Chapter 4. The Thermodynamics of Real Systems

4.1 Criteria for Spontaneous Processes and for Equilibrium：The Gibbs and Helmholtz Energies

1. Criteria for Spontaneous Process in Closed Systems

由 $T_{\text{surr}}\mathrm{d}S \ge \mathrm{d}q$ 出發

$T_{\text{surr}}\mathrm{d}S \ge \mathrm{d}U - \mathrm{d}w$

通式 $\boxed{\mathrm{d}U - \mathrm{d}w - T_{\text{surr}}\mathrm{d}S \le 0}$ 結合第一、二定律之 criteria

(1) isolated system $\mathrm{d}U = \mathrm{d}w = 0$

故 $\Delta S_{\text{isol.}} \ge 0$

(2) constant S, $\mathrm{d}w = 0$ (即：constant V for simple system)

$(\mathrm{d}U)_{\text{S, V}} \le 0$

(3) constant T, V 之 simple system, $\mathrm{d}w = 0$, $T_{\text{surr}} = T$

$\mathrm{d}U - T\mathrm{d}S \le 0$ $\boxed{\text{定義 } A = U - TS}$, $\mathrm{d}(A)_{\text{T, V}} \le 0$

Helmholtz Free Energy

(4) constant T, P 之 simple system, $P_{\text{ext}} = P$, $T_{\text{surr}} = T$

$\mathrm{d}U + P\mathrm{d}V - T\mathrm{d}S$ 定義 $\boxed{G = U + PV - TS}$, $\mathrm{d}(G)_{\text{T, P}} \le 0$

Gibbs Free Energy

$G = H - TS = A + PV$

亦即：$$\underset{\text{isolated system}}{(\mathrm{d}S)_{\text{U, V}} \ge 0},\ \underbrace{(\mathrm{d}U)_{\text{S, V}} \le 0,\ (\mathrm{d}A)_{\text{T, V}} \le 0,\ (\mathrm{d}G)_{\text{T, P}} \le 0}_{\substack{\text{對 simple system 而言} \\ \text{(即只作 } PV \text{ work)}}}$$

<對於 G, A 強調一下此時已 implicitly 考慮 surrounding 之 ΔS >

$$\begin{tikzcd}
U \arrow[r, "\text{考慮 } PV \text{ work}"] \arrow[d, "\text{考慮 } S"'] & H \arrow[d, "\text{考慮 } S"] \\
A \arrow[r, "\text{考慮 } PV \text{ work}"'] & G
\end{tikzcd}$$

<Note>

(1) $(\Delta G)_{\text{T, P}} \le 0$ 表示 $\Delta H - T\Delta S \le 0$

低溫時，ΔH 重要，所以 Berthlot 才會誤以爲 $\Delta H \le 0$ 是自發反應之條件
高溫時，$T\Delta S$ 重要，亦即 $\Delta S \ge 0$ 決定是否自發

(2) 再強調一下，此時已 implicitly 考慮到 surrounding

constant T, P時，由 $\Delta S_{\mathrm{sys}}+\Delta S_{\mathrm{surr}}=\Delta S_{\mathrm{sys}}+\dfrac{\Delta q_{\mathrm{surr}}}{T_{\mathrm{surr}}}=\Delta S_{\mathrm{sys}}-\dfrac{\Delta q_{\mathrm{sys}}}{T_{\mathrm{surr}}}$

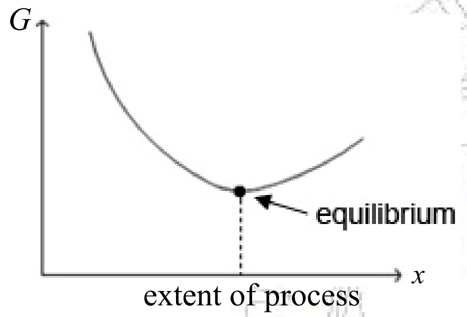
$$=\Delta S_{\mathrm{sys}}-\frac{\Delta H_{\mathrm{sys}}}{T}=-\frac{\Delta G_{\mathrm{sys}}}{T}\ge 0$$

$$\boxed{\text{即定溫定壓下 } \Delta G\le 0\text{ , 和 } \Delta S_{\mathrm{sys}}+\Delta S_{\mathrm{surr}}\ge 0 \text{ 意義相同}}$$

2. Criteria for a Closed Simple System at Equilibrium

由上知，任何 spontaneous process 都會使 A or G 降低，直至平衡 (only for simple system)

故 $\boxed{\begin{array}{l}(\mathrm{d}G)_{\mathrm{T,\,P}}=0\\ (\mathrm{d}^2G)_{\mathrm{T,\,P}}\ge 0\end{array}}$ $\boxed{\begin{array}{l}(\mathrm{d}A)_{\mathrm{T,\,V}}=0\\ (\mathrm{d}^2A)_{\mathrm{T,\,V}}\ge 0\end{array}}$



§ 以 G 為例，在定溫下水汽化為水蒸氣

$\Delta G=\Delta H-T\Delta S=0$ at equilibrium

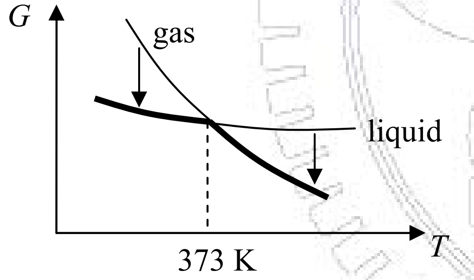
水汽化，ΔH 及 ΔS 均為正

373 K 時，$\Delta H=T\Delta S$

大於 373 K 時，第二項 ($T\Delta S$) 變大，$\Delta G<0$，汽化是 spontaneous，即 gas 是 equilibrium state

小於 373 K 時，第一項 (ΔH) 較大，$\Delta G>0$，即汽化不會自動發生

但 ΔG (condensation) < 0，液化是自發的，即：liquid 是 equilibrium state



3. Maximum Work <A 及 G 之意義>

$$\boxed{\mathrm{d}U-\mathrm{d}w-T_{\mathrm{surr}}\mathrm{d}S\le 0}$$

(1) constant T 時，$\mathrm{d}U-T\mathrm{d}S-\mathrm{d}w\le 0$，即 $\boxed{(\mathrm{d}A)_{\mathrm{T}}\le \mathrm{d}w}$

或 $\boxed{w_{\mathrm{surr}}\le -(\Delta A)}$，等號在平衡時成立

Maximum work can be done on the surrounding in an isothermal process.

☆ 只是給 limit, reversible 步驟時是 max，否則 w_{surr} 較小

ΔA 是不變的 (不管是否 reversible), w_{surr} 則會變

(2) 將 work 分為 PV work 及其他 work (如：電功，表面張力)

$$\mathrm{d}w=\underbrace{-P_{ext}\mathrm{d}V}_{\text{compression work}}+\underbrace{\mathrm{d}w_{\mathrm{net}}}_{\text{net work}}$$

通式改爲 $dU - T_{surr}dS + P_{ext}dV - dw_{net} \le 0$

constant T, P 時, $dU - TdS + PdV \le dw_{net}$

即 $(dG)_{T,P} \le dw_{net}$, 或 $\boxed{w_{surr\,(net)} \le -(\Delta G)}$ ← Maximum non-PV work at constant T, P

$(dG)_{T,P} = dw_{net}$ at equilibrium

(3) 例：$2Hg_{(l)} + Cl_{2(g)} \rightarrow Hg_2Cl_{2(s)}$ $\Delta H = -63.3$ kcal mol^{-1}, $\boxed{\Delta S = -43.5 \text{ cal K}^{-1}}$ mol^{-1}

① $\Delta G = \Delta H - T\Delta S = -63.3 - 298 \times (-43.5) \times 10^{-3}$

$= -50.4$ kcal mol^{-1} (ΔS 之正負決定 ΔH 較 ΔG 爲大或小)

② constant P 下作反應, 則放熱 63.3 kcal mol^{-1} $(-\Delta H)$

③ 用 reversible electrochemical cell, 則放熱較小 (部分能量變爲電功)

$\Delta q_{surr} = (\Delta S_{surr})T_{surr} = (-\Delta S_{sys})T = 43.5 \times 298 \times 10^{-3} = 12.9$ kcal mol^{-1}

其中 $\Delta S_{surr} = -\Delta S_{sys}$, 而所作電功 $-w_{net} = 50.4$ kcal mol^{-1} $(-\Delta G)$

④ 在②之情形, $\Delta S_{surr} = \dfrac{63.3 \times 10^3}{298} = 212.4$ cal K^{-1}mol^{-1}, $\Delta S_{sys} + \Delta S_{surr} > 0$, 自動發生

⑤ 如 cell 不是 reversible, 則所作電功較少, 放熱較多

($TdS = -12.9$ kcal mol^{-1} $> dq$, 放熱爲 $-dq > 12.9$ kcal mol^{-1})

4. 生物化學之熱力學

$$\begin{cases} \Delta G < 0 & \text{exergonic reaction} \\ \Delta G > 0 & \text{endergonic reaction} \end{cases}$$

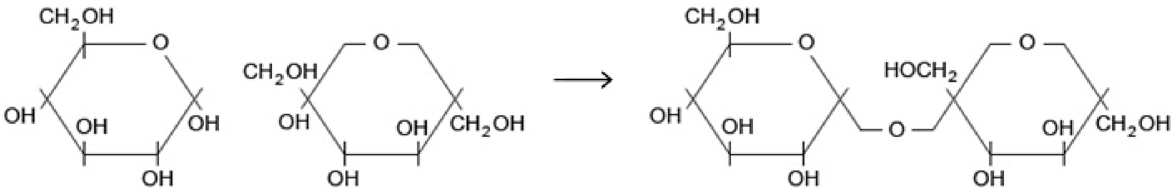
在生命體中, 有很多反應是 $\Delta G > 0$ 的,

但可以靠一些 $\Delta G < 0$ 之反應與之 couple, 使之 $\Delta G_{total} < 0$

例：

$ATP + H_2O \rightarrow ADP + HPO_4^{-2} + H^+$ $\Delta G° = -29.3$ kJ mol^{-1}

glucose + fructose $\rightarrow$ sucrose + H_2O $\Delta G° = 23.0$ kJ mol^{-1}



故 ATP＋glucose → ADP＋glucose 1- phosphate

↓ ＋fructose

sucrose

即：ATP＋glucose＋fructose → sucrose＋ADP

$\Delta G = 23.0 - 29.3 = -6.3\ \text{kJ mol}^{-1}$ 可發生

ESA 1896

4.2 Fundamental Relations for Closed Simple Systems

Simple (只有 $P\mathrm{d}V$), closed system, reversible process

$$P_{\text{ext}} = P,\ T_{\text{surr}} = T,\ \mathrm{d}q \xrightarrow{\text{才可}} T\mathrm{d}S$$

$$\begin{aligned}\mathrm{d}U &= \mathrm{d}q_{\text{rev}} - P\mathrm{d}V \\ &= T\mathrm{d}S - P\mathrm{d}V\end{aligned}$$

$$\boxed{\begin{aligned}\mathrm{d}U &= T\mathrm{d}S - P\mathrm{d}V \\ \mathrm{d}H &= T\mathrm{d}S + V\mathrm{d}P \\ \mathrm{d}A &= -S\mathrm{d}T - P\mathrm{d}V \\ \mathrm{d}G &= -S\mathrm{d}T + V\mathrm{d}P\end{aligned}}$$

即：

$$\left(\frac{\partial U}{\partial S}\right)_{\mathrm{V}} = T \quad , \quad \left(\frac{\partial U}{\partial V}\right)_{\mathrm{S}} = -P$$

$$\left(\frac{\partial H}{\partial S}\right)_{\mathrm{P}} = T \quad , \quad \left(\frac{\partial H}{\partial P}\right)_{\mathrm{S}} = V$$

$$\left(\frac{\partial A}{\partial T}\right)_{\mathrm{V}} = -S\ , \quad \left(\frac{\partial A}{\partial V}\right)_{\mathrm{T}} = -P$$

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

4.3 Additional Useful Thermodynamic Identities

1. Maxwell Relations:

由 $\left(\frac{\partial^2 U}{\partial S\partial V}\right) \underset{\text{即}U\text{是exact}}{=} \left(\frac{\partial^2 U}{\partial V\partial S}\right)$ 知 $-\left(\frac{\partial P}{\partial S}\right)_{\mathrm{V}} = \left(\frac{\partial T}{\partial V}\right)_{\mathrm{S}}$ 或 $-\left(\frac{\partial S}{\partial P}\right)_{\mathrm{V}} = \left(\frac{\partial V}{\partial T}\right)_{\mathrm{S}}$

同理 $\left(\frac{\partial T}{\partial P}\right)_{\mathrm{S}} = \left(\frac{\partial V}{\partial S}\right)_{\mathrm{P}}$ 或 $\left(\frac{\partial P}{\partial T}\right)_{\mathrm{S}} = \left(\frac{\partial S}{\partial V}\right)_{\mathrm{P}}$

$\left(\frac{\partial S}{\partial V}\right)_{\mathrm{T}} = \left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}}$ 或 $\left(\frac{\partial V}{\partial S}\right)_{\mathrm{T}} = \left(\frac{\partial T}{\partial P}\right)_{\mathrm{V}} \xrightarrow{\text{回顧}} \mathrm{d}S = \frac{C_{\mathrm{V}}}{T}\mathrm{d}T + \left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}}\mathrm{d}V$

$\left(\frac{\partial S}{\partial P}\right)_{T} = -\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}}$ 或 $\left(\frac{\partial P}{\partial S}\right)_{T} = -\left(\frac{\partial T}{\partial V}\right)_{\mathrm{P}} \xrightarrow{\text{回顧}} \mathrm{d}S = \frac{C_{\mathrm{P}}}{T} - \left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}}\mathrm{d}P$

每一式子, 如：$\left(\frac{\partial P}{\partial T}\right)_{\mathrm{S}} = \left(\frac{\partial S}{\partial V}\right)_{\mathrm{P}}$, P. V和T. S成對存在,

而"下面"的constant either 是 reverse, 如：$S,\ V \rightarrow V,\ S$ $\left[\text{例：}-\left(\frac{\partial P}{\partial S}\right)_{\mathrm{V}} = \left(\frac{\partial T}{\partial V}\right)_{\mathrm{S}}\right]$

或是 $T, S \rightarrow \mathrm{V},\ P$ $\left[\text{例：}\left(\frac{\partial P}{\partial T}\right)_{\mathrm{S}} = \left(\frac{\partial S}{\partial V}\right)_{\mathrm{P}}\right]$

(只是爲了那些不求甚解的同學, 其實真正懂了, 根本不必如此背)

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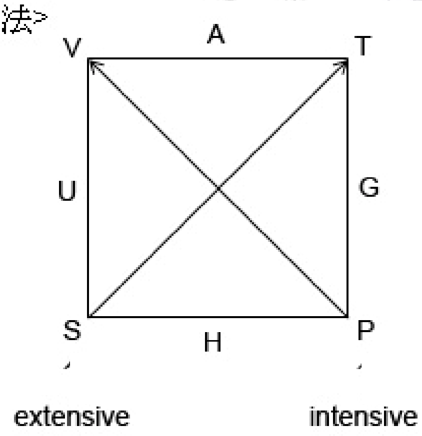


(↗ 所指即爲負值)

逆時針：

“A Very Ugly Shrimp Has Pretty Good Taste”

順時針：

“The Green Plant Has Strong UV Absorption”

或

交大應化系是“A Terribly Good Place Having Such Unusual Values”

取每一字之第一字母即依序爲左圖之各 state parameter

由此圖可導出 ① 基本式, 如

$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$ (看最左邊一行, U是 function of S 和 V, 箭頭射向 V, 故 $P\mathrm{d}V$ 爲負號)

② Maxwell relations：如$-\left(\frac{\partial P}{\partial S}\right)_{\mathrm{V}} = \left(\frac{\partial T}{\partial V}\right)_{\mathrm{S}}$

將圖中間畫一根垂直切線, 再逆時針轉 90°, 正負號由兩個箭頭方向是否一致決定

2. 補證明

① $\left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} = \left(\frac{\partial U}{\partial V}\right)_{\mathrm{S}} + \left(\frac{\partial U}{\partial S}\right)_{\mathrm{V}}\left(\frac{\partial S}{\partial V}\right)_{\mathrm{T}} = -P + T\left(\frac{\partial S}{\partial V}\right)_{\mathrm{T}} = T\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} - P$

② $\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} = -T\left(\frac{\partial S}{\partial P}\right)_{\mathrm{T}} + V\left(\frac{\partial P}{\partial P}\right)_{\mathrm{T}} = -T\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} + V$

③ $C_{\mathrm{P}} - C_{\mathrm{V}} = \alpha^2 VT/\kappa_T$, 如講義第二章所列

3.將 partial derivative 表爲α, κ_{T}, C_{P}, P, V, T 之系統性方法：

(1) 如有 U, A, H, G 將其變爲“分子”(偏微分之上方) 再消去

如：$\left(\frac{\partial U}{\partial T}\right)_{\mathrm{V}} = C_{\mathrm{V}}$, $\left(\frac{\partial H}{\partial T}\right)_{\mathrm{P}} = C_{\mathrm{P}}$

有時要彼此互變：看“分母”及“constant”，兩個 parameter 最適用於何 state function 爲“分子”，如：T, P 適用於 G 之微分

故 $\left(\frac{\partial H}{\partial T}\right)_{\mathrm{P}} \rightarrow \left(\frac{\partial G}{\partial T}\right)_{\mathrm{P}} + \left(\frac{\partial TS}{\partial T}\right)_{\mathrm{P}} = -S + S + T\left(\frac{\partial S}{\partial T}\right)_{\mathrm{P}} = T\left(\frac{\partial S}{\partial T}\right)_{\mathrm{P}}$

(2) 如有 S, 則 ① 用 Maxwell relation 消去

② 用$\left(\frac{\partial S}{\partial T}\right)_{\mathrm{V}} = \frac{C_{\mathrm{V}}}{T}$, $\left(\frac{\partial S}{\partial T}\right)_{\mathrm{P}} = \frac{C_{\mathrm{P}}}{T}$, 因爲$\left(\frac{\partial S}{\partial T}\right)_{\mathrm{V}} = \left(\frac{\partial S}{\partial U}\right)_{\mathrm{V}}\left(\frac{\partial U}{\partial T}\right)_{\mathrm{V}} = \frac{1}{T}C_{\mathrm{V}}$

(3) 如有 V, 則變爲 $\alpha \left[= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]$, 及 $\kappa_T \left[= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{\mathrm{T}}\right]$

(4) 如有C_{V}, 則利用$C_{\mathrm{P}} - C_{\mathrm{V}} = \alpha^2 VT/\kappa_T$

〈例 1〉 $\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial P}\right)_{\mathrm{H}} = \frac{-\left(\partial H/\partial P\right)_{\mathrm{T}}}{\left(\partial H/\partial T\right)_{\mathrm{P}}} = -\frac{\left(\frac{\partial G}{\partial P}\right)_{\mathrm{T}} + T\left(\frac{\partial S}{\partial P}\right)_{\mathrm{T}}}{C_{\mathrm{P}}} = -\frac{V - T\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}}}{C_{\mathrm{P}}}$

〈例 2〉 Adiabatic Free Expansion $\rightarrow U$ constant

$$\mu_{\mathrm{J}} = \left(\frac{\partial T}{\partial V}\right)_{\mathrm{U}} = -\frac{\left(\partial U/\partial V\right)_{\mathrm{T}}}{\left(\partial U/\partial T\right)_{\mathrm{V}}} = -\frac{\left(\partial A/\partial V\right)_{\mathrm{T}} + T\left(\partial S/\partial V\right)_{\mathrm{T}}}{C_{\mathrm{V}}}$$

$$= -\frac{-P + T\left(\partial P/\partial T\right)_{\mathrm{V}}}{C_{\mathrm{V}}} = \frac{P}{C_{\mathrm{V}}} - \frac{T\alpha}{C_{\mathrm{V}}\kappa_T} = \frac{\left(P\kappa_{\mathrm{T}} - \alpha T\right)}{C_{\mathrm{V}}\kappa_{\mathrm{T}}}$$

①如爲 ideal gas, $C_{\mathrm{V}} = \frac{3}{2}\mathrm{R}$, $\alpha = \frac{1}{T}$, $\kappa_T = \frac{1}{P}$, 則 $\left(\frac{\partial T}{\partial V}\right)_{\mathrm{U}} = 0$

②如爲 vdW gas, 且 C_{V} 是 constant, 因 $P = \frac{\mathrm{R}T}{V-b} - \frac{a}{V^2}$, $\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} = \frac{\mathrm{R}}{V-b}$

$$\left(\frac{\partial T}{\partial V}\right)_{\mathrm{U}} = \frac{1}{C_{\mathrm{V}}}\left(P - \frac{\mathrm{R}T}{V-b}\right) = \frac{-a}{C_{\mathrm{V}}V^2}$$

$\mathrm{d}T = \frac{-a}{C_{\mathrm{V}}V^2}\mathrm{d}V$, $\Delta T = \frac{a}{C_{\mathrm{V}}}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$, 和上一章結果一致

〈例 3〉 Reversible Adiabatic Process $\rightarrow S$ constant

$$\left(\frac{\partial T}{\partial P}\right)_{\mathrm{S}} = \frac{-\left(\partial S/\partial P\right)_{\mathrm{T}}}{\left(\partial S/\partial T\right)_{\mathrm{P}}} = \frac{\left(\partial V/\partial T\right)_{\mathrm{P}}}{\frac{1}{T}C_{\mathrm{P}}} = \frac{\alpha VT}{C_{\mathrm{P}}}$$

① 對 ideal gas 而言, $\alpha = {}^{1}\!/_{T}$, $\left(\frac{\partial T}{\partial P}\right)_{\mathrm{S}} = \frac{V}{C_{\mathrm{P}}} = \frac{\mathrm{R}T}{C_{\mathrm{P}}P}$

$$\frac{\mathrm{d}T}{T} = \frac{R}{C_{\mathrm{P}}}\frac{\mathrm{d}P}{P} \ , \ \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\mathrm{R}/C_{\mathrm{P}}}$$

② vdW 式子因α不易求, 可考慮 $\left(\frac{\partial T}{\partial V}\right)_{\mathrm{S}} = \frac{-\left(\frac{\partial S}{\partial V}\right)_{\mathrm{T}}}{\left(\frac{\partial S}{\partial T}\right)_{\mathrm{V}}} = -\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} \Big/ C_{\mathrm{V}}/T = -T\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} \Big/ C_{\mathrm{V}}$

$$= \frac{-\mathrm{R}T}{(V-b)}, \ 故 \ \frac{\mathrm{d}T}{T} = \frac{-\mathrm{d}V}{V-b}\left(\frac{\mathrm{R}}{C_v}\right), \ \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2-b}{V_1-b}\right)^{-\mathrm{R}/C_{\mathrm{v}}}$$

〈例 4〉 Isothermal Process → T constant

$$\left(\frac{\partial U}{\partial P}\right)_{\mathrm{T}} = \left(\frac{\partial G}{\partial P}\right)_{\mathrm{T}} + T\left(\frac{\partial S}{\partial P}\right)_{\mathrm{T}} - \left(\frac{\partial PV}{\partial P}\right)_{\mathrm{T}} = V + T\left(\frac{\partial S}{\partial P}\right)_{\mathrm{T}} - V - P\left(\frac{\partial V}{\partial P}\right)_{\mathrm{T}}$$

$$= -T\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} + PV\kappa_T = V\left(\kappa_T P - \alpha\ T\right)$$

① 對 ideal gas , $\left(\frac{\partial U}{\partial P}\right)_{\mathrm{T}} = 0$

② 對 vdW gas , 複雜, 用 $\left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}}$ 較方便

$$\searrow \left(\frac{\partial A}{\partial V}\right)_{\mathrm{T}} + T\left(\frac{\partial S}{\partial V}\right)_{\mathrm{T}} = -P + T\left(\frac{\partial P}{\partial T}\right)_{\mathrm{T}}$$

4. 計算ΔS之另一方法

① $\left(\frac{\partial S}{\partial P}\right)_{\mathrm{T}} = -\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}}$ ideal gas ⇒ $V = \frac{\mathrm{R}T}{P}$ 故 $\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} = \frac{R}{P}$, $\mathrm{d}S = \frac{-R}{P}\mathrm{d}P$, $\Delta S = -\mathrm{R}\ln\frac{P_2}{P_1} = R\ln\frac{V_2}{V_1}$

$\left(\frac{\partial S}{\partial V}\right)_{\mathrm{T}} = \left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}}$

② $\left(\frac{\partial S}{\partial T}\right)_{\mathrm{V}} = \left(\frac{\partial S}{\partial U}\right)_{\mathrm{V}}\left(\frac{\partial U}{\partial T}\right)_{\mathrm{V}} = \frac{C_{\mathrm{V}}}{T}$, $\Delta S = \int\frac{C_{\mathrm{V}}}{T}\mathrm{d}T$

③ $\left(\frac{\partial S}{\partial T}\right)_{\mathrm{P}} = \frac{C_{\mathrm{P}}}{T}$, $\Delta S = \int\frac{C_{\mathrm{P}}}{T}\mathrm{d}T$

上一章之通式亦可由 $dS = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V = \frac{C_{\mathrm{V}}}{T}\mathrm{d}T + \left(\frac{\partial P}{\partial T}\right)_V \mathrm{d}V$ 得到

4.4 Gibbs Energy Calculation

1. ΔG之 pressure dependence:

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P \ , \ \left(\frac{\partial G}{\partial P}\right)_{\mathrm{T}} = V$$

故定溫下, $\Delta G = \int_{P_1}^{P_2} V\mathrm{d}P$

(1) ideal gas, $\mathrm{d}G = \frac{\mathrm{R}T}{P}\mathrm{d}P$, $\boxed{\Delta G = \mathrm{R}T \ln \frac{P_2}{P_1}}$

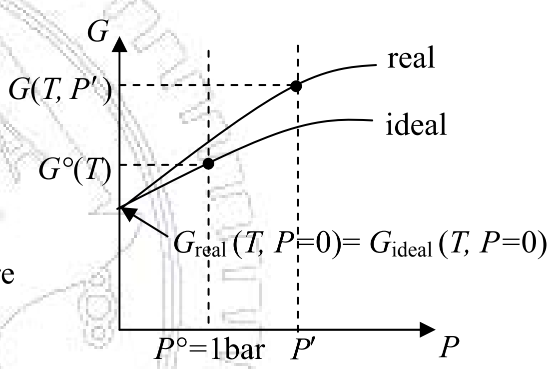
$$G(T,\ P) = G°(T) + \mathrm{R}T\ \ln\left(P/P°\right) = G°(T) + \mathrm{R}T \ln P \text{ (in bar)} \quad \left(\text{用}P/P°\text{較好, ln內之參數應無單位}\right)$$

standard state ($P = 1$ bar)

☆ 如用 1atm 爲 reference state, 則 $G^{\mathrm{atm}} = G° + \mathrm{R}T\ln 1.01325 = G° + 0.01316\ \mathrm{R}T$

at 298 K, $G^{\mathrm{atm}} - G° = 7.8$ cal mol^{-1}或32.6 J mol^{-1}, 相差不是很大

(2) Real gas :



$$G(T,\ P) = G°(T) + \mathrm{R}T \ln\left(\frac{f}{P°}\right)$$

此即fugacity之定義

ideal gas之 fugacity即爲 pressure

① $P \to 0$ 時,由 (1) 之式知 G 變爲$-\infty$, 不太好

② 對 real gas, 可視爲" ideal" 或 " corrected" vapor pressure

③ 此時之standard state是一個 hypothetical state
(如以前所述 $\Delta H°$ 之 standard state)

$$G_{\mathrm{real}}(T,\ P') - G°(T) = \mathrm{R}T\ \ln \frac{f'}{P°}$$

$$= G_{\mathrm{real}}(T, P') - \lim_{P''\to 0}\left[G_{\mathrm{real}}(T,\ P'') - G_{\mathrm{ideal}}(T,\ P'')\right] - G°(T)$$

$$= G_{\mathrm{real}}(T, P') - G_{\mathrm{real}}(T, P=0) - \left[G°(T) - G_{\mathrm{ideal}}(T, P=0)\right]$$

$$= \int_0^{P'} V_{\mathrm{real}}\mathrm{d}P - \int_0^{P°}\frac{\mathrm{R}T}{P}\mathrm{d}P \qquad (\text{好像是 } P° \xrightarrow[\text{ideal gas}]{} 0 \xrightarrow[\text{real gas}]{} P')$$

$$= \int_0^{P'} V_{\mathrm{real}}\mathrm{d}P - \int_0^{P'}\frac{\mathrm{R}T}{P}\mathrm{d}P - \int_{P'}^{P°}\frac{\mathrm{R}T}{P}\mathrm{d}P$$

$$= \int_0^{P'} V_{\mathrm{real}}\mathrm{d}P - \int_0^{P'}\frac{\mathrm{R}T}{P}\mathrm{d}P - \mathrm{R}T\ \ln\frac{P°}{P'}$$

故 $\mathrm{R}T\ \ln\frac{f'}{P°} + \mathrm{R}T\ \ln\frac{P°}{P'} = \int_0^{P'}\left(V_{\mathrm{real}} - \frac{\mathrm{R}T}{P}\right)\mathrm{d}P$

$$\boxed{\mathrm{R}T\ \ln\frac{f'}{P'} = \int_0^{P'}\left(V_{\mathrm{real}} - \frac{\mathrm{R}T}{P}\right)\mathrm{d}P}$$

ideal gas 的 f

$\mathrm{R}T \ln f$ 與 $\mathrm{R}T \ln P$之差異即爲 $\int \Delta V\mathrm{d}P$

$V_{\mathrm{real}} - V_{\mathrm{ideal}}$

或 $G_{\mathrm{real}}(T, P') = \underbrace{G°(T) + \mathrm{R}T \ln\frac{P'}{P°}}_{\text{ideal}} + \int_0^{P'}\left(V_{\mathrm{real}} - \frac{\mathrm{R}T}{P}\right)\mathrm{d}P$

如用 $PV = \mathrm{R}T + BP$, 則 $V = \frac{\mathrm{R}T}{P} + B$, 或 $P = \frac{\mathrm{R}T}{V - B}$

$$\mathrm{R}T \ln\frac{f'}{P'} = \int_0^{P'} B\,\mathrm{d}P = BP'$$

故 $f' = P'e^{BP'/\mathrm{R}T}$ 〈常用的 f 與 P 之關係式〉

(3) solid or liquid 如 V 幾乎不隨 P 而變, 則

$$G(T, P) = G^\circ(T) + V(P - P^\circ)$$

standard state 即 pure substance at P°

2. ΔG 之 temperature dependence

① $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P$, 故 $\left(\frac{\partial G}{\partial T}\right)_\mathrm{P} = -S = \frac{G - H}{T}$

但 $\left(\frac{\partial G/T}{\partial T}\right)_\mathrm{P} = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_\mathrm{P} - \frac{G}{T^2} = \frac{G - H}{T^2} - \frac{G}{T^2} = \frac{-H}{T^2}$ Gibbs-Helmholz Equation

或是 $\left(\frac{\partial G/T}{\partial 1/T}\right)_\mathrm{P} = \left(\frac{\partial G/T}{\partial T}\right)_\mathrm{P}\left(\frac{\partial T}{\partial 1/T}\right)_\mathrm{P} = -T^2\left(\frac{\partial G/T}{\partial T}\right)_\mathrm{P} = H$

對於化學反應, $\boxed{\left(\frac{\partial \Delta G/T}{\partial 1/T}\right)_\mathrm{P} = \Delta H}$ 或 $\boxed{\left(\frac{\partial \Delta G/T}{\partial T}\right)_\mathrm{P} = \frac{-\Delta H}{T^2}}$

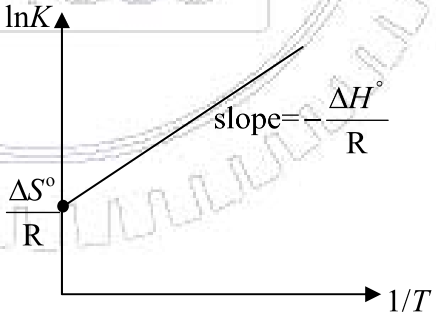
即：G 與 H 並不是毫不相關的, 粗略講即是因 ΔS 決定 ΔG 之 temperature dependence, 使得 ΔH 也和 ΔG 之 temperature dependence 相關

以後會教到 $\Delta G^\circ = -\mathrm{R}T\ln K$

故 $\left(\frac{\partial \ln K}{\partial 1/T}\right) = -\frac{\Delta H^\circ}{\mathrm{R}}$

$$\ln K = -\frac{\Delta H^\circ}{\mathrm{R}T} + \text{intercept}$$

$$= -\frac{\Delta G^\circ}{\mathrm{R}T} = -\frac{\Delta H^\circ}{\mathrm{R}T} + \frac{T\Delta S^\circ}{\mathrm{R}T}$$



② 如 $C_\mathrm{P} = a + bT + CT^{-2}$

則 $\Delta H = \int C_\mathrm{P}\mathrm{d}T = \int a + bT + CT^{-2}\mathrm{d}T = a(T - T_0) + \frac{b}{2}(T^2 - T_0^2) - C\left(\frac{1}{T} - \frac{1}{T_0}\right)$

$$= \Delta H_0 + aT + \frac{b}{2}T^2 - CT^{-1}$$

其中 $\Delta H_0 = -\left(aT_0 + \frac{b}{2}T_0^2 - C\frac{1}{T_0}\right)$

故 $\dfrac{\Delta H}{T^2}=\dfrac{\Delta H_0}{T^2}+\dfrac{a}{T}+\dfrac{b}{2}-\dfrac{C}{T^3}$

$-\dfrac{\Delta G}{T}=\int\dfrac{\Delta H}{T^2}\mathrm{d}T=\dfrac{-\Delta H_0}{T}+a\ln T+\dfrac{b}{2}T+\dfrac{C}{2T^2}+I$, I 是 $\dfrac{\Delta H_0}{T_0}-a\ln T_0-\dfrac{b}{2}T_0-\dfrac{C}{2T_0^{\,2}}$

$$\Delta G=\Delta H_0-aT\ln T-\frac{b}{2}T^2-\frac{C}{2}\frac{1}{T}-IT$$

欲知 $\Delta G(T)$, 可由 $\left\{\begin{array}{l}\text{某一}T\text{之}\Delta H\\ C_\mathrm{P}(T)\\ \text{某一}T\text{之}\Delta G\end{array}\right.$ 或 $\left\{\begin{array}{l}C_\mathrm{P}(T)\\ \text{某一}T\text{之}\Delta S\\ \text{某一}T\text{之}\Delta G\text{ 或 }\Delta H\end{array}\right.$

另法：用 $\Delta S=\int\dfrac{C_\mathrm{P}}{T}\mathrm{d}T$，再用 $\Delta G=\Delta H-T\Delta S$ 更快

$$\Delta S=\int\frac{a}{T}+b+cT^{-3}\mathrm{d}T=a\ln T+bT-\frac{c}{2}T^{-2}+J$$

$$\Delta G=\Delta H_0+aT+\frac{b}{2}T^2-cT^{-1}-T\left(a\ln T+bT-\frac{c}{2}T^{-2}+J\right)$$

$$=\Delta H_0-aT\ln T-\frac{b}{2}T^2-\frac{c}{2}\frac{1}{T}+\left(a-\mathrm{J}\right)T$$

4.5 Multicomponent System

$\begin{cases}\text{single component system-由 } P, V, T \text{ 中 2 個 variable 描述} \\ \text{c-component system- c+1 for single phase (不含總 mole 數)}\end{cases}$

(c − p+2 for p-phase, 以後說明)

↑ 未必就等於 species 之數目, 如：$2NO_2 = N_2O_4$ 平衡, 只能算 1 個 component

課本用 c+2 是包含總 mole 數

原來 $G\,(P,\ T) \rightarrow G\,(P,\ T,\ n_1,\ n_2,\ \cdots,\ n_C)$ ，其中有一個 n_j 是 redundant (多餘的)

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,\,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,\,n} dP + \sum_{i=1}^{c}\left(\frac{\partial G}{\partial n_i}\right)_{T,\,P,\,n'} dn_i$$

(n 表全部之 n_j; n' 表除了 n_i 外之 n_j)

$$= -SdT + VdP + \sum_{i=1}^{c}\mu_i dn_i$$

$\mu_i = \left(\dfrac{\partial G}{\partial n_i}\right)_{T,\,P,\,n'}$ chemical potential

$$\text{同理 } dA = -SdT - PdV + \sum_{i=1}^{c}\left(\frac{\partial A}{\partial n_i}\right)_{T,\,V,\,n'} dn_i \cdots\cdots$$

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,\,V,\,n'} = \left(\frac{\partial U}{\partial n_i}\right)_{S,\,V,\,n'} = \left(\frac{\partial H}{\partial n_i}\right)_{S,\,P,\,n'}$$

extensive

Partial Molar Quantity: $\overline{Y}_i = \left(\dfrac{\partial Y}{\partial n_i}\right)_{T,\,P,\,n'}$ ←通常 T, P hold constant 者才算是, 故上面 3 個不是

intensive

① 以前之式子均能適用, 只要 $G \rightarrow \mu_i$, $H,\ U,\ A,\ S,\ V \rightarrow \overline{H}_i$, $\overline{U}_i$, ……etc.

② 對於 1-component system , $\overline{Y}_i = \overline{Y} = Y/n$, 即 $Y = n\overline{Y}_i$

③ 對於 c-component system , $Y = \sum_{i=1}^{c} n_i \overline{Y}_i$

或 $\overline{Y} = \dfrac{1}{n}Y = \sum_{i=1}^{c}\dfrac{n_i}{n}\overline{Y}_i = \sum_{i=1}^{c} x_i\overline{Y}_i = \overline{Y}$ ，其中 $\overline{Y}$ 爲總 mole 數爲 1 之量，

x_i 爲 ith component 之 mole fraction

④ $\overline{Y}_i$ 是 concentration dependent

4.6 Euler’s Theorem and the Gibbs-Duhem Relation

1. 如 $f\left(\lambda x_1,\ \lambda x_2,\cdots,\ \lambda x_c\right)=\lambda^k f\left(x_1,\ x_2,\cdots,\ x_c\right)$

f 即爲 homogeneous function of degree k, 令 k=1 即和上式相同

Euler's Theorem: $kf=\sum_{i=1}^{c} x_i\left(\frac{\partial f}{\partial x_i}\right)_{x'}$

(證明：兩邊對 λ 微分, $\sum_i \left(\frac{\partial f}{\partial \lambda x_i}\right)_{x'} \underbrace{\left(\frac{\partial \lambda x_i}{\partial \lambda}\right)_{x'}}_{=x_i} = k\lambda^{k\text{-}1} f$ ，再令 $\lambda=1$)

2. Gibbs-Duhem Relation

因 $Y=\sum_{i=1}^{c} n_i\overline{Y}_i$

$$dY=\sum_i n_i \mathrm{d}\overline{Y}_i+\sum_i \overline{Y}_i \mathrm{d}n_i$$

又 $\mathrm{d}Y=\left(\frac{\partial Y}{\partial T}\right)_{\mathrm{P,\,n}}\mathrm{d}T+\left(\frac{\partial Y}{\partial P}\right)_{\mathrm{T,\,n}}\mathrm{d}P+\sum_{i=1}^{c}\overline{Y}_{\mathrm{i}}\mathrm{d}n_{\mathrm{i}}$

故 $\boxed{\sum_i n_i \mathrm{d}\overline{Y}_i=\left(\frac{\partial Y}{\partial T}\right)_{\mathrm{P,\,n}}\mathrm{d}T+\left(\frac{\partial Y}{\partial P}\right)_{\mathrm{T,\,n}}\mathrm{d}P}$

generalized Gibbs-Duhem relation

$\boxed{\sum_i n_i \mathrm{d}\overline{Y}_i=0}$ at constant $T,\ P$

如 Y 爲 G, 即 $\sum_i n_i \mathrm{d}\mu_i=0$

Gibbs-Duhem relation

(1) 以 volume 爲例： 用 binary system (含 n_A mole 的 A 及 n_B mole 的 B)

$$\overline{V}_\mathrm{A}=\left(\frac{\partial V}{\partial n_\mathrm{A}}\right)_{\mathrm{T,\,P,\,n_B}}\quad,\quad \overline{V}_\mathrm{B}=\left(\frac{\partial V}{\partial n_\mathrm{B}}\right)_{\mathrm{T,\,P,\,n_A}}$$

$$V=n_\mathrm{A}\overline{V}_\mathrm{A}+n_\mathrm{B}\overline{V}_\mathrm{B}$$

而 Gibbs Duhem equation $\Rightarrow$ ① $\frac{\mathrm{d}\overline{V}_\mathrm{A}}{\mathrm{d}\overline{V}_\mathrm{B}}=\frac{-n_B}{n_\mathrm{A}}$ 即 $\overline{V}_\mathrm{A}$ 及 $\overline{V}_\mathrm{B}$ 是相關的

② $\mathrm{d}V=\overline{V}_\mathrm{A}\mathrm{d}n_\mathrm{A}+\overline{V}_\mathrm{B}\mathrm{d}n_B$

① $\Delta V_{\mathrm{mix}}=V-(n_\mathrm{A}V_\mathrm{A}^\bullet+n_\mathrm{B}V_\mathrm{B}^\bullet)$, 其中 g 表 pure substance

$$=(n_\mathrm{A}\overline{V}_\mathrm{A}+n_\mathrm{B}\overline{V}_\mathrm{B})-n_\mathrm{A}\overline{V}^\bullet_\mathrm{A}-n_B\overline{V}^\bullet_\mathrm{B}=\boxed{n_\mathrm{A}(\overline{V}_\mathrm{A}-\overline{V}^\bullet_\mathrm{A})+n_\mathrm{B}(\overline{V}_\mathrm{B}-\overline{V}^\bullet_\mathrm{B})}$$

適用於任何 state function , 如：$G,\ H$

② $\overline{V}_\mathrm{A}$ 與 $\overline{V}_\mathrm{B}$ 之關係

$$\mathrm{d}\overline{V}_\mathrm{A} = \frac{-n_\mathrm{B}}{n_\mathrm{A}}\mathrm{d}\overline{V}_\mathrm{B} = \frac{x_\mathrm{B}}{x_\mathrm{B}-1}\mathrm{d}\overline{V}_\mathrm{B} \text{ , 因 } x_\mathrm{B} = {}^{n_\mathrm{B}}\!\big/\!{}_{n_\mathrm{A}+n_\mathrm{B}} \text{ , } 1-x_\mathrm{B} = {}^{n_\mathrm{A}}\!\big/\!{}_{n_\mathrm{A}+n_\mathrm{B}}$$

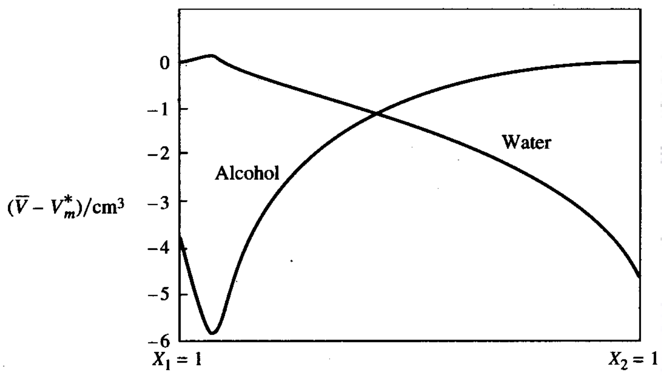
故 $\int \mathrm{d}\overline{V}_\mathrm{A} = \int \frac{x_\mathrm{B}}{x_\mathrm{B}-1}\mathrm{d}\overline{V}_\mathrm{B} = -\int \frac{x_\mathrm{B}}{1-x_\mathrm{B}}\mathrm{d}\overline{V}_\mathrm{B}$

(1) 由其中之一 $\overline{V}_i$ 的變化即已決定另一 $\overline{V}_i$ 之變化

(2) 一個有 max., 另一個即有 min.

(3) 與軸之交點即爲 $V_\mathrm{A}^\bullet$ 及 $V_\mathrm{B}^\bullet$

(4) 在 x = 0.5 時, slope 等値異號



(a)

以 H_2O/C_2H_5OH 爲例 (圖 a, H_2O 爲 1, C_2H_5OH 爲 2)

For C_2H_5OH, min. 在 $x_2 = 0.064$

即 $\frac{0.064\times 46}{0.064\times 46 + 0.936\times 18} = 15\%$ by weight

③ $\overline{V}_i$ 可以是負值 (即：B 加入使總體積變小)

如：$MgSO_4$, 由於 electrostriction使水結構被破壞

(2) Free energy of mixing：

用氣體 mixing 來說明, $G = G^\circ + \mathrm{R}T\ln\frac{P}{P^\circ} \to \mu = \mu^\circ + \mathrm{R}T\ln\frac{P}{P^\circ}$

$$\begin{cases} \text{混合前 } x_1\mu_1^\bullet + x_2\mu_2^\bullet \\ \text{混合後 } x_1(\mu_1^\bullet + \mathrm{R}T\ln x_1) + x_2(\mu_2^\bullet + \mathrm{R}T\ln x_2) = 0 \end{cases}$$

$$\frac{P_\mathrm{f}}{P_\mathrm{i}} = \frac{n_1}{n_1+n_2}$$

$$\Delta G = x_1\mathrm{R}T\ln x_1 + x_2\mathrm{R}T\ln x_2$$
$$= \mathrm{R}T\sum_i x_i \ln x_i$$

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_\mathrm{P} = -\mathrm{R}\sum_i x_i\ln x_i$$

$$\Delta H = 0$$

另一作法：

定溫 $\Delta G = \Delta H - T\Delta S = -T\Delta S$

3. Determination of Partial Molar Quantities (Experimental)

① Method of intercepts

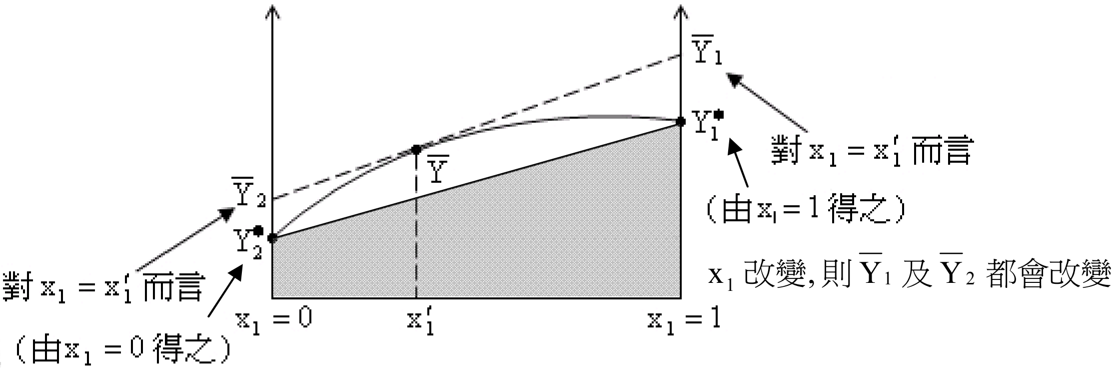
$$\overline{Y} = x_1\overline{Y}_1 + x_2\overline{Y}_2 = (\overline{Y}_1 - \overline{Y}_2)x_1 + \overline{Y}_2 \qquad (\text{因 } x_2 = 1 - x_1)$$

$$\text{又} \left(\frac{\partial \overline{Y}}{\partial x_1}\right)_{T,\,P} = \overline{Y}_1 - \overline{Y}_2 + x_1\frac{\partial \overline{Y}_1}{\partial x_1} - x_1\frac{\partial \overline{Y}_2}{\partial x_1} + \frac{\partial \overline{Y}_2}{\partial x_1}$$

(注意：Y_i是 concentration dependent)

$$= \overline{Y}_1 - \overline{Y}_2 + \underbrace{x_1\frac{\partial \overline{Y}_1}{\partial x_1} + x_2\frac{\partial \overline{Y}_2}{\partial x_1}}_{=0 \quad \text{from Gibbs-Duhem relation}} = \overline{Y}_1 - \overline{Y}_2$$

$$\text{故} \quad \overline{Y} = \left(\frac{\partial \overline{Y}}{\partial x_1}\right)x_1 + \overline{Y}_2$$



x_1 改變, 則 $\overline{Y}_1$ 及 $\overline{Y}_2$ 都會改變

如要準確, 則可用 $\Delta\overline{Y}_{\text{mix}}$ 作圖 (即：把上圖中之灰色部分切掉,拉平)

參考課本Figure 4.3

$$\Delta\overline{Y}_{\text{mix}} = \overline{Y} - x_1\overline{Y}_1^\bullet - x_2\overline{Y}_2^\bullet$$

$$= \overline{Y} - \left[Y_2^\bullet + x_1(\overline{Y}_1^\bullet - \overline{Y}_2^\bullet)\right]$$

$x_1 = 0$ ：左截距 $= \overline{Y} - \overline{Y}_2^\bullet = \overline{Y}_2 - \overline{Y}_2^\bullet$

$x_1 = 1$ ：右截距 $= \overline{Y} - \overline{Y}_1^\bullet = \overline{Y}_1 - \overline{Y}_1^\bullet$

※注意※

左圖和上圖是不同的系統，並非由上圖可得到左圖。

Apparent molar quantity method (以 volume 爲例)

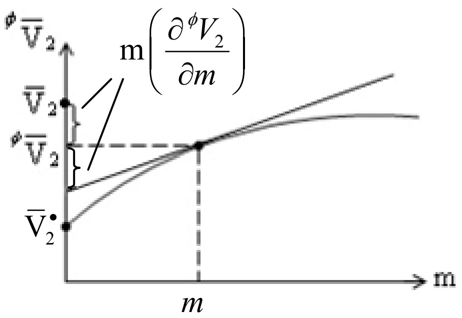
Apparent molar volume $\quad {}^{\phi}\overline{V}_2 = \dfrac{V - n_1\overline{V}_1^\bullet}{n_2}$

即加入 $\underset{\text{(solute)}}{\text{"2"}}$ 使得總 volume 之增加量

如 $n_1 = \frac{1000}{M_1}$，則 $n_2 = m$

$$V = m\,{}^{\phi}\overline{V}_2 + \frac{1000}{M_1}\overline{V}_1^{\bullet}$$

$$\overline{V}_2 = \left(\frac{\partial V}{\partial m}\right) = {}^{\phi}\overline{V}_2 + m\left(\frac{\partial\,{}^{\phi}V_2}{\partial m}\right)$$



即：把 ${}^{\phi}\overline{V}_2$ 值再加上截距與 ${}^{\phi}\overline{V}_2$ 之差值可得 $\overline{V}_2$