

# 8

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## Ideal Solutions

*—a seven-percent solution—*

Sherlock Holmes

Solution properties can be described by changes in thermodynamic quantities on mixing or by partial molar thermodynamic quantities. The Gibbs–Duhem equation relates changes in the latter quantities for different components of a solution. Different methods for determining partial molar quantities are discussed. The ideal solution applies to solutions of very similar components and gives Raoult’s law for the vapor pressure of all components. The ideally dilute solution applies to all solutions in the limit of infinite dilution. In the ideally dilute solution, Raoult’s law holds for the solvent and Henry’s law for solutes. The boiling points, freezing points, and osmotic pressure of ideally dilute solutions are colligative properties; they depend only on properties of the solvent and the total concentration of solutes. Distribution coefficients for a solute between two solvents are the ratios of the Henry’s law constants for these solvents. Vapor-pressure and boiling-point phase diagrams are shown for ideal solutions and may be used to determine the concentrations of coexisting phases. Solid–liquid equilibria, including eutectic mixtures, can also be described by such diagrams.

A solution is a homogeneous multicomponent phase. Of course, the idea of homogeneity depends on the scale of observation. When the nonuniformities are of the order of molecular dimensions, we have the true solutions that will be discussed in this chapter. When they are somewhat larger than the wavelength of light, they can be observed, and then we say that the system is composed of more than a single phase. In between these limits are systems with inhomogeneities in the range from a few nanometers to approximately a micron. Such systems are dominated by surface interactions and are called colloids. Colloidal inhomogeneities generally will not be visible to the naked eye; such systems will appear homogeneous. However, they have special properties and therefore they will be briefly discussed in [Chapter 11](#).

## 8.1 Measures of Concentration

Most of chemistry and engineering and all of biology deals with multicomponent systems. For systems with more than one component, the relative amounts of the various components are important thermodynamic variables. Measures of concentration may apply to the entire system or to a homogeneous region of the system (i.e., a phase). A multicomponent phase is called a *solution*. Because gaseous mixtures are homogeneous,<sup>1</sup> they are solutions. The component at highest concentration in a solution is usually called the *solvent* (designated by subscript *A*) and the other components the *solutes* (designated by subscript *i* or, collectively, by the subscript *B*). One of the most fundamental measures of concentration is the *mole fraction*, introduced for gaseous solutions in [Chapter 1](#), and defined by

$$x_i \equiv \frac{n_i}{n} \quad (1)$$

*Molarity* is defined as

$$c_i = \frac{n_i}{V} \quad (2)$$

where *V* is the volume of the solution in liters. It is a very convenient concentration unit, due to the ease of transferring precise volumes of liquid solutions. For thermodynamics, molarity is less useful because the volume of a given solution undergoes small changes with temperature, changing the molarity of the solution. A closely related measure of concentration, the *molality*, is defined as the moles of solute per kilogram of the solvent:

$$m_i \equiv \frac{n_i}{n_A M_A} \quad (3)$$

where *M<sub>A</sub>* is the molecular weight of the solvent (in kg/mol). *m<sub>i</sub>* does not vary with temperature. Because 1 L of dilute aqueous solution has a mass close to 1 kg

and is almost all water, molarities and molalities are numerically similar for such solutions. When concentrations are given as a percent, such as in Sherlock Holmes' seven-percent solution, the mass of solute per mass of solution ( $\times 100$ ) is implied.

It is important to be able to convert among the different concentration units. Conversions between molality and mole fraction are performed by considering a solution containing 1 kg of solvent:

$$x_i = \frac{m_i}{\sum_i m_i + 1/M_A}, \quad m_i = \frac{n_i}{n_A M_A} = \frac{x_i}{x_A M_A} \quad (4)$$

The conversion between molarity and mole fraction involves the density,  $\rho$ , of the solution and is (by calculating the mole fraction of 1 L of solution)

$$x_i = \frac{c_i}{[(\rho - \sum_{i \neq A} c_i M_i)/M_A] + \sum_{i \neq A} c_i} \quad (5)$$

## 8.2 Partial Molar Quantities

Extensive properties of multicomponent phases (solutions) are related to the amount of material in the phase, but may not be just the sum of the properties of the constituent components. Probably the best known example of this difference is the observation that mixing 1.0 L of ethanol with 1.0 L of water at standard temperature and pressure (STP) produces 1.93 L of water–ethanol solution. We define the difference between an extensive property of the solution and the sum of the properties of its pure components as the property change of mixing for the solution:

$$\Delta_{\text{mix}} X \equiv X - \sum_i n_i X_{i,m}^* \quad (6)$$

where  $X_{i,m}^*$  is a molar property of a pure component. There is a volume change of mixing,  $\Delta_{\text{mix}} V$  of  $-0.07$  L for the above water–ethanol solution. The word “change” is often omitted in discussing these quantities. Thus, we use the terminology “volume of mixing” and the “Gibbs free energy of mixing.” The “heat of mixing” is taken to mean the enthalpy change on mixing. In ideal gas mixtures, where interactions are negligible, we have seen that  $\Delta_{\text{mix}} V$  is zero. However, in [Chapter 4](#), we saw that, even for ideal gases,  $\Delta_{\text{mix}} S$  is not zero, and this also holds for  $\Delta_{\text{mix}} A$  and  $\Delta_{\text{mix}} G$ , to which  $\Delta_{\text{mix}} S$  contributes. In order to use Eq. (6), we must develop methods of calculating extensive properties of solutions.

To calculate a general extensive property,  $X$ , of a solution, we start with a differential relation for  $X$ :

$$dX = \left( \frac{\partial X}{\partial P} \right)_{T, n_i} dP + \left( \frac{\partial X}{\partial T} \right)_{P, n_i} dT + \sum_i \left( \frac{\partial X}{\partial n_i} \right)_{P, T, n_{j \neq i}} dn_i \quad (7)$$

For  $c$  components in a phase, this equation has  $c + 2$  terms, one more than given by the phase rule, because its integration requires the size of the phase as well as its intensive variables. The quantity  $(\partial X / \partial n_i)_{P, T, n_{j \neq i}}$  is called the *partial molar  $X$  with respect to  $i$*  and given the symbol  $\bar{X}_i$ :

$$\bar{X}_i \equiv \left( \frac{\partial X}{\partial n_i} \right)_{P, T, n_{j \neq i}} \quad (8)$$

These partial molar quantities are the key quantities used to describe the properties of solutions.

We have previously introduced one particular partial molar quantity. In Eq. (9) of [Chapter 6](#), the chemical potential was given as

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{P, T, n_{j \neq i}} \equiv \bar{G}_i \quad (9)$$

This shows that the chemical potential of a component is just its partial molar Gibbs free energy. Note that the definitions of the chemical potential in terms of other thermodynamic variables, given in Chapter 6, Eq. (8), are not partial molar quantities because pressure and temperature are not the variables held constant in these derivatives.

Partial molar quantities are ratios of two extensive variables and are, therefore, intensive variables. As intensive variables they are independent of the size of the system and dependent only on other intensive variables. We can take our partial derivatives to be dependent on  $P$ ,  $T$ , and  $c - 1$  concentrations and write Eq. (7) as

$$dX = \left( \frac{\partial X}{\partial P} \right)_{T, n_i} dP + \left( \frac{\partial X}{\partial T} \right)_{P, n_i} dT + \sum_i \bar{X}_i(P, T, c_j) dn_i \quad (10)$$

Consider a process beginning with a very small system at given  $P$ ,  $T$ , and  $c_j$ 's and, holding  $P$  and  $T$  constant, adding the components of the system in the proper ratio to keep the system concentrations constant. Integrating Eq. (10) for this process, the first two terms drop out, giving

$$X_f - X_0 = \sum_i \int_0^f \bar{X}_i dn_i \quad (11)$$

The partial molar quantities are constant during the process and may be taken out of the integrals, and the limit may be taken in which the initial size of the system (and the extensive variables  $X_0$  and the  $n_{i,0}$ 's) go to zero:

$$X = \sum_i \bar{X}_i n_i \quad (12)$$

where the subscript  $f$  has been dropped for simplicity. Equation (11) of [Chapter 6](#) is just Eq. (11) written for the Gibbs free energy.

A useful relation can be derived by considering the change in  $X$  upon arbitrary additions of material to the system at constant  $T$  and  $P$ . Because concentrations change upon such addition, we must, in using Eq. (12) consider changes in the partial molar quantities as well as changes in the number of moles:

$$dX = \sum_i \bar{X}_i dn_i + \sum_i n_i d\bar{X}_i \quad (13)$$

However, Eq. (10) tells us that a perfectly general expression for  $dX$  at constant  $T$  and  $P$  is

$$dX = \sum_i \bar{X}_i dn_i \quad (14)$$

The only way that these two relations can be reconciled is if

$$\sum_i n_i d\bar{X}_i = 0 \quad (15)$$

Equation (15) is called the general *Gibbs–Duhem relation*. Because it tells us that there is a relation between the partial molar quantities of a solution, we will learn how to use it to determine a  $\bar{X}_i$  when all other  $\bar{X}_{j \neq i}$  have been determined. (In a two-component system, knowing  $\bar{X}_{\text{solvent}}$  determines  $\bar{X}_{\text{solute}}$ .) This type of relationship is required by the phase rule because, at constant  $T$ ,  $P$ , and  $c$  components, a single-phase system has only  $c - 1$  degrees of freedom.

Many relations that hold between extensive thermodynamic variables also hold between the corresponding partial molar quantities. In particular, we have

$$\bar{G}_i = \mu_i = \bar{H}_i - T\bar{S}_i \quad (16)$$

$$\left( \frac{\partial \mu_i}{\partial P} \right)_{T, c_j} = \bar{V}_i \quad (17)$$

$$\left( \frac{\partial \mu_i}{\partial T} \right)_{P, c_j} = -\bar{S}_i \quad (18)$$

The first relation follows directly by taking the partial derivative of  $G = H - TS$  with respect to  $n_i$  (holding  $P$ ,  $T$ , and the other  $n_j$ 's constant). The latter two relations can be proved by reversing the order of differentiating with respect to  $n_i$  and with  $T$  and  $P$  respectively.

Use of Eq. (12) in Eq. (6) allows us to calculate changes of thermodynamic function on mixing:

$$\Delta_{\text{mix}}X = \sum_i n_i \bar{X}_i - \sum_i n_i X_{m,i}^* = \sum_i n_i (\bar{X}_i - X_{m,i}^*) \quad (19)$$

This shows that nonzero mixing properties of solutions result from partial molar quantities not being equal to the molar properties of the pure components. From a microscopic point of view, nonzero volumes of mixing could be due to the components of a solution fitting each other better or more poorly than they fit themselves. Nonzero energy and enthalpy of mixing result if the forces between molecules of different components are different than those between molecules of the same component. For  $S$ ,  $A$ , and  $G$ , an additional term results from the “randomness” of the solution compared to the pure components, which, in [Chapter 4](#), was shown to give an entropy of mixing of  $-nR \sum_j X_j \ln X_j$ .

It can easily be shown that simple thermodynamic relationships also hold for changes of thermodynamic functions on mixing. For example,

$$\Delta_{\text{mix}}G = \Delta_{\text{mix}}H - T\Delta_{\text{mix}}S \quad (20)$$

$$\left( \frac{\partial \Delta_{\text{mix}}G}{\partial P} \right)_{T,c_j} = \Delta_{\text{mix}}V \quad \text{and} \quad \left( \frac{\partial \Delta_{\text{mix}}G}{\partial T} \right)_{P,c_j} = -\Delta_{\text{mix}}S \quad (21)$$

### 8.3 Measurement of Partial Molar Quantities

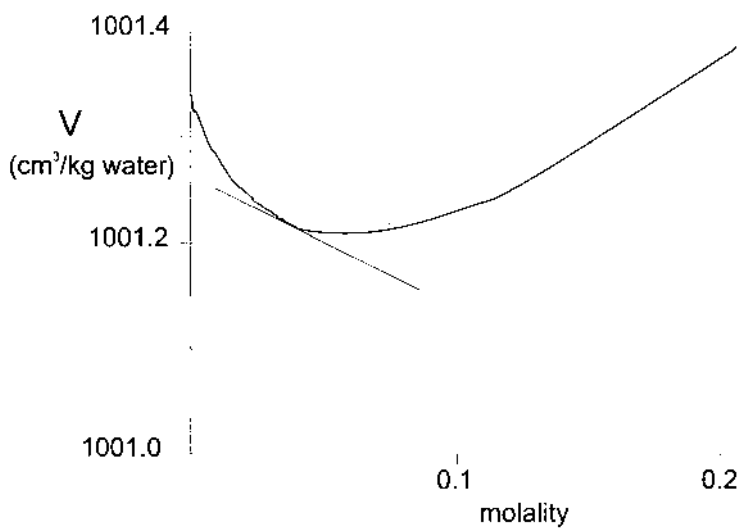
The measurement of partial molar quantities will be illustrated with reference to partial molar volumes. We can measure absolute volumes of solution and, thus, can determine partial molar volumes directly from its definition:

$$\bar{V}_i(P, T, c_j) \equiv \left( \frac{\partial V}{\partial n_i} \right)_{P,T,n_{j \neq i}} \quad (22)$$

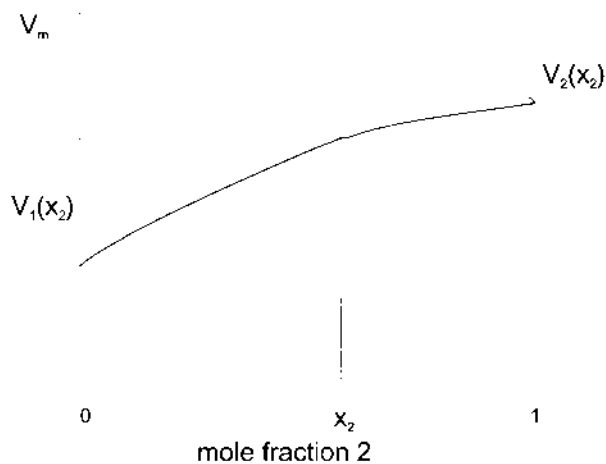
For binary solutions, this is just the slope of the plot at constant  $T$  and  $P$  of the volume of the solution versus its molality. This is illustrated in [Fig. 1](#) for an aqueous  $\text{MgSO}_4$  solution. Note that at low concentration, the partial molar volume of  $\text{MgSO}_4$  in aqueous solution is *negative*.

An alternative definition of  $\bar{V}_i$  is the change of volume of a solution upon adding 1 mol of component  $i$  in the limit in which the solution volume is so large that its concentration is unchanged by the addition. Using such large volumes is usually impractical, but smaller additions and volumes can be used. This method avoids the difficulty of measuring slopes of curves.

In a binary solution (two components), the partial molar volumes of the components can be determined from a plot of the molar volume of the solution versus mole fraction, as shown in [Fig. 2](#).



**Figure 1** Volume of the solution versus its molality.



**Figure 2** Molar volume of the solution versus mole fraction.

Using Eq. (12), we have

$$V_m = \frac{V}{n_1 + n_2} = \frac{n_1 \bar{V}_1 + n_2 \bar{V}_2}{n_1 + n_2} \quad (23)$$

Writing this in terms of mole fractions, we have

$$V_m(x_2) = x_1 \bar{V}_1(x_2) + x_2 \bar{V}_2(x_2) = \bar{V}_1(x_2) + x_2 [\bar{V}_2(x_2) - \bar{V}_1(x_2)] \quad (24)$$

where, in this expression, we have explicitly indicated that the partial molar volumes are functions of the concentration of the binary solution. The tangent line to the curve of Eq. (24) at  $x_2$  has slope  $\bar{V}_2(x_2) - \bar{V}_1(x_2)$  and its intercepts with  $x_2 = 0$  and  $x_2 = 1$  are  $\bar{V}_1(x_2)$  and  $\bar{V}_2(x_2)$ , respectively, as shown in Fig. 2.

### 8.3.1 Partial Molar Gibbs Free Energies

Partial molar Gibbs free energies (chemical potentials) can most easily be measured by taking advantage of the equality of chemical potentials in different phases at equilibrium. The chemical potential of a component of a solution is its chemical potential in the vapor that is in equilibrium with the solution. Thus, if the component has a measurable vapor pressure, it can be used to determine its chemical potential in the solution. Assuming that the vapor can be considered an ideal gas, its chemical potential is determined by its vapor pressure:

$$\mu_{i,l} = \mu_{i,g} = \mu_{i,g}^0 + RT \ln\left(\frac{P_i}{P^0}\right) \quad (25)$$

where  $\mu_{i,g}^0$  is the chemical potential of the 1.0-bar pure component in the gas phase. Because zeros of energy are arbitrary, this quantity is usually fixed by setting the chemical potentials of the *elements* in their reference states<sup>2</sup> equal to zero. A similar relation holds for the pure component:

$$\mu_{i,l}^* = \mu_{i,g}^* = \mu_{i,g}^0 + RT \ln\left(\frac{P_i^*}{P^0}\right) \quad (26)$$

where  $P_i^*$  is the vapor pressure of pure  $i$ . Subtracting Eq. (24) from Eq. (23) gives

$$\mu_{i,l} - \mu_{i,l}^* = \bar{G}_i - G_{m,i}^* = RT \ln\left(\frac{P_i}{P_i^*}\right) \quad (27)$$

For nonideal vapors, fugacities must be used. From Eq. (51) of Chapter 6,

$$\mu_{i,l} - \mu_{i,l}^* = \bar{G}_i - G_{m,i}^* = RT \ln\left(\frac{f_i}{f_i^*}\right) \quad (28)$$

Strictly speaking, this holds only for both the solution and pure component under the vapor pressure of component  $i$ . However, because the molar volumes of solutions are small, the result is little changed at other pressures.



In a binary solution, the Gibbs-Duhem relation [Eq. (15)] determines the variation of a partial molar property of one component in terms of the variation of the partial molar quantity of the other component. This relation is useful for obtaining chemical potentials in binary solutions when only one of the components has a measurable vapor pressure. Applying Eq. (15) to chemical potentials in a binary solution,

$$n_B d\mu_B = -n_A d\mu_A \quad (29)$$

Dividing by  $n = n_A + n_B$  and using  $x_B = 1 - x_A$  gives

$$d\mu_B = -\frac{x_A}{1 - x_A} d\mu_A \quad (30)$$

Integration of this equation will be discussed in [Chapter 9](#).

## 8.4 The Ideal Solution

In our study of gases, the ideal gas model was both simple and useful. It neglects all interactions between molecules. Obviously, a model neglecting all intermolecular interactions can have little validity for liquid or solid solutions, which are held together by cohesive forces. The simplest model for such solutions, the ideal solution, allows interactions between molecules, but it assumes that they are the same between any two species in the solution. Thus, for a binary solution,  $A-A$ ,  $B-B$  and  $A-B$  interactions are equal.  $A$  and  $B$  molecules are also required to have similar size and shape. This model rarely provides a good fit to data. (Very similar species, such as benzene–toluene, and mixtures of isomers and isotopic variations of molecules are a few examples where it does fit.) However, it does provide a good reference point against which the behavior of real solutions can be measured. Deviations from ideal solution behavior can tell us something about the interactions in systems.

Because thermodynamics describes macroscopic behaviors, we need a macroscopic definition of the ideal solution in addition to the microscopic description given above. We define an ideal solution as one that, for each of its components, at all  $T$  and  $P$  and over the entire range of concentrations,

$$\mu_i \stackrel{\text{i.s.}}{=} \mu_i^* + RT \ln x_i \quad (31)$$

Equation (31) implies that the properties of the solution change smoothly into those of pure component  $i$  as  $x_i \rightarrow 1$ . The pure components of an ideal solution must, therefore, have the same phase as the solution. Standard states of an ideal liquid solution are thus just the pure liquid components at the given  $T$  and  $P$ . Comparing Eq. (31) with the normal form of the chemical potential given in Eq. (47) of [Chapter 6](#),  $\mu = \mu^0 + RT \ln a$ , we see that, for the ideal solution, the

activity of every component is just its mole fraction. The other partial molar quantities of the components of an ideal solution are as follows:

$$\bar{V}_i = \left( \frac{\partial \mu_i}{\partial P} \right)_{T, n_i} \stackrel{\text{i.s.}}{=} \left( \frac{\partial \mu_i^*}{\partial P} \right)_{T, n_i} = V_{m,i}^* \quad (32)$$

$$\bar{S}_i = - \left( \frac{\partial \mu_i}{\partial T} \right)_{P, n_i} \stackrel{\text{i.s.}}{=} - \left( \frac{\partial \mu_i^*}{\partial T} \right)_{P, n_i} - R \ln x_i = S_{m,i}^* - R \ln x_i \quad (33)$$

$$\bar{H}_i = \mu_i + T\bar{S}_i = \mu_i^* + RT \ln x_i + T(S_{m,i}^* - R \ln x_i) = H_{m,i}^* \quad (34)$$

From Eq. (19), the Gibbs free energy of mixing of an ideal solution is

$$\Delta_{\text{mix}} G = \sum_i n_i (\mu_i - \mu_i^*) \stackrel{\text{i.s.}}{=} RT \sum_i n_i \ln x_i \quad (35)$$

and from Eqs. (32)–(34), we obtain

$$\Delta_{\text{mix}} V \stackrel{\text{i.s.}}{=} \Delta_{\text{mix}} H \stackrel{\text{i.s.}}{=} 0 \quad (36)$$

$$\Delta_{\text{mix}} S \stackrel{\text{i.s.}}{=} -R \sum_i n_i \ln x_i = -nR \sum_i x_i \ln x_i \quad (37)$$

Expression (37) is the same result that holds for the ideal gas, where the entropy of mixing results entirely from the increase in randomness of the mixture. It is necessarily positive because all  $x_i < 1$  and  $\ln x_i < 0$ . All of the thermodynamic properties of mixing of an ideal solution result from this randomness; there are no energy effects.

In order to find the vapor pressure of a component of an ideal solution, we equate its chemical potential in the solution with that in the vapor in equilibrium with the solution. Assuming that the vapor is ideal, this gives

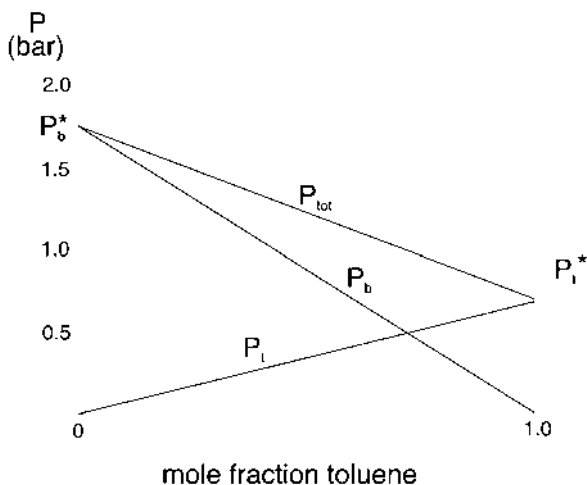
$$\mu_{i,l} \stackrel{\text{i.s.}}{=} \mu_i^* + RT \ln x_i = \mu_{i,g}, = \mu_i^0 + RT \ln (P_i/P^0) \quad (38)$$

where  $\mu_i^0$  is the chemical potential of 1.0 bar vapor. We do the same for the pure liquid component:

$$\mu_i^* = \mu_{i,g}^* = \mu_i^0 + RT \ln (P_i^*/P^0) \quad (39)$$

Substituting Eq. (39) into Eq. (38) gives

$$P_i \stackrel{\text{i.s.}}{\stackrel{\text{i.g.}}{=}} x_i P_i^* \quad (40)$$



**Figure 3** Vapor-pressure diagram of benzene–toluene solutions.

which is known as *Raoult's law*. The total vapor pressure of the components of a solution obeying Raoult's law is  $\sum_i P_i = \sum_i x_i P_i^*$ . For a binary solution, this becomes

$$P = x_A P_A^* + x_B P_B^* = P_A^* + x_B (P_B^* - P_A^*) \quad (41)$$

The vapor pressure of such a solution varies linearly with  $x_B$  from  $P_A^*$  to  $P_B^*$ . This behavior is illustrated in the *vapor-pressure diagram* of benzene–toluene solutions shown in Fig. 3.

## 8.5 The Ideally Dilute Solution

Whereas the ideal solution model applies over the entire range of concentrations, but only for very similar components, the ideally dilute solution model applies to any solution, but only over a very limited range of concentrations. From a microscopic point of view, the ideally dilute solution holds as long as solute molecules are almost always completely surrounded by solvent molecules and rarely interact with other solute molecules.

The applicable concentration range of the ideally dilute approximation depends on the size of the solute molecules, because, obviously, large polymer molecules will interact at much lower concentrations than will smaller species. For ionic solutes, the range of applicable concentrations is so small that it is practically useless, and even in this range, allowance must be made for the

ionization of the solute. Ionic solutions will be considered in detail in [Chapter 10](#). For small, nonionized solutes, the ideally dilute solution approximation can usually be used up to total solute mole fractions of 0.01–0.1, depending on the accuracy required.

Calling the solvent component  $A$  and a solute component  $i$ , we define the ideally dilute solution as one that has, in a range around infinite dilution,

$$\mu_A^{\text{id.s.}} = \mu_A^0 + RT \ln x_A \quad (42)$$

$$\mu_i^{\text{id.s.}} = \mu_i^0 + RT \ln x_i \quad (43)$$

Comparison with the standard form for the chemical potential,  $\mu = \mu^0 + RT \ln a$  [Eq. 47 of [Chapter 6](#)], shows that in the ideally dilute solution activities are equal to mole fractions for both solvent and solute. In order to find the standard state of the solvent in the ideally dilute solution, we note that at  $x_A = 1$  (infinite dilution, within the range of applicability of the model), we have  $\mu_A^0 = \mu_A^*$ . The standard state of the solvent in the ideally dilute solution is pure solvent, just like the standard states of all components in an ideal solution. The solvent in the ideally dilute solution behaves just like a component of the ideal solution. Although it is also true that  $\mu_i^0$  becomes  $\mu_i^*$  at  $x_i = 1$ , this is clearly outside the realm of applicability of Eq. (43). In order to avoid this difficulty, in determining  $\mu_i^0$  we make measurements at very low values of  $x_i$  and extrapolate to  $x_i = 1$  using  $\mu_i^0 = \mu_i - RT \ln x_i$ , as if the high dilution behavior held to  $x_i = 1$ . In other words, our standard state for a solute in the ideally dilute solution is the *hypothetical* state of pure solute with the behavior of the solute in the infinitely dilute solution.

It is more common to use molality or molarity as the concentration unit for the solute in the ideally dilute solution. The relevant equations are then

$$\mu_i^{\text{id.s.}} = \mu_i^0 + RT \ln m_i \quad (44)$$

$$\mu_i^{\text{id.s.}} = \mu_i^0 + RT \ln c_i \quad (45)$$

where  $m_i$  and  $c_i$  are the numerical values of the solute molality and molarity, respectively.<sup>3</sup> The standard state for the solute in these cases is the *hypothetical* state of a 1.0 *m* or a 1.0 *M* solution, with the solute behaving as it does in the infinitely dilute solution.

As shown in Example 1, the chemical potential of a solute can be of a more complicated form than given by Eqs. (43)–(45), even though the solution shows ideally dilute behavior. This can result from a transformation of the substance when it dissolves in the solution.

**Example 1.**  $\text{N}_2\text{O}_4$  almost completely dissociates into  $\text{NO}_2$  in dilute aqueous solution. What is the chemical potential and activity of  $\text{N}_2\text{O}_4$  in such solutions?

*Solution:* The reaction is  $\text{N}_2\text{O}_4 \leftrightarrow 2\text{NO}_2$ . If the nominal molality of the solution is  $m_{\text{N}_2\text{O}_4}$ , the solution actually contains  $2m_{\text{N}_2\text{O}_4}$  of  $\text{NO}_2$  and practically no  $\text{N}_2\text{O}_4$ . We then have

$$\begin{aligned}\mu_{\text{N}_2\text{O}_4} &= 2\mu_{\text{NO}_2} = 2(\mu_{\text{NO}_2}^0 + RT \ln m_{\text{NO}_2}) = 2(\mu_{\text{NO}_2}^0 + RT \ln 2m_{\text{N}_2\text{O}_4}) \\ &= 2\mu_{\text{NO}_2}^0 + RT \ln(2m_{\text{N}_2\text{O}_4})^2 = \mu_{\text{N}_2\text{O}_4}^0 + RT \ln(2m_{\text{N}_2\text{O}_4})^2\end{aligned}$$

This shows that the activity of  $\text{N}_2\text{O}_4$  in this solution is  $(2m_{\text{N}_2\text{O}_4})^2$ .

We will see in [Chapter 10](#), when we deal with the dissociation of electrolytes into ions, that, in general, the chemical potential of a dissociating solute is the chemical potential of its component parts, whereas the activity of the solute is the product of the component parts.

In order to find the vapor pressures above the ideally dilute solution, we equate the chemical potentials of the components in the solution with those in the vapor. Because the solvent in the ideally dilute solution behaves just like a component of an ideal solution, its vapor pressure follows Raoult's law. For the solute in an ideally dilute solution, we obtain

$$\mu_{i,l} \stackrel{\text{id.s.}}{=} \mu_{i,l}^0 + RT \ln x_i = \mu_{i,g} = \mu_{i,g}^0 + RT \ln(P_i/P^0) \quad (46)$$

which can be rearranged to

$$RT \ln\left(\frac{P_i}{x_i P^0}\right) = \mu_{i,l}^0 - \mu_{i,g}^0 \quad (47)$$

or

$$\frac{P_i}{x_i P^0} = \exp\left(\frac{\mu_{i,l}^0 - \mu_{i,g}^0}{RT}\right) \quad (48)$$

The standard chemical potential  $\mu_{i,l}^0$  depends on  $T$  and  $P$ , and  $\mu_{i,g}^0$  depends on  $T$ , but both are independent of concentration. Equation (51) can thus be written as

$$P_i = x_i K_i \quad \text{with } K_i = P^0 \exp\left(\frac{\mu_{i,l}^0 - \mu_{i,g}^0}{RT}\right) \quad (49)$$

This equation is known as *Henry's law* and  $K_i$  is known as the Henry's law constant (more exactly as the *mole fraction-based Henry's law constant*).  $K_i$  depends on the particular solute–solvent combination being considered, as well as the temperature and the total pressure. However, it does not depend on the solution concentration. Using Eq. (4), the partial pressure can be expressed in terms of the molality as

$$P_i = K_i \frac{m_i}{m_i + 1/M_A} \quad (50)$$

Because the ideally dilute solution approximation only holds in the limit of very dilute solutions (i.e., where  $m_i \ll 1/M_A$ ), this becomes

$$P_i = K_i M_A m_i = K_{m,i} m_i \quad (51)$$

where  $K_{m,i}$  is the *molality-based Henry's law constant* of component  $i$  in the given solution. In a similar manner, a Henry's law constant can also be defined in terms of concentration expressed as molarity.

Henry's law is also used to find the amount of a gas that dissolves at equilibrium in a solvent at a known partial pressure of the gas. The solubility of the gas is proportional to the inverse of the Henry's law constants, as we have defined them in Eqs. (49) and (51). The reader is cautioned, however, that sometimes the Henry's law constant is defined so that solubilities are directly proportional to the Henry's law constants. The units listed for the constant indicate the definition used in any tabulation. Some Henry's law constants are given in Table 1.

Solubilities of gases usually decrease as the temperature increases, indicating that solubility is exothermic. Solutes with higher boiling points generally have greater solubility. (See Question 14.) Unusually large solubility may result in cases in which there are specific (e.g., hydrogen-bonding) interactions between solute and solvent. Helium shows much greater solubility than expected from its boiling point due to its ability to fit into cavities in solvents.

**TABLE 1** Mole-fraction-Based Henry's Law Constants  $K_i$  ( $10^9$  Pa) at 298 K

Solute	Solvent	
	Water	Benzene
Argon	3.73	
Carbon dioxide	0.167	0.0114
Helium	14.93	
Hydrogen	7.12	0.367
Hydrogen sulfide	0.057	
Nitrogen	8.68	0.239
Oxygen	4.40	
Methane	3.74	
Benzene	0.0300	
Naphthalene	0.0024	

Source: Data from A James, M Lord. VNR Index of Chemical and Physical Data. New York: Van Nostrand Reinhold 1992, p 495.

## 8.6 Freezing-Point Depression, Boiling-Point Elevation and Osmotic Pressure

We often have a situation in which the solvent in a solution can equilibrate with another phase, whereas the solutes are confined to the solution. This will occur with vaporization if the solutes are non-volatile, it will occur with freezing if the solute is excluded from the crystal lattice of the solid solvent, and it will occur with osmosis if only solvent can pass through a semipermeable membrane. For vaporization and freezing, when the solvent is pure ( $x_A = 1$ ), these equilibrations occur at the normal boiling point ( $T_b^*$ ) and freezing point ( $T_f^*$ ) of the solvent, whereas for osmosis, equilibration across a semipermeable membrane occurs when pure solvent is at the same pressure on both sides of the membrane.

If solute is added to a solvent, the mole fraction of solvent and its escaping tendency from the liquid, as measured by its chemical potential or activity, is reduced. We will see that in order to reestablish equilibrium with the other phase, there must be a reduction in freezing point, an elevation of boiling point or an increase in osmotic pressure. Because the addition of solute reduces the escaping tendency of the solvent from a solution, it extends the realm of stability of the solution. Thus, the addition of antifreeze (ethylene glycol) to water in a car's radiator both lowers the freezing point and raises the boiling point of the liquid in the radiator, both of which are beneficial for the cooling system.

Considering freezing, equilibrium requires that the chemical potential of the solvent in solution equal that of the (pure) solid solvent:

$$\mu_{A,s}^* = \mu_{A,l} = \mu_{A,l}^* + RT \ln a_A \quad (52)$$

or

$$\ln a_A = \frac{\mu_{A,s}^* - \mu_{A,l}^*}{RT} = -\frac{\Delta_{\text{fus}}G^*}{RT} \quad (53)$$

Taking the derivative with respect to  $T^{-1}$  and using Eq. (29) of Chapter 4,

$$\left( \frac{\partial \ln a_A}{\partial T^{-1}} \right)_p = -\frac{1}{R} \left( \frac{\partial (T^{-1} \Delta_{\text{fus}}G^*)}{\partial T^{-1}} \right)_p = -\frac{\Delta_{\text{fus}}H^*}{R} \quad (54)$$

Separating variables and integrating from the pure solvent (with  $a_A = 1$  and  $T_f = T_f^*$ ) gives

$$\ln a_A = -\frac{\Delta_{\text{fus}}H^*}{R} \left( \frac{1}{T_f} - \frac{1}{T_f^*} \right) \approx -\frac{\Delta_{\text{fus}}H^*}{R} \left( \frac{\theta_f}{(T_f^*)^2} \right) \quad (55)$$

where we have substituted  $T_f^*$  for  $T_f$  in the denominator in the final step because  $T_f^* - T_f \equiv \theta_f$ , the *freezing-point depression*, is quite small. Equation (55) also gives the activity of solvent in solution in equilibrium with solid  $A$  at various

temperatures below the freezing point. A similar analysis of the boiling point gives, in terms of the *boiling-point elevation*,  $\theta_b = T_b - T_b^*$ :

$$\ln a_A = \frac{\Delta_{\text{vap}} H^*}{R} \left( \frac{1}{T_b} - \frac{1}{T_b^*} \right) \approx - \frac{\Delta_{\text{vap}} H^*}{R} \left( \frac{\theta_b}{(T_b^*)^2} \right) \quad (56)$$

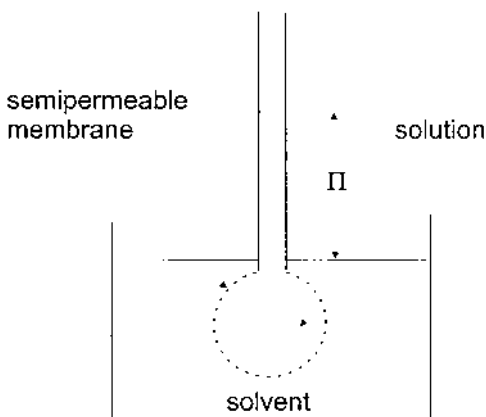
*Osmosis* is the selective passage of particular components of a solution through a *semipermeable membrane*. Usually, it is the solvent that passes through the membrane, because the solute is blocked. However, some membranes also allow small solute molecules to pass through as well and only block the passage of macromolecular solute molecules. The *osmotic pressure* of a solution is the pressure difference produced at equilibrium across the membrane, with the solution on one side of the membrane and pure solvent on the other side. As shown in Fig. 4, the reduced activity of the solvent in solution is compensated for by an increase in the pressure of the solution:

$$\mu_A^*(P) = \mu_A^*(P') + RT \ln a_A \quad (57)$$

where  $P$  is the pressure on the pure solvent side of the membrane and  $P'$  is the pressure on the solution side of the membrane. This can be written as

$$\ln a_A = \frac{\mu_A^*(P) - \mu_A^*(P')}{RT} = \frac{1}{RT} \int_{P'}^P \left( \frac{\partial \mu_A^*}{\partial P} \right)_T dP = - \frac{\Pi V_m^*}{RT}. \quad (58)$$

In the last step, the excellent approximation of constant molar volume of the solvent has been made.  $\Pi$ , the osmotic pressure, is  $P' - P$ . We see that the activity of the solvent in solution can be determined by measuring the freezing-



**Figure 4** Osmotic pressure.



point depression, boiling-point elevation, or osmotic pressure of the solution, as well as by measuring the vapor pressure of solvent above the solution.

Particularly simple forms of the equations for the freezing-point depression, boiling-point elevation, and osmotic pressure are obtained when the solution is ideal or when it is sufficiently dilute, so that the ideally dilute solution approximation is appropriate. In both of these cases, the activity of the solvent is equal to its mole fraction, so that

$$\ln a_A = \ln x_A = \ln(1 - \sum x_i) \equiv \ln(1 - x_B) \quad (59)$$

The  $\sum x_i$  extends over all the solute species and is designated as  $x_B$ , which we have previously used to designate the mole fraction of the single solute in a binary solution. At a concentration small enough to make the ideally dilute solution approximation, it is usually sufficient to use only the first term in the Taylor series approximation of  $\ln(1 - x_B)$ ,<sup>4</sup>

$$\ln a_A = -x_B \quad (60)$$

Equation (55) for the freezing-point depression then becomes

$$\theta_f = \frac{R(T_f^*)^2 x_B}{\Delta_{\text{fus}} H^*} \quad (61)$$

whereas Eq. (56) for the boiling-point elevation becomes

$$\theta_b = \frac{R(T_b^*)^2 x_B}{\Delta_{\text{vap}} H^*} \quad (62)$$

Equation (58) for the osmotic pressure becomes

$$\Pi = \frac{RTx_B}{V_m^*} \quad (63)$$

Freezing-point depression, boiling-point elevation and osmotic pressure are known as *colligative properties*, because they are dependent on the properties of the *solvent* and the total mole fraction of all solutes, but are independent of any particular property of the solutes. Equations (61)–(63) are usually written in terms of  $m_B$ , the sum of the molalities of all the solutes, which for ideally dilute solutions is related to  $x_B$  by

$$x_B = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A} = m_B M_A$$

where  $M_A$  is the molecular weight of the solvent (in units of kg/mol). This gives

$$\theta_f = K_f m_B, \quad K_f = \frac{R(T_f^*)^2 M_A}{\Delta_{\text{fus}} H^*} \quad (64)$$

$$\theta_b = K_b m_B, \quad K_b = \frac{R(T_b^*)^2 M_A}{\Delta_{\text{vap}} H^*} \quad (65)$$

$$\Pi = \left( \frac{RT M_A}{V_m^*} \right) m_B \quad (66)$$

$m_B$  is the total molality of the solution.  $K_f$  and  $K_b$ , the molal freezing-point depression and boiling-point elevation constants, respectively, depend only on the properties of the *solvent* and are usually evaluated by calibration, as in the following example.

**Example 2.** The freezing point of pure benzene is 5.45°C. The addition of 0.52 g of cyclohexane to 100.0 g of benzene forms a solution with freezing point 5.13°C. If 0.81 g of an unknown compound is added to 100.0 g of benzene, the resulting freezing point is 5.21°C. What is the molecular weight of the unknown compound?

*Solution:* First, we calculate the molality of the cyclohexane solution:

$$\frac{0.52 \text{ g}_{\text{chex}}}{100 \text{ g}_{\text{benz}}} \frac{\text{mol}_{\text{chex}}}{84 \text{ g}_{\text{chex}}} \frac{1000 \text{ g}_{\text{benz}}}{\text{kg}_{\text{benz}}} = 0.062 \text{ m}$$

The freezing depression constant of benzene is then

$$K_f = \frac{(5.45 - 5.13)^\circ\text{C}}{0.062 \text{ m}} = 5.2^\circ\text{C}/\text{m}$$

The molality of the solution of unknown is then calculated:

$$\frac{(5.45 - 5.21)^\circ\text{C}}{5.2^\circ\text{C}/\text{m}} = 0.046 \text{ m} = 0.046 \text{ mol}_x/\text{kg}_{\text{benz}}$$

From this, the molecular weight of the unknown compound is calculated:

$$\frac{0.81 \text{ g}_x}{100 \text{ g}_{\text{benz}}} \frac{\text{kg}_{\text{benz}}}{0.046 \text{ mol}_x} \frac{1000 \text{ g}_{\text{benz}}}{\text{kg}_{\text{benz}}} = \frac{180 \text{ g}_x}{\text{mol}_x}$$

When doing calculations with colligative properties, it is usually advantageous to make measurements at a number of concentrations and extrapolate the results to zero concentration, where the ideally dilute solution theory is clearly applicable.

A few values of  $K_f$  and  $K_b$  are given in [Table 2](#). For a macromolecular solution, the ideally dilute approximation holds only up to such low molality that freezing-point depression and boiling-point elevation are useless for determining

**TABLE 2.** Freezing-point depression and boiling-point elevation constants

Solvent	$K_f$ (K kg/mol)	$K_b$ (K kg/mol)
Water	1.86	0.51
Benzene	5.12	2.53
Naphthalene	5.94	5.8
Carbon tetrachloride	30.0	4.95

polymer molecular weights by the method of Example 2. Osmotic pressure, however, is measurable even for very dilute solutions.

Equation (63) for osmotic pressure is usually rewritten by substituting  $x_B \approx n_B/n_A$  and then taking the volume of the solvent,  $n_A V_m^*$ , as approximately equal to the volume of the solution:

$$\Pi = \frac{RTn_B}{V} \quad (67)$$

This equation is easy to remember because it has the same form as the ideal gas law. Note that it depends only on the concentration of the solution and is independent of any specific properties of both the solute and the solvent. However, if the osmotic pressure is established by a rise of the level of the solution, as in Fig. 4, this rise will be dependent on the density of the solution (approximately the density of the solvent). Example 3 shows how even small concentrations of macromolecular solutes in solution can produce readily measurable osmotic pressures.

**Example 3.** What is the osmotic pressure at 25°C of a solution having a density of 0.8 g/mL and containing 1.5 g of a polymer of molecular weight 12,000 per liter of solution? How high will the solution rise to establish this pressure?

*Solution:*

$$\pi = \frac{0.082 \text{ l atm}}{\text{mol K}} 298 \text{ K} \frac{1.5 \text{ g}}{\text{L}} \frac{\text{mol}}{12,000 \text{ g}} = 3.0 \times 10^{-3} \text{ atm}$$

The rise of the solution is

$$h = (3.0 \times 10^{-3} \text{ atm}) \frac{760 \text{ mm Hg}}{\text{atm}} \frac{13.6 \text{ mm solution}}{0.8 \text{ mm Hg}} \\ = 31 \text{ mm solution}$$

which is easily measurable.

Synthetic polymers are often produced with a range of degree of polymerization and molecular weight. As shown next, a molecular weight determined for such a polymer by measurement of osmotic pressure is a *number-average* molecular weight.

In the ideally dilute limit, colligative properties depend on the *total* solute mole fraction or molality. If there are a number of different solutes present, this can be expressed as (for the case of freezing-point depression)

$$\theta_f = K_f m_B = K_f \sum_i m_i \quad (68)$$

Expressing  $m_B$  in terms of  $w_B$ , the total mass of all solutes added to a 1 kg of solvent,

$$m_B = \frac{w_B}{M_B} = \sum_i m_i \quad (69)$$

where  $M_B$  is the appropriate “average” molecular weight of the solutes. From this, we obtain

$$M_B = \frac{w_B}{\sum_i m_i} = \frac{\sum_i m_i M_i}{m_B} = \sum_i f_i M_i \quad (70)$$

where  $f_i = m_i/m_B$  is the fraction of the moles (or molecules) of the solute that have molecular weight  $M_i$ . The type of average given in Eq. (70) is a number average. Thus, when a molecular weight is determined from a colligative property, as illustrated in Examples 2 and 3, a *number-average molecular weight* is obtained (i.e., all molecules contribute equally). This average is to be distinguished from molecular weights determined by physical methods, such as light scattering, in which the contributions of different molecules are proportional to their size, giving a *mass-average molecular weight*. By measuring different averages of the molecular weight, information about the distribution of the masses of molecules can be obtained.

## 8.7 Distribution of a Solute Between Two Solvents

Liquid-phase extraction is a procedure by which some fraction of a solute is taken out of solution by shaking the solution with a different solvent (in which the solute usually has greater solubility). The analysis of this process assumes that the shaking is sufficient so that equilibrium is established for the solute,  $i$ , between the two solutions. At equilibrium, the chemical potentials of the solute in the two solutions are equal. Assuming ideally dilute solutions, we can write

$$\mu_{i,1} = \mu_{i,1}^0 + RT \ln x_1 = \mu_{i,2}^0 + RT \ln x_2 \quad (71)$$

Defining  $K_{12}$ , the *distribution coefficient* of solute between solute 1 and solute 2, as

$$K_{12} \equiv \frac{x_1}{x_2} \quad (72)$$

we obtain

$$\ln K_{12} = -\frac{(\mu_{i,1}^0 - \mu_{i,2}^0)}{RT} = -\frac{\Delta_{\text{trans}} G^\circ}{RT} \quad (73)$$

where  $\Delta_{\text{trans}} G^\circ$  is the standard free-energy change for transfer of one mole of  $i$  from solvent 2 to solvent 1. Equation (73) can be written as

$$K_{12} = \exp\left(\frac{\mu_{i,2}^0 - \mu_{i,1}^0}{RT}\right) = \exp\left(\frac{\mu_{i,2}^0 - \mu_{i,g}^0}{RT}\right) \exp\left(\frac{\mu_{i,1}^0 - \mu_{i,g}^0}{RT}\right)^{-1} \quad (74)$$

where  $\mu_{i,g}^0$  is the standard (1.0 bar) chemical potential of  $i$  in the gas phase. Referring to Eq. (49), this becomes

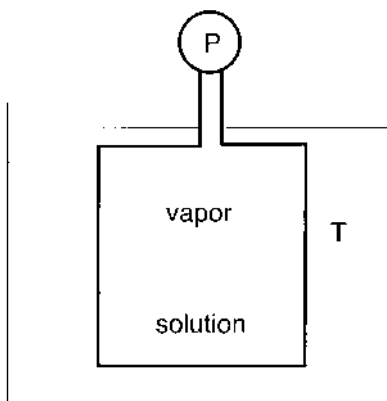
$$K_{12} = \frac{K_2}{K_1} \quad (75)$$

(i.e., the distribution coefficient is the ratio of Henry's law coefficients for the solute in the two solvents). Note that the solute has a greater tendency to be distributed into the solvent in which it has the lower Henry's law constant (because it has a lower escaping tendency from that solvent).

Equation (75) may be derived more simply by using an alternative measure of escaping tendency, the partial pressure of  $i$  above the solution. This partial pressure must be equal above the two solutions between which the distribution of  $i$  is equilibrated (Problem 18). Extraction is not a colligative property because it is the solute, not the solvent, that is distributing between the two phases. The distribution coefficient, like the Henry's law constants, depends on the identity of the solutes, as well as that of the solvent.

## 8.8 Phase Diagram of a Binary Ideal Solution

In [Chapter 6](#), we found that phase diagrams were an effective way of communicating information concerning phase transformations of single-component systems. These diagrams are even more essential when dealing with the more complicated phase transformations of multicomponent systems. A binary system has two components. For a binary solution in equilibrium with its vapor, there are two degrees of freedom ( $f = 2 - 2 + 2 = 2$ ). If we investigate the phase diagram at a particular temperature, there is only one additional degree of freedom. A thermostat for preparing such a system is shown in [Fig. 5](#). The container

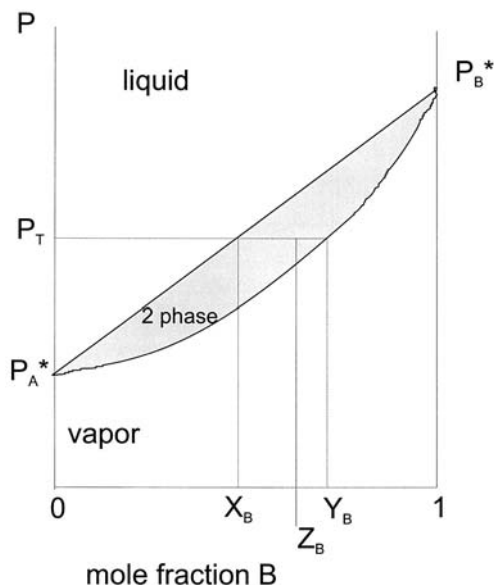


**Figure 5** Thermostat for preparing a binary system.

containing the solution in equilibrium with its vapor is equipped with a pressure gauge and it is assumed that all of the air has been removed from the container.<sup>5</sup> Because there is only a single degree of freedom, reading the pressure on the gauge determines the concentration,  $x_B$ , of the liquid phase. For an ideal solution, Eq. (41) gives the relation between these two intensive variables. With only a single degree of freedom, the pressure measurement must also determine the concentration of the vapor phase. In fact, the vapor-phase mole fraction of  $B$ ,  $y_B = P_B/P$ , can be easily calculated (see Problem 6). Both the liquid and vapor mole fractions as a function of  $P$  are plotted in Fig. 6, known as a *pressure versus concentration liquid–vapor-phase diagram*, or more simply as a *vapor-pressure diagram*. Following convention, pressure is plotted as the  $y$ -axis of this graph.

The concentrations of both the liquid phase,  $x_B$ , and the vapor phase,  $y_B$ , are determined by the pressure. The line relating vapor pressure to liquid-phase concentration is called the *bubble-point line*, because when the pressure on the liquid is reduced to this value, bubbles appear. The lower line, which relates vapor pressure to the vapor-phase concentration, is called the *dew-point line* because when vapor is compressed to give this pressure, liquid droplets appear on surfaces.

The overall concentration of the system,  $z_B$ , is not determined by the pressure because the overall concentration depends on the relative amounts of the two phases and is not an intensive degree of freedom of the system. Nevertheless, the overall concentration, being the weighted average of the liquid and vapor-phase concentrations, must lie between the bubble-point line and the dew-point line on a horizontal line at  $P$ . This line is known as the *tie line* (because it “ties together” the coexisting phases) and it lies in the region between the liquid and vapor curves, which is called the *two-phase region*. In this book, two-phase



**Figure 6** Lever rule.

regions will be shaded, but often in the literature they are not distinguished from single-phase regions. If the system consists mainly of the liquid phase, the point representing the overall concentration lies very close to the liquid curve on the tie line; whereas if it is mainly vapor phase, the point lies very close to the vapor line. In fact, the mole-weighted deviation of the mole fractions of these phases from that of the overall mole fraction balances around the system mole fraction.<sup>6</sup> This gives rise to the *lever rule*, which, referring to Fig. 6, can be written as

$$n_g(y_B - z_B) = n_l(z_B - x_B) \quad (76)$$

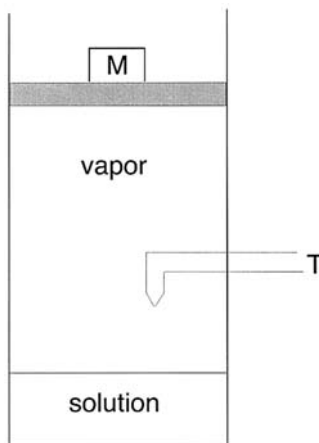
A more formal proof of this simple method of determining the relative amounts of the phases from the concentrations of the phases and the system is treated in Problem 7. Tie lines are not provided on phase diagrams, but are drawn by the user of the diagram at the pressure of interest.

It is important to note that the system consists of two phases only in the two-phase region. If the point representing the overall concentration and the pressure lies above the liquid curve in Fig. 6, the system consists only of liquid with  $x_B = z_B$ . With only a single phase, the system has three degrees of freedom, which are most conveniently taken as  $T$ ,  $P$ , and  $x_B = z_B$ . Thus, at a given temperature, pressure and composition can both be varied, as long as the system remains in this one-phase region. In a similar manner, at pressures that put the

point representing the system below the vapor curve in Fig. 6, only a single vapor phase, with  $y_B = z_B$ , exists.

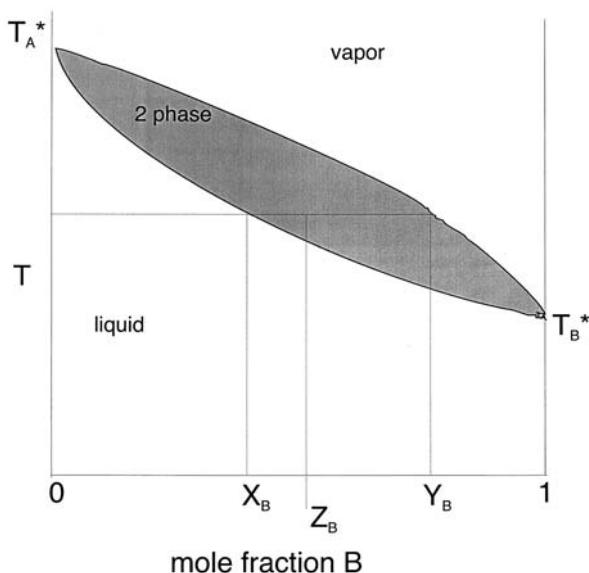
An alternative method of studying two-component systems is by holding the pressure constant and allowing the temperature to vary. An apparatus for doing this is shown in Fig. 7. The constant pressure is completely established by the mass,  $M$ , on the weightless piston (and by atmospheric pressure). The system temperature is measured by the thermocouple. The *temperature–concentration liquid-vapor phase diagram* which describes this binary system at a given pressure is called a *boiling-point diagram* and is shown in Fig. 8. Note that the liquid region is at the bottom of the boiling-point diagram, whereas it is at the top of the vapor-pressure diagram. The two-phase region is enclosed by the bubble-point curve on the bottom and the dew-point curve on the top. Neither of these curves is a straight line, as there is no Raoult's law for boiling points. Note that in this ideal solution, the addition of small amounts of the more volatile component ( $B$ ) to the less volatile component ( $A$ ) *lowers* the boiling point of the solution. This is in contrast to the boiling-point elevation discussed regarding colligative properties, where it was assumed that only one component of the solution (the solvent) was volatile. Because the temperature is uniform throughout the system, when liquid and vapor coexist at equilibrium, these two phases are connected by a horizontal tie line. Tie lines and the lever rule may be used to determine the relative amounts of coexisting phases on boiling-point diagrams, just as they are used on vapor-pressure diagrams.

The tie line between liquid and vapor concentration shows that the vapor is enriched in the more volatile component. This is the basis for the process of



**Figure 7** Apparatus for the two-component system allowing the temperature to vary.



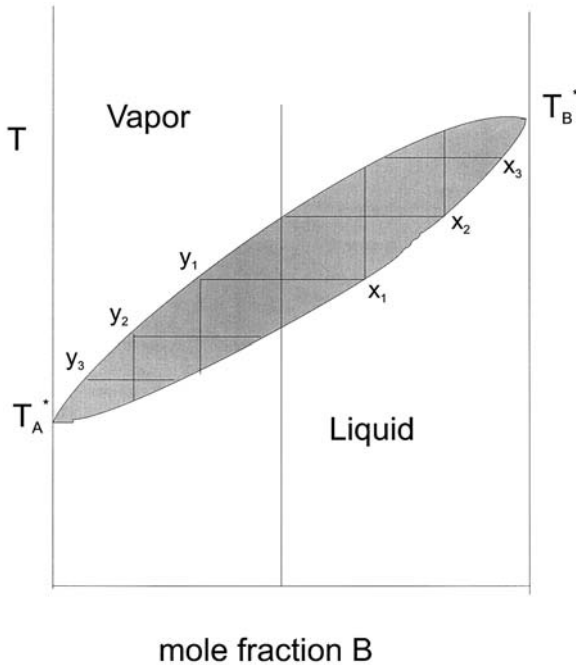


**Figure 8** Boiling-point diagram.

*distillation*, where a solution is separated into two solutions: one enriched in the more volatile component (obtained by condensing the vapor) and the other enriched in the less volatile component. If these two solutions are then each subjected to additional distillation steps, further separation of the original solution into its two components is possible. In Fig. 9, this process is illustrated for the case in which, at each stage of distillation, half of the volume of solution is converted into vapor.  $x_1, x_2, x_3, \dots$  are the successive liquid-phase concentrations and  $y_1, y_2, y_3, \dots$  are the successive vapor phase concentrations. As can be seen, after a number of steps, separation into nearly pure components is achieved. Successive distillation is extremely tedious and practically never performed. *Fractional distillation* is a continuous method for carrying out successive distillations by continuously condensing and evaporating solutions in a distillation column. Industrial distillation columns may achieve more than 100 successive liquid–vapor equilibrations (each liquid–vapor equilibration is known as a *theoretical plate*; see Problem 21), with resulting excellent separation of binary solutions into their components.

### 8.8.1 Solid–Liquid Equilibrium

Phase diagrams can present information on liquid–solid equilibrium, as well as on liquid–vapor equilibrium. At fixed pressure, a pure liquid freezes at a definite



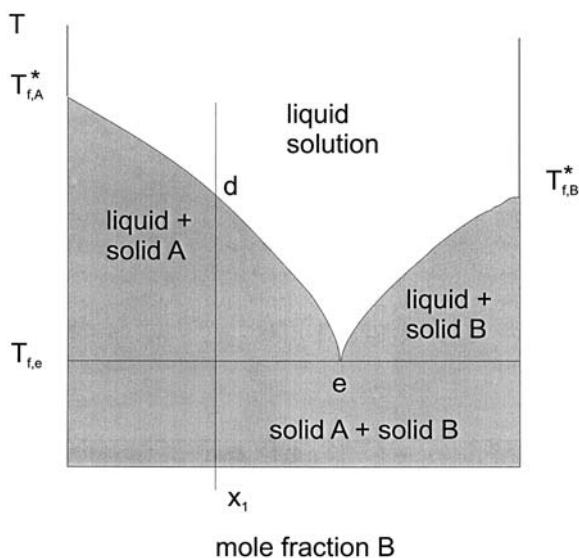
**Figure 9** Distillation process.

temperature. When  $B$  is added to liquid  $A$ , forming a very dilute solution, the freezing point of the solution is lowered. This behavior is shown in Fig. 10, where on the left-hand side of the diagram, it is assumed that the solid that freezes out is pure  $A$ . (A solid solution is not formed). The two-phase region represents equilibrium between pure  $A$  and the liquid solution.

This phenomenon can also be looked at in terms of the dissolution of solid  $A$  in the solution (even though  $A$ , because it is present at a greater concentration, would usually be considered the solvent of this solution). As the temperature is lowered, the solubility of  $A$  in the solution decreases. If the solution is ideal, we can use Eq. (55) with  $a_A = x_A$  to calculate the solubility of  $A$  in the solution at temperatures below the freezing point of  $A$ :

$$\ln x_A = \frac{\Delta_{\text{fus}} H_A^*}{R} \left( \frac{1}{T_{f,A}^*} - \frac{1}{T} \right) \quad (77)$$

Equation (77) provides solubilities at temperatures much lower than  $T_{f,A}^*$  with reasonable accuracy only in rare cases in which solutions follow ideal behavior.



**Figure 10** Solid–liquid phase diagram.

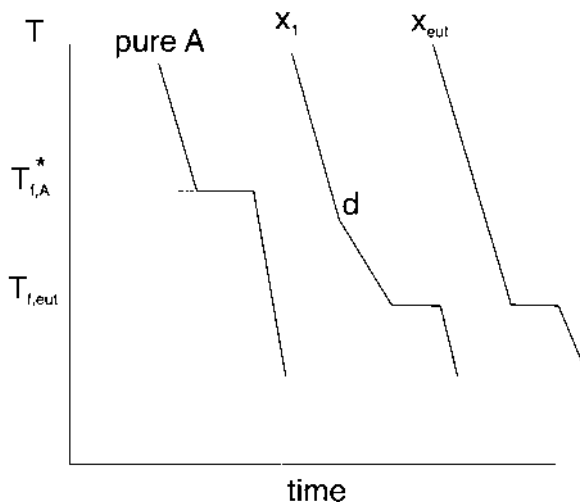
However, the general form of the curve on the left-hand side of Fig. 10 is followed even in nonideal systems. Looking at the right-hand side of Fig. 10, we see that as *A* is added to pure *B*, the freezing point of the solution is also lowered. (We have also assumed that *B* does not form solid solutions.) Alternatively, this can be described as reducing the solubility of *B* in the solution as the temperature of the solution is lowered below the freezing point of pure *B*. At an intermediate concentration, the two solubility curves in Fig. 10 meet at point *e* and a solution with the lowest freezing point is obtained. This solution is known as the *eutectic* and the concentration and temperature at point *e*, is known as the eutectic concentration and temperature.

It is interesting to consider what happens as solutions of different concentrations are cooled. The pure components, of course, freeze at a single temperature, and temperature remains constant until all of the liquid is frozen. As the solution of concentration  $x_1$  is cooled, pure *A* begins to freeze out at point *d*, and the solution becomes more enriched in *B*. Microscopic investigation shows that fairly large crystals of *A* are formed at this point. With further cooling, the concentration of the remaining solution moves along the curve *d*–*e*. The relative amounts of pure *A* and the solution can be obtained by drawing the tie line at the appropriate temperature and using the lever rule. When the eutectic temperature at point *e* is reached, pure solid *B* begins to appear. There are now three phases in

equilibrium: pure solid  $A$ , pure solid  $B$ , and the solution of the eutectic composition. Because pressure is fixed, the phase rule tells us that there are  $f = 2 - 3 + 2 - 1$  (pressure) = 0 degrees of freedom. On a two-component phase diagram, the condition of three phases in equilibrium is represented by a horizontal line on the diagram.<sup>7</sup> No further reduction of temperature can occur until all the remaining eutectic solution is converted into  $A$  and  $B$ .

Microscopic investigation of the solid formed when a eutectic freezes indicates that it is a mixture of very fine particles of pure  $A$  and pure  $B$ , rather than a solid solution of  $A$  and  $B$ . If a solution that has the eutectic composition is cooled, freezing occurs at a single concentration, just like a pure component. A eutectic can be distinguished from a pure component either by microscopic inspection of the solid or by adding one of the pure components. In the eutectic case, the freezing point of the solution will be increased by this addition, rather than decreased, as occurs for a pure substance.

The structure of phase diagrams can be investigated by *thermal analysis*. This is performed by measuring *cooling curves*, which are temperature versus time diagrams for the cooling of the substance from the molten state. Assuming a constant rate of heat loss from the system, the slope of the cooling curve is inversely proportional to the heat capacity of the system. The cooling curve for pure component  $A$  for the solution of composition  $x_1$ , and for a solution of the eutectic composition are shown in Fig. 11. The cooling curves of the pure component and the eutectic both show horizontal segments as the liquid is



**Figure 11** Cooling curve for component  $A$ , solution of composition  $x_1$ , and solution of the eutectic composition.

converted into solid at the melting point and the *eutectic halt*, respectively. The system can be considered to have infinite heat capacity at these temperatures. The solution of concentration  $x_1$  first shows a *break* (a sudden change in slope) in its cooling curve at point d, as additional heat must be removed for solidification, and then a halt, as the remaining eutectic is converting into a solid. By determining the cooling curves at different concentrations, the phase boundaries can be determined.

## Questions

1. Which of the following properties of a given solution will change as the temperature of the solution is increased?

- (a) Density
- (b) Molarity
- (c) Molality
- (d) Mole fraction
- (e) Partial pressure (of a gaseous solution)

2. Dissolving a gas in a liquid can be thought of as a two-step process: First, cavities are made in the liquid and then the gas molecules are placed in the cavities. Wolfenden and Radzicka (Science 265:936, 1994) have noted that the solubility of water in cyclohexane at 26°C is equal to the concentration of water vapor in equilibrium with liquid water at this temperature. Show that this observation implies that the Gibbs free energy to make water-sized cavities in cyclohexane is equal to the Gibbs free energy of attraction of water molecules to cyclohexane in these cavities.

3. For which of the following solutions at 298 K would you expect Raoult's law to be a good approximation for all components:

- (a)  $\text{C}_2\text{H}_5^{35}\text{Cl}-\text{C}_2\text{H}_5^{37}\text{Cl}$
- (b) Benzene-toluene
- (c) Benzene-naphthalene
- (d) Benzene- $\text{CCl}_4$

4. For a solid, there is often a "solubility" (i.e., a maximum amount that will dissolve in a solvent at a given temperature). Is there a "solubility" for a gas in a solvent? What is the difference?

5. The maximum pressure in an auto radiator is determined by the release pressure of the radiator cap. Do a phase-rule analysis and determine whether each of the following statements is true or false:

- (a) With just water in the radiator, the maximum temperature is completely determined by the release pressure.
- (b) With a water-ethylene glycol (antifreeze) solution in the radiator, the maximum temperature can be varied by changing the concentration of the solution.

6. The heat of solution for NaCl in water is 3.9 kJ/mol. Because this process is endothermic, how can you explain the large solubility of NaCl in water? Will this solubility increase or decrease as the temperature is increased?

7. For an ideal solution, is each of the following greater than, less than, or equal to zero or is there no way to tell?

- (a) The partial pressure of the less volatile component minus the vapor pressure of pure less volatile component
- (b) The partial pressure of the more volatile component minus the vapor pressure of pure less volatile component
- (c) The total pressure above the solution minus the vapor pressure of the less volatile component
- (d) The total pressure above the solution minus the vapor pressure of the more volatile component

8. Show that in the ideal solution limit, for a group of solvents obeying Trouton's law, the fractional change of boiling point produced by a given mole fraction of solute is the same for all the solvents.

9. The Henry's law constant of  $N_2$  in water reaches a maximum value at  $\sim 60^\circ\text{C}$ . What does this imply will happen as water in equilibrium with the  $N_2$  of air is heated from room temperature to  $60^\circ\text{C}$ ?

10. Referring to Fig. 5, if at fixed temperature there are two nonreacting, nonvolatile solutes in an ideally dilute solution,

- (a) does measuring the pressure of the solution determine  $x_B$ ?
- (b) does measuring the pressure completely determine the system?

11. Referring to Fig. 6, if the pressure over a liquid of mole fraction of  $B$  of 0.4 is slowly reduced, what is the mole fraction of the first drop of vapor that is formed? If the reduction in pressure continues so that the liquid is continuously converted into gas, what is the mole fraction of  $B$  in the last drop of liquid to evaporate?

12. Before ethylene glycol [melting point (mp) =  $-13^\circ\text{C}$ ; boiling point (bp) =  $199^\circ\text{C}$ ] became widely adopted as automobile radiator antifreeze, methanol (bp =  $65^\circ\text{C}$ ) was used for this purpose. Methanol is less expensive. However, unlike ethylene glycol, it is not an "all-season" coolant and must be removed from the radiation in hot weather. Explain this difference.

13. Assuming that you have a very accurate and sensitive thermocouple, how would you use it to determine the freezing point of a solution?

14. Although Raoult's law is not accurate for the solubility of gases in solvents, its use can explain some rough trends in solubility. Using Raoult's law show that the solubility of a gas in a liquid is

- (a) proportional to the partial pressure of the gas
- (b) reduced as temperature is increased
- (c) greater for gases with higher boiling points.

## Problems

1. An amount of NaCl is dissolved in water at 25°C to make a 0.0200 *M* solution. What is the molarity of this solution at 80°C? You can take the thermal expansion coefficient as that of water,  $2.1 \times 10^{-4} \text{ K}^{-1}$ , over the temperature range of this problem. What is the molality of the solution at 25°C and 80°C?
2. An aqueous solution containing 45.02 g of NaCl per liter of solution has a density of 1.029 kg/L. Calculate the molarity, molality, and mole fraction of the solution.
3. Derive Eq. (5) and find an expression for  $c_i$  in terms of the mole fractions in the solution.
4. In 1.0 *M* methanol in water solution, how far apart, on average, are the methanol molecules? Treating the water molecules as spheres of 0.3 nm diameter, how many water molecules on the average are between two methanol molecules?
5. Derive Eq. (21).
6. Show that the mole fraction of *B* in the vapor phase above an ideal binary solution consisting of components *A* and *B* with vapor pressures  $P_A^*$  and  $P_B^*$  is  $y_B = P_B^*(P - P_A^*)/P(P_B^* - P_A^*)$ , when the solution vapor pressure is *P*.
7. Prove Eq. (76). (Suggestion: Write the number of moles of *B* in the system,  $n_B$ , in two different ways: as  $z_B$  times the total moles of the system and as the sum of the moles of *B* in each phase. Equate these two expressions for  $n_B$ .)
8. Derive Eq. (54).
9. Assume that benzene and naphthalene form an ideal solution and that the solids are pure components (no solid solutions are formed) with melting points at 1.0 atm pressure of 5.5°C and 80.5°C. Estimate the composition and melting point of the benzene–naphthalene eutectic using Eq. (77).
10. What is the entropy change when 20 g of benzene and 20 g of toluene are mixed to form an ideal solution?
11. The vapor pressures of benzene and toluene at 90°C are 1034 and 413 torr, respectively. What is the mole fraction of benzene in the benzene–toluene solution that boils at 90°C?
12. A trimeric protein,  $\mathbf{P}_3$ , dissociates completely into three monomer units in solution. What is the chemical potential and activity of  $\mathbf{P}_3$  in terms of those of the monomer?
13. Reverse osmosis is a process whereby seawater can be purified by passing the water molecules through a semipermeable membrane. What is the minimum amount of work that must be done to obtain 1.0 L of pure water by reverse osmosis, starting with seawater that is 0.7 *M* NaCl? Compare this work with the energy required to vaporize the water in a distillation process.
14. An air-breathing creature might be able to breathe with its lungs filled with a liquid, if concentrations (mol/L) of oxygen in the liquid were comparable to the concentration of oxygen in ambient air. What Henry's law constant for oxygen would be required for a

liquid so that it contains an oxygen concentration equal to the air when it is equilibrated with ambient air?

15. Show that for a substance obeying Trouton's rule, the boiling-point elevation constant is proportional to the boiling point.

16. Pure benzene freezes at 5.50°C and has a density of 0.876 g/mL. A solution of 1.7 g of nitrobenzene in 250 mL benzene freezes at 5.18°C. What is the molality-based freezing-point depression constant of benzene and at what temperature does a solution containing 3.2 g of bromobenzene in 250 mL of benzene freeze? (You may make the ideally dilute approximation for both these solutions.)

17. The Henry's law constants of N<sub>2</sub> and O<sub>2</sub> in water at 0°C are  $5.2 \times 10^{-4} \text{ atm}^{-1}$  and  $2.8 \times 10^{-4} \text{ atm}^{-1}$ , respectively. What is the freezing point of water in equilibrium with 1.0 atm air (78% N<sub>2</sub> and 21% O<sub>2</sub>)?

18. Derive Eq. (75) by equating the partial pressure of solute above the two solutions between which it is equilibrated.

19. Show that

$$\frac{d \ln K_{12}}{dT} = \frac{\Delta_{\text{trans}} H^\circ}{RT^2}$$

where  $K_{12}$  is the distribution coefficient of a solute between solvents 1 and 2 and  $\Delta_{\text{trans}} H^\circ$  is the standard molar enthalpy change for transfer of the solute from solvent 2 to solvent 1.

20. Show that the chemical potentials for the ideal solution satisfy the Gibbs–Duhem relation [Eq. (29)].

21. A *theoretical plate* is defined as the degree of separation attained for an infinitesimal vaporization at equilibrium (i.e., the concentration of liquid in a theoretical plate is that of the first bit of vapor to be formed from the liquid in the previous one). Using this definition, approximately how many theoretical plates would be required to achieve a separation into a vapor with  $x_B = 0.1$  and a liquid with  $x_B = 0.9$  for the system described by the boiling-point diagram in Fig. 9.

22.\* In the ideal macromolecular solution, the solute molecules consist of a large number,  $x$ , of segments, but each segment has size and attractive interactions similar to that of the solvent molecules. Several statistical theories have given as the entropy of mixing of such a solution from  $n_A$  mol of solvent and  $n_B$  mol of macromolecule

$$\Delta_{\text{mix}} S = -R \left[ n_A \ln \left( \frac{n_A}{n_A + x n_B} \right) + n_B \ln \left( \frac{n_B}{n_A + x n_B} \right) \right]$$

(See PJ Flory. Principles of Polymer Chemistry. Ithaca, NY Cornell Press, (1953, pp 495–503.)  $\Delta_{\text{mix}} H$  is zero.



- (a) Use the Gibbs free energy of this solution to show that

$$\mu_A = \mu_A^0 + RT \ln\left(\frac{n_A}{n_A + xn_B}\right) + RT\left(1 - \frac{n_A + n_B}{n_A + xn_B}\right)$$

$$\mu_B = \mu_B^0 + RT \ln\left(\frac{xn_B}{n_A + xn_B}\right) + RT\left(1 - \frac{x(n_A + n_B)}{n_A + n_B}\right)$$

- (b) Show that these chemical potentials satisfy the Gibbs–Duhem relation [Eq. (29)].
- (c) Show that for a very dilute solution,  $\ln a_A \approx -x_B$ , as would be required to give Eqs. (61)–(63) for the colligative properties of such a solution.
23. What are  $\Delta_{\text{mix}}H$ ,  $\Delta_{\text{mix}}S$ , and  $\Delta_{\text{mix}}G$  of an ideally dilute solution?

## Notes

1. There are some exceptions to this for fluids above the critical temperature. See RP Gordon. J Chem Educ 49:249, 1972.
2. As discussed in [Chapter 7](#), the reference states of elements are chosen as the state that the element is stable in at 1.0 bar pressure and the temperature of interest.
3. Some authors write this as  $m_i/m^0$  and  $c_i/c^0$ , where  $m^0 = 1.0 \text{ molal}$  and  $c^0 = 1.0 \text{ molar}$ .
4.  $\ln(1 - x_B) = -x_B - \frac{1}{2}x_B^2 - \dots$ .
5. From the result obtained in [Chapter 6](#), we do not expect the presence of atmospheric pressure to appreciably affect the vapor pressure of the solution.
6. In much the same way that the average grade in a three-student class with grades of 60, 60, and 90 is 70 [ $2(70 - 60) = 90 - 70$ ].
7. This should distinguished from a horizontal line drawn in a two-phase region of the diagram by the reader to connect two phases that are at equilibrium.