Chapter 6   Thermodynamic Properties of Fluids

§6-1. Property relations for homogeneous phases

1. The first law for a closed system of n moles is:

$$dU = dQ + dW$$

(1) For the special case of a reversible process,

$$dU = dQ_{rev} + dW_{rev}$$

$$dQ_{rev} = TdS \qquad \text{---------2nd law}$$

(2) For P-V work only:

$$dW_{rev} = -PdV$$

$$\therefore dU = TdS - PdV$$

2. Define:

(1) ●$H \equiv U + PV$

　●$A \equiv U - TS$　　$\therefore$

　●$G \equiv H - TS$

◆$dU = TdS - PdV$

◆$dH = TdS + VdP$

◆$dA = -SdT - PdV$

◆$dG = -SdT + VdP$

※※不但要會證明，且先
決條件要清楚！

(2) For a function of two variables, $F(x, y,) = xy$

Then, $dF = d(xy) = x\,dy + y\,dx$

↳The total derivative of a function of multiple variables, $F(x, y, z, ...)$ is

defined as:

$$dF = (\partial F/\partial x)_{y,z\text{----}}\,dx + (\partial F/\partial y)_{x,z\text{----}}\,dy + (\partial F/\partial z)_{x,y\,\text{----}}\,dz + \text{------}$$

$$\therefore d(x^3 y^2) =$$

而 $dU = TdS - PdV;\ dH = TdS + VdP;\ dA = -SdT - PdV;\ dG = -SdT + VdP$

所以：

❶$dU = (\dfrac{\partial}{\partial}\text{---})\,dS - (\dfrac{\partial}{\partial}\text{---})\,dV$

$$dU = TdS - PdV$$

$(\dfrac{\partial}{\partial}\text{---}) = T\ ;\ (\dfrac{\partial}{\partial}\text{---}) = -P$

❷$dH = (\dfrac{\partial}{\partial}\text{---})\,dS + (\dfrac{\partial}{\partial}\text{---})\,dP$

$$dH = TdS + VdP$$

$(\dfrac{\partial}{\partial}\text{---}) = T\ ;\ (\dfrac{\partial}{\partial}\text{---}) = V$

❸ $dA = (\frac{\partial}{\partial}\text{---})\, dT + (\frac{\partial}{\partial}\text{---})\, dV$

$dA = -SdT - PdV$

$(\frac{\partial}{\partial}\text{---}) = -S\ ;\ (\frac{\partial}{\partial}\text{---}) = -P$

❹ $dG = (\frac{\partial}{\partial}\text{---})\, dT + (\frac{\partial}{\partial}\text{---})\, dP$

$dG = -SdT + VdP$

$(\frac{\partial}{\partial}\text{---}) = -S\ ;\ (\frac{\partial}{\partial}\text{---}) = V$

(3)The Maxwell Relationships:

❶任何一函數 F(x, y, z)都可應用

$dF = (\partial F/\partial x)_{y,z\text{----}}\, dx + (\partial F/\partial y)_{x,z\text{----}}\, dy + (\partial F/\partial z)_{x,y}\text{----}\, dz + \text{------}$

而變成：

$dF = A\, dx + B\, dy + C\, dz$

❷但不是隨便一個 $M\, dx + N\, dy + Q\, dz$ 都可變成 dF 的形式。

※ $d(3xy^2 + x^3y) = A\, dx + B\, dy$ →A = _____ B = _____

$x^2y\, dx + 4xy^3\, dy = dG$ → G = _____

❸若 $M\, dx + N\, dy = dF$ 是成立的

↳稱之為 exact differential → $(\partial M/\partial y)_x = (\partial N/\partial x)_y$

∴ $6x^2y^5dx + 10x^3y^4dy$ →

$3x^2y^4dx + 5x^4y^2\, dy$ →

❹The Maxwell Relationships:

● The four equations, $dU = TdS – PdV$; $dH = TdS + VdP$; $dA = -SdT – PdV$; $dG = -SdT + VdP$, are all exact differentials.

↳◆ $dU = TdS – PdV$ is a exact differential → $(\frac{\partial T}{\partial V})_S = -(\frac{\partial P}{\partial S})_V$

◆ $dH = TdS + VdP$ is a exact differential → $(\frac{\partial}{\partial}\text{---}) = (\frac{\partial}{\partial}\text{---})$

◆ $dA = -SdT – PdV$ is a exact differential → $(\frac{\partial}{\partial}\text{---}) = (\frac{\partial}{\partial}\text{---})$

◆ $dG = -SdT + VdP$ is a exact differential → $(\frac{\partial}{\partial}\text{---}) = (\frac{\partial}{\partial}\text{---})$

3. Enthalpy and entropy as functions of T and P:

(1)在均勻相中，把 enthalpy and entropy 表示成 T、P 的函數

↳得到最有用的物性關係式

(2)以 1 mol 為基量：

❶ $(\frac{\partial H}{\partial T})_P = C_p$

$dH = TdS + VdP \rightarrow (\frac{\partial H}{\partial T})_P = T(\frac{\partial S}{\partial T})_P$
$\left.\right\}$ $(\frac{\partial S}{\partial T})_P = \frac{C_p}{T}$

❷ but $(\frac{\partial V}{\partial T})_P = -(\frac{\partial S}{\partial P})_T$

$dH = TdS + VdP \rightarrow (\frac{\partial H}{\partial P})_T = T(\frac{\partial S}{\partial P})_T + V = -T(\frac{\partial V}{\partial T})_P + V = V - T(\frac{\partial V}{\partial T})_P$

重要的熱力學狀態方程式

❸ The functional relations chosen here for H and S are

H = H(T, P) and S = S(T, P)

∴ $dH = (\frac{\partial H}{\partial T})_P dT + (\frac{\partial H}{\partial P})_T dP$ $dS = (\frac{\partial S}{\partial T})_P dT + (\frac{\partial S}{\partial P})_T dP$

∴ $dH = C_p dT + \left[V - T(\frac{\partial V}{\partial T})_P\right] dP$

$dS = C_p \frac{dT}{T} - (\frac{\partial V}{\partial T})_P dP$

4. Alternative Forms for Liquids:

(1) Chapter 3:
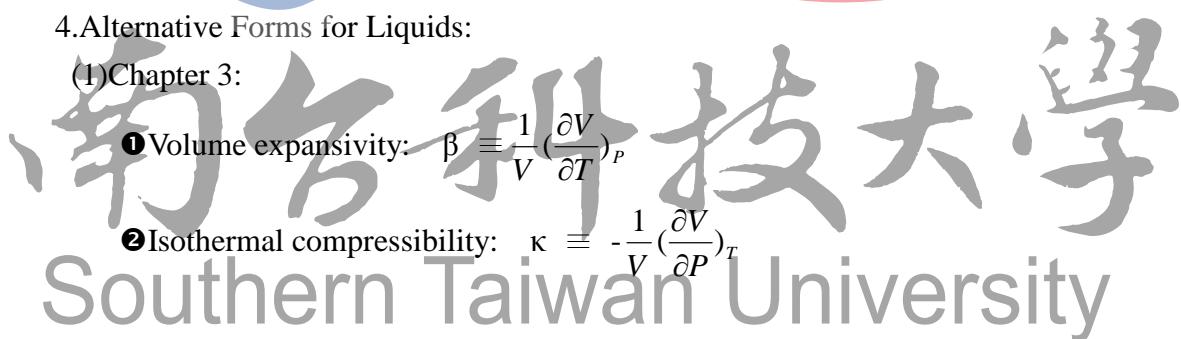
❶ Volume expansivity: $\beta \equiv \frac{1}{V}(\frac{\partial V}{\partial T})_P$

❷ Isothermal compressibility: $\kappa \equiv -\frac{1}{V}(\frac{\partial V}{\partial P})_T$

(2) $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P = -\beta V$

$(\frac{\partial H}{\partial P})_T = T(\frac{\partial S}{\partial P})_T + V = T(-\beta V) + V = (1-\beta T)V$

$(\frac{\partial H}{\partial P})_T = T(\frac{\partial S}{\partial P})_T + V = V - T(\frac{\partial V}{\partial T})_P$
$\left.\right\}$ $V - T(\frac{\partial V}{\partial T})_P = (1-\beta T)V$

$$\therefore\ dH = C_p\,dT + \left[V - T(\frac{\partial V}{\partial T})_P\right]dP = C_p\,dT + (1-\beta T)V dP$$

$$dS = C_p\frac{dT}{T} - (\frac{\partial V}{\partial T})_P\,dP = C_p\frac{dT}{T} - \beta V\,dP$$

5.Internal energy and entropy as functions of T and P:

以 1 mol 為基量：

(1) $dU = TdS - PdV$

↪ ● $\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$

● $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$

(2)However,

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \quad \therefore \left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V = \frac{C_V}{T}$$

重要的熱力學狀態方程式

One of Maxwell's equations:

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

(3) The functional relations chosen here for U and S are

$$U = U(T, V) \quad \text{and} \quad S = S(T, V)$$

$$\therefore dU = (\frac{\partial U}{\partial T})_V\,dT + (\frac{\partial U}{\partial V})_T\,dV \ ; \quad dS = (\frac{\partial S}{\partial T})_V\,dT + (\frac{\partial S}{\partial V})_T\,dV$$

$$\therefore dU = C_V\,dT + [T\left(\frac{\partial P}{\partial T}\right)_V - P]\,dV$$

$$dS = \frac{C_V}{T}\,dT + \left(\frac{\partial P}{\partial T}\right)_V\,dV$$

Chapter 3 ➔ $(\frac{\partial P}{\partial T})_V = \frac{\beta}{\kappa}$ ----------詳見 Example 3-1

$$\therefore dU = C_V\,dT + [\frac{\beta}{\kappa}T - P]\,dV \qquad dS = \frac{C_V}{T}\,dT + \frac{\beta}{\kappa}\,dV$$

Example 6-1:

Show the Joule-Thomson coefficient $\mu_{JT} = \left(\dfrac{\partial T}{\partial P}\right)_H = \dfrac{1}{C_P}[T\left(\dfrac{\partial V}{\partial T}\right)_P - V]$

Sol:

$$dH = \left(\dfrac{\partial H}{\partial T}\right)_P dT + \left(\dfrac{\partial H}{\partial P}\right)_T dP$$

∵ Joule-Thomson 實驗過程是 H 不變

$$\therefore\ 0 = \left(\dfrac{\partial H}{\partial T}\right)_P dT + \left(\dfrac{\partial H}{\partial P}\right)_T dP$$

$$\therefore\ 0 = \left(\dfrac{\partial H}{\partial T}\right)_P \left(\dfrac{\partial T}{\partial P}\right)_H + \left(\dfrac{\partial H}{\partial P}\right)_T$$

$$\therefore\ \mu_{JT} = \left(\dfrac{\partial T}{\partial P}\right)_H = -\left(\dfrac{\left(\dfrac{\partial H}{\partial P}\right)_T}{\left(\dfrac{\partial H}{\partial T}\right)_P}\right) = -\dfrac{\left(\dfrac{\partial H}{\partial P}\right)_T}{Cp} = -\dfrac{\left(\dfrac{\partial H}{\partial P}\right)_T}{Cp}$$

$$= -\dfrac{1}{C_P}[V - T\left(\dfrac{\partial V}{\partial T}\right)_P] = \dfrac{1}{C_P}[T\left(\dfrac{\partial V}{\partial T}\right)_P - V]$$

Example 6-2:

證明 ideal gas 的 internal energy 只和溫度 T 成 $dU = n\hat{C}_v dT$ 的關係而與體積 V 無關。

Sol: ∵ $dU = (\dfrac{\partial U}{\partial T})_V dT + (\dfrac{\partial U}{\partial V})_T dV$

而 $(\dfrac{\partial U}{\partial T})_V = C_V$

$dU = TdS - PdV$ ➜ $(\dfrac{\partial U}{\partial V})_T = T\left(\dfrac{\partial S}{\partial V}\right)_T - P = T\left(\dfrac{\partial P}{\partial T}\right)_V - P$

∴ $dU = C_V dT + [T\left(\dfrac{\partial P}{\partial T}\right)_V - P]dV$

Example 6-3:

Show thermodynamically that $\Pi_T = \left(\dfrac{\partial U}{\partial V}\right)_T = 0$ for a perfect gas, and derive its value

for a van der Waals gas.

Example 6-4:

Derive $\left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\beta}{\kappa}\right) - P$

where $\beta =$ The *expansion coefficient* of a gas $= \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$

$\kappa =$ The *isothermal compressibility* of a gas $= -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$

Sol:

$$\left(\frac{\partial A}{\partial B}\right)_C \left(\frac{\partial B}{\partial C}\right)_A \left(\frac{\partial C}{\partial A}\right)_B = -1$$

Example 6-5:

Prove that $\left(\dfrac{\partial U}{\partial T}\right)_P = C_P - P\left(\dfrac{\partial V}{\partial T}\right)_P$

Example 6-6:

Derive the Joule coefficient $\left(\dfrac{\partial T}{\partial V}\right)_U$ for a van der Waals gas.

6. The Helmholtz and Gibbs free energy:

(1)由 2nd law 知：

$$dS \geqq \dfrac{dQ}{T}$$ irrev. → 大於
                            rev. → 等於   <u>此式被稱為 Clausius inequality</u>

●<u>For a spontaneous process or irreversible process:</u>

$$dS > \dfrac{dQ}{T}$$ ➔ $dQ < TdS$ or $dQ - TdS < 0$

only P-V work ➔ 1st law: $dU = dQ + dW = dQ - PdV$

$$dU + PdV - TdS < 0$$

∴V, S 若保持不變 ➔ $(dU)_{V,S} < 0$

◆自發程序若發生在系統的體積與 entropy 不變時，則內能要減少。

◆把 $dS \geqq \dfrac{dQ}{T}$ 轉換成另一種表示 $(dU)_{V,S} \leqq 0$ irrev. → 小於
                                                                rev. → 等於

❀若 T, V 為定值 ➔ $dU + PdV - TdS < 0$ 可變成

$$dU - d(TS) < 0$$ or $d(U - TS) < 0$

但 $A = U - TS$ ➔ $(dA)_{T,V} < 0$

◆自發程序若發生在系統的溫度與體積不變時，則 Helmholtz free energy 要減少。

◆把 $dS \geqq \dfrac{dQ}{T}$ 轉換成另一種表示 $(dA)_{T,V} \leqq 0$ irrev. → 小於
                                                                rev. → 等於

❀若 T, P 為定值 ➔ $dU + PdV - TdS < 0$ 可變成

$$dU + d(PV) - d(TS) < 0$$ or $d(U+PV) - d(TS) < 0$

即 $d(H - TS) < 0$ 但 $G = H - TS$ ➔ $(dG)_{T,P} < 0$

6-7

◆自發程序若發生在系統的溫度與壓力不變時，則 Gibbs free energy 要減少。

◆把 dS $\geq \dfrac{dQ}{T}$ 轉換成另一種表示 $(dG)_{T,P} \leqq 0$　　irrev. → 小於
　　　　　　　　　　　　　　　　　　　　　　　　　　　　　rev. → 等於

※※由於一般的反應或程序最常在恆溫、恆壓下進行，所以，以 G 值來判斷該
　反應(程序)是否為自發為最重要。

(2)Maximum work and Helmholtz free energy：
　❶一個系統對外作可逆 work 時 ➔ 最大的 work ➔ 即 $W_{rev.} = W_{max}$
　❷isothermal & reversible 的條件下：

　　$dS = \dfrac{dQ_{rev}}{T}$　➔ $dQ_{rev} = TdS$

　　$dA = dU - d(TS) = dU - TdS = dQ_{rev} + dW_{rev} - TdS = TdS + dW_{rev} - TdS$

　　　$= dW_{rev} = dW_{max}$

　　∴$\Delta A = W_{max}$　➔ΔA 是一個程序進行時，所能做的最大 work。

　　∴Helmholtz free energy 又被稱為 work function。

(3) reversible 的條件下：

　　$dU = dQ_{rev} + dW$(各種功)

　　　　$= TdS + (-PdV + dW_{net})$　　W_{net} = 除了 P-V work 之外的所有 work。

　　∴$dG = dH - d(TS) = d(U + PV) - d(TS) = dU + d(PV) - d(TS)$

　　　　$= [TdS + (-PdV + dW_{net})] + [PdV + VdP] - [TdS + SdT]$

　　　　$= -SdT + VdP + dW_{net}$

　　∴恆溫、恆壓、可逆程序時：

　　$dG = dW_{net}$　or　$\Delta G = W_{net}$

　　∴恆溫、恆壓、可逆程序時，Gibbs free energy 的變化等於 P-V work 之
　　　外的所有 work。

(4)Basic calculating of ΔG:

　❶一般從 G = H - TS 的定義即可求得 ΔG。

　❷在 isothermal 下，有時需考慮以下的 case：

　　$dG = -SdT + VdP = VdP$ ➔ $\Delta G = \int dG = \displaystyle\int_{P1}^{P2} VdP$

　　①for ideal gases：　$\Delta G = \int dG = \displaystyle\int_{P1}^{P2}\left(\dfrac{nRT}{P}\right)dP = nRT \ln\left(\dfrac{P_2}{P_1}\right)$

　　②for liquid or solid：$\Delta G = V(P_2 - P_1)$

Example 6-7:

Calculate q, W, ΔU, ΔH, ΔS, and ΔG for the conversion of 3 moles of H_2O from liquid water to water vapor at 1 atm, 100℃?

Example 6-8:

Two moles of an ideal gas expands from 3 atm, 49.2 liters to 1 atm isothermally and reversibly. Find q, W, ΔU, ΔH, ΔS, and ΔG for this process?

Example 6-9:

計算下列程序的自由能變化？

$$H_2O_{(\ell, -10℃)} \rightarrow H_2O_{(\ell, -10℃)}$$

水在 –10℃ 之 vapor pressure：2.149 mm-Hg；冰在 –10℃ 之 vapor pressure 為 1.950 mm-Hg。

❸Gibbs free energies of Chemical Reactions

①We define standard free energies of formation $\Delta_f G^o$ similarly to the enthalpies of formation, $\Delta_f H^o$.

↪●$\Delta_f G^o$ 和 $\Delta_f H^o$ 具有類似的特色。

●且求 $\Delta_{rxn} G^o$ 與求 $\Delta_{rxn} H^o$ 的計算方式相同。

$\Delta_{rxn} H^o = \Sigma \gamma_j \times \Delta_f H^o(products) - \Sigma \gamma_i \times \Delta_f H^o(reactants)$

$\Delta_{rxn} G^o = \Sigma \gamma_j \times \Delta_f G^o(products) - \Sigma \gamma_i \times \Delta_f G^o(reactants)$

②若 chemical reaction 是在恆溫下進行，若可以求出此反應的$\Delta_{rxn} S^o$ 與 $\Delta_{rxn} H^o$，則 $\Delta_{rxn} G^o = \Delta_{rxn} H^o - T \Delta_{rxn} S^o$

Example 6-10:

Determine $\Delta_{rxn}G(298K)$ for the following chemical reaction:

$$2\ H_{2[g]} + O_{2[g]} \rightarrow 2\ H_2O_{[\ell]}$$
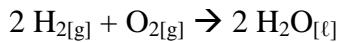
	$H_{2[g]}$	$O_{2[g]}$	$H_2O_{[\ell]}$
$\Delta_f H^o$, kJ/ml	0	0	-285.83
S^o, J/mol·K	130.68	205.14	69.91
$\Delta_f G^o$, kJ/mol	0	0	-237.13

Sol:

❹Focus on ΔG ---The variation of the Gibbs free energy with temperature

①Gibbs-Helmholtz equation:

● $G = H - TS$　or $H = G + TS$

● $\left[\dfrac{\partial\left(\dfrac{G}{T}\right)}{\partial T}\right]_P = \dfrac{T(\dfrac{\partial G}{\partial T})_P - G(\dfrac{\partial T}{\partial T})}{T^2} = \dfrac{T(\dfrac{\partial G}{\partial T})_P - G}{T^2}$

● $\because \left(\dfrac{\partial G}{\partial T}\right)_P = -S$　$\therefore \left[\dfrac{\partial\left(\dfrac{G}{T}\right)}{\partial T}\right]_P = \dfrac{T(\dfrac{\partial G}{\partial T})_P - G}{T^2} = \dfrac{-TS - G}{T^2} = -\dfrac{H}{T^2}$

●● $\left[\dfrac{\partial\left(\dfrac{G}{T}\right)}{\partial T}\right]_P = -\dfrac{H}{T^2}$ or $\left[\dfrac{\partial\left(\dfrac{\Delta G}{T}\right)}{\partial T}\right]_P = -\dfrac{\Delta H}{T^2}$ or $\left[\dfrac{\partial\left(\dfrac{\Delta G}{T}\right)}{\partial(\dfrac{1}{T})}\right]_P = \Delta H$

is called the Gibbs-Helmholtz equation.

② $\because \left[\dfrac{\partial\left(\dfrac{\Delta G}{T}\right)}{\partial T}\right]_P = -\dfrac{\Delta H}{T^2}$　　$\therefore \int_1^2 d(\dfrac{\Delta G}{T}) = -\int_{T_1}^{T_2}(\dfrac{\Delta H}{T^2})dT$

$\therefore \dfrac{\Delta G_2}{T_2} - \dfrac{\Delta G_1}{T_1} = -\int_{T_1}^{T_2}(\dfrac{\Delta H}{T^2})dT$

Example 6-11:

知標準生成自由能，$\Delta G^{o}_{NO(g)}$=20.7 kcal/mol；$\Delta G^{o}_{NO2(g)}$=12.4 cal/mol。標準生成焓，
$\Delta H^{o}_{NO(g)}$=21.6 kcal/mol；$\Delta H^{o}_{NO2(g)}$=8.1 cal/mol。且 O_2 的 Cp =6.5；NO 的 C_p =7.0；
NO_2 的 C_p =9.0[單位皆是 (cal/mol·K)]，求 1 atm, 100℃時，

$$2\ NO_{(g)} + O_{2(g)} \rightarrow 2\ NO_{2(g)}\ 之\ \Delta G?$$
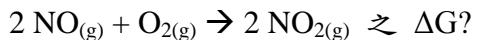
※標準生成自由能、標準生成焓---等，若沒特別說明→ 就當成 1 atm、25℃。

7. The Gibbs energy as a generating function:

(1)∵ dG = - SdT + VdP

∴G = G(P, T) 的函數關係是存在的。

∴The special [or canonical(正則)] variables for the Gibbs energy are
temperature and pressure.

$$(2)d(\frac{G}{RT}) = \frac{1}{RT}dG - \frac{G}{RT^2}dT = \frac{1}{RT}(VdP - SdT) - \frac{H-TS}{RT^2}dT$$
$$= \frac{V}{RT}dP - \frac{H}{RT^2}dT$$
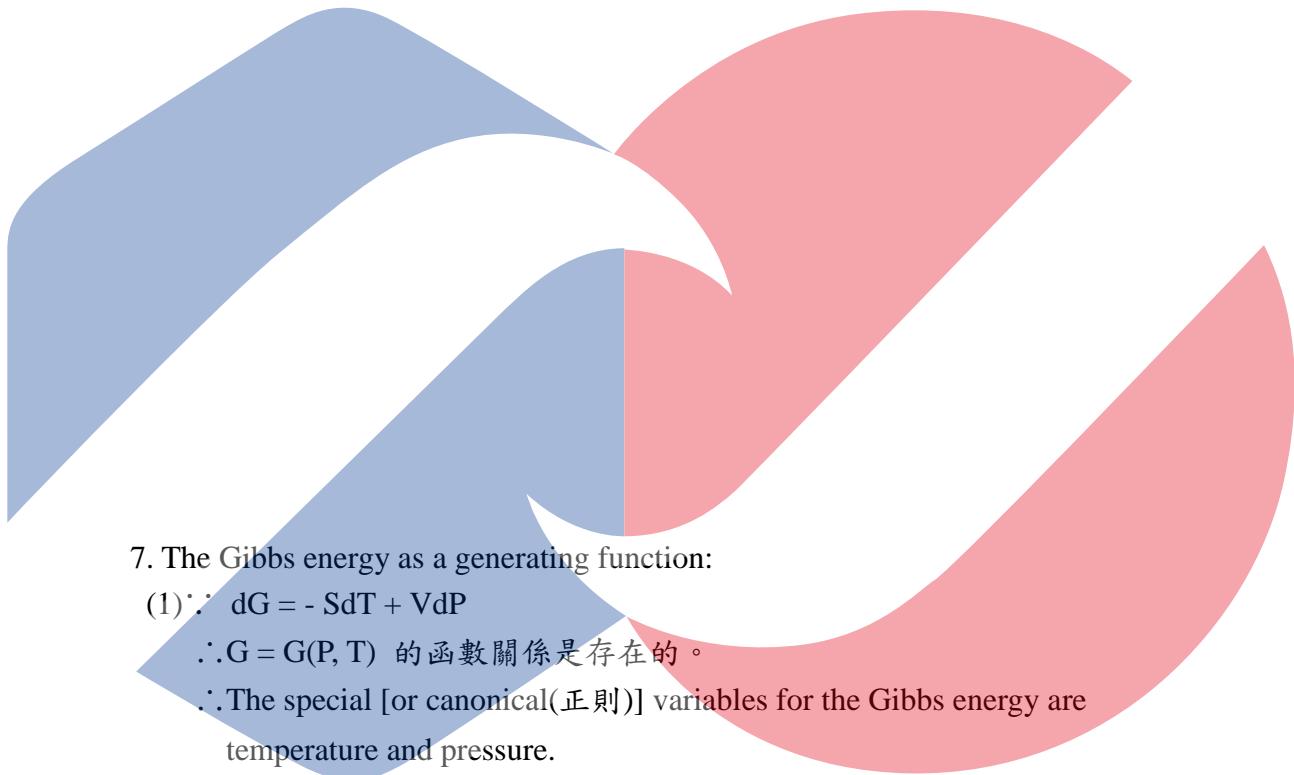
§6-2. Residual properties

1. Define:

(1)the residual Gibbs energy $G^R \equiv G - G^{ig}$

G：actual gas 的 Gibbs free energy。

G^{ig}：ideal-gas 的 Gibbs energy。

> ●全都是在 1mol 且同
> 溫同壓的條件下。

(2)the residual volume $V^R \equiv V - V^{ig} = V - (RT/P)$

For real gas: Z =(PV/RT) ➔ V = ZRT/P

$$\therefore V^R \equiv V - V^{ig} = V - (RT/P) = \frac{RT}{P}(Z-1)$$

(3)The definition for the generic residual property is:

$$M^R \equiv M - M^{ig}$$

●M 與 M^{ig} 分別為 1 mol 的 actual gas 與 ideal-gas 的 extensive property，如 V、U、H、S 與 G。且必需為同溫、同壓下的數值。

2.∵ G = H − TS ➔ $G^R = H^R - TS^R$

$$d(\frac{G}{RT}) = \frac{V}{RT}dP - \frac{H}{RT^2}dT$$

●at constant temperature

◆real gas: $d(\frac{G}{RT}) = \frac{V}{RT}dP$

◆ideal gas: $d(\frac{G^{ig}}{RT}) = \frac{V^{ig}}{RT}dP$

$$\therefore d(\frac{G^R}{RT}) = \frac{V^R}{RT}dP \quad ➔ \quad \frac{G^R}{RT} = \int \frac{V^R}{RT}dP = \int \frac{1}{RT}[\frac{RT}{P}(Z-1)]dP$$

$$= \int (Z-1)\frac{dP}{P}$$

∴求 Residual properties，除了知道定義之外，先會求 real gas 與 ideal gas 的性質，再互相減扣即可。所以，§6-3 不再介紹。

§6-3. Two-phase systems

1. Point X-- two phases α and β of a pure species coexist at T , P in equilibrium,

$$\Delta \widehat{G} = 0 \quad ➔ \quad \widehat{G}_\alpha = \widehat{G}_\beta \quad (取 1 \text{ mole } 為基量)$$

●當溫度變成 T + dT 時，

α phase 的 Gibbs energy = $\widehat{G}_\alpha + d\widehat{G}_\alpha$

β phase 的 Gibbs energy = $\widehat{G}_\beta + d\widehat{G}_\beta$
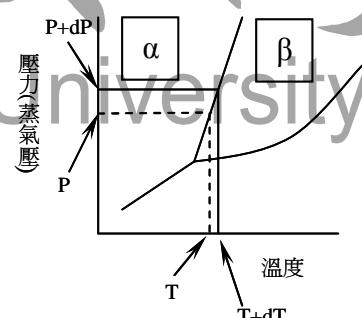
但仍要保持 α 與 β phase 的向平衡

$\Leftrightarrow \therefore \widehat{G}_\alpha + d\widehat{G}_\alpha = \widehat{G}_\beta + d\widehat{G}_\beta$

即 $d\widehat{G}_\alpha = d\widehat{G}_\beta$

但 $d\widehat{G} = -\widehat{S}dT + \widehat{V}dP$ ➔ $-\widehat{S}_\alpha dT + \widehat{V}_\alpha dP = -\widehat{S}_\beta dT + \widehat{V}_\beta dP$

$\therefore \dfrac{dP}{dT} = \dfrac{\widehat{S}_\beta - \widehat{S}_\beta}{\widehat{V}_\beta - \widehat{V}_\alpha} = \dfrac{\Delta S}{\Delta V}$

另一方面，$\widehat{G} = \widehat{H} - T\widehat{S}$ ➔ 定溫時，$\Delta\widehat{G} = \Delta\widehat{H}_{tr} - T\Delta\widehat{S}$ ⎫
⎬ $\Delta\widehat{S} = \dfrac{\Delta\widehat{H}_{tr}}{T}$
但既然任何 phase line 的點都代表相平衡 ➔ $\Delta\widehat{G} = 0$ ⎭

$\therefore \dfrac{dP}{dT} = \dfrac{\Delta\widehat{H}_{tr}}{T\Delta\widehat{V}}$

※ $\dfrac{dP}{dT} = \dfrac{\Delta\widehat{H}_{vap}}{T(\widehat{V}_g - \widehat{V}_\ell)}$ ----- liquid-vapor equilibrium ⎫

※ $\dfrac{dP}{dT} = \dfrac{\Delta\widehat{H}_{fus}}{T(\widehat{V}_\ell - \widehat{V}_s)}$ ----- solid-liquid equilibrium ⎬ Clapeyron eq.

※ $\dfrac{dP}{dT} = \dfrac{\Delta\widehat{H}_{sub}}{T(\widehat{V}_g - \widehat{V}_s)}$ ----- solid-vapor equilibrium ⎭

Example 6-12:
已知水和冰的密度分別是 0.917 g/cm^3 與 1 g/cm^3，而水的凝固熱為-6008 J/mol，
則壓力為 100 atm 時，水的 melting point 為多少？

2.考慮 liquid-vapor equilibrium：

$$\frac{dP}{dT} = \frac{\Delta \widehat{H}_{vap}}{T(\widehat{V}_g - \widehat{V}_\ell)}$$

(1) $\widehat{V}_g >> \widehat{V}_\ell$ ➜ $\dfrac{dP}{dT} = \dfrac{\Delta \widehat{H}_{vap}}{T\widehat{V}_g}$

(2)把 vapor 視為 ideal gas ➜ $\widehat{V}_g = RT/P$

$$\therefore \frac{dP}{dT} = \frac{\Delta \widehat{H}_{vap}}{T\widehat{V}_g} = \frac{P\Delta \widehat{H}_{vap}}{RT^2} \quad \text{or} \quad \frac{1}{P}dP = = \frac{\Delta \widehat{H}_{vap}}{R}\frac{1}{T^2}dT$$

$$\int_{P_1}^{p_2} \frac{1}{P}dP = \int_{T_1}^{T_2} \frac{\Delta \widehat{H}_{vap}}{R}\frac{1}{T^2}dT$$

$$ln\frac{P_2}{P_1} = -\frac{\Delta \widehat{H}_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

同理 $ln\dfrac{P_2}{P_1} = -\dfrac{\Delta \widehat{H}_{sub}}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ ⎫ Clausius-Clapeyron equation

(3) $\dfrac{dP}{dT} = \dfrac{P\Delta \widehat{H}_{vap}}{RT^2}$ ➜ $\displaystyle\int \frac{dP}{P} = \int \frac{\Delta \widehat{H}_{vap}}{RT^2}dT + C$

$$ln\,P = -\frac{\Delta \widehat{H}_{vap}}{R}\left(\frac{1}{T}\right) + C$$

$$y = mx + c$$

Slope = -ΔH/R

ln P

1/T
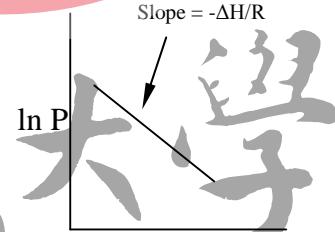
以 $ln\,P$ 對 1/T 作圖得 slope $= -\dfrac{\Delta \widehat{H}_{vap}}{R}$ 之直線
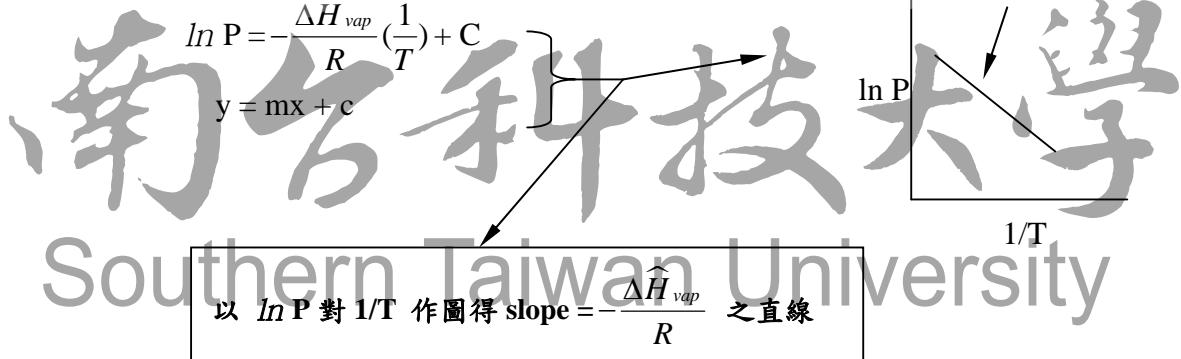
Example 6-13:

Find the boiling point of water at 750 mm-Hg if the heat of the vaporization of water is 539 cal/g at 100℃, 1atm.

Example 6-14:

The normal boiling point of toluene is 110.6℃. Find the vapor pressure of toluene at 77℃ if the heat of vaporization is 33.69 kJ/mol.

Example 6-15:

已知固體苯在 243K 及 273K 的飽和蒸氣壓為 2.24 與 24.498 mm-Hg；液體苯在 303K 及 283K 的飽和蒸氣壓為 119 與 46.4 mm-Hg。請求出苯的(A)熔融熱 (B)triple point？   (A)2487cal/mol   (B)39.6 mm-Hg; 280K

Example 6-16:

The vapor pressure of water at varius temperature are listed in the following table. Calculate the heat of vaporization of water.

| T(K)	365	350	325	300
P(atm)	0.75	0.411	0.132	0.04

sol：將上面的 Table 改成 1/T 與 lnP

1/T	2.74×10^{-3}	2.86×10^{-3}	3.08×10^{-3}	3.33×10^{-3}
ln P	-0.288	-0.889	-2.025	-3.219

再以 *ln*P 對 1/T 作圖，求其 slope

y = -4982.7x + 13.355
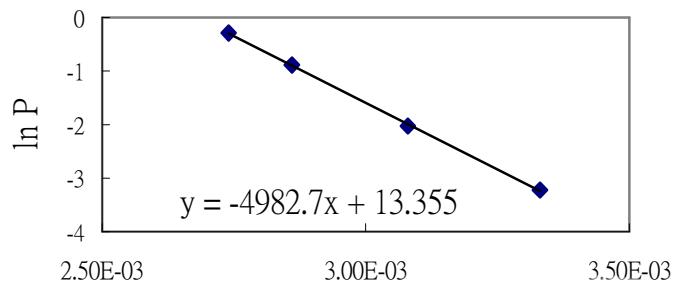
$$\text{slope} = -4982.7 = -\frac{\Delta \widehat{H}_{vap}}{R} \longrightarrow \Delta \widehat{H}_{vap} = 4982.7 \times 8.314 = 41426 \text{ J/mol}$$

●不可以從 Table 中，任意找兩組數據代入

$$ln\frac{P_2}{P_1} = -\frac{\Delta \widehat{H}_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{ 來求} \Delta \widehat{H}_{vap} \text{。}$$