Chaper 2. Work, Heat and Energy：The First Law

2.1 Work and The State of a System

1. Historical Notes :

(1) 1783 年，Lavoisier—反對 phlogiston theory (燃燒係損失燃素)，推廣 caloric theory (substance of heat, constant in universe, flows from warmer to colder bodies)

(2) 1798 年，Ben Thompson (Count Rumford)在 München, boring (鑽)炮管
(神聖羅馬帝國)

初期認爲 ①金屬屑含熱小，故磨後產生金屬屑會放熱
test→ 改用不銳利的刀，產生較小之金屬屑，但產生更多之熱
②空氣在金屬表面運動所生
test→ 1799 Humphry Davy 真空中磨擦冰塊，冰溶解。認爲是”動作”產生熱 (此時尚無”work”之概念) (後來發現其實是真空有漏)。
去測量一匹馬一小時可產生多少熱
用今日之單位：$\boxed{1\ \text{cal} \approx 5.46\ \text{joule}}$ (而非 4.184 joule)

(3) 1840 年，能量守恆僅在 mechanical system 中被接受，
功和熱可以互換亦被接受，但”守恆”則不爲人知

(4) Julius Robert Mayer，1814 年生，藥劑師之子
1832-1838 年唸大學藥劑系 (但化學老師很好，打下化學基礎)
論文係有關蛔蟲藥，看不出對熱力學之潛力
1840 年當船醫，熱帶(Surabaya)人靜脈血很紅 (誤以爲是動脈)
當地醫師告知是正常，因在熱帶需較少 O_2 維持體溫
開始思索：吃等量之食物，可產生不等量之熱→是否 熱+功 即守恆

初期：思路不清，把力、momentum、work、energy 都搞混了，投稿被退
到 1842 年，Annalen der Chemie and Pharmazie 才接受其論文：
由 365 m 高處落下之物體作之功，相當於將等重之水加熱1℃ (0 至1℃)
用今日之單位：$\boxed{1\ \text{cal} \approx 3.56\ \text{J}}$

(5) James Prescott Joule
1818 年生於 Manchester 附近，父親是 brewer，師事 Dalton，20 歲即有自己之實驗室
1840 年 $Q = I^2 Rt$ (J)，電流生熱；其後又量：壓縮氣體、壓液體通過小管、轉 paddle 加熱。
1849 年 Royal Society 宣讀 ”On the Mechanical Equivalent of Heat”

$772\ \text{ft} \cdot 1\ \text{lb} \cdot 1\ \text{lb}.\ H_2O \cdot 1 \Rightarrow 1\ \text{cal}\ \boxed{= 4.154\ \text{J}\ ,}$ 後來改進到 4.18 J

2. Work

(1) 熱力學之源起 係對 macroscopic 觀察而來
based on empirical law，如同古典力學
不像量子力學或統計需要一些假設才可以成立，因此不會被推翻
但是：若由 microscopic 出發，也可以導出相同的結果。

(2) Work 之定義：

Carnot : weight × height lifted = work

Coriolis : work done on the object (= force) × distance the object is moved (in the direction of the force)

即：$\boxed{\mathrm{d}w = F_z \cdot \mathrm{d}z}$ 在 z 軸上的 work

如果力和位移不同方向，則 $\mathrm{d}w = \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{r} = |F| \cdot |\mathrm{d}r| \cdot \cos\alpha$

① 正負號：規定 work done on the system 爲正

即：以 system 爲中心，視 work 爲 energy 之一種

因此如果 system ”對外作功”，則 work 爲負

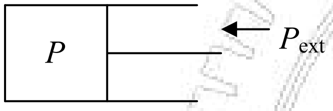
② infinitesimal process : 用積分

$$w = \int_c F \cdot \mathrm{d}s = \int_c \left(F_x \mathrm{d}x + F_y \mathrm{d}y + F_z \mathrm{d}z\right)$$

↖ line integral，沿著 path 積分

即 work 是 P_{ext} vs. V_{path} 下之積分

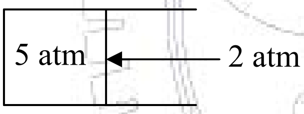
③ 對 closed fluid system (如：piston)

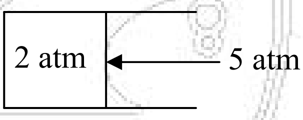


$$\mathrm{d}w = F_{\text{ext}}\mathrm{d}z = \frac{F_{\text{ext}}}{A} A\mathrm{d}z = -P_{\text{ext}}\mathrm{d}V$$

是 P_{ext}，而非 P_{opposing} 或 P_{system}

問：





|→ 膨脹, $w = -2\,\Delta V$, 爲負値　　←| 壓縮, $w = -5\,\Delta V$, 爲正値

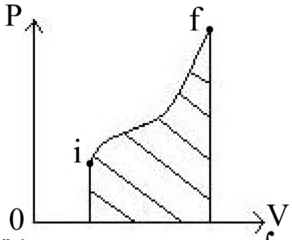
④ Free expansion：$w = 0$

⑤ Reversible work　　☆Maximum work 的觀念

(A) $P_{\text{sys}} = P_{\text{ext}}$

故 $\boxed{\mathrm{d}w_{\text{rev}} = -P\mathrm{d}V}$

(B)



path 是 well defined

work 即爲 path 下面之面積 (之負值)

$$\begin{cases} \text{對 ideal gas: } w_{\text{rev}} = -\int P\mathrm{d}V = -\int \dfrac{n\mathrm{R}T}{V}\mathrm{d}V = -n\mathrm{R}T\ln\dfrac{V_2}{V_1} \\ \text{對 vdW gas: } P = \dfrac{n\mathrm{R}T}{V-b} - \dfrac{n^2a}{V^2},\quad w_{\text{rev}} = n\mathrm{R}T\ln\dfrac{V_1-b}{V_2-b} - n^2a\left(\dfrac{1}{V_2} - \dfrac{1}{V_1}\right) \end{cases}$$

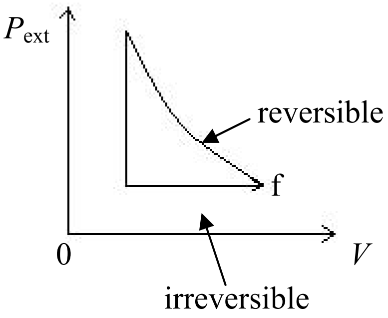
課本 Eq. 2.1-13 缺一負號

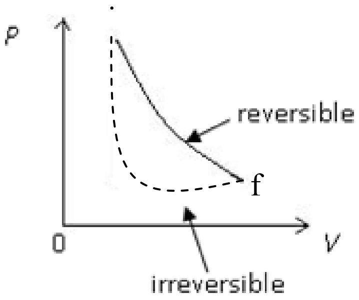
⑥ Work 與 path 有關

即：不能只知 initial 及 final state

如要定一個物質之 ”work”，則要知 “history”，不好

例





work 不同，但到達相同 final state

即：work 不是 state function

3. 其它的功

	intensive	extensive	
hydrostatic	P	V	$-PdV$
surface	γ	A	$\gamma\ dA$
elongation	f	L	fdL
electrical	ϕ	Q	$\phi\ dQ$
gravitational	ψ	m	$\psi\ dm$

4. Exact differential

數學上 $df(x,y) = M(x,y)dx + N(x,y)dy$

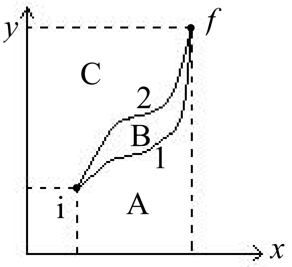
$\left(\frac{\partial M(x,y)}{\partial y}\right)_x = \left(\frac{\partial N(x,y)}{\partial x}\right)_y$ ，則 df 係 exact

① 如表爲 $df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$ 則爲 exact

因爲 $\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right)$

② $\int_c df$ 與 path 無關

$\int_{path\,1} df = A + (B + C)$ ， $\int_{path\,2} df = (A + B) + C$



只與初/末態有關

df 爲 exact, 則稱 f 爲 state function

③ $\oint df = 0$

④ $f(x,y,z) \Rightarrow df = L\,dx + M\,dy + N\,dz$

則 $\left(\frac{\partial L}{\partial y}\right)_{x,z} = \left(\frac{\partial M}{\partial x}\right)_{y,z}$, $\left(\frac{\partial L}{\partial z}\right)_{x,y} = \left(\frac{\partial N}{\partial x}\right)_{y,z}$, $\left(\frac{\partial M}{\partial z}\right)_{x,y} = \left(\frac{\partial N}{\partial y}\right)_{x,z}$

2.2 Heat

以前的人對 heat 和 temperature 觀念不清

到 Joseph Black (1728-1799) 才弄清楚其分別

但仍有 heat 是 “imponderable fluid” (無法稱重的流體) 之錯誤觀念

1. $dq = C dT$　　C : heat capacity

$= cm dT$　　c : specific heat (capacity), m：mass

molar heat capacity

$C_{p,m} = C_p / n$　(const. P)

$C_{v,m} = C_v / n$　(const. V)

C 永遠爲正 (即吸熱後不可再降溫)

$$q = \int dq = \int C dT = C \Delta T \quad \text{if } C \text{ constant 或 } \Delta T \text{不大}$$

2. phase change：$\Delta T = 0$ 但仍有 q(latent heat), (相變化時，吸熱但溫度不變)

例： 水　0°C , 1 atm,　$q = 79.72\ \text{cal g}^{-1}$　或　$333.5\ \text{kJ kg}^{-1}$

100°C , 1atm,　$q = 539.55\ \text{cal g}^{-1}$　或　$2257.5\ \text{kJ kg}^{-1}$

2.3 Internal Energy：The First Law of Thermodynamics

1. First Law 許多種不同的說法：

(1) For a closed system and for any process that begins and ends with equilibrium states,

ΔU is defined as $\Delta U = q + w$ and is a state function, 即：$\oint \mathrm{d}U = 0$

↖

internal energy 或 thermodynamic energy

(2) 較 sophisticated 的說法： (由 "功" 的觀點出發)

If the state of an otherwise isolated system is changed from A to B by the performance of work, the amount of work required depends solely on the initial and the final state, not on the path.

此時定義 $\mathrm{d}U = \mathrm{d}w_{\mathrm{ad}}$

原是 $\text{đ}w$ (path dependent, 用 đ 表示) 在 special case 變爲 $\mathrm{d}w$ (path independent, 用 d 表示)

q 之定義即變爲 $q = w_{ad} - w = \Delta U - w$

↖

diathermal

推論：

(3) For an isolated system, $\Delta U = 0$ → Energy is conserved for the Universe.

(4) It is impossible to construct a perpetual motion machine to produce work by a cyclic process without any change in the surrounding.

即：不可能無中生有

"Perpetual motion machine of the first kind" 產生的能量較其吸收的能量更多

2. <Note> : ① 1st law 可視爲功與熱的能量守恆定律

但廣義而言， $E_{total} = V_{\mathrm{g}} + m_0 c^2 + U$

↖ internal energy

↖ gravitational potential

將質能互換及重力位能包含進來

對 closed system，則 $E_{\mathrm{total}} = U + \text{constant}$

② 1st law 談的是 ΔU，而非 U 之絕對值

③ 對 ideal gas, $U = \frac{3}{2}\mathrm{R}T$ 只是 T 之函數

亦即：ideal gas 之 isothermal process $\Delta U = 0$

"classical" molecules：

在常溫下，rotation 要考慮，vibration 並不重要

因此
$$\begin{cases} U \approx \frac{5}{2}\mathrm{R}T & \text{for diatomic or linear polyatomic gas} \\ U \approx 3\,\mathrm{R}T & \text{for nonlinear polyatomic gas} \end{cases}$$

↖

◇1 確實之值要用統計熱力學計算或作實驗

◇2 不包含化學能 (鍵能之變化)

2.4 Calculation of Amounts of Heat and Energy Changes

1. Heat Capacity C_V

$$dq = dU - dw = dU + P_{ext}dV$$
$$= dU \quad (\text{if } dV = 0)$$

即：$(dq)_V = (dU)_V = \left(\frac{\partial U}{\partial T}\right)_V dT = C_V dT$

或 $\underbrace{C_V = \left(\frac{\partial U}{\partial T}\right)_V}_{\text{定義}} = \left(\frac{\partial q}{\partial T}\right)_V$

↑ simple system (即:只作 PV 功)

Note: 只考慮 PV work 才成立
若有其他功 (如：電功)
則 $dq_V \neq dU$

2. Dependence of ΔU on T or V

$U(T, V)$ for 1-component system

不是很理想，學了 2nd law 即知 $U(S, V)$較好。

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \text{對 ideal gas } \left(\frac{\partial U}{\partial V}\right)_T = 0$$

↑ heat capacity ↑ internal pressure

Note: $\left(\frac{\partial U}{\partial T}\right)_V dT$ 不是 dq
only constant V 時才是

3. Joule Experiment

1843 年，Joule 想測 $\left(\frac{\partial U}{\partial V}\right)_T$

Internal pressure

$$\left(\frac{\partial U}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial U}{\partial T}\right)_V = -\mu_J C_V$$

故 $\mu_J = 0$ for ideal gas

如果 $\mu_j < 0$，則 $\left(\frac{\partial U}{\partial V}\right)_T > 0$

↑ cooling on expansion

量 Joule coefficient $\mu_J = \left(\frac{\partial T}{\partial V}\right)_U$

system = 球 + water bath

q = 0 因絕熱

w = 0 因 free expansion

其實 $\left(\frac{\partial T}{\partial V}\right)_U = \frac{-\left(\partial U/\partial V\right)_T}{\left(\partial U/\partial T\right)_V} = -\frac{a/V^2}{C_V} = -\frac{a}{C_V V^2}$ for vdW gas

實驗中, $P = 22$ atm, 水有 16 [illegible]，太多了，故量不出 ΔT

參考課本Figure 2.5

2.5 Enthalpy

1. 引出 C_P 及 H

實驗上常在 constant P 下進行， $P = P_{ext}$, if heat is added slowly

$\mathrm{d}q = \mathrm{d}U + P_{ext}\mathrm{d}V = \mathrm{d}U + \mathrm{d}(PV) = \mathrm{d}(U + PV)$ for 定壓

定義 enthalpy (焓) $H = U + PV$, 也是 state function

則 $\underline{(\mathrm{d}q)_P = (\mathrm{d}H)_P}$ for simple system

simple system

$$\text{定義}\quad C_P = \left(\frac{\partial q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$= \left[\left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\right] + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$= \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P = \text{ideal } P\cdot\left(\frac{\partial V}{\partial T}\right)_P$$

利用 2_{nd} law, 則

$$= T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

$$= \frac{-T\left(\partial V/\partial T\right)_P^2}{\left(\partial V/\partial P\right)_V} = \frac{\alpha^2 VT}{\kappa_T}$$

$$\text{或}\quad = \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V$$

2. Joule-Thomson Experiment

1852-62 年

$$\text{量}\quad \left(\frac{\partial H}{\partial P}\right)_T = -\frac{\left(\partial T/\partial P\right)_H}{\left(\partial T/\partial H\right)_P} = -\mu_{JT}C_P$$

Joule-Thomson coefficient , $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$ for ideal gas , $\mu_{JT} = 0$

1, 2 各表 initial 及 final；R, L 各表右邊及左邊

$q = 0$, 假設 $V_{L2} = 0$, $V_{R1} = 0$

左邊 $w = -P_L(V_{L2} - V_{L1}) = +P_L V_L$

右邊 $w = -P_R(V_{R2} - V_{R1}) = -P_R V_R$

$w = P_L V_L - P_R V_R = -\Delta(PV) = \Delta U$ (因 q=0)

$\Delta H = \Delta U + \Delta(PV) = 0$

參考課本 Figure 2.8

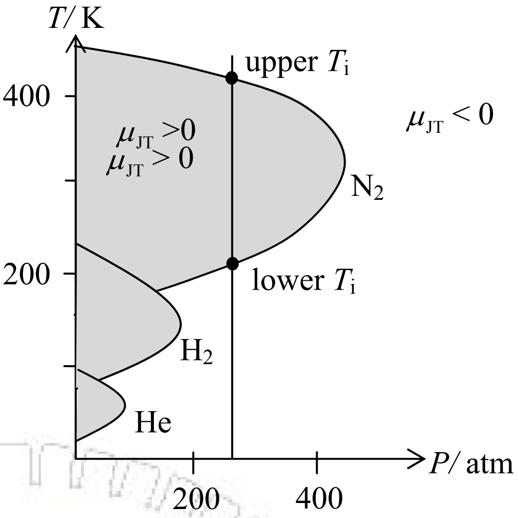
μ_{JT} 爲正表示 cooling on expansion

除了 Ar, H_2 及 He 外，room temp. 之 $\mu_{JT} > 0$

inversion temp. 723 K 195 K 44.8 K

$\begin{cases}\text{應用：液化氣體} \\ \text{冰箱 (還利用 vaporization)}\end{cases}$

	μ_{JT} (K/atm) 0 °C	T_i
He	−0.06	44.8 K
N_2	0.266	621 K
H_2	−0.03 at 298 K	195 K
CO_2	1.369	1500 K
C_2H_5Cl	5.22	



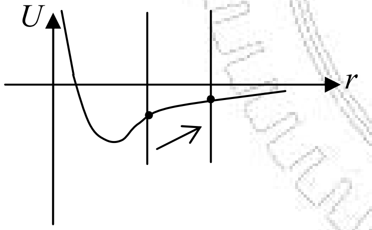
3. 如果不是 simple system：

	如有電功，則 $\Delta U = q + w + w'$ (w' 為電功)	只有 PV 功 (simple system)
① constant volume 下	$q_v = \Delta U - w'$	$q_V = \Delta U$
② constant pressure 下	$q_P = \Delta H - w'$	$q_P = \Delta H$
③ adiabatic 情況下，PV work	$w = \Delta U - w'$	$w = \Delta U$

2.5A 補充教材

1. Internal Pressure $\left(\frac{\partial U}{\partial V}\right)_T$

分子非 ideal 時，有 interaction potential



定容：r 固定

定壓：expansion 時 r 變大

亦即：吸的熱有一部分要供給分子以抗拒 ”引力”

由第二定律：$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P}$

$\uparrow$ P 之修正項 $\uparrow$ ideal P $\uparrow$ real P

ideal P 即 $P \propto T$, =對 T 一次微分再乘 T

回想 vdWgas,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} = \frac{a}{V^2}$$ 即是 P 之修正項

§ 如是 virial, $\frac{PV}{RT} = 1 + \frac{B}{V}$ 則 $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{R}{V} + \frac{BR}{V^2} + \frac{B'RT}{V^2}\right) - P = \underline{\frac{RT^2}{V^2}\left(\frac{dB}{dT}\right)}$

$$\searrow P = \frac{RT}{V} + \frac{BRT}{V^2}$$

$$\uparrow B' = \left(\frac{dB}{dT}\right)$$

2. 最有用的通式

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

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

定容之吸熱 改變 V 時抗拒分子引力之吸熱 (不含－PdV 項)

同理 $(-P \to V, dV \to dP)$，

因此 $\Delta U = C_V \Delta T$，只在：

① C_V 不隨 T 而變

② $dV = 0$ 或 $\left(\frac{\partial U}{\partial V}\right)_T = 0$

③ 沒 phase change

(當然對 ideal gas, $\Delta U = C_v \Delta T$)

如令 $a = 0$，$P = \frac{RT}{V-b}$，$PV = RT + Pb$

$V = \frac{RT}{P} + b$，$T\left(\frac{\partial V}{\partial T}\right)_P = V - b$

則 $\left(\frac{\partial H}{\partial P}\right)_T \cong b$

"excluded volume

對vdW, $P = \frac{RT}{V-b} - \frac{a}{V^2}, P(V-b)V^2 = V^2RT - a(V-b)$

微分($P = \text{constant}$)

得 $3PV^2dV - 2bPVdV = RV^2dT + 2RTVdV - adV$

$$\left(\frac{dV}{dT}\right)_P = \frac{RV^2}{3PV^2 - 2bPV - 2RTV + a}$$

$$V - T\left(\frac{dV}{dT}\right)_P = V - \frac{RTV^2}{3PV^2 - 2bPV - 2RTV + a}$$

$$= \frac{3PV^3 - 2bPV^2 - 3RTV + aV}{3PV^2 - 2bPV - 2RTV + a}$$

如果 a=0, 則 RT=$P(V-b)$

$$V - T\left(\frac{\partial V}{\partial T}\right)_P = \frac{3PV^3 - 2bPV^2 - 3PV^3 + 3bPV^2}{3PV^2 - 2bPV - 2PV^2 + 2bPV}$$

$= b$, 和左邊一致

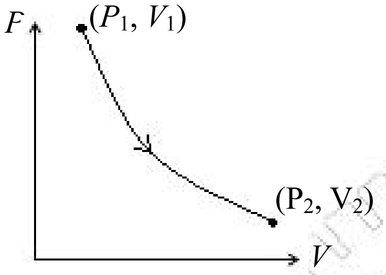
2.6 Application to Ideal Gas

Ideal Gas 之性質：

$$\begin{cases} U(T)\ \text{function of T only，故}\left(\partial U\big/\partial V\right)_T = 0 \quad \left(\partial C_V\big/\partial V\right)_T = 0 \\ H(T)\ \text{function of T only，故}\left(\partial H\big/\partial P\right)_T = 0 \quad \left(\partial C_P\big/\partial P\right)_T = 0 \end{cases}$$

但是 $\left(\frac{\partial U}{\partial V}\right)_P \neq 0$ 因 $\left(\frac{\partial U}{\partial V}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T + \left(\frac{\partial U}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P = 0 + \frac{C_V P}{R} \neq 0$

(1) Reversible Isothermal Process



$$\Delta T = 0 \ \Rightarrow \Delta U = \Delta H = 0$$

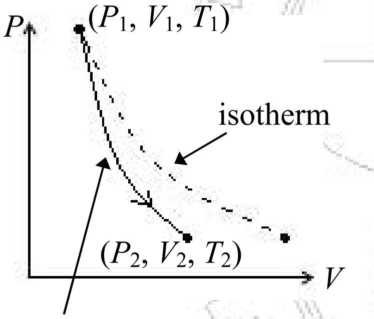
$$w = \int -P_{ext}dV \underset{\text{reversible}}{=} -\int PdV \underset{\text{ideal gas}}{=} -\int \frac{nRT}{V}dV = -nRT\ \ln\frac{V_2}{V_1}$$

$$q = -w = nRT\ \ln\frac{V_2}{V_1} \text{ 或 } nRT\ \ln\frac{P_1}{P_2}$$

靠所吸得之熱 → 全部拿來作功

如：想用錢就找父母拿，因此口袋之錢不變

(2) Reversible Adiabatic Process



此曲線永遠在 isotherm 之下

$$q = 0\ ,\ \Delta U = w$$

$$\underset{\text{ideal gas}}{C_V dT} = -P_{ext}dV \underset{\substack{\nearrow \\ \text{reversible}}}{=} -PdV \underset{\text{ideal gas}}{=} -\frac{RT}{V}dV$$

$$\int\frac{C_V}{T}dT = -\int\frac{R}{V}dV$$

因爲 $C_V = \text{constant}$

所以 $C_V\ \ln\frac{T_2}{T_1} + R\ \ln\frac{V_2}{V_1} = 0,\ \ln\frac{T_2}{T_1} = \frac{-R}{C_V}\ \ln\frac{V_2}{V_1}$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_1}\right)^{-R/C_V} = \left(\frac{V_1}{V_2}\right)^{R/C_V} = \left(\frac{V_1}{V_2}\right)^{\gamma-1},\ \gamma = \frac{C_P}{C_V}\quad (=\frac{5}{3}\ \text{for ideal gas})$$

但 $\left(\frac{T_2}{T_1}\right) = \frac{P_2V_2}{P_1V_1}$ (for ideal gas) $\longrightarrow$ $\boxed{P_1V_1^{\gamma} = P_2V_2^{\gamma}}$ (與 $PV = nRT$ 並不牴觸)

另可導出 $\boxed{\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{1-\frac{1}{\gamma}}}$ c.f. $\boxed{\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{1-\gamma}}$

故 $\Delta U = w = C_V\left(T_2 - T_1\right)$ （T_2由上式決定 ）

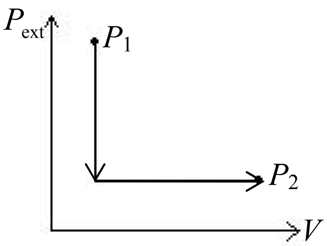
$\Delta H = C_P\left(T_2 - T_1\right)$

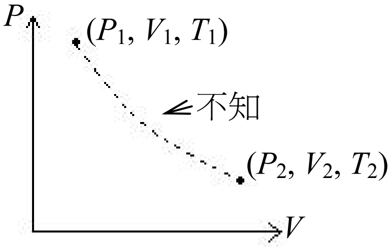
靠降低自身之溫度來作功，沒有外援

例如：父母斷絕經費來源，必須省飯錢餓肚子才可買東西

(3) Irreversible Adiabatic Process

P_{ext} 突降至 P_2 後，維持 const.

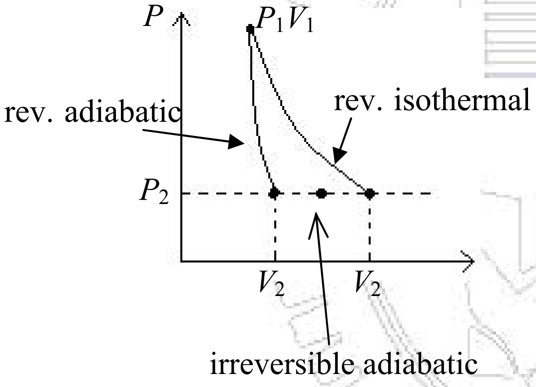




$$q = 0 \text{ , } w = -\int P_{\text{ext}}\,\mathrm{d}V = -P_2(V_2 - V_1) = \Delta U$$

假設 $C_V = \frac{3}{2}R$ 爲constant，則 $C_V(T_2 - T_1) = -P_2(V_2 - V_1), \frac{3}{2}R(T_2 - T_1) = -RT_2 + P_2\frac{RT_1}{P_1}$

$$\frac{5}{2}RT_2 = \frac{3}{2}RT_1 + \frac{P_2}{P_1}RT_1$$



① 和 reversible adiabatic expansion 比：

less work done → less cooling

② 如果 $P_2 \to 0$,則 $V_2 \to \infty$

故 $P_2\Delta V$ 不是 zero， $P_2\Delta V \cong P_2V_2$

$P_2 = 0$, 則 $T_2 = 0.6\,T_1$,不能變 0 K

因爲 $\underset{\underset{C_V}{\uparrow}}{\frac{3}{2}RT_1}$ 之能量變爲 $\underset{\underset{C_P}{\uparrow}}{\frac{5}{2}RT_2}$

c.f. reversible 時， $P_2 \to 0$, $T_2 \to 0$

2.7 Application to Non-Ideal Gas

此時 $\left(\partial U/\partial V\right)_{\mathrm{T}} \neq 0$，$= T\left(\partial P/\partial T\right)_{\mathrm{V}} - P$

用通式：

$$\Delta U = \int C_{\mathrm{V}}\mathrm{d}T + \int\left[T\left(\partial P/\partial T\right)_{\mathrm{V}} - P\right]\mathrm{d}V \qquad \mathrm{vdW}: P = \frac{\mathrm{R}T}{V\text{-}b} - \frac{a}{V^2}$$

$$\Delta H = \int C_{\mathrm{P}}\mathrm{d}T + \int\left[V - T\left(\partial V/\partial T\right)_{\mathrm{P}}\right]\mathrm{d}P$$

For vdW gas, $\left(\partial U/\partial V\right)_T = T\left(\partial P/\partial T\right)_{\mathrm{V}} - P = T\cdot\dfrac{\mathrm{R}}{V-b} - P = \dfrac{a}{V^2}$

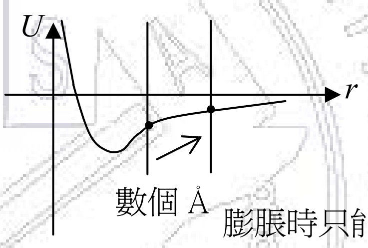
$$\left(\partial H/\partial P\right)_{\mathrm{T}} = V - T\left(\partial V/\partial T\right)_{\mathrm{P}} \approx b$$

(1) Reversible Isothermal Process

$$\Delta U = 0 + \int \frac{a}{V^2}\mathrm{d}V = -\frac{a}{V}\Big|_{\mathrm{i}}^{\mathrm{f}} = \frac{a}{V_1} - \frac{a}{V_2}$$ ← 膨脹時通常爲正值

$$w = -\int P_{\mathrm{ext}}\mathrm{d}V = -\int P\mathrm{d}V = -\int\left(\frac{\mathrm{R}T}{V-b} - \frac{a}{V^2}\right)\mathrm{d}V$$

$$= -\mathrm{R}T\ \ln\frac{V_2-b}{V_1-b} - \underline{a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)}$$



膨脹時只能作比 ideal gas 少的功
部份能量要拿來克服引力

$$q = \Delta U - w = RT\ \ln\frac{V_2-b}{V_1-b}$$

在 w 而不在 q 項內
因爲作功改變了 internal P
但吸熱並不會直接改變

$$\Delta H = \Delta U + \Delta(PV) = \frac{-a}{V_2} + \frac{a}{V_1} + \left(\mathrm{R}T\frac{V_2}{V_2-b} - \frac{a}{V_2}\right) - \left(\mathrm{R}T\frac{V_1}{V_1-b} - \frac{a}{V_1}\right)$$

$$= \frac{-2a}{V_2} + \frac{2a}{V_1} + b\mathrm{R}T\left(\frac{1}{V_2-b} - \frac{1}{V_1-b}\right) \qquad 因\ \frac{V_2}{V_2-b} = 1 + \frac{b}{V_2-b}$$

(2) Reversible Adiabatic Process

$q = 0, \Delta U = w$

$$C_{\mathrm{V}}\mathrm{d}T + \left\{T\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} - P\right\}\mathrm{d}V = -P_{\mathrm{ext}}\mathrm{d}V = -P\mathrm{d}V$$

假設 C_{V} constant，$C_{\mathrm{V}}\mathrm{d}T = -T\left(\dfrac{\partial P}{\partial T}\right)_{\mathrm{V}}\mathrm{d}V$

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

for vdW gas , $\frac{C_V}{T}\,\mathrm{d}T=-\frac{R}{V-b}\,\mathrm{d}V$, $\ln\frac{T_2}{T_1}=-\frac{\mathrm{R}}{C_V}\ln\frac{V_2-b}{V_1-b}$

$$\left.\begin{array}{l} \left(\frac{T_2}{T_1}\right)=\left(\frac{V_1-b}{V_2-b}\right)^{\gamma-1} \\[2ex] \left(\frac{T_2}{T_1}\right)=\frac{\left(P_2+\frac{a}{V_2^2}\right)(V_2-b)}{\left(P_1+\frac{a}{V_1^2}\right)(V_1-b)} \end{array}\right\}\rightarrow \left(P+\frac{a}{V^2}\right)(V-b)^{\gamma}=\text{constant}$$

2.8 Calculation of Enthalpy Changes of Process without Chemical Reaction

1. 隨 T 之變化

(1) constant P: 即求 $\left(\frac{\partial H}{\partial T}\right)_{\mathrm{p}} = C_{\mathrm{p}} \quad \Delta H = \int C_{\mathrm{P}}\, dT$

A. ideal gas, $C_{\mathrm{P}} = \frac{5}{2}\mathrm{R}$

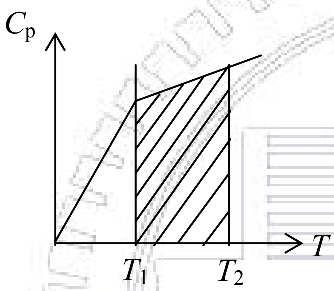
B. 一般把 C_{P} 表爲 $C_{\mathrm{P}}(T) = a + bT + \frac{c}{T^2}$ 見課本 p.1212 (Table

則 $\Delta H = \int a + bT + \frac{c}{T^2}\,\mathrm{d}T$

$$= a(T_2 - T_1) + \frac{1}{2}b\left(T_2{}^2 - T_1{}^2\right) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

故欲知 ΔH at any T，要知 $C_{\mathrm{P}}(T)$ 及某一 T 之 H 值

C. graphical method 或 numerical interaction



D. 考慮 phase change

$\Delta_{\mathrm{fus}}H$ 或 $\Delta_{\mathrm{vap}}H$ (習慣上用 ΔH_{fus} 或 ΔH_{vap})

(2) constant V, 即求 $\left(\frac{\partial H}{\partial T}\right)_{\mathrm{V}}$

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

$$= C_{\mathrm{P}}\left(1 - \mu_{\mathrm{JT}}\frac{\alpha}{\kappa_{\mathrm{T}}}\right), \quad \mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial P}\right)_{\mathrm{H}}$$

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

2. 隨 P 之變化 at constant T

$$\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} = -\mu_{\mathrm{JT}}C_{\mathrm{P}} \quad 或是 \quad \mathrm{V} - T\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} = V(1 - \alpha T)$$

如是 virial equation, $z = \frac{PV}{\mathrm{R}T} = 1 + B(T)\frac{1}{V}$

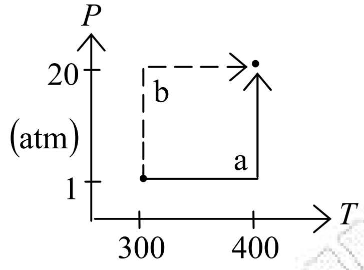
$$V = \frac{\mathrm{R}T}{P} + B(T)\frac{\mathrm{R}T}{PV} \approx \frac{\mathrm{R}T}{P} + B(T)$$

$$\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}}=\frac{\mathrm{R}T}{P}+B(T)-T\left(\frac{\mathrm{R}}{P}+\frac{\partial B(T)}{\partial T}\right)=B(T)-T\left(\frac{\partial B(T)}{\partial T}\right)$$

$$\mathrm{vdW}: B=b-\frac{a}{\mathrm{R}T}\text{，則}\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}}=b-\frac{a}{\mathrm{R}T}-T\left(\frac{a}{\mathrm{R}T^{2}}\right)=b-\frac{2a}{RT}$$

3. 利用假想的步驟求Δ H

(1) 例：1 mole Ar (1 atm, 300K) → (20 atm, 400K)



理論上 path a 或 b 均可

但實際上高壓時非 ideal gas，故用 a 較好

① constant P, $\Delta H=\frac{5}{2}\mathrm{R}\cdot\Delta T=\frac{5}{2}\times 8.314\times 100=2078.5\ \mathrm{J\,mol^{-1}}$

② constant T, $\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}}=B-T\left(\frac{\partial B}{\partial T}\right)$

例：用 vdW equation,

$$\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}}=b-\frac{a}{\mathrm{R}T}-\frac{a}{\mathrm{R}T}=b-\frac{2a}{\mathrm{R}T}$$

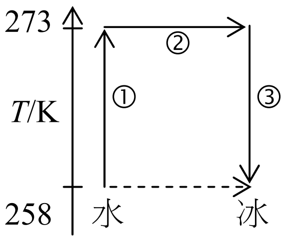
$$=3.219\times 10^{-5}\times 10^{3}-2\times\frac{0.1363\times 10^{3}}{8.3145\times 673}=-0.0172\ \ell\,\mathrm{mol^{-1}}$$

$$\Delta H=(20-1)\times(-0.0172)\ \ell\cdot\mathrm{atm}\times\left(\frac{0.082}{8.314}\right)^{-1}\frac{\mathrm{J}}{\ell\cdot\mathrm{atm}}$$

$$=19\times(-1.745)=-33\ \mathrm{J}$$

故①+② $=2045\ \mathrm{J\,mol^{-1}}$

(2) Irreversible 之例：1 atm, −15°C 下，水結冰



假設 C_{P} 不隨 T 而改變太多

① $\int_{258}^{273}C_{\mathrm{P}}(\ell)\mathrm{d}T=76.1\ \mathrm{J\,K^{-1}\,mol^{-1}}\times 15=1140\ \mathrm{J\,mol^{-1}}$

② $18.02\ \mathrm{g\,mol^{-1}}\times(-333.5)\ \mathrm{J\,g^{-1}}=-6010\ \mathrm{J\,mol^{-1}}$

③ $\int_{273}^{258}C_{\mathrm{P}}(s)\mathrm{d}T=37.15\ \mathrm{J\,K^{-1}\,mol^{-1}}\times 15=-557\ \mathrm{J\,mol^{-1}}$

$\Delta\mathrm{H}=$①+②+③$=-5427\ \mathrm{J\,mol^{-1}}$

2.9 Enthalpy Changes for Chemical Reactions

1. $\begin{cases} \text{exothermic 放熱 , } \Delta H < 0 \\ \text{endothermic 吸熱 , } \Delta H > 0 \end{cases}$

把 equation 寫成 $\sum_{i=1}^{c} v_i F_i = 0$

$\uparrow$ 係數 $\quad \uparrow$ Formula for *i*th species

−: for reactant

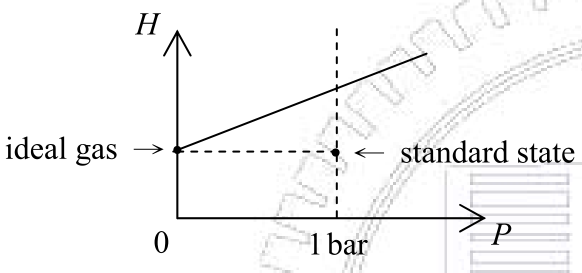
+ : for product

則 $\Delta H = \sum_{i=1}^{c} v_i H_m(i)$

2. 定 standard-state

(1) liquid 或 solid : pure substance at 1 bar and 298 K

(2) gas :1 bar 之 ideal gas (假想，未必存在，亦即要 correct for non-ideal effect)



3. $\Delta H°$ standard-state enthalpy change

$\Delta H_f°$

_D_Dd___________ŷĬƧƧ_________________^(/)____

_____________________$\Delta_f H°(i)$

$$\Delta H° = \sum_{i=1}^{c} v_i \left(\Delta H_f°(i)\right)$$

參考課本Figure 2.10

4. $T-$dependence

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_p \mathrm{d}T$$

5. adiabatic reaction

參考課本Figure 2.11

ΔH 造成溫度變化

$\Delta H_1 = \Delta H_2 + \Delta H_3 = 0$

$\Delta H_3 = \int_{T_1}^{T_2} \sum_{i=1}^{c} v_i C_p(i) \mathrm{d}T = -\Delta H_2$

2.10 Energy Changes of Chemical Reaction

1. $\Delta U = \Delta H - \Delta PV$ 忽略$(\ell),(\mathrm{s})$之體積

   $\approx \Delta H - (\Delta n)\mathrm{R}T$ Δn : gas之mole數變化

2. Bomb Calorimeter

   constant V之實驗

$$\text{由 } C_\mathrm{V}, \Delta T \rightarrow q = -C_\mathrm{V}(\Delta T) = \Delta U$$

$$\downarrow$$

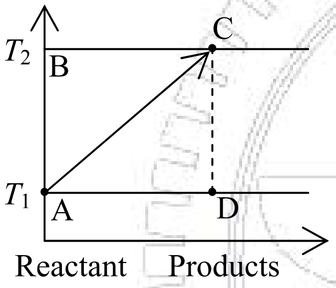
$$\Delta H = \Delta U + (\Delta n)\mathrm{R}T$$

修正：① product 在高溫→反應前溫度

② $\Delta H(T)$不一定是 constant → 用$C_\mathrm{P}(T)$修正

③ P也不是 1 bar，但修正量不大

④ heat of combustion of wire



實驗：$\mathrm{A} \rightarrow \mathrm{C}$, 但 $\Delta U_\mathrm{AC} = 0$

溫度$\mathrm{T_1}$, ΔU 要的是 $\mathrm{A} \rightarrow \mathrm{D}$, 即$\Delta U_\mathrm{AD}$

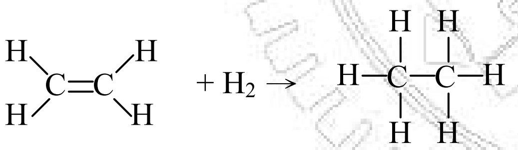
$$\Delta U_\mathrm{AD} + \Delta U_\mathrm{DC} = \Delta U_\mathrm{AC}$$

$$\text{故 } \Delta U_\mathrm{AD} = -\Delta U_\mathrm{DC} = -\int_{\mathrm{T_1}}^{\mathrm{T_2}} C_\mathrm{V}^{\text{Product}}\,\mathrm{d}T$$

$$\text{而 } T_2 \text{ 之 } \Delta U = \Delta U_\mathrm{BC} = -\int C_\mathrm{V}^{\text{Reactant}}\,\mathrm{d}T$$

3. Average Bond Energies (自己讀)

例：



查 Table A.9, 破壞 C=C 613 生成 C—C −348 kJ $\mathrm{mol^{-1}}$

H—H 436 2C—H −(2×413) kJ $\mathrm{mol^{-1}}$

⇒ −125 kJ $\mathrm{mol^{-1}}$ 實際 −134.5 kJ $\mathrm{mol^{-1}}$

Sidney Bensen : Bond Group Additivity Rule

$2\times(\mathrm{Cd})(\mathrm{H_2})$: $2\times 6.78 = 13.56$ kcal $\mathrm{mol^{-1}}$

$2\times(\mathrm{C})(\mathrm{H_3})$: $-10.2\times 2 = -20.4$

$+0.8$ gauche correction

$\Delta H = -33.16$ kcal $\mathrm{mol^{-1}}$ $= -138.7$ kJ $\mathrm{mol^{-1}}$