Ch 8 Thermodynamic Potentials

8.1 Introduction

到目前為止，能量的 state variables 有2個：the internal energy U
the enthalpy H

能量函數 (state variables) 稱作 therodynamic potentials.

The role of the therodynamic potentials is to determine the equilibrium states of systems under prescribed constrain

對於所有可能的 processes，共需要4種 thermodynamic potentia

① U：The Internal energy
② H：The Enthalpy
③ F：The Helmholtz function
④ G：The Gibbs function

Consider the combined 1st and 2nd laws：$dU = TdS - PdV$ (8
There are 2 conjugate pairs：
(T, S), (P, V)

從此2 pairs 中各取一獨立變數共有4種取法。

8.2 The Legendre Transformation

Consider the function $Z = Z(x, y) \Rightarrow dZ = X\,dx + Y\,dy$ (8.5)

$$Z \text{ is exact differential} \Rightarrow \begin{bmatrix} X = \dfrac{\partial Z}{\partial x} \\ \\ Y = \dfrac{\partial Z}{\partial y} \end{bmatrix} \quad (8.8)$$

其中 (x, X), (y, Y) are canonically conjugate pairs.

We wish to replace (x, y) by (X, Y) as independent variabl
定義新函數：

$$M(X, Y) = Z - xX - yY \quad (8.6)$$

$$\Rightarrow dM = \underbrace{dZ - X\,dx - Y\,dy}_{\overset{\shortparallel}{0}} - x\,dX - y\,dY$$

$$\Rightarrow dM = -x\,dX - y\,dY \quad (8.7)$$

$$M \text{ is exact differential} \Rightarrow \begin{bmatrix} -x = \dfrac{\partial M}{\partial X} \\ \\ -y = \dfrac{\partial M}{\partial Y} \end{bmatrix} \quad (8.9)$$

(8.6) is the transformation that takes us from a function of one pair of variables to the other.

(8.5), (8.7) give reciprocity relations (8.8), (8.9)

If we wish to replace only one of the variable y by its canonically conjugate Y, we must consider the function

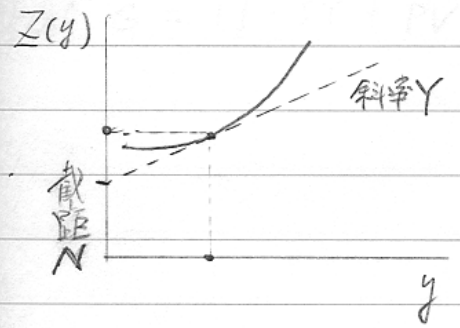
$$N(x, Y) = Z - yY \tag{8.10}$$

$$dN = dZ - Y dy - y dY$$

(8.5) 代入 $\Rightarrow dN = X dx - y dY$ (8.11)

with reciprocity relations : $\left[\begin{array}{l} \frac{\partial N}{\partial x} = X \\ \frac{\partial N}{\partial Y} = -y \end{array}\right]$ (8.12)

欲對轉換更有感覺，考慮曲線函數 $Z(y)$，曲線上每一點之座標由 (y, z) 表示。



$\Rightarrow$ 曲線上的斜率函數 $Y(y) = \frac{dZ}{dy}$

$dZ(y) = Y(y) dy$

每個 (y, z) 都可找到一切線：斜率 Y，截距 N

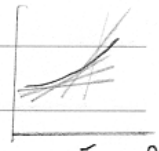


Fig 8.1

於是我們可以將 (y, Z) 轉換成 (Y, N) 來敘述此曲線兩組座標間的關係為：

$$Y = \frac{Z - N}{y - 0} \Rightarrow \text{截距 } N = Z - yY$$

$$\Rightarrow dN = dZ - d(yY) = dZ - y dY - Y dy = -y dY$$

$$\Rightarrow y = \frac{-dN}{dY}$$

8.3 Definition of the Thermodynamic Potentials

由 1st 及 2nd laws $\Rightarrow$ $dU = TdS - PdV$, $U(S,V)$

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

① 設 $H = U + PV$ $\Rightarrow$ $dH = dU + PdV + VdP$

$$dH = TdS + VdP \ , \quad H(S,P)$$

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

② 設 $F = U - ST$ $\Rightarrow$ $dF = dU - TdS - SdT$

$$dF = -PdV - SdT$$

$$\left(\frac{\partial F}{\partial V}\right)_T = -P \ , \quad \left(\frac{\partial F}{\partial T}\right)_V = -S$$

③ 設 $G = U - ST + PV$ $\Rightarrow$ $dG = dU - SdT - TdS + PdV + VdP$

$$dG = -SdT + VdP$$

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

8.4 The Maxwell Relations

因4種 Thermodynamic Potentials 均為 state variable,
他們的 differentials 均為 exact

$$\Rightarrow \quad dU = T\,dS - P\,dV \qquad T = \left(\frac{\partial U}{\partial S}\right)_V, \quad -P = \left(\frac{\partial U}{\partial V}\right)_S \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 U}{\partial V \partial S}$$

$$dH = T\,dS + V\,dP \qquad T = \left(\frac{\partial H}{\partial S}\right)_P, \quad V = \left(\frac{\partial H}{\partial P}\right)_S \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P = \frac{\partial^2 H}{\partial P \partial S}$$

$$dF = -S\,dT - P\,dV \qquad S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad -P = \left(\frac{\partial F}{\partial V}\right)_T \qquad -\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial^2 F}{\partial V \partial T}$$

$$dG = -S\,dT + V\,dP \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P, \quad V = \left(\frac{\partial G}{\partial P}\right)_T \qquad -\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 G}{\partial P \partial T}$$

詳情參閱 P135 TABLE 8.1

Reciprocity Relations

Maxwell Relations

No.

Thermodynamic Potentials

由熱力學 1st law: $dU = TdS - PdV$

$\Rightarrow$

The internal energy $U = U(S,V)$

定義: $H = U + PV$, $dH = TdS + VdP$, $H = H(S,P)$

定義: $F = U - TS$, $dF = -SdT - PdV$, $F = F(T,V)$

定義: $G = U - TS + PV$, $dG = -ST + VdP$, $G = G(T,P)$

由不平衡 ↓ 系統在不同熱力變數被選作控制變因時
有相對應的 Thermodynamic Potential 必須為最小值.

① S and V constant $dS = dV = 0$ $dU \le 0$ U 最小化

② S and P constant $dS = dP = 0$ $dH \le 0$ H 最小化

③ T and V constant $dT = dV = 0$ $dF \le 0$ F 最小化

④ T and P constant $dT = dP = 0$ $dG \le 0$ G 最小化

⑤ Adiabatic $đQ = dU + PdV$ $dS \ge 0$ S 最大化
$= TdS = 0$

系統熱增加 熱流入 ↓不可逆功轉成熱

ow ⑤ $đQ = 0$ 時, 系統由不平衡趨向平衡: $TdS = đQ + \varepsilon + \delta$ ← 內部功轉成熱.

因 $đQ = 0 \Rightarrow TdS = \varepsilon + \delta \ge 0 \Rightarrow (dS)_{ad} \ge 0$

↖等號表示原為平衡態.

因而絕熱系統是否達平衡之指標為 S 極大化.

No.

初態與終態均為平衡態時，不可逆源自於外界作功轉成熱.

由 1st law: $dU = \begin{bmatrix} đQ_r - đW_r \\ đQ - đW \end{bmatrix} = TdS - PdV$

$đW$是系統對外作功

$đQ_r = TdS$ 是可逆過程系統吸熱.

$đW_r$ 是可逆過程系統對外作功.

$đQ = TdS - \varepsilon$ 是一般狀況下系統吸熱,

其中 $\varepsilon \geq 0$ 是外界對系統作的不可逆功，在系統內完全轉成熱.

故系統實際得到的熱 $TdS = đQ + \varepsilon$ 功轉成熱

實際熱流入

因 $đQ_r - đW_r = đQ - đW = đQ_r - \varepsilon - đW$

$\Rightarrow (-đW) - (-đW_r) = \varepsilon \geq 0$

外界對系統作的功 − 外界對系統作的可逆功. = 不可逆功轉成的熱.

系統由不平衡趨向平衡，過程為不可逆之內部功轉成熱.

ow ① $dV = 0 \Rightarrow$ 外界與系統間沒作功. ($đW = 0$) (~~不逆功~~)

$dS \geq 0 \Rightarrow$ 系統內無熱增加 ($TdS = 0$).

此時若系統在不平衡狀態，為趨向平衡內部功轉成熱,

設有 $\delta \geq 0$ 的功轉成熱, (按 2nd law 此過程無法反轉)(此為自然發生過程不

又因 $TdS = 0$, 系統內無熱增加, $\Rightarrow$ 此功轉成的熱 $\delta > 0$ 必須流出.

即 $TdS = đQ + \delta$, 要求 $TdS = 0$, $\delta \geq 0 \Rightarrow đQ = -\delta \leq 0$

系統與外界無作功時: $\underbrace{dU}_{\text{系統內能變化}} = \underbrace{đQ}_{\text{流入熱}} - \underbrace{đW}_{=0} = đQ = -\delta \leq 0$

等號成立表示原為平衡

若外界對系統作不可逆功 $\varepsilon > 0$, 但無可逆功.

$\Rightarrow \underbrace{TdS}_{\text{系統熱增加}} = \underbrace{đQ}_{\text{熱流入}} + \underbrace{\varepsilon}_{\text{不可逆功轉成熱}} + \delta \leftarrow$ 內部功轉成熱.

因 $TdS = 0 \Rightarrow đQ = -\varepsilon - \delta \leq 0$ 熱流出.

$\Rightarrow \underbrace{dU}_{\text{系統內能變化}} = đQ - đW = (-\varepsilon - \delta) - (PdV - \varepsilon) = -\delta - P\overset{0}{\overset{\parallel}{dV}} = -\delta \leq 0.$ 因 $dV = 0$

等號表示原為平衡

因而 $dV = dS = 0$ 系統是否達平衡之指標為 U 極小化.

No.

ow ② $dP=0$, $dV\neq 0$. ⇒ 外界與系統間有相互作功.($dW\neq 0$)

$dS=0$ ⇒ 系統內無熱增加 ($TdS=0$)

若此時系統在不平衡狀態,為趨向平衡自然發生過程為不可逆之內部功轉成熱

設內部有 $\delta>0$ 之功轉成熱, 又因 $TdS=0$, 系統內無熱增加

⇒ 此功 $\delta>0$ 轉成的熱必須流出去.

即 $TdS = đQ + \delta$, 要求 $TdS=0$, $\delta\geq 0$ ⇒ $đQ = -\delta \leq 0$

系統與外界互有作功, 但 P 恆定時 (設外界與系統間均為可逆功)

能變化 ⇒ $dU = đQ - đW = -\delta - PdV$ = 視 dV 而定, 無規律性.

焓之變化 ⇒ $dH = d[U+PV] = đQ + \underset{\overset{\shortparallel}{0}}{VdP} = -\delta \leq 0$.

等號成立表示原為平衡態.

P 恆定, 系統與外界間有可逆功與不可逆功 ($\varepsilon\geq 0$),

⇒ $TdS = đQ + \varepsilon + \delta$ ← 內部功轉成熱.

系統熱增加 熱流入 不可逆功轉成熱

因 $TdS=0$ ⇒ $đQ = -\varepsilon-\delta \leq 0$ 熱流出.

能變化 ⇒ $dU = đQ - đW = (-\varepsilon-\delta) - (PdV-\varepsilon) = -\delta - PdV$ 無規律

焓之變化 ⇒ $dH = d[U+PV] = đQ - (-\varepsilon) + VdP$

$= (-\varepsilon-\delta) - (-\varepsilon) + VdP = -\delta \leq 0$

等號表示原為平衡態

因而 $dP=dS=0$ 系統是否達到平衡之指標: H 極小化.

The change in U is the heat flow in an isochoric reversible process.
The change in H is the heat flow in an isobaric reversible process.

若系統與環境之溫度不同, 熱(流入流出)必然只能由高溫流向低溫,
同時發生宇宙總 Entropy 淨增加. 上述 show①, show② 並未考慮
此種情況.

show①, show② 中, 熱必為流出, 必然 $T_{系統} \geq T_{環境}$
若 $T_{系} > T_{環}$, 則熱流出為另一不可逆過程.

③ $dV=0 \Rightarrow$ 外界系統間沒作功. ($đW=0$)

$dT=0,\ TdS\neq 0 \Rightarrow$ 系統熱可增減.

若此時系統在不平衡狀態, 為趨向平衡, 自然發生 (不可逆之) 內部功轉成熱.

設內部有 $\delta>0$ 之功轉成熱, 則系統內熱增加: $TdS = đQ + \delta$

$\Rightarrow$ 實際流入系統的熱 $đQ = TdS - \delta$.

$\Rightarrow$ 系統內能變化 $dU = đQ - đW = (TdS-\delta) - \overset{0}{\overset{\shortparallel}{PdV}} = TdS - \delta$ 無規律

Helmholtz Free Energy $F = U - TS$

系統由不平衡趨向平衡過程 F 之變化 $dF = d[U-TS]$

$$= -S\underset{0}{\underset{\shortparallel}{dT}} - \delta - P\underset{0}{\underset{\shortparallel}{dV}} = -\delta \leq 0$$

等號表示原為平衡態

若外界對系統間無可逆作功, 但外界給予系統不可逆功 $\varepsilon>0$.

$\Rightarrow$ 系統內熱增加 $TdS = đQ + \varepsilon + \delta$ ← 為達平衡之內部功轉成熱.

$\Rightarrow$ 實際流入系統的熱 $đQ = TdS - \varepsilon - \delta$

$\Rightarrow$ 系統內能變化 $dU = đQ - đW = (TdS - \varepsilon - \delta) - (\overset{0}{\overset{\shortparallel}{PdV}} - \delta)$

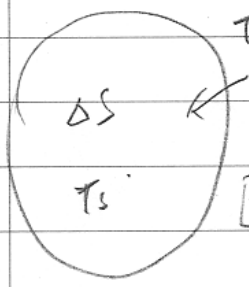
$$= TdS - \delta$$

$\Rightarrow$ 系統由不平衡趨向平衡過程 $dF = d[U-TS]$

$$= -SdT - \delta - PdV = -\delta \leq 0.$$

A.H. Carter P134, 8.5

考慮系統在 $dT=dV=0$ 條件下, [由不平衡 → 平衡 由平衡初態到平衡終態] 過程中熱量 $Q>0$ 由高溫的外界流入低溫的系統, 環境 Entropy 變化 ΔS_0, 系統 ΔS.



$\boxed{T_s<T}$

由 2nd law: $\Delta S + \Delta S_0 \geq 0$

因 $\Delta S_0 = \frac{-Q}{T} \Rightarrow \Delta S \geq \frac{Q}{T} \Rightarrow T\Delta S \geq Q$ (不等溫或不平衡都不成立)

由 1st law: $\Delta U = Q - W \Rightarrow W = -\Delta U + Q \leq -\Delta U + T\Delta S$

因 $F = U - TS \Rightarrow \Delta F = \Delta U - T\Delta S - S\Delta T \Rightarrow (\Delta F)_T = \Delta U - T\Delta S$

由上兩行 $\Rightarrow W \leq -(\Delta F)_T \Rightarrow$ 對外作功 $\leq$ 系統 F 的減少

當系統與外界間不作功時, 体積亦不變 $\Rightarrow (\Delta F)_{TV} \leq 0$. ($F \leq F_0$)

ΔF in an isothermal reversible process is the work done on or by the system. The decrease in F equals the maximum energy that can be freed in an isothermal process and made available work. 因此稱 F 為 the free energy (Helmholtz).

$dT=dV=0$ 系統是否達平衡之指標: ΔF 極小.

No.

ow ④ $dP=0,\ dV\neq 0 \Rightarrow$ 外界此系統間有相互作功. ($dW\neq 0$)

$dT=0,\ TdS\neq 0 \Rightarrow$ 系統熱可增減.

若此時系統在不平衡狀態, 在趨向平衡過程中, 發生不可逆內部功轉成熱

設內部有 $\delta>0$ 之功轉成熱, 則系統內熱增加: $TdS = dQ+\delta$

$\Rightarrow$ 實際流入系統的熱 $dQ = TdS-\delta$

$\Rightarrow$ 系統內能變化 $dU = dQ - dW = (TdS-\delta) - PdV$ 無規律.

Gibbs Free Energy $G = U - TS + PV$

系統由不平衡趨向平衡過程 G 之變化 $dG = d[U-TS+PV]$

$$= -\delta - S\cancel{dT}^{0} + V\cancel{dP}^{0}$$

$$= -\delta \leq 0$$

等號表示原為平衡態.

若過程中外界施此系統不可逆功 ε, 則結果相同, 詳見 Show③.

A.H. Carter P136, 8.6

考慮系統在 $dT=dP=0$ 下, [由不平衡 → 平衡 / 由平衡初態 → 平衡終態] 過程中, 熱量 $Q>0$

由高溫之外界流入低溫之系統, 環境 Entropy 變化 ΔS_0, 系統 ΔS.

由 2nd law: $\Delta S + \Delta S_0 \geq 0$.

因 $\Delta S_0 = \frac{-Q}{T} \Rightarrow \Delta S \geq \frac{Q}{T} \Rightarrow T\Delta S \geq Q$ 不等溫或不平衡態等號都不成立.

由 1st law: $\Delta U = Q - W \Rightarrow Q = \Delta U + W = \Delta U + \overbrace{P\Delta V}^{\text{可逆功}}$

由上兩行 $\Rightarrow \Delta U + P\Delta V = Q \leq T\Delta S \Rightarrow \Delta U + P\Delta V - T\Delta S \leq 0$.

因 $G = U + PV - TS \Rightarrow \Delta G = \Delta U + P\Delta V + \cancel{V\Delta P}^{0} - T\Delta S - \cancel{S\Delta T}^{0}$

由上兩行 $\Rightarrow (\Delta G)_{T,P} \leq 0. \Rightarrow G_f \leq G_i$ for 平衡態轉換.

$dT=dP=0$ 系統是否平衡之指標: ΔG 極小.

若考慮可逆功 $W = P\Delta V + \underbrace{B\Delta M}_{-W_{nm}}$.

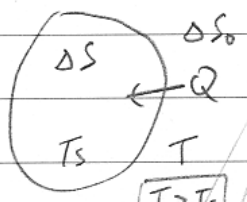
$T\Delta S \geq Q$

$\Delta U = Q - W \Rightarrow Q = \Delta U + W = \Delta U + P\Delta V + B\Delta M$

$\Rightarrow \Delta U + P\Delta V - T\Delta S \leq B\Delta M = -W_{nm}$

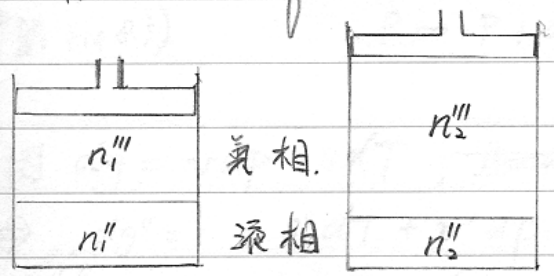
$\Rightarrow (\Delta G)_{T,P} \leq B\Delta M = -W_{nm} \Rightarrow W_{nm} \leq -(\Delta G)_{T,P}$

The decrease in G is equal to the maximum energy that can be freed in an isothermal, isobaric process and made available for nonmechanical work



若以 $T_s>T$ Q流出來分析, 結果完全相同.

8.7 Application of the Gibbs Function to Phase Transitions.



固定 T, P

兩相達平衡

設有2種可能的平衡態.

$\begin{matrix} n_1'' \\ n_2'' \end{matrix}$ 與 $\begin{matrix} n_1''' \\ n_2''' \end{matrix}$ 分別表在 " 與 ''' 相 mole (液 氣)

物質守衡 $\Rightarrow \underbrace{n_1'' + n_1'''}_{\text{狀態1.}} = \underbrace{n_2'' + n_2'''}_{\text{狀態2.}}$

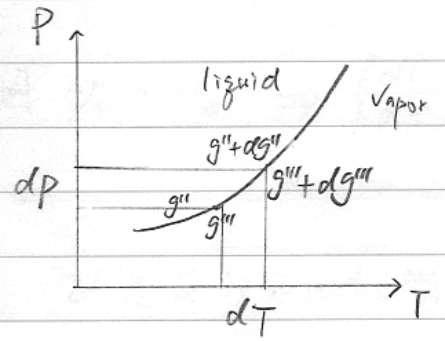
The specific Gibbs functions of phase" (liquid) and phase''' (vapor) are defined a

g'' g'''

state 1 $G_1 = n_1'' g'' + n_1''' g'''$

state 2 $G_2 = n_2'' g'' + n_2''' g'''$

Suppose that a reversible transition takes place from state 1 to state 2. Since $(\Delta G)_{T,P} = 0. \Rightarrow G_1 = G_2. \Rightarrow g'' = g'''$.



The specific Gibbs function is the same for the two phases.

參閱 P25, P26
Fig2.3, Fig2.4

在任何兩相交界上, 兩相的 specific Gibbs function 均相等. $g''=g'''$
但在兩相交界上, 不同點的 g 不同.

沿兩相交界滑動 $\left[\begin{array}{l} T \to T+dT \\ P \to P+dP \end{array}\right] \Rightarrow g \to g+dg \left\{\begin{array}{l} g''+dg'' \\ g'''+dg''' \end{array}\right. \xrightarrow{\text{因 } g''=g'''} dg''=dg'''$

(仍然都是平衡態)

(參閱 Fig 8.3)

因 $dg = vdp - sdT$，~~且 P, T 固定~~.

$$\Rightarrow \quad dg'' = -s''dT + v''dp = -s'''dT + v'''dp = dg'''$$

$$\Rightarrow \quad (s''' - s'')dT = (v''' - v'')dp$$

$$\Rightarrow \quad \frac{dP}{dT} = \frac{s''' - s''}{v''' - v''} \qquad (8.28)$$

由 Entropy 定義： $s''' - s'' = \dfrac{l_{23}}{T} > 0$ ← Latent heat $= đq = du + Pdv$

$$\Rightarrow \text{液氣界線變化關係} \quad \left(\frac{dP}{dT}\right)_{23} = \frac{l_{23}}{T(v''' - v'')} > 0 \ (\text{liquid-vapor}) \qquad (8.30)$$

此為 Clausius - Clapeyron equation.

$$\left(\frac{dP}{dT}\right)_{13} = \frac{l_{13}}{T(v''' - v')} > 0 \ (\text{solid-vapor}) \qquad (8.31)$$

$$\left(\frac{dP}{dT}\right)_{12} = \frac{l_{12}}{T(v'' - v')} \begin{array}{l} >0 \\ <0 \text{ 水} \end{array} \ (\text{solid-liquid}) \qquad (8.32)$$

特例 因 $v_{冰} > v_{水} \Rightarrow \left(\dfrac{dP}{dT}\right)_{冰水} < 0$.

於是可決定兩相間界面曲線

例 水 → 水蒸氣.

考慮 P 不大時, 水 → 蒸氣 : $v''' \gg v''$, $l_{23} > 0$.

考慮蒸氣為 an ideal gas.

$$\Rightarrow \left(\frac{dP}{dT}\right)_{23} \doteq \frac{l_{23}}{T v'''} \underline{\underline{\quad v''' = \frac{RT}{P} \quad}} \frac{l_{23} P}{R T^2}$$

近似考慮 l_{23} 與溫度無關 $\Rightarrow \dfrac{dP}{dT} = \dfrac{l_{23}}{R} \dfrac{P}{T^2}$

$$\int_{P_0}^{P} \frac{dP}{P} = \frac{l_{23}}{R} \int_{T_0}^{T} \frac{dT}{T^2}$$

$$\Rightarrow P = P_0 \, e^{-\frac{l_{23}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)}$$

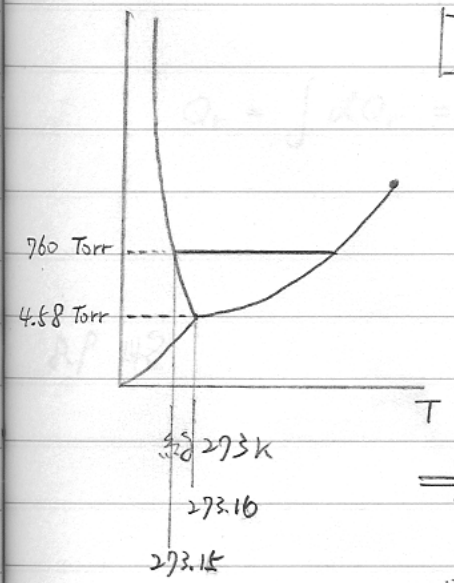
(T_0, P_0) 為兩相邊界線上某固定點.

Why the ice point of water (273.15 K) is 0.01 K below the triple point (273.16 K) :

$$dT = \frac{T(v'' - v')}{l_{12}} dP$$

$\boxed{\text{因 } dT \to 0 \Rightarrow \Delta T \propto \Delta P}$

$$\Delta T = \frac{T(v'' - v')}{l_{12}} \Delta P$$



$l_{12} = 80$ 卡/克 $= 80 \times 4.182 \times 1000$ J/kg $= 3.34 \times 10^5$ J/kg

$v'' = 10^{-3}$ m³/kg

$v' = 1.09 \times 10^{-3}$ m³/kg

$\Delta P = 10^5$ Pa

$$\Rightarrow \Delta T = \frac{273(1 - 1.09) \times 10^{-3}}{3.34 \times 10^5} \times 10^5 = -0.0074 \text{ K}$$

另由於 air 溶於冰與水當中, 熔點再降 0.0023 K.

$\Rightarrow$ 熔點共下降 $0.0097 \text{ K} \doteq 0.01 \text{ K}$

8.8 An application of the Maxwell Relations.

考慮 an ideal gas, $\begin{pmatrix}\text{isothermal}\\ \text{reversible}\end{pmatrix}$ $P_0 \to P$ $\Rightarrow$ 獨立變數取 T, P

$\Rightarrow S = S(T, P)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P \cancel{dT}^{\,0} + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$\Rightarrow dQ_r = TdS = T\left(\frac{\partial S}{\partial P}\right)_T dP$, S 不是可觀測量，算不下去了。

由 Table 8.1, the Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

$$\Rightarrow dQ_r = -T\left(\frac{\partial V}{\partial T}\right)_P dP$$

For an ideal gas $PV = nRT$ $\Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$

$$\Rightarrow dQ_r = \frac{-nRT}{P} dP$$

$$Q_r = \int dQ_r = -nRT\int \frac{dP}{P} = -nRT\ln\left(\frac{P}{P_0}\right)$$

8.9 略.