Lecture # 23

Colligative properties cont'd: Osmotic pressure

\[ \Delta P = \Pi \]

Goal: Get \( \Pi (x_A) \)

[Diagram: U-shaped container with a semi-permeable membrane, solvent on one side and solution on the other side, \( P \), \( x_A \)]

Phase equilibria

\[ \text{MB, pure} (P) = \text{MB, mix} (P + \Pi, x_A) \]

1. \( P \rightarrow P + \Pi \)

\[ \text{MB, pure} (P + \Pi) = \frac{\partial \text{MB}}{\partial P} \int_{P}^{P+\Pi} \partial P \]

Get \( \frac{\partial \text{MB}}{\partial P} \) from Maxwell Relation:

\[ d\mu = -s dT + \nu \omega dP + \mu dN \]

\( \text{const} \Rightarrow \frac{1}{2} \nabla \cdot v = \frac{1}{2} \nabla (P_v \rho) \)

\( \text{molal volume} \)

\( \nu_B = \text{constant} \)

\[ \text{MB, pure} (P + \Pi) = \text{MB, pure} (P) + \nu_B \Pi \]
2. Add Solute

\[ \mu_{B, \text{mix}} (P+\Pi, y_B) = \mu_{B, \text{soln}} (P) + u_B \Pi + RT \ln y_B x_B \]

Thus

\[ -u_B \Pi = RT \ln y_B x_B \]

For dilute solution

\[ x_A \ll 1 \]

\[ x_B \rightarrow 1 \text{ thus } y_B \rightarrow 1 \]

\[ \ln (1-x_A) \approx -x_A \]

\[ \Pi = \frac{RT x_A}{u_B} \]

Usually prefer to use in terms of \( C_A \) moles/l

\[ \text{for } x_A \ll 1, \quad x_A = \frac{N_A}{N_B} \quad \text{ and } \quad V = N_B u_B \]

\[ \Pi = RT \left( \frac{N_A}{N_B} \right) = C_A RT \frac{V}{N_B} \]

\[ \Pi = C_A RT \]
Solute & Phase Partitioning

What if you add a lipophilic dye to the oil/water (salad dressing) mix we discussed before. Now a 3-component system. Call dye "$s" = solute.

\[
oil = B, \quad x_{SB}
\]
\[
water = A, \quad x_{SA}
\]

at eqm \( M_s(A) = M_s(B) \)

\[
\frac{2wss}{2} + kT \left[ \ln x_{SA} + x_{SA}(1-x_{SA})^2 \right] = \frac{2wss}{2} + kT \left[ \ln x_{SB} + x_{SB}(1-x_{SB})^2 \right]
\]

reverse

\[
\ln \frac{x_{SB}}{x_{SA}} = x_{SA}(1-x_{SA})^2 - x_{SB}(1-x_{SB})^2
\]

\[
\ln K^B_A \leftarrow \text{Partition Coefficient}
\]

Usually, you measure \( K^B_A \)

Think about this exp.: Tiny bit of dye

Tiny bit of dye

\[
\frac{K^B_A}{x_{SA}} = 100
\]

\[
K^B_A = \frac{x_{SB}}{x_{SA}} = 100
\]

10,000X (saturation)

\[
K^B_A = \frac{0.002}{2 \times 10^{-5}} = 100
\]

\[
K^B_A = \frac{10}{2 \times 10^{-4}} = 100
\]