Boiling-Point Elevation

The normal boiling point of a pure liquid or a solution is the temperature at which the vapor pressure reaches 1 atm. Because a dissolved solute reduces the vapor pressure, the temperature of the solution must be increased to make it boil. That is, the boiling point of a solution is higher than that of the pure solvent. This phenomenon, referred to as boiling-point elevation, provides an alternative method for determining molar masses.

The vapor-pressure curve of a dilute solution lies slightly below that for the pure solvent. In Figure 6.9, \( \Delta P_1 \) is the decrease of vapor pressure at \( T_b \), and \( \Delta T_b \) is the change in temperature necessary to hold the vapor pressure at 1 atm (in other words, \( \Delta T_b = T_b^\prime - T_b \) is the increase in boiling point caused by addition of solute to the pure solvent). For small concentrations of nondissociating solutes, the two curves are parallel, so

\[
- \frac{\Delta P_1}{\Delta T_b} = \text{slope of curve} = S
\]

\[
\Delta T_b = - \frac{\Delta P_1}{S} = \frac{X_b P_i}{S}
\]

\[
= \frac{1}{S}\left(\frac{n_2}{n_1 + n_2}\right) \quad \text{(from Raoult's law, with } P_i = 1 \text{ atm)}
\]

\[\text{FIGURE 6.9 The vapor pressure of the solvent above a dilute solution is lower than that of the pure solvent at all temperatures. As a result, in order for the solution to boil (i.e., for the vapor pressure to reach 1 atm), a higher temperature is required for the solution than for the pure solvent. This amounts to an elevation of the boiling point.}\]

The constant \( S \) is a property of the pure solvent only, because it is the slope of the vapor pressure curve \( - \Delta P_i / \Delta T_b \) near 1 atm pressure. In other words, \( S \) is independent of the solute species involved.

For very dilute solutions, \( n_1 \gg n_2 \), and this may be simplified to

\[
\Delta T_b = \frac{1}{S} \frac{n_2}{n_1} = \frac{1}{S} \frac{m_2/M_2}{m_1/M_1}
\]

where \( m_1 \) and \( m_2 \) are the masses of solvent and solute (in grams) and \( M_1 \) and \( M_2 \) are their molar masses in grams per mole. Because \( M_1 \), like \( S \), is a property of the solvent only, it is convenient to combine the two and define a new constant \( K_b \) through

\[
K_b = \frac{M_1}{(1000 \text{ g kg}^{-1})S}
\]

Then

\[
\Delta T_b = K_b \left(\frac{m_2/M_2}{m_1/(1000 \text{ g kg}^{-1})}\right)
\]

Because \( m_1 \) is measured in grams, \( m_1/(1000 \text{ g kg}^{-1}) \) is the number of kilograms of solvent. Also, \( m_2/M_2 \) is the number of moles of solute. The expression in parentheses is therefore the molality (\( m \)) of the solution.

\[
\Delta T_b = K_b m \quad \text{[6.4]}
\]