Chapter1. The Behavior of Gases and Liquids

1.1 Introduction

1. Systems – any object that we wish to study
   - macroscopic – 巨觀, P. V. T
   - microscopic – 微觀, 速度分布

2. Mathematical Functions

   精確描述不同參數之關係
   - independent variable – one to which we can assign a value
   - dependent variable -

   例： $PV = n\mathrm{R}T$

   $V = n\mathrm{R}T/P$，此時 V 是 dependent variable

   P, T, n 是 independent variable

   但 $P = \mathrm{nR}T/V$，此時 P 是 dependent variable

   可用 $P = P(T, V, n)$表示

   ↑ independent variable

   或 $P = f(T, V, n)$

3. 顯示 function 之方法 —作圖

   (1) 2-D 圖：可表示 1 個 independent variable

   如：$P = V^{-1}(n\mathrm{R}T)$

   ↑ 視爲 constant

   不同溫度可畫不同曲線

   參考課本Figure 1.1 (a)

   (2) 3-D 圖：可表示 2 個 independent variables

   ①每一個切面即爲 2-D 圖

   ②切面不一定要平行或垂直於軸

   參考課本Figure 1.1 (b)

4. Units of Measurements

   (1) 使用正確單位的重要性

   以 1999 "Mars Climate Orbit"撞毀爲例，把英制和米制搞混

   (2) SI unit：International System of Units

   七個基本單位

   ①長度 — m (meter)

   ②質量 — kg (kilogram)

   ③時間 — s (second)

④溫度 — K (kelvin)
⑤電流 — A (ampere)
⑥照度 — cd (candela)
⑦數量 — mol (mole)

其他爲導出單位 (derived units)

⑧力 — N (Newton) $1\ \mathrm{N} = 1\ \mathrm{kg\ m\ s^{-2}}$
⑨壓力 — Pa (Pascal) $1\ \mathrm{Pa} = 1\ \mathrm{N\ m^{-2}} = 1\ \mathrm{kg\ m^{-1}\ s^{-2}}$
⑩能量 — J (Joule) $1\ \mathrm{J} = 1\ \mathrm{Nm} = 1\ \mathrm{kg\ m^{2}\ s^{-2}}$

(3) Non-SI unit

①壓力： 1 atm = 101325 Pa (定義)
= 760 Torr (定義)
1 bar = 100000 Pa (定義)
②能量： 1 cal = 4.184 J (定義)

(4) 常數

①Avogadro's constant $N_{Av} = 6.02214\times10^{23}\ \mathrm{mol^{-1}}$
②Ideal gas constant $R = 8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}$
$= 1.9872\ \mathrm{cal\ K^{-1}\ mol^{-1}}$
$= 0.08205\ \mathrm{L\ atm\ K^{-1}\ mol^{-1}}$
$= N_{Av}\, k_B$
Boltzmann's constant $k_B = 1.3807\times10^{-23}\ \mathrm{J\ K^{-1}}$

5. Problem Solving Techniques

自己讀，注意 ① 有效數字
② 數字是否有意義

1.2. 一些定義及觀念：

1. System and Surrounding

{ system: the part of the physical world under consideration
  surrounding: all the rest of the universe

system + surrounding = universe

2. Types of Systems

	matter	heat	work
open system	○		
closed system	×		
adiabatic system		×	
isolated system	×	×	×

3. 描述 system：state

A. equilibrium state : none of its thermodynamic properties changes with time
(只用少數 variable 即可描述)

B. steady state : matter or energy flows, but properties independent of time
例：flow system 之 P, T, n

C. metastable state : practically no change with time of observation
例：① H_2 與 O_2 混合氣，② supercooled water，③ diamond vs. graphite

4. State Variables (functions)— 對 macrostate 而言，例如：P、T、V、ρ

(state function 只和目前之 state 有關，和 history 無關。以後再詳述。)

{ intensive variable— independent of mass, can be measured at a point
  extensive variable— dependent of mass, should be measured as a whole

亦可由 combine 2 個 identical systems 後，是否變 2 倍而知。

intensive	extensive
P	V
ε	Q
σ	A
T	S

§ 2 個 extensive variables 相除可以變成 intensive

例如：$\rho = m/V$，$V_m = V/n$ (molar volume)

5. Equation of State – 描述各 variable 間之關係

$P \quad n\mathrm{R}T/V$

dependent variable　　n, T, V 係 indep. variable

→ $P = f(n,T,V)$ 或 $P(n,T,V)$

對於一個單組成單相平衡態之流體(氣體或液體)，需要 3 個參數描述之(P, V, T, n 中任選 3 個)
而 equation of state 即描述各參數之關係

6. Process— an occurrence that changes the state of a system

通常要有 driving force 才會改變；例：壓力使體積改變，溫差使溫度改變，

reversible- direction can be reversed at ant point by some infinitesimal change in the surrounding

① all intermediate state are quasi-equilibrium state

任何時候均可以用 *variable* 描述

② quasi-static process- infinitesimal rate change

irreversible- 有可能中間過程的 state 無法描述 (未達平衡)

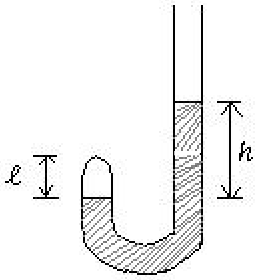
* spontaneous process 是 irreversible

1.3. Real Gas

1. Ideal Gas Law 之歷史

1660 Robert Boyle – 定溫下 $P \propto 1/V$

J 形管實驗



ℓ (cm)	h (cm)
20	10
19.5	36.8
19	64.9

$(h+h_0)\,\ell$ =constant

即 $P \cdot V$=constant

h_0=1033.6 cm for $H_2O_{(\ell)}$

自己試著由上數據導式子

1787 Alexandre Cesar Charles – $P \propto T$ at const. V，但未發表

1802 Joseph Gay-Lussac – $V \propto T$

$V = V_0(1+\alpha_0\theta)$, 其中 V_0 爲 273 K 之體積

當時量α_0 = 1/267，而非 1/237.15

用不同氣體量 $V_{100°C}/V_{0°C}$ = K = 1.375 (應是 373.15/273.15 = 1.366) const. for all gases

由此導出絕對溫度 $T = \dfrac{1}{\alpha_0} + \theta$ 故 $T_0 = \dfrac{1}{\alpha_0}$

$$\Rightarrow V = V_0\left(1+\frac{1}{T_0}(T-T_0)\right) = V_0 T / T_0$$ 如同上式

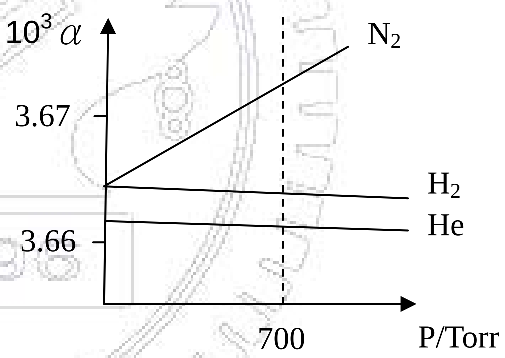
後來儀器精良後發現：

α 隨 $\begin{cases} \text{氣體而變} \\ P \end{cases}$

$$\frac{1}{\alpha_0} = 3.661\times10^{-3}$$

亦即 $PV \neq nRT$

需要修正，但以 ideal gas 爲參考指標



2. Virial Equation

(1) 偏離 ideal gas 之指標

z: compressibility 或稱 compression factor

$$z = \frac{PV}{nRT} = \frac{PV_m}{RT}$$ 隨 $\begin{cases} T \\ P \\ \text{Gas} \end{cases}$ 而變

參考課本Figure 1.3

(2) Virial Equation

$$z = \frac{PV}{n\mathrm{R}T} = 1 + B_2(T)\frac{n}{V} + B_3(T)\left(\frac{n}{V}\right)^2 + \ldots \qquad \text{low } \frac{n}{V}\text{ 時，} z \to 1 \quad \cdots\cdots①$$

$$= 1 + B_2(T)\frac{1}{V_m} + B_3(T)\left(\frac{1}{V_m}\right)^2 + \ldots$$

$$\text{或 } z = 1 + A_2{}'(T)P + A_3{}'(T)P^2 + \ldots \qquad \text{low } P\text{ 時，} z \to 1 \quad \cdots\cdots②$$

$$\text{或 } PV_m = \mathrm{R}T + A_2(T)P + A_3(T)P^2 + \ldots$$

理論上也可用$=1+C_2\left(\frac{1}{T}\right)+C_3\left(\frac{1}{T^2}\right)+\ldots$　　high T 時，$z \to 1$

但實際上不易用，因修正項太大，除非$T \to \infty$，不易求

由①, $P = \mathrm{R}T\left(\frac{n}{V}\right)\left[1 + B_2\frac{n}{V} + B_3\left(\frac{n}{V}\right)^2\right]$

代入②, $z = 1 + A_2{}'\left\{\mathrm{R}T\left(\frac{n}{V}\right)\left[1 + B_2\left(\frac{n}{V}\right) + \ldots\right]\right\} + A_3{}'\mathrm{R}^2T^2\left(\frac{n^2}{V^2}\right)\left[1 + B_2\left(\frac{n}{V}\right) + \ldots\right]^2$

$$= 1 + A_2{}'\mathrm{R}T\left(\frac{n}{V}\right) + \left(B_2A_2{}'\mathrm{R}T + A_3{}'\mathrm{R}^2T^2\right)\left(\frac{n}{V}\right)^2 + \ldots$$

$$\downarrow$$

$$B_3 = B_2A_2{}'\mathrm{R}T + A_3{}'\mathrm{R}^2T^2 = B_2{}^2 + A_3{}'\mathrm{R}^2T^2$$

故 $\boxed{A_2{}' = B_2 / \mathrm{R}T}$ $\boxed{A_3{}' = \left(B_3 - B_2{}^2\right) / \mathrm{R}^2T^2}$

或 $\boxed{A_2 = B_2, \quad A_3 = \left(B_3 - B_2{}^2\right) / RT}$

<註> $B_2(T)$其實可與 interaction potential relate, $B_2(T) = 2\pi L\sigma^3\int_0^\infty\left(1 - e^{-u/kT}\right)r^2\mathrm{d}r$

$$= 2\pi L\sigma^3/3 \qquad \text{for hard sphere}$$

3. van der Waals Equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = n\mathrm{R}T \qquad \text{或 } P = \frac{n\mathrm{R}T}{V\text{-}nb} - \frac{an^2}{V^2} \qquad \text{或 } \left(P + \frac{a}{V_m{}^2}\right)(V_m - b) = \mathrm{R}T$$

↖ intensive variable

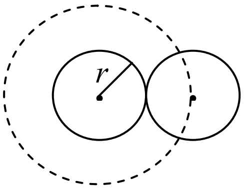
<說明>：① P,V 是實際量得的量

②括弧內是 ideal gas，故 P 要 + , V 要 −

↑　↑

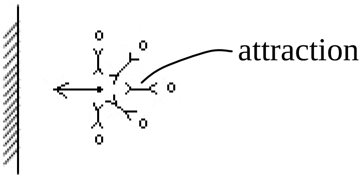
分子間的引力　分子佔有的體積

b 之意義：excluded volume



$$\frac{4}{3}\pi(2r)^3\cdot\frac{1}{2}=\frac{16}{3}\pi r^3 \text{或} \frac{2}{3}\pi d^3$$

a 之意義：internal pressure (以後會再討論)



對某一特定分子

$$\text{attraction} \propto \frac{n}{V}$$

$$\text{total attraction} \propto \left(\frac{n}{V}\right)^2$$

另一種看法

$$\left(\begin{array}{c} \text{P}' \propto \text{No. of pairs} \\ \propto \left(\frac{n}{V}\right)^2 \end{array} \right)$$

例： Cl_2 $P = 19.57$ atm, $V = 1\,\ell$, $T = 300$ K

$P = 45.64$ atm, $V = 1\,\ell$, $T = 600$ K

問 $V = 2\,\ell$, $T = 600$ K 時, $P = ?$

Question：mixture 時, 怎麼辦？ $a = a_1x_1{}^2 + 2a_{12}x_1x_2 + a_2x_2{}^2$

$$b = b_1x_1{}^2 + 2b_{12}x_1x_2 + b_2x_2{}^2$$

可導出 $a_{12} = \sqrt{a_1a_2}$, $b_{12} = \left[\frac{1}{2}\left(b_1{}^{1/3} + b_2{}^{1/3}\right)\right]^3$

§ van der Waals eq.之優點: even 它其實不是最準確的 eq.

① virial eq.只適用於 ideal-gas-like 之 case, vdw 則適用較大範圍

② 亦適用於 liq.→ continuity of state 的觀念

③ 正確指出 critical region 之性質

④ 簡單的式子, 又有可以接受的物理概念

⑤ a, b 可由實驗(P_c, T_c, V_c)求得，詳見 1.4 節

4. 其他的 equation of state

(1) Berthlot $\left(P + \frac{A}{TV_m{}^2}\right)(V_m - b) = \mathrm{R}T$, 即：$a \rightarrow A/T$

(2) Dieterici $P\,\mathrm{e}^{a/V_\mathrm{m}\mathrm{R}T}(V_\mathrm{m} - b) = \mathrm{R}T$, 其實有 $\left(P + \frac{a}{V_\mathrm{m}{}^2}\right)$ 之意思

$$\text{因 } P\left(1 + \frac{a}{V_\mathrm{m}{}^2P}\right) \approx P\left(1 + \frac{a}{V_\mathrm{m}\mathrm{R}T}\right) \approx Pe^{a/V_mRT}$$

(3) Redlich-Kwong $\left(P + \frac{a}{\sqrt{T}}\frac{1}{V_\mathrm{m}(V_\mathrm{m} + b)}\right)(V_\mathrm{m} - b) = \mathrm{R}T$

(4) Redlich - Kwong - Soave $\left[P + a\alpha(T)\frac{1}{V_\mathrm{m}(V_\mathrm{m} + b)}\right](V_\mathrm{m} - b) = \mathrm{R}T$

其中 $T \quad 1 \quad m \quad 1 - \sqrt{T/T_\mathrm{C}} \quad {}^2$

(5) Beattie - Bridgeman 5個parameters 誤差可到 0.5% 以下

$$PV_\mathrm{m} = \mathrm{R}T\left(1 - \frac{c}{T^3V_\mathrm{m}}\right)\left(1 + \frac{B_0}{V_\mathrm{m}} - \frac{bB_0}{V_\mathrm{m}}\right) - \frac{A_0}{V_\mathrm{m}}\left(1 - \frac{a}{V_\mathrm{m}}\right)$$

5. 各 equation 與 virial equation 之關係:

	vdw	Berthlot	Dieterici	Beattie-Bridgeman
B_2	$b-a/RT$	$b-A/RT^2$	$b-a/RT$	$B_0-\frac{A_0}{RT}-\frac{c}{T^3}$
B_3	b^2	b^2	$b^2-\frac{ab}{RT}+\frac{a^2}{2R^2T^2}$	$\frac{A_0a}{RT}-B_0b-\frac{B_0c}{T^3}$
T_B	a/bR	$\sqrt{A/bR}$	a/bR	自解之

Boyle Temp: Boyle's Law holds 之溫度

即 ① B = 0 之 T 或 ② z 之 slope 為 $0\big|_{P\to 0}$ 時, 即 $B'=0$, 因 $y=\frac{1}{V_m}$, $\left.\frac{\partial z}{\partial y}\right|_{y\to 0}=0$

見課本 P.25 Example 1.10

6. 以 van der Walls Equation 解釋 z之變化

$$z=\frac{PV_m}{RT}=\left(\frac{RT}{V_m-b}-\frac{a}{V_m^{\ 2}}\right)\frac{V_m}{RT}$$

$$=\frac{V_m}{V_m-b}-\frac{a}{RTV_m}$$

$$=\frac{1}{1-by}-\frac{ay}{RT} \quad \text{,其中 } y=1/V_m$$

因 a, b 為正值，故上式之第一項是正值，第二項為負

高溫時，第二項不重要，故 $z>1$

很低溫時，第二項較重要，故 $z<1$

參考課本Figure 1.3

1.4 Coexistence of Phase and the Critical Point

1. PVT surface

對單一個 species 而言, P-V-T 有一個關係 → equation of state

參考課本Figure 1.7

$P(V, T)$

3-dimensional surface

(1) Isotherms (上述之 3-D 圖用 2-D 來表示)

參考課本Figure 1.5

解釋：
- isotherm
- tie line
- V_g , V_ℓ
- gas slope 與 liquid slope 之不同
- law of rectilinear diameter
- critical point

問：T 變大時爲何 V_ℓ 變大，而 V_g 變小

(liquid 膨脹；gas 因 K.E.變大，得更靠近才變成 liquid)。

不能用 $V_g = nRT/P$ ，因爲此時 P 不是 constant。

Critical point : PV curve 之反曲點

strong scattering of light ← (解釋 Fig. 1.6)

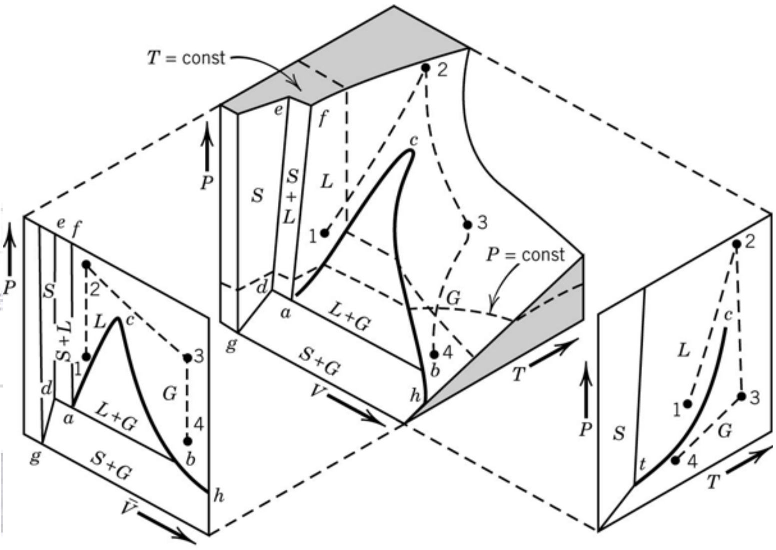
infinite heat capacity

infinite compressibility

(2) Phase diagram

參考課本Figure 1.4

解釋：
- triple point
- 2-phase coexistence curve
- 1-phase region
- normal f.p.及 b.p.
- liquefy gas without phase
- 大於 T_c 或 P_c 即無法有〝相變化〞



由 phase diagram 即可知是否會昇華

CO_2 之 triple point 在 5.112 atm 及 216.5 K

昇華點：194.6°K 即 −78.5°C

2. 由 van der Waals gas 求 critical parameters (爲了簡化，V_m 均以 V 表示)

$$P=\frac{\mathrm{R}T}{V-b}-\frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial V}\right)_T=0\Rightarrow\frac{-\mathrm{R}T}{(V-b)^2}+\frac{2a}{V^3}=0 \qquad —①$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T=0\Rightarrow\frac{2\mathrm{R}T}{(V-b)^3}-\frac{6a}{V^4}=0 \qquad —②$$

$$\frac{①}{②}\quad \frac{V-b}{2}=\frac{V}{3}\quad \text{即}\ 3V_c-3b=2V_c \quad \boxed{V_c=3b}$$

在硬球模型中，
b 是球體積之 4 倍，
V_c 是球體積之 12 倍

代入① $$\frac{-\mathrm{R}T_c}{4b^2}+\frac{2a}{27b^3}=0 \qquad \boxed{T_c=\frac{8a}{27b\mathrm{R}}}$$

代入 van der Waals equation, $$P_c=\frac{8a}{27b\cdot 2b}-\frac{a}{9b^2}=\boxed{\frac{a}{27b^2}=P_c}$$ 即：$P_c=\frac{1}{3}\frac{a}{V_c^2}$

①實驗上常可由 P_c , T_c , V_c 求 a 及 b $\boxed{a=3P_cV_c^2}$, $\boxed{b=\frac{1}{3}V_c}$

②對 van der Waals gas , $z_c=\frac{P_cV_c}{\mathrm{R}\,T_c}=\frac{3}{8}=0.375$

但實驗上 z_c 在 0.25~0.3 之間

各 parameter 之關係(以 P_c , T_c 表之)：

	vdw	Berthlot	Dieterici	Beattie-Bridgeman
a	$\frac{27R^2T_c^2}{64P_c}$	$\frac{27R^2T_c^3}{64P_c}$	$\frac{4R^2T_c^2}{e^2P_c}$	$\frac{R^2T_c^{5/2}}{9\left(2^{1/3}-1\right)P_c}$
b	$RT_c/8P_c$	$RT_c/8P_c$	$\frac{RT_c}{e^2P_c}$	$\left(2^{1/3}-1\right)RT_c/3P_c$
z_c	$3/8$	$3/8$	$\frac{2}{e^2}=0.27$	
P_c	$a/27b^2$		$\left(a/4b^2\right)e^{-2}$	
V_c	$3b$		$2b$	
T_c	$8a/27bR$		$a/4bR$	

3. Law of Corresponding State

不用〝絕對〞的概念， 而用〝相對〞的概念, 以大人、小孩搬磚爲例

用 reduced parameter

$$P_R=\frac{P}{P_c}\ ,\ T_R=\frac{T}{T_c}\ ,\ V_R=\frac{V}{V_c}$$

即 $$P=\frac{a}{27b^2}P_R\ ,\ V=3b\,V_R\ ,\ T=\frac{8a}{27bR}T_R$$

以 van der Waals equation 爲例： 利用 $\boxed{b=\frac{1}{3}V_c\ ,\ a=3P_cV_c^2\ ,\ R=\frac{8P_cV_c}{3\,T_c}}$

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

$$\left(P+3\frac{P_cV_c^2}{V^2}\right)\left(V-\frac{V_c}{3}\right)=\frac{8P_cV_c}{3T_c}T$$

上式除以 P_cV_c：

$$\left(\frac{P}{P_c}+3\frac{V_c^2}{V^2}\right)\left(\frac{V}{V_c}-\frac{1}{3}\right)=\frac{8}{3}\frac{T}{T_c}$$

$$\boxed{\text{即}\left(P_r+\frac{3}{V_r^2}\right)\left(V_r-\frac{1}{3}\right)=\frac{8}{3}T_r}$$

用處：有一個 universal curve 可適用所有之 gas

<注意> 此係 vdW 之 Law of Corresponding State ，

每一個 eq. of state 均有其各自的 Law of Corresponding State。

但真正最精確的應是由實驗得來，如課本 P. 34 之 Fig. 1.9

參考課本Figure 1.9

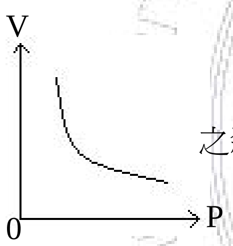
4. 如果沒有 equation of state，對特定之”區域”可由實驗上得知 state variable 之關係

(1) isothermal compressibility $\boxed{\text{永遠爲正}}$

$$\beta \text{ 或 } \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n}$$

乘 $\frac{1}{V}$ 使之變爲 intensive

即



之斜率

對 ideal gas: $\kappa_T = -\frac{1}{V}\left(-\frac{nRT}{P^2}\right) = \frac{1}{P}$

但如爲 liquid，則很小

例：水 298 K, 1 atm 之 $\kappa_T = 4.52\times10^{-5}$ bar^{-1}

(2) coefficient of thermal expansion $\boxed{\text{不一定爲正}}$，如：0–3.98°C之水

或 thermal expansivity

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n}$$

ideal gas: $\alpha = 1/T$

水: $\alpha = 2.57\times10^{-4}$ K^{-1}

如是小變化，可用ΔT，ΔV代入

否則，要知$\alpha(T)$

對 solid 而言，常常用 coefficient of linear thermal expansion

$$\alpha_L = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_P$$

$\alpha_L = \frac{1}{3}\alpha$ (課本有證明, P.19)

1.5 相關之數學

1. 基本微分：

$$f = f(x), \quad \text{則 } df = \frac{df}{dx}dx$$

differential of *f* derivative of *f*

$$\frac{df}{dx} = \lim_{h\to 0}\frac{f(x+h)-f(x)}{h}$$

2.基本的 partial differential (看課本 Appendix B)

$f = f(x,y,z)$ 含超過一個variable

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z}dx + \left(\frac{\partial f}{\partial y}\right)_{x,z}dy + \left(\frac{\partial f}{\partial z}\right)_{x,y}dz$$

partial derivatives

下標之 variable 表示 constant

例： $dV = \frac{nR}{P}dT - \frac{nRT}{P^2}dP + \frac{RT}{P}dn$ for ideal gas

以 *P*, *V*, *T* 三個 parameter 爲例

$$V(P\,,\,T) \Rightarrow dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \text{ ——— } ①$$

$$P(V\,,\,T) \Rightarrow dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \text{ ——— } ②$$

由 ① 解 d*P*

$$dP = \frac{-\left(\partial V/\partial T\right)_P}{\left(\partial V/\partial P\right)_T}dT + \frac{1}{\left(\partial V/\partial P\right)_T}dV$$

與 ② 比較，得

(1) $\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T}$ (理所當然) 因爲 x , y 軸可互換

(2) $\left(\frac{\partial P}{\partial T}\right)_V = \frac{-\left(\partial V/\partial T\right)_P}{\left(\partial V/\partial P\right)_T}$ 或 $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V$ 或 $\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P = -1$

由①中，令 $dV = 0$ 亦可

①式對 *T* 微分，with *E* constant

(3) $$\boxed{\left(\frac{dV}{dT}\right)_E = \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_E}$$

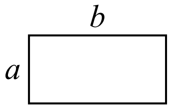
3. General rules :

(1) $\left(\frac{\partial A}{\partial B}\right)_C = \frac{1}{\left(\partial B/\partial A\right)_C}$

(2) $\left(\frac{\partial A}{\partial B}\right)_{\mathrm{C}}=-\frac{\left(\partial A/\partial C\right)_{\mathrm{B}}}{\left(\partial B/\partial C\right)_{\mathrm{A}}}=-\frac{\left(\partial C/\partial B\right)_{\mathrm{A}}}{\left(\partial C/\partial A\right)_{\mathrm{B}}}$ 或 $\left(\frac{\partial A}{\partial B}\right)_{\mathrm{C}}\left(\frac{\partial B}{\partial C}\right)_{\mathrm{A}}\left(\frac{\partial C}{\partial A}\right)_{\mathrm{B}}=-1$, cyclic rule

(3) $\left(\frac{\partial A}{\partial B}\right)_{\mathrm{C}}=\left(\frac{\partial A}{\partial B}\right)_{\mathrm{X}}+\left(\frac{\partial A}{\partial X}\right)_{\mathrm{B}}\left(\frac{\partial X}{\partial B}\right)_{\mathrm{C}}$， 記住″修正項″爲 $\left(\frac{\partial A}{\partial X}\right)_{\mathrm{B}}\left(\frac{\partial X}{\partial B}\right)_{\mathrm{C}}$，變換constant 之變數

<例>：① 周長一定，何時面積最大？



$p=2a+2b$ ， $A=ab$

即：$\left(\frac{\partial A}{\partial a}\right)_{\mathrm{p}}=0$ 不能用 $ab=A$ 代入微分，因 $b=f(a)$

用 $\left(\frac{\partial A}{\partial a}\right)_{\mathrm{p}}=\left(\frac{\partial A}{\partial a}\right)_{\mathrm{b}}+\left(\frac{\partial A}{\partial b}\right)_{\mathrm{a}}\left(\frac{\partial b}{\partial a}\right)_{\mathrm{p}}=b+a\cdot(-1)=b-a=0$

↖ $\frac{-\left(\frac{\partial P}{\partial a}\right)_{\mathrm{b}}}{\left(\frac{\partial P}{\partial b}\right)}=-1$

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

$=\frac{+\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}}}{\left(-\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_{\mathrm{T}}}=\frac{\alpha}{\kappa_{\mathrm{T}}}$ 或 $\frac{\alpha}{\beta}$