Chapter 6. The Thermodynamics of Solutions

6.1 Ideal Solutions

$\mu_i(T,\ P) = \mu_i^\bullet(T,\ P) + \mathrm{R}T\ln x_i$ for 每一 component

(可視爲 definition, 也可用 entropy of mixing 觀念導出來)

〈Note〉 此時, standard state 即爲 pure substance at $T,\ P$

因 $x_i = 1$時, $\mu_i(T,\ P) = \mu_i^\bullet(T,\ P)$

(1) Raoult's Law： $P_i = P_i^\bullet x_i$

先說明P_i及$P_i^\bullet$

$$\begin{cases} \text{pure substance} & \text{蒸汽壓 } P_i^\bullet \text{ (課本用 } P_i^*\text{)} \\ \text{mixture} & \text{蒸汽壓 } P_i \end{cases}$$

ideal solution 遵守 Raoult's law

〈證明〉：基本知識：$\mu_\mathrm{g} = \mu_\mathrm{g}{}^\circ + \mathrm{R}T\ln\left(P_i/P^\circ\right)$ for gas (ideal gas)

$\mu_l = \mu^\bullet(T,\ P) + \mathrm{R}T\ln x_i$ for solution (P 即 solution 之 vapor pressure)

☆ 但 P 未必就是 $P^\bullet$ (vapor pressure of pure liquid)，不過 μ 的 P-dependence 很小

又 $\mu_\ell^\bullet(T,\ P^\bullet) - \mu_\ell^\bullet(T,\ P) = \overline{V}^\bullet(P^\bullet - P)$ 對 liquid

Pure liquid 時, 蒸汽壓爲 $P_i^\bullet$, $\mu_l = \mu_\mathrm{g}$

故 $\mu_i^\bullet(T,\ P_i^\bullet) = \mu_i{}^\circ + \mathrm{R}T\ \ln\left(P_i^\bullet/P^\circ\right)$

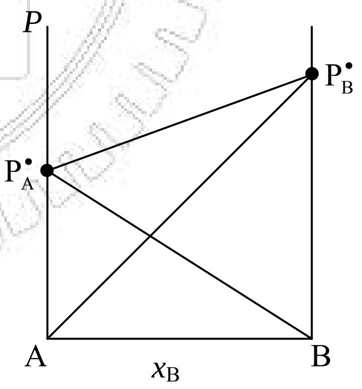
Solution時, 蒸汽壓爲 P_i, $\mu_l = \mu_\mathrm{g}$

即 $\mu_i^\bullet(T,\ P_i) + \mathrm{R}T\ln x_i = \mu_i{}^\circ + \mathrm{R}T\ln\left(P_i/P^\circ\right)$

$$\mu_i^\bullet(T,\ P_i^\bullet)\overset{\text{可忽略}}{\boxed{-\overline{V}^\bullet(P_i^\bullet - P_i)}} + \mathrm{R}T\ln x_i = \mu_i{}^\circ + \mathrm{R}T\ln\left(P_i/P^\circ\right)$$

$$\mu_i{}^\circ + \mathrm{R}T\ln\left(P_i^\bullet/P^\circ\right) + \mathrm{R}T\ln x_i = \mu_i{}^\circ + \mathrm{R}T\ln\left(P_i/P^\circ\right)$$

故 $\boxed{P_i = P_i^\bullet x_i}$



(2) ideal solution 之 mixing 與 ideal gas 相似

$$G_{(soln)} = \sum_{i=1}^{c} n_i\mu_i = \sum_{i=1}^{c} n_i\left[\mu_i^{\bullet} + RT\ln x_i\right],\ \mu_i = \mu_i^{\bullet} + RT\ln x_i$$

$$故\begin{cases} \overline{S_i} = \overline{S_i^{\bullet}} - R\ln x_i \qquad 因\ \overline{S_i} = -\left(\dfrac{\partial\mu_i}{\partial T}\right)_{\mathrm{P,\,n}} = -\left(\dfrac{\partial\mu_i^{\bullet}}{\partial T}\right)_{\mathrm{P,\,n}} - \mathrm{R}\ln x_i \\ \left.\begin{array}{l} \overline{H_i} = \overline{H_i^{\bullet}} \\ \overline{V_i} = \overline{V_i^{\bullet}} \end{array}\right\} 均不隨濃度改變,\ 因 \begin{cases} \overline{H_i} = \overline{\mu_i} + T\overline{S_i} = \overline{\mu_i^{\bullet}} + \mathrm{R}T\ln x_i + T\left(\overline{S_i^{\bullet}} - \mathrm{R}\ln x_i\right) = \overline{\mu_i^{\bullet}} + T\overline{S_i^{\bullet}} \\ \overline{V_i} = \left(\dfrac{\partial\mu_i}{\partial P}\right)_{\mathrm{T}} = \left(\dfrac{\partial\mu_i^{\bullet}}{\partial P}\right)_{\mathrm{T}} \end{cases} \end{cases}$$

又 $G_{(\mathrm{unmix})} = \sum n_i\mu_i^{\bullet}$ 故 $\boxed{\Delta G_{\mathrm{mix}} = \mathrm{R}T\sum_{i=1}^{c} n_i(\ln x_i)}$

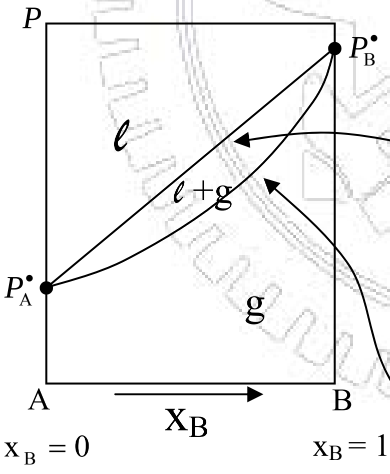
故 $\Delta S_{\mathrm{mix}} = -\left(\dfrac{\partial\Delta G_{\mathrm{mix}}}{\partial T}\right)_{\mathrm{P}} = \boxed{-\mathrm{R}\sum_{i=1}^{c} n_i\ln x_i}$ 或用 $\Delta S_{\mathrm{mix}} = S_{\mathrm{soln}} - S_{\mathrm{pure}}$

$\Delta H_{\mathrm{mix}} = 0$ 證法仿上, 用 $\Delta H = \Delta G + T\Delta S$ 或用 $\dfrac{-H}{T^2} = \left(\dfrac{\partial \mu/T}{\partial T}\right)_{\mathrm{P}}$

$\Delta V_{\mathrm{mix}} = 0$ 用 $V_i = \left(\dfrac{\partial\mu_i}{\partial P}\right)_{\mathrm{T}}$ 或用 $\Delta V_{\mathrm{mix}} = V_{\mathrm{soln}} - V_{\mathrm{pure}}$

(3) Phase diagram of 2-component ideal solutions

① Pressure-composition phase diagrams



"P" →
在 liq. 表外壓
在有 gas 時
表蒸氣壓

x_{A}, x_{B} 爲 soln.之 mole fraction

For gas phase $P_{\mathrm{T}} = P_{\mathrm{A}}^{\bullet}x_{\mathrm{A}} + P_{\mathrm{B}}^{\bullet}x_{\mathrm{B}}$

$\boxed{P_{\mathrm{T}} = P_{\mathrm{A}}^{\bullet} + (P_{\mathrm{B}}^{\bullet} - P_{\mathrm{A}}^{\bullet})x_{\mathrm{B}}}$ 直線, 實用上 $\boxed{x_{\mathrm{B}} = \dfrac{P_{\mathrm{T}} - P_{\mathrm{A}}^{\bullet}}{P_{\mathrm{B}}^{\bullet} - P_{\mathrm{A}}^{\bullet}}}$

composition of vapor

$$x_{\mathrm{A}}^{(\mathrm{v})} = \frac{P_{\mathrm{A}}}{P_{\mathrm{T}}} = \frac{P_{\mathrm{A}}^{\bullet}x_{\mathrm{A}}}{P_{\mathrm{A}}^{\bullet}x_{\mathrm{A}} + P_{\mathrm{B}}^{\bullet}x_{\mathrm{B}}} \quad 和\ x_{\mathrm{A}}\ 不同$$

$$x_{\mathrm{B}}^{(\mathrm{v})} = \frac{P_{\mathrm{B}}}{P_{\mathrm{T}}} = \frac{P_{\mathrm{B}}^{\bullet}x_{\mathrm{B}}}{P_{\mathrm{A}}^{\bullet}x_{\mathrm{A}} + P_{\mathrm{B}}^{\bullet}x_{\mathrm{B}}} \quad 和\ x_{\mathrm{B}}\ 不同$$

$$x_{\mathrm{B}}^{(\mathrm{v})} = \frac{P_{\mathrm{B}}^{\bullet}}{P_{\mathrm{T}}}x_{\mathrm{B}}$$

故 $P_{\mathrm{T}} = \dfrac{P_{\mathrm{A}}^{\bullet}P_{\mathrm{B}}^{\bullet}}{P_{\mathrm{A}}^{\bullet} + x_{\mathrm{A}}^{(\mathrm{v})}(P_{\mathrm{B}}^{\bullet} - P_{\mathrm{A}}^{\bullet})} = \boxed{\dfrac{P_{\mathrm{A}}^{\bullet}P_{\mathrm{B}}^{\bullet}}{P_{\mathrm{B}}^{\bullet} + x_{\mathrm{B}}^{(\mathrm{v})}(P_{\mathrm{A}}^{\bullet} - P_{\mathrm{B}}^{\bullet})}}$ 曲線

在 $x_{\mathrm{A}} \to 0$, $P_{\mathrm{T}} \to P_{\mathrm{B}}^{\bullet}$

$x_{\mathrm{B}} \to 0$, $P_{\mathrm{T}} = P_{\mathrm{A}}^{\bullet}$

其他 x 值 , P_{T} 線在上面直線之右邊

由 $P_{\mathrm{T}} = P_{\mathrm{A}}^{\bullet} + (P_{\mathrm{B}}^{\bullet} - P_{\mathrm{A}}^{\bullet})x_{\mathrm{B}}$

$= P_{\mathrm{A}}^{\bullet} + (P_{\mathrm{B}}^{\bullet} - P_{\mathrm{A}}^{\bullet})x_{\mathrm{B}}^{(\mathrm{v})}\dfrac{P_{\mathrm{T}}}{P_{\mathrm{B}}^{\bullet}}$ 而來

$$P_{\mathrm{B}}^{\bullet}P_{\mathrm{T}} = P_{\mathrm{A}}^{\bullet}P_{\mathrm{B}}^{\bullet} + (P_{\mathrm{B}}^{\bullet} - P_{\mathrm{A}}^{\bullet})x_{\mathrm{B}}^{(\mathrm{v})}P_{\mathrm{T}}$$

$$因爲\ \frac{1}{x_A^{(v)}} = 1 + \frac{P_B^{\bullet} x_B}{P_A^{\bullet} x_A} = 1 + \frac{P_B^{\bullet}(1-x_A)}{P_A^{\bullet} x_A}$$

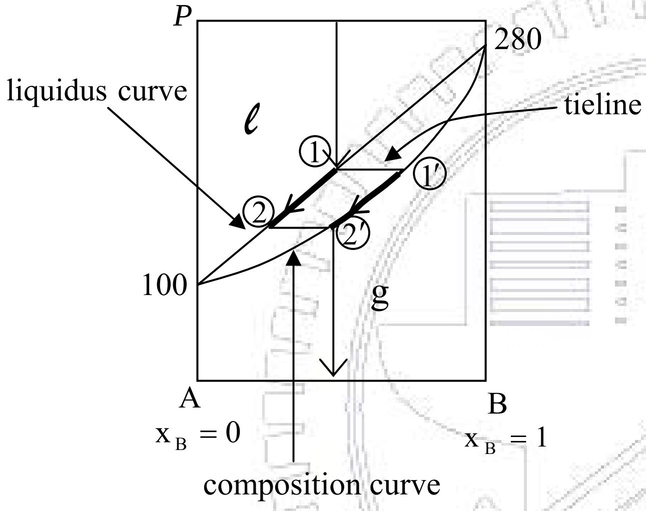
$$= 1 - \frac{P_B^{\bullet}}{P_A^{\bullet}}\left(1 - \frac{1}{x_A}\right)$$

$1 - \frac{1}{x_A^{(v)}} = \frac{P_B^{\bullet}}{P_A^{\bullet}}\left(1 - \frac{1}{x_A}\right)$，$P_B^{\bullet}$ 大於 $P_A^{\bullet}$ 時，則 $1 - \frac{1}{x_A^{(v)}}$ 小於 $1 - \frac{1}{x_A}$

即 $x_A^{(v)}$小於 x_A, 或 $x_B^{(v)}$大於 x_B

討論此 phase diagram

(對特定之 *T*)



binary ideal solution

(1) phase rule f : c − p + 2 = 4 − p
  p = 1 時, f = 3, 要知 P, T, x_A (或 x_B)
  p = 2 時, f = 2, 要知 P 及 T (或 x_A 或 x_B)
  p = 3 時, f = 1, 要知 P 或 T (此相圖看不到)

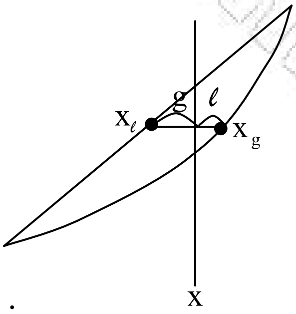
(2) 用 liquid (solution) 慢慢減壓爲例
  點 ① 時, 開始 vaporize, 組成爲 ①′, x_B~0.74
  (因 B 較 volatile)

(3) 繼續降壓, 則 liquid 組成隨 ① → ②
  vapor 組成隨 ①′ → ②′
  liq.及 vapor mole 比由 lever rule 決定

(4) 到最後一滴 liquid, 組成爲 ②, 此時 vapor 組成 ②′
  近似於原先之 liquid

(5) 再降壓則全部 vaporize

〈lever rule〉



在 ℓ + g region 設有 n_ℓ mole 之 liquid 組成爲 x_ℓ

n_g mole 之 vapor 組成爲 x_g

平均組成爲 x

則 $(n_l + n_g)x = n_l x_l + n_g x_g$

$$\frac{n_l}{n_g} = \frac{x_g - x}{x - x_l}$$

<學例>：

(a) $P_B^{\bullet} = 280$ Torr, $P_A^{\bullet} = 100$ Torr at 60°C, A = 2-Me-propanol, B = 2-propanol

$x_B = 0.5 = x_A$ 時, $P_A = 50$ Torr, $P_B = 140$ Torr, $P_T = 190$ Torr

$x_A^{(v)} = 50/190 = 0.26$, $x_B^{(v)} = 140/190 = 0.74$

(b) 如 $P_T = 160$ Torr, 則 $x_B = \frac{160-100}{280-100} = \frac{60}{180} = \frac{1}{3}$

$$x_B^{(v)} = \frac{280\times\frac{1}{3}}{160} = 0.58$$

自己練習算出 liq. 及 vapor 之 mole 數比例

(c) 在何壓力下最後一滴 solution vaporize?

代公式, $P_T = \dfrac{280\cdot 100}{280-180\,x_B^{(v)}} = \dfrac{28000}{280-90} = \dfrac{28000}{190}$

或由觀念上來解: $x_B^{(v)} = 0.5 = \dfrac{280\cdot x_B}{P_T}$, 又 $x_B = \dfrac{P_T-100}{280-100}$

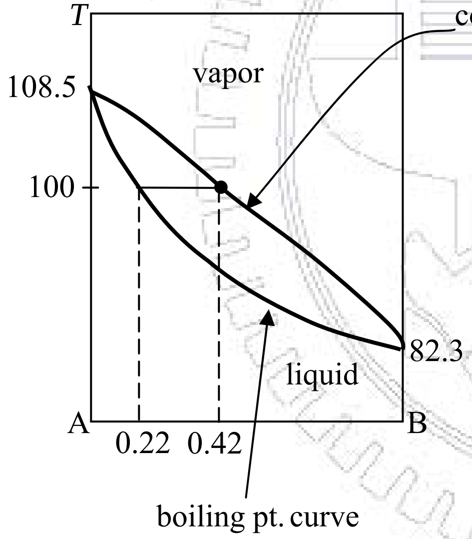
解 $\begin{cases} 280\,x_B = 0.5\,P_T \\ 180\,x_B = P_T - 100 \end{cases}$

$$560\,x_B = P_T \ ,\ x_B = \frac{100}{560-180} = \frac{100}{380}$$

$$P_T = \frac{56000}{380} = 147.4 \text{ Torr}$$

② Temperature-composition phase diagrams (T vs. x_B)

〈 P = 760 Torr 〉



〈 Boiling point curve〉

$$760 = P_A^{\bullet} x_A + P_B^{\bullet}(1-x_A)$$

或 $x_A = \dfrac{760-P_B^{\bullet}}{P_A^{\bullet}-P_B^{\bullet}}$

例：at 100°C, $P_A^{\bullet} = 570$ Torr (methyl propanol)

$P_B^{\bullet} = 1440$ Torr (propanol-2)

則 $x_A = \dfrac{760-1440}{570-1440} = \dfrac{680}{870} = 0.782$

$x_B = 0.22$

〈 Condensation curve〉

$$x_A^{(v)} = 570\times 0.782 \big/ 760 = 0.585\ ,\ x_B^{(v)} = 0.415$$

Constant - pressure distillation:

參考課本Figure 6.5

最後是蒸出 pure B
↑
more volatile component

3-dimensional diagram

參考課本Figure 6.4

全圖 (包括 solid, liquid, 及 vapor)

參考課本 Figure 6.7

6.2 Henry’s Law and Dilute Nonelectrolyte Solution

for non-ideal solution 但是”ideally dilute ” solution

參考課本Figure 6.9

1. Henry’s Law

① Raoult’s law 在 $x_1 \to 0$ (for “2”) 或 $x_2 \to 0$ (for “1”)時，大致成立

即：nearly pure component 近乎 ideal

即：solvent in a dilute solution obeys Raoult’s law

② Henry’s law 在 $x_2 \to 0$ 時 (for “2”)

即：solute in a dilute solution obeys Henry’s Law

$$\boxed{P_i = k_i x_i}$$

也可用 m，則 $k_i \to k_i^{(m)}$

但 standard state 就不同了

不是用 $P_i^{\bullet}$ as in ideal solution

此時 $\mu_{i(\text{soln})} = \mu_{i(\text{vap})} = \mu^{\circ}_{i(\text{gas})} + RT\ln\frac{P_i}{P^{\circ}}$

$$= \mu^{\circ}_{i(\text{gas})} + RT\ln\frac{k_i x_i}{P^{\circ}}$$

$$= \boxed{\mu^{\circ}_{i(\text{gas})} + RT\ln\frac{k_i}{P^{\circ}}} + RT\ln x_i$$

$\mu_i^{(H)}$

$$= \mu_i^{(H)} + RT\ln x_i$$

假想 (不存在) 的 standard state

即具 k_i vapor pressure 之 pure substance

〈這樣子才可寫成與 ideal solution一樣的式子〉

滿足 Henry’s Law 也可視爲是 ideal soln.

只是 reference state 不同

<應用>：(1) Nernst distribution law 在 2 個 phase 中 (如：萃取)

$$K_\mathrm{d} = \frac{x_i^{(\mathrm{II})}}{x_i^{(\mathrm{I})}} \quad \text{定義}$$

但 $\mu_i^{(\mathrm{I})} = \mu_{i(\mathrm{I})}^{(\mathrm{H})} + RT \ln x_i^{(\mathrm{I})}$

$\mu_i^{(\mathrm{II})} = \mu_{i(\mathrm{II})}^{(\mathrm{H})} + RT \ln x_i^{(\mathrm{II})}$

平衡時

$$\mu_i^{(\mathrm{I})} = \mu_i^{(\mathrm{II})},\ \mu_{i(\mathrm{I})}^{(\mathrm{H})} - \mu_{i(\mathrm{II})}^{(\mathrm{H})} = \mathrm{R}T \ln x_i^{(\mathrm{II})} - RT \ln x_i^{(\mathrm{I})} = \mathrm{R}T \ln K_\mathrm{d}$$

$$\text{故 } K_\mathrm{d} = \exp\left[\frac{\mu_{i(\mathrm{I})}^{(\mathrm{H})} - \mu_{i(\mathrm{II})}^{(\mathrm{H})}}{\mathrm{R}T}\right] = \exp\left[\ln \frac{k_i^{(\mathrm{I})}}{k_i^{(\mathrm{II})}}\right] = \frac{k_i^{(\mathrm{I})}}{k_i^{(\mathrm{II})}} \leftarrow \text{反比關係}$$

(2) CO_2 溶於水, $k_\mathrm{m}^{(\mathrm{H})} = 29.4\ \mathrm{bar\ m}^{\circ -1}$

則 P_{CO_2} =1 bar 時, $1 = k_\mathrm{m}^{(\mathrm{H})} \cdot m$

故 $m = 0.034\ \mathrm{m}^\circ$

Solvent obeys Raoult's law 但 solute obeys Henry's law 是否違背 Gibbs-Duhem eq.？

Gibbs-Duhem：原是 $n_1\, \mathrm{d}\mu_1 + n_2\, \mathrm{d}\mu_2 = 0$, 可寫成 $x_1 \left(\frac{\partial \mu_1}{\partial x_2}\right)_{\mathrm{T,\,P}} + x_2 \left(\frac{\partial \mu_2}{\partial x_2}\right)_{\mathrm{T,\,P}} = 0$

$$\left(\frac{\partial \mu_2}{\partial x_2}\right)_{\mathrm{T,\,P}} = \mathrm{R}T\left(\frac{\partial \ln x_2}{\partial x_2}\right) = \frac{\mathrm{R}T}{x_2},\ \text{故 } x_2\left(\frac{\partial \mu_2}{\partial x_2}\right)_{\mathrm{T,\,P}} = \frac{x_2 \mathrm{R}T}{x_2} = \mathrm{R}T$$

$$x_1\left(\frac{\partial \mu_1}{\partial x_2}\right)_{\mathrm{T,\,P}} = -x_1\left(\frac{\partial \mu_1}{\partial x_1}\right)_{\mathrm{T,\,P}},\ \text{即} -x_1\left(\frac{\partial \mu_1}{\partial x_1}\right)_{\mathrm{T,\,P}} + \mathrm{R}T = 0$$

$$\text{故}\left(\frac{\partial \mu_1}{\partial x_1}\right)_{\mathrm{T,\,P}} \mathrm{d}x_1 = \frac{\mathrm{R}T}{x_1}\mathrm{d}x_1$$

由 $x_1 = 1$ 積分到 $x_1 = x_1' = 1 - x_2'$

$$\mu_1\left(x_1'\right) - \mu_1\left(x_1 = 1\right) = \mathrm{R}T\left[\ln\left(x_1'\right) - \ln(1)\right]$$

即 $\mu_1\left(x_1\right) = \mu_1^\bullet + \mathrm{R}T \ln x_1$, 和 Raoult's law 一樣

6.3 Activity and activity coefficients

不遵守 Raoult’s law 或 Henry’s law 者如何描述？

1. Non-ideal solution-activity

$\mu_i = \mu_i^{\circ} + \mathrm{R}T \ln a_i$ 此即 a_i 之原始定義 (類似氣態中之 fugacity vs. P)

a_i 可用 mole fraction x_i 或 P_i/P°, m_i/m°, c_i/c° 表之

① 沒有 dimension

② $a = 1$ for standard state

activity 中文雖叫“ 活性”，但其實即“ideal 濃度 (相對於 reference state)”

(1) a for a pure solid or liquid

因 standard state 爲 pure substance at P° (1 bar)

故 $a = 1$ for $P = 1$ bar

$P \neq \mathrm{P}^{\circ}$ 時,
$$\mu_i(P) = \mu_i^{\circ} + \overline{V_i^{\bullet}}(P - \mathrm{P}^{\circ})$$
$$= \mu_i^{\circ} + \mathrm{R}T \ln a_i$$

故 $\boxed{a_i = \exp\left[\dfrac{\overline{V_i^{\bullet}}(P-\mathrm{P}^{\circ})}{\mathrm{R}T}\right]} \approx 1$ 除非壓力很大

〈例〉: 2 atm, 298.15 K $H_2O_{(l)}$ 之 $a = \exp\left[\dfrac{1.805\times10^{-5}\times(2-1)\times101325}{8.3145\times298.15}\right]$
$$= \exp(0.0007378)$$
$$a = 1.000738 \approx 1$$

但 100 atm, $a \approx 1.074$

(2) a for an ideal gas

對 ideal gas: $\mu_i = \mu_i^{\circ} + \mathrm{R}T \ln P_i/\mathrm{P}^{\circ}$

故 $\boxed{a_i = P_i/\mathrm{P}^{\circ}}$

(3) a for a non-ideal gas 似上, 但 $P_i \to f_i$

activity coefficient

$\boxed{a_i = f_i/\mathrm{P}^{\circ}}$, $\gamma_i = \dfrac{a_i(\text{real})}{a_i(\text{ideal})} = \boxed{\dfrac{f_i}{P_i}}$, ideal gas 之 $\gamma_i = 1$

故 $\mu_i = \mu_i^{\circ} + \mathrm{R}T \ln \dfrac{\gamma_i P_i}{\mathrm{P}^{\circ}}$ ，就不必用 fugacity 了

(4) a for an ideal solution :

$a_i = x_i$, 故 $\mu_i^{\circ} = \mu_i^{\bullet}$

應是 solid 但還沒有變 solid

但此時 solute 之 reference state 即爲 supercooled (metastable)

例：naphthalene in benzene

參考課本Figure 6.8

<Note> 此時 standard P 是 at the pressure of the solution, 而非某一特定之 P

ideal

$\mu_{ig}^{o} + RT \ln P_i = \mu_{il}^{\bullet} + RT \ln x_i$

pure : $\mu_{ig}^{o} + RT \ln P_i^{\bullet} = \mu_{il}^{\bullet}$

Raoult's law

$\mu_{ig}^{o} + RT \ln P_i^{\bullet} x_i = \mu_{il}^{\bullet} + RT \ln x_i$

即 $\mu_{ig}^{o} + RT \ln P_i^{\bullet} = \mu_{il}^{\bullet}$

省略 "i", $\mu_{g}^{o} + RT \ln P^{\bullet} = \mu_{l}^{\bullet}$, 即 pure substance 之 liq. 與 vap. 之平衡

(5) a for a non-ideal solution

(A) Convention I

不分 solvent 和 solute, 只看 mole fraction

即 std. state 爲 pure substance at the T, P of the solution.

solution gas

此時 $\mu_{il}^{o} + RT \ln a_i = \mu_{ig}^{o} + RT \ln P_i / P^{o}$

$\downarrow \quad \|$

$\mu_{ig}^{o} + RT \ln \frac{P_i^{\bullet}}{P^{o}} + RT \ln a_i^{(I)}$, 故 $\boxed{P_i = P_i^{\bullet} a_i}$, 即 : $\boxed{a_i^{(I)} = \frac{P_i}{P_i^{\bullet}}}$

似 Raoult's law

$$\gamma_i^{(I)} = \boxed{\frac{a_i}{x_i}} = \frac{P_i}{P_i^{\bullet} x_i} = \boxed{\frac{P_i}{P_{i(\text{ideal})}}}$$

定義

compare, 觀念上很重要

a 是和 ref.比, 或可視爲"ideal"之 mole fraction

γ 是和 ideal 狀態下比

〈例 1〉 $x = 0.25$, vap pressure = 60 torr for pure liquid

= 48 torr for solution

$$a = \frac{48}{60} = 0.8$$

$$\gamma = \frac{0.80}{0.25} = 3.2$$

或 $\gamma = \dfrac{48}{60 \times 0.25} = \dfrac{48}{15} = 3.2$

〈例 2〉 對 solute 而言, 如果 obey Henry's law, 但用convention I, 則 $a_2^{(\mathrm{I})} = k_2^{(\mathrm{H})} x_2 / P_2^{\bullet}$

$$\gamma_2^{(\mathrm{I})} = k_2^{(\mathrm{H})} x_2 / P_2^{\bullet} x_2 = k_2^{(\mathrm{H})} / P_2^{\bullet}$$

對 solvent 而言, 如果 obey Raoult's law, 則 $a_1^{(\mathrm{I})} = P_1^{\bullet} x_1 / P_1^{\bullet} = x_1$

$$\gamma_1^{(\mathrm{I})} = P_1^{\bullet} x_1 / P_1^{\bullet} x_1 = 1$$

(B) Convention II

分 solvent 與 solute, solvent 通常是“1”, solute 是“2”

① solvent 與 convention I 相同

$$\gamma_1^{(\mathrm{II})} = \gamma_1^{(\mathrm{I})} = \frac{P_1}{P_1^{\bullet} x_1}$$

② solute 用 Henry’s law 之 derivation

$$\mu_i^{\mathrm{o(II)}} = \mu_i^{\mathrm{o(H)}} = \mu_i^{\mathrm{o(g)}} + RT \ln \frac{k_i^{(\mathrm{H})}}{\mathrm{P^o}}$$

而 $\mu_i = \mu_i^{\mathrm{o(II)}} + \mathrm{R}T \ln a_i^{(\mathrm{II})}$ 要成立,

故 $\mu_i^{\mathrm{o(g)}} + \mathrm{R}T \ln \dfrac{k_i^{(\mathrm{H})}}{\mathrm{P^o}} + \mathrm{R}T \ln a_i^{(\mathrm{II})} = \mu_i^{\mathrm{o(g)}} + \mathrm{R}T \ln \dfrac{P_i}{\mathrm{P^o}}$

即 $\boxed{P_i = k_i a_i^{(\mathrm{II})}}$ 即把 Henry's law 中之 x_i 用 a_i 取代

$$\boxed{\gamma_i^{(\mathrm{II})} = a_i^{(\mathrm{II})} \big/ x_i = P_i \big/ k_i^{(\mathrm{H})} x_i = 1}$$

§ 通常選擇 $\gamma \to 1$ 之 convention $\to \mu_i = \mu_i^{\mathrm{o(II)}} + \mathrm{R}T \ln x_i$

<Note>此時，對 solute 而言，如 obey Henry’s law, 使用 convention II，

則 $a_2^{(\mathrm{II})} = k_2^{(\mathrm{H})} x_2 / k_2^{(\mathrm{H})} = x_2$

(6) Express activity coefficients with other concentration expressions

(A) molality: m 1000g solvent 含 *m* mole 之 solute, 單位以 m°表之 (即：1 *m*)

$x_2 = \dfrac{m}{m + {}^{1}\!/\!_{M_1}}$, $x_1 = \dfrac{{}^{1}\!/\!_{M_1}}{m + {}^{1}\!/\!_{M_1}}$, M_1 爲 solvent 之分子量 (in kg)

故 $\dfrac{m}{x_2} = \dfrac{{}^{1}\!/\!_{M_1}}{x_1}$, $m = \dfrac{x_2}{x_1 M_1}$, $\boxed{x_2 = x_1 M_1 m} \approx M_1 m$ if $x_1 \to 1$

故 Henry's law 可表爲 $P_2 = k_2^{(\mathrm{H})} m M_1 x_1$

$= k_2^{(\mathrm{m})} m$, 即 $k_2^{(\mathrm{m})} = k_2^{(\mathrm{H})} M_1 x_1$

$$\mu_2 = \mu_2^{\circ(\mathrm{II})} + \mathrm{R}T \ln \gamma_2^{(\mathrm{II})} x_2$$

$$= \mu_2^{\circ(\mathrm{II})} + \mathrm{R}T \ln \gamma_2^{(\mathrm{II})} m x_1 M_1,\ (\gamma_2^{(\mathrm{II})} = 1,\ m = 1\,\mathrm{m}^\circ,\ x_1 \square 1 \text{時爲 } \mu_2^{\circ(\mathrm{m})})$$

$$= \underbrace{\mu_2^{\circ(\mathrm{II})} + \mathrm{R}T \ln M_1 \mathrm{m}^\circ}_{\mu_i^{\mathrm{o(m)}}} + \mathrm{R}T \ln \underbrace{\frac{\gamma_2^{(\mathrm{II})} x_1 m}{\mathrm{m}^\circ}}_{a_i^{(\mathrm{m})}},\ \mathrm{m}^\circ = 1 \text{ mol kg}^{-1}$$

$$= \mu_2^{\circ(\mathrm{m})} + \mathrm{R}T \ln (\gamma^{(\mathrm{m})}\, {}^{m}\!/\!_{\mathrm{m}^\circ}) \qquad \gamma^{(\mathrm{m})} = \gamma^{(\mathrm{II})} x_1$$

molality activity coefficient

(B) molarity(課本稱”concentration”)description, 即 M

$x_2 \square \dfrac{c}{c + \dfrac{1}{\overline{V}}} \square c\overline{V}$ (V_1 in liter)

則要使 $\mu_2 = \mu_2^{\mathrm{o(c)}} + \mathrm{R}T \ln \dfrac{\gamma_2^{\mathrm{o(c)}} c}{\mathrm{c}^\circ}$ 成立，$\mathrm{c}^\circ = 1 \text{ mol L}^{-1}$

但 $\mu_2 = \mu_2^{\mathrm{o(II)}} + \mathrm{R}T \ln \gamma_2^{(\mathrm{II})} c\overline{V}$, ($\gamma_2^{(\mathrm{II})} = 1$, c=1 c°, $V \approx V_1^\bullet$ 時爲 $\mu_2^{\mathrm{o(c)}}$)

$$= \mu_2^{\mathrm{o(II)}} + \mathrm{R}T \ln \frac{\gamma_2^{(\mathrm{II})} c\overline{V}}{\mathrm{c}^\circ V_1^\bullet} \cdot V_1^\bullet \mathrm{c}^\circ = \underbrace{\mu_2^{\mathrm{o(II)}} + \mathrm{R}T \ln V_1^\bullet \mathrm{c}^\circ}_{\mu_2^{\mathrm{o(c)}}} + \mathrm{R}T \ln \underbrace{\frac{\gamma_2^{(\mathrm{II})} \overline{V}}{V_1^\bullet}}_{\gamma_2^{(\mathrm{c})}} \frac{c}{\mathrm{c}^\circ}$$

故 $\mu_2^{\mathrm{o(c)}} = \mu_2^{\mathrm{o(II)}} + \mathrm{R}T \ln \overline{V_1^\bullet} \mathrm{c}^\circ$, $\gamma_2^{(\mathrm{c})} = \dfrac{\gamma_2^{(\mathrm{II})} \overline{V}}{\overline{V_1^\bullet}}$

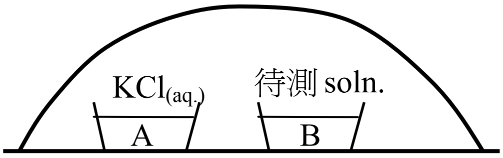
6.4 The activity of Nonvolatile Solutes

nonvolatile 物質蒸汽壓很低，不易量

通常可利用 (1) Gibbs-Duhem, (2) Debye-Hückel, (3) 電化學方法 來算

(1) isopiestic method

$KCl_{(aq.)}$是 reference solution (A), 待測 solution 爲 (B)



密閉久置於恆溫下，兩者平衡

solvent 是 1, solute 是 2, $\mu_1^{(A)} = \mu_1^{(B)} = \mu_{1g} \Rightarrow a_1^{(A)} = a_1^{(B)}$

$$\gamma_1^{(B)} = \frac{a_1^{(B)}}{x_1^{(B)}} = \frac{a_1^{(A)}}{x_1^{(B)}} = \frac{\gamma_1^{(A)} x_1^{(A)}}{x_1^{(B)}}$$

可由實驗測得, $\gamma_1^{(A)}$ 已知

因 $x_1 \mathrm{d}\ln(a_1) + x_2 \mathrm{d}\ln(a_2) = 0$ (Gibbs-Duhem, $x_1\mathrm{d}\mu_1 + x_2\mathrm{d}\mu_2 = 0$)

用 Convention II, $a_1 = \gamma_1 x_1$, $a_2 = \gamma_2 x_2$ (省略"(II)")

又 $x_i \mathrm{d}\ln x_i = \mathrm{d}x_i$

故 $x_1 \mathrm{R}T\ \mathrm{d}\ln\gamma_1 + \mathrm{R}T\ \mathrm{d}x_1 + x_2\mathrm{R}T\ \mathrm{d}\ln\gamma_2 + \mathrm{R}T\ \mathrm{d}x_2 = 0$

$$x_1\ \mathrm{d}\ln\gamma_1 + x_2\ \mathrm{d}\ln\gamma_2 = 0$$

$$\mathrm{d}\ln\gamma_2 = -\frac{x_1}{x_2}\mathrm{d}\ln\gamma_1 = -\frac{x_1}{1-x_1}\mathrm{d}\ln(\gamma_1)$$

由 $x_1 = x_1'' \approx 1$, 積分到 $x_1 = x_1'$

則 $\ln\gamma_2(x_1') = -\int_{x_1''}^{x_1'} \frac{x_1}{1-x_1}\ \mathrm{d}\ln\gamma_1$

對於電解質溶液之應用，於第八章再說

(2) Debye-Hückel Theory

第八章再討論

6.5 Thermodynamic Functions of Nonideal Solutions

1. Partial molar quantities

$$\mu_i = \mu_i^{\bullet} + \mathrm{R}T\ln a_i = \mu_i^{\bullet} + \mathrm{R}T\ln \gamma_i^{(\mathrm{I})} x_i$$

$$\bar{S}_i = -\left(\frac{\partial \mu_i}{\partial T}\right)_{\mathrm{P,\,n}} = -\left(\frac{\partial \mu_i^{\bullet}}{\partial T}\right)_{\mathrm{P,\,n}} - \mathrm{R}\ln \gamma_i^{(\mathrm{I})} x_i - \mathrm{R}T\left(\frac{\partial \ln \gamma_i^{(\mathrm{I})} x_i}{\partial T}\right)_{\mathrm{P,\,n}}$$

$$= \left(S_i^{\bullet} - \mathrm{R}\ln x_i\right) - \mathrm{R}\ln \gamma_i^{(\mathrm{I})} - \mathrm{R}T\left(\frac{\partial \ln \gamma_i^{(\mathrm{I})}}{\partial T}\right)_{\mathrm{P,\,n}}$$

$$= S_i^{(\mathrm{ideal})} - \mathrm{R}\ln \gamma_i^{(\mathrm{I})} - \mathrm{R}T\left(\frac{\partial \ln \gamma_i^{(\mathrm{I})}}{\partial T}\right)_{\mathrm{P,\,n}}$$

由 $\bar{H}_i = \mu_i + T\bar{S}_i$ 可得

$$\bar{H}_i = H_i^{\bullet} - \mathrm{R}T^2\left(\frac{\partial \ln \gamma_i^{(\mathrm{I})}}{\partial T}\right)_{\mathrm{P,\,n}}$$

及 $\bar{V}_i = V_i^{\bullet} + \mathrm{R}T\left(\dfrac{\partial \ln \gamma_i^{(\mathrm{I})}}{\partial P}\right)_{\mathrm{T,\,n}}$

2. Thermodynamic Function of Nonideal Solution

$$G_{\mathrm{soln}} = \sum_{i=1}^{c} n_i\left[\mu_i^{\mathrm{o}} + \mathrm{R}T\ln a_i\right]$$

$$\rightarrow \quad \Delta G_{\mathrm{mix}} = \mathrm{R}T\sum_{i=1}^{c} n_i \ln a_i$$

$$= \mathrm{R}T\sum_{i=1}^{c}(n_i \ln x_i + n_i \ln \gamma_i)$$

$$= \Delta G_{\mathrm{mix}}^{\mathrm{ideal}} + \underbrace{\mathrm{R}T\sum_{i=1}^{c} n_i \ln \gamma_i}_{G^{\mathrm{E}} = G_{(\mathrm{actual})} - G_{(\mathrm{ideal})}}$$

excess Gibbs energy

同理 $S^{\mathrm{E}} = -\mathrm{R}\sum n_i \ln \gamma_i - \mathrm{R}T\sum n_i\left(\dfrac{\partial \ln \gamma_i}{\partial T}\right)_{\mathrm{P,\,n}}$

$$H^{\mathrm{E}} = \Delta H_{\mathrm{mix}} = -\mathrm{R}T^2\sum n_i\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{\mathrm{P,\,n}}$$

$$V^{\mathrm{E}} = \Delta V_{\mathrm{mix}} = \mathrm{R}T\sum n_i\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{\mathrm{T,\,n}}$$

3. Enthalpy change of solution：

(1) integral heat of solution

$$\Delta H_{\mathrm{int,\,1}} = \frac{\Delta H_{\mathrm{mix}}}{n_1},\ \Delta H_{\mathrm{int,\,2}} = \frac{\Delta H_{\mathrm{mix}}}{n_2}$$

(2) differential heat of solution for solute

$$\Delta H_{\text{diff, 2}} = \left(\frac{\partial \Delta H_{\text{mix}}}{\partial n_2}\right)_{\text{T, P, n'}} = \overline{H_2} - \overline{H_2^{\bullet}}$$

4. Tabulated thermodynamics properties for solutes

$$\Delta H_f^{\circ}(i,\ \text{soln.}) = \overline{H_i^{\circ}} - H^{\circ}(\text{elements})$$

通常用 m° 爲濃度單位

$$\Delta \text{G}_f(i,\ \text{soln.}) = \mu_i^{\circ} - G^{\circ}(\text{elements})$$

可由 Table A8 查出：

ao 表示 aqueous solute, not ionized

ai 表示 aqueous electrolyte solute, ionized

6.6 Phase Diagrams of Non-ideal mixtures

見投影片

1. Liq.-vap. Phase diagram
   distillation-theoretical plate

參考課本Figure 6.11

ethanol-diethyl ether, 20℃
positive deviation–壓力較 Raoult's law 高（要看上面之curve)

參考課本Figure 6.12

ethanol-diethyl ether, 1.84 atm
boiling point 較 ideal 低 (要看下面之 curve)

參考課本Figure 6.13

ethanol-benzene
positive deviation 有 azeotropes (共沸物)
在交點上，液態和氣態組成之斜率相同，兩個 phase 之組成相同

參考課本Figure 6.14

acetone-$CHCl_3$
negative deviation
azeotropes–不可能從一邊 distill 到另一邊
討論 excess ΔG
negative– A-B 較穩定
negative deviation 例：dioxane/water
positive– A-B 較不穩定
例：HCl/H_2O

參考課本Figure 6.15

兩個 liq. phase 共存
T_c：upper critical soln. pt.或 upper consolute pt.
在 T_c以上之溫度爲 1-phase
也有可能有 upper 及 lower T_c，如：水及 nicotine, T_c=61.5℃及 233.0℃
upper–因 thermal motion 克服能障
lower–形成 complex，如：triethylamine

參考課本Figure 6.16

Positive deviation 太嚴重
2-phase 區延伸到 liq.-vap.區
在 97.9℃–2 個 liq. phase, 1 個 gas phase
$f=2-3+2=1$ (P or T 中之一個)
steam distillation–furfural
b.p.~160 ℃, 加水後可在 97.9 ℃ bol, 冷凝後, 20℃, x ≈0.78

108.6°C, 80% H_2O 78°C, 4% 水 再乾燥去水

2. Solid-liq. phase diagram

參考課本Figure 6.17

Au-Cu 在固態及液態均可互溶
可利用 zone refining 來純化：圓柱狀固態通過高溫爐,（一個”zone”）熔解再冷凝
例：冰塊外面 clear 裡面霧霧的
↑
先感受到低溫

參考課本Figure 6.18

參考課本Figure 6.19

Au-Cu
solid solution α and β
eutectic point–凝固點較純物質低

cooling curve
水平線–phase transition of “pure” substance
eutectic point
DSC–differential scanning calorimetry, 用加熱測 C_p 以知相變化

xylene-bromobenzene
兩個 solid 幾乎 insoluble
solder: 67% tin 33% Pb, 183°C 溶
冰/鹽: 23% NaCl 77% H_2O, $-21.1°C$ { 結冰時撒鹽水
低於冰點

參考課本Figure 6.20

3. Solid-liq. phase diagram with compounds

參考課本Figure 6.21

形成固體化合物
aniline (A) and phenol (P)
形成 AP (1：1 of A：P) 固體，但 $A_{(s)}$和 $P_{(s)}$不共存
但液體 AP 不存在，熔解後形成相同比例之 solution (congruent melting)，似兩個相圖之加成

參考課本 Figure 6.22

形成四個化合物：$LaCu_6$, $LaCu_4$, $LaCu_2$ 及 LaCu
congruent melting：$LaCu_2$ 及 $LaCu_6$
incongruent melting：LaCu 及 $LaCu_4$
(液態組成改變，且有新的固體產生)
A, B 爲 peritectic point–三相共存，其參數在定壓下是無法改變的 (f=1)
如：735°C 的 $LaCu_4$
或 551°C 的 LaCu

4. 3-component phase diagram

參考課本Figure 6.23

利用 (x_1, x_2, x_3) 表濃度 $x_1+x_2+x_3$ 是定值

參考課本Figure 6.24

H_2O, acetone, ethyl acetate 三種組成，在 30℃及 1atm. Tie line 不必

參考課本Figure 6.25

有 compound 形成
各區之組成要能說出

相互平行

6.7 Colligative (tied together) Properties (依數性質)

只和濃度有關，和分子之 identity 無關，主要有四種

(1) FP depression (2) BP elevation (3) vapor pressure lowering (4) osmotic pressure

(1) FP depression 以 solvent 爲“A”，考慮 A 之凝固

$$\mu_{\mathrm{A(l)}} = \mu_{\mathrm{A(s)}} \quad \text{at FP}$$

$$\mu^{\bullet}_{\mathrm{A(l)}} + \mathrm{R}T \ln a_{\mathrm{A}} = \mu^{\bullet}_{\mathrm{A(s)}} \quad \text{for solution}$$

〈條件 1〉 ideal solution，則

$$\mu^{\bullet}_{\mathrm{A}(l)} + \mathrm{R}T \ln x_{\mathrm{A}} = \mu^{\bullet}_{\mathrm{A(s)}}$$

$$\mu^{\bullet}_{\mathrm{A}(l)}\big/T + \mathrm{R} \ln x_{\mathrm{A}} = \mu^{\bullet}_{\mathrm{A(s)}}\big/T \text{，又} \left(\frac{\partial \mu/T}{\partial T}\right) = \frac{-H}{T^2}$$

$$\frac{-H^{\bullet}_{\mathrm{A}(l)}}{T^2} + \mathrm{R}\frac{\mathrm{d}\ln x_A}{\mathrm{d}T} = \frac{-H^{\bullet}_{\mathrm{A(s)}}}{T^2}$$

$$\frac{\mathrm{d}\ln x_A}{\mathrm{d}T} = \frac{H^{\bullet}_{\mathrm{A}(l)} - H^{\bullet}_{\mathrm{A(s)}}}{\mathrm{R}T^2} = \frac{\Delta H_{\mathrm{fus}}}{\mathrm{R}T^2}$$

〈條件 2〉 ΔH_{fus} 在此 ΔT 中變化不大

$$\ln x_{\mathrm{A}}\Big|_1^{x_{\mathrm{A}}} = \frac{\Delta H_{\mathrm{fus}}}{\mathrm{R}}\left(\frac{-1}{T}\right)\Bigg|_{T^{\bullet}}^{T}$$

即 $$\boxed{\ln x_{\mathrm{A}} = \frac{\Delta H_{\mathrm{fus}}}{\mathrm{R}}\left(\frac{1}{T^{\bullet}} - \frac{1}{T}\right)}$$

是 solvent 之 ΔH_{fus}

和 solute 無關

其中 $T^{\bullet}$ 爲 normal FP

① $\left.\begin{array}{l} x_{\mathrm{A}} < 1 \\ \Delta H_{\mathrm{fus}} > 0 \end{array}\right\}$ 故 $\dfrac{1}{T^{\bullet}} - \dfrac{1}{T} < 0$，即 $T^{\bullet} > T$

FP depression

② 如爲 BP elevation，其實可看爲 Clausius-Clapeyron Eq. $\ln\dfrac{P_2}{P_1} = \dfrac{-\Delta H}{\mathrm{R}}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$

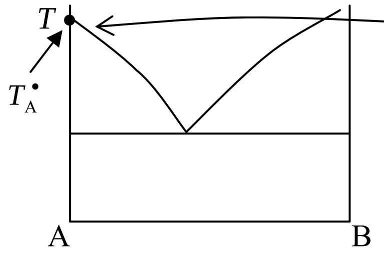
$P_1 = P_1^{\bullet}$，T_1 即 $T^{\bullet}$

$P_2 = P_1^{\bullet} x_2$，即可導出上式

③ <另解> 看成反應 $\mathrm{A_{(s)}} = \mathrm{A_{(soln)}}$，$\Delta G^{\circ} = -\mathrm{R}T\ln K = -\mathrm{R}T\ln x_{\mathrm{A}}$ 也可

④ 此亦爲“solubility”之問題

ideal solution
與 solute 無關
non-ideal solution
則有關



靠近 x_{A}=1 之曲線
即上述 equation 所描述
此 curve 亦表示 A 之”solubility”
(另一 component 不一定是 B)

〈條件 3〉 $x_\mathrm{A} \approx 1$ 時, $x_\mathrm{A} = 1 - x_\mathrm{B}$, x_B 很小

則 $\ln x_\mathrm{A} = \ln(1 - x_\mathrm{B}) \approx -x_\mathrm{B}$

故 $\frac{\Delta H_\mathrm{fus}}{\mathrm{R}}\left(\frac{T - T^\bullet}{TT^\bullet}\right) \cong -x_\mathrm{B}$, 令 $\Delta T = T^\bullet - T$

$$\frac{\Delta T}{T^{\bullet 2}}\frac{\Delta H_\mathrm{fus}}{\mathrm{R}} = x_\mathrm{B} \qquad x_\mathrm{B} = \frac{m_\mathrm{B}}{\frac{1}{M_\mathrm{A}} + m_\mathrm{B}} \approx m_\mathrm{B} M_\mathrm{A}$$

$$\Delta T = \frac{\mathrm{R}T^{\bullet 2}}{\Delta H_\mathrm{fus}} x_\mathrm{B} \cong \frac{\mathrm{R}T^{\bullet 2}}{\Delta H_\mathrm{fus}} M_\mathrm{A} m_\mathrm{B} = K_\mathrm{fA} m_\mathrm{B}$$

$$K_\mathrm{fA} = \frac{M_\mathrm{A}\mathrm{R}T^{\bullet 2}}{\Delta H_\mathrm{fus}}$$ (如果用 SI unit)

$$= \frac{\mathrm{R}T^{\bullet 2}}{\lambda_\mathrm{f}}$$ (如果 λ_f 爲 1000 g solvent 之 ΔH)

〈例〉: 水 1g 之 $\Delta H_\mathrm{f} = 80$ cal $\quad \frac{1.987 \times (273.15)^2}{80 \times 10^3} = 1.86$

(2) BP Elevation 類似 FP depression

$$\mu^\bullet_{\mathrm{A(l)}} + \mathrm{R}T \ln x_\mathrm{A} = \mu^\bullet_{\mathrm{A(g)}} \quad \text{at BP}$$

$$\nwarrow + \mathrm{R}T \ln P \quad 但 \ P = 1 \text{ at BP}$$

故 $\Delta T = K_\mathrm{bA} m_\mathrm{B} = \frac{M_\mathrm{A}\mathrm{R}T_\mathrm{b}^{\bullet 2}}{\Delta H_\mathrm{vap}} m_\mathrm{B} = \frac{\mathrm{R}T_\mathrm{b}^{\bullet 2}}{\lambda_\mathrm{vap}} m_\mathrm{B}$

(3) Vapor Pressure lowering

$P_\mathrm{total} = P_\mathrm{solvent} + P_\mathrm{solute} \approx P_\mathrm{solvent}$ if solute 是 non-volatile

$= x_\mathrm{A} P_\mathrm{A}^\bullet$ if ideal solution

故 $\Delta P = P_\mathrm{A}^\bullet - x_\mathrm{A} P_\mathrm{A}^\bullet = x_\mathrm{B} P_\mathrm{A}^\bullet$

(4) Osmotic Pressure

參考課本Figure 6.26

$$\mu_{右邊} = \mu_{左邊}$$

$$\mu_\mathrm{A}^\bullet(T, P) = \mu_\mathrm{A}^\bullet(T, P + \Pi) + \mathrm{R}T \ln a_\mathrm{A}$$

但 $\mu_\mathrm{A}^\bullet(T, P + \Pi) - \mu_\mathrm{A}^\bullet(T, P) = \int_P^{P+\Pi} \overline{V_\mathrm{A}^\bullet} \mathrm{d}P = \Pi \overline{V_\mathrm{A}^\bullet}$

故 $\Pi \overline{V_\mathrm{A}^\bullet} = -\mathrm{R}T \ln x_\mathrm{A} \approx \mathrm{R}T x_\mathrm{B}$

$$\Pi = \frac{x_\mathrm{B}}{\overline{\overline{V_\mathrm{A}^\bullet}}} \mathrm{R}T$$

但 $x_{\mathrm{B}} = \dfrac{n_{\mathrm{B}}}{n_{\mathrm{A}} + n_{\mathrm{B}}} \approx \dfrac{n_{\mathrm{B}}}{n_{\mathrm{A}}}$, $V = n_{\mathrm{A}}\overline{V_{\mathrm{A}}} + n_{\mathrm{B}}\overline{V_{\mathrm{B}}} \approx n_{\mathrm{A}}\overline{V_{\mathrm{A}}^{\bullet}}$

〈條件 1〉 ideal soln

〈條件 2〉 diluted soln

故 $\Pi = \dfrac{n_{\mathrm{B}}}{V}\mathrm{R}T = c_{\mathrm{B}}\mathrm{R}T$

$\boxed{\text{也叫 van't Hoff Eq.}}$

如果不 ideal 則用 $\Pi = \mathrm{i}c\mathrm{R}T$

Note: $\Pi\overline{V_{\mathrm{A}}^{\bullet}} = x_{\mathrm{B}}\mathrm{R}T = -\mathrm{R}T\ln a_{\mathrm{A}}$

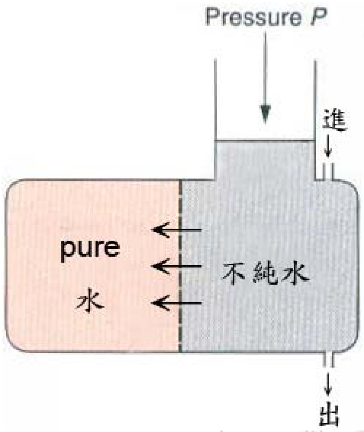
$\Pi V = n_{\mathrm{B}}\mathrm{R}T \quad (V \approx n_{\mathrm{A}}\overline{V_{\mathrm{A}}^{\bullet}})$

對於算 a_{A} 很有用,
常可由 Π 來測 a of solvent
(不是 solute)

〈例〉: 海水中 $\left[\mathrm{Cl^-}\right] = 0.55\ M$, $\left[\mathrm{Na^+}\right] \approx 0.47\ M$, 故 $c \approx 1\ M$

$\Pi = 1 \times 0.082 \cdot 300 = 24.6$ atm

§ Reverse Osmosis



① 一般 membrane 可承受 200 psi

$$\frac{200}{14.7} = 13.6\ \text{atm} = c \cdot 0.082 \cdot 300$$

$$c = 0.55\ M$$

② RO 之 work $= \Pi V$

$$= 13.6 \cdot 18 \times 10^{-3} \times \frac{8.314}{0.082} = 25\ \mathrm{J\ mol^{-1}}$$

蒸餾水 而 $\Delta H_{\mathrm{v}} \approx 539 \times 18 \times 4.184 = 40600\ \ \mathrm{J\ mol^{-1}}$

但要考慮 catridge 之更新,
馬達之 efficiency, 鍋爐之溫水再利用