Chapter 5 Phase Equilibrium

5.1 The Fundamental Fact of Phase Equilibrium

1. 基本定義及名詞

① phase－a region of system inside which intensive properties do not change abruptly as a function of position

② $\begin{cases}\text{condensed phase- liquid, solid}\\ \text{vapor phase}\end{cases}$

allotropy 同素異形體

polymorphism 多相性

有時要分辨很曖昧，如：$\begin{cases}\text{diamond 與 graphite}\\ O_2 \text{ 與 } O_3\end{cases}$

是 phase 或結構?

↑ 課本認爲 gas 只有一種 phase

2. 相平衡之特性

以 I 及 II 表不同 phase, $dG = dG^{(I)} + dG^{(II)}$

對 2- phase 之 closed system $dn_i^{(I)} = -dn_i^{(II)}$ 因 $n_i^{(I)} + n_i^{(II)} = n_i$

$i = 1, 2, \cdots\cdots$ (表 compoent)

$$\text{故}\quad dG = -S^{(I)}dT + V^{(I)}dP + \sum_{i=1}^{c}\mu_i^{(I)}dn_i^{(I)}$$

$$+\ (-S^{(II)}dT + V^{(II)}dP + \sum_{i=1}^{c}\mu_i^{(II)}dn_i^{(II)})$$

定溫定壓下，$dT = dP = 0$

$$= \sum_{i=1}^{c}(\mu_i^{(I)} - \mu_i^{(II)})dn_i^{(I)} = 0 \quad (\text{平衡時})$$

指partial molar G

故 $\boxed{\mu_i^{(I)} = \mu_i^{(II)}}$ at equilibrium

如未達平衡，則 $dG < 0$ 爲 spontaneous process

① 如 $\mu_i^{(I)} > \mu_i^{(II)}$，則 $dn_i^{(I)} < 0$

② 如 $\mu_i^{(I)} < \mu_i^{(II)}$，則 $dn_i^{(I)} > 0$

} 即：物質由高 μ 流向低 μ

此即爲何叫 μ 爲〝chemical potential〞之故

5.2 The Gibbs Phase Rule

(1) 對 1-phase, c-component, 要 $c + 2$ variables (含總 mole 數)

但如只有 intensive variable, 則只要 $c + 1$ (總 mole 數可省掉，或是 $\sum_i x_i = 1$)

(2) p-phase, c-component

f: number of independent intensive variables (degree of freedom)

$\boxed{f = c - p + 2}$ Gibbs phase rule

<理由 A>：原要 $cp+2$ variable

$$但\begin{cases}各\ \text{phase}中\sum_i x_i=1 & 有\ p\ 個\text{equation}\\ 同一\ \text{component}\ 在各\ \text{phase}\ 之\ \mu_i\ 相等 & 有\ c(p-1)\ 個\text{equation}\end{cases}$$

即 $\mu_1^{(\mathrm{I})}=\mu_1^{(\mathrm{II})}=\mu_1^{(\mathrm{III})}=\cdots\cdots=\mu_1^{(\mathrm{N})}$, $cp+2-p-c(p-1)=c-p+2$

<理由 B>：

$$\begin{cases}每一\ \text{component}\ 在各\ \text{phase}\ 中\ \mu_i\ 相等,\ 只需一個\ \mu,\ 共\ c\ 個 & \\ 每一\ \text{phase}\ 中,\ \sum_i x_i=1\ ,\ 有\ p\ 個\ \text{equation} & -p\\ 加上\ T\ 及\ P & +2\end{cases}$$

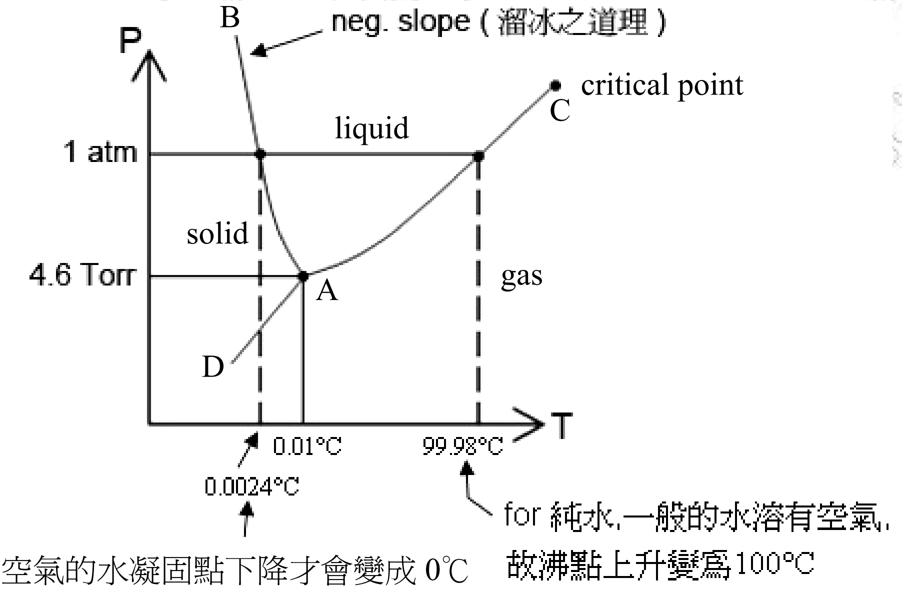
<Mortimer 用>： $f=p(\underset{\substack{\uparrow\\ 含\ T,P}}{c}+1)-(p-1)(\underset{\substack{\uparrow\\ 含\ T,P,\ \mu_i}}{c}+2)=c-p+2$ (較不容易理解)

<Note>： f 並不包含總 mole 數
但在算 c 時，如看成“濃度”之 parameter 數，則包含總 mole 數 (下一節詳述 c 之算法)
此多出來的一個 parameter，在 single phase ($p=1$)時就減掉了

例： 1-component system:

$p=1$, $f=2$ (P,V,T 中任2個)
$p=2$, $f=1$ 兩相之平衡(即下圖中之三條曲線) e.g. specify P or T for $H_2O_{(l),(g)}$
$p=3$, $f=0$ triple point(即下圖中之點A) P,T 是固定的, 不能變

以水之 phase diagram 說明：



同理.溶有空氣的水凝固點下降才會變成 0℃

(3) number of component

$c=$ number of substance $-$ number of relations

① 化學平衡
② 電性中和
③ 化學計量 (含：配製時之比例)

另一種看法即：需要多少種 substance (mixture)來準備

例： ① H_2, O_2, H_2O 混合物 $c = 3$

如有催化劑促其達平衡 $c = 2$ catalyst 不算

如原來放入 2:1 之 H_2：O_2 $c = 1$ (或：先放 H_2O 及 catalyst)

即：需要一種 substance 來 prepare

② NaCl, NaBr 溶於水, $c = 3$ 即： Na^+ , Cl^- , Br^-

<算法 1>: 有 H_2O, Na^+, Cl^-, Br^-, $c = 4$, 但 $[Na^+] = [Cl^-] + [Br^-]$, 故 $c = 3$

<算法 2>: 有 H_2O, $H^+, OH^-, Na^+, Cl^-, Br^-$, $c = 6$, 但 $H_2O = H^+ + OH^-$, $[H^+] = [OH^-]$,
$[Na^+] = [Cl^-] + [Br^-]$, 故 $c = 3$

<算法 3>: $c = 3$ 因可以用上述三種物質製備

<Note>: c 是仍考慮總 mole 數是一個 parameter 的

③ 如果 solution 中含 $Na^+, K^+, Cl^-, Br^-, Li^+$, 則 $c = 5$

因爲可以用 NaCl,KCl,KBr,LiCl加水

但 Na^+, Cl^-, K^+, Br^-, $c = 4$ (KCl , NaCl , KBr , NaBr 只要其中3個再加H_2O即可)

故 5－1 = 4 (電中性)

④ Ca^{+2} 及 Cl^- in H_2O, 則 $c = 2$ (因電中性, 故 $c = 3 - 1$)

或考慮非用 $CaCl_2$ 及水配不可

如果是飽和水溶液, 則 $c = 1$, $f = 1 - 2 + 2 = 1$ (溫度或壓力)

雖是水及固體兩種, 但濃度是固定的, 故只要知水之 mole 數

5.3 Phase equilibrium in 1-component systems

平衡時，$G^{\mathrm{I}} = G^{\mathrm{II}}$，如果改變一下溫度 dT，則 dP 會隨之而變

達到新的平衡後，$G'^{\mathrm{I}} = G'^{\mathrm{II}}$，故 $dG^{\mathrm{I}} = dG^{\mathrm{II}}$

$$-S^{(\mathrm{I})}dT + V^{(\mathrm{I})}dP = -S^{(\mathrm{II})}dT + V^{(\mathrm{II})}dP$$

$\boxed{\dfrac{dP}{dT} = \dfrac{\Delta S}{\Delta V}}$ Clapeyron Equation, $\Delta S = S^{(\mathrm{II})} - S^{(\mathrm{I})}$, $\Delta V = V^{(\mathrm{II})} - V^{(\mathrm{I})}$

Note: 其實即爲 Maxwell relation $\left(\dfrac{\partial P}{\partial T}\right)_{\mathrm{V}} = \left(\dfrac{\partial S}{\partial V}\right)_{\mathrm{T}}$

(1) solid-liquid equilibrium (描述上頁相圖之曲線 AB)

$\Delta S/\Delta V$ 幾乎是 constant

$$P_2 - P_1 = \frac{\Delta S}{\Delta V}(T_2 - T_1) \approx \frac{\Delta H}{\Delta V}\frac{\Delta T}{T}$$

或是 $\dfrac{dP}{dT} = \dfrac{\Delta H}{T\Delta V}$，$(P_2 - P_1) = \dfrac{\Delta H}{\Delta V}\ln\dfrac{T_2}{T_1}$

〈例〉: $\mathrm{D_{ice}} = 0.9917\ \mathrm{g/cm^3}$ $\Delta H_{\mathrm{f}} = 333.5\ \mathrm{J/g} = 333.5\ \mathrm{m^3Pa/g}$

$\mathrm{D_{water}} = 0.9998\ \mathrm{g/cm^3}$ $\Rightarrow 3291\ \mathrm{cm^3 \cdot atm/g}$

400 atm 冰之 mp ?

$$(400-1)\cdot\frac{\left(\dfrac{1}{0.9998} - \dfrac{1}{0.9917}\right)}{3291} = \ln\frac{T_2}{273.15}$$

$$-1.09\times10^{-2} = \ln\frac{T_2}{273.15}\ ,\quad T_2 = 270.2\ \mathrm{K}，低了 2\mathrm{K}$$

☆ 此即溜冰之道理

$50\,\mathrm{kg}$ 在 $5\times0.2\,\mathrm{cm^2}$ 冰刀上，即 $\mathrm{P} = \dfrac{50\times9.8}{1\times10^{-4}} = 4.8\times10^{6}\ \mathrm{Pascal} \approx 48\,\mathrm{atm}$

$\Delta T \approx 0.35\mathrm{K}$

(2) 液相與氣相之平衡 (描述上頁相圖之曲線 AC)

$\Delta V \approx \dfrac{\mathrm{R}T}{P}$，故 $\dfrac{dP}{dT} = \dfrac{\Delta H}{\mathrm{R}T^2/P}$

$\dfrac{dP}{P} = \dfrac{\Delta H}{\mathrm{R}}\dfrac{dT}{T^2}$，$\boxed{\ln\dfrac{P_2}{P_1} = \dfrac{-\Delta H}{\mathrm{R}}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)}$ 假設 ΔH 不隨 T 變太多

Clausius - Clapeyron equation

非常重要的式子，可計算液體在不同溫度之蒸氣壓 (如知道沸點及 ΔH_{vap})

〈另解 1〉 $\mu_g = \mu_l$

$$\mu_g^\circ + RT\ln P/P^\circ = \mu_l^\circ + V_m(P - P^\circ) \quad \approx \mu_l^\circ$$

$$\ln\frac{P}{P^\circ} = \frac{\mu_l^\circ - \mu_g^\circ}{RT} = \frac{-\Delta G_v^\circ}{RT},\ \Delta G_v^\circ = \mu_g^\circ - \mu_l$$

$$\frac{\Delta G_v^\circ}{T} = -R\ \ln\frac{P}{P^\circ} \quad ，但 \quad \frac{\partial\, \Delta G_v^\circ/T}{\partial\, 1/T} = \Delta H_v$$

$$故 \quad \frac{d\ \ln P}{d\ 1/T} = \frac{-\Delta H_v}{R} \quad , \quad \ln\frac{P_2}{P_1} = \frac{-\Delta H_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

〈另解 2〉 $A_{(l)} = A_{(g)}$ ， $K_v = P_A = P$ 以 P 表 A 之蒸汽壓

$$\frac{\partial \ln K_v}{\partial \frac{1}{T}} = \frac{-\Delta H_v}{R} \quad 即\ \ln\frac{P_2}{P_1} = \frac{-\Delta H_V}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

<Note>固相與氣相之平衡(昇華, 上頁相圖之曲線 AD)和(2)類似，只是 ΔH 係 enthalpy of sublimation(昇華熱)因 $\Delta H_{sub} > \Delta H_{vap}$，故斜率較曲線 AC 大

(3) vapor pressure and external pressure

上面之討論係只考慮系統中只有 pure substance, 沒有其他分子

如沒有其他分子, 則 $\mu_g^\circ + RT\ln P_1/P^\circ = \mu_l^\circ + V_m(P_1 - P^\circ)$

因只有 pure substance, 則 $P_1' = P_1$

如果有其他分子, 如果總壓是 P_2'，蒸汽壓是 P_2，則 $\mu_g^\circ + RT\ln P_2/P^\circ = \mu_l^\circ + V_m(P_2' - P^\circ)$

故 $\boxed{RT\ln\frac{P_2}{P_1} = V_m(P_2' - P_1)}$ 故一般壓力大, vapor pressure 變大

§ 因爲高壓(有其他分子)時, liquid 的 μ 變得較 gas 大, 故 μ_{liq} 要變小、 μ_g 要變大才會平衡, 即蒸氣壓變大

例： 298.15 K ，$H_2O_{(l)}$ 蒸汽壓爲 23.756 Torr

$$1\,atm 空氣下,\ RT\ln\frac{P_2}{23.756} = 18.05\cdot(760 - 23.756)\ cm^3\cdot Torr$$

$$= 18.05\times10^{-6}\times736\times\frac{101325}{760}\ \ Pascal\cdot m^3$$

$$\ln\frac{P_2}{23.756} = \frac{18.05\times10^{-6}\times736\times101325/760}{8.314\times298.15} = 7.14\times10^{-4}$$

$$P = 23.756\ e^{7.14\times10^{-4}} = 23.773\ \ Torr, \quad 增加 0.017\ Torr$$

☆ 假設空氣不溶於水

5.4 The Gibbs Energy and Phase Transitions

(1) 爲何 1 atm 下， $\begin{cases} 372\ \text{K 時，水較穩定} \\ 374\ \text{K 時，} H_2O_{(g)}\ \text{較穩定} \end{cases}$ ？

參考課本Figure 5.5

<說明 1>

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

但 $S_{vap} > S_{liquid}$ ， 故 G_{vap} 之 slope 負值較大 (高溫時more negative)

<說明 2>

$$G = H - TS$$

TS ↑ 高溫時，此項重要，S 大的會使 G more negative

H ↑ 低溫時，此項重要，H 小的會使 G more negative

(2) 爲何定溫下，加大壓力水蒸氣會液化？

參考課本Figure 5.6

<說明 1>

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$V_{gas} > V_{liquid}$ ，故 G_{vap} 之slope大，故高壓時 G_{liquid} 較小

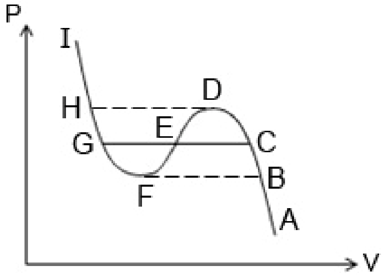
<說明 2>

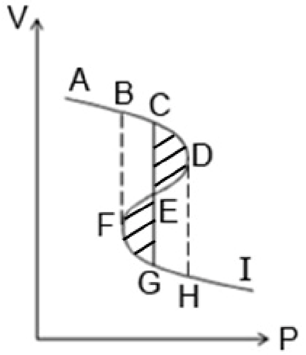
$$G = U + PV - TS$$

TS ↑ 低壓時，此項重要，S 大的使 G more negative

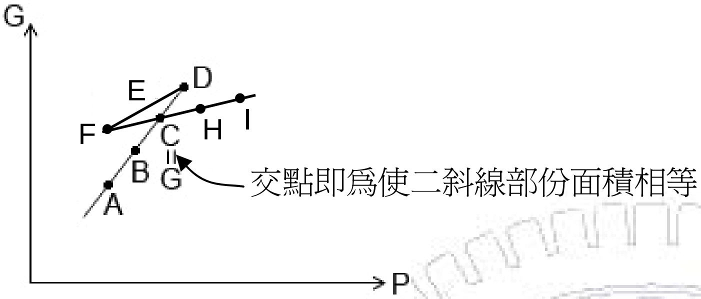
PV ↑ 高壓時，此項重要，V 小的會使 G more negative

(3) van der Waals Equation

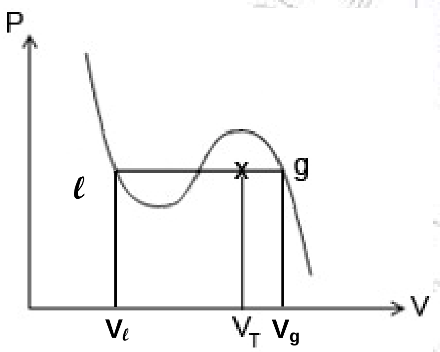




$$\begin{aligned} dG &= -SdT + VdP \\ &= VdP \text{ at constant } T \\ \Delta G &= \int VdP \end{aligned}$$



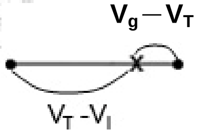
§ Lever Rule



$$V_T = x_g V_g + x_\ell V_\ell = (x_g + x_\ell) V_T$$

故 $x_g(V_g - V_T) = x_\ell(V_T - V_\ell)$

$$\frac{x_g}{x_\ell} = \frac{V_T - V_\ell}{V_g - V_T}$$



$x_g : x_\ell$

(4) stability 之 criteria

① $\left(\partial S / \partial T\right)_V > 0$ 即 $C_V > 0$

② $\left(\partial P / \partial V\right)_T < 0$ 即 $\beta > 0$　詳見 Callen Chapter 8

Berry Chapter 19

故上節之 vdW 圖中的 D-E-F 部分不 stable

(5) Classification of Phase Transitions

① First-order phase transition

G continuous , 但至少 1 個 1st derivative (S 或 V)是 discontinuous

C_p 及 β 均 $\rightarrow \infty$ at phase transition

因 S 變 T 不變, V 變 P 不變

參考課本Figure 5.5 參考課本Figure 5.8 參考課本Figure 5.7

參考課本Figure 5.9 參考課本Figure 5.10

在 phase transition 時,
2nd derivative $\rightarrow \infty$

② Second-order phase transition

G 及 1st derivative 是 continuous , 但至少一個 2nd-derivative 是 discontinuous

C_p 及 β finite break

參考課本Figure 5.11 參考課本Figure 5.12

不多見, 通常在 $\left.\begin{array}{c}\text{normal}\\ \text{superconducting}\end{array}\right\}$ state間出現

③ order-disorder (通常不算是 1st or 2nd order)

如： β-brass. $(\mathrm{Zn}:\mathrm{Cu} \approx 1:1)$ 742 K 有 order-disorder transition (ordered 時, 各 Cu 原子在 Zn cubic cell 中間)

④ lambda transition (He II)

參考課本Figure 5.13

C_P 會 reach ∞ (似 1st order)
但是慢慢上昇的，而非突然上昇 (不似 1st order)

5.5 Surface in One-Component System

(1) Surface Tension

定義 $dw=\underset{\text{surface tension}}{\gamma}\,\underset{\text{area}}{da}$ 把分子從 bulk 帶到 surface 所作之功

參考課本Figure 5.16

假想用鐵絲圈將液體慢慢拉出,

$dU = TdS + 2L\gamma\,dx$ (兩個surface)

$dw_{rev} = dU - dq_{rev} = dU - TdS = 2L\gamma\,dx = F_{rev}dx$

故 $\gamma = F_{rev}/2L$

γ 是force per unit length exerted by surface,故稱爲surface tension

故 $dG = -SdT + VdP + \gamma da$

① constant T, P 下, $dG = \gamma\,da$,故 minimize a 可減少 G

因此水滴是球形的, 2 個水滴樂於合併成 1 個

② $\gamma = \left(\frac{\partial G}{\partial a}\right)_{T,P} = \left(\frac{\partial A}{\partial a}\right)_{T,V} = \left(\frac{\partial U}{\partial a}\right)_{S,V}$,可視爲單位表面積之量, 如同〝表面積世界〞中的 μ

③ $\left(\frac{\partial \gamma}{\partial T}\right)_V = \left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial a}\right)_{T,V}\right]_V = \left[\frac{\partial}{\partial a}\left(\frac{\partial A}{\partial T}\right)_V\right]_{T,V} = -\left(\frac{\partial S}{\partial a}\right)_{T,V} = -S_S$ (surface entropy)

即 $S_S = -\left(\frac{\partial \gamma}{\partial T}\right)_V$, γ 似 chemical potential

→ 即 “molar” quantity

把 γ 視爲單位面積之 A at constant T, V

G at constant T, P

就如 μ 是單位 mole 之 G at constant T, P

④ $U_S = \left(\frac{\partial U}{\partial a}\right)_{T,V}$ (非 γ), $A_S = \left(\frac{\partial A}{\partial a}\right)_{T,V} = \gamma$

故 $A_S = U_S - TS_S$

即 $\gamma = U_S - TS_S = U_S + T\left(\frac{\partial \gamma}{\partial T}\right)_V$, $U_S = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_V$

由 surface tension 導出 surface energy

(2) Bubble Pressure / Surface Pressure

$$V = \frac{4}{3}\pi r^3, \quad dV = 4\pi r^2 dr,$$

$$a = 4\pi r^2, \quad da = 8\pi r dr, \quad 故 da = \frac{2}{r}dV$$

$$dA = -SdT - PdV + \underset{\substack{\uparrow \\ \text{surface pressure}}}{\frac{2\gamma}{r}}dV$$

參考課本Figure 5.18

surface pressure 與 $\begin{cases} r \text{ 成反比} \\ \gamma \text{ 成正比} \end{cases}$

泡泡變大, r 大 ；P_s 小, 就破了

<另一種看法>

piston 內有一小水滴

由 piston 內的氣體和液體的觀點：

$$dw_{\text{rev}} = -P^{(g)}dV^{(g)} - P^{(\ell)}dV^{(\ell)} + \gamma\, da$$

(氣體不必計入 surface tension)

由 piston 之觀點：

$$dw_{\text{rev}} = -P^{(g)}dV = -P^{(g)}(dV^{(g)} + dV^{(\ell)})$$

$$故 (P^{(\ell)} - P^{(g)})\mathrm{d}V^{(\ell)} = \gamma\,\mathrm{d}a = \frac{2\gamma}{r}\mathrm{d}V$$

即 $\boxed{(P^{(\ell)} - P^{(g)}) = \frac{2\gamma}{r}}$ Laplace equation

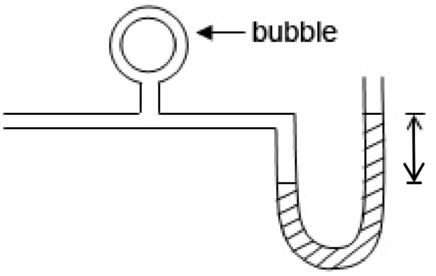
<例>

1 μm 之 droplet at 25°C ($\gamma = 0.07197\ \text{Nm}^{-2}$)

$$P^{(\ell)} - P^{(g)} = \frac{2 \times 0.07197}{1 \times 10^{-6}} = 1.44 \times 10^5\ \text{Nm}^{-2} = 1.42\ \text{atm}$$

但 1 mm 之 droplet, $P^{(\ell)} - P^{(g)} = 1.42 \times 10^{-3}$ atm

<例>



$\Delta P = \frac{4\gamma}{r}$ 因爲有 2 層 surface

(3) Capillary Rise　重力=表面張力

參考課本Figure 5.17 (b)　　$1\text{st approximation} : mg = \underset{\substack{\uparrow \\ \text{密度}}}{\rho}\,(ha)g = \frac{2\gamma}{r}a,$　其中r爲毛細管半徑

故　$\gamma = \frac{1}{2}\rho\, ghr$

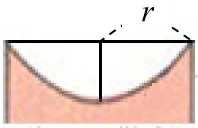
或　$h = \frac{2\gamma}{\rho\, gr}$　$\left(\begin{array}{l}\text{隨}\ \gamma\ \text{成正比} \\ \ \rho,\ r\ \text{成反比}\end{array}\right)$

修正：① ρ應是 $\rho_\ell - \rho_v$　　liquid與vapor的ρ之差

② 修正meniscus

<1>假設半球，凸出部分

$$= r\left(\pi r^2\right) - \frac{1}{2}\frac{4}{3}\pi r^3 = \frac{1}{3}\pi r^3 = \frac{1}{3}ar$$



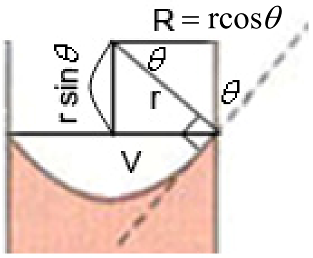
$$\rho\,(ha)g + \rho(\frac{1}{3}ar)g = \frac{2\gamma}{r}a$$

$$\rho\, a(h + \frac{1}{3}r)g = \frac{2\gamma}{r}a$$

$$\gamma = \frac{1}{2}\rho\, g(h + \frac{1}{3}r)r$$

<2>不是半球,而是θ角

即$\gamma = \left(h + \frac{r\cos\theta}{3}\right)(\rho_\ell - \rho_v)\frac{rg}{2}$



(4) Effect of droplet size on vapor pressure

planar liquid 即：平常一般之 liquid surface

$$dG = -SdT + VdP + \gamma\, da + \mu^{(p)} dn$$

$$dV = \bar{V} dn$$

對球型液滴, $da = \frac{2}{r} dV = \frac{2\bar{V}}{r} dn$

即 μ 之修正

□ $dG = -SdT + VdP + \left[\mu^{(p)} + \frac{2\bar{V}\gamma}{r}\right] dn$

定溫定壓下, □ liquid $\mu^{(d)} = \mu^{(p)} + \frac{2\bar{V}\gamma}{r}$

□ vapor $\mu = \mu^{\circ} + RT \ln\frac{P}{P^{\circ}}$

$$\mu^{(d)} = \mu^{\circ} + \mathrm{R}T \ln\frac{P^{(d)}}{P^{\circ}} \quad \text{(droplet)}$$

$$\mu^{(p)} = \mu^{\circ} + \mathrm{R}T \ln\frac{P^{(p)}}{P^{\circ}} \quad \text{(planar)}$$

故 $\mu^{\circ} + \mathrm{R}T \ln\frac{P^{(p)}}{P^{\circ}} + \frac{2\bar{V}\gamma}{r} = \mu^{\circ} + \mathrm{R}T \ln\frac{P^{(d)}}{P^{\circ}}$, $\boxed{\ln\frac{P^{(d)}}{P^{(p)}} = \frac{2\bar{V}\gamma}{\mathrm{R}Tr}}$ 故 r 愈小, γ 愈大 } $P^{(d)}$ 愈大

例： 298.15 K， $H_2O_{(l)}$ $P = 23.756$ Torr, γ=0.07197 N m^{-2}

但 $r = 2.54\times10^{-8}$ m 或 0.025 μm 時

則 $\frac{P^{(d)}}{P^{(p)}} = \mathrm{e}^{\frac{2\times1.806\times10^{-5}\times0.07197}{8.314\times298.15\times2.5\times10^{-8}}}$

$P^{(d)} = 24.756$torr

小 droplet 蒸氣壓較平衡蒸氣壓大

Note:

① 對水中之氣泡(cavity), 蒸氣壓變小

$$\ln\frac{P^{(c)}}{P^{(p)}} = -\frac{2\bar{V}\gamma}{\mathrm{R}Tr}$$

故可以放沸石避免 superheat liquid (for 平滑, 無塵之 container, 不會有 cavity)

② 爲何雨滴會變大？

vap. pressure 大
↓
變小

vap. pressure 小
↓
變大

③ 人造雨用 AgI/acetone 噴出 nozzle ,

1 g AgI → 10^{15} droplet, heterogeneous nucleation

5.6 Surface in Multicomponent Systems

1. Density profile near the surface region

(1) 1-component system

參考課本Figure 5.19 (a)

z_0 之決定：使 shaded area 相等

(2) 2-component system

參考課本Figure 5.19 (b)

如果依上法決定 component 之 z_0 ,
則兩個 component 之 z_0 不會相同
通常用 solvent 爲基準來定 z_0

此時定義 surface excess $n_i^{(\sigma)}$

$$n_i^{(\sigma)} = n_i - n_i^{(\mathrm{I})} - n_i^{(\mathrm{II})}$$

亦即：$n_i^{(\sigma)} > 0$, accumulation at surface

$n_i^{(\sigma)} < 0$, avoid the surface

2. Thermodynamics

$$dG^{(\mathrm{I})} = -S^{(\mathrm{I})}dT + V^{(\mathrm{I})}dP + \sum \mu_i dn_i^{(\mathrm{I})}$$

$$dG^{(\mathrm{II})} = -S^{(\mathrm{II})}dT + V^{(\mathrm{II})}dP + \sum \mu_i dn_i^{(\mathrm{II})}$$

$$dG = -SdT + VdP + \sum \mu_i dn_i + \gamma\, da$$

故 $d\left[G - G^{(\mathrm{I})} - G^{(\mathrm{II})}\right] = -\left[S - S^{(\mathrm{I})} - S^{(\mathrm{II})}\right]dT + \underbrace{\left[V - V^{(\mathrm{I})} - V^{(\mathrm{II})}\right]}_{=0}dP + \gamma\, da + \sum \mu_i d\left[n_i - n_i^{(\mathrm{I})} - n_i^{(\mathrm{II})}\right]$

即 $dG^{(\sigma)} = -S^{(\sigma)}dT + \gamma\, da + \sum \mu_i dn_i^{(\sigma)}$

$dG^{(\sigma)}$即surface Gibb's energy

在定溫定壓下, $G^{(\mathrm{I})} = \sum \mu_i n_i^{(\mathrm{I})}; G^{(\mathrm{II})} = \sum \mu_i n_i^{(\mathrm{II})}$

$$G = \gamma\, a + \sum \mu_i n_i$$

故 $G^{(\sigma)} = \gamma\, a + \sum \mu_i n_i^{(\sigma)}$

因此可導出新的 Gibb's -Duhem equation:

$$a d\gamma + \sum n_i^{(\sigma)} d\mu_i = 0$$

或 $d\gamma = -\sum \Gamma_i^{(\sigma)} d\mu_i$, 其中$\Gamma_i^{(\sigma)} = \dfrac{n_i^{(\sigma)}}{a}$ surface concentration

意義：如果增加compoent i (即增加μ_i)會減少γ, 則$\Gamma_i^{(\sigma)}$爲正 , compoent i聚集在interface,
此即surfactant之工作原理。反之, 如果增加compoent i使γ 增加, 則compoent i會避開interface

3. $d\gamma = -\Gamma_2^{(\sigma)} d\mu_2 - \Gamma_1^{(\sigma)} d\mu_1 = -\Gamma_2^{(\sigma)} d\mu_2$ (solvent 1 之$\Gamma_1 = 0$)

故$\Gamma_2^{(\sigma)} = -\left(\dfrac{\partial \gamma}{\partial \mu_2}\right)$