

熱力學(Thermodynamics)

Dynamical action of heat \Rightarrow *System* $\xleftrightarrow[\text{Work}]{\text{Heat}}$ *Surrounding*

\Rightarrow Change of macroscopic variables (宏觀變數：壓力、體積、溫度)

- 熱力學第零定律 \Rightarrow 熱平衡(CH 18)
- 熱力學第一定律 \Rightarrow 能量守恆(CH 19)
- 熱力學第二定律 \Rightarrow 自然界不可逆過程(CH21)
- 氣體動力論 \Rightarrow 以統計概念探討宏觀現象(CH20)

✦ 溫標(Temperature Scales) $\Rightarrow T_F = \frac{9}{5}T_C + 32^\circ F$

	攝氏溫標 T_C (Celsius scale)	華氏溫標 T_F (Fahrenheit scale)	凱氏溫標 (Kelvin scale)
凝固點	0°C	32°F	273K
沸點	100°C	212°F	373K

✦ 熱力學第零定律(The Zeroth Law of Thermodynamics)

— 熱平衡(Thermal equilibrium)現象之描述(確認溫度狀態變數)，即
兩物體分別與第三物體達至熱平衡，則該兩物體也必互為熱平衡。

※補充說明：

1. 兩系統只要溫度相同(不一定接觸)，則該兩系統必互為熱平衡。
2. 熱平衡不代表其它狀態變數(如壓力、體積)一定相同。
3. 當一系統的狀態變數不隨時間改變時，則該系統處於熱平衡。

★ 理想氣體狀態方程式 — 描述宏觀變數之關係

- 定溫下，氣體的壓力與體積成反比： $PV = \text{常數}$ 。(Robert Boyle)
- 定壓下，氣體的體積與溫度成正比： $V \propto T$ 。(Charles and Gay-Lussac)
- 定容下，氣體的壓力與溫度成正比： $P \propto T$ 。(Gay-Lussac)

$$V \propto T \quad \& \quad P \propto T \Rightarrow PV \propto T$$

- PV 值由存在氣體分子數 N 決定

$$\Rightarrow V \propto N \quad (P \& T \text{ is given}), \quad P \propto N \quad (V \& T \text{ is given}) \Rightarrow PV \propto N$$

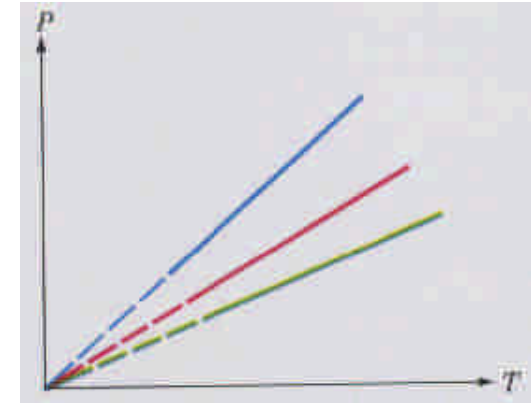
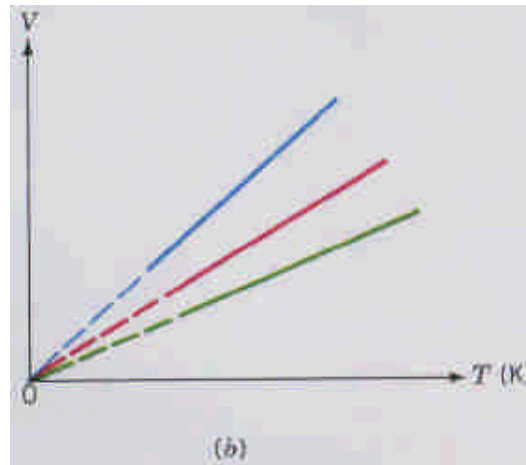
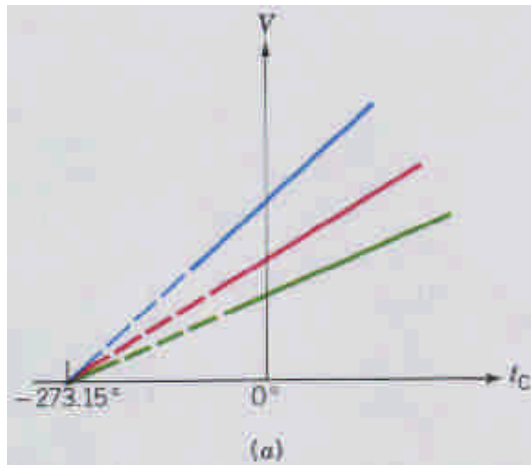


Fig.18.4

Fig.18.3

- 理想氣體狀態方程式(The equation of state for an ideal gas)：

$$\Rightarrow PV=NkT \quad (k=1.38\times 10^{-23} \text{ J/K})$$

$$\Rightarrow PV=nRT \quad (N=nN_A, \quad N_A=6.02\times 10^{23} \text{ mol}^{-1}, \quad R=kN_A=8.314 \text{ J/mol}\cdot\text{K})$$

- 當真實氣體(約為大氣壓力)相當稀薄且溫度(約為室溫)遠大於其液化溫度，其仍可趨近理想氣體。

✦ 熱膨脹(Thermal Expansion)－隨溫度上升而膨脹

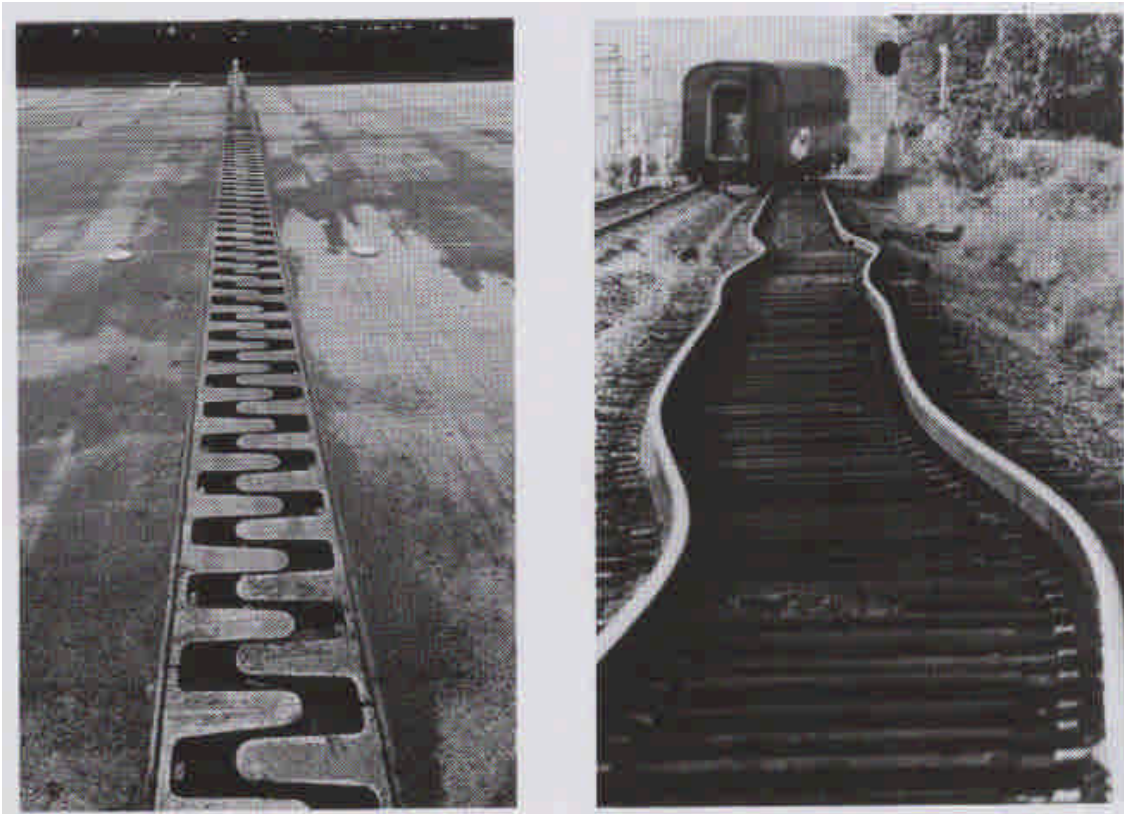


Fig.18.7

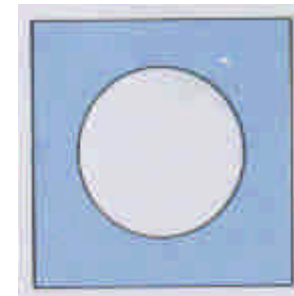
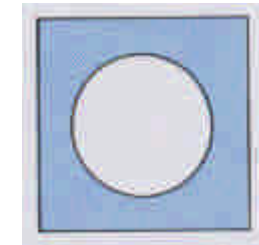


Fig.18.8

$$\alpha = \frac{\Delta L / L_0}{\Delta T} \quad (\text{The coefficient of linear expansion})$$

$$\beta = \frac{\Delta V / V_0}{\Delta T} \quad (\text{The coefficient of volume expansion})$$

●Application :

➤複合金屬熱膨脹

⇒利用熱膨脹係數不同來設計溫度感應開關，如恆溫器、電路阻斷器及化油器塞子控制器等。

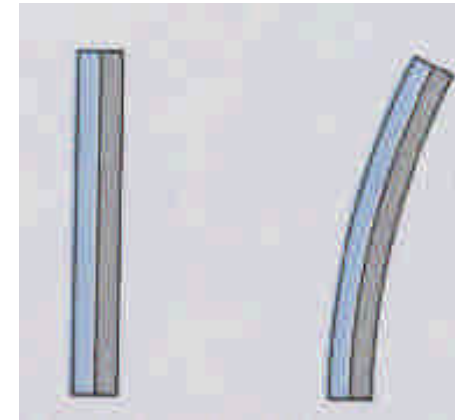


Fig.18.9

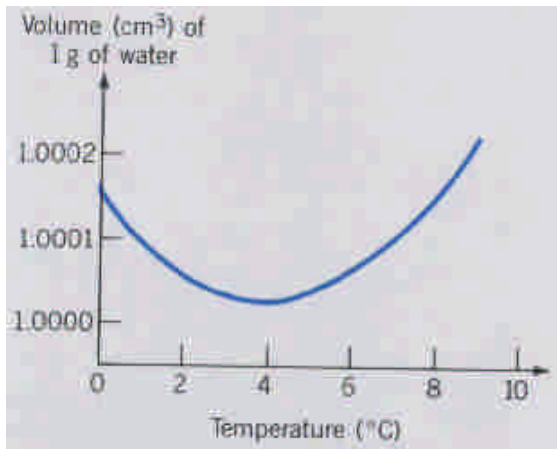


Fig.18.10

➤湖面結冰原因

⇒因水在 $0^{\circ}\text{C} \sim 4^{\circ}\text{C}$ 隨溫度減小而體積反增大，即密度變小，故湖面水冷卻至 4°C ，便不再下沉直至結冰。

➤原子位能井函數與熱膨脹關係

⇒對稱(虛線)→非對稱(實線)⇒原子振動能量隨溫度增加($E_2 > E_1$)⇒平均位置增大($\bar{r}_2 > \bar{r}_1$)⇒原子間距增大

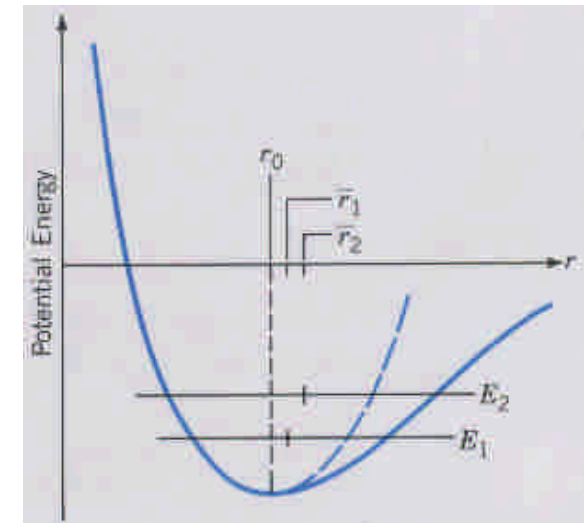
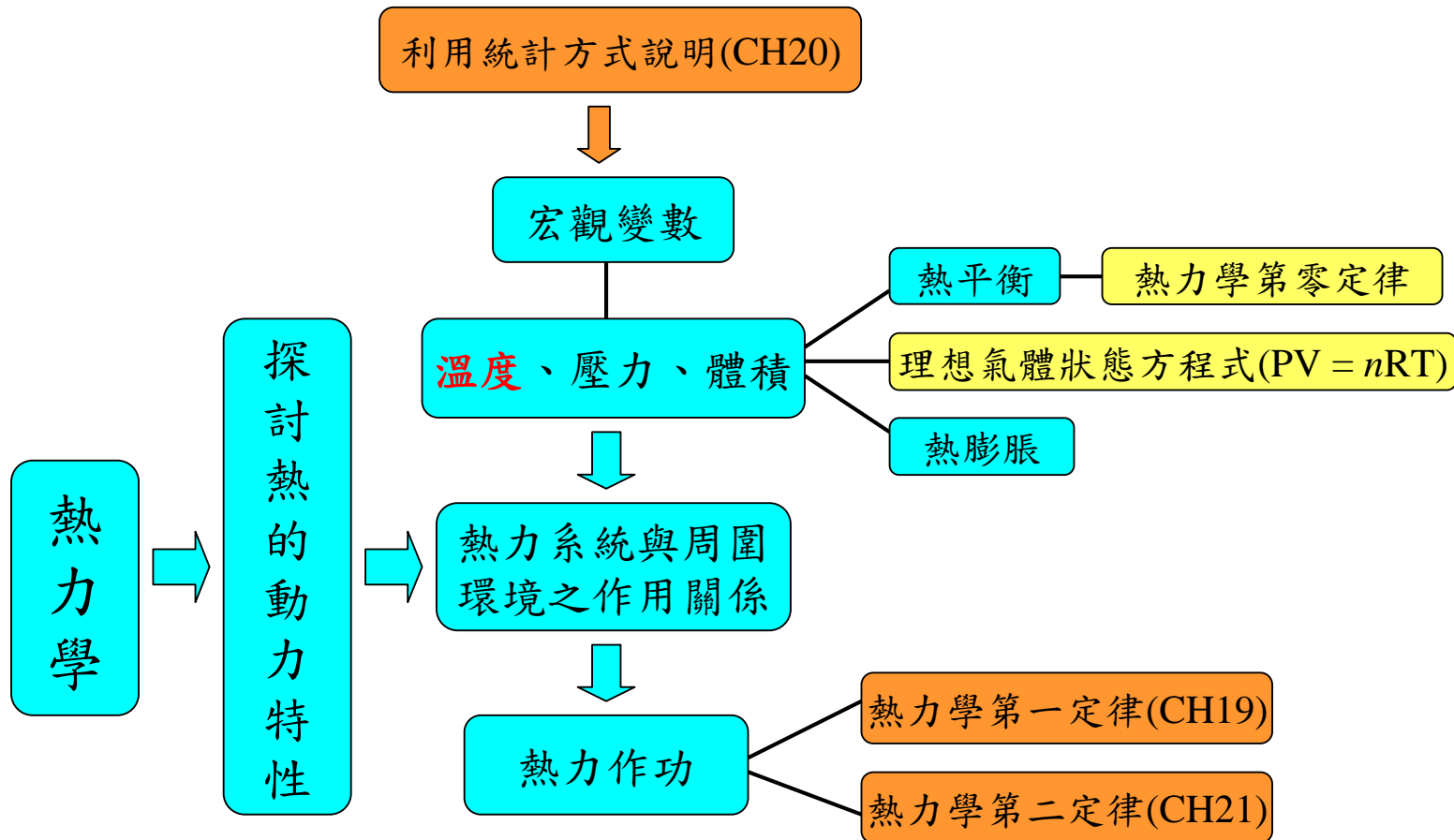


Fig.18.11

本章重要觀念發展脈絡彙整





熱的性質

熱(heat) \Rightarrow 溫度 \Rightarrow 熱質(the caloric theory) \Rightarrow 摩擦(或做功)生熱 \Rightarrow 內能



比熱

- 熱容量(Heat capacity) = $\frac{\Delta Q}{\Delta T}$
- $\Delta Q = mc\Delta T$, c 爲比熱(specific heat)

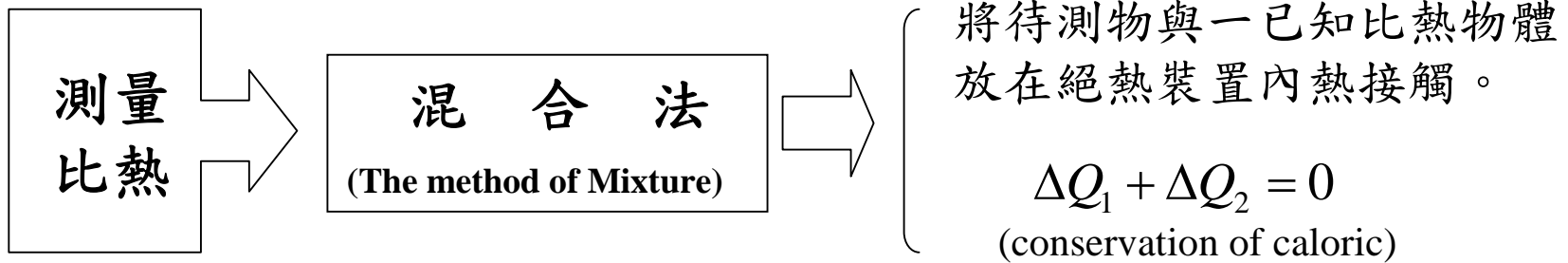
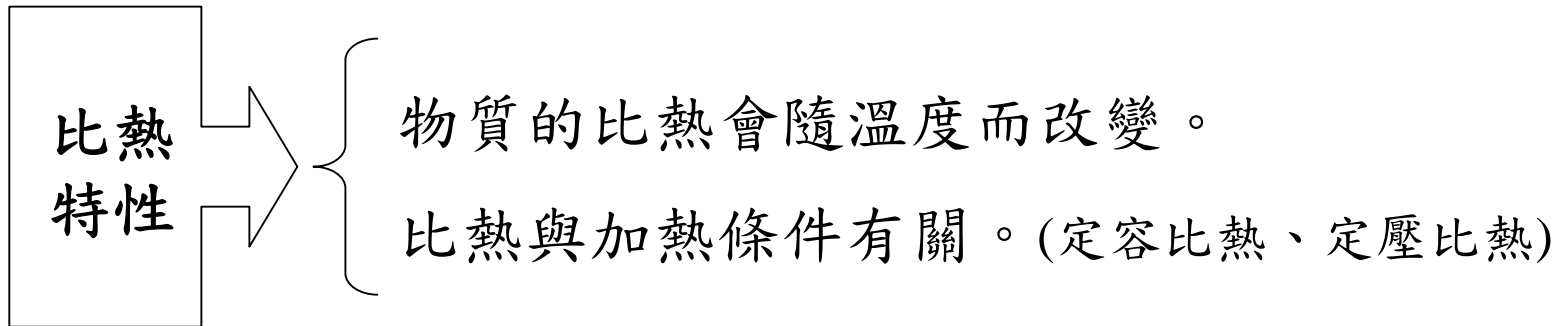
$$\text{熱容量} = \frac{\Delta Q}{\Delta T} = \frac{mc\Delta T}{\Delta T} = mc \Rightarrow c = \frac{1}{m} \frac{\Delta Q}{\Delta T} \text{ (單位質量的熱容量)}$$

- $\Delta Q = nC\Delta T$, C 爲莫耳比熱(molar specific heat)

$$\text{熱容量} = \frac{\Delta Q}{\Delta T} = nC \quad (n = m/M, \text{ } M \text{ 爲分子量})$$

$$\Rightarrow C = \frac{1}{n} \frac{\Delta Q}{\Delta T} \text{ (每莫耳的熱容量)}$$

- c 與 C 之關係 $\Rightarrow nC = mc \Rightarrow C = (m/n)c = Mc$



✦ 潛熱(Latent Heat) — 溫度未改變，但發生相改變。($\Delta Q = mL$)

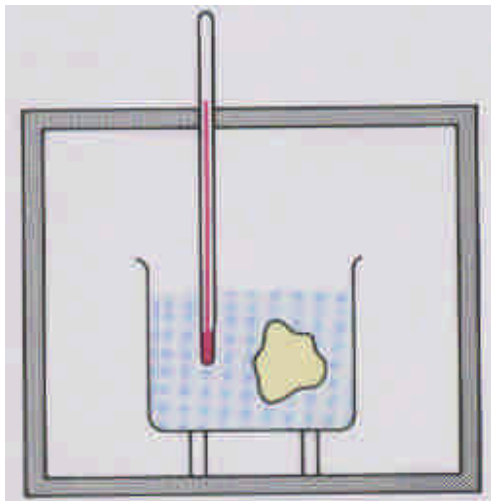


Fig.19.2

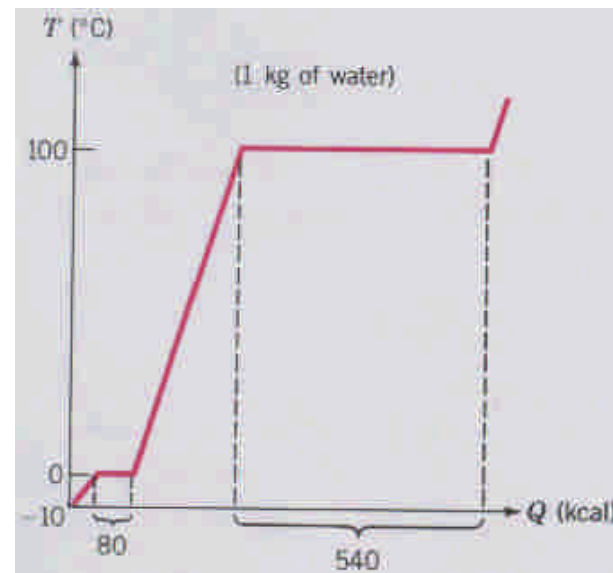


Fig.19.3

TABLE 19.1 SPECIFIC HEATS (20 °C AND 1 ATM)

	c (J/kg·K)	C (J/mol·K)
Aluminum	900	24.3
Copper	385	24.4
Gold	130	25.6
Steel/Iron	450	25.0
Lead	130	26.8
Mercury	140	28.0
Water	4190	75.4
Ice (−10 °C)	2100	38

From 1 Cal=4.186 J , it can be obtained

$$\text{Aluminum} = 900(\text{J/kg} \cdot \text{K}) = 0.9(\text{J/g} \cdot \text{K}) = 0.21(\text{cal/g} \cdot \text{K})$$

$$\text{Copper} = 385(\text{J/kg} \cdot \text{K}) = 0.385(\text{J/g} \cdot \text{K}) = 0.092(\text{cal/g} \cdot \text{K})$$

TABLE 19.2 LATENT HEATS (AT 1 ATM)

	Melting Temperature °C	Latent Heat of Fusion (J/kg)	Boiling Temperature °C	Latent Heat of Vaporization (J/kg)
Aluminum	660	24.5×10^3	2450	$11,390 \times 10^3$
Copper	1083	134×10^3	1187	5065×10^3
Gold	1063	64.5×10^3	2660	1580×10^3
Lead	327	24.5×10^3	1750	870×10^3
Water	0	334×10^3	100	2260×10^3
	K		K	
Helium	3.5	5.23×10^3	4.2	20.9×10^3
Hydrogen	13.8	58.6×10^3	20.3	452×10^3
Nitrogen	63.2	25.5×10^3	77.3	201×10^3
Mercury	234	11.8×10^3	630	272×10^3

$$\text{water} \Rightarrow \begin{cases} \text{Fusion: } 334 \times 10^3 \text{ (J/kg)} \approx 80000 \text{ (cal/kg)} = 80 \text{ (kcal/kg)} \\ \text{Vaporization: } 2260 \times 10^3 \text{ (J/kg)} \approx 540 \text{ (kcal/kg)} \end{cases}$$

✦ 熱功當量(The Mechanical Equivalent of Heat) — Mayer & Joule

- Heat is energy，由溫度差造成能量轉移。

(Work is energy，由位移所造成。)

- $1 \text{ Cal} = 4.186 \text{ J}$ (or $1 \text{ Btu} = 778 \text{ ft}\cdot\text{lb}$)

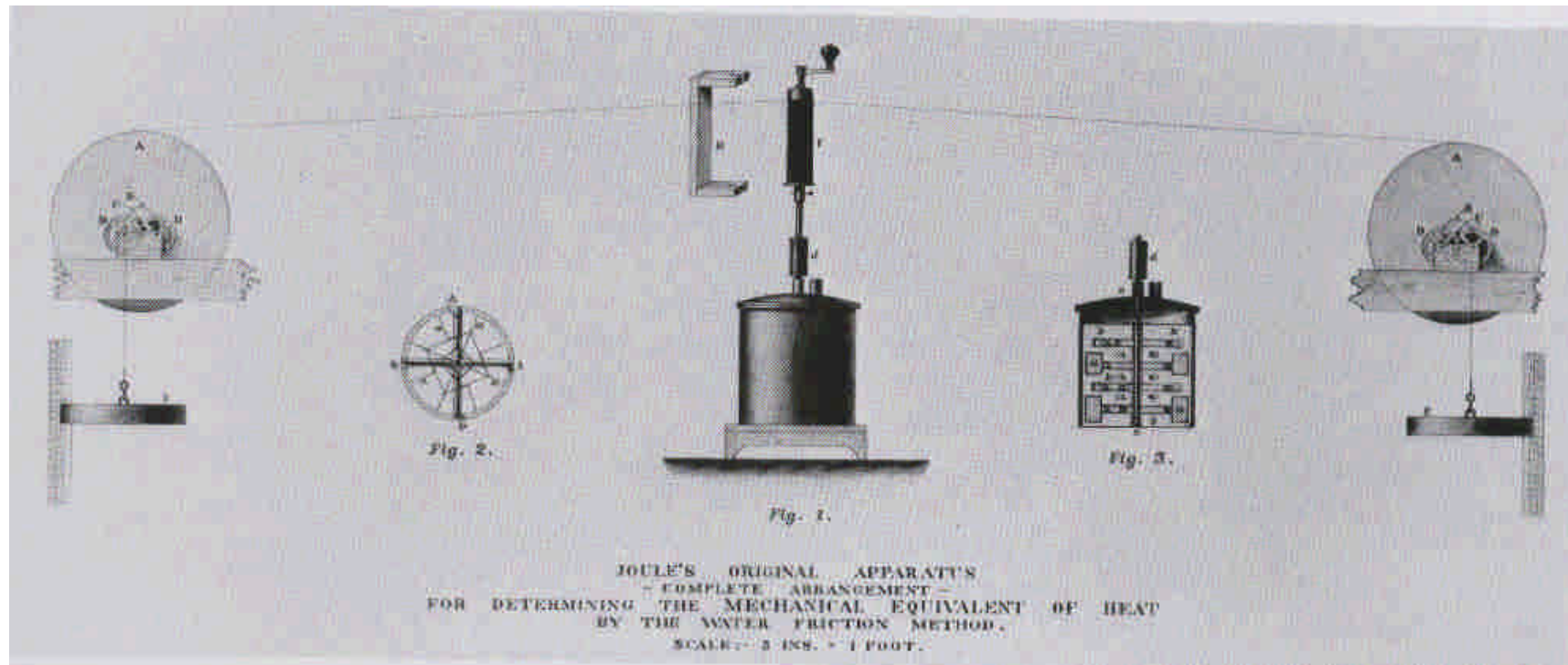


Fig.19.4

✦ Work (功) in Thermodynamics

➤ Quasi-static process (準靜過程) — 近似平衡的過程。

➤ $dW = Fdx = PAdx = PdV \Rightarrow W = \int_{V_i}^{V_f} PdV$ (考慮氣體做功)

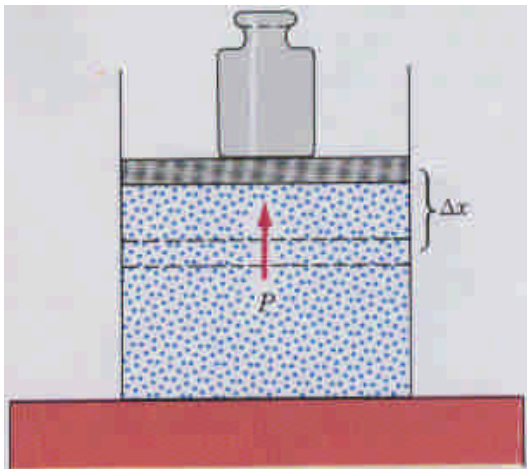


Fig.19.5

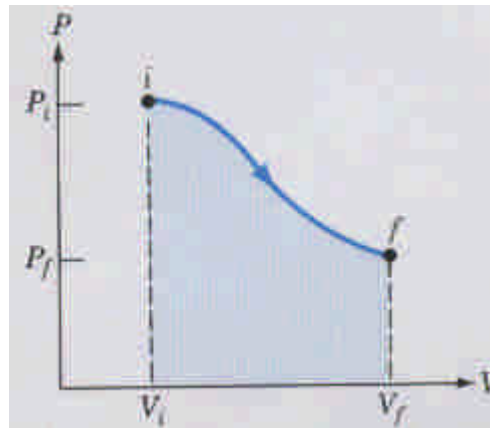
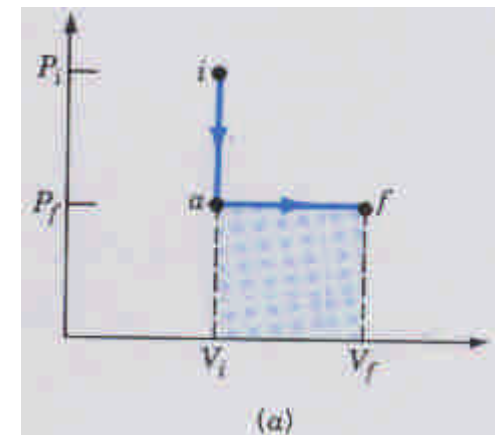


Fig.19.6

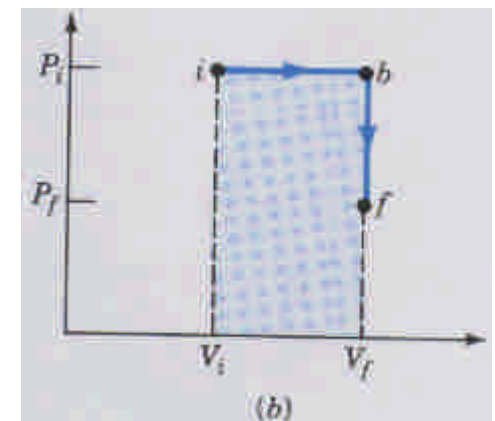


(a)
Fig.19.7

• Isobaric Work (定壓做功) — ($P=\text{const.}$)

1. 熱力路徑不同，做功大小不同。

2. 自由膨脹 (Free expansion) 不會做功。 (see Fig.19.8)



(b)

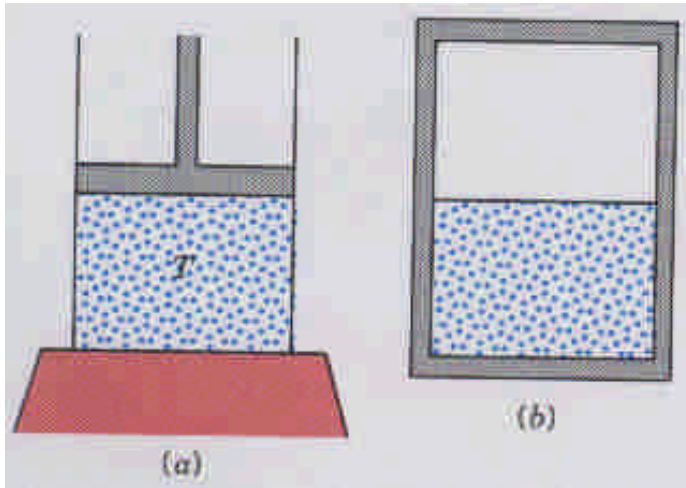


Fig.19.8

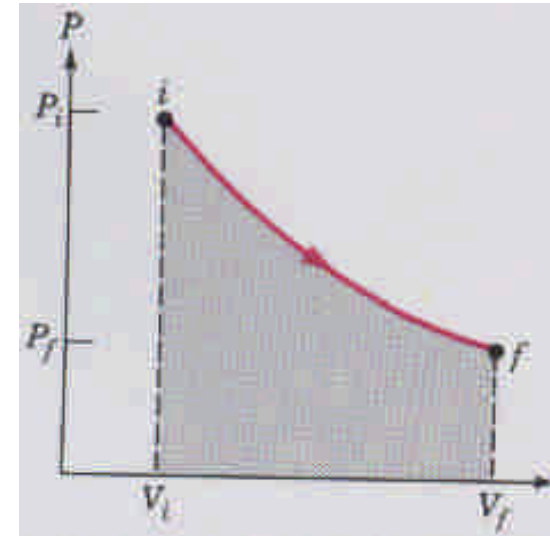


Fig.19.9

- Isothermal Work (定溫作功) – ($T = \text{const.}$)

For ideal gas, $PV = nRT \Rightarrow P = nRT / V$ (see Fig.19.9)

$$W = \int_{V_i}^{V_f} P dV = nRT \int_{V_i}^{V_f} dV / V = nRT \ln(V_f / V_i)$$

- Adiabatic Work (絕熱作功) – ($Q = 0 \Rightarrow \Delta U = -W$)

For ideal gas, $PV^\gamma = K \Rightarrow P = K / V^\gamma$ (參考 Example 19.6)

$$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} K dV / V^\gamma = \frac{K}{\gamma - 1} \left(\frac{1}{V_1^{\gamma-1}} - \frac{1}{V_2^{\gamma-1}} \right) = \frac{1}{\gamma - 1} (P_1 V_1 - P_2 V_2)$$

✦ 熱力學第一定律(The first law of thermodynamics)

$$\Delta U = Q - W \quad ,$$

$$\left\{ \begin{array}{l} \Delta U \text{ 為系統內能變化量 (導入內能觀念)} \\ Q \text{ 為系統與環境交換熱} \\ W \text{ 為系統對環境作功} \end{array} \right.$$

※Note：若考慮環境對系統作功，則 $\Delta U = Q + W$

- 若有摩擦力或熱力過程非準靜，則內能 U 僅與最初或最終的系統平衡狀態有關。
- 內能是所有可能儲藏在系統內各種能量的總合，但不包含與系統質量中心有關的動能與位能。
- 隨機運動相關的動能及位能(即所謂的熱能)，可能來自於部分內能，但內能並非就是熱能。

● Application :

- 孤立系統(Isolated System)

$$Q = 0 \text{ and } W = 0 \Rightarrow \Delta U = 0 \text{ or } U = \text{const.}$$

➤ 循環過程(Cyclic Process)

$$\Delta U = 0 \text{ (狀態未變)} \Rightarrow Q = W$$

➤ 定容過程(Constant-volume Process)

$$W = 0 \text{ (}\because V=\text{const.} \Rightarrow dV=0) \Rightarrow \Delta U = Q$$

➤ 絕熱過程(Adiabatic Process)－類似絕熱做功

$$Q = 0 \text{ (考慮可能的絕熱裝置或過程時間短暫)} \Rightarrow \Delta U = -W$$

➤ 絕熱自由膨脹(Adiabatic free expansion)

$$Q = 0 \text{ and } W = 0 \Rightarrow \Delta U = 0 \text{ (} U=\text{const.} \Rightarrow T=\text{const. for ideal gas)}$$

$$(\because P = 0 \Rightarrow W = \int P dV = 0)$$

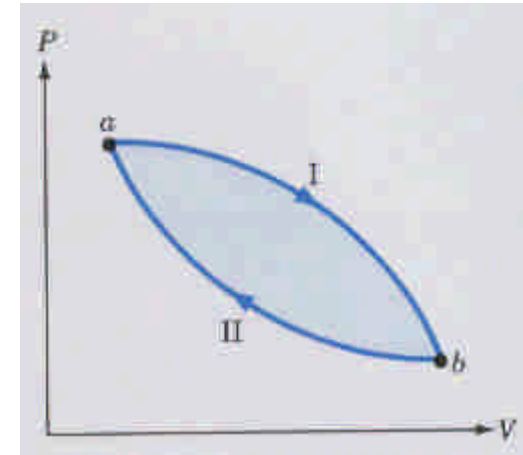


Fig.19.10

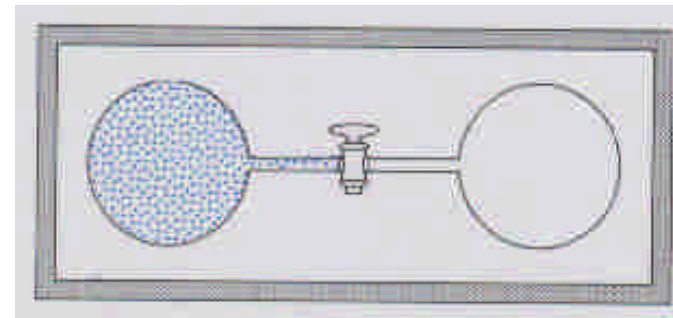


Fig.19.11

✦ 理想氣體(Ideal Gases)

- 比熱(Specific Heats) — C_v 與 C_p 的關係

$$Q_v = nC_v\Delta T$$

$$\Delta U = nC_v\Delta T \quad (\because \text{定容 } V = \text{const.} \Rightarrow W = 0)$$

$$Q_p = nC_p\Delta T$$

$$nC_p\Delta T = \Delta U + W$$

$$nC_p\Delta T = nC_v\Delta T + P\Delta V$$

$$C_p - C_v = R \quad (\because P = \text{const.} \Rightarrow P\Delta V = nR\Delta T)$$

- 絕熱準靜過程(Adiabatic Quasi-static Process)

$$PV^\gamma = \text{const.}, \quad \text{其中 } \gamma = \frac{C_p}{C_v}$$

準靜－考慮微量變化 \Rightarrow 溫度 dT , 體積 dV , $dW=pdV$

$$\begin{aligned}\text{由熱力學第一定律 } \Rightarrow dU &= dQ - dW \xrightarrow{dQ=0} dU = -dW \\ \Rightarrow nC_v dT &= -PdV\end{aligned}\quad (1)$$

$$\begin{aligned}\text{由理想氣體狀態方程 } \Rightarrow PV &= nRT \Rightarrow d(PV) = nRdT \\ \Rightarrow PdV + VdP &= nRdT\end{aligned}\quad (2)$$

$$\begin{aligned}\text{將(1)式代入(2)式，消去}dT \Rightarrow PdV + VdP &= -PRdV / C_v \\ \Rightarrow P(C_v + R)dV + C_v VdP &= 0\end{aligned}$$

$$\begin{aligned}\text{For ideal gas, } C_v + R = C_p \Rightarrow PC_p dV + C_v VdP &= 0 \\ \Rightarrow \left(\frac{C_p}{C_v}\right)PdV + VdP &= 0\end{aligned}$$

$$\begin{aligned}\text{Let } \gamma = \frac{C_p}{C_v} \Rightarrow \gamma \frac{dV}{V} + \frac{dP}{P} &= 0 \Rightarrow \gamma \ln V + \ln P = \text{const.} \Rightarrow \ln V^\gamma + \ln P = \text{const.} \\ \Rightarrow \ln PV^\gamma &= \text{const.} \Rightarrow \textcolor{red}{PV^\gamma = \text{const.}}\end{aligned}$$

- Discussion:

$$d(PV^\gamma) = 0 \Rightarrow V^\gamma dP + \gamma PV^{\gamma-1} dV = 0 \Rightarrow dP/dV = -\gamma P/V$$

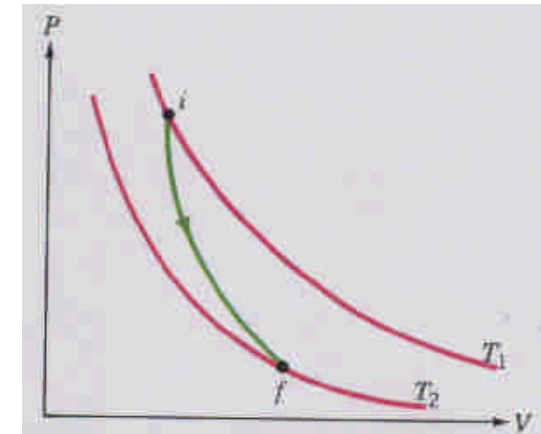
Fig.19.12

For an isothermal process ($\gamma = 1$)

$$\Rightarrow dP/dV = -P/V \Rightarrow PV = \text{const.}$$

For an adiabatic process ($\gamma > 1$)

$$\Rightarrow \gamma = C_p / C_v > 1 \quad (\because C_p > C_v)$$



✦ 熱傳輸(Heat Transport)

- 傳導(conduction) { 藉由原子振盪能量傳輸熱
藉由大量自由電子傳輸熱

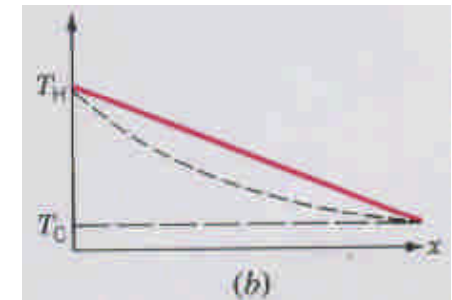


Fig.19.13

$$\frac{dQ}{dt} = -\kappa A \frac{dT}{dx} = \kappa A \frac{T_H - T_C}{L} = A \frac{\Delta T}{R} \quad (R = L/\kappa \text{ 為熱阻(thermal resistance)})$$

其中 κ 為熱傳導率(thermal conductivity), A 為接觸面積, dT/dx 為溫度梯度(通常為負值)

Example:

$$\Delta T = \left(\frac{R}{A} \right) \frac{dQ}{dt} \Rightarrow \Delta T_1 + \Delta T_2 = \frac{1}{A} \left(\frac{L_1}{\kappa_1} + \frac{L_2}{\kappa_2} \right) \frac{dQ}{dt}$$
$$= \frac{1}{A} (R_1 + R_2) \frac{dQ}{dt}$$

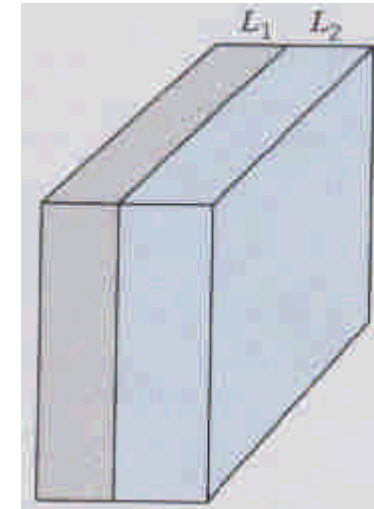


Fig.19.15

●對流(convection) \Rightarrow 藉由分子或原子的集體移動(流體運動)傳輸熱

\Rightarrow { 自然對流(free convection)－流體密度隨溫度改變而造成冷暖空氣流動。
強迫對流(forced convection)－利用風扇或幫浦造成流體流動。

$$\frac{dQ}{dt} = hA\Delta T \quad , \quad h \text{ 爲對流係數}$$

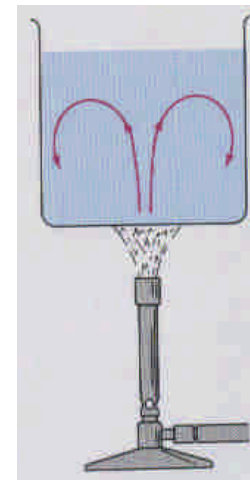


Fig.19.16

●輻射(radiation) \Rightarrow 不需介質參與熱的傳輸，係由電磁波傳輸。

\Rightarrow 物體可同時發射與吸收輻射能，好的發射體也是好的接收體

$$\frac{dQ}{dt} = e\sigma AT^4, \quad \text{其中 } e \text{ 爲發射率(emissivity), } \sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$$

發射率(或吸收率)與物體表面性質有關。

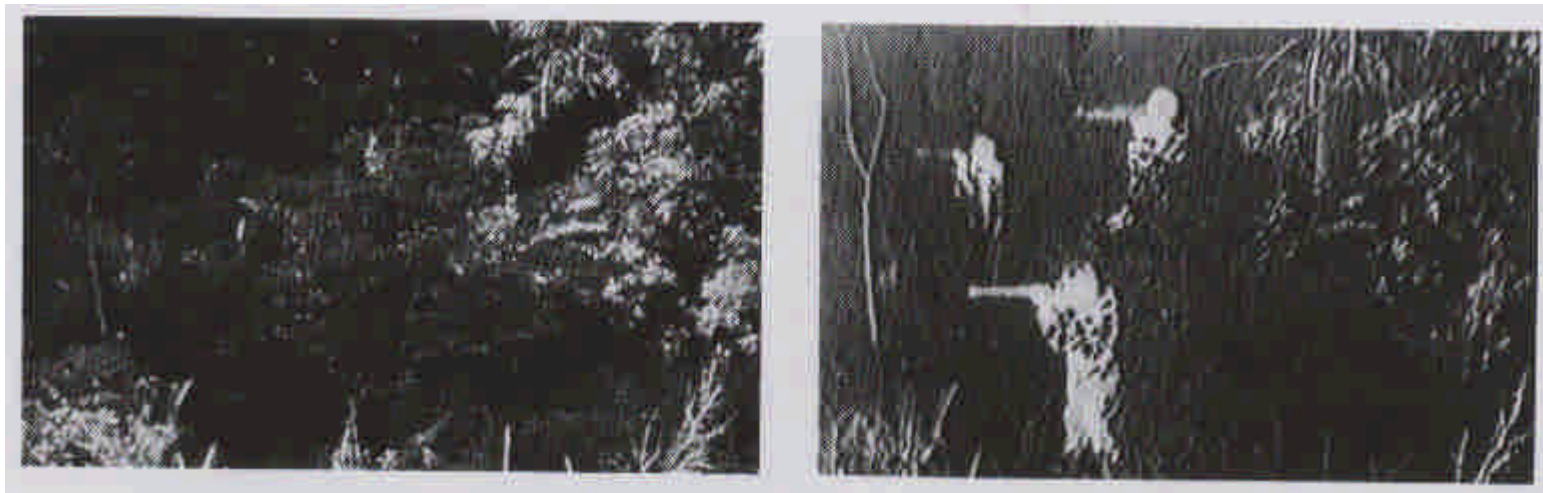


Fig.19.17

本章重要觀念發展脈絡彙整

