L17 Colligative properties

i) fp ↓, bp ↑
ii) osmotic pressure
iii) solubility

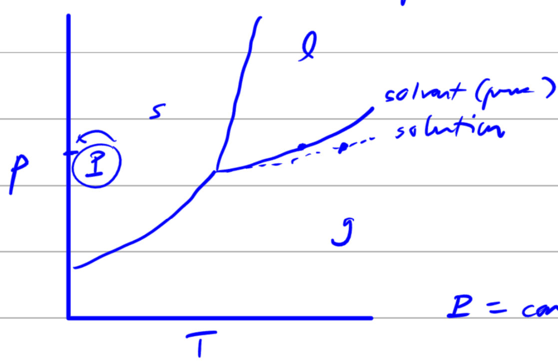
all result from same fundamental relation

$$\mu_i < \mu_i^* \ (\text{or } \mu^0)$$

(solution) (pure solvent)

1) bp elevation: $\mu_{soln} < \mu_{solv}$, but μ_{vap} the same

T_{bp} must increase



SOLV.	SOLN.
$P = p^*$	$P = p$
T lower	T higher

$p_{solv} > p_{soln}$ at all temps

P = confining pressure

Empirically: $\Delta T_b = K_b b$ ← molality (mol solute / kg solv.)

change in T_b; ebullioscopic

Why? at eqb. $\mu_A(l) = \mu_A^*(g)$

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

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At bp, $p = 1$ atm $\quad \mu_A^*(g) = \mu_A^o(g)$

$$\therefore \quad \mu_A^o(g) = \mu_A^o(l) + RT\ln x_A$$

For 1 mole: $\mu^o = G^o$

sub in, $\div T$: $\quad \dfrac{G_A^o(g) - G_A^o(l)}{T} = R\ln x_A$

diff wrt T (G-H eqn) $\left(\frac{\partial(G^{\circ}/T)}{\partial T}\right)_p = \frac{-H^{\circ}}{T^2}$

so: $\frac{-H_A^{\circ}(g) + H_A^{\circ}(l)}{T^2} = R\frac{\partial}{\partial T}(\ln x_A)$

$$-\frac{\Delta_{vap}H^{\circ}}{RT^2} = \frac{\partial}{\partial T}(\ln x_A)$$

assume: $\Delta_{vap}H^{\circ}$ const over small range

$T^* =$ normal bp for pure substance $(x_A = 1)$

$$d\ln x_A = -\frac{\Delta_{vap}H}{RT^2}\,dT$$

$$\int_1^{x_A} d\ln x_A = -\frac{\Delta_{vap}H}{R}\int_{T^*}^{T}\frac{1}{T^2}\,dT$$

$$\ln x_A = -\frac{\Delta_{vap}H}{R}\left(-\frac{1}{T} + \frac{1}{T^*}\right)$$

$$= -\frac{\Delta_{vap}H}{R}\left(\frac{T - T^*}{TT^*}\right)$$

for small ΔT, $\Delta T = T - T^*$, $TT^* \approx (T^*)^2$

$$\ln x_A = -\frac{\Delta_{vap}H\,\Delta T}{R(T^*)^2}$$

solute: $\ln(1 - x_B) = -\frac{\Delta_{vap}H\,\Delta T}{R(T^*)^2}$

x_B is small
$\ln(1-x) \simeq -x$

$$x_B = \frac{\Delta_{vap}H\,\Delta T}{R(T^*)^2}$$

$$\Delta T = \frac{R(T^*)^2}{\Delta_{vap}H}\cdot x_B$$

$$b = \frac{n_B}{n_A M_A} \simeq \frac{n_B}{(n_A + n_B)M_B} = \frac{n_B}{nM_B} = \frac{x_B}{M_B}$$

$$\Delta T = \underbrace{\frac{M_A R (T^*)^2}{\Delta_{vap} H}}_{K_b} b$$