

## 12.4: Colligative Properties of a Dilute Solution

The **colligative properties** of a solution are usually considered to be:

1. Note that all four properties are defined by an equilibrium between the liquid solution and a solid, liquid, or gas phase of the pure solvent. The properties called colligative (Latin: *tied together*) have in common a dependence on the concentration of solute particles that affects the solvent chemical potential.

Figure 12.3 illustrates the freezing-point depression and boiling-point elevation of an aqueous solution. At a fixed pressure, pure liquid water is in equilibrium with ice at the freezing point and with steam at the boiling point. These are the temperatures at which  $\text{H}_2\text{O}$  has the same chemical potential in both phases at this pressure. At these temperatures, the chemical potential curves for the phases intersect, as indicated by open circles in the figure. The presence of dissolved solute in the solution causes a lowering of the  $\text{H}_2\text{O}$  chemical potential compared to pure water at the same temperature. Consequently, the curve for the chemical potential of  $\text{H}_2\text{O}$  in the solution intersects the curve for ice at a lower temperature, and the curve for steam at a higher temperature, as indicated by open triangles. The freezing point is depressed by  $\Delta T_f$ , and the boiling point (if the solute is nonvolatile) is elevated by  $\Delta T_b$ .

Although these expressions provide no information about the activity coefficient of a solute, they are useful for estimating the solute molar mass. For example, from a measurement of any of the colligative properties of a dilute solution and the appropriate theoretical relation, we can obtain an approximate value of the solute molality  $m_B$ . (It is only approximate because, for a measurement of reasonable precision, the solution cannot be extremely dilute.) If we prepare the solution with a known amount  $n_A$  of solvent and a known mass of solute, we can calculate the amount of solute from  $n_B = n_A M_A m_B$ ; then the solute molar mass is the solute mass divided by  $n_B$ .

### 12.4.1 Freezing-point depression

As in Sec. 12.2.1, we assume the solid that forms when a dilute solution is cooled to its freezing point is pure component A.

Equation 12.3.6 gives the general dependence of temperature on the composition of a binary liquid mixture of A and B that is in equilibrium with pure solid A. We treat the mixture as a solution. The solvent is component A, the solute is B, and the temperature is the freezing point  $T_f$ :

$$\left( \frac{\partial T_f}{\partial x_A} \right)_p = \frac{T_f^2}{\Delta_{\text{sol},A}H} \left[ \frac{\partial(\mu_A/T)}{\partial x_A} \right]_{T,p} \quad (12.4.1)$$

Consider the expression on the right side of this equation in the limit of infinite dilution. In this limit,  $T_f$  becomes  $T_f^*$ , the freezing point of the pure solvent, and  $\Delta_{\text{sol},A}H$  becomes  $\Delta_{\text{fus},A}H$ , the molar enthalpy of fusion of the pure solvent.

To deal with the partial derivative on the right side of Eq. 12.4.1 in the limit of infinite dilution, we use the fact that the solvent activity coefficient  $\gamma_A$  approaches 1 in this limit. Then the solvent chemical potential is given by the Raoult's law relation

$$\mu_A = \mu_A^* + RT \ln x_A \quad (12.4.2)$$

(solution at infinite dilution)

where  $\mu_A^*$  is the chemical potential of A in a pure-liquid reference state at the same  $T$  and  $p$  as the mixture. (At the freezing point of the mixture, the reference state is an unstable supercooled liquid.)

If the solute is an electrolyte, Eq. 12.4.2 can be derived by the same procedure as described in Sec. 9.4.6 for an ideal-dilute binary solution of a nonelectrolyte. We must calculate  $x_A$  from the amounts of all species present at infinite dilution. In the limit of infinite dilution, any electrolyte solute is completely dissociated to its constituent ions: ion pairs and weak electrolytes are completely dissociated in this limit. Thus, for a binary solution of electrolyte B with  $\nu$  ions per formula unit, we should calculate  $x_A$  from

$$x_A = \frac{n_A}{n_A + \nu n_B} \quad (12.4.3)$$

where  $n_B$  is the amount of solute formula unit. (If the solute is a nonelectrolyte, we simply set  $\nu$  equal to 1 in this equation.)

From Eq. 12.4.2, we can write

$$\left[ \frac{\partial(\mu_A/T)}{\partial x_A} \right]_{T,p} \rightarrow R \quad \text{as } x_A \rightarrow 1 \quad (12.4.4)$$

In the limit of infinite dilution, then, Eq. 12.4.1 becomes

$$\lim_{x_A \rightarrow 1} \left( \frac{\partial T_f}{\partial x_A} \right)_p = \frac{R(T_f^*)^2}{\Delta_{\text{fus},A}H} \quad (12.4.5)$$

It is customary to relate freezing-point depression to the solute concentration  $c_B$  or molality  $m_B$ . From Eq. 12.4.3, we obtain

$$1 - x_A = \frac{\nu n_B}{n_A + \nu n_B} \quad (12.4.6)$$

In the limit of infinite dilution, when  $\nu n_B$  is much smaller than  $n_A$ ,  $1 - x_A$  approaches the value  $\nu n_B/n_A$ . Then, using expressions in Eq. 9.1.14, we obtain the relations

$$\begin{aligned} dx_A &= -d(1 - x_A) = -\nu d(n_B/n_A) \\ &= -\nu V_A^* dc_B \\ &= -\nu M_A dm_B \end{aligned} \quad (12.4.7)$$

(binary solution at infinite dilution)

which transform Eq. 12.4.5 into the following (ignoring a small dependence of  $V_A^*$  on  $T$ ):

$$\lim_{c_B \rightarrow 0} \left( \frac{\partial T_f}{\partial c_B} \right)_p = -\frac{\nu V_A^* R(T_f^*)^2}{\Delta_{\text{fus},A}H} \quad (12.4.8)$$

$$\lim_{m_B \rightarrow 0} \left( \frac{\partial T_f}{\partial m_B} \right)_p = -\frac{\nu M_A R(T_f^*)^2}{\Delta_{\text{fus},A}H} \quad (12.4.1)$$

We can apply these equations to a nonelectrolyte solute by setting  $\nu$  equal to 1.

As  $c_B$  or  $m_B$  approaches zero,  $T_f$  approaches  $T_f^*$ . The freezing-point depression (a negative quantity) is  $\Delta T_f = T_f - T_f^*$ . In the range of molalities of a dilute solution in which  $(\partial T_f / \partial m_B)_p$  is given by the expression on the right side of Eq. 12.4.8, we can write

$$\Delta T_f = -\frac{\nu M_A R(T_f^*)^2}{\Delta_{\text{fus},A}H} m_B \quad (12.4.9)$$

The **molal freezing-point depression constant** or cryoscopic constant,  $K_f$ , is defined for a binary solution by

$$K_f \stackrel{\text{def}}{=} -\lim_{m_B \rightarrow 0} \frac{\Delta T_f}{\nu m_B} \quad (12.4.10)$$

and, from Eq. 12.4.9, has a value given by

$$K_f = \frac{M_A R(T_f^*)^2}{\Delta_{\text{fus},A}H} \quad (12.4.11)$$

The value of  $K_f$  calculated from this formula depends only on the kind of solvent and the pressure. For  $\text{H}_2\text{O}$  at 1 bar, the calculated value is  $K_b = 1.860 \text{ K kg mol}^{-1}$  (Prob. 12.4).

In the dilute binary solution, we have the relation

$$\Delta T_f = -\nu K_f m_B \quad (12.4.12)$$

(dilute binary solution)

This relation is useful for estimating the molality of a dilute nonelectrolyte solution ( $\nu=1$ ) from a measurement of the freezing point. The relation is of little utility for an electrolyte solute, because at any electrolyte molality that is high enough to give a measurable depression of the freezing point, the mean ionic activity coefficient deviates greatly from unity and the relation is not accurate.

## 12.4.2 Boiling-point elevation

We can apply Eq. 12.3.6 to the boiling point  $T_b$  of a dilute binary solution. The pure phase of A in equilibrium with the solution is now a gas instead of a solid. (We must assume the solute is nonvolatile or has negligible partial pressure in the gas phase.) Following the procedure of Sec. 12.4.1, we obtain

$$\lim_{m_B \rightarrow 0} \left( \frac{\partial T_b}{\partial m_B} \right)_p = \frac{\nu M_A R (T_b^*)^2}{\Delta_{\text{vap},A} H} \quad (12.4.13)$$

where  $\Delta_{\text{vap},A} H$  is the molar enthalpy of vaporization of pure solvent at its boiling point  $T_b^*$ .

The **molal boiling-point elevation constant** or ebullioscopic constant,  $K_b$ , is defined for a binary solution by

$$K_b \stackrel{\text{def}}{=} \lim_{m_B \rightarrow 0} \frac{\Delta T_b}{\nu m_B} \quad (12.4.14)$$

where  $\Delta T_b = T_b - T_b^*$  is the boiling-point elevation. Accordingly,  $K_b$  has a value given by

$$K_b = \frac{M_A R (T_b^*)^2}{\Delta_{\text{vap},A} H} \quad (12.4.15)$$

For the boiling point of a dilute solution, the analogy of Eq. 12.4.12 is

$$\Delta T_b = \nu K_b m_B \quad (12.4.16)$$

(dilute binary solution)

Since  $K_f$  has a larger value than  $K_b$  (because  $\Delta_{\text{fus},A} H$  is smaller than  $\Delta_{\text{vap},A} H$ ), the measurement of freezing-point depression is more useful than that of boiling-point elevation for estimating the molality of a dilute solution.

## 12.4.3 Vapor-pressure lowering

In a binary two-phase system in which a solution of volatile solvent A and nonvolatile solute B is in equilibrium with gaseous A, the vapor pressure of the solution is equal to the system pressure  $p$ .

Equation 12.3.7 gives the general dependence of  $p$  on  $x_A$  for a binary liquid mixture in equilibrium with pure gaseous A. In this equation,  $\Delta_{\text{sol},A} V$  is the molar differential volume change for the dissolution of the gas in the solution. In the limit of infinite dilution,  $-\Delta_{\text{sol},A} V$  becomes  $\Delta_{\text{vap},A} V$ , the molar volume change for the vaporization of pure solvent. We also apply the limiting expressions of Eqs. 12.4.4 and 12.4.7. The result is

$$\lim_{c_B \rightarrow 0} \left( \frac{\partial p}{\partial c_B} \right)_T = -\frac{\nu V_A^* R T}{\Delta_{\text{vap},A} V} \quad \lim_{m_B \rightarrow 0} \left( \frac{\partial p}{\partial m_B} \right)_T = -\frac{\nu M_A R T}{\Delta_{\text{vap},A} V} \quad (12.4.17)$$

If we neglect the molar volume of the liquid solvent compared to that of the gas, and assume the gas is ideal, then we can replace  $\Delta_{\text{vap},A} V$  in the expressions above by  $V_A^*(g) = RT/p_A^*$  and obtain

$$\lim_{c_B \rightarrow 0} \left( \frac{\partial p}{\partial c_B} \right)_T \approx -\nu V_A^* p_A^* \quad \lim_{m_B \rightarrow 0} \left( \frac{\partial p}{\partial m_B} \right)_T \approx -\nu M_A p_A^* \quad (12.4.18)$$

where  $p_A^*$  is the vapor pressure of the pure solvent at the temperature of the solution.

Thus, approximate expressions for vapor-pressure lowering in the limit of infinite dilution are

$$\Delta p \approx -\nu V_A^* p_A^* c_B \quad \text{and} \quad \Delta p \approx -\nu M_A p_A^* m_B \quad (12.4.19)$$

We see that the lowering in this limit depends on the kind of solvent and the solution composition, but not on the kind of solute.

## 12.4.4 Osmotic pressure

The osmotic pressure  $\Pi$  is an intensive property of a solution and was defined in Sec. 12.2.2. In a dilute solution of low  $\Pi$ , the approximation used to derive Eq. 12.2.11 (that the partial molar volume  $V_A$  of the solvent is constant in the pressure range from  $p$  to  $p + \Pi$ ) becomes valid, and we can write

$$\Pi = \frac{\mu_A^* - \mu_A}{V_A} \quad (12.4.20)$$

In the limit of infinite dilution,  $\mu_A^* - \mu_A$  approaches  $-RT \ln x_A$  (Eq. 12.4.2) and  $V_A$  becomes the molar volume  $V_A^*$  of the pure solvent. In this limit, Eq. 12.4.20 becomes

$$\Pi = -\frac{RT \ln x_A}{V_A^*} \quad (12.4.21)$$

from which we obtain the equation

$$\lim_{x_A \rightarrow 1} \left( \frac{\partial \Pi}{\partial x_A} \right)_{T,p} = -\frac{RT}{V_A^*} \quad (12.4.22)$$

The relations in Eq. 12.4.7 transform Eq. 12.4.22 into

$$\lim_{c_B \rightarrow 0} \left( \frac{\partial \Pi}{\partial c_B} \right)_{T,p} = \nu RT \quad (12.4.23)$$

$$\lim_{m_B \rightarrow 0} \left( \frac{\partial \Pi}{\partial m_B} \right)_{T,p} = \frac{\nu RT M_A}{V_A^*} = \nu \rho_A^* RT \quad (12.4.24)$$

Equations 12.4.23 and 12.4.24 show that the osmotic pressure becomes independent of the kind of solute as the solution approaches infinite dilution. The integrated forms of these equations are

$$\Pi = \nu c_B RT \quad (12.4.25)$$

(dilute binary solution)

$$\Pi = \frac{RT M_A}{V_A^*} \nu m_B = \rho_A^* RT \nu m_B \quad (12.4.26)$$

(dilute binary solution)

Equation 12.4.25 is **van't Hoff's equation** for osmotic pressure. If there is more than one solute species,  $\nu c_B$  can be replaced by  $\sum_{i \neq A} c_i$  and  $\nu m_B$  by  $\sum_{i \neq A} m_i$  in these expressions.

In Sec. 9.6.3, it was stated that  $\Pi/m_B$  is equal to the product of  $\phi_m$  and the limiting value of  $\Pi/m_B$  at infinite dilution, where  $\phi_m = (\mu_A^* - \mu_A)/RT M_A \sum_{i \neq A} m_i$  is the osmotic coefficient. This relation follows directly from Eqs. 12.2.11 and 12.4.26.

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