

## 12.2: Solvent Chemical Potentials from Phase Equilibria

Section 9.6.3 explained how we can evaluate the activity coefficient  $\gamma$  of a nonelectrolyte solute of a binary solution if we know the variation of the osmotic coefficient of the solution from infinite dilution to the molality of interest. A similar procedure for the mean ionic activity coefficient of an electrolyte solute was described in Sec. 10.6.

The physical measurements needed to find the osmotic coefficient  $\gamma$  of a binary solution must be directed to the calculation of the quantity  $\Delta\mu$ , the difference between the chemical potentials of the pure solvent and the solvent in the solution at the temperature and pressure of interest. This difference is positive, because the presence of the solute reduces the solvent's chemical potential.

To calculate  $\gamma$  from  $\Delta\mu$ , we use Eq. 9.6.16 for a nonelectrolyte solute, or Eq. 10.6.1 for an electrolyte solute. Both equations are represented by  $\Delta\mu = RT \ln \gamma$  where  $\gamma$  for a nonelectrolyte is  $\gamma$  and for an electrolyte is the number of ions per formula unit.

The sequence of steps, then, is (1) the determination of  $\Delta\mu$  over a range of molality at constant  $T$  and  $P$ , (2) the conversion of these values to  $\gamma$  using Eq. 12.2.1, and (3) the evaluation of the solute activity coefficient by a suitable integration from infinite dilution to the molality of interest.

A measurement of  $\Delta\mu$  also gives us the solvent activity coefficient, based on the pure-solvent reference state, through the relation  $\Delta\mu = RT \ln \gamma_s$  (Eq. 9.5.15).

Sections 12.2.1 and 12.2.2 will describe freezing-point and osmotic-pressure measurements, two much-used methods for evaluating  $\gamma$  in a binary solution at a given  $T$  and  $P$ . The isopiestic vapor-pressure method was described in Sec. 9.6.4. The freezing-point and isopiestic vapor-pressure methods are often used for electrolyte solutions, and osmotic pressure is especially useful for solutions of macromolecules.

### 12.2.1 Freezing-point measurements

This section explains how we can evaluate  $\gamma$  for a solution of a given composition at a given  $T$  and  $P$  from the freezing point of the solution combined with additional data obtained from calorimetric measurements.

Consider a binary solution of solvent A and solute B. We assume that when this solution is cooled at constant pressure and composition, the solid that first appears is pure A. For example, for a dilute aqueous solution the solid would be ice. The temperature at which solid A first appears is  $T_f$ , the freezing point of the solution. This temperature is lower than the freezing point  $T_f^0$  of the pure solvent, a consequence of the lowering of  $\Delta\mu$  by the presence of the solute. Both  $T_f$  and  $T_f^0$  can be measured experimentally.

Let  $T$  be a temperature of interest that is equal to or greater than  $T_f$ . We wish to determine the value of  $\gamma$ , where  $\gamma_s$  refers to pure liquid solvent and  $\gamma$  refers to the solution.

A second method for evaluating  $\gamma$  uses the solution property called *osmotic pressure*. A simple apparatus to measure the osmotic pressure of a binary solution is shown schematically in Fig. 12.2. The system consists of two liquid phases separated by a semipermeable membrane. Phase  $\gamma_s$  is pure solvent and phase  $\gamma$  is a solution with the same solvent at the same temperature. The semipermeable membrane is permeable to the solvent and impermeable to the solute.

The presence of the membrane makes this system different from the multiphase, multicomponent system of Sec. 9.2.7, used there to derive conditions for transfer equilibrium. By a modification of that procedure, we can derive the conditions of equilibrium for the present system. We take phase  $\gamma$  as the reference phase because it includes both solvent and solute. In order to prevent expansion work in the isolated system, both pistons shown in the figure must be fixed in stationary positions. This keeps the volume of each phase constant:  $V$ . Equation 9.2.41, expressing the total differential of the entropy in an isolated multiphase, multicomponent system, becomes  $dS = 0$ . In an equilibrium state, the coefficients  $\left(\frac{\partial S}{\partial T}\right)_V$  and  $\left(\frac{\partial S}{\partial P}\right)_V$  must be zero. Therefore, in an equilibrium state the temperature is the same in both phases and the solvent has the same chemical potential in both phases. The presence of the membrane, however, allows the pressures of the two phases to be unequal in the equilibrium state.

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Suppose we start with both phases shown in Fig. 12.2 at the same temperature and pressure. Under these conditions, the value of  $\mu_{\text{solvent}}^{\text{solution}}$  is less in the solution than in the pure liquid, and a spontaneous flow of solvent will occur through the membrane from the pure solvent to the solution. This phenomenon is called *osmosis* (Greek for *push*). If we move the right-hand piston down slightly in order to increase the pressure  $P_{\text{solution}}$  of the solution in phase  $\text{solution}$ ,  $\mu_{\text{solvent}}^{\text{solution}}$  increases in this phase. The **osmotic pressure** of the solution,  $\Pi$ , is defined as the additional pressure the solution must have, compared to the pressure  $P_{\text{pure solvent}}$  of the pure solvent at the same temperature, to establish an equilibrium state with no flow of solvent in either direction through the membrane:  $\Pi = P_{\text{solution}} - P_{\text{pure solvent}}$ .

In practice, the membrane may not be completely impermeable to a solute. All that is required for the establishment of an equilibrium state with different pressures on either side of the membrane is that solvent transfer equilibrium be established on a short time scale compared to the period of observation, and that the amount of solute transferred during this period be negligible.

The osmotic pressure  $\Pi$  is an intensive property of a solution whose value depends on the solution's temperature, pressure, and composition. Strictly speaking,  $\Pi$  in an equilibrium state of the system shown in Fig. 12.2 refers to the osmotic pressure of the solution at pressure  $P_{\text{pure solvent}}$ , the pressure of the pure solvent. In other words, the osmotic pressure of a solution at temperature  $T$  and pressure  $P_{\text{pure solvent}}$  is the additional pressure that would have to be exerted on the solution to establish transfer equilibrium with pure solvent that has temperature  $T$  and pressure  $P_{\text{pure solvent}}$ . A solution has the property called osmotic pressure regardless of whether this additional pressure is actually present, just as a solution has a freezing point even when its actual temperature is different from the freezing point.

Because in an equilibrium state the solvent chemical potential must be the same on both sides of the semipermeable membrane, there is a relation between chemical potentials and osmotic pressure given by  $\mu_{\text{solvent}}^{\text{solution}}(T, P_{\text{pure solvent}} + \Pi) = \mu_{\text{solvent}}^{\text{pure}}(T, P_{\text{pure solvent}})$ . We can use this relation to derive an expression for  $\Pi$  as a function of  $P_{\text{pure solvent}}$ . The dependence of  $\Pi$  on pressure is given according to Eq. 9.2.49 by  $\left(\frac{\partial \mu_{\text{solvent}}^{\text{solution}}}{\partial P}\right)_T = V_{\text{solvent}}^{\text{solution}}$  where  $V_{\text{solvent}}^{\text{solution}}$  is the partial molar volume of the solvent in the solution. Rewriting this equation in the form  $\left(\frac{\partial \Pi}{\partial P_{\text{pure solvent}}}\right)_T = -\frac{V_{\text{solvent}}^{\text{solution}}}{RT}$  and integrating at constant temperature and composition from  $P_{\text{pure solvent}}$  to  $P_{\text{pure solvent}} + \Pi$ , we obtain  $\Pi = \frac{RT}{V_{\text{solvent}}^{\text{solution}}} \ln \frac{P_{\text{pure solvent}} + \Pi}{P_{\text{pure solvent}}}$ . Substitution from Eq. 12.2.7 changes this to  $\Pi = \frac{RT}{V_{\text{solvent}}^{\text{solution}}} \ln \frac{a_{\text{solvent}}^{\text{pure}}}{a_{\text{solvent}}^{\text{solution}}}$  which is the desired expression for  $\Pi$  at a single temperature and pressure. To evaluate the integral, we need an experimental value of the osmotic pressure  $\Pi$  of the solution. If we assume  $\Pi$  is constant in the pressure range from  $P_{\text{pure solvent}}$  to  $P_{\text{pure solvent}} + \Pi$ , Eq. 12.2.10 becomes simply  $\Pi = \frac{RT}{V_{\text{solvent}}^{\text{solution}}} \ln \frac{a_{\text{solvent}}^{\text{pure}}}{a_{\text{solvent}}^{\text{solution}}}$ .

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