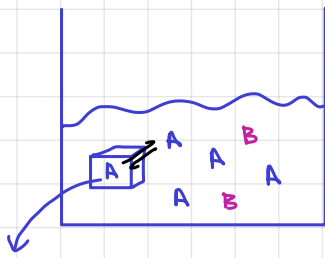


Ch 25] Freezing Point depression



Solvent: A     solute: B

Equil: free energy of A(s) and A(sol) are equal at equilibrium. namely,  $T = T_{\text{fusion}}$

Why isn't B crystalizing in A?  
Crystalizing is for purity so why isn't impurity B going in?  
Stacking  $\rightarrow$  A doesn't accommodate B.

Crystal structure of A doesn't support defects

$$M_A^*(s) = M_A^{\text{sol}} = M_A^*(l) + RT_{\text{fus}} \ln X_A$$

$$M_A^*(l) - M_A^*(s) = -RT_{\text{fus}} \ln X_A$$

$$\Delta \bar{G}_{\text{fus}}^* = -RT_{\text{fus}} \ln X_A$$

$$\frac{\Delta G}{T_{\text{fus}}} = -R \ln X_A$$

$$\frac{\Delta \bar{H}_{\text{fus}}^*}{T_{\text{fus}}} - \frac{\Delta \bar{H}_{\text{fus}}^*}{T_{\text{fus}}^*} = -R \ln X_A = -R \ln(1 - X_B)$$

Taylor series  $\rightarrow -X_B$

the key is they are different temp.

$$\Delta \bar{H}_{\text{fus}}^* \left( \frac{T_{\text{fus}}^* - T_{\text{fus}}}{T_{\text{fus}} T_{\text{fus}}^*} \right) = R X_B = R \frac{n_B}{n_A + n_B}$$

mol fraction is part over total  
got rid of

$$\frac{\Delta \bar{H}_{\text{fus}}^* \cdot \Delta T_{\text{fus}}}{T_{\text{fus}}^* T_{\text{fus}}^*} = R \frac{n_B}{n_A} = R \left( \frac{m M_A}{1000} \right)$$

molality =  $\frac{n_B}{1 \text{ kg of A}}$

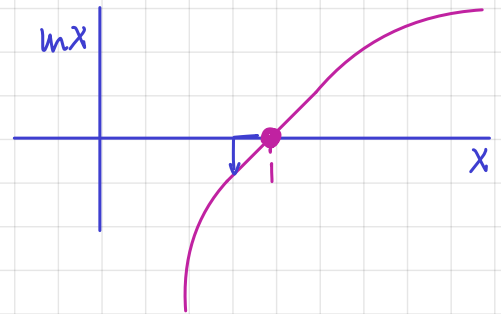
$$\Delta T_{\text{fus}} = \text{freezing point depression} = \left( \frac{R M_A}{1000} \frac{T_{\text{fus}}^{*2}}{\Delta \bar{H}_{\text{fus}}^*} \right) m = K_f m$$

$$\Delta G = \Delta H - T \Delta S$$

$$\frac{\Delta G}{T} = \frac{\Delta H}{T} - \Delta S$$

$$\Delta G_{\text{fus}}^* = 0 \text{ at } T_{\text{fus}}^*$$

$$\Rightarrow \Delta \bar{S}_{\text{fus}} = \frac{\Delta \bar{H}_{\text{fus}}^*}{T_{\text{fus}}^*}$$



# Osmotic pressure

Equilibrium:

star bc / pure liquid A

$$M_A^*(l) = M_A(sol) \stackrel{\text{height}}{=} M_A^*(l) + RT \ln X_A$$

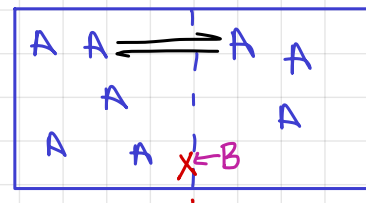
there is an inequality

different pressure

$$M = \bar{G}$$

$$dG = VdP - SdT$$

$$\frac{\partial G}{\partial P} = V \Rightarrow \frac{\partial M_A}{\partial P} = \bar{V}_A$$



membrane blocks B

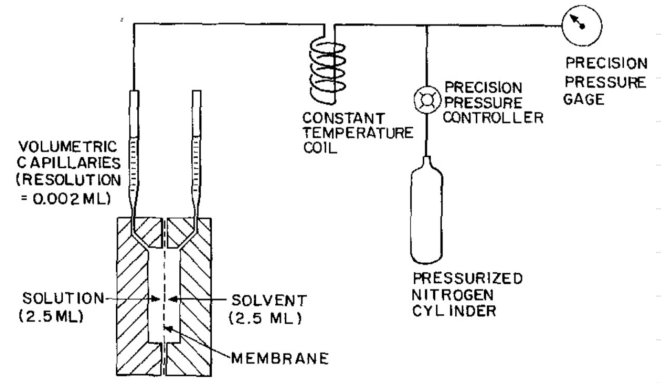


FIG. 1. Schematic diagram of high-pressure membrane osmometer system.