Freezing point depression : $A = $ solvent
$B = $ solute

Solid solvent is in equilibrium with the solvent in the solution.

$$\mu_A^*(s) = \mu_A(sol) = \mu_A^*(l) + RT \ln a_A$$

Now, $\mu_A^*(s) - \mu_A^*(l) = -\Delta \bar{G}_{fusion}$ (pure substance)

$$\Rightarrow -\frac{\Delta \bar{G}_{fus}}{RT} = \ln a_A \Rightarrow -\frac{1}{R} \underbrace{\frac{\partial \Delta \bar{G}_{fus}/T}{\partial T}\bigg)_P}_{-\frac{\Delta \bar{H}_{fus}}{T^2} \text{ from Gibbs-Helmholtz}} = \frac{\partial \ln a_A}{\partial T}\bigg)_P$$

Recall (Raoults Law) that
$a_A \to x_A$ as $x_A \to 1$.
We now integrate from

T_{fus}^* (pure liquid, $x_A = 1 \Rightarrow a_A = 1$) to T_{fus} (solution)
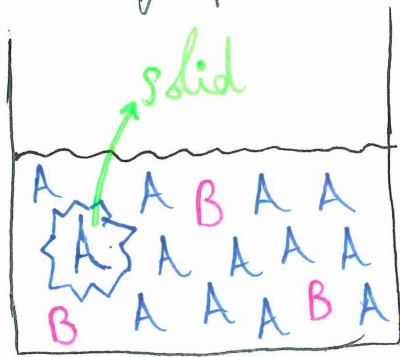
which gives $\ln a_A \bigg|_1^{a_A} = \int_{T_{fus}^*}^{T_{fus}} \frac{\Delta \bar{H}_{fus}}{RT^2} dT = \ln a_A$

Now, assume $\Delta \bar{H}_{fus}$ independent of T, and
put $\ln a_A = \ln x_A = \ln(1 - x_B) = -x_B$ for x_B small

to get $-x_B = \frac{\Delta \bar{H}_{fus}}{R}\left(\frac{1}{T_{fus}^*} - \frac{1}{T_{fus}}\right) = \frac{\Delta \bar{H}_{fus}}{R} \cdot \frac{T_{fus} - T_{fus}^*}{T_{fus} T_{fus}^*}$

Freezing point depression, A = solvent, B = solute (68a)

• Solid is pure A because crystal doesn't support "B" defects.

• Component A in equilibrium at T_{fus}

$$\Rightarrow \mu_A^*(s) = \mu_A^{sol} = \mu_A^*(l) + RT_{fus}\ln x_A$$

· using Raoult's Law

$\Delta \bar{G}_{fus} \equiv \mu_A^*(l) - \mu_A^*(s)$ for the pure substance A.

$$= 0 \text{ at } T_{fus}^* \Rightarrow \Delta\bar{S}_{fus} = \frac{\Delta\bar{H}_{fus}}{T_{fus}^*}$$

Thus $\dfrac{\Delta\bar{G}_{fus}}{T_{fus}} = -R\ln x_A = \dfrac{\Delta\bar{H}_{fus}}{T_{fus}} - \Delta\bar{S}_{fus} = \Delta\bar{H}_{fus}\left(\dfrac{1}{T_{fus}} - \dfrac{1}{T_{fus}^*}\right)$

Use a Taylor series: $\ln x_A = \ln(1 - x_B) = -x_B$ for x_B small

to get $\quad x_B = \dfrac{\Delta\bar{H}_{fus}}{R} \cdot \dfrac{(T_{fus}^* - T_{fus})}{T_{fus}\, T_{fus}^*}$

Set $\Delta T_{fus} = T_{fus}^* - T_{fus}$ and approx. $T_{fus} T_{fus}^* = T_{fus}^{*2}$

to get $X_B = \dfrac{\Delta \bar{H}_{fus}}{R} \cdot \dfrac{\Delta T_{fus}}{T_{fus}^{*2}}$

Next change from mole fraction to molality, m.

$$m \equiv \frac{n_B}{1 \, kg \, of \, A} = \frac{n_B}{1000 \, g \, of \, A}$$

and $X_B \equiv \dfrac{n_B}{n_A + n_B} \approx \dfrac{n_B}{n_A} = \dfrac{m \, M_A}{1000}$ (assume n_B small)
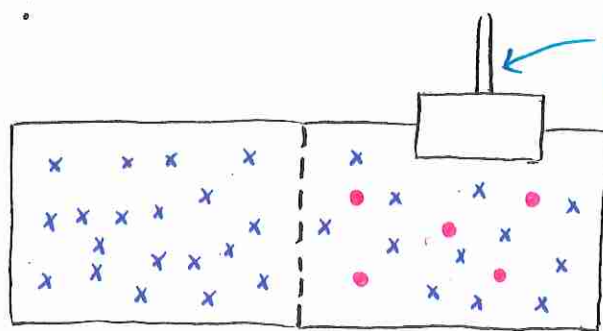
M_A = molar mass of A

Finally, get $\Delta T_{fus} = \left[\dfrac{M_A}{1000} \cdot \dfrac{R T_{fus}^{*2}}{\Delta \bar{H}_{fus}} \right] \cdot m = k_f \, m$

Similarly, $\Delta T_{vap} = k_b \, m$ with $k_b = \dfrac{M_A}{1000} \cdot \dfrac{R T_{vap}^{*2}}{\Delta \bar{H}_{vap}}$

for the boiling point elevation

Osmotic Pressure :

piston

$x = $ solvent $= 1$

$\bullet = $ solute $= 2$

Usually the solvent is water.

↳ semipermeable membrane. won't let solute pass through.

At equilibrium the chemical potential of water must be equal on the two sides.

On the right we have $\mu_i^{sol} = \mu_i^*(\ell) + RT \ln a_1$

For $x_1 < 1$, $\mu_i^{sol} < \mu_i^*(\ell)$

Therefore somehow we must raise μ_i^{sol}.

De know $\left(\dfrac{\partial \mu_1}{\partial P}\right)_T = \bar{V}_1$ So we can increase the pressure on the piston in order to raise μ_i^{sol}.

Equil. : $\mu_i^*(\ell, P) = \mu_i^*(\ell, P+\pi) + RT \ln a_1$

Now, $\mu_i^*(\ell, P+\pi) = \mu_i^*(\ell, P) + \displaystyle\int_P^{P+\pi} \left(\dfrac{\partial \mu_i^*}{\partial P}\right)_T dP$

$= \mu_i^*(\ell, P) + \pi \bar{V}_i^*$ (assume incompressible)

$\Rightarrow \pi \bar{V}_1^* + RT \ln a_1 = 0$

put $\ln a_1 = \ln x_1 = \ln(1-x_2) = -x_2$ for x_2 small $\quad$ (71)

Also put $x_2 = \dfrac{n_2}{n_1+n_2} \simeq \dfrac{n_2}{n_1}$

and put $n_1 \bar{V}_1^* \simeq V$ (dilute solution)

yielding $\quad \pi \bar{V}_1^* = RT x_2 = RT \dfrac{n_2}{n_1}$

$$\Rightarrow \pi V = n_2 RT$$

$$\Rightarrow \pi = cRT \qquad c = \dfrac{n_2}{V} = \text{molarity of the solution}$$

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ex 2.20 g of a polymer is dissolved in enough water to make 300 mL of solution. The osmotic pressure is found to be 7.45 torr at 20°C.

$\qquad$ Determine the polymer's molar mass.

$$\pi = cRT = \dfrac{7.45 \text{ torr}}{760 \text{ torr atm}^{-1}} = 0.0098 \text{ atm}$$

$$c = \dfrac{\pi}{RT} = \dfrac{0.0098 \text{ atm}}{(0.082)(293K)} = 4.07 \times 10^{-4} \, M$$

In 1 L of solution we would have $2.20 g \left(\dfrac{1000 \text{ mL}}{300 \text{ mL}} \right)$

$\qquad\qquad = 7.33$ g of polymer.

Thus the molar mass is $\dfrac{7.33 \text{ g} L^{-1}}{4.07 \times 10^{-4} \text{ mol } L^{-1}} = 18000 \text{ g mol}^{-1}$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad = 18 \text{ kDa}.$

For a strong electrolyte that dissociates into ν ions, we modify the colligative properties expressions :

$$\Delta T_{fus} = \nu k_f m \quad ; \quad \Delta T_{vap} = \nu k_f m \quad ; \quad \Pi = \nu c R T$$

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For a 2 molal aqueous solution of sucrose, to use $\Pi = c R T$ we should compute c first :

$$c = \frac{2 \text{ moles}}{1000 \text{ g } H_2O} \cdot \frac{1000 g}{1.003 L} = 1.994 M \quad \text{using density at 298 K} \left\{ 0.997 \, g/mL \right.$$

$$\Pi = (1.994 M)(0.082)(298 K) = 48.7 \, atm$$

If we account for non-ideal behavior it turns out $\Pi = 58.0 \, atm$ is about 20% higher