2} - (0.1673)\frac{7m^{5/2}}{5} + (0.0206)\frac{4m^3}{3}\end{aligned}$$

Thus, at 1.00 molal, $\ln\gamma_\pm = -0.4234$, or $\gamma_\pm = 0.655$.

The formulas we derived in Section 25–3 for the colligative properties of solutions of nonelectrolytes take on a slightly different form for solutions of electrolytes. The difference lies in Equation 25.21 for x_2. For a strong electrolyte that dissociates into ν_+ cations and ν_- anions per formula unit, the mole fraction of solute particles is given by

$$x_2 = \frac{\nu m}{\dfrac{1000\ \mathrm{g\cdot kg^{-1}}}{M_1} + \nu m} \approx \frac{\nu m M_1}{1000\ \mathrm{g\cdot kg^{-1}}} \qquad (25.44)$$

Note that the right side here contains a factor of ν. If this expression for x_2 is carried through in derivations of the formulas for the colligative effects, we obtain

$$\Delta T_{\mathrm{fus}} = \nu K_{\mathrm{f}} m \qquad (25.45)$$

$$\Delta T_{\mathrm{vap}} = \nu K_{\mathrm{b}} m \qquad (25.46)$$

and

$$\Pi = \nu cRT \qquad (25.47)$$

EXAMPLE 25–10

A 0.050-molal aqueous solution of $K_3Fe(CN)_6$ has a freezing point of −0.36°C. How many ions are formed per formula unit of $K_3Fe(CN)_6$?

SOLUTION: We can solve Equation 25.45 for ν to obtain

$$\nu = \frac{\Delta T_{\mathrm{fus}}}{K_{\mathrm{f}} m} = \frac{0.36^\circ\mathrm{C}}{(1.86\ ^\circ\mathrm{C\cdot kg\cdot mol^{-1}})(0.050\ \mathrm{mol\cdot kg^{-1}})} = 3.9$$

Thus, the dissolution process of $K_3Fe(CN)_6$ can be written as

$$\mathrm{K_3Fe(CN)_6} \xrightarrow{\mathrm{H_2O(l)}} 3\,\mathrm{K^+(aq)} + \mathrm{Fe(CN)_6^{3-}(aq)}$$

25–6. The Debye–Hückel Theory Gives an Exact Expression for $\ln\gamma_\pm$ for Very Dilute Solutions

In the previous section, we expressed the osmotic coefficient for solutions of electrolytes in the form $\phi = 1 + am^{1/2} + bm + \cdots$ rather than as a simple polynomial in m as we did for sucrose in Section 25–2. The reason we did so is that in 1925, Peter Debye and Erich Hückel showed theoretically that at low concentrations, the logarithm of the activity coefficient of ion j is given by

$$\ln\gamma_j = -\frac{\kappa q_j^2}{8\pi\varepsilon_0\varepsilon_r k_{\mathrm{B}}T} \qquad (25.48)$$

and that the logarithm of the mean ionic activity coefficient is given by (see Problems 25–50 through 25–58)

$$\ln\gamma_\pm = -|q_+q_-|\frac{\kappa}{8\pi\varepsilon_0\varepsilon_r k_\text{B}T} \tag{25.49}$$

where $q_+ = z_+e$ and $q_- = z_-e$ are the charges on the cations and anions, ε_r is the (unitless) relative permittivity of the solvent, and κ is given by

$$\kappa^2 = \sum_{j=1}^{s}\frac{q_j^2}{\varepsilon_0\varepsilon_r k_\text{B}T}\left(\frac{N_j}{V}\right) \tag{25.50}$$

where s is the number of ionic species and N_j/V is the number density of species j. If we convert N_j/V to molarity, Equation 25.50 becomes

$$\kappa^2 = N_A(1000\ \text{L}\cdot\text{m}^{-3})\sum_{j=1}^{s}\frac{q_j^2c_j}{\varepsilon_0\varepsilon_r k_\text{B}T} \tag{25.51}$$

It is customary to define a quantity I_c, called the *ionic strength*, by

$$I_c = \frac{1}{2}\sum_{j=1}^{s}z_j^2c_j \tag{25.52}$$

where c_j is the molarity of the jth ionic species, in which case (Problem 25–46)

$$\kappa^2 = \frac{2e^2N_A(1000\ \text{L}\cdot\text{m}^{-3})}{\varepsilon_0\varepsilon_r k_\text{B}T}\left(I_c/\text{mol}\cdot\text{L}^{-1}\right) \tag{25.53}$$

EXAMPLE 25–11

First show that κ has units of m^{-1} and then show that $\ln\gamma_\pm$ in Equation 25.49 is unitless, as it must be.

SOLUTION: We start with Equation 25.50. The units of q_j are C, ε_0 are $\text{C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$, k_B are $\text{J}\cdot\text{K}^{-1} = \text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}\cdot\text{K}^{-1}$, T are K, and N_j/V are m^{-3}. Therefore, the units of κ^2 are

$$\kappa^2 \sim \frac{(\text{C}^2)(\text{m}^{-3})}{(\text{C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3})(\text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}\cdot\text{K}^{-1})(\text{K})} = m^{-2}$$

or

$$\kappa \sim \text{m}^{-1}$$

Using Equation 25.49 for $\ln\gamma_\pm$,

$$\ln\gamma_\pm \sim \frac{(\text{C}^2)(\text{m}^{-1})}{(\text{C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3})(\text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}\cdot\text{K}^{-1})(\text{K})} = \text{unitless}$$

Equation 25.49 is called the Debye–Hückel limiting law because it is the exact form that $\ln\gamma_\pm$ takes on for all electrolyte solutions for sufficiently low concentrations. Just what is meant by "sufficiently low concentrations" depends upon the system. Note that $\ln\gamma_\pm$ goes as κ in Equation 25.49, that κ goes as $I_c^{1/2}$ in Equation 25.53, and that $I_c^{1/2}$ goes as $c^{1/2}$ in Equation 25.52. Consequently, $\ln\gamma_\pm$ varies as $c^{1/2}$. This $c^{1/2}$ dependence is typical for electrolyte solutions, so when we curve fit ϕ in Section 25–5, we fit it to a polynomial in $c^{1/2}$ (or $m^{1/2}$) instead of c (or m).

Most of the experimental data for $\ln\gamma_\pm$ are given in terms of molality rather than molarity. In Figure 25.6, we plot $\ln\gamma_\pm$ versus $m^{1/2}$ for a number of 1–1 electrolytes. Note that all the curves merge into a single straight line at small concentrations, in accord with the limiting law nature of Equation 25.49. At small concentrations where the limiting law is valid, the molality and molarity scales differ by only a multiplicative constant, so a linear plot in $c^{1/2}$ is also linear in $m^{1/2}$ (Problem 25–5).

The quantity κ in Equation 25.50 is a central quantity in the Debye–Hückel theory and has the following physical interpretation. Consider an ion with charge q_i situated at the origin of a spherical coordinate system. According to Debye and Hückel (see also Problem 25–51), the net charge in a spherical shell of radius r and thickness dr surrounding this central ion is

$$p_i(r)dr = -q_i\kappa^2re^{-\kappa r}dr \tag{25.54}$$

If we integrate this expression from 0 to ∞, we obtain

$$\int_0^\infty p_i(r)dr = -q_i\kappa^2\int_0^\infty re^{-\kappa r}dr = -q_i$$

This result simply says that the total charge surrounding an ion of charge q_i is equal and of the opposite sign to q_i. In other words, it expresses the electroneutrality of the

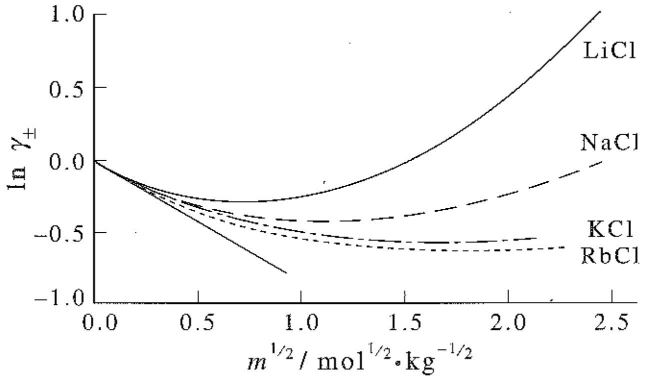


FIGURE 25.6

Values of $\ln\gamma_\pm$ versus $m^{1/2}$ for aqueous alkali halide solutions at 25°C. Note that even though the four curves are different, they all merge into one, the Debye–Hückel limiting law (Equation 25.49) at small concentrations.

solution. Equation 25.54, which is plotted in Figure 25.7, shows that there is a diffuse shell of net charge of opposite sign surrounding any given ion in solution. We say that Equation 25.54 describes an *ionic atmosphere* about the central ion. Furthermore, the maximum in the curve in Figure 25.7 occurs at $r = \kappa^{-1}$, so we say that κ^{-1}, which Example 25–11 shows has units of m, is a measure of the thickness of the ionic atmosphere.

For a 1–1 electrolyte in aqueous solution at 25°C, a handy formula for κ is (Problem 25–53)

$$\frac{1}{\kappa} = \frac{304 \text{ pm}}{(c/\text{mol}\cdot\text{L}^{-1})^{1/2}} \tag{25.55}$$

where c is the molarity of the solution. The thickness of the ionic atmosphere in a 0.010 molar solution is approximately 3000 pm, or about 10 times the size of a typical ion.

For an aqueous solution at 25°C, Equation 25.49 becomes (Problem 25–59)

$$\ln \gamma_{\pm} = -1.173|z_+z_-|(I_c/\text{mol}\cdot\text{L}^{-1})^{1/2} \tag{25.56}$$

According to Equation 25.52, I_c is related to the concentration, but the relation itself depends upon the type of electrolyte. For example, for a 1–1 electrolyte, $z_+ = 1$, $z_- = -1$, $c_+ = c$, and $c_- = c$, so $I = c$. For a 1–2 electrolyte such as $CaCl_2$, $z_+ = 2$, $z_- = -1$, $c_+ = c$, and $c_- = 2c$, so $I_c = \frac{1}{2}(4c + 2c) = 3c$. Generally, I_c is equal to some numerical factor times c, where the value of the numerical factor depends upon the type of salt. Therefore, Equation 25.56 says that a plot of $\ln \gamma_{\pm}$ versus $c^{1/2}$ should be a straight line and that the slope of the line should depend upon the type of electrolyte. The slope will be -1.173 for a 1–1 electrolyte and $-(1.173)(2)(3^{1/2}) = -4.06$ for a 1–2 electrolyte. Figure 25.8 shows a plot of $\ln \gamma_{\pm}$ versus $c^{1/2}$ for NaCl(aq) and $CaCl_2$(aq). Notice that the plots are indeed linear for small concentrations and that deviations from linear behavior occur at higher concentrations [$c^{1/2} \approx 0.05 \text{ mol}\cdot\text{L}^{-1}$ or $c = 0.003 \text{ mol}\cdot\text{L}^{-1}$ for $CaCl_2$(aq) and $c^{1/2} \approx 0.15 \text{ mol}\cdot\text{L}^{-1}$ or $c = 0.02 \text{ mol}\cdot\text{L}^{-1}$ for NaCl(aq)]. The slopes of the two linear portions are in the ratio of 4.06 to 1.17.

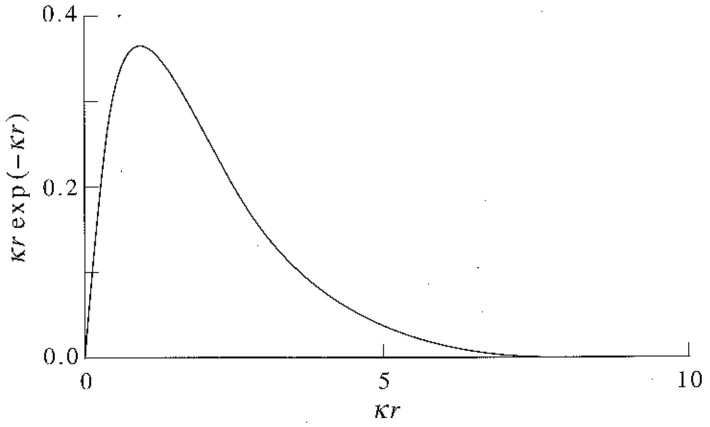


FIGURE 25.7
A plot of the net charge in a spherical shell of radius r and thickness dr surrounding a central ion of charge q_i. This plot illustrates the ionic atmosphere that surrounds each ion in solution. The maximum here corresponds to $r = \kappa^{-1}$.

25–7. The Mean Spherical Approximation Is an Extension of the Debye–Hückel Theory to Higher Concentrations

The Debye–Hückel theory assumes that the ions are simply point ions (zero radii) and that they interact with a purely coulombic potential [$U(r) = z_+z_-e^2/4\pi\varepsilon_0\varepsilon_r r$]. In addition, the solvent is considered a continuous medium with a uniform relative permittivity ε_r (78.54 for water at 25°C). Although the assumptions of point ions and a continuum solvent may seem crude, they are quite satisfactory when the ions are far apart from each other on the average, as they are in very dilute solutions. Consequently, the Debye–Hückel expression for $\ln \gamma_{\pm}$ given by Equation 25.49 is exact in the limit of small concentrations. There is no corresponding theory for solutions of nonelectrolytes because, being neutral species, nonelectrolyte molecules do not interact with each other to any significant extent until they approach each other relatively closely, where the solvent can hardly be assumed to be a continuous medium.

Figure 25.8 emphasizes that the Debye–Hückel theory is a limiting law. It should not be considered a quantitative theory with which to calculate activity coefficients except at very low concentrations. Nevertheless, the Debye–Hückel theory has played an invaluable role as a strict limiting law that all electrolyte solutions obey. In addition, any theory that attempts to describe solutions at higher concentrations must reduce to Equation 25.49 for small concentrations. Many attempts have been made to construct

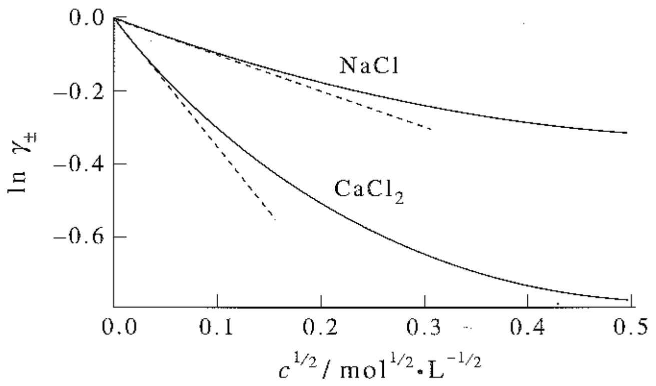


FIGURE 25.8
A plot of the logarithm of the mean ionic activity coefficient ($\ln \gamma_{\pm}$) for NaCl(aq) and $CaCl_2$(aq) at 25°C versus $c^{1/2}$. Note that both curves approach the Debye–Hückel limiting law (the straight lines) as the molarity goes to zero.

theories for more concentrated electrolyte solutions, but most have met with only limited success. One early attempt is called the Extended Debye–Hückel theory, in which Equation 25.49 is modified to be

$$\ln \gamma_{\pm} = -\frac{1.173|z_+z_-|(I_c/\mathrm{mol{\cdot}L^{-1}})^{1/2}}{1+(I_c/\mathrm{mol{\cdot}L^{-1}})^{1/2}} \tag{25.57}$$

This expression becomes Equation 25.49 in the limit of small concentrations because $I_c^{1/2}$ becomes negligible compared with unity in the denominator of Equation 25.57 in this limit.

EXAMPLE 25–12

Use Equation 25.57 to calculate $\ln \gamma_{\pm}$ for 0.050 molar LiCl(aq), and compare the result with that obtained from Equation 25.49. The accepted experimental value is −0.191.

SOLUTION: For a 1–1 salt such as LiCl, $I_c = c$, so

$$\ln \gamma_{\pm} = -1.173(0.050)^{1/2} = -0.262$$

and

$$\ln \gamma_{\pm} = -\frac{1.173(0.050)^{1/2}}{1+(0.050)^{1/2}} = -0.214$$

Although Equation 25.57 provides some improvement over the Debye–Hückel limiting law, it is not very accurate even at 0.050 molar. At 0.200 molar, Equation 25.57 gives −0.362 for $\ln \gamma_{\pm}$ versus the experimental value of −0.274.

Another semiempirical expression for $\ln \gamma_{\pm}$ that has been widely used to fit experimental data is

$$\ln \gamma_{\pm} = -\frac{1.173|z_+z_-|(I_c/\,\mathrm{mol{\cdot}L^{-1}})^{1/2}}{1+(I_c/\,\mathrm{mol{\cdot}L^{-1}})^{1/2}} + Cm \tag{25.58}$$

where C is a parameter whose value depends upon the electrolyte. Although Equation 25.58 can be used to fit experimental $\ln \gamma_{\pm}$ data up to one molar or so, C is still strictly an adjustable parameter.

In the 1970s, significant advances were made in the theory of electrolyte solutions. Most of the work on these theories is based on a model called the *primitive model*, in which the ions are considered hard spheres with charges at their centers and the solvent is considered a continuous medium with a uniform relative permittivity. In spite of the obvious deficiencies of this model, it addresses the long-range coulombic interactions between the ions and their short-range repulsion. These turn out to be major considerations, and as we will see, the primitive model can give quite satisfactory agreement with experimental data over a fairly large concentration range.

Most of these theories that have been developed require numerical solutions to fairly complicated equations, but one is notable in that it provides analytic expressions for the various thermodynamic properties of electrolyte solutions. The name of this theory, the mean spherical approximation (MSA), derives from its original formulation, and the theory can be viewed as a Debye–Hückel theory in which the finite (nonzero) size of the ions is accounted for in a fairly rigorous manner. A central result of the mean spherical approximation is that

$$\ln \gamma_{\pm} = \ln \gamma_{\pm}^{\mathrm{el}} + \ln \gamma^{\mathrm{HS}} \tag{25.59}$$

where $\ln \gamma_{\pm}^{\mathrm{el}}$ is an electrostatic (coulombic) contribution to $\ln \gamma_{\pm}$ and $\ln \gamma^{\mathrm{HS}}$ is a hard-sphere (finite-size) contribution. For solutions of 1–1 electrolytes, $\ln \gamma_{\pm}^{\mathrm{el}}$ is given by

$$\ln \gamma_{\pm}^{\mathrm{el}} = \frac{x(1+2x)^{1/2} - x - x^2}{4\pi\rho d^3} \tag{25.60}$$

where ρ is the number density of charged particles, d is the sum of the radius of a cation and an anion, and $x = \kappa d$, where κ is given by Equation 25.53. Although it is not obvious by casual inspection, Equation 25.59 reduces to the Debye–Hückel limiting law, Equation 25.49, in the limit of small concentrations (Problem 25–60). The hard sphere contribution to $\ln \gamma_{\pm}$ is given by

$$\ln \gamma^{\mathrm{HS}} = \frac{4y - \dfrac{9}{4}y^2 + \dfrac{3}{8}y^3}{\left(1 - \dfrac{y}{2}\right)^3} \tag{25.61}$$

where $y = \pi\rho d^3/6$.

In spite of the fact that Equations 25.60 and 25.61 are somewhat lengthy, they are easy to use because once d has been chosen, they give $\ln \gamma_{\pm}$ in terms of the molarity c. Figure 25.9 shows experimental values of $\ln \gamma_{\pm}$ for NaCl(aq) at 25°C and $\ln \gamma_{\pm}$ as calculated from Equation 25.59 with $d = 320$ pm.

Given essentially one adjustable parameter (the sum of the ionic radii), the agreement is seen to be quite good. We also show the results for the more commonly seen Equation 25.57 in Figure 25.9.

Problems

25-1. The density of a glycerol/water solution that is 40.0% glycerol by mass is 1.101 $\mathrm{g{\cdot}mL^{-1}}$ at 20°C. Calculate the molality and the molarity of glycerol in the solution at 20°C. Calculate the molality at 0°C.

25-2. Concentrated sulfuric acid is sold as a solution that is 98.0% sulfuric acid and 2.0% water by mass. Given that the density is 1.84 $\mathrm{g{\cdot}mL^{-1}}$, calculate the molarity of concentrated sulfuric acid.

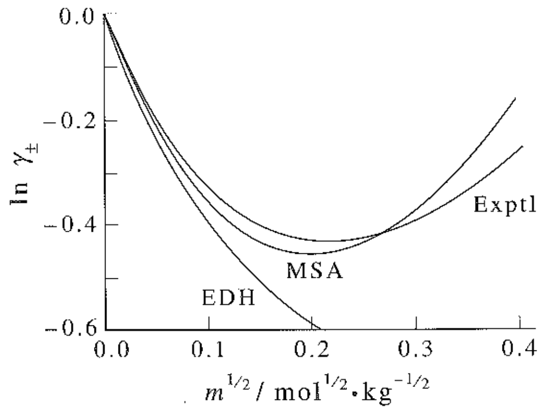


FIGURE 25.9
A comparison of $\ln\gamma_{\pm}$ from the mean spherical approximation (Equation 25.59) with experimental data for NaCl(aq) at 25°C. The line labelled EDH is the extended Debye–Hückel theory result, Equation 25.57. The value of d, the sum of the radii of the cation and anion, is taken to be 320 pm.

25-3. Concentrated phosphoric acid is sold as a solution that is 85% phosphoric acid and 15% water by mass. Given that the molarity is 15 $\text{mol}\cdot\text{L}^{-1}$, calculate the density of concentrated phosphoric acid.

25-4. Calculate the mole fraction of glucose in an aqueous solution that is 0.500 molal in glucose.

25-5. Show that the relation between molarity and molality for a solution with a single solute is

$$c = \frac{(1000\ \text{mL}\cdot\text{L}^{-1})\rho m}{1000\ \text{g}\cdot\text{kg}^{-1} + mM_2}$$

where c is the molarity, m is the molality, ρ is the density of the solution in $\text{g}\cdot\text{mL}^{-1}$, and M_2 is the molar mass ($\text{g}\cdot\text{mol}^{-1}$) of the solute.

25-6. The *CRC Handbook of Chemistry and Physics* has tables of "concentrative properties of aqueous solutions" for many solutions. Some entries for CsCl(s) are

A/%	$\rho/\text{g}\cdot\text{mL}^{-1}$	$c/\text{mol}\cdot\text{L}^{-1}$
1.00	1.0058	0.060
5.00	1.0374	0.308
10.00	1.0798	0.641
20.00	1.1756	1.396
40.00	1.4226	3.380

where A is the mass percent of the solute, ρ is the density of the solution, and c is the molarity. Using these data, calculate the molality at each concentration.

25-7. Derive a relation between the mass percentage (A) of a solute in a solution and its molality (m). Calculate the molality of an aqueous sucrose solution that is 18% sucrose by mass.

25-8. Derive a relation between the mole fraction of the solvent and the molality of a solution.

25-9. The volume of an aqueous sodium chloride solution at 25°C can be expressed as

$$V/\text{mL} = 1001.70 + (17.298\ \text{kg}\cdot\text{mol}^{-1})m + (0.9777\ \text{kg}^2\cdot\text{mol}^{-2})m^2 - (0.0569\ \text{kg}^3\cdot\text{mol}^{-3})m^3$$

$$0 \le m \le 6\ \text{mol}\cdot\text{kg}^{-1}$$

where m is the molality. Calculate the molarity of a solution that is 3.00 molal in sodium chloride.

25-10. If x_2^{∞}, m^{∞}, and c^{∞} are the mole fraction, molality, and molarity, respectively, of a solute at infinite dilution, show that

$$x_2^{\infty} = \frac{m^{\infty}M_1}{1000\ \text{g}\cdot\text{kg}^{-1}} = \frac{c^{\infty}M_1}{(1000\ \text{mL}\cdot\text{L}^{-1})\rho_1}$$

where M_1 is the molar mass ($\text{g}\cdot\text{mol}^{-1}$) and ρ_1 is the density ($\text{g}\cdot\text{mL}^{-1}$) of the solvent. Note that mole fraction, molality, and molarity are all directly proportional to each other at low concentrations.

25-11. Consider two solutions whose solute activities are a_2' and a_2'', referred to the same standard state. Show that the difference in the chemical potentials of these two solutions is independent of the standard state and depends only upon the ratio a_2'/a_2''. Now choose one of these solutions to be at an arbitrary concentration and the other at a very dilute concentration (essentially infinitely dilute) and argue that

$$\frac{a_2'}{a_2''} = \frac{\gamma_{2x}x_2}{x_2^{\infty}} = \frac{\gamma_{2m}m}{m^{\infty}} = \frac{\gamma_{2c}c}{c^{\infty}}$$

25-12. Use Equations 25.4, 25.11, and the results of the previous two problems to show that

$$\gamma_{2x} = \gamma_{2m}\left(1 + \frac{mM_1}{1000\ \text{g}\cdot\text{kg}^{-1}}\right) = \gamma_{2c}\left(\frac{\rho}{\rho_1} + \frac{c[M_1 - M_2]}{\rho_1[1000\ \text{mL}\cdot\text{L}^{-1}]}\right)$$

where ρ is the density of the solution. Thus, we see that the three different activity coefficients are related to one another.

25-13. Use Equations 25.4, 25.11, and the results of Problem 25–12 to derive

$$\gamma_{2m} = \gamma_{2c}\left(\frac{\rho}{\rho_1} - \frac{cM_2}{\rho_1[1000\ \text{mL}\cdot\text{L}^{-1}]}\right)$$

Given that the density of an aqueous citric acid ($M_2 = 192.12\ \text{g}\cdot\text{mol}^{-1}$) solution at 20°C is given by

$$\rho/\text{g}\cdot\text{mL}^{-1} = 0.99823 + (0.077102\ \text{L}\cdot\text{mol}^{-1})c$$

$$0 \le c < 1.772\ \text{mol}\cdot\text{L}^{-1}$$

plot γ_{2m}/γ_{2c} versus c. Up to what concentration do γ_{2m} and γ_{2c} differ by 2%?

25-14. The *CRC Handbook of Chemistry and Physics* gives a table of mass percent of sucrose in an aqueous solution and its corresponding molarity at 25°C. Use these data to plot molality versus molarity for an aqueous sucrose solution.

25-15. Using the data in Table 25.2, calculate the activity coefficient of water (on a mole fraction basis) at a sucrose concentration of 3.00 molal.

25-16. Using the data in Table 25.2, plot the activity coefficient of water against the mole fraction of water.

25-17. Using the data in Table 25.2, calculate the value of ϕ at each value of m and reproduce Figure 25.2.

25-18. Fit the data for the osmotic coefficient of sucrose in Table 25.2 to a 4th-degree polynomial and calculate the value of γ_{2m} for a 1.00-molal solution. Compare your result with the one obtained in Example 25–5.

25-19. Using the data for sucrose given in Table 25.2, determine the value of $\ln \gamma_{2m}$ at 3.00 molal by plotting $(\phi - 1)/m$ versus m and determining the area under the curve by numerical integration (MathChapter G) rather than by curve fitting ϕ first. Compare your result with the value given in Table 25.2.

25-20. Equation 25.18 can be used to determine the activity of the solvent at its freezing point. Assuming that ΔC_P^* is independent of temperature, show that

$$\Delta_{\text{fus}}\overline{H}(T) = \Delta_{\text{fus}}\overline{H}(T_{\text{fus}}^*) + \Delta\overline{C}_P^*(T - T_{\text{fus}}^*)$$

where $\Delta_{\text{fus}}\overline{H}(T_{\text{fus}}^*)$ is the molar enthalpy of fusion at the freezing point of the pure solvent (T_{fus}^*) and $\Delta\overline{C}_P^*$ is the difference in the molar heat capacities of liquid and solid solvent. Using Equation 25.18, show that

$$-\ln a_1 = \frac{\Delta_{\text{fus}}\overline{H}(T_{\text{fus}}^*)}{R(T_{\text{fus}}^*)^2}\theta + \frac{1}{R(T_{\text{fus}}^*)^2}\left(\frac{\Delta_{\text{fus}}\overline{H}(T_{\text{fus}}^*)}{T_{\text{fus}}^*} - \frac{\Delta\overline{C}_P^*}{2}\right)\theta^2 + \cdots$$

where $\theta = T_{\text{fus}}^* - T_{\text{fus}}$.

25-21. Take $\Delta_{\text{fus}}\overline{H}(T_{\text{fus}}^*) = 6.01\ \text{kJ}\cdot\text{mol}^{-1}$, $\overline{C}_P^{\text{l}} = 75.2\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and $\overline{C}_P^{\text{s}} = 37.6\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ to show that the equation for $-\ln a_1$ in the previous problem becomes

$$-\ln a_1 = (0.00968\ \text{K}^{-1})\theta + (5.2 \times 10^{-6}\ \text{K}^{-2})\theta^2 + \cdots$$

for an aqueous solution. The freezing point depression of a 1.95-molal aqueous sucrose solution is 4.45°C. Calculate the value of a_1 at this concentration. Compare your result with the value in Table 25.2. The value you calculated in this problem is for 0°C, whereas the value in Table 25.2 is for 25°C, but the difference is fairly small because a_1 does not vary greatly with temperature (Problem 25–61).

25-22. The freezing point of a 5.0-molal aqueous glycerol (1,2,3-propanetriol) solution is −10.6°C. Calculate the activity of water at 0°C in this solution. (See Problems 25–20 and 25–21.)

25-23. Show that replacing T_{fus} by T_{fus}^* in the denominator of $(T_{\text{fus}} - T_{\text{fus}}^*)/T_{\text{fus}}^* T_{\text{fus}}$ (see Equation 25.20) gives $-\theta/(T_{\text{fus}}^*)^2 - \theta^2/(T_{\text{fus}}^*)^3 + \cdots$ where $\theta = T_{\text{fus}}^* - T_{\text{fus}}$.

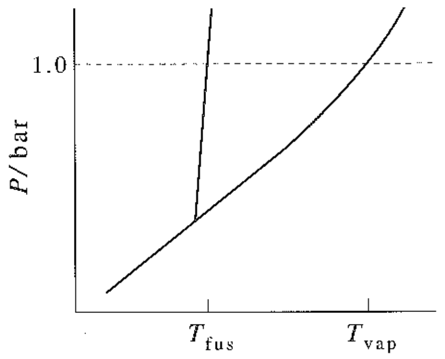
25-24. Calculate the value of the freezing point depression constant for nitrobenzene, whose freezing point is 5.7°C and whose molar enthalpy of fusion is $11.59\ \text{kJ}\cdot\text{mol}^{-1}$.

25-25. Use an argument similar to the one we used to derive Equations 25.22 and 25.23 to derive Equations 25.24 and 25.25.

25-26. Calculate the boiling point elevation constant for cyclohexane given that $T_{\text{vap}} = 354$ K and $\Delta_{\text{vap}}\overline{H} = 29.97\ \text{kJ}\cdot\text{mol}^{-1}$.

25-27. A solution containing 1.470 g of dichlorobenzene in 50.00 g of benzene boils at 80.60°C at a pressure of 1.00 bar. The boiling point of pure benzene is 80.09°C, and the molar enthalpy of vaporization of pure benzene is $32.0\ \text{kJ}\cdot\text{mol}^{-1}$. Determine the molecular mass of dichlorobenzene from these data.

25-28. Consider the following phase diagram for a typical pure substance. Label the region corresponding to each phase. Illustrate how this diagram changes for a dilute solution of a nonvolatile solute.



Now demonstrate that the boiling point increases and the freezing point decreases as a result of the dissolution of the solute.

25-29. A solution containing 0.80 g of a protein in 100 mL of a solution has an osmotic pressure of 2.06 torr at 25°C. What is the molecular mass of the protein?

25-30. Show that the osmotic pressure of an aqueous solution can be written as

$$\Pi = \frac{RT}{\overline{V}^*}\left(\frac{m}{55.506\ \text{mol}\cdot\text{kg}^{-1}}\right)\phi$$

25-31. According to Table 25.2, the activity of the water in a 2.00-molal sucrose solution is 0.95807. What external pressure must be applied to the solution at 25.0°C to make the activity of the water in the solution the same as that in pure water at 25.0°C and 1 atm? Take the density of water to be $0.997\ \text{g}\cdot\text{mL}^{-1}$.

25-32. Show that $a_2 = a_\pm^2 = m^2\gamma_\pm^2$ for a 2–2 salt such as $CuSO_4$ and that $a_2 = a_\pm^4 = 27m^4\gamma_\pm^4$ for a 1–3 salt such as $LaCl_3$.

25-33. Verify the following table:

Type of salt	Example	I_m
1–1	KCl	m
1–2	$CaCl_2$	$3m$
2–1	K_2SO_4	$3m$
2–2	$MgSO_4$	$4m$
1–3	$LaCl_3$	$6m$
3–1	Na_3PO_4	$6m$

Show that the general result for I_m is $|z_+z_-|(\nu_+ + \nu_-)m/2$.

25-34. Show that the inclusion of the factor ν in Equation 25.41 allows $\phi \to 1$ as $m \to 0$ for solutions of electrolytes as well as nonelectrolytes. [*Hint*: Realize that x_2 involves the total number of moles of solute particles (see Equation 25.44)].

25-35. Use Equation 25.41 and the Gibbs–Duhem equation to derive Equation 25.42.

25-36. The osmotic coefficient of $CaCl_2(aq)$ solutions can be expressed as

$$\begin{aligned}\phi = 1.0000 &- (1.2083\ \text{kg}^{1/2}\cdot\text{mol}^{-1/2})m^{1/2} + (3.2215\ \text{kg}\cdot\text{mol}^{-1})m \\ &- (3.6991\ \text{kg}^{3/2}\cdot\text{mol}^{-3/2})m^{3/2} + (2.3355\ \text{kg}^2\cdot\text{mol}^{-2})m^2 \\ &- (0.67218\ \text{kg}^{5/2}\cdot\text{mol}^{-5/2})m^{5/2} + (0.069749\ \text{kg}^3\cdot\text{mol}^{-3})m^3 \\ &\qquad 0 \le m \le 5.00\ \text{mol}\cdot\text{kg}^{-1}\end{aligned}$$

Use this expression to calculate and plot $\ln\gamma_\pm$ as a function of $m^{1/2}$.

25-37. Use Equation 25.43 to calculate $\ln\gamma_\pm$ for NaCl(aq) at 25°C as a function of molality and plot it versus $m^{1/2}$. Compare your results with those in Table 25.4.

25-38. In Problem 25–19, you determined $\ln\gamma_{2m}$ for sucrose by calculating the area under the curve of $\phi - 1$ versus m. When dealing with solutions of electrolytes, it is better numerically to plot $(\phi - 1)/m^{1/2}$ versus $m^{1/2}$ because of the natural dependence of ϕ on $m^{1/2}$. Show that

$$\ln\gamma_\pm = \phi - 1 + 2\int_0^{m^{1/2}} \frac{\phi - 1}{m^{1/2}}\,dm^{1/2}$$

25-39. Use the data in Table 25.4 to calculate $\ln\gamma_\pm$ for NaCl(aq) at 25°C by plotting $(\phi - 1)/m^{1/2}$ against $m^{1/2}$ and determine the area under the curve by numerical integration (MathChapter G). Compare your values of $\ln\gamma_\pm$ with those you obtained in Problem 25-37 where you calculated $\ln\gamma_\pm$ from a curve-fit expression of ϕ as a polynomial in $m^{1/2}$.

25-40. Don Juan Pond in the Wright Valley of Antarctica freezes at −57°C. The major solute in the pond is $CaCl_2$. Estimate the concentration of $CaCl_2$ in the pond water.

25-41. A solution of mercury(II) chloride is a poor conductor of electricity. A 40.7-g sample of $HgCl_2$ is dissolved in 100.0 g of water, and the freezing point of the solution is found to be −2.83°C. Explain why $HgCl_2$ in solution is a poor conductor of electricity.

25-42. The freezing point of a 0.25-molal aqueous solution of Mayer's reagent, K_2HgI_4, is found to be −1.41°C. Suggest a possible dissociation reaction that takes place when K_2HgI_4 is dissolved in water.

25-43. Given the following freezing-point depression data, determine the number of ions produced per formula unit when the indicated substance is dissolved in water to produce a 1.00-molal solution.

Formula	$\Delta T/\text{K}$
$PtCl_2\cdot 4NH_3$	5.58
$PtCl_2\cdot 3NH_3$	3.72
$PtCl_2\cdot 2NH_3$	1.86
$KPtCl_3\cdot NH_3$	3.72
K_2PtCl_4	5.58

Interpret your results.

25-44. An aqueous solution of NaCl has an ionic strength of 0.315 mol·L^{-1}. At what concentration will an aqueous solution of K_2SO_4 have the same ionic strength?

25-45. Derive the "practical" formula for κ^2 given by Equation 25.53.

25-46. Some authors define ionic strength in terms of molality rather than molarity, in which case

$$I_m = \frac{1}{2}\sum_{j=1}^{s} z_j^2 m_j$$

Show that this definition modifies Equation 25.53 for dilute solutions to be

$$\kappa^2 = \frac{2e^2 N_A (1000\ \text{L}\cdot\text{m}^{-3})\rho}{\varepsilon_0\varepsilon_r kT}(I_m/\text{mol}\cdot\text{kg}^{-1})$$

where ρ is the density of the solvent (in g·mL^{-1}).

25-47. Show that

$$\ln\gamma_\pm = -1.171|z_+z_-|(I_m/\text{mol}\cdot\text{kg}^{-1})^{1/2}$$

for an aqueous solution at 25°C, where I_m is the ionic strength expressed in terms of molality. Take ε_r to be 78.54 and the density of water to be 0.99707 g·mL^{-1}.

25-48. Calculate the value of $\ln\gamma_\pm$ for a 0.010-molar NaCl(aq) solution at 25°C. The experimental value is −0.103. Take $\varepsilon_r = 78.54$ for $H_2O(l)$ at 25°C.

25-49. Derive the general equation

$$\phi = 1 + \frac{1}{m}\int_0^m m' d \ln \gamma_\pm$$

(*Hint*: See the derivation in Problem 25–35.) Use this result to show that

$$\phi = 1 + \frac{\ln \gamma_\pm}{3}$$

for the Debye–Hückel theory.

In the next nine problems we will develop the Debye–Hückel theory of ionic solutions and derive Equations 25.48 and 25.49.

25-50. In the Debye–Hückel theory, the ions are modeled as point ions, and the solvent is modeled as a continuous medium (no structure) with a relative permittivity ε_r. Consider an ion of type i (i = a cation or an anion) situated at the origin of a spherical coordinate system. The presence of this ion at the origin will attract ions of opposite charge and repel ions of the same charge. Let $N_{ij}(r)$ be the number of ions of type j (j = a cation or an anion) situated at a distance r from the central ion of type i (a cation or an anion). We can use a Boltzmann factor to say that

$$N_{ij}(r) = N_j e^{-w_{ij}(r)/k_\mathrm{B}T}$$

where N_j/V is the bulk number density of j ions and $w_{ij}(r)$ is the interaction energy of an i ion with a j ion. This interaction energy will be electrostatic in origin, so let $w_{ij}(r) = q_j\psi_i(r)$, where q_j is the charge on the ion of type j and $\psi_i(r)$ is the electrostatic potential due to the central ion of type i.

A fundamental equation from physics that relates a spherically symmetric electrostatic potential $\psi_i(r)$ to a spherically symmetric charge density $\rho_i(r)$ is Poisson's equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_i}{dr}\right) = -\frac{\rho_i(r)}{\varepsilon_0\varepsilon_r} \qquad (1)$$

where ε_r is the relative permittivity of the solvent. In our case, $\rho_i(r)$ is the charge density around the central ion. First, show that

$$\rho_i(r) = \frac{1}{V}\sum_j q_j N_{ij}(r) = \sum_j q_j C_j e^{-q_j\psi_i(r)/k_\mathrm{B}T}$$

where C_j is the bulk number density of species j ($C_j = N_j/V$). Linearize the exponential term and use the condition of electroneutrality to show that

$$\rho_i(r) = -\psi_i(r)\sum_j \frac{q_j^2 C_j}{k_\mathrm{B}T} \qquad (2)$$

Now substitute $\rho_i(r)$ into Poisson's equation to get

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_i}{dr}\right) = \kappa^2\psi_i(r) \qquad (3)$$

where

$$\kappa^2 = \sum_j \frac{q_j^2 C_j}{\varepsilon_0\varepsilon_r k_\mathrm{B}T} = \sum_j \frac{q_j^2}{\varepsilon_0\varepsilon_r k_\mathrm{B}T}\left(\frac{N_j}{V}\right) \qquad (4)$$

Show that Equation 3 can be written as

$$\frac{d^2}{dr^2}[r\psi_i(r)] = \kappa^2[r\psi_i(r)]$$

Now show that the only solution for $\psi_i(r)$ that is finite for large values of r is

$$\psi_i(r) = \frac{Ae^{-\kappa r}}{r} \qquad (5)$$

where A is a constant. Use the fact that if the concentration is very small, then $\psi_i(r)$ is just Coulomb's law and so $A = q_i/4\pi\varepsilon_0\varepsilon_r$ and

$$\psi_i(r) = \frac{q_i e^{-\kappa r}}{4\pi\varepsilon_0\varepsilon_r r} \qquad (6)$$

Equation 6 is a central result of the Debye–Hückel theory. The factor of $e^{-\kappa r}$ modulates the resulting Coulombic potential, so Equation 6 is called a *screened Coulombic potential*.

25-51. Use Equations 2 and 6 of the previous problem to show that the net charge in a spherical shell of radius r surrounding a central ion of type i is

$$p_i(r)dr = \rho_i(r)4\pi r^2 dr = -q_i\kappa^2 r e^{-\kappa r}dr$$

as in Equation 25.54. Why is

$$\int_0^\infty p_i(r)dr = -q_i$$

25-52. Use the result of the previous problem to show that the most probable value of r is $1/\kappa$.

25-53. Show that

$$r_\mathrm{mp} = \frac{1}{\kappa} = \frac{304\ \mathrm{pm}}{(c/\mathrm{mol\cdot L^{-1}})^{1/2}}$$

where c is the molarity of an aqueous solution of a 1–1 electrolyte at 25°C. Take $\varepsilon_r = 78.54$ for H_2O(l) at 25°C.

25-54. Show that

$$r_\mathrm{mp} = \frac{1}{\kappa} = 430\ \mathrm{pm}$$

for a 0.50-molar aqueous solution of a 1–1 electrolyte at 25°C. Take $\varepsilon_r = 78.54$ for H_2O(l) at 25°C.

25-55. How does the thickness of the ionic atmosphere compare for a 1–1 electrolyte and a 2–2 electrolyte?

25-56. In this problem, we will calculate the total electrostatic energy of an electrolyte solution in the Debye–Hückel theory. Use the equations in Problem 25–50 to show that the number of ions of type j in a spherical shell of radii r and $r+dr$ about a central ion of type i is

$$\left(\frac{N_{ij}(r)}{V}\right)4\pi r^2dr = C_je^{-q_j\psi_i(r)/k_\mathrm{B}T}4\pi r^2dr \approx C_j\left(1-\frac{q_j\psi_i(r)}{k_\mathrm{B}T}\right)4\pi r^2dr \qquad (1)$$

The total Coulombic interaction between the central ion of type i and the ions of type j in the spherical shell is $N_{ij}(r)u_{ij}(r)4\pi r^2dr/V$ where $u_{ij}(r) = q_iq_j/4\pi\varepsilon_0\varepsilon_r r$. To determine the electrostatic interaction energy of all the ions in the solution with the central ion (of type i), U_i^el, sum $N_{ij}(r)u_{ij}(r)/V$ over all types of ions in a spherical shell and then integrate over all spherical shells to get

$$\begin{aligned}U_i^\mathrm{el} &= \int_0^\infty\left(\sum_j\frac{N_{ij}(r)u_{ij}(r)}{V}\right)4\pi r^2dr\\ &= \sum_j\frac{C_jq_iq_j}{\varepsilon_0\varepsilon_r}\int_0^\infty\left(1-\frac{q_j\psi_i(r)}{k_\mathrm{B}T}\right)rdr\end{aligned}$$

Use electroneutrality to show that

$$U_i^\mathrm{el} = -q_i\kappa^2\int_0^\infty\psi_i(r)rdr$$

Now, using Equation 6 of Problem 25–50, show that the interaction of all ions with the central ion (of type i) is given by

$$U_i^\mathrm{el} = -\frac{q_i^2\kappa^2}{4\pi\varepsilon_0\varepsilon_r}\int_0^\infty e^{-\kappa r}dr = -\frac{q_i^2\kappa}{4\pi\varepsilon_0\varepsilon_r}$$

Now argue that the total electrostatic energy is

$$U^\mathrm{el} = \frac{1}{2}\sum_i N_iU_i^\mathrm{el} = -\frac{Vk_\mathrm{B}T\kappa^3}{8\pi}$$

Why is there a factor of 1/2 in this equation? Wouldn't you be overcounting the energy otherwise?

25-57. We derived an expression for U^el in the previous problem. Use the Gibbs–Helmholtz equation for A (Problem 22–23) to show that

$$A^\mathrm{el} = -\frac{Vk_\mathrm{B}T\kappa^3}{12\pi}$$

25-58. If we assume that the electrostatic interactions are the sole cause of the nonideality of an electrolyte solution, then we can say that

$$\mu_j^\mathrm{el} = \left(\frac{\partial A^\mathrm{el}}{\partial n_j}\right)_{T,V} = RT\ln\gamma_j^\mathrm{el}$$

or that

$$\mu_j^\mathrm{el} = \left(\frac{\partial A^\mathrm{el}}{\partial N_j}\right)_{T,V} = k_\mathrm{B}T\ln\gamma_j^\mathrm{el}$$

Use the result you got for A^el in the previous problem to show that

$$k_\mathrm{B}T\ln\gamma_j^\mathrm{el} = -\frac{\kappa q_j^2}{8\pi\varepsilon_0\varepsilon_r}$$

Use the formula

$$\ln\gamma_\pm = \frac{\nu_+\ln\gamma_+ + \nu_-\ln\gamma_-}{\nu_+ + \nu_-}$$

to show that

$$\ln\gamma_\pm = -\left(\frac{\nu_+q_+^2 + \nu_-q_-^2}{\nu_+ + \nu_-}\right)\frac{\kappa}{8\pi\varepsilon_0\varepsilon_rk_\mathrm{B}T}$$

Use the electroneutrality condition $\nu_+q_+ + \nu_-q_- = 0$ to rewrite $\ln\gamma_\pm$ as

$$\ln\gamma_\pm = -|q_+q_-|\frac{\kappa}{8\pi\varepsilon_0\varepsilon_rk_\mathrm{B}T}$$

in agreement with Equation 25.49.

25-59. Derive Equation 25.56 from Equation 25.49.

25-60. Show that Equation 25.59 reduces to Equation 25.49 for small concentrations.

25-61. In this problem, we will investigate the temperature dependence of activities. Starting with the equation $\mu_1 = \mu_1^* + RT\ln a_1$, show that

$$\left(\frac{\partial\ln a_1}{\partial T}\right)_{P,x_1} = \frac{\overline{H}_1^* - \overline{H}_1}{RT^2}$$

where $\overline{H}_1^*$ is the molar enthalpy of the pure solvent (at one bar) and $\overline{H}_1$ is its partial molar enthalpy in the solution. The difference between $\overline{H}_1^*$ and $\overline{H}_1$ is small for dilute solutions, so a_1 is fairly independent of temperature.

25-62. Henry's law says that the pressure of a gas in equilibrium with a nonelectrolyte solution of the gas in a liquid is proportional to the molality of the gas in the solution for sufficiently dilute solutions. What form do you think Henry's law takes on for a gas such as HCl(g) dissolved in water? Use the following data for HCl(g) at 25°C to test your prediction.

$P_\mathrm{HCl}/10^{-11}$ bar	$m_\mathrm{HCl}/10^{-3}$ mol·kg^{-1}
0.147	1.81
0.238	2.32
0.443	3.19
0.663	3.93
0.851	4.47
1.08	5.06
1.62	6.25
1.93	6.84
2.08	7.12