Osmotic Equilibria

- Species 2, solute - cannot cross the membrane
- Species 1, solvent - can pass through

\[ \Pi = \text{"osmotic pressure"} \]

At equilibrium, \( \Psi_1 (T, P + \Pi, x_1) = \Psi_1 (T, P, \text{pure}) \Rightarrow \)

\[ x_1 \frac{\partial \Psi_1}{\partial \Pi} (T, P + \Pi) = \frac{\partial \Psi_1}{\partial \Pi} (T, P) \]

\[ \frac{\partial \ln \Psi_1}{\partial P} \Bigg|_T = \frac{V_1}{R T} \Rightarrow \Psi_1 (T, P + \Pi) = \Psi_1 (T, P) \exp \left( \frac{\Pi V_1}{R T} \right) \]

\[ \ln \Psi_1 = 1 \Rightarrow \Pi = -\frac{RT}{V_1} \ln (\Psi_1 x_1) \]

For dilute solutions, \( \Psi_1 \approx 1, \ln (1-x_2) \approx -x_2 \Rightarrow \)

\[ \Pi = \frac{RT}{V_1} x_2 = \frac{RTN_2}{V_1N} \Rightarrow \frac{\Pi V}{RTN_2} = \text{or} \]

\[ \Pi = \frac{RT \text{C}_2}{V_1N} \text{[mol/m}^3] \]

**Numerical Estimate (Ex. 9.7)**

Seawater, 3.5\% w/w NaCl, \( P = 1030 \text{ kPa} \)

\[ x_{\text{NaCl}} = \frac{3.5 \text{ g} / 58.4 \text{ g/mol}}{3.5/58.4 + 96.5/18.0} = 0.011 \]

However, \( \text{NaCl} \) dissociates into \( \text{Na}^+ \) and \( \text{Cl}^- \),

So \( x_{\text{H}_{2}O} = 1 - 2 \times 0.011 = 0.978 \) and assume \( x_{\text{H}_{2}O} = 1 \)
\[ \Pi = -RT/V \ln x_1 \Rightarrow \Pi = 32 \text{ bar} \]

Application: desalination of sea water by “reverse osmosis” — applying \( P > 32 \text{ bar} \) on salty water to push water to the right and make it drinkable.

**Membrane Osmometry (Ex. 9.8)**

\[ \Delta h = 3.2 \text{ cm} \]

\[ 0.2 \text{ g} / \text{kg of H}_2\text{O} \]

\[ M_W = ? \]

\[ \Pi = \rho g \Delta h = \frac{RT}{V_1} \]

\[ x_2 \Rightarrow x_2 = 2.3 \times 10^{-6} \]

\[ x_2 = \frac{w_2/M_2}{w_2/M_2 + w_1/M_1} \Rightarrow M_2 = \frac{w_2 M_1}{w_1 x_2} = \frac{0.2 \text{ g} \cdot 18 \text{ g/mol}}{100 \text{ g} \cdot 2.3 \times 10^{-6} \text{ g/mol}} = 15,900 \text{ g/mol} \]

Small mole fractions give measurable \( \Delta h \)

**Virial Expansion of \( \Pi \)**

Osmotic pressure measurements at moderate concentrations can be used to obtain solute-solute interactions:

By analogy to the virial equation of state:

\[ \frac{\Pi V}{RT} = 1 + B(T) \rho_2 + \ldots \]

\( V \): volume of solution

\( \rho_2 \): molal conc. of solute

\( B > 0 \): repulsive between solute molecules

\( B < 0 \): attractive
Colligative properties: properties that depend on the mole fractions (but not the nature) of a solute. Osmotic pressure is a colligative property. Also:

- Boiling Point Elevation / Freezing Point Depression

\[ \mu_{i, I}(T, P, x_i) = \mu_{i, II}(T, P) \Rightarrow RT \ln(\gamma_i x_i) + \mu_{i, I}(T, P) = \mu_{i, II}(T, P) \]

\[ \Rightarrow RT \ln(\gamma_i x_i) = -\Delta \mu(T, P) \quad (i) \]

\[ \Delta \mu(T_{\text{pure}}, P) = \mu_{i} - \mu_{II} = 0 \quad \text{at pure component} \]

\[ \frac{\partial (\mu/T)}{\partial T} \bigg|_P = -\frac{\beta G}{T^2} + \frac{1}{T} \frac{\partial \beta G}{\partial T} \bigg|_P = -\frac{6 + TS}{T^2} = -\frac{H}{T^2} \]

\[ \Rightarrow \frac{\partial (\Delta \mu/T)}{\partial T} \bigg|_P = -\frac{H}{T^2} \]

18. \( \Delta H = H_I - H_{II} \) is independent of \( T \),

\[ \frac{\Delta H(T)}{T} - \frac{\Delta H(T_{\text{pure}})}{T_{\text{pure}}} = \Delta H \left( \frac{1}{T} - \frac{1}{T_{\text{pure}}} \right) \quad (i) \]

\[ \Rightarrow RT \ln(\gamma_i x_i) = -\frac{\Delta H(T_{\text{pure}})}{RT_{\text{pure}} T} \]
For dilute solutions, \( x_2 \approx 1 \ln x_2 \approx \ln(1-x_2) \approx -x_2 \)

\[ T = T_{\text{pure}} \quad \therefore \quad -x_2 = -\frac{\Delta H (T_{\text{pure}}-T)}{R T_{\text{pure}}} \implies \]

\[ T = T_{\text{pure}} - \frac{x_2 R T_{\text{pure}}}{\Delta H} \]

For melting, \( \Delta H = h_1 - h_2 = h(\text{liq.}) - h(\text{solid}) > 0 \)

\[ T < T_{\text{pure}} : \text{freezing point depression} \]

For boiling, \( \Delta H = h_1 - h_2 = h(\text{liq.}) - h(\text{vapor}) < 0 \)

\[ T > T_{\text{pure}} : \text{boiling point elevation} \]

Example: freezing point depression for solution of polymer in example 9.8

\( x_2 = 2.3 \cdot 10^{-6} \quad \Delta H = 601 \text{ KJ/mol} \quad T_{\text{pure}} = 273 \text{ K} \)

\[ T - T_{\text{pure}} = -\frac{2.3 \cdot 10^{-6} \cdot 8.314 \cdot \frac{J}{mol \cdot K} \cdot 273^2 \cdot 2}{6011 \frac{J}{mol}} = 2.4 \cdot 10^{-4} \text{ K} \]

(too small to measure accurately)