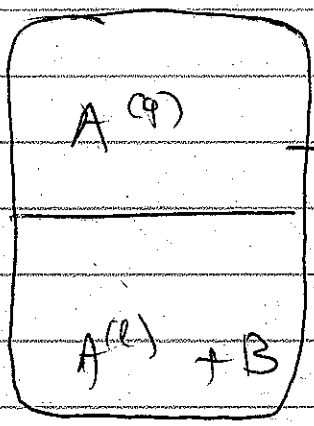
<u>Colligative props</u>: effect of dissolved species on solvent properties like boiling point and freezing point

$$\boxed{\text{Effect on boiling point.}}$$



$\mu_A^*(g)$

$\mu_A(l)$

$x_A + x_B = 1$

$$\mu_A(g) = \mu_A^*(l) + RT \ln x_A =$$

$$= \mu_A^*(l) + RT \ln(1 - X_B)$$

If we assume $X_B \ll 1 \Rightarrow \ln(1 - X_B) \simeq -X_B$
(Taylor expansion)

So:

$$\mu_A(g) = \mu_A^*(l) - RT \; X_B$$

$$\mu_A(g) - \mu_A^*(l) = -RT X_B \Rightarrow X_B = \frac{\mu_A^*(l) - \mu_A(g)}{RT} =$$

$$= \frac{\Delta G^{vaporization}}{RT}$$

Now, if there is a small amount of x_B in, the boiling point will be T, while for pure A, the boiling point will be T_b. so:

$$0 \; (= x_B) = \frac{+\Delta G_{vap}(T_b)}{R T_b}$$

$$x_B = \frac{\Delta G_{vap}(T)}{RT}$$

assume $\Delta G_{vap} \simeq$ const

$$\Rightarrow \quad x_B = \frac{\Delta G_{vap}}{R}\left\{\frac{1}{T} - \frac{1}{T_b}\right\}$$

defining $\delta T = T - T_b$ and assuming $T T_b \simeq T^2$

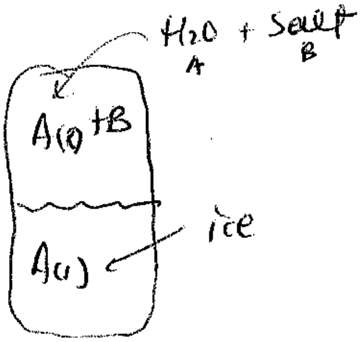
we get:

$$x_B = (\delta T)\frac{\Delta G_{vap}}{RT^2} \Rightarrow \boxed{\delta T = \underbrace{\left(\frac{RT^2}{\Delta G_{vap}}\right)}_{k_B} x_B}$$

So the temperature depression is proportional to the amount of dissolved stuff.

k_B depends only on T, solvent

Freezing point depression



$$\mu_A(l) = \mu_{(A)}(s)$$

$$\mu_A(l) = \mu_A^*(s) \quad \checkmark \text{ b/c } \mu_A(s) \simeq \text{const.} \quad ①$$

but

$$\mu_A(l) = \mu_A^*(l) + RT\ln X_A = \mu_A^*(l) + RT\ln(1-X_B)$$

$$\ln(1-X_B) \simeq -X_B \quad (\text{if } X_B \text{ small}) \Big\} \Rightarrow$$

$$\Rightarrow \mu_A(l) \simeq \mu_A^*(l) - RT X_B \quad ②$$

①,② ⇒ So $\mu_A^*(l) - RT X_B = \mu_A^*(s)$

similar fashion to boiling point depression:

$$\delta T = \underbrace{\left(\frac{RT_f^{*2}}{\Delta H_{melt}}\right)}_{\text{cryoscopic constant } K_f} X_B$$