

Ch 9 The Chemical Potential and Open Systems.

本章考慮開放系統，有粒子進出系統。

9.1 The Chemical Potential.

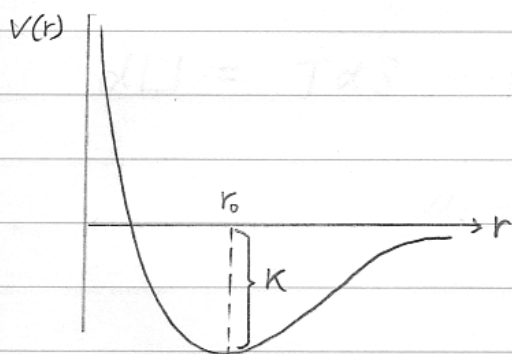
$$\textcircled{dn} \quad dE = \mu dn$$

定義：若 dn kmole 物質流入系統，
至使系統增加能量 dE ，

$$\text{則 } dE = \mu dn$$

其中 μ 稱為 chemical potential.

The chemical potential is associated with intermolecular forces.
例 庫倫力.



$$E = K + V$$

總動位
能能能

設粒子在 $r \rightarrow \infty$ 時靜止，動能，位能均為 0。
當粒子移入系統，位能 改出成 動能 轉成內

P152 第 2 段 \rightarrow 例數第 2 段，舉例： $\mu = -0.43 \text{ eV}$

這是一般 μ 的大小。

1st & 2nd law 結合的式子要增加考慮 μdn .

$$dU = TdS - PdV + \mu dn$$

$\downarrow \quad \rightarrow$ kJ/mole.
J/kilomole

$U = U(S, V, n)$ 3個獨立變數.

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \underbrace{\left(\frac{\partial U}{\partial n}\right)_{S,V}}_{\mu} dn$$

The chemical potential is defined as the internal energy per kilomole added under conditions of constant entropy and volume.

若不只一種粒子:

$$dU = TdS - PdV + \sum_{j=1}^m \mu_j dn_j \quad (9.4)$$

$$\mu_j = \left(\frac{\partial U}{\partial n_j}\right)_{S,V, \underbrace{n_1, n_2, \dots}_{\text{除了 } n_j \text{ 外所有 } n_i}} \quad (9.5)$$

Euler's theorem for homogenous functions

若 $\lambda f(x, y, z) = f(\lambda x, \lambda y, \lambda z)$

則 $f = x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y} + z \frac{\partial f}{\partial z}$

proof: $\frac{\partial}{\partial \lambda} [\lambda f(x, y, z)] = \frac{\partial}{\partial \lambda} f(\lambda x, \lambda y, \lambda z)$

$$f(x, y, z) = \frac{\partial f}{\partial (\lambda x)} \frac{d(\lambda x)}{d\lambda} + \frac{\partial f}{\partial (\lambda y)} \frac{d(\lambda y)}{d\lambda} + \frac{\partial f}{\partial (\lambda z)} \frac{d(\lambda z)}{d\lambda}$$

$$= x \frac{\partial f(\lambda x, \lambda y, \lambda z)}{\partial (\lambda x)} + y \frac{\partial f(\lambda x, \lambda y, \lambda z)}{\partial (\lambda y)} + z \frac{\partial f(\lambda x, \lambda y, \lambda z)}{\partial (\lambda z)}$$

若欲 $\frac{\partial f(\lambda x, \lambda y, \lambda z)}{\partial (\lambda x)}$ 與 λ 無關 \Rightarrow

$$\frac{\partial f(\lambda x, \lambda y, \lambda z)}{\partial \lambda x} = \frac{\partial f(x, y, z)}{\partial x}$$

$U = U(S, V, n_1, n_2, \dots)$: U 及所有獨立變數均為 extensive properties

$$\Rightarrow \lambda U(S, V, n) = U(\lambda S, \lambda V, \lambda n)$$

$$\Rightarrow U = S \left(\frac{\partial U}{\partial S} \right)_{V, n_k} + V \left(\frac{\partial U}{\partial V} \right)_{S, n_k} + \sum_{j=1}^m n_j \left(\frac{\partial U}{\partial n_j} \right)_{S, V, n_{k \neq j}} \quad (9.8)$$

由 PIB5, Table 8.1 : $\left(\frac{\partial U}{\partial S} \right)_{V, n_k} = T$, $\left(\frac{\partial U}{\partial V} \right)_{S, n_k} = -P$

由 PIB3, (9.5) : $\left(\frac{\partial U}{\partial n_j} \right)_{S, V, n_k} = \mu_j$

$$\Rightarrow U = ST - PV + \sum_{j=1}^m \mu_j n_j \quad (9.10)$$

$$\text{因 } G = U - ST + PV \Rightarrow G = \sum_{j=1}^m \mu_j n_j \quad (9.11)$$

由 (9.10) $dU = Tds + SdT - PdV - VdP + \sum_{j=1}^m (\mu_j dn_j + n_j d\mu_j)$

又因 (9.4) $dU = Tds - PdV + \sum_{j=1}^m \mu_j dn_j$

$$\Rightarrow SdT - VdP + \sum_{j=1}^m n_j d\mu_j = 0 \quad \text{Gibbs-Duhem equation} \quad (9.13)$$

T 及 P 固定時, 由 (9.13) $\Rightarrow \sum_{j=1}^m n_j d\mu_j = 0 \xrightarrow{(9.11)} (dG)_{T, P} = \sum_{j=1}^m \mu_j dn_j \quad (9.14)$

由上述理論結果, 將做一些應用討論。

P.2 Phase Equilibrium

T_A	T_B
P_A	P_B
V_A	V_B
U_A	U_B
n_A	n_B

Insulated system 中有相同物質的兩相 (例如: 冰, 水).

兩相達成平衡的條件在 P138, Table 8.2, 第5項

因本系統 $dQ=0$.

本系統 n, V, U 固定.

$$\Rightarrow n_A + n_B = n$$

$$V_A + V_B = V$$

$$U_A + U_B = U$$

系統平衡條件: $S_A + S_B = S$ (maximum)

$$\Rightarrow dS = dS_A + dS_B = 0$$

$$\text{由 (P.4) 1st \& 2nd law} \Rightarrow \begin{cases} dS_A = \frac{1}{T_A} (dU_A + P_A dV_A - \mu_A dn_A) \\ dS_B = \frac{1}{T_B} (dU_B + P_B dV_B - \mu_B dn_B) \end{cases}$$

$$\text{因 } dn_B = -dn_A, dV_B = -dV_A, dU_B = -dU_A$$

$$\Rightarrow \left(\frac{1}{T_A} - \frac{1}{T_B} \right) dU_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B} \right) dV_A - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B} \right) dn_A = 0. \quad (\text{P.23})$$

系統平衡條件

因 dU_A, dV_A, dn_A 隨意變動 (P.23) 均成立.

$$\Rightarrow \text{相平衡時} \quad T_A = T_B, \quad P_A = P_B, \quad \mu_A = \mu_B$$

Δn_A	$\rightarrow \Delta n_B = -\Delta n_A$
T	T
P	P

若兩相間等溫，等壓。

若系統原來未達平衡，

在 phase A, 粒子數比平衡時多了 Δn_A

而 phase A 要減 Δn_A , phase B 要加 Δn_A 才會平衡。

$$\Delta S = \Delta S_A + \Delta S_B \geq 0$$

$$\text{由 (P.23) } T_A = T_B, P_A = P_B \Rightarrow = \frac{-\mu_A}{T} (-\Delta n_A) - \frac{\mu_B}{T} (\Delta n_A) \geq 0.$$

$$= \frac{\Delta n_A}{T} (\mu_A - \mu_B) \geq 0$$

$\Rightarrow \mu_A > \mu_B$ 粒子由高位能流到低位能。

9.3 The Gibbs Phase Rule

考慮平衡系統有 k 種物質，各有 π 種 phases.

相共存現象(自然界)在 P157 下面，

Let μ_i^r be the chemical potential of the i th constituent in the r th phase.

$$\text{由 (P.11)} \Rightarrow G = \sum_{i=1}^k \sum_{r=1}^{\pi} \mu_i^r n_i^r \quad (\text{P.31})$$

由 Table P.2: T, P 固定下，表平衡時 $(dG)_{TP} = 0$.

$$\text{由 (P.13) 固定 } T, P \text{ 下} \xrightarrow{\quad} \sum_{i=1}^k \sum_{r=1}^{\pi} n_i^r d\mu_i^r = 0. \quad (\text{P.33})$$

$$\text{再由 (P.15)} \Rightarrow (dG)_{TP} = \sum_{i=1}^k \sum_{r=1}^{\pi} \mu_i^r dn_i^r = 0, \quad T \text{ and } P \text{ fixed.} \quad (\text{P.32})$$

由於考慮 closed system, 粒子數守衡:

$$\sum_{r=1}^{\pi} dn_i^r = 0, \text{ for } i=1, 2, 3, \dots, k. \quad (P.34)$$

為說明上的方便, 簡化系統為 2 constituents, 2 phases.

(P.32) 可化作:

$$(dG)_{TP} = \mu_1^\alpha dn_1^\alpha + \mu_1^\beta dn_1^\beta + \mu_2^\alpha dn_2^\alpha + \mu_2^\beta dn_2^\beta = 0. \quad (P.35)$$

由 (P.34) 粒子數守衡, (P.35) 化作:

$$(\mu_1^\alpha - \mu_1^\beta) dn_1^\alpha + (\mu_2^\alpha - \mu_2^\beta) dn_2^\alpha = 0. \quad (P.37)$$

$$\text{因 } dn_1^\alpha \text{ 及 } dn_2^\alpha \text{ 是任意的} \Rightarrow \mu_1^\alpha = \mu_1^\beta; \mu_2^\alpha = \mu_2^\beta \quad (P.38)$$

\Rightarrow 在 T, P 固定下的平衡狀態, 各種粒子的所有 phases 的 chemical potentials 均要相同.

由於封閉系統, 各種物質 mole 數守衡.

$$n_1^\alpha + n_1^\beta = n_1 \quad \& \quad n_2^\alpha + n_2^\beta = n_2 \quad (P.39)$$

$$\left. \begin{aligned} \text{可方便的用分數表示法: } x_1^\alpha &= \frac{n_1^\alpha}{n_1}, & x_1^\beta &= \frac{n_1^\beta}{n_1} \\ x_2^\alpha &= \frac{n_2^\alpha}{n_2}, & x_2^\beta &= \frac{n_2^\beta}{n_2} \end{aligned} \right\} \quad (P.40)$$

上述 2 constituents, 2 phases 系統共有 $T, P, x_1^\alpha, x_2^\alpha$ 4 個獨立變數.

又有 (P.38) 兩平衡方程, 故獨立變數減成 2 個.

△

上述的一般狀況即為 Gibbs phase rule. (無化學反應)

固定 T, P , 粒子數不守恒 系統平衡, 在趨向平衡過程中 $\sum_{i=1}^{\pi} dN_i^r \neq 0$

For a multiconstituent, multiphase system with T and P fixed, the condition for equilibrium is

$$\mu_i^k = \mu_i^p = \mu_i^r = \dots = \mu_i^{\pi}, \quad i = 1, 2, \dots, k \quad (9.42)$$

數

The kilomole fractions: $x_j^r = \frac{n_j^r}{\sum_{i=1}^k n_i^r}, \quad j = 1, 2, \dots, k \quad (9.43)$
 r 相內 i^{th} 種成份之 kilomole fraction $r = 1, 2, \dots, \pi$

上述 kilomole fractions 共有 $k\pi$ 個. 另有 π 個關係式:

r 相內所有成份的 kilomole fraction 和為 1 $\sum_{i=1}^k x_i^r = 1, \quad r = 1, 2, \dots, \pi \quad (9.44)$

故系統共有 $2 + k\pi - \pi$ 個獨立變數.

另 (9.42) 有 $k(\pi-1)$ 個平衡方程.

定義系統的 degree of freedom $f = (2 + k\pi - \pi) - k(\pi-1) = 2 + k - \pi$

例 1: 最簡系統, $k=1$ 種成份, $\pi=1$ 個相 $\Rightarrow f=2$.

P, V, T 三變數, $PV=RT$ 關係式 $\Rightarrow 2$ 獨立變數.

P25
Fig 2.3

例 2: 2 種成份混合成氣相 ($k=2, \pi=1$) $\Rightarrow f=3$

可取 P, T 及其中一種成份的 kilomole fraction 為獨立變數.

另一種成份的 kilomole fraction 即被確定.

$T=1$ 之後, 系統即處於平衡狀態.

若只固定 P, T , 兩種成份的 mole 分率是任意的.

例 3. Water in equilibrium with its saturated vapor.

$$k=1, \pi=2. \Rightarrow f=1.$$

給定 T , 則飽和蒸氣壓 P 就被確定。反之亦然。

液相的量
並不確定

例 4. 水的三相點, $k=1, \pi=3 \Rightarrow f=0.$

故其 T, P 均為確定值。

若為 closed system. 達平衡時只有 ~~兩個~~ 獨立變數。

(自然 TP 固定)

Proof: 達平衡時: $\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi, \quad i=1, 2, \dots, k$ (A)

粒子數守恒: $\sum_{r=1}^{\pi} dn_i^r = 0, \quad i=1, 2, \dots, k$

定義 kilomole fraction: $x_i^\alpha = \frac{n_i^\alpha}{\sum_{r=1}^{\pi} n_i^r}, \quad i=1, 2, \dots, k$
 $\alpha=1, 2, \dots, \pi$

$$\sum_{r=1}^{\pi} x_i^r = 1, \quad i=1, 2, \dots, k \quad (B)$$

T, P 加上 $\{x_i^r\}$ 共有 $k\pi + 2$ 個變數。

(B) 有 k 個等式, (A) 有 $k(\pi-1)$ 個等式。

$$\Rightarrow \text{獨立變數 } 2 + k\pi - k - k(\pi-1) = 2.$$

考慮 P138, Fig 8.2, 開放系統只有一獨立變數 T .

對閉系統有二獨立變數 T, V .

9.4 Chemical Reactions

化學反應式, 例: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

可寫成 $\Rightarrow 2\text{H}_2\text{O} - 2\text{H}_2 - \text{O}_2 = 0$.

所有化學反應式可一般化表示為: $\sum_{j=1}^m \nu_j M_j = 0$.

上例中 $\nu_{\text{H}_2\text{O}} = 2$, $\nu_{\text{H}_2} = -2$, $\nu_{\text{O}_2} = -1$.

$$dN_{\text{H}_2} : dN_{\text{O}_2} : dN_{\text{H}_2\text{O}} = -2 : -1 : 2$$

若化學反應在定 T, P 下.

$$\begin{aligned} \text{由 Gibbs-Duhem eq (9.13): } & SdT - Vdp + \sum_{j=1}^m n_j d\mu_j = 0. \\ & \Rightarrow \sum_{j=1}^m n_j d\mu_j = 0. \end{aligned}$$

又因 at equilibrium $(dG)_{T,P} = 0$, $G = \sum_{j=1}^m \mu_j n_j \Rightarrow \sum_{j=1}^m \mu_j dn_j$

$$\Rightarrow \sum_{j=1}^m \mu_j \nu_j = 0. \text{ for chemical equilibrium in a reaction.}$$

$$\Rightarrow \mu_{\text{H}_2\text{O}} = \frac{1}{2}(2\mu_{\text{H}_2} + \mu_{\text{O}_2})$$

9.5 Mixing Processes

考慮 2 種不同 ideal gas 的混合現象,
因固定 T, P , 故依然用 Gibbs function 來討論.

氣體總壓力 P , 第 j 種氣體之分壓 $P_j = x_j P$
where x_j is the kilomole fraction of j th constituent gas.

$$P_j = \frac{n_j RT}{V}, \quad P = \frac{n RT}{V} = \left(\sum_j n_j \right) \frac{RT}{V}$$

$$\text{Gibbs function } G = \sum_j n_j g_j \quad (9.51)$$

where g_j is the specific Gibbs function. for the j th constituent

下面要求 g :

For an ideal gas, 由 (4.13), (4.14), 可逆時: $T ds = c_p dT - v dp$

$$v = \frac{RT}{P} \text{ 代入 } \Rightarrow ds = c_p \frac{dT}{T} - R \frac{dP}{P}$$

$$\Rightarrow s = c_p \ln T - R \ln P + s_0$$

$$\Rightarrow g = u + Pv - Ts = h - Ts$$

$$(4.2P) \quad h = c_p T + h_0$$

$$\begin{aligned} \Rightarrow g = h - Ts &= c_p T + h_0 - T [c_p \ln T - R \ln P + s_0] \\ &= c_p T + h_0 - c_p T \ln T + RT \ln P - Ts_0 \\ &= RT [\ln P + \phi] \quad (P.5-2) \end{aligned}$$

$$\text{where } \phi = \left[\frac{c_p}{R} (1 - \ln T) + \frac{h_0}{RT} - \frac{s_0}{R} \right] = \phi(T)$$

ϕ depends on T only.

下面要求 2 種 ideal gas 混合時 Gibbs function 的變化。

initial state i

n_1	n_2
T, P	T, P



final state f

$n = n_1 + n_2$
$T, P = P_1 + P_2$

diaphragm

總量為兩種量之和。

溫度不變，

總壓為兩分壓和。

每種氣體壓力因體積增大而減

$$G_i = n_1 g_{1i} + n_2 g_{2i}$$

$$= n_1 RT [\ln P + \phi_1] + n_2 RT [\ln P + \phi_2]$$

$$G_f = n_1 g_{1f} + n_2 g_{2f}$$

$$= n_1 RT [\ln P_1 + \phi_1] + n_2 RT [\ln P_2 + \phi_2]$$

$$= n_1 RT [\ln(x_1 P) + \phi_1] + n_2 RT [\ln(x_2 P) + \phi_2]$$

$$= n_1 RT [\ln P + \phi_1 + \ln x_1] + n_2 RT [\ln P + \phi_2 + \ln x_2]$$

$$= n_1 g_1 + n_1 RT \ln x_1 + n_2 g_2 + n_2 RT \ln x_2$$

$$\Delta G = G_f - G_i = RT(n_1 \ln x_1 + n_2 \ln x_2) \\ = nRT(x_1 \ln x_1 + x_2 \ln x_2) \quad \Downarrow \text{For an ideal gas, 各種氣體量的比值等於分壓比. (9.5')}$$

注意：因 $x_1 + x_2 = 1$, $0 \leq x_1, x_2 \leq 1 \Rightarrow \ln x_1, \ln x_2 \leq 0$.
 $\Rightarrow \Delta G < 0$.

從 state i \rightarrow state f, entropy 的變化可由 reciprocity relation:

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

$$\Rightarrow \Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P \Rightarrow \Delta S = -nR(x_1 \ln x_1 + x_2 \ln x_2) > 0 \quad (9.5'')$$

當兩種不同氣體混合時, $\Delta G < 0$, $\Delta S > 0$. 這如所預期.

但兩相同氣體混合時, 理當 $\Delta G = 0$, $\Delta S = 0$,

結果用 (9.5') 及 (9.5'') 確得到意外的結果: Gibbs paradox.

$$\begin{array}{|c|c|} \hline P & P \\ \hline V, T & V, T \\ \hline n_1 = n_2 & \end{array} \Rightarrow \begin{array}{|c|} \hline P, V, T \\ \hline n = n_1 + n_2 \\ \hline \end{array} \Rightarrow x_1 = x_2 = \frac{1}{2}$$

$$\Rightarrow \Delta S = nR \ln 2 > 0.$$

此理論將在統計力學中討論.

直觀上, different or distinguishable 氣體混合時 S 增加.