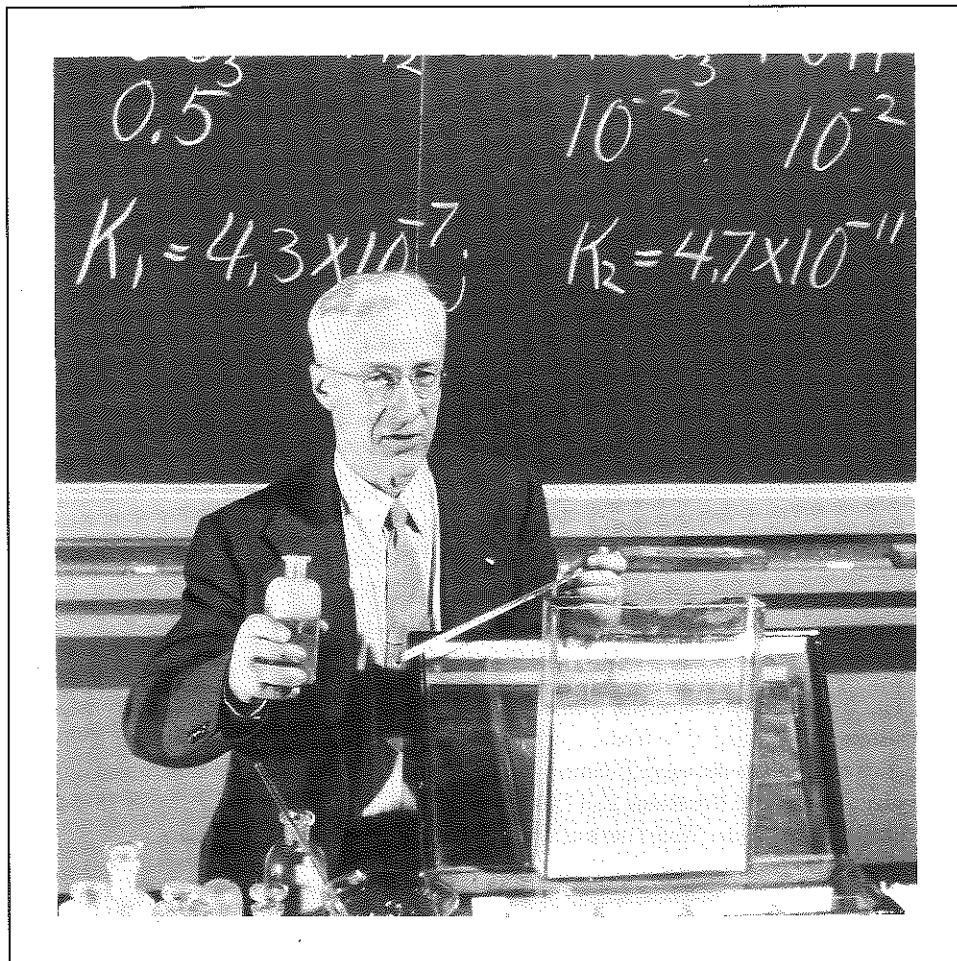# Solutions I: Liquid-Liquid Solutions

Joel Hildebrand was born in Camden, NJ, on November 16, 1881, and died in 1983. He received his Ph.D. in chemistry from the University of Pennsylvania in 1906. After spending a year at the University of Berlin with Nernst, he returned to the University of Pennsylvania as an instructor. In 1913, he joined the Department of Chemistry at the University of California at Berkeley, where he stayed for the remainder of his life. Although he officially retired in 1952, he remained professionally active until his death, publishing his last paper in 1981. Hildebrand made significant contributions to the fields of liquids and nonelectrolyte solutions. He retained a long interest in deviations from ideal solutions (Raoult's law) and the theory of regular solutions. His books, *The Solubility of Nonelectrolytes* and *Regular Solutions*, published with Robert Scott, were standard references in the field. Hildebrand was a famed, excellent teacher of general chemistry at Berkeley. His general chemistry text, *Principles of Chemistry*, influenced other schools to place greater emphasis on principles and less on the memorization of specific material in the teaching of general chemistry. Hildebrand was a great lover of the outdoors and especially enjoyed skiing and camping. He managed the U.S. Olympic Ski Team in 1936, was President of the Sierra Club from 1937 to 1940, and wrote a book on camping with his daughter Louise, *Camp Catering* or, *How to rustle grub for hikers, campers, mountaineers, canoeists, hunters, skiers, and fishermen.*

In this and the next chapter, we will apply our thermodynamic principles to solutions. This chapter focuses on solutions that consist of two volatile liquids, such as alcohol–water solutions. We will first discuss partial molar quantities, which provide the most convenient set of thermodynamic variables to describe solutions. This discussion will lead to the Gibbs–Duhem equation, which gives us a relation between the change in the properties of one component of a solution in terms of the change in the properties of the other component. The simplest model of a solution is an ideal solution, in which both components obey Raoult's law over the entire composition range. Although a few solutions behave almost ideally, most solutions are not ideal. Just as nonideal gases can be described in terms of fugacity, nonideal solutions can be described in terms of a quantity called activity. Activity must be calculated with respect to a specific standard state, and in Section 24–8 we introduce two commonly-used standard states: a solvent, or Raoult's law standard state, and a solute, or Henry's law standard state.

24–1. Partial Molar Quantities Are Important Thermodynamic Properties of Solutions

Up to this point, we have discussed the thermodynamics of only one-component systems. We will now discuss the thermodynamics of multicomponent systems, although, for simplicity, we will discuss only systems of two components. Most of the concepts and results we will develop are applicable to multicomponent systems. Let's consider a solution consisting of n_1 moles of component 1 and n_2 moles of component 2. The Gibbs energy of this solution is a function of T and P and the two mole numbers n_1 and n_2. We emphasize this dependence of G on these variables by writing $G = G(T, P, n_1, n_2)$. The total derivative of G is given by

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP$$

$$+ \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_1} dn_2 \qquad (24.1)$$

If the composition of the solution is fixed, so that $dn_1 = dn_2 = 0$, then Equation 24.1 is the same as Equation 22.30, and we have

$$\left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} = -S(P, T, n_1, n_2)$$

and

$$\left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} = V(P, T, n_1, n_2)$$

As in the previous chapter, the partial derivatives of G with respect to mole numbers are called chemical potentials, or partial molar Gibbs energies. The standard notation for chemical potential is μ, so we can write Equation 24.1 as

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 \tag{24.2}$$

where

$$\mu_j = \mu_j(T, P, n_1, n_2) = \left(\frac{\partial G}{\partial n_j}\right)_{T,P,n_{i\neq j}} = \overline{G}_j \tag{24.3}$$

We will see that the chemical potential of each component in the solution plays a central role in determining the thermodynamic properties of the solution.

Other extensive thermodynamic variables have associated partial molar values, although only the partial molar Gibbs energy is given a special symbol and name. For example, $(\partial S/\partial n_j)_{T,P,n_{i\neq j}}$ is called the partial molar entropy and is denoted by $\overline{S}_j$, and $(\partial V/\partial n_j)_{T,P,n_{i\neq j}}$ is called the partial molar volume and is denoted by $\overline{V}_j$. Generally, if $Y = Y(T, P, n_1, n_2)$ is some extensive thermodynamic property, then its associated partial molar quantity, denoted by $\overline{Y}_j$, is by definition

$$\overline{Y}_j = \overline{Y}_j(T, P, n_1, n_2) = \left(\frac{\partial Y}{\partial n_j}\right)_{T,P,n_{i\neq j}} \tag{24.4}$$

Physically, the partial molar quantity $\overline{Y}_j$ is a measure of how Y changes when n_j is changed while keeping T, P, and the other mole numbers fixed.

Partial molar quantities are intensive thermodynamic quantities. In fact, for a pure system, the chemical potential is just the Gibbs energy per mole. We can use the intensive property of partial molar quantities to derive one of the most important relations for solutions. As a concrete example, we will consider a *binary solution*, that is, one composed of two different liquids. The Gibbs energy of a binary solution (Equation 24.2) is

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2$$

At constant T and P, we have

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \tag{24.5}$$

Now, imagine that we increase the size of the system uniformly by means of a scale parameter λ such that $dn_1 = n_1 d\lambda$ and $dn_2 = n_2 d\lambda$. Note that as we vary λ from 0 to 1, the number of moles of components 1 and 2 varies from 0 to n_1 and 0 to n_2, respectively. Because G depends extensively on n_1 and n_2, we must have that $dG = Gd\lambda$. Therefore, the total Gibbs energy varies from 0 to some final value G as λ is varied. Introducing $d\lambda$ into Equation 24.5 gives

$$\int_0^1 Gd\lambda = \int_0^1 n_1\mu_1 d\lambda + \int_0^1 n_2\mu_2 d\lambda$$

Because G, n_1, and n_2 are final values (and so do not depend upon λ) and μ_1 and μ_2 are intensive variables (and so do not depend upon the size parameter λ), we can write the above equation as

$$G \int_0^1 d\lambda = n_1\mu_1 \int_0^1 d\lambda + n_2\mu_2 \int_0^1 d\lambda$$

or, upon integration,

$$G(T, P, n_1, n_2) = \mu_1 n_1 + \mu_2 n_2 \tag{24.6}$$

Note that $G = \mu n$ for a one-component system, which shows once again that μ is the Gibbs energy per mole for a pure system, or more generally, that the partial molar quantity of any extensive thermodynamic quantity of a pure substance is its molar value.

Partial molar quantities have a particularly nice physical interpretation in terms of volume, for which the equivalent equation to Equation 24.6 would be

$$V(T, P, n_1, n_2) = \overline{V}_1 n_1 + \overline{V}_2 n_2 \tag{24.7}$$

Now, when 1-propanol and water are mixed, the final volume of the solution is not equal to the sum of the volumes of pure 1-propanol and water. We can use Equation 24.7 to calculate the final volume of a solution of any composition if we know the partial molar volumes of 1-propanol and water at that composition. Figure 24.1 shows the partial molar volumes of 1-propanol and water as a function of the mole fraction of 1-propanol in 1-propanol/water solutions at 20°C. We can use this figure to estimate the final volume of solution when 100 mL of 1-propanol is mixed with 100 mL of water at 20°C. The densities of 1-propanol and water at 20°C are 0.803 g·mL^{-1} and 0.998 g·mL^{-1}, respectively. Using these densities, we see that 100 mL each of 1-propanol and water corresponds to a mole fraction of 1-propanol of 0.194. Referring
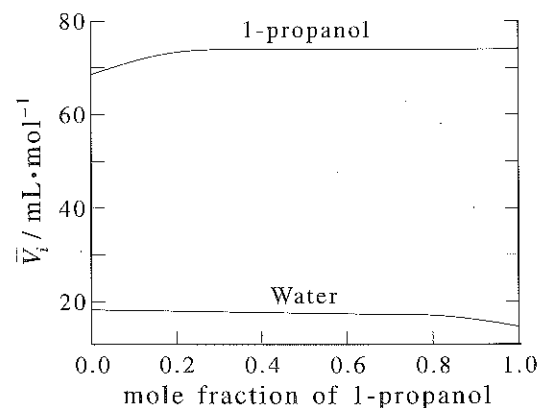
FIGURE 24.1
The partial molar volumes of 1-propanol and water in a 1-propanol/water solution at 20°C plotted against the mole fraction of 1-propanol in the solution.

to Figure 24.1, we see that this corresponds to roughly $\overline{V}_{1\text{-propanol}} = 72$ mL·mol^{-1} and $\overline{V}_{water} = 18$ mL·mol^{-1}. Thus, the final volume of the solution is

$$V = n_1 \overline{V}_{1\text{-propanol}} + n_2 \overline{V}_{water}$$
$$= \left(\frac{80.3 \text{ g}}{60.09 \text{ g·mol}^{-1}} \right) (72 \text{ mL·mol}^{-1}) + \left(\frac{99.8 \text{ g}}{18.02 \text{ g·mol}^{-1}} \right) (18 \text{ mL·mol}^{-1})$$
$$= 196 \text{ mL}$$

compared with a total volume of 200 mL before mixing. Problems 24–8 through 24–12 involve the determination of partial molar volumes from solution data.

24–2. The Gibbs–Duhem Equation Relates the Change in the Chemical Potential of One Component of a Solution to the Change in the Chemical Potential of the Other

Most of our thermodynamic formulas for single-component systems (pure substances) have analogous formulas in terms of partial molar quantities. For example, if we start with $G = H - TS$ and differentiate with respect to n_j keeping T, P, and $n_{i \neq j}$ fixed, we obtain

$$\left(\frac{\partial G}{\partial n_j} \right)_{T,P,n_{i \neq j}} = \left(\frac{\partial H}{\partial n_j} \right)_{T,P,n_{i \neq j}} - T \left(\frac{\partial S}{\partial n_j} \right)_{T,P,n_{i \neq j}}$$

or

$$\mu_j = \overline{G}_j = \overline{H}_j - T\overline{S}_j \tag{24.8}$$

Furthermore, by using the fact that cross second partial derivatives are equal, we get

$$\overline{S}_j = \left(\frac{\partial S}{\partial n_j} \right)_{T,P,n_{i \neq j}} = \frac{\partial}{\partial n_j} \left(-\frac{\partial G}{\partial T} \right)_{P,n_i} = -\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial n_j} \right)_{T,P,n_{i \neq j}} = -\left(\frac{\partial \mu_j}{\partial T} \right)_{P,n_i}$$

and

$$\overline{V}_j = \left(\frac{\partial V}{\partial n_j} \right)_{T,P,n_{i \neq j}} = \frac{\partial}{\partial n_j} \left(\frac{\partial G}{\partial P} \right)_{T,n_i} = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_j} \right)_{T,P,n_{i \neq j}} = \left(\frac{\partial \mu_j}{\partial P} \right)_{T,n_i}$$

If we substitute these two results into

$$d\mu_j = \left(\frac{\partial \mu_j}{\partial T} \right)_{P,n_i} dT + \left(\frac{\partial \mu_j}{\partial P} \right)_{T,n_i} dP$$

we obtain

$$d\mu_j = -\overline{S}_j dT + \overline{V}_j dP \tag{24.9}$$

which is an extension of Equation 22.30 to multicomponent systems.

EXAMPLE 24–1
Derive an equation for the temperature dependence of $\mu_j(T, P)$ in analogy with the Gibbs–Helmholtz equation (Equation 22.60).

SOLUTION: The Gibbs–Helmholtz equation is (Equation 22.60)

$$\left(\frac{\partial G/T}{\partial T} \right)_{P,n_i} = -\frac{H}{T^2}$$

Now differentiate with respect to n_j and interchange the order of differentiation on the left side to get

$$\left(\frac{\partial \mu_j/T}{\partial T} \right)_P = -\frac{\overline{H}_j}{T^2}$$

where $\overline{H}_j$ is the partial molar enthalpy of component j.

We will now derive one of the most useful equations involving partial molar quantities. First we differentiate Equation 24.6

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + n_1 d\mu_1 + n_2 d\mu_2$$

and subtract Equation 24.5 to get

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \qquad \text{(constant } T \text{ and } P) \tag{24.10}$$

If we divide both sides by $n_1 + n_2$, we have

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \qquad \text{(constant } T \text{ and } P) \qquad (24.11)$$

where x_1 and x_2 are mole fractions. Either of Equations 24.10 or 24.11 is called the *Gibbs–Duhem equation*. The Gibbs–Duhem equation tells us that if we know the chemical potential of one component as a function of composition, we can determine the other. For example, suppose we were to know that

$$\mu_2 = \mu_2^* + RT \ln x_2 \qquad 0 \leq x_2 \leq 1$$

over the whole range of x_2 (0 to 1). A superscript * is the IUPAC notation for a property of a pure substance, so in this equation, $\mu_2^* = \mu_2(x_2 = 1)$ is the chemical potential of pure component 2. We can differentiate μ_2 with respect to x_2 and substitute into Equation 24.11 to get

$$d\mu_1 = -\frac{x_2}{x_1} d\mu_2 = -RT \frac{x_2}{x_1} d \ln x_2$$

$$= -RT \frac{x_2}{x_1} \frac{dx_2}{x_2} = -RT \frac{dx_2}{x_1} \qquad (0 \leq x_2 \leq 1)$$

But $dx_2 = -dx_1$ (because $x_1 + x_2 = 1$), so

$$d\mu_1 = RT \frac{dx_1}{x_1} \qquad (0 \leq x_1 \leq 1)$$

where $0 \leq x_1 \leq 1$ because $0 \leq x_2 \leq 1$. Now integrate both sides from $x_1 = 1$ (pure component 1) to arbitrary x_1 to get

$$\mu_1 = \mu_1^* + RT \ln x_1 \qquad (0 \leq x_1 \leq 1)$$

where $\mu_1^* = \mu_1(x_1 = 1)$. We will see later in this chapter that this result says that if one component of a binary solution obeys Raoult's law over the complete concentration range, the other component does also.

EXAMPLE 24–2
Derive a Gibbs–Duhem type of equation for the volume of a binary solution.

SOLUTION: We start with Equation 24.7, which is the analog of Equation 24.6

$$V(T, P, n_1, n_2) = n_1 \overline{V}_1 + n_2 \overline{V}_2$$

and differentiate (at constant T and P) to obtain

$$dV = n_1 d\overline{V}_1 + \overline{V}_1 dn_1 + n_2 d\overline{V}_2 + \overline{V}_2 dn_2$$

Subtract the analog of Equation 24.5

$$dV = \overline{V}_1 dn_1 + \overline{V}_2 dn_2 \qquad \text{(constant } T \text{ and } P)$$

---

to obtain

$$n_1 d\overline{V}_1 + n_2 d\overline{V}_2 = 0 \qquad \text{(constant } T \text{ and } P)$$

This equation says that if we know the change in the partial molar volume of one component of a binary system over a range of composition, we can determine the change in the partial molar volume of the other component over the same range.

24–3. At Equilibrium, the Chemical Potential of Each Component Has the Same Value in Each Phase in Which the Component Appears

Consider a binary solution of two liquids that is in equilibrium with its vapor phase, which contains both components. Examples are a solution of 1-propanol and water or a solution of benzene and toluene, each in equilibrium with its vapor. We wish to generalize our treatment in the previous chapter, in which we treated a pure liquid in equilibrium with its vapor phase, and develop the criterion for equilibrium in a binary solution. The Gibbs energy of the solution and its vapor is

$$G = G^{\text{sln}} + G^{\text{vap}}$$

Let n_1^{sln}, n_2^{sln} and n_1^{vap}, n_2^{vap} be the mole numbers of each component in each phase. For generality, let j denote either component 1 or 2, so n_j denotes the number of moles of component j. Now suppose that dn_j moles of component j are transferred from the solution to the vapor at constant T and P, so that $dn_j^{\text{vap}} = +dn_j$ and $dn_j^{\text{sln}} = -dn_j$. The accompanying change in the Gibbs energy is

$$dG = dG^{\text{sln}} + dG^{\text{vap}}$$

$$= \left(\frac{\partial G^{\text{sln}}}{\partial n_j^{\text{sln}}} \right)_{T, P, n_{i \neq j}} dn_j^{\text{sln}} + \left(\frac{\partial G^{\text{vap}}}{\partial n_j^{\text{vap}}} \right)_{T, P, n_{i \neq j}} dn_j^{\text{vap}}$$

$$= \mu_j^{\text{sln}} dn_j^{\text{sln}} + \mu_j^{\text{vap}} dn_j^{\text{vap}} = (\mu_j^{\text{vap}} - \mu_j^{\text{sln}}) dn_j^{\text{vap}}$$

If the transfer from the solution to the vapor occurs spontaneously, then $dG < 0$. Furthermore, $dn_j^{\text{vap}} > 0$, so μ_j^{vap} must be less than μ_j^{sln} in order that $dG < 0$. Therefore, molecules of component j move spontaneously from the phase of higher chemical potential (solution) to that of lower chemical potential (vapor). Similarly, if $\mu_j^{\text{vap}} > \mu_j^{\text{sln}}$, then molecules of component j move spontaneously from the vapor phase to the solution phase ($dn_j^{\text{vap}} < 0$). At equilibrium, where $dG = 0$, we have that

$$\mu_j^{\text{vap}} = \mu_j^{\text{sln}} \qquad (24.12)$$

Equation 24.12 holds for each component. Although we have discussed a solution in equilibrium with its vapor phase, our choice of phases was arbitrary, so Equation 24.12 is valid for the equilibrium between any two phases in which component j occurs.

The important result here is that Equation 24.12 says that the chemical potential of each component in the liquid solution phase can be measured by the chemical potential of that component in the vapor phase. If the pressure of the vapor phase is low enough that we can consider it to be ideal, then Equation 24.12 becomes

$$\mu_j^{\text{sln}} = \mu_j^{\text{vap}} = \mu_j^{\circ}(T) + RT \ln P_j \tag{24.13}$$

where the standard state is taken to be $P_j^{\circ} = 1$ bar. For *pure* component j, Equation 24.13 becomes

$$\mu_j^*(l) = \mu_j^*(\text{vap}) = \mu_j^{\circ}(T) + RT \ln P_j^* \tag{24.14}$$

where the superscript $*$ represents pure (liquid) component j. Thus, for example, $\mu_j^*(l)$ is the chemical potential and P_j^* is the vapor pressure of pure j. If we subtract Equation 24.14 from Equation 24.13, we obtain

$$\mu_j^{\text{sln}} = \mu_j^*(l) + RT \ln \frac{P_j}{P_j^*} \tag{24.15}$$

Equation 24.15 is a central equation in the study of binary solutions. Note that $\mu_j^{\text{sln}} \rightarrow \mu_j^*$ as $P_j \rightarrow P_j^*$. Strictly speaking, we should use fugacities (Section 22–8) instead of pressures in Equation 24.15, but usually the magnitudes of vapor pressures are such that pressures are quite adequate. For example, the vapor pressure of water at 293.15 K is 17.4 torr, or 0.0232 bar.

24–4. The Components of an Ideal Solution Obey Raoult's Law for All Concentrations

A few solutions have the property that the partial vapor pressure of each component is given by the simple equation

$$P_j = x_j P_j^* \tag{24.16}$$

Equation 24.16 is called *Raoult's law*, and a solution that obeys Raoult's law over the entire composition range is said to be an *ideal solution*.

The molecular picture behind an ideal binary solution is that the two types of molecules are randomly distributed throughout the solution. Such a distribution will occur if (1) the molecules are roughly the same size and shape, and (2) the intermolecular forces in the pure liquids 1 and 2 and in a mixture of 1 and 2 are all similar. We expect ideal-solution behavior only when the molecules of the two components are similar. For example, benzene and toluene, o-xylene and p-xylene, hexane and heptane, and bromoethane and iodoethane form essentially ideal solutions. Figure 24.2 depicts an ideal solution, in which the two types of molecules are randomly distributed. The mole fraction x_j reflects the fraction of the solution surface that is occupied by
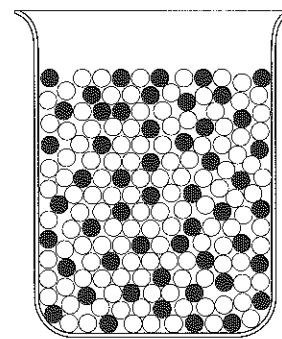
FIGURE 24.2
A molecular depiction of an ideal solution. The two types of molecules are distributed throughout the solution in a random manner.

j molecules. Because the j molecules on the surface are the molecules that can escape into the vapor phase, the partial pressure P_j is just $x_j P_j^*$.

According to Raoult's law (Equation 24.16) and Equation 24.15, the chemical potential of component j in the solution is given by

$$\mu_j^{\text{sln}} = \mu_j^*(l) + RT \ln x_j \tag{24.17}$$

Equation 24.17 also serves to define an ideal solution if it is valid for all values of x_j ($0 \leq x_j \leq 1$). Furthermore, we showed in Section 24–2 that if one component obeys Equation 24.17 from $x_j = 0$ to $x_j = 1$, then so does the other.

The total vapor pressure over an ideal solution is given by

$$P_{\text{total}} = P_1 + P_2 = x_1 P_1^* + x_2 P_2^* = (1 - x_2)P_1^* + x_2 P_2^*$$
$$= P_1^* + x_2(P_2^* - P_1^*) \tag{24.18}$$

Therefore, a plot of P_{total} against x_2 (or x_1) will be a straight line as shown in Figure 24.3.
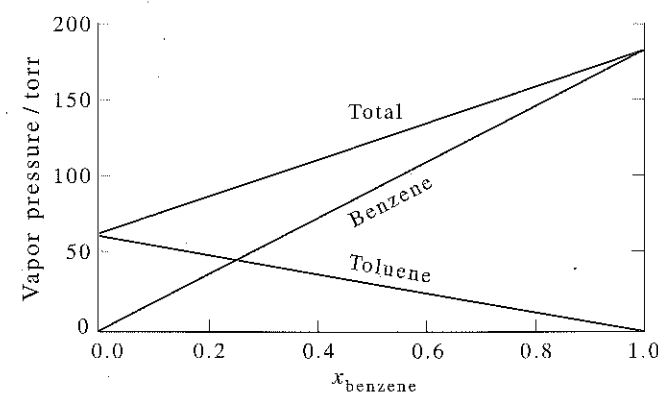

FIGURE 24.3
A plot of P_{total} against x_{benzene} for a solution of benzene and toluene at 40°C. This plot shows that a benzene/toluene solution is essentially ideal.

EXAMPLE 24–3

1-propanol and 2-propanol form essentially an ideal solution at all concentrations at 25°C. Letting the subscripts 1 and 2 denote 1-propanol and 2-propanol, respectively, and given that $P_1^* = 20.9$ torr and $P_2^* = 45.2$ torr at 25°C, calculate the total vapor pressure and the composition of the vapor phase at $x_2 = 0.75$.

SOLUTION: We use Equation 24.18:

$$P_{total}(x_2 = 0.75) = x_1 P_1^* + x_2 P_2^*$$

$$= (0.25)(20.9 \text{ torr}) + (0.75)(45.2 \text{ torr})$$

$$= 39.1 \text{ torr}$$

Let y_j denote the mole fraction of each component in the vapor phase. Then, by Dalton's law of partial pressures,

$$y_1 = \frac{P_1}{P_{total}} = \frac{x_1 P_1^*}{P_{total}} = \frac{(0.25)(20.9 \text{ torr})}{39.1 \text{ torr}} = 0.13$$

Similarly,

$$y_2 = \frac{P_2}{P_{total}} = \frac{x_2 P_2^*}{P_{total}} = \frac{(0.75)(45.2 \text{ torr})}{39.1 \text{ torr}} = 0.87$$

Note that $y_1 + y_2 = 1$. Also note that the vapor is richer than the solution in the more volatile component.

Problem 24–15 has you expand Example 24–3 by calculating P_{total} as a function of x_2 (the mole fraction of 2-propanol in the liquid phase) and as a function of y_2 (the mole fraction of 2-propanol in the vapor phase), and then plotting P_{total} against x_2 and y_2. The resulting plot, which is shown in Figure 24.4, is called a *pressure-composition diagram*. The upper curve shows the total vapor pressure as a function of the composition of the liquid phase (the liquid curve), and the lower curve shows the total vapor pressure as a function of the composition of the vapor phase (the vapor curve). Now let's see what happens when you start at the point P_a, x_a in Figure 24.4 and lower the pressure. At the point P_a, x_a, the pressure exceeds the vapor pressure of the solution, so the region above the liquid curve consists of one (liquid) phase. As the pressure is lowered, we reach the point A, where liquid starts to vaporize. Along the line AB, the system consists of liquid and vapor in equilibrium with each other. At the point B, all the liquid has vaporized, and the region below the vapor curve consists of one (vapor) phase.

Let's consider the point C in the liquid-vapor region. Point C lies on a line connecting the composition of liquid ($x_2 = 0.75$) and vapor ($y_2 = 0.87$) phases that we calculated in Example 24–3. Such a line is called a *tie line*. The overall composition of the two-phase (liquid-vapor) system is x_a. We can determine the relative amounts
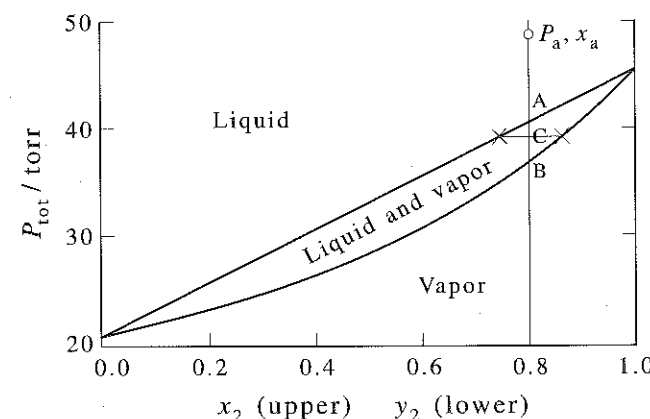

FIGURE 24.4

A pressure-composition diagram for a 1-propanol/2-propanol solution, which forms an essentially ideal solution at 25°C. This figure can be calculated using the approach in Example 24–3. The upper curve (called the liquid curve) represents P_{total} versus x_2, the mole fraction of 2-propanol in the liquid phase, and the lower curve (called the vapor curve) represents P_{total} versus y_2, the mole fraction of 2-propanol in the vapor phase. The two points marked by $\times$ represent the values of x_2 and y_2 from Example 24–3.

of liquid and vapor phase in the following way. The mole fractions in the liquid and vapor phases are

$$x_2 = \frac{n_2^l}{n_1^l + n_2^l} = \frac{n_2^l}{n^l} \quad \text{and} \quad y_2 = \frac{n_2^{vap}}{n_1^{vap} + n_2^{vap}} = \frac{n_2^{vap}}{n^{vap}}$$

where n^{vap} and n^l are the total number of moles in the vapor and liquid phases, respectively. The overall mole fraction at x_a is given by the total number of moles of component 2 divided by the total number of moles

$$x_a = \frac{n_2^l + n_2^{vap}}{n^l + n^{vap}}$$

Using a material balance of the number of moles of component 2, we have

$$x_a(n^l + n^{vap}) = x_2 n^l + y_2 n^{vap}$$

or

$$\frac{n^l}{n^{vap}} = \frac{y_2 - x_a}{x_a - x_2} \tag{24.19}$$

This equation represents what is called the *lever rule* because $n^{vap}(y_2 - x_a) = n^l(x_a - x_2)$ can be interpreted as a balance of each value of "n" times the distance from each curve to the point C in Figure 24.4. Note that $n^l = 0$ when $x_a = y_2$ (vapor curve) and that $n^{vap} = 0$ when $x_a = x_2$ (liquid curve).

EXAMPLE 24–4

Calculate the relative amounts of liquid and vapor phases at an overall composition of 0.80 for the values in Example 24–3.

SOLUTION: In this case, $x_a = 0.80$, $x_2 = 0.75$, and $y_2 = 0.87$ (see Example 24–3), so

$$\frac{n^l}{n^{vap}} = \frac{0.87 - 0.80}{0.80 - 0.75} = 1.6$$

According to Example 24–3, the mole fraction of 2-propanol in the vapor phase in equilibrium with a 1-propanol/2-propanol solution is greater than the mole fraction of 2-propanol in the solution. We can display the composition of the solution and vapor phases at various temperatures by a diagram called a *temperature-composition diagram*. To construct such a diagram, we choose some total ambient pressure such as 760 torr and write

$$760 \text{ torr} = x_1 P_1^* + x_2 P_2^* = x_1 P_1^* + (1 - x_1)P_2^*$$
$$= P_2^* - x_1(P_2^* - P_1^*)$$

or

$$x_1 = \frac{P_2^* - 760 \text{ torr}}{P_2^* - P_1^*}$$

We then choose some temperature between the boiling points of the two components and solve the above equation for x_1, the compositon of the solution that will give a total pressure of 760 torr. A plot of temperature against x_1 shows the boiling temperature (at $P_{total} = 760$ torr) of a solution as a function of its composition (x_1). Such a curve, labeled the solution curve, is shown in Figure 24.5. For example, at $t = 90°C$, P_1^* (the vapor pressure of 1-propanol) $= 575$ torr and P_2^* (the vapor pressure of 2-propanol) $= 1027$ torr. Therefore,

$$x_1 = \frac{P_2^* - 760 \text{ torr}}{P_2^* - P_1^*} = \frac{1027 \text{ torr} - 760 \text{ torr}}{1027 \text{ torr} - 575 \text{ torr}} = 0.59$$

The point corresponding to $t = 90°C$ and $x_1 = 0.59$ is labeled by point a in Figure 24.5. We can also calculate the corresponding composition of the vapor phase as a function of temperature. The mole fraction of component 1 in the vapor phase is given by Dalton's law

$$y_1 = \frac{P_1}{760 \text{ torr}} = \frac{x_1 P_1^*}{760 \text{ torr}}$$
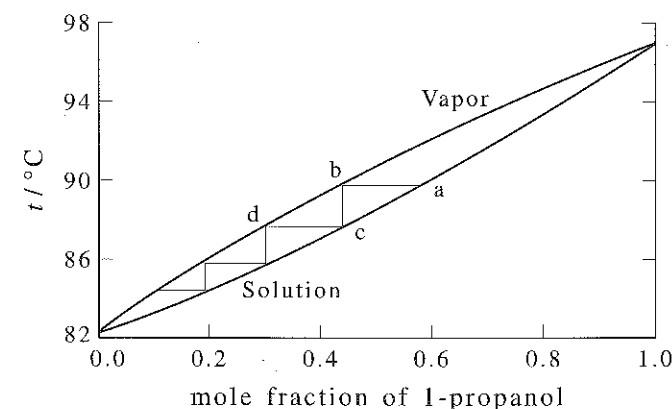

FIGURE 24.5

A temperature-composition diagram of a 1-propanol/2-propanol solution, which is essentially an ideal solution. The boiling point of 1-propanol is 97.2°C and that of 2-propanol is 82.3°C.

because the total pressure is taken (arbitrarily) to be 760 torr. We saw above that $x_1 = 0.59$ at 90°C, so we have that

$$y_1 = (0.59)(575 \text{ torr})/(760 \text{ torr}) = 0.45$$

which is labelled by point b in Figure 24.5.

EXAMPLE 24–5

The vapor pressures (in torr) of 1-propanol and 2-propanol as a function of the Celsius temperature, t, are given by the empirical formulas

$$\ln P_1^* = 18.0699 - \frac{3452.06}{t + 204.64}$$

and

$$\ln P_2^* = 18.6919 - \frac{3640.25}{t + 219.61}$$

Use these formulas to calculate x_1 and y_1 at 93.0°C, and compare your results with the values given in Figure 24.5.

SOLUTION: At 93.0°C,

$$\ln P_1^* = 18.0699 - \frac{3452.06}{93.0 + 204.64} = 6.472$$

or $P_1^* = 647$ torr. Similarly, $P_2^* = 1150$ torr. Therefore,

$$x_1 = \frac{P_2^* - 760 \text{ torr}}{P_2^* - P_1^*} = \frac{1150 \text{ torr} - 760 \text{ torr}}{1150 \text{ torr} - 647 \text{ torr}} = 0.77$$

and

$$y_1 = \frac{x_1 P_1^*}{760 \text{ torr}} = \frac{(0.77)(647 \text{ torr})}{760 \text{ torr}} = 0.65$$

in agreement with the values shown in Figure 24.5.

The temperature-composition diagram can be used to illustrate the process of fractional distillation, in which a vapor is condensed and then re-evaporated many times (Figure 24.6). If we were to start with a 1-propanol/2-propanol solution that has a mole fraction of 0.59 in 1-propanol (point a in Figure 24.5), the mole fraction of 1-propanol in the vapor will be 0.45 (point b). If this vapor is condensed (point c) and then re-evaporated, then the mole fraction of 1-propanol in the vapor phase will be about 0.30 (point d). As this process is continued, the vapor becomes increasingly richer in 2-propanol, eventually resulting in pure 2-propanol. A fractional distillation column differs from an ordinary distillation column in that the former is packed with glass beads, which provide a large surface area for the repeated condensation-evaporation process.

We can calculate the change in thermodynamic properties upon forming an ideal solution from its pure components. Let's take the Gibbs energy as an example. We define the Gibbs energy of mixing by

$$\Delta_{mix}G = G^{sln}(T, P, n_1, n_2) - G_1^*(T, P, n_1) - G_2^*(T, P, n_2) \quad (24.20)$$

Condenser

Pure liquid to collection flask

Column packed with glass rings

Insulation

Glass wool plug

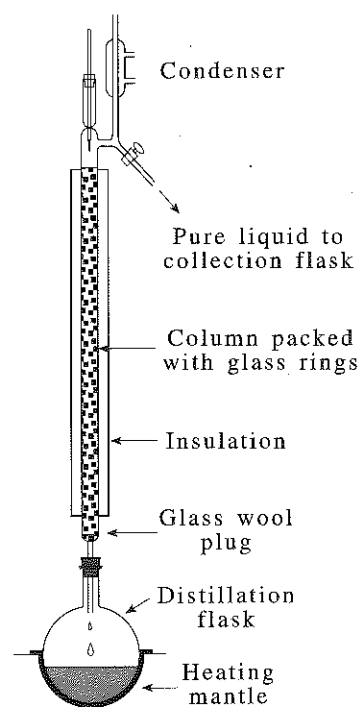Distillation flask

Heating mantle

FIGURE 24.6
A simple fractional distillation column. Because repeated condensation and re-evaporation occur along the entire column, the vapor becomes progresively richer in the more volatile component as it moves up the column.

where G_1^* and G_2^* are the Gibbs energies of the pure components. Using Equation 24.17 for an ideal solution gives

$$\Delta_{mix}G^{id} = n_1\mu_1^{sln} + n_2\mu_2^{sln} - n_1\mu_1^* - n_2\mu_2^*$$
$$= RT(n_1 \ln x_1 + n_2 \ln x_2) \quad (24.21)$$

This quantity is always negative because x_1 and x_2 are less than one. In other words, an ideal solution will always form spontaneously from its separate components. The entropy of mixing of an ideal solution is given by

$$\Delta_{mix}S^{id} = -\left(\frac{\partial \Delta_{mix}G^{id}}{\partial T}\right)_{P,n_1,n_2} = -R(n_1 \ln x_1 + n_2 \ln x_2) \quad (24.22)$$

Note that this result for an ideal solution is the same as Equation 20.26 for the mixing of ideal gases. This similarity is due to the fact that in both cases the molecules in the final solution are randomly mixed. Nevertheless, you should realize that an ideal solution and a mixture of ideal gases differ markedly in the interactions involved. Although the molecules do not interact in a mixture of ideal gases, they interact strongly in an ideal solution. In an ideal solution, the interactions in the mixture and those in the pure liquids are essentially identical.

The volume change upon mixing of an ideal solution is given by

$$\Delta_{mix}V^{id} = \left(\frac{\partial \Delta_{mix}G^{id}}{\partial P}\right)_{T,n_1,n_2} = 0 \quad (24.23)$$

and the enthalpy of mixing is (see Equations 24.21 and 24.22)

$$\Delta_{mix}H^{id} = \Delta_{mix}G^{id} + T\Delta_{mix}S^{id} = 0 \quad (24.24)$$

Therefore, there is no volume change upon mixing, nor is there any energy as heat absorbed or evolved when an ideal solution is formed from its pure components. Both Equations 24.23 and 24.24 result from the facts that the molecules are roughly the same size and shape (hence $\Delta_{mix}V^{id} = 0$) and that the various interaction energies are the same (hence $\Delta_{mix}H^{id} = 0$). Equations 24.23 and 24.24 are indeed observed to be true experimentally for ideal solutions. For most solutions, however, $\Delta_{mix}H$ and $\Delta_{mix}V$ do not equal zero.

24–5. Most Solutions Are Not Ideal

Ideal solutions are not very common. Figures 24.7 and 24.8 show vapor pressure diagrams for carbon disulfide/dimethoxymethane $[(CH_3O)_2CH_2]$ solutions and tri-chloromethane/acetone solutions, respectively. The behavior in Figure 24.7 shows so-called positive deviations from Raoult's law because the partial vapor pressures
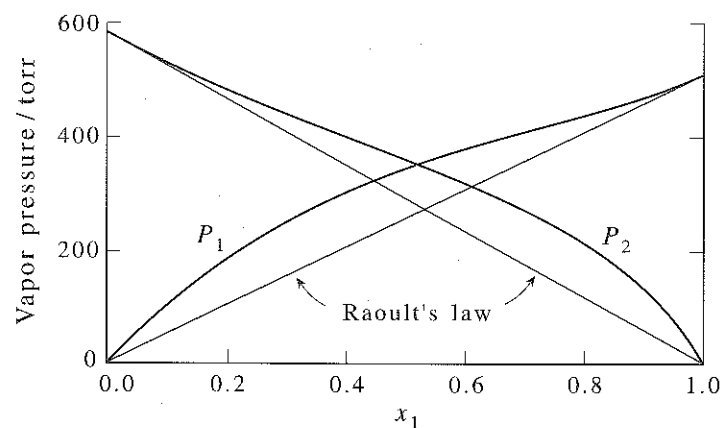
FIGURE 24.7
The vapor pressure diagram of a carbon disulfide/dimethoxymethane solution at 25°C. This system shows positive deviations from ideal, or Raoult's law, behavior.
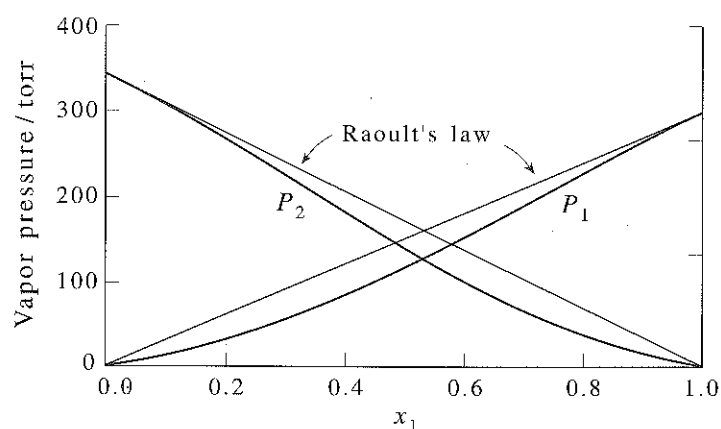

FIGURE 24.8
The vapor pressure diagram of a trichloromethane/acetone solution at 25°C. This system shows negative deviations from ideal, or Raoult's law, behavior.

of carbon disulfide and dimethoxymethane are greater than predicted on the basis of Raoult's law. Physically, positive deviations occur because carbon disulfide–dimethoxymethane interactions are more repulsive than either carbon disulfide–carbon disulfide or dimethoxymethane–dimethoxymethane interactions. Negative deviations, on the other hand, like those shown in Figure 24.8 for a trichloromethane/acetone solution, are due to stronger unlike-molecule interactions than like-molecule interactions. Problem 24–36 asks you to show that if one component of a binary solution exhibits positive deviations from ideal behavior, then the other component must do likewise.
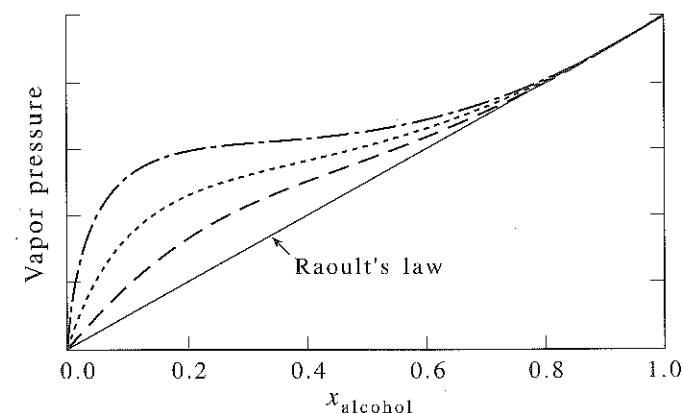
FIGURE 24.9
The vapor pressure diagram of alcohol/water solutions as a function of the number of carbon atoms in the alcohols, showing increasing deviation from ideal behavior. The dashed line corresponds to methanol, the dotted line to ethanol, and the dashed-dotted line to 1-propanol.

Figure 24.9 shows plots of methanol, ethanol, and 1-propanol vapor pressures in alcohol/water solutions. Note that the positive deviation from ideal behavior increases with the size of the hydrocarbon part of the alcohol. This behavior occurs because the water–hydrocarbon (repulsive) interactions become increasingly prevalent as the size of the hydrocarbon chain increases.

There are some important features to notice in Figures 24.7 and 24.8. Let's focus on component 1. The vapor pressure of component 1 approaches its Raoult's law value as x_1 approaches 1. In an equation, we have that

$$P_1 \longrightarrow x_1 P_1^* \quad \text{as} \quad x_1 \longrightarrow 1 \tag{24.25}$$

Although we deduced Equation 24.25 from Figures 24.7 and 24.8, it is generally true. Physically, this behavior may be attributed to the fact that there are so few component-2 molecules that most component-1 molecules see only other component-1 molecules, so that the solution behaves ideally. Raoult's law behavior is *not* observed for component 1 as $x_1 \to 0$ in Figures 24.7 and 24.8, however. Although not easily seen in Figures 24.7 and 24.8, the vapor pressure of component 1 as $x_1 \to 0$ is linear in x_1, but the slope is not equal to P_1^* as in Equation 24.25. We emphasize this behavior by writing

$$P_1 \longrightarrow k_{H,1} x_1 \quad \text{as} \quad x_1 \longrightarrow 0 \tag{24.26}$$

In the special case of an ideal solution, $k_{H,1} = P_1^*$, but ordinarily $k_{H,1} \neq P_1^*$. Equation 24.26 is called *Henry's law*, and $k_{H,1}$ is called the *Henry's law constant* of component 1. As $x_1 \to 0$, the component-1 molecules are completely surrounded by component-2 molecules, and the value of $k_{H,1}$ reflects the intermolecular interactions between the two components. As $x_1 \to 1$, on the other hand, the component-1

molecules are completely surrounded by component-1 molecules, and P_1^* is what reflects the intermolecular interactions in the pure liquid. Although we have focussed our discussion on component 1 in Figures 24.7 and 24.8, the same situtation holds for component 2. Equations 24.25 and 24.26 can be written as

$$P_j \longrightarrow x_j P_j^* \quad \text{as } x_j \longrightarrow 1$$
$$P_j \longrightarrow x_j k_{H,j} \quad \text{as } x_j \longrightarrow 0 \tag{24.27}$$

Thus, in a vapor pressure diagram of a solution of two volatile liquids, the vapor pressure of each component approaches Raoult's law as the mole fraction of that component approaches one and Henry's law as the mole fraction approaches zero.

EXAMPLE 24-6
The vapor pressure (in torr) of component 1 over a binary solution is given by

$$P_1 = 180 x_1 e^{x_2^2 + \frac{1}{2} x_2^3} \qquad 0 \le x_1 \le 1$$

Determine the vapor pressure (P_1^*) and the Henry's law constant ($k_{H,1}$) of pure component 1.

SOLUTION: In the limit that $x_1 \to 1$, the exponential factor $\to 1$ because $x_2 \to 0$ as $x_1 \to 1$. Therefore,

$$P_1 \longrightarrow 180 x_1 \quad \text{as} \quad x_1 \longrightarrow 1$$

so $P_1^* = 180$ torr. As $x_1 \to 0$, on the other hand, the exponential factor approaches $e^{3/2}$ because $x_2 \to 1$ as $x_1 \to 0$. Thus, we have

$$P_1 \longrightarrow 180 e^{3/2} x_1 = 807 x_1 \quad \text{as} \quad x_1 \longrightarrow 0$$

and $k_{H,1} = 807$ torr.

We will now show that the Henry's law behavior of component 2 as $x_2 \to 0$ is a thermodynamic consequence of the Raoult's law behavior of component 1 as $x_1 \to 1$. To prove this connection, we will start with the Gibbs–Duhem equation (Equation 24.11)

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \qquad \text{(constant } T \text{ and } P)$$

Now, assuming that the vapor phase may be treated as an ideal gas, both chemical potentials can be expressed as

$$\mu_j(T, P) = \mu_j^\circ(T) + RT \ln P_j$$

(Recall that the argument of the logarithm is actually P_j/P°, where P° is one bar.) Now this form of $\mu_j(T, P)$ allows us to write

$$d\mu_1 = RT \left(\frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} dx_1$$

and

$$d\mu_2 = RT \left(\frac{\partial \ln P_2}{\partial x_2} \right)_{T,P} dx_2$$

Substitute these two expressions into the Gibbs–Duhem equation to get

$$x_1 \left(\frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} dx_1 + x_2 \left(\frac{\partial \ln P_2}{\partial x_2} \right)_{T,P} dx_2 = 0 \tag{24.28}$$

But $dx_1 = -dx_2$ (because $x_1 + x_2 = 1$), so Equation 24.28 becomes

$$x_1 \left(\frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} = x_2 \left(\frac{\partial \ln P_2}{\partial x_2} \right)_{T,P} \tag{24.29}$$

which is another form of the Gibbs–Duhem equation. If component 1 obeys Raoult's law as $x_1 \to 1$, then $P_1 \to x_1 P_1^*$ and $(\partial \ln P_1/\partial x_1)_{T,P} = 1/x_1$, so the left side of Equation 24.29 becomes unity. Thus, we have the condition

$$x_2 \left(\frac{\partial \ln P_2}{\partial x_2} \right)_{T,P} = 1 \quad \text{as} \quad x_1 \to 1 \text{ or } x_2 \to 0$$

We now integrate this expression indefinitely to get

$$\ln P_2 = \ln x_2 + \text{constant} \quad \text{as} \quad x_1 \to 1 \text{ or } x_2 \to 0$$

or

$$P_2 = k_{H,2} x_2 \quad \text{as} \quad x_2 \to 0$$

Thus, we see that if component 1 obeys Raoult's law as $x_1 \to 1$, then component 2 must obey Henry's law as $x_2 \to 0$. Problem 24–32 has you prove the converse: if component 2 obeys Henry's law as $x_2 \to 0$, then component 1 must obey Raoult's law as $x_1 \to 1$.

24–6. The Gibbs–Duhem Equation Relates the Vapor Pressures of the Two Components of a Volatile Binary Solution

The following example shows that if we know the vapor pressure curve of one of the components over the entire composition range, we can calculate the vapor pressure of the other component.

EXAMPLE 24–7

The vapor pressure curve of one of the components (say component 1) of a nonideal binary solution can often be represented empirically by (see Figure 24.10)

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3} \qquad 0 \leq x_1 \leq 1$$

where α and β are parameters that are used to fit the data. Show that the vapor pressure of component 2 is necessarily given by

$$P_2 = x_2 P_2^* e^{\gamma x_1^2 + \delta x_1^3} \qquad 0 \leq x_2 \leq 1$$

where $\gamma = \alpha + 3\beta/2$ and $\delta = -\beta$. Notice that the parameters α and β must in some manner reflect the extent of the nonideality of the solution because both P_1 and P_2 reduce to the ideal solution expressions when $\alpha = \beta = 0$. Furthermore, note that $P_1 \rightarrow x_1 P_1^* e^{\alpha + \beta}$ as $x_1 \rightarrow 0$ ($x_2 \rightarrow 1$), so the Henry's law constant of component 1 is $k_{H,1} = P_1^* e^{\alpha + \beta}$. Similarly, we find that $k_{H,2} = P_2^* e^{\alpha + \beta/2}$.

SOLUTION: We use the Gibbs–Duhem equation

$$d\mu_2 = -\frac{x_1}{x_2} d\mu_1$$

along with (Equation 24.13)

$$\begin{aligned}
\mu_1 &= \mu_1^\circ + RT \ln P_1 \\
&= \mu_1^\circ + RT \ln P_1^* + RT \ln x_1 \\
&\quad + \alpha RT (1 - x_1)^2 + \beta RT (1 - x_1)^3
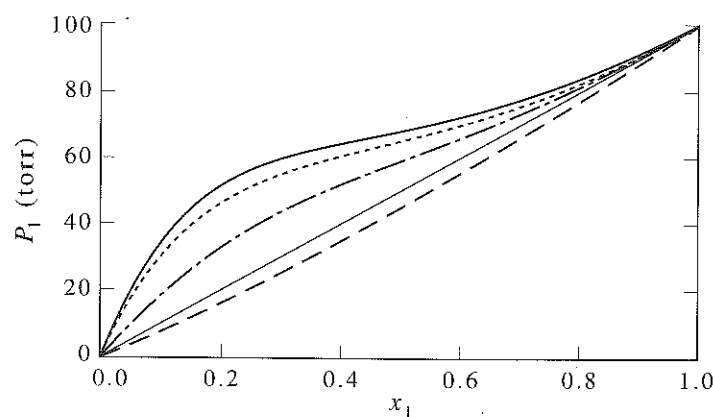\end{aligned}$$

FIGURE 24.10
A plot of $P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$ for $P_1^* = 100$ torr and various values of α and β. The values of α and β for the five curves, top to bottom, are 1.0, 0.60; 0.80, 0.60; 0.60, 0.20; 0,0 (ideal solution); and −0.80, 0.60.

Differentiate this equation with respect to x_1 and substitute the result into the above Gibbs–Duhem equation to obtain

$$\begin{aligned}
d\mu_2 &= -\frac{x_1}{x_2} RT \left[\frac{dx_1}{x_1} - 2\alpha(1 - x_1)dx_1 - 3\beta(1 - x_1)^2 dx_1 \right] \\
&= RT \left[-\frac{dx_1}{x_2} + 2\alpha x_1 dx_1 + 3\beta x_1(1 - x_1)dx_1 \right]
\end{aligned}$$

Now change variables from x_1 to x_2

$$d\mu_2 = RT \left[\frac{dx_2}{x_2} - 2\alpha(1 - x_2)dx_2 - 3\beta x_2(1 - x_2)dx_2 \right]$$

and integrate from $x_2 = 1$ to arbitrary x_2 and use the fact that $\mu_2 = \mu_2^*$ when $x_2 = 1$ to get

$$\begin{aligned}
\mu_2 - \mu_2^* &= RT \left[\ln x_2 + \alpha(1 - x_2)^2 - \frac{3\beta}{2}(x_2^2 - 1) + \beta(x_2^3 - 1) \right] \\
&= RT \left[\ln x_2 + \alpha x_1^2 + \frac{3\beta}{2}x_1^2 - \beta x_1^3 \right]
\end{aligned}$$

Using the fact that $\mu_2 = \mu_2^\circ + RT \ln P_2$ and that $\mu_2^* = \mu_2^\circ + RT \ln P_2^*$, we see that

$$\ln P_2 = \ln P_2^* + \ln x_2 + \alpha x_1^2 + \frac{3\beta}{2}x_1^2 - \beta x_1^3$$

or

$$P_2 = x_2 P_2^* e^{(\alpha + 3\beta/2)x_1^2 - \beta x_1^3}$$

We could also have used Equation 24.29 to do this problem (Problem 24–33).

Figure 24.11 shows the boiling-point diagram of a benzene/ethanol system, in which the boiling points of benzene/ethanol solutions (at one atm) are plotted against the mole fraction of ethanol. Figure 24.11 shows that if you were to start with a solution with an ethanol mole fraction of 0.2, for example, then repeated evaporation–condensation would lead to a mixture consisting of a mole fraction of about 0.4 that cannot be separated by further fractional distillation.

Such a mixture, for which there is no change in composition upon boiling, is called an *azeotrope*. Thus, it is not possible to achieve a separation of a benzene/ethanol solution by distillation into pure benzene and pure ethanol. If we start out at an ethanol mole fraction of 0.2, we would obtain a separation of pure benzene and the azeotrope. Similarly, if we started out with an ethanol mole fraction of 0.8, we would achieve a separation of pure ethanol and the benzene/ethanol azeotrope.

As our final topic in this section on nonideal solutions, let's consider the case in which the positive deviations from ideal behavior become increasingly large, as often occurs as the temperature is lowered. Figure 24.12 illustrates typical vapor pressure behavior for a series of temperatures, where $T_3 > T_c > T_2 > T_1$. The vertical axis is P_2 / P_2^*, so each curve is "normalized" by the vapor pressure of pure component 2 at each
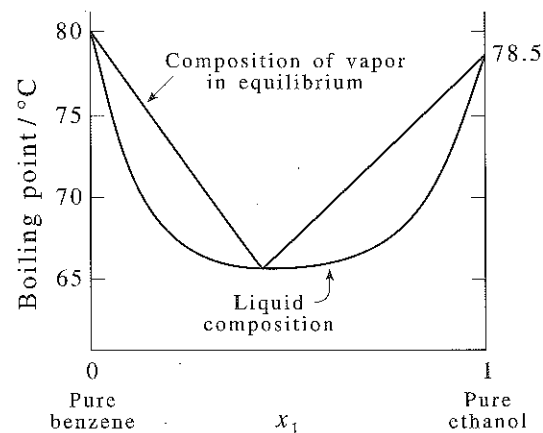
984

FIGURE 24.11
The boiling-point diagram of a benzene/ethanol solution, showing the occurrence of an azeotropic solution at an ethanol mole fraction of about 0.4. The quantity x_1 is the mole fraction of ethanol.
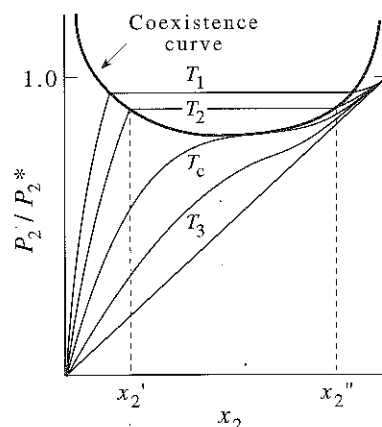

FIGURE 24.12
An illustration of the critical behavior of a binary solution as a function of temperature $(T_3 > T_c > T_2 > T_1)$.

temperature. Therefore, all the curves meet at $P_2/P_2^* = 1$ at $x_2 = 1$. For temperature T_3, which is greater than T_c, the slope of the P_2 versus x_2 curve is everywhere positive. At T_c, the curve has an inflection point, where $\partial P_2/\partial x_2 = 0$ and $\partial^2 P_2/\partial x_2^2 = 0$. For the temperatures T_1 and T_2, which are less than T_c, the curves have a horizontal portion that becomes wider as the temperature is lowered. The temperature T_c is called the *critical temperature* or *consulate temperature*, and as we will now discuss, the consulate temperature is the temperature below which the two liquids are not miscible in all proportions.

Let's follow the T_2 curve in Figure 24.12 as we start with pure component 1 ($x_2 = 0$) and add component 2. Up to the point x_2', the added component 2 simply

24–6. The Gibbs–Duhem Equation Relates the Vapor Pressures of the Two Components   985

dissolves in component 1 to form a single solution phase. Above the concentration x_2', however, two separate or immiscible solution phases form, one of composition x_2' and one of composition x_2''. As x_2 is increased from x_2' to x_2'', the two phases must maintain a constant mole fraction of component 2 (x_2' and x_2'') and therefore, the relative proportions of the two phases change, with the volume of the phase of composition x_2'' increasing and the volume of the phase of composition x_2' decreasing. The overall composition of the two phases together is given by the value of x_2. When $x_2 > x_2''$, we obtain a single solution phase.

We can derive a lever rule to calculate the relative amounts of the two phases in the following way. Consider some overall composition x_2, which lies between x_2' and x_2''. Let n_1', n_2' and n_1'', n_2'' be the number of moles of the two components in the phases of composition x_2' and x_2'', respectively. Then, the mole fraction of component 2 in each phase is

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

and the overall mole fraction of component-2 is

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

Using material balance of the number of moles of component 2 allows us to write

$$x_2(n_1' + n_1'' + n_2' + n_2'') = x_2'(n_1' + n_2') + x_2''(n_1'' + n_2'')$$

We can rearrange this material balance equation to give

$$\frac{n'}{n''} = \frac{n_1' + n_2'}{n_1'' + n_2''} = \frac{x_2'' - x_2}{x_2 - x_2'} \tag{24.30}$$

Equation 24.30 gives the relative total number of moles in each phase. Note that if $x_2 = x_2''$, then $n' = 0$, and if $x_2 = x_2'$, then $n'' = 0$. As Equation 24.30 shows, when x_2 reaches x_2'', the phase of composition x_2' disappears, and there is a single solution phase of composition $x_2 = x_2''$. For $x_2 \geq x_2''$, there is a single solution phase of composition x_2. Thus, at a temperature T_2, the two liquids are immiscible when x_2 is between x_2' and x_2'' but are miscible for $x_2 < x_2'$ and $x_2 > x_2''$. Similar behavior occurs at other temperatures less than T_c, and Figure 24.12 summarizes this behavior. The heavy curve in Figure 24.12 is called a *coexistence curve*. Points inside the coexistence curve represent two solution phases, whereas points below the coexistence curve represent one solution phase. Problem 24–43 has you determine the coexistence curve for a simple model system.

We can display the results illustrated by Figure 24.12 in a temperature-composition diagram (Figure 24.13a). The curve separating the one-phase region from the two-phase region is the coexistence curve. The temperature T_c, the temperature above which the two liquids are totally miscible, is the consulate temperature. The coexistence curve in
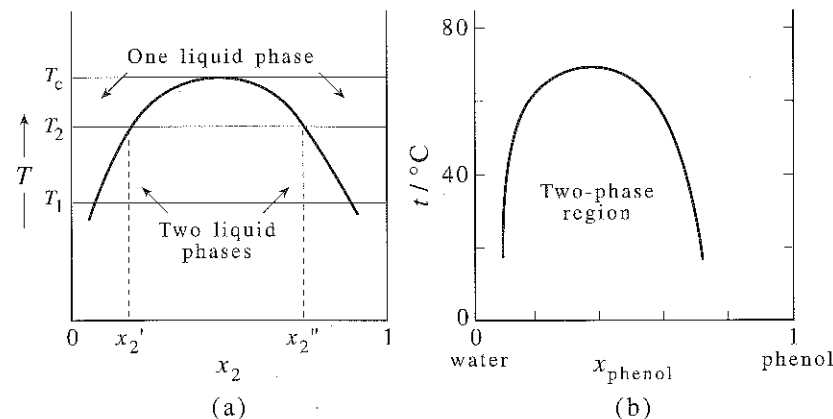
FIGURE 24.13
(a) A temperature-composition diagram for the system illustrated in Figure 24.12.
(b) A temperature-composition diagram for a water/phenol system.

Figure 24.13a looks "upside down" compared with the one in Figure 24.12, but note that the temperature decreases as you go up in Figure 24.12, whereas they decrease as you go down in Figure 24.13. Figure 24.13b shows a coexistence curve for a water/phenol system.

24–7. The Central Thermodynamic Quantity for Nonideal Solutions Is the Activity

The chemical potential of component j in a liquid solution is given by (Equation 24.15)

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln \frac{P_j}{P_j^*} \tag{24.31}$$

if we assume, as usual, that the vapor pressures involved are low enough that the vapors can be considered to behave ideally (otherwise, we replace the partial pressures by partial fugacities). An ideal solution is one in which $P_j = x_j P_j^*$ for all concentrations, so that Equation 24.31 becomes

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln x_j \quad \text{(ideal solution)} \tag{24.32}$$

Equation 24.31 is still valid for a nonideal solution, but the relation between P_j/P_j^* and composition is more complicated than simply $P_j = x_j P_j^*$. For example, we saw in Example 24–7 that partial vapor pressure data are often fit by an expression like

$$P_1 = x_1 P_1^* \exp(\alpha x_2^2 + \beta x_2^3 + \cdots) \tag{24.33}$$

The exponential factor here accounts for the nonideality of the system. The chemical potential of component 1 in this case is given by

$$\mu_1 = \mu_1^* + RT \ln x_1 + \alpha RT x_2^2 + \beta RT x_2^3 + \cdots \tag{24.34}$$

In Section 22–8, we introduced the idea of fugacity to preserve the form of the thermodynamic equations we had derived for ideal gases. We will follow a similar procedure for solutions, using an ideal solution as our standard.

To carry over the form of Equation 24.32 to nonideal solutions, we define a quantity called the *activity* by the equation

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln a_j \tag{24.35}$$

where μ_j^* is the chemical potential, or the molar Gibbs energy, of the pure liquid. Equation 24.35 is the generalization of Equation 24.32 to nonideal solutions. The first of Equations 24.27 says that $P_j = x_j P_j^*$, as $x_j \to 1$. If we substitute this result into Equation 24.31, we obtain

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln x_j \qquad (\text{as } x_j \to 1)$$

If we compare this equation with Equation 24.35, which is valid at all concentrations, we can define the activity of component j by

$$a_j = \frac{P_j}{P_j^*} \qquad \text{(ideal vapor)} \tag{24.36}$$

such that $a_j \to x_j$ as $x_j \to 1$. In other words, the activity of a pure liquid is unity (at a total pressure of one bar and at the temperature of interest). For an ideal solution, $P_j = x_j P_j^*$ for all concentrations, and so the activity of component i in an ideal solution is given by $a_j = x_j$. In a nonideal solution, a_j still is equal to P_j/P_j^*, but this ratio is no longer equal to x_j, although $a_j \to x_j$ as $x_j \to 1$.

According to Equations 24.33 and 24.36, the activity of component 1 can be represented empirically by

$$a_1 = x_1 e^{\alpha x_2^2 + \beta x_2^3 + \cdots}$$

Note that $a_1 \to 1$ as $x_1 \to 1$ ($x_2 \to 0$). The ratio a_j/x_j can be used as a measure of the deviation of the solution from ideality. This ratio is called the *activity coefficient* of component j and is denoted by γ_j:

$$\gamma_j = \frac{a_j}{x_j} \tag{24.37}$$

If $\gamma_j = 1$ for all concentrations, the solution is ideal. If $\gamma_j \neq 1$, the solution is not ideal. For example, the partial vapor pressures of chlorobenzene in equilibrium with a chlorobenzene/1-nitropropane solution at 75°C are listed below:

x_1	0.119	0.289	0.460	0.691	1.00
P_1/torr	19.0	41.9	62.4	86.4	119

According to these data, the vapor pressure of pure chlorobenzene at 75°C is 119 torr, so the activities and activity coefficients are as follows:

x_1	0.119	0.289	0.460	0.691	1.00
$a_1(= P_1/P_1^*)$	0.160	0.352	0.524	0.726	1.00
$\gamma_1(= a_1/x_1)$	1.34	1.22	1.14	1.05	1.00

Figure 24.14 shows the activity coefficient of chlorobenzene in 1-nitropropane at 75°C plotted against the mole fraction of chlorobenzene.

Activity is really just another way of expressing chemical potential because the two quantities are directly related to each other through $\mu_j = \mu_j^* + RT \ln a_j$. Therefore, just as the chemical potential of one component of a binary solution is related to the chemical potential of the other component by way of the Gibbs-Duhem equation, the activities are related to each other by

$$x_1 d \ln a_1 + x_2 d \ln a_2 = 0 \qquad (24.38)$$

For example, if $a_1 = x_1$ over the entire composition range, meaning that component 1 obeys Raoult's law over the entire composition range, then

$$d \ln a_2 = -\frac{x_1}{x_2}\frac{dx_1}{x_1} = -\frac{dx_1}{x_2} = \frac{dx_2}{x_2}$$

Integrate from $x_2 = 1$ to arbitrary x_2 and use the fact that $a_2 \rightarrow 1$ as $x_2 \rightarrow 1$ to get
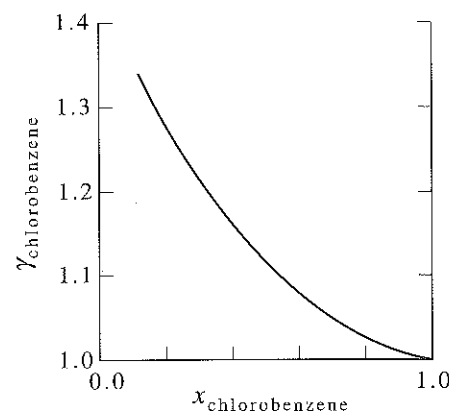
$$\ln a_2 = \ln x_2$$

FIGURE 24.14
The activity coefficient of chlorobenzene in 1-nitropropane at 75°C plotted against the mole fraction of chlorobenzene.

or $a_2 = x_2$. Thus, we see once again that if one component obeys Raoult's law over the entire composition range, the other component will also.

EXAMPLE 24–8
Show that if

$$a_1 = x_1 e^{\alpha x_2^2}$$

then

$$a_2 = x_2 e^{\alpha x_1^2}$$

SOLUTION: We first differentiate $\ln a_1$ with respect to x_1:

$$d \ln a_1 = \frac{dx_1}{x_1} - 2\alpha(1 - x_1)dx_1$$

and substitute into Equation 24.38 to obtain

$$d \ln a_2 = -\frac{x_1}{x_2}\left(\frac{dx_1}{x_1} - 2\alpha x_2 dx_1\right)$$
$$= -\frac{dx_1}{x_2} + 2\alpha x_1 dx_1$$

Now change the integration variable from x_1 to x_2:

$$d \ln a_2 = \frac{dx_2}{x_2} - 2\alpha(1 - x_2)dx_2$$

and integrate from $x_2 = 1$ (where $a_2 = 1$) to arbitrary x_2:

$$\ln a_2 = \ln x_2 + \alpha(1 - x_2)^2$$

or

$$a_2 = x_2 e^{\alpha x_1^2}$$

24–8. Activities Must Be Calculated with Respect to Standard States

In one sense, there are two types of binary solutions, those in which the two components are miscible in all proportions and those in which they are not. Only in the latter case are the designations "solvent" and "solute" unambiguous. As we will see in this section, the different nature of these two types of solutions leads us to define different standard states.

Although we have not said so explicitly, we have tacitly assumed both components of the solutions we have considered thus far exist as pure liquids at the temperatures of the solutions. We have defined the activity of each component by (Equation 24.36)

$$a_j = \frac{P_j}{P_j^*} \qquad \text{(ideal vapor)} \qquad (24.39)$$

so that $a_j \to x_j$ as $x_j \to 1$ and $a_j = 1$ when $P_j = P_j^*$. An activity defined by Equation 24.39 is said to be based upon a solvent, or Raoult's law standard state. Because of the relation (Equation 24.35) $\mu_j = \mu_j^* + RT \ln a_j$, the chemical potential of component j is also based upon a solvent, or Raoult's law, standard state. You need to realize that activities or chemical potentials are meaningless unless it is clear just what has been used as the standard state. If the two liquids are miscible in all proportions, there is no distinction between solvent and solute and a solvent standard state is normally used. If, on the other hand, one component is sparingly soluble in the other, then picking a standard state based upon Henry's law instead of Raoult's law is more convenient. To see how we define the activity in this case, we start with Equation 24.31

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln \frac{P_j}{P_j^*} \qquad (24.40)$$

Because component j is sparingly soluble, we use the second of Equations 24.27, which says that $P_j \to x_j k_{H,j}$ as $x_j \to 0$, where $k_{H,j}$ is the Henry's law constant of component j. If we substitute the limiting value $x_j k_{H,j}$ into Equation 24.40 for P_j, we obtain

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln \frac{x_j k_{H,j}}{P_j^*} \qquad (x_j \to 0)$$

$$\doteq \mu_j^* + RT \ln \frac{k_{H,j}}{P_j^*} + RT \ln x_j \qquad (x_j \to 0) \qquad (24.41)$$

We define the activity of component j by

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln \frac{k_{H,j}}{P_j^*} + RT \ln a_j \qquad (24.42)$$

so that $a_j \to x_j$ as $x_j \to 0$, as can be seen by comparing Equations 24.41 and 24.42. Equation 24.42 becomes equivalent to Equation 24.35 if we define a_j by

$$a_j = \frac{P_j}{k_{H,j}} \qquad \text{(ideal vapor)} \qquad (24.43)$$

and choose the standard state such that

$$\mu_j^* = \mu_j^* + RT \ln \frac{k_{H,j}}{P_j^*}$$

or such that $k_{H,j} = P_j^*$. The standard state in this case requires that $k_{H,j} = P_j^*$. This standard state may not exist in practice, so it is called a hypothetical standard state. Nevertheless, the definition of activity involving Henry's law for dilute components given by Equation 24.43 is natural and useful.

The numerical value of an activity or an activity coefficient depends upon the choice of standard state. Table 24.1 lists vapor pressure data for carbon disulfide/dimethoxymethane solutions at 35.2°C, and these data are plotted in Figure 24.15. Notice that both curves approach Raoult's law as their corresponding mole fractions approach unity. The dashed lines in the figure represent the linear regions as the corresponding mole fractions approach zero. The slopes of these lines give the Henry's law constant for each component. The values come out to be $k_{H,CS_2} = 1130$ torr and $k_{H,dimeth} = 1500$ torr. We can use these values and the values of the vapor pressures of the pure components to calculate activities and activity coefficients based upon each standard state. For example, Table 24.1 gives $P_{CS_2} = 407.0$ torr and $P_{dimeth} = 277.8$ torr at $x_{CS_2} = 0.6827$. Therefore,

$$a_{CS_2}^{(R)} = \frac{P_{CS_2}}{P_{CS_2}^*} = \frac{407.0 \text{ torr}}{514.5 \text{ torr}} = 0.7911$$

TABLE 24.1
Vapor pressure data of carbon disulfide/dimethoxymethane solutions at 35.2°C

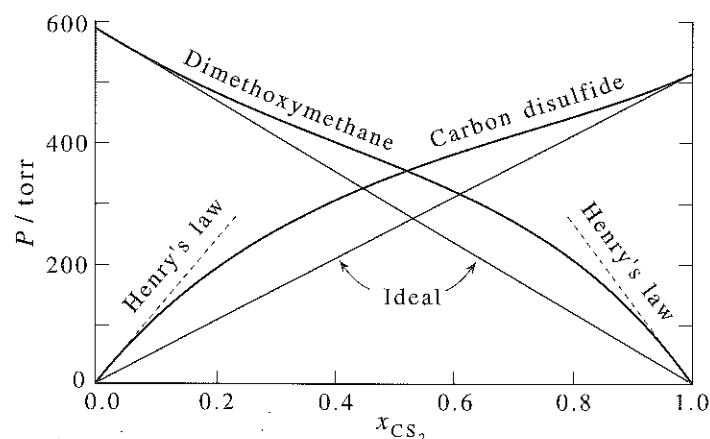| x_{CS_2}	P_{CS_2}/torr	P_{dimeth}/torr
0.0000	0.000	587.7
0.0489	54.5	558.3
0.1030	109.3	529.1
0.1640	159.5	500.4
0.2710	234.8	451.2
0.3470	277.6	412.7
0.4536	324.8	378.0
0.4946	340.2	360.8
0.5393	357.2	342.2
0.6071	381.9	313.3
0.6827	407.0	277.8
0.7377	424.3	250.1
0.7950	442.3	217.4
0.8445	458.1	184.9
0.9108	481.8	124.2
0.9554	501.0	65.1
1.0000	514.5	0.000

FIGURE 24.15
Vapor pressures of carbon disulfide and dimethoxymethane over their solutions at 35.2°C. The solid straight lines represent ideal behavior, and the dashed lines represent the Henry's law behavior for each component as the corresponding mole fractions approach zero.

and

$$a_{dimeth}^{(R)} = \frac{P_{dimeth}}{P_{dimeth}^*} = \frac{277.8 \text{ torr}}{587.7 \text{ torr}} = 0.4727$$

with

$$\gamma_{CS_2}^{(R)} = \frac{a_{CS_2}^{(R)}}{x_{CS_2}} = \frac{0.7911}{0.6827} = 1.159$$

and

$$\gamma_{dimeth}^{(R)} = \frac{a_{dimeth}^{(R)}}{x_{dimeth}} = \frac{0.4727}{0.3173} = 1.490$$

where the superscript (R) simply emphasizes that these values are based upon a Raoult's law, or solvent, standard state.

Similarly,

$$a_{CS_2}^{(H)} = \frac{P_{CS_2}}{k_{H,CS_2}} = \frac{407.0 \text{ torr}}{1130 \text{ torr}} = 0.360$$

$$a_{dimeth}^{(H)} = \frac{P_{dimeth}}{k_{H,dimeth}} = \frac{277.8 \text{ torr}}{1500 \text{ torr}} = 0.185$$

$$\gamma_{CS_2}^{(H)} = \frac{a_{CS_2}^{(H)}}{x_{CS_2}} = \frac{0.360}{0.6827} = 0.527$$

and

$$\gamma_{dimeth}^{(H)} = \frac{a_{dimeth}^{(H)}}{x_{dimeth}} = \frac{0.185}{0.3173} = 0.583$$

where the superscript (H) simply emphasizes that these values are based upon a Henry's law, or solute, standard state. Figure 24.16a shows the Raoult's law, or solvent-based, activities, and Figure 24.16b shows the Henry's law, or solute-based, activities plotted against the mole fraction of carbon disulfide. We will see in the next chapter that a solute, or Henry's law, standard state is particularly appropriate for a substance that does not exist as a liquid at one bar and at the temperature of the solution under study.

The activity coefficients based upon the Raoult's law standard state (which is the usual standard state for miscible liquids) are plotted in Figure 24.17. Notice that $\gamma_{CS_2} \to 1$ as $x_{CS_2} \to 1$ and that it goes to 2.2 as $x_{CS_2} \to 0$. Both of these limiting values may be deduced from the definition of γ_j (Equation 24.37)

$$\gamma_j = \frac{a_j}{x_j} = \frac{P_j}{x_j P_j^*}$$

Now $P_j \to P_j^*$ as $x_j \to 1$, and so $\gamma_j \to 1$ as $x_j \to 1$. At the other limit, however, $P_j \to x_j k_{H,j}$ as $x_j \to 0$, so we see that $\gamma_j \to k_{H,j}/P_j^*$ as $x_j \to 0$. The value of k_H for $CS_2(l)$ is 1130 torr, so $\gamma_{CS_2} \to k_{H,CS_2}/P_{CS_2}^* = (1130 \text{ torr}/514.5 \text{ torr}) = 2.2$, in agreement with Figure 24.17. The activity coefficient of dimethoxymethane approaches 2.5 as $x_{dimeth} \to 0$ ($x_{CS_2} \to 1$), in agreement with $\gamma_{dimeth} \to k_{H,dimeth}/P_{dimeth}^* = (1500 \text{ torr}/587.7 \text{ torr}) = 2.5$.
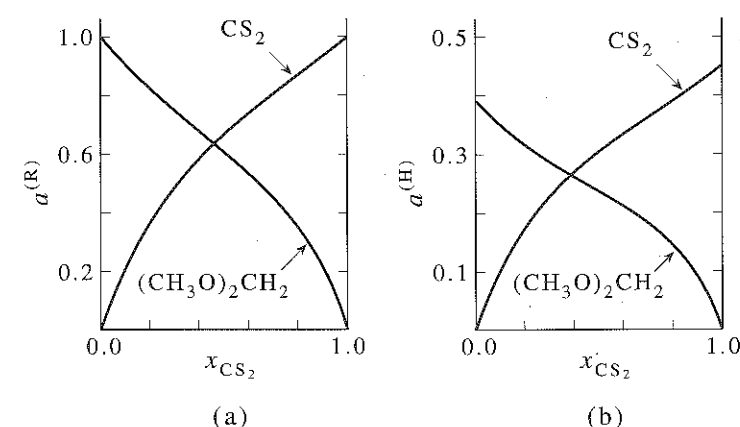

FIGURE 24.16
(a) The Raoult's law activities of carbon disulfide and dimethoxymethane in carbon disulfide/dimethoxymethane solutions at 35.2°C plotted against the mole fraction of carbon disulfide. (b) The Henry's law activities for the same system.
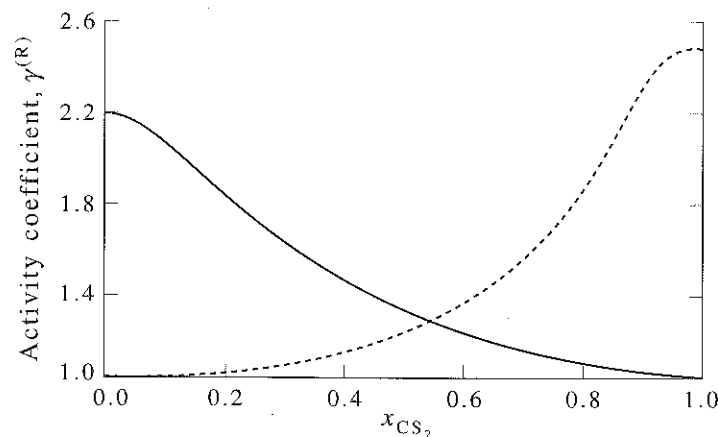
FIGURE 24.17
The Raoult's law activity coefficients of carbon disulfide (solid line) and dimethoxymethane (dashed line) plotted against x_{CS_2} for carbon disulfide/dimethoxymethane solutions at 35.2°C.

24–9. We Can Calculate the Gibbs Energy of Mixing of Binary Solutions in Terms of the Activity Coefficients

Recall from Equation 24.21 that

$$\Delta_{mix} G = n_1 \mu_1^{sln} + n_2 \mu_2^{sln} - n_1 \mu_1^* - n_2 \mu_2^*$$

But, according to Equations 24.35 and 24.37,

$$\mu_j^{sln} = \mu_j^* + RT \ln a_j = \mu_j^* + RT \ln x_j + RT \ln \gamma_j \qquad (24.44)$$

so

$$\Delta_{mix} G/RT = n_1 \ln x_1 + n_2 \ln x_2 + n_1 \ln \gamma_1 + n_2 \ln \gamma_2 \qquad (24.45)$$

If we divide Equation 24.45 by the total number of moles, $n_1 + n_2$, we obtain the *molar Gibbs energy of mixing*, $\Delta_{mix}\overline{G}$.

$$\Delta_{mix}\overline{G}/RT = x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \qquad (24.46)$$

The first two terms here represent the Gibbs energy of mixing of an ideal solution.

EXAMPLE 24–9
Use Equation 24.46 to derive a formula for $\Delta_{mix}\overline{G}$ for a binary solution in which the vapor pressure can be expressed by

$$P_1 = x_1 P_1^* e^{\alpha x_2^2} \qquad \text{and} \qquad P_2 = x_2 P_2^* e^{\alpha x_1^2}$$

SOLUTION: According to the above expressions for P_1 and P_2,

$$\gamma_1 = \frac{P_1}{x_1 P_1^*} = e^{\alpha x_2^2} \qquad \text{and} \qquad \gamma_2 = \frac{P_2}{x_2 P_2^*} = e^{\alpha x_1^2}$$

Substitute these expressions into Equation 24.46 to obtain

$$\Delta_{mix}\overline{G}/RT = x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2^2 + \alpha x_2 x_1^2$$

But

$$x_1 x_2^2 + x_2 x_1^2 = x_1 x_2 (x_1 + x_2) = x_1 x_2$$

so

$$\Delta_{mix}\overline{G}/RT = x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2 \qquad (24.47)$$

Molecular theories of binary solutions show that the parameter α, which is unitless, has the form of an energy divided by RT. Therefore, we will write α as w/RT, where w is a constant whose value we will not need. With this substitution, Equation 24.47 can be written as

$$\frac{\Delta_{mix}\overline{G}}{w} = \frac{RT}{w}(x_1 \ln x_1 + x_2 \ln x_2) + x_1 x_2 \qquad (24.48)$$

Figure 24.18 shows plots of $\Delta_{mix}\overline{G}/w$ for several values of RT/w. Note that the slopes of all the curves equal zero at the midpoint, $x_1 = x_2 = 1/2$. The curve for $RT/w = 0.50$ is special in the sense that curves for values of RT/w greater than 0.50
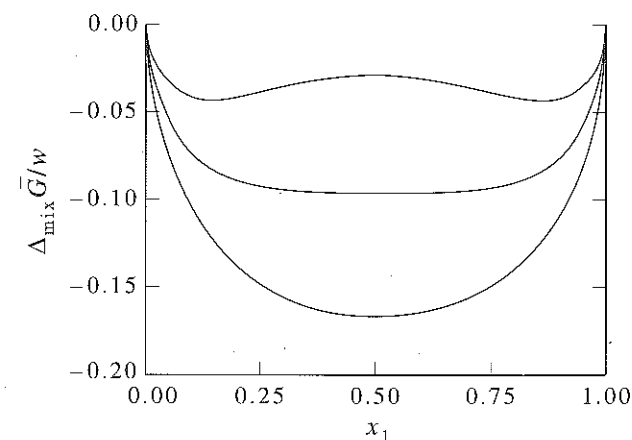

FIGURE 24.18
Plots of $\Delta_{mix}\overline{G}/w$ for $RT/w = 0.60$ (bottom curve), $RT/w = 0.50$ (middle curve), and $RT/w = 0.40$ (top curve).

are concave upward for all values of x_1, whereas curves for values of RT/w less than 0.50 are concave downward at $x_1 = 1/2$. In mathematical terms, $\partial^2(\Delta_{mix}\overline{G}/w)/\partial x_1^2$ is positive (a minimum) at $x_1 = x_2 = 1/2$ for the curves that lie below the curve with $RT/w = 0.50$, whereas $\partial^2(\Delta_{mix}\overline{G}/w)/\partial x_1^2$ is negative (a maximum) at $x_1 = x_2 = 1/2$ for curves that lie above it. The region where $\partial^2(\Delta_{mix}\overline{G}/w)/\partial x_1^2$ is negative is similar to the loops of the van der Waals equation or the Redlich–Kwong equation when $T < T_c$ (Figure 16.8), and in this case corresponds to a region in which the two liquids are not miscible. The critical value $RT/w = 0.50$ corresponds to a solution critical temperature, T_c, where the two liquids are miscible in all proportions at temperatures above $T_c = 0.50w/R$ and immiscible at temperatures below $T_c = 0.50w/R$.

Let's consider the curve with $RT/w = 0.40$ in Figure 24.18. The two minima represent two immiscible solutions in equilibrium with each other. The compositions of these two solutions are given by the values of x_1 at each minimum. Using Equation 24.47, we have

$$\frac{\partial(\Delta_{mix}\overline{G}/w)}{\partial x_1} = \frac{RT}{w}[\ln x_1 - \ln(1 - x_1)] + (1 - 2x_1) = 0 \qquad (24.49)$$

as the condition for the extrema of $\Delta_{mix}\overline{G}/w$. First note that $x_1 = 1/2$ solves Equation 24.49 for any value of RT/w, which accounts for the fact that all the curves in Figure 24.18 have either a maximum or a minimum at $x_1 = 1/2$. By plotting $(RT/w)[\ln x_1 - \ln(1 - x_1)] + (1 - 2x_1)$ against x_1 for various values of RT/w, you can see that only $x_1 = 1/2$ satisfies Equation 24.49 for $RT/w \geq 0.50$, whereas two other roots occur for $RT/w < 0.50$. The two roots give the composition of the two miscible solutions in equilibrium with each other. For the case in which $RT/w = 0.40$, the two values of x_1 are 0.145 and 0.855. Figure 24.19 shows the mole fraction of component 1 in each of the two immiscible solutions as a function of temperature (RT/w). Note that Figure 24.19 is similar to Figure 24.13.

EXAMPLE 24–10

Use Equation 24.49 to calculate the composition of the two immiscible solutions in equilibrium with each other at a temperature given by $RT/w = 0.40$.

SOLUTION: We use the Newton–Raphson method that we introduced in Math-Chapter G. The function $f(x)$ of Equation G.1 is

$$f(x) = \frac{RT}{w}[\ln x - \ln(1 - x)] + 1 - 2x$$

Equation G.1 becomes

$$x_{n+1} = x_n - \frac{\dfrac{RT}{w}[\ln x_n - \ln(1 - x_n)] + 1 - 2x_n}{\dfrac{RT}{w}\left[\dfrac{1}{x_n(1 - x_n)}\right] - 2}$$

with $RT/w = 0.40$. For one of the solutions, we start with $x_0 = 0.100$ and get

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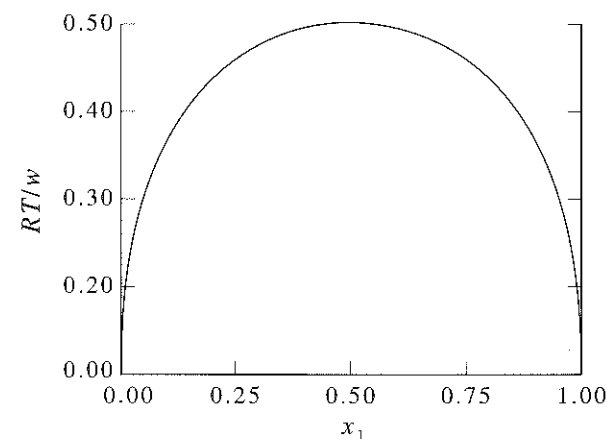
FIGURE 24.19
A temperature-composition diagram for a binary system for which $\Delta_{mix}\overline{G}/w = (RT/w)(x_1 \ln x_1 + x_2 \ln x_2) + x_1 x_2$ (Equation 24.48). The curve gives the compositions of the two immiscible solutions as a function of temperature. There is only one homogeneous phase in the region above the curve, and there are two immiscible solutions in equilibrium with each other in the region below the curve.

n	x_n	$f(x_n)$	$f'(x_n)$
0	0.100	−0.07889	2.4444
1	0.132	−0.01695	1.4851
2	0.144	−0.001370	1.2509
3	0.145	−0.000017	1.2305
4	0.145		

For the other solution, we start with $x_0 = 0.900$ and get

n	x_n	$f(x_n)$	$f'(x_n)$
0	0.900	0.07889	2.4444
1	0.868	0.01695	1.4851
2	0.856	0.00137	1.2509
3	0.855	0.000017	1.2305
4	0.855		

in agreement with Figure 24.19.

Many solutions can be described by the Equation 24.47, and such solutions are called *regular solutions*. Problems 24–37 through 24–45 involve regular solutions.

To focus on the effect of nonideality, we define an *excess Gibbs energy of mixing*, G^E:

$$G^E = \Delta_{mix}G - \Delta_{mix}G^{id} \tag{24.50}$$

We see from Equation 24.45 that

$$G^E/RT = n_1 \ln \gamma_1 + n_2 \ln \gamma_2$$

If we divide by the total number of moles $n_1 + n_2$, we obtain the *molar excess Gibbs energy of mixing*, $\overline{G}^E$:

$$\overline{G}^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \tag{24.51}$$

For $\Delta_{mix}\overline{G}$ given by Equation 24.47,

$$\overline{G}^E/RT = \alpha x_1 x_2 \tag{24.52}$$

According to Equation 24.52, a plot of $\overline{G}^E$ against x_1 is a parabola that is symmetric about the vertical line at $x_1 = 1/2$.

We can use γ_{CS_2} and γ_{dimeth} that we calculated for Figure 24.17 to calculate the value of $\overline{G}^E$ for a carbon disulfide/dimethoxymethane solution at 35.2°C, which is shown in Figure 24.20. Note that the plot of $\overline{G}^E$ versus x_{CS_2} is not symmetric about $x_{CS_2} = 1/2$. This asymmetry implies that $\beta \neq 0$ in the empirical vapor pressure formula (Equation 24.33).

We will continue our discussion of solutions in the next chapter, where we focus on solutions in which the two components are not soluble in all proportions. In particular,
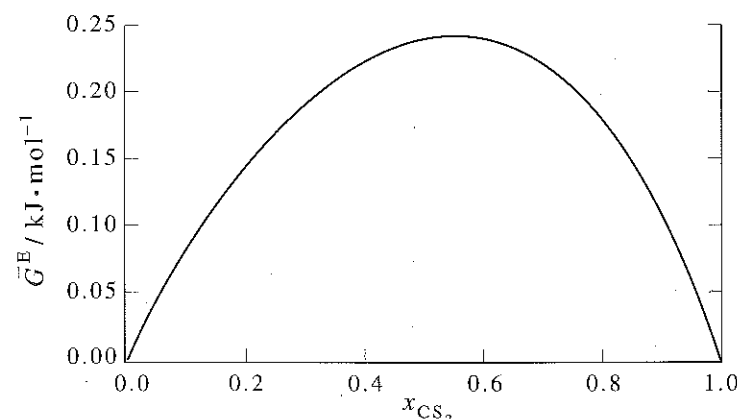

FIGURE 24.20
The molar excess Gibbs energy of mixing of carbon disulfide/dimethoxymethane solutions at 35.2°C plotted against the mole fraction of carbon disulfide.

we will discuss solutions of solids in liquids, where the terms *solute* and *solvent* are meaningful.

Problems

24-1. In the text, we went from Equation 24.5 to 24.6 using a physical argument involving varying the size of the system while keeping T and P fixed. We could also have used a mathematical process called *Euler's theorem*. Before we can learn about Euler's theorem, we must first define a *homogeneous function*. A function $f(z_1, z_2, \ldots, z_N)$ is said to be homogeneous if

$$f(\lambda z_1, \lambda z_2, \ldots, \lambda z_N) = \lambda f(z_1, z_2, \ldots, z_N)$$

Argue that extensive thermodynamic quantities are homogeneous functions of their extensive variables.

24-2. Euler's theorem says that if $f(z_1, z_2, \ldots, z_N)$ is homogeneous, then

$$f(z_1, z_2, \ldots, z_N) = z_1 \frac{\partial f}{\partial z_1} + z_2 \frac{\partial f}{\partial z_2} + \cdots + z_N \frac{\partial f}{\partial z_N}$$

Prove Euler's theorem by differentiating the equation in Problem 24-1 with respect to λ and then setting $\lambda = 1$.

Apply Euler's theorem to $G = G(n_1, n_2, T, P)$ to derive Equation 24.6. (*Hint:* Because T and P are intensive variables, they are simply irrelevant variables in this case.)

24-3. Use Euler's theorem (Problem 24-2) to prove that

$$Y(n_1, n_2, \ldots, T, P) = \sum n_j \overline{Y}_j$$

for any extensive quantity Y.

24-4. Apply Euler's theorem to $U = U(S, V, n)$. Do you recognize the resulting equation?

24-5. Apply Euler's theorem to $A = A(T, V, n)$. Do you recognize the resulting equation?

24-6. Apply Euler's theorem to $V = V(T, P, n_1, n_2)$ to derive Equation 24.7.

24-7. The properties of many solutions are given as a function of the mass percent of the components. If we let the mass percent of component 2 be A_2, derive a relation between A_2 and the mole fractions, x_1 and x_2.

24-8. The *CRC Handbook of Chemistry and Physics* gives the densities of many aqueous solutions as a function of the mass percentage of solute. If we denote the density by ρ and the mass percentage of component 2 by A_2, the *Handbook* gives $\rho = \rho(A_2)$ (in $g \cdot mL^{-1}$). Show that the quantity $V = (n_1 M_1 + n_2 M_2)/\rho(A_2)$ is the volume of the solution containing n_1 moles of component 1 and n_2 moles of component 2, where M_j is the molar mass of component j. Now show that

$$\overline{V}_1 = \frac{M_1}{\rho(A_2)} \left[1 + \frac{A_2}{\rho(A_2)} \frac{d\rho(A_2)}{dA_2} \right]$$

and

$$\overline{V}_2 = \frac{M_2}{\rho(A_2)}\left[1 + \frac{(A_2 - 100)}{\rho(A_2)}\frac{d\rho(A_2)}{dA_2}\right]$$

Show that

$$V = n_1\overline{V}_1 + n_2\overline{V}_2$$

in agreement with Equation 24.7.

24-9. The density (in $g \cdot ml^{-1}$) of a 1-propanol/water solution at $20°C$ as a function of A_2, the mass percentage of 1-propanol, can be expressed as

$$\rho(A_2) = \sum_{j=0}^{7}\alpha_j A_2^j$$

where

$$\alpha_0 = 0.99823 \qquad\qquad \alpha_4 = 1.5312 \times 10^{-7}$$

$$\alpha_1 = -0.0020577 \qquad\quad \alpha_5 = -2.0365 \times 10^{-9}$$

$$\alpha_2 = 1.0021 \times 10^{-4} \qquad \alpha_6 = 1.3741 \times 10^{-11}$$

$$\alpha_3 = -5.9518 \times 10^{-6} \qquad \alpha_7 = -3.7278 \times 10^{-14}$$

Use this expression to plot $\overline{V}_{H_2O}$ and $\overline{V}_{1\text{-propanol}}$ versus A_2, and compare your values with those in Figure 24.1.

24-10. Given the density of a binary solution as a function of the mole fraction of component 2 $[\rho = \rho(x_2)]$, show that the volume of the solution containing n_1 moles of component 1 and n_2 moles of component 2 is given by $V = (n_1M_1 + n_2M_2)/\rho(x_2)$, where M_j is the molar mass of component j. Now show that

$$\overline{V}_1 = \frac{M_1}{\rho(x_2)}\left[1 + \left(\frac{x_2(M_2 - M_1) + M_1}{M_1}\right)\frac{x_2}{\rho(x_2)}\frac{d\rho(x_2)}{dx_2}\right]$$

and

$$\overline{V}_2 = \frac{M_2}{\rho(x_2)}\left[1 - \left(\frac{x_2(M_2 - M_1) + M_1}{M_2}\right)\frac{1 - x_2}{\rho(x_2)}\frac{d\rho(x_2)}{dx_2}\right]$$

Show that

$$V = n_1\overline{V}_1 + n_2\overline{V}_2$$

in agreement with Equation 24.7.

24-11. The density (in $g \cdot mL^{-1}$) of a 1-propanol/water solution at $20°C$ as a function of x_2, the mole fraction of 1-propanol, can be expressed as

$$\rho(x_2) = \sum_{j=0}^{4}\alpha_j x_2^j$$

where

$$\alpha_0 = 0.99823 \qquad\qquad \alpha_3 = -0.17163$$

$$\alpha_1 = -0.48503 \qquad\qquad \alpha_4 = -0.01387$$

$$\alpha_2 = 0.47518$$

Use this expression to calculate the values of $\overline{V}_{H_2O}$ and $\overline{V}_{1\text{-propanol}}$ as a function of x_2 according to the equation in Problem 24-10.

24-12. Use the data in the *CRC Handbook of Chemistry and Physics* to curve fit the density of a water/glycerol solution to a fifth-order polynomial in the mole fraction of glycerol, and then determine the partial molar volumes of water and glycerol as a function of mole fraction. Plot your result.

24-13. Just before Example 24–2, we showed that if one component of a binary solution obeys Raoult's law over the entire composition range, the other component does also. Now show that if $\mu_2 = \mu_2' + RT\ln x_2$ for $x_{2,\min} \leq x_2 \leq 1$, then $\mu_1 = \mu_1' + RT\ln x_1$ for $0 \leq x_1 < 1 - x_{2,\min}$. Notice that for the range over which μ_2 obeys the simple form given, μ_1 obeys a similarly simple form. If we let $x_{2,\min} = 0$, we obtain $\mu_1 = \mu_1^* + RT\ln x_1$ ($0 \leq x_1 \leq 1$).

24-14. Continue the calculations in Example 24–3 to obtain y_2 as a function of x_2 by varying x_2 from 0 to 1. Plot your result.

24-15. Use your results from Problem 24–14 to construct the pressure-composition diagram in Figure 24.4.

24-16. Calculate the relative amounts of liquid and vapor phases at an overall composition of 0.50 for one of the pair of values, $x_2 = 0.38$ and $y_2 = 0.57$, that you obtained in Problem 24–14.

24-17. In this problem, we will derive analytic expressions for the pressure-composition curves in Figure 24.4. The liquid (upper) curve is just

$$P_{\text{total}} = x_1P_1^* + x_2P_2^* = (1 - x_2)P_1^* + x_2P_2^* = P_1^* + x_2(P_2^* - P_1^*) \tag{1}$$

which is a straight line, as seen in Figure 24.4. Solve the equation

$$y_2 = \frac{x_2P_2^*}{P_{\text{total}}} = \frac{x_2P_2^*}{P_1^* + x_2(P_2^* - P_1^*)}$$

for x_2 in terms of y_2 and substitute into Equation (1) to obtain

$$P_{\text{total}} = \frac{P_1^*P_2^*}{P_2^* - y_2(P_2^* - P_1^*)}$$

Plot this result versus y_2 and show that it gives the vapor (lower) curve in Figure 24.4.

24-18. Prove that $y_2 > x_2$ if $P_2^* > P_1^*$ and that $y_2 < x_2$ if $P_2^* < P_1^*$. Interpret this result physically.

24-19. Tetrachloromethane and trichloroethylene form essentially ideal solutions at 40°C at all concentrations. Given that the vapor pressure of tetrachloromethane and trichloroethylene at 40°C are 214 torr and 138 torr, respectively, plot the pressure-composition diagram for this system (see Problem 24–17).

24-20. The vapor pressures of tetrachloromethane (1) and trichloroethylene (2) between 76.8°C and 87.2°C can be expressed empirically by the formulas

$$\ln(P_1^*/\text{torr}) = 15.8401 - \frac{2790.78}{t + 226.4}$$

and

$$\ln(P_2^*/\text{torr}) = 15.0124 - \frac{2345.4}{t + 192.7}$$

where t is the Celsius temperature. Assuming that tetrachloromethane and trichloroethylene form an ideal solution at all compositions, calculate the values of x_1 and y_1 at 82.0°C (at an ambient pressure of 760 torr).

24-21. Use the data in Problem 24–20 to construct the entire temperature-composition diagram of a tetrachloromethane/trichlororethylene solution.

24-22. The vapor pressures of benzene and toluene between 80°C and 110°C as a function of the Kelvin temperature are given by the empirical formulas

$$\ln(P_{\text{benz}}^*/\text{torr}) = -\frac{3856.6 \text{ K}}{T} + 17.551$$

and

$$\ln(P_{\text{tol}}^*/\text{torr}) = -\frac{4514.6 \text{ K}}{T} + 18.397$$

Assuming that benzene and toluene form an ideal solution, use these formulas to construct a temperature-composition diagram of this system at an ambient pressure of 760 torr.

24-23. Construct the temperature-composition diagram for 1-propanol and 2-propanol in Figure 24.5 by varying t from 82.3°C (the boiling point of 2-propanol) to 97.2°C (the boiling point of 1-propanol), calculating the values of (1) P_1^* and P_2^* at each temperature (see Example 24–5), (2) x_1 according to $x_1 = (P_2^* - 760)/(P_2^* - P_1^*)$, and (3) y_1 according to $y_1 = x_1 P_1^*/760$. Now plot t versus x_1 and y_1 on the same graph to obtain the temperature-composition diagram.

24-24. Prove that $\overline{V}_j = \overline{V}_j^*$ for an ideal solution, where $\overline{V}_j^*$ is the molar volume of pure component j.

24-25. The volume of mixing of miscible liquids is defined as the volume of the solution minus the volume of the individual pure components. Show that

$$\Delta_{\text{mix}}\overline{V} = \sum_i x_i(\overline{V}_i - \overline{V}_i^*)$$

at constant P and T, where $\overline{V}_i^*$ is the molar volume of pure component i. Show that $\Delta_{\text{mix}}\overline{V} = 0$ for an ideal solution (see Problem 24–24).

24-26. Suppose the vapor pressures of the two components of a binary solution are given by

$$P_1 = x_1 P_1^* e^{x_2^2/2}$$

and

$$P_2 = x_2 P_2^* e^{x_1^2/2}$$

Given that $P_1^* = 75.0$ torr and $P_2^* = 160$ torr, calculate the total vapor pressure and the composition of the vapor phase at $x_1 = 0.40$.

24-27. Plot y_1 versus x_1 for the system described in the previous problem. Why does the curve lie below the straight line connecting the origin with the point $x_1 = 1$, $y_1 = 1$? Describe a system for which the curve would lie above the diagonal line.

24-28. Use the expressions for P_1 and P_2 given in Problem 24–26 to construct a pressure-composition diagram.

24-29. The vapor pressure (in torr) of the two components in a binary solution are given by

$$P_1 = 120x_1 e^{0.20x_2^2 + 0.10x_2^3}$$

and

$$P_2 = 140x_2 e^{0.35x_1^2 - 0.10x_1^3}$$

Determine the values of P_1^*, P_2^*, $k_{\text{H,1}}$, and $k_{\text{H,2}}$.

24-30. Suppose the vapor pressure of the two components of a binary solution are given by

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$$

and

$$P_2 = x_2 P_2^* e^{(\alpha + 3\beta/2)x_1^2 - \beta x_1^3}$$

Show that $k_{\text{H,1}} = P_1^* e^{\alpha + \beta}$ and $k_{\text{H,2}} = P_2^* e^{\alpha + \beta/2}$.

24-31. The empirical expression for the vapor pressure that we used in Examples 24–6 and 24–7, for example,

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3 + \cdots}$$

is sometimes called the *Margules equation*. Use Equation 24.29 to prove that there can be no linear term in the exponential factor in P_1, for otherwise P_2 will not satisfy Henry's law as $x_2 \to 0$.

24-32. In the text, we showed that the Henry's law behavior of component 2 as $x_2 \to 0$ is a direct consequence of the Raoult's law behavior of component 1 as $x_1 \to 1$. In this problem, we will prove the converse: the Raoult's law behavior of component 1 as $x_1 \to 1$ is a direct consequence of the Henry's law behavior of component 2 as $x_2 \to 0$. Show that the chemical potential of component 2 as $x_2 \to 0$ is

$$\mu_2(T, P) = \mu_2^\circ(T) + RT \ln k_{\text{H,2}} + RT \ln x_2 \qquad x_2 \to 0$$

Differentiate μ_2 with respect to x_2 and substitute the result into the Gibbs-Duhem equation to obtain

$$d\mu_1 = RT\frac{dx_1}{x_1} \qquad x_2 \longrightarrow 0$$

Integrate this expression from $x_1 = 1$ to $x_1 \approx 1$ and use the fact that $\mu_1(x_1 = 1) = \mu_1^*$ to obtain

$$\mu_1(T, P) = \mu_1^*(T) + RT\ln x_1 \qquad x_1 \to 1$$

which is the Raoult's law expression for chemical potential.

24-33. In Example 24-7, we saw that if

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$$

then

$$P_2 = x_2 P_2^* e^{(\alpha + 3\beta/2)x_1^2 - \beta x_1^3}$$

Show that this result follows directly from Equation 24.29.

24-34. Suppose we express the vapor pressures of the components of a binary solution by

$$P_1 = x_1 P_1^* e^{\alpha x_2^2}$$

and

$$P_2 = x_2 P_2^* e^{\beta x_1^2}$$

Use the Gibbs–Duhem equation or Equation 24.29 to prove that α must equal β.

24-35. Use Equation 24.29 to show that if one component of a binary solution obeys Raoult's law for all concentrations, then the other component also obeys Raoult's law for all concentrations.

24-36. Use Equation 24.29 to show that if one component of a binary solution has positive deviations from Raoult's law, then the other component must also.

The following nine problems develop the idea of a regular solution.

24-37. If the vapor pressures of the two components in a binary solution are given by

$$P_1 = x_1 P_1^* e^{wx_2^2/RT} \quad \text{and} \quad P_2 = x_2 P_2^* e^{wx_1^2/RT}$$

show that

$$\Delta_{\text{mix}}\overline{G}/w = \Delta_{\text{mix}}G/(n_1 + n_2)w = \frac{RT}{w}[x_1\ln x_1 + x_2\ln x_2] + x_1 x_2$$

$$\Delta_{\text{mix}}\overline{S}/R = \Delta_{\text{mix}}S/(n_1 + n_2)R = -(x_1\ln x_1 + x_2\ln x_2)$$

and

$$\Delta_{\text{mix}}\overline{H}/w = \Delta_{\text{mix}}H/(n_1 + n_2)w = x_1 x_2$$

A solution that satisfies these equations is called a *regular solution*. A statistical thermodynamic model of binary solutions shows that w is given by

$$w = N_A(\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12})$$

where ε_{ij} is the interaction energy between molecules of components i and j. Note that $w = 0$ if $\varepsilon_{12} = (\varepsilon_{11} + \varepsilon_{22})/2$, which means that energetically, molecules of components 1 and 2 "like" the opposite molecules as well as their own.

24-38. Prove that $\Delta_{\text{mix}}\overline{G}$, $\Delta_{\text{mix}}\overline{S}$, and $\Delta_{\text{mix}}\overline{H}$ in the previous problem are symmetric about the point $x_1 = x_2 = 1/2$.

24-39. Plot $P_1/P_1^* = x_1 e^{wx_2^2/RT}$ versus x_1 for $RT/w = 0.60$, 0.50, 0.45, 0.40, and 0.35. Note that some of the curves have regions where the slope is negative. The following problem has you show that this behavior occurs when $RT/w < 0.50$. These regions are similar to the loops of the van der Waals equation or the Redlich–Kwong equation when $T < T_c$ (Figure 16.8), and in this case correspond to regions in which the two liquids are not miscible. The critical value $RT/w = 0.50$ corresponds to a solution critical temperature.

24-40. Differentiate $P_1 = x_1 P_1^* e^{w(1-x_1)^2/RT}$ with respect to x_1 to prove that P_1 has a maximum or a minimum at the points $x_1 = \frac{1}{2} \pm \frac{1}{2}(1 - \frac{2RT}{w})^{1/2}$. Show that $RT/w < 0.50$ for either a maximum or a minimum to occur. Do the positions of these extrema when $RT/w = 0.35$ correspond to the plot you obtained in the previous problem?

24-41. Plot $\Delta_{\text{mix}}\overline{G}/w$ in Problem 24-37 versus x_1 for $RT/w = 0.60$, 0.50, 0.45, 0.40, and 0.35. Note that some of the curves have regions where $\partial^2\Delta_{\text{mix}}\overline{G}/\partial x_1^2 < 0$. These regions correspond to regions in which the two liquids are not miscible. Show that $RT/w = 0.50$ is a critical value, in the sense that unstable regions occur only when $RT/w < 0.50$. (See the previous problem.)

24-42. Plot both $P_1/P_1^* = x_1 e^{\alpha x_2^2}$ and $P_2/P_2^* = x_2 e^{\alpha x_1^2}$ for $RT/w = 1/\alpha = 0.60$, 0.50, 0.45, 0.40, and 0.35. Prove that the loops occur for values of $RT/w < 0.50$.

24-43. Plot both $P_1/P_1^* = x_1 e^{\alpha x_2^2}$ and $P_2/P_2^* = x_2 e^{\alpha x_1^2}$ for $RT/w = 1/\alpha = 0.40$. The loops indicate regions in which the two liquids are not miscible, as explained in Problem 24-39. Draw a horizontal line connecting the left-side and the right-side intersections of the two curves. This line, which connects states in which the vapor pressure (or chemical potential) of each component is the same in the two solutions of different composition, corresponds to one of the horizontal lines in Figure 24.12. Now set $P_1/P_1^* = x_1 e^{\alpha x_2^2}$ equal to $P_2/P_2^* = x_2 e^{\alpha x_1^2}$ and solve for α in terms of x_1. Plot $RT/w = 1/\alpha$ against x_1 and obtain a coexistence curve like the one in Figure 24.19.

24-44. The molar enthalpies of mixing of solutions of tetrachloromethane (1) and cyclohexane (2) at 25°C are listed below.

x_1	$\Delta_{mix}\overline{H}/\text{J}\cdot\text{mol}^{-1}$
0.0657	37.8
0.2335	107.9
0.3495	134.9
0.4745	146.7
0.5955	141.6
0.7213	118.6
0.8529	73.6

Plot $\Delta_{mix}\overline{H}/x_2$ against x_1 according to Problem 24–37. Do tetrachloromethane and cyclohexane form a regular solution?

24-45. The molar enthalpies of mixing of solutions of tetrahydrofuran and trichloromethane at 25°C are listed below.

x_{THF}	$\Delta_{mix}\overline{H}/\text{J}\cdot\text{mol}^{-1}$
0.0568	-0.469
0.1802	-1.374
0.3301	-2.118
0.4508	-2.398
0.5702	-2.383
0.7432	-1.888
0.8231	-1.465
0.9162	-0.802

Do tetrahydrofuran and trichloromethane form a regular solution?

24-46. Derive the equation

$$x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 = 0$$

by starting with Equation 24.11. Use this equation to obtain the same result as in Example 24–8.

24-47. The vapor pressure data for carbon disulfide in Table 24.1 can be curve fit by

$$P_1 = x_1(514.5\ \text{torr})e^{1.4967x_2^2-0.68175x_2^3}$$

Using the results of Example 24–7, show that the vapor pressure of dimethoxymethane is given by

$$P_2 = x_2(587.7\ \text{torr})e^{0.4741x_1^2+0.68175x_1^3}$$

Now plot P_2 versus x_2 and compare the result with the data in Table 24.1. Plot $\overline{G}^E$ against x_1. Is the plot symmetric about a vertical line at $x_1 = 1/2$? Do carbon disulfide and dimethoxymethane form a regular solution at 35.2°C?

24-48. A mixture of trichloromethane and acetone with $x_{acet} = 0.713$ has a total vapor pressure of 220.5 torr at 28.2°C, and the mole fraction of acetone in the vapor is $y_{acet} = 0.818$. Given that the vapor pressure of pure trichloromethane at 28.2°C is 221.8 torr, calculate the activity and the activity coefficient (based upon a Raoult's law standard state) of trichloromethane in the mixture. Assume the vapor behaves ideally.

24-49. Consider a binary solution for which the vapor pressure (in torr) of one of the components (say component 1) is given empirically by

$$P_1 = 78.8x_1 e^{0.65x_2^2+0.18x_2^3}$$

Calculate the activity and the activity coefficient of component 1 when $x_1 = 0.25$ based on a solvent and a solute standard state.

24-50. Some vapor pressure data for ethanol/water solutions at 25°C are listed below.

$x_{ethanol}$	$P_{ethanol}/\text{torr}$	P_{water}/torr
0.00	0.00	23.78
0.02	4.28	23.31
0.05	9.96	22.67
0.08	14.84	22.07
0.10	17.65	21.70
0.20	27.02	20.25
0.30	31.23	19.34
0.40	33.93	18.50
0.50	36.86	17.29
0.60	40.23	15.53
0.70	43.94	13.16
0.80	48.24	9.89
0.90	53.45	5.38
0.93	55.14	3.83
0.96	56.87	2.23
0.98	58.02	1.13
1.00	59.20	0.00

Plot these data to determine the Henry's law constant for ethanol in water and for water in ethanol at 25°C.

24-51. Using the data in Problem 24–50, plot the activity coefficients (based upon Raoult's law) of both ethanol and water against the mole fraction of ethanol.

24-52. Using the data in Problem 24–50, plot $\overline{G}^E/RT$ against x_{H_2O}. Is a water/ethanol solution at 25°C a regular solution?

24-53. Some vapor pressure data for a 2-propanol/benzene solution at 25°C are

$x_{2\text{-propanol}}$	$P_{2\text{-propanol}}/\text{torr}$	$P_{\text{total}}/\text{torr}$
0.000	0.0	94.4
0.059	12.9	104.5
0.146	22.4	109.0
0.362	27.6	108.4
0.521	30.4	105.8
0.700	36.4	99.8
0.836	39.5	84.0
0.924	42.2	66.4
1.000	44.0	44.0

Plot the activities and the activity coefficients of 2-propanol and benzene relative to a Raoult's law standard state versus the mole fraction of 2-propanol.

24-54. Using the data in Problem 24–53, plot $\overline{G}^{E}/RT$ versus $x_{2\text{-propanol}}$.

24-55. *Excess thermodynamic quantities* are defined relative to the values the quantities would have if the pure components formed an ideal solution at the same given temperature and pressure. For example, we saw that (Equation 24.47)

$$\frac{G^{E}}{(n_1 + n_2)RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

Show that

$$\frac{S^{E}}{(n_1 + n_2)R} = -(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) - T\left(x_1 \frac{\partial \ln \gamma_1}{\partial T} + x_2 \frac{\partial \ln \gamma_2}{\partial T}\right)$$

24-56. Show that

$$\frac{G^{E}}{(n_1 + n_2)} = wx_1 x_2$$

$$\frac{S^{E}}{(n_1 + n_2)R} = 0$$

and

$$\frac{H^{E}}{(n_1 + n_2)} = wx_1 x_2$$

for a regular solution (see Problem 24–37).

24-57. Example 24–7 expresses the vapor pressures of the two components of a binary solution as

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$$

and

$$P_2 = x_2 P_2^* e^{(\alpha + 3\beta/2)x_1^2 - \beta x_1^3}$$

Show that these expressions are equivalent to

$$\gamma_1 = e^{\alpha x_2^2 + \beta x_2^3} \quad \text{and} \quad \gamma_2 = e^{(\alpha + 3\beta/2)x_1^2 - \beta x_1^3}$$

Using these expressions for the activity coefficients, derive an expression for $\overline{G}^{E}$ in terms of α and β. Show that your expression reduces to that for $\overline{G}^{E}$ for a regular solution.

24-58. Prove that the maxima or minima of $\Delta_{\text{mix}}\overline{G}$ defined in Problem 24–37 occur at $x_1 = x_2 = 1/2$ for any value of RT/w. Now prove that

$$\frac{\partial^2 \Delta_{\text{mix}}\overline{G}}{\partial x_1^2} \begin{cases} > 0 & \text{for } RT/w > 0.50 \\ = 0 & \text{for } RT/w = 0.50 \\ < 0 & \text{for } RT/w < 0.50 \end{cases}$$

at $x_1 = x_2 = 1/2$. Is this result consistent with the graphs you obtained in Problem 24–41?

24-59. Use the data in Table 24.1 to plot Figures 24.15 through 24.17.