

Ch 3 The First Law of Thermodynamics

3.1 Configuration Work

Configuration Work: the work = product of some intensive variables and the change in some extensive variables through a reversible process.

設 Y_i : intensive, X_i : extensive:

$$\delta W = \sum_i Y_i dX_i$$

因 δW 的值與 system 的狀態有關, 故稱作 configuration work.
 $\int \delta W$ 的值與所選的路徑有關, $\oint \delta W \neq 0$

Appendix A

A2 Exact and Inexact Differentials

只有一個獨立變數 $\oint f(x) dx = 0$

proof: 設 $f(x) = \frac{d}{dx} z(x)$



$$\int_a^b f(x) dx = \int_a^b \left(\frac{d}{dx} z(x) \right) dx = z(b) - z(a)$$

$$\oint_C dz = \int_a^b dz + \int_b^a dz = \int_a^b dz - \int_a^b dz = 0$$

有 2 個獨立變數時: $z = z(x, y)$

$$dz = M(x, y) dx + N(x, y) dy$$

如果 $dz = Mdx + Ndy$ 是 exact;

$dz = Mdx + Ndy$ 是 inexact

$$\textcircled{1} \frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

$$\textcircled{1} \frac{\partial M}{\partial y} \neq \frac{\partial N}{\partial x}$$

$$\textcircled{2} \oint_c dz = 0$$

$$\textcircled{2} \oint_c dz \neq 0$$

$$\textcircled{3} \int_a^b dz \text{ is independent of path}$$

$$\textcircled{3} \int_a^b dz \text{ is dependent of path}$$

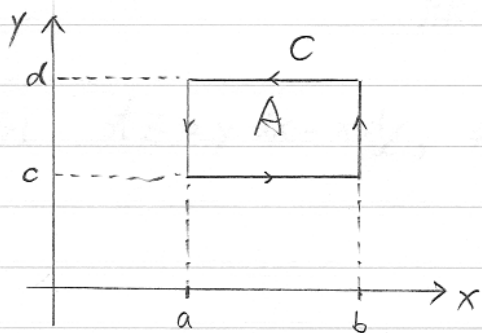
(A.29) P398

In thermodynamics all state variables are exact differentials.

However, some thermodynamic quantities (work, heat) are inexact differentials.

Proof:

在 xy 平面上取一矩形面積.



$$\textcircled{1} \iint_A \frac{\partial N}{\partial x} dx dy = \int_c^d \int_a^b \frac{\partial N}{\partial x} dx dy$$

$$= \int_c^d [N(b, y) - N(a, y)] dy$$

$$= \int_c^d N(b, y) dy + \int_d^c N(a, y) dy$$

$$\boxed{\int_a^b N(x, c) dy = \int_b^a N(x, d) dy = 0} \Rightarrow \oint_c N dy$$

$$\begin{aligned}
 \textcircled{2} \iint_A \frac{-\partial M}{\partial y} dx dy &= - \int_a^b \int_c^d \frac{\partial M}{\partial y} dy dx \\
 &= - \int_a^b [M(x, d) - M(x, c)] dx \\
 &= \int_a^b M(x, d) dx + \int_a^b M(x, c) dx
 \end{aligned}$$

$$\boxed{0 = \int_a^c M(a, y) dy = \int_c^d M(b, y) dy} \Rightarrow = \oint_C M dx$$

$$\textcircled{1}, \textcircled{2} \Rightarrow \oint dZ = \oint_C (M dx + N dy) = \iint_A \left(\frac{\partial N}{\partial x} - \frac{\partial M}{\partial y} \right) dx dy$$

故 $\oint dZ = 0$ 的條件是 $\frac{\partial N}{\partial x} = \frac{\partial M}{\partial y}$, 此時 dZ 稱作 exact.

例: $dZ = \left(\frac{\partial Z}{\partial x} \right) dx + \left(\frac{\partial Z}{\partial y} \right) dy$ 就是 exact, 其 $\frac{\partial}{\partial y} \left(\frac{\partial Z}{\partial x} \right) = \frac{\partial}{\partial x} \left(\frac{\partial Z}{\partial y} \right)$

例: $dZ = y dx - x dy$ 是 inexact. $\frac{\partial}{\partial y}(y) \neq \frac{\partial}{\partial x}(-x)$

Δ An integrating factor: An inexact differential 乘上 an integrating factor 就變為 exact.

例 $dZ = y dx - x dy$, 乘上 $\frac{1}{y^2} \Rightarrow dZ = \frac{dx}{y} - \frac{x}{y^2} dy$ is exact

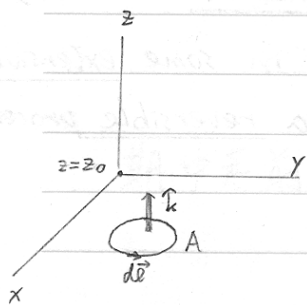
$$\text{where: } \frac{\partial}{\partial y} \left(\frac{1}{y} \right) = \frac{\partial}{\partial x} \left(\frac{-x}{y^2} \right)$$

對於一個 inexact differential 可找到很多個 integrating factor.

若 $dG(x,y) = F_x(x,y,z=z_0)dx + F_y(x,y,z=z_0)dy$

則對 xy 平面上任意封閉路徑積分 $\oint dG = 0$ 必須 $\frac{\partial F_x}{\partial y} = \frac{\partial F_y}{\partial x}$
 $(z=z_0 \text{ 處})$

Proof: 設 $\vec{F}(x,y,z) = F_x(x,y,z)\hat{i} + F_y(x,y,z)\hat{j} + F_z(x,y,z)\hat{k}$



在 $z=z_0$ 的 xy 平面上, 任意選取一平面 A , 由 Stoke theory:

$$\oint \vec{F} \cdot d\vec{r} = \int_A (\nabla \times \vec{F}) \cdot d\vec{a} = \int_A (\nabla \times \vec{F}) \cdot (\hat{k} da)$$

$$\text{因 } \nabla \times \vec{F} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ F_x & F_y & F_z \end{vmatrix} = \hat{i} \left(\frac{\partial F_z}{\partial y} - \frac{\partial F_y}{\partial z} \right) + \hat{j} \left(\frac{\partial F_x}{\partial z} - \frac{\partial F_z}{\partial x} \right) + \hat{k} \left(\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} \right)$$

$$\text{又因 } \vec{F} \cdot d\vec{r} = (F_x\hat{i} + F_y\hat{j} + F_z\hat{k}) \cdot (\hat{i}dx + \hat{j}dy) = F_xdx + F_ydy$$

$$\Rightarrow \oint (F_xdx + F_ydy) = \int_A \left(\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} \right) da$$

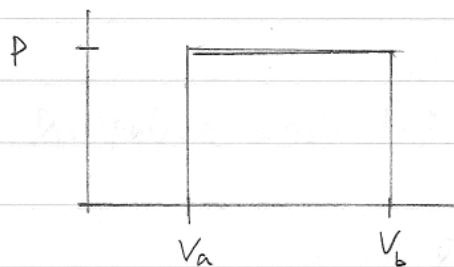
因 $da > 0$, 要求對任意封閉路徑做積分使 $\oint dG = \oint (F_xdx + F_ydy) = 0$

$$\text{必然 } \frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} = 0, \text{ 即 } \frac{\partial F_y}{\partial x} = \frac{\partial F_x}{\partial y}$$

Configuration work listed on TABLE 3.1

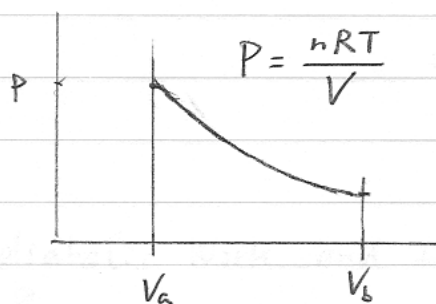
以 ideal gas 膨脹為例說明 $\int P dv = \int \delta W$

① Isobaric process (reversible) from V_a to V_b .



$$W = \int_{V_a}^{V_b} P dv = P(V_b - V_a)$$

② Isothermal process (reversible) from V_a to V_b .



$$\begin{aligned} W &= \int_{V_a}^{V_b} P dv \\ &= \int_{V_a}^{V_b} \frac{nRT}{V} dv \\ &= nRT \ln\left(\frac{V_b}{V_a}\right) \end{aligned}$$

作功與路徑有關。

3.2 Dissipative Work

Reversible process 只有 configuration work.

Irreversible process 有 configuration work + dissipative work.

13.1 Dissipative work 1.: ^{扭矩}Stirring work Fig 3.5 流体中轉動.

$$dW = -\tau d\theta$$

2. Electric work Fig 3.6.

$$dW = -I^2 R dt$$

3.3 Adiabatic Work and Internal Energy

實驗結果

The total work done in all adiabatic process between two equilibrium states is independent of the path.

$$\square \int_a^b dU = U_b - U_a = -\int_a^b dW_{ad} = -W_{ad}$$

$\Rightarrow dU = dW_{ad}$, dU 是 exact, dW_{ad} 必然也是 exact.

實際上 $dU = -dW + dQ$

3.4 Heat

Fig 3.8 (a) 中, 若絕熱, 則 $dU = \delta W_{\text{ad}}$, δW_{ad} is exact now.

Fig 3.8 (b) 中, 若無作功, 則 $dU = \delta Q$, δQ is exact now

若同時有作功及熱流: $dU = -\delta W + \delta Q$.

注意 $\oint dU = 0$.

熱傳播方式: 傳導, 對流, 輻射. 不同溫度間才會有熱流.

無作功, 熱流入物體 $\Rightarrow Q = \Delta U \Rightarrow$
 ① 溫度上升.
 ② 相變化, 冰 \rightarrow 水.

3.5 Units of Heat

SI unit: joule (J)

1 kilocalorie (kcal) \equiv 1 kg 的水由 14.5°C to 15.5°C .

$$1 \text{ J} = 2.39 \times 10^{-4} \text{ kcal}$$

$$1 \text{ kcal} = 4184 \text{ J}$$

3.6 The Mechanical equivalent of Heat

~~無~~ Configuration work, ~~無~~ dissipative work, ~~有~~ heat.

$$\Delta U = Q$$

~~無~~ Configuration work, ~~有~~ dissipative work, ~~無~~ heat.

$$\Delta U = |W_d|$$

兩者等效, 微觀下, 機械能轉到 random 分子動能 \Rightarrow 溫度增加.

3.7 Summary of the First Law.

1. Energy is conserved.

2. U is an extensive state variable.

3. $dU = \delta Q - \delta W$

3.8 Some calculations of work

$$\text{First Law: } \delta W = \delta Q - dU$$

$$\boxed{P, V, T} \quad f(P, V, T) = 0 \quad 2 \text{ 獨立變數} \Rightarrow V = V(T, P)$$

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

$$\text{因 } \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P, \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\Rightarrow dV = \beta V dT - \kappa V dP$$

$$\Rightarrow \delta W = \beta P V dT - \kappa P V dP \quad (\text{useful}) \quad (3.8)$$

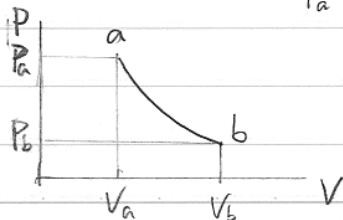
$$\text{例 1. ideal gas: } \beta = \frac{1}{T}, \quad \kappa = \frac{1}{P}$$

$$\text{由 (3.8)} \quad \delta W = PV \frac{dT}{T} - PV \frac{dP}{P} = nR dT - nRT \frac{dP}{P} \quad (3.9)$$

↖ 變數取 T, P, 故將 V 代換掉

For isothermal expansion: $dT = 0$

$$W = -nRT \int_{P_a}^{P_b} \frac{dP}{P} = nRT \ln \frac{P_a}{P_b}, \quad P_a > P_b \text{ 膨脹}$$
$$= nRT \ln \frac{V_b}{V_a}; \quad PV = nRT = \text{常數}$$



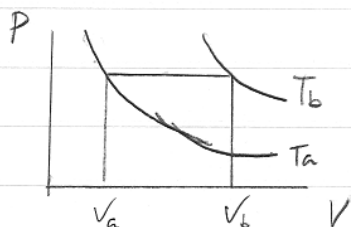
2. For isobaric expansion: $dp=0$

$$W = nR \int_{T_a}^{T_b} dT = nR(T_b - T_a)$$

$$= P(V_b - V_a)$$

$$PV = nRT$$

$$T = \frac{P}{nR} V$$



體積增大來自於溫度上升

例 2. solid, 10g Cu, isothermally quasi-statically compressed at 0°C , from 1 atm to 1000 atm

由(8.8) $dW = -\kappa PV dp$

$$W = -\kappa V \int_{P_i}^{P_f} dp = -\frac{\kappa V}{2} (P_f^2 - P_i^2)$$

↓
近似不變

For copper, $\kappa = 7.5 \times 10^{-12} \text{ Pa}^{-1}$ at 0°C , $\rho = 8.93 \text{ g/cm}^3$

$$\Rightarrow V = \frac{m}{\rho} = \frac{10 \text{ g}}{8.93 \text{ g/cm}^3} = 1.12 \text{ cm}^3 = 1.12 \times 10^{-6} \text{ m}^3$$

$$W = -\frac{\kappa V}{2} (P_f^2 - P_i^2) = -\frac{7.5 \times 10^{-12} \times 1.12 \times 10^{-6}}{2} \left[(1.01 \times 10^8)^2 - 1 \right]$$

$$= -4.3 \times 10^{-2} \text{ J}$$

↑ Cu塊對外界作負功, 外界對Cu作正功.