

Using Colligative Properties to Find the Solute Molar Mass

- The molar mass of the solute can be obtained by measuring one of the colligative properties of the solution, the mass of the solute and the mass of the solvent (or the volume of the solution)
 - ΔP and ΔT_b are not very sensitive to changes in the solute concentration (rarely used for molar mass determinations)
 - ΔT_f is more sensitive especially when solvents with large k_f constants are used
 - Π is most sensitive and can be used for substances with low molar solubility such as large biomolecules

Example: The T_f of camphor is 179.80°C and its k_f is 39.7°C/m . When **200.0 mg** of a compound (X) are added to **100.0 g** of camphor, its freezing point drops to **179.29°C**. What is the molar mass of X?

→ **Calc. the m of X:**

$$\Delta T_f = k_f m \rightarrow m = \frac{\Delta T_f}{k_f} = \frac{(179.80 - 179.29)^\circ\text{C}}{39.7^\circ\text{C/m}} = 0.013 \frac{\text{mol}}{\text{kg}}$$

→ **Calc. the number of moles of X:**

$$m = \frac{\text{mol}(X)}{\text{kg}(\text{camphor})} \rightarrow 0.013 \frac{\text{mol}}{\text{kg}} \times 0.1000 \text{ kg} = 0.0013 \text{ mol}$$

→ **Calc. the molar mass of X:**

$$MW = \frac{\text{grams}(X)}{\text{mol}(X)} \rightarrow \frac{0.2000 \text{ g}}{0.0013 \text{ mol}} = \boxed{160 \text{ g/mol}}$$

Example: A **3.0 g** polymer sample is dissolved in enough benzene to produce **150. mL** of solution. If the solution's osmotic pressure is **0.0119 atm** at **25°C**, what is the average MW of the polymer?

Calc. M of the solution:

$$M = \frac{\Pi}{RT} = \frac{0.0119 \text{ atm}}{0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K} \times 298 \text{ K}} = 4.87 \times 10^{-4} \frac{\text{mol}}{\text{L}}$$

→ **Calc. the number of moles of the polymer:**

$$M = \frac{\text{mol}(\text{pol})}{L(\text{soln})} \rightarrow 4.87 \times 10^{-4} \frac{\text{mol}}{\text{L}} \times 0.150 \text{ L} = 7.30 \times 10^{-5} \text{ mol}$$

→ **Calc. the molar mass of the polymer:**

$$MW = \frac{\text{grams}(\text{polym})}{\text{mol}(\text{polym})} \rightarrow \frac{3.0 \text{ g}}{7.30 \times 10^{-5} \text{ mol}} = \boxed{41000 \text{ g/mol}}$$

Volatile Nonelectrolyte Solutions

- No dissociation; both solvent and solute have vapor pressures (mixtures of volatile organic compounds)
- Raoult's law can be applied to the vapor pressures of both the solute and the solvent

$$P_{\text{solv}} = X_{\text{solv}} P_{\text{solv}}^\circ \quad P_{\text{solute}} = X_{\text{solute}} P_{\text{solute}}^\circ$$

⇒ The presence of each component lowers the vapor pressure of the other component

 - The total pressure over the solution is the sum of the partial pressures of the solute and the solvent

$$P_{\text{tot}} = P_{\text{solv}} + P_{\text{solute}} = X_{\text{solv}} P_{\text{solv}}^\circ + X_{\text{solute}} P_{\text{solute}}^\circ$$

– The mole fractions of the solute and solvent in the vapor phase above the solution can be calculated using Dalton's law

$$P_{\text{solvent}} = X_{\text{solvent}}^{\text{vap}} P_{\text{tot}} \quad P_{\text{solute}} = X_{\text{solute}}^{\text{vap}} P_{\text{tot}}$$

$$X_{\text{solvent}}^{\text{vap}} = \frac{P_{\text{solvent}}}{P_{\text{tot}}} \quad X_{\text{solute}}^{\text{vap}} = \frac{P_{\text{solute}}}{P_{\text{tot}}}$$

Example: The equilibrium vapor pressures of pure benzene and toluene are **95.1** and **28.4 torr**, respectively at 25°C. Calculate the total pressure, partial pressures and mole fractions of benzene and toluene over a solution of **1.0 mol** of benzene in **3.0 mol** of toluene at 25°C.

$$X_b = \frac{1.0}{1.0 + 3.0} = 0.25 \quad X_t = \frac{3.0}{1.0 + 3.0} = 0.75$$

$$P_b = X_b P_b^{\circ} = 0.25 \times 95.1 \text{ torr} = \boxed{24 \text{ torr}}$$

$$P_t = X_t P_t^{\circ} = 0.75 \times 28.4 \text{ torr} = \boxed{21 \text{ torr}}$$

$$P_{\text{tot}} = P_b + P_t = 24 + 21 = \boxed{45 \text{ torr}}$$

$$X_b^{\text{vap}} = \frac{P_b}{P_{\text{tot}}} = \frac{24}{45} = \boxed{0.53} \quad X_t^{\text{vap}} = \frac{P_t}{P_{\text{tot}}} = \frac{21}{45} = \boxed{0.47}$$

⇒ The mole fractions of the solute and solvent in the vapor phase are different from those in the liquid phase → **The vapor phase is enriched with the more volatile component** → Condensation of the vapors leads to a solution which is enriched with the more volatile component → **distillation**

Electrolyte Solutions

- The solute dissociates to ions
- The number of particles in the solution is greater than the one implied by the solute concentration

• The formulas for the colligative properties must be modified

- **van't Hoff factor (*i*)** – accounts for the dissociation of the solute
- *i* is determined experimentally as a ratio of the measured colligative property versus the one expected for a nonelectrolyte

$$\Delta P = i(X_{\text{solute}} P_{\text{solute}}^{\circ}) \quad \Delta T_b = i(k_b m)$$

$$\Pi = i(MRT) \quad \Delta T_f = i(k_f m)$$

- For ideal solutions (very dilute solutions), the ideal value of *i* represents the number of moles of particles to which a mole of the solute dissociates
- For real solutions, *i* is smaller than the ideal value
- The deviation is due to clustering of cations and anions (**ionic atmosphere**) which reduces the “effective” concentration of particles → (*i* × *Conc.*)

Example: Select the solution with the higher osmotic pressure: **0.1M NaCl** or **0.08M CaCl₂**

→ Calculate the effective concentrations:

$$\rightarrow 0.1\text{M NaCl} \rightarrow i \times M = 2 \times 0.1 = 0.2$$

$$\rightarrow 0.08\text{M CaCl}_2 \rightarrow i \times M = 3 \times 0.08 = 0.24 \text{ (higher)}$$

⇒ **0.08M CaCl₂** has higher Π ($\Pi = i \times MRT$)