、分子間相互作用を反映

質量作用の法則

$$nA + mB \rightleftarrows lC$$

$$\Delta G = l\mu_C - n\mu_A - m\mu_B$$

$$= l(\mu_C^\ominus + RT\ln a_C)$$

$$-n(\mu_A^\ominus + RT\ln a_A)$$

$$-m(\mu_B^\ominus + RT\ln a_B)$$

$$= \cdots\cdots$$

$$= \Delta G^\ominus + RT\ln\left(\frac{a_C{}^l}{a_A^n\, a_B^m}\right)$$

↑

$$l\mu_C^\ominus - n\mu_A^\ominus - m\mu_B^\ominus$$

平衡　$\Delta G = 0$　　　$K = e^{-\Delta G^\circ/RT}$

$$\Delta G^\ominus = -RT\ln K$$

$$K = \frac{a_C^l}{a_A^n\, a_B^m}$$ 平衡定数

$a_i \leftarrow p_i$, $[i]$

Gibbs-Helmholtzの式

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

GのT依存性 $\longleftrightarrow$ H (熱, P一定)

(導出1) $dG = -S\,dT + V\,dP + \mu\,dN$

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

よって $G = H - TS \rightarrow \frac{\partial G}{\partial T} = \overbrace{\frac{\partial H}{\partial T} - T\frac{\partial S}{\partial T}}^{=0} - S$

$$= H + T\left(\frac{\partial G}{\partial T}\right)_{P,N} \iff (*)$$

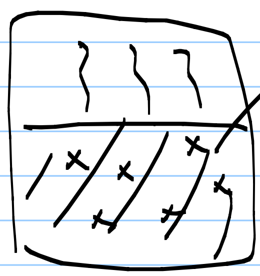
(導出2) $G = H - TS$

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

$G(T,P,N)$
$H(S,P,N)$
$S(U,V,N)$

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

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