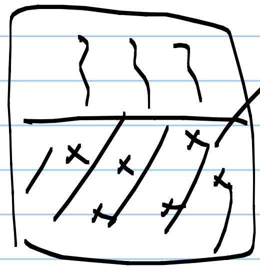
$$\frac{G}{T} = \frac{H}{T} - S \qquad G(T, P, N) \quad H(S, P, N) \quad S(U, V, N)$$

$$\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_{P,N} = -\frac{H}{T^2}$$

$$\underbrace{\frac{1}{T}\left(\frac{\partial H}{\partial T}\right) - \left(\frac{\partial S}{\partial T}\right)}_{=0} - \frac{H}{T^2}$$

蒸気圧降下と沸点上昇



不揮発性溶質 (solute)

モル分率 x_s

溶媒 (solvent) $x_v = 1 - x_s$

蒸気圧 $p_v = x_v p_v^*$ ← 純溶媒の〜

Raoultの法則

$x_v < 1$ より $p_v < p_v^*$ 蒸気圧降下

不揮発性溶質 → 溶媒の蒸発を妨げる

溶媒と蒸気の平衡

→ $\mu_v(\text{liq}) = \mu_v(\text{gas})$

$$\mu_v^*(\text{liq}) + RT \ln x_v = \mu_v^*(\text{gas})$$

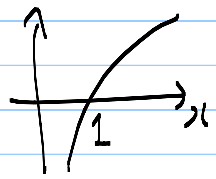
$$\ln x_v = \frac{\mu_v^*(\text{gas}) - \mu_v^*(\text{liq})}{RT}$$

$$= \frac{\Delta G^*(\text{vap})}{nRT} \quad \cdots\cdots (1)$$

vaporization

希薄 → $x_s \ll 1$, $x_v \approx 1$

$$\ln x_v = \ln(1 - x_s) \approx -x_s$$



$\frac{\partial}{\partial T}$ より

$$-\frac{\partial x_s}{\partial T} = \frac{1}{nR}\frac{\partial}{\partial T}\left(\frac{\Delta G^*(\mathrm{vap})}{T}\right)$$

$$= -\frac{\Delta H^*(\mathrm{vap})}{nRT^2}$$ ← 蒸発熱

G-H式 → (=)

$$\Delta H^*(\mathrm{vap})/n = \Delta H^*_m(\mathrm{vap})$$

モル蒸発熱

純溶媒 → 溶液

$x_s = 0$ 　　 $x_s > 0$

T_b^* 　　 T_b 　 $(\Delta T_b = T_b - T_b^*)$

$$x_s = \int_{T_b^*}^{T_b} \frac{\Delta H^*_m(\mathrm{vap})}{RT^2}\, dT$$

変化は小さいとして ΔH^*_m は一定とすると

$$= \frac{\Delta H^*_m(\mathrm{vap})}{R}\left(\frac{1}{T_b^*} - \frac{1}{T_b}\right)$$

$$\frac{\Delta T_b}{T_b^* T_b} \approx \frac{\Delta T_b}{T_b^{*2}}$$

$$\Delta T_b = \frac{RT_b^{*2}}{\Delta H^*_m(\mathrm{vap})} x_s$$

G-H式を使わない導出

① $$-x_s = \frac{\Delta G^*(\mathrm{vap})}{nRT}$$

$\Delta G = \Delta H - T\Delta S$ を用いて.

$$-x_s = \frac{\Delta H^*(vap)}{nRT} - \frac{\Delta S^*(vap)}{nR} \quad \cdots ②$$

$x_s = 0 \longrightarrow x_s > 0$

$T_b^* \qquad\qquad T_b$

$$0 = \frac{\Delta H^*(vap)}{nRT_b^*} - \frac{\Delta S^*(vap)}{nR} \quad \cdots ③$$

②③より

$$x_s = \frac{\Delta H_m^*(vap)}{R}\left(\frac{1}{T_b} - \frac{1}{T_b^*}\right)$$

以下同様

$\Delta H_m^*(vap)$の決定

← Clausius－Clapeyronの式