

Ch 4 Applications of the First Law

4.1 Heat Capacity

A process, 將 Q 加入 system, system 由一個平衡態轉到另一個平衡態, 伴隨溫度上升 ΔT , 定義 The heat capacity

$$C \equiv \lim_{\Delta T \rightarrow 0} \left(\frac{Q}{\Delta T} \right) = \frac{dQ}{dT}$$

The heat capacity is not truly a derivative,

because Q is not a state variable, and dQ is not an exact differential. C 的值與 process 的條件有關.

Specific heat: $c \equiv \frac{1}{n} \left(\frac{dQ}{dT} \right) = \frac{d\epsilon}{dT} \quad \frac{J}{\text{kmole} \cdot K}$

(1) At constant volume: $C_v \equiv \left(\frac{d\epsilon}{dT} \right)_v$

(2) At constant pressure: $C_p \equiv \left(\frac{d\epsilon}{dT} \right)_p$

Fig 4.1

P5-4

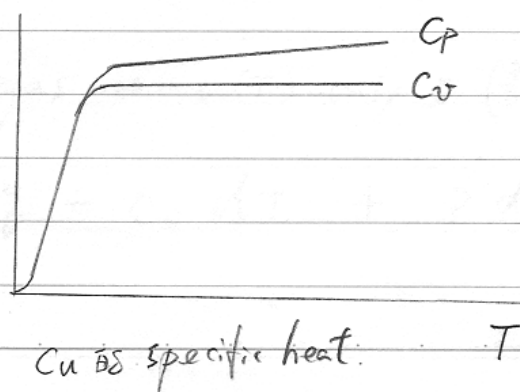


Fig 16.1, P281

Law of Dulong-Petit

4.2 Mayer's eq.

To find the relationship between c_v and c_p for an ideal gas.

For a reversible process, the first law

$$dU = \delta Q - PdV \quad (4.3)$$

$$du = \delta q - p dv \quad (4.4)$$

P, v, T

$$u = u(v, T) \quad (4.5)$$

取 v, T 為獨立變數
才能求 c_v

$$pv = RT \quad (4.6)$$

$$\text{由 (4.5)} \quad du = \left(\frac{\partial u}{\partial v}\right)_T dv + \left(\frac{\partial u}{\partial T}\right)_v dT \quad (4.7)$$

$$(4.7) \text{ 代入 (4.4)} \Rightarrow \delta q = \left(\frac{\partial u}{\partial T}\right)_v dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right] dv \quad (4.8)$$

$$c_v \equiv \left(\frac{\delta q}{dT}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v \quad (\text{定容, 不作功, } \delta q = du) \quad (4.9)$$

$$\Rightarrow \delta q = c_v dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right] dv$$

For an ideal gas $u = u(T)$ only $\therefore \left(\frac{\partial u}{\partial v}\right)_T = 0$

$$\Rightarrow \delta q = c_v dT + p dv \quad (4.11)$$

欲將變數由 v 換成 p , 用 $Pv = RT$

$$\Rightarrow Pdv + vdp = R dT$$

$$\Rightarrow Pdv = R dT - vdp \quad \text{代入 (4.11) 換掉 } dv$$

$$\Rightarrow d\epsilon = C_v dT + R dT - vdp$$

$$= (C_v + R) dT - vdp$$

$$C_p \equiv \left(\frac{d\epsilon}{dT} \right)_p = C_v + R.$$

$$\Rightarrow C_p = C_v + R \quad \text{Mayer's eq} \quad (4.14)$$

定義 The ratio of specific heat capacities $\gamma \equiv \frac{C_p}{C_v}$

在室溫, for monatomic gas $C_p = \frac{5}{2}R$, $C_v = \frac{3}{2}R$, $\gamma = 1.67$

for diatomic gas $C_p = \frac{7}{2}R$, $C_v = \frac{5}{2}R$, $\gamma = 1.40$.

Ideal gas 內部, 因 $u(T)$ only. $C_v = \left(\frac{\partial u}{\partial T} \right)_v = \frac{du}{dT}$

$$du = C_v dT \Rightarrow u - u_0 = \int_{T_0}^T C_v dT$$

$$\text{若 } C_v \text{ 與 } T \text{ 無關} \Rightarrow u = u_0 + C_v (T - T_0) \quad (4.16)$$

各種氣體在^(可用)理想氣體近似, p, T range 中均可用上式.

4.3 Enthalpy and Heat of Transformation,

The heat of transformation is the heat transfer accompanying a phase change, 相變所吸收的熱。

A phase change is an isothermal and isobaric process, but the volume changes.

相變過程對外作功 $W = p(v_2 - v_1)$

內能微元變量 $du = \sigma_f - p dv$

相變過程之內能總變量： $(u_2 - u_1) = l - p(v_2 - v_1)$
 \uparrow 總吸熱

$l = (u_2 + Pv_2) - (u_1 + Pv_1)$ is latent heat (潛熱) of transform per kilomole associated with a given phase change.

定義 能量函數 h : specific enthalpy

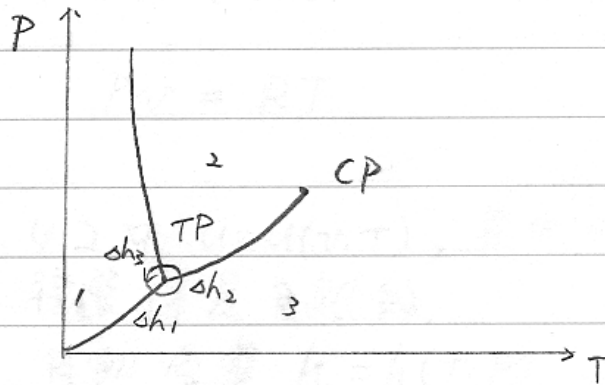
$$h \equiv u + pv, \quad h \text{ is state variable.}$$

$$\Rightarrow \mathcal{L} = h_2 - h_1$$

相變所吸收的熱為兩相 enthalpy 的差

因 h is state function: $\oint dh = 0$.

例 1



極接近 TP, 繞 TP - 圈. 會經過 3 個相變:

solid \rightarrow vapor

$$\Delta h_1 = l_{13}$$

vapor \rightarrow liquid

$$\Delta h_2 = l_{32} = -l_{23}$$

liquid \rightarrow solid

$$\Delta h_3 = l_{21} = -l_{12}$$

$$\oint dh = 0 = \Delta h_1 + \Delta h_2 + \Delta h_3$$

$$\Rightarrow 0 = l_{13} - l_{23} - l_{12}$$

例 2 TABLE 4.1 冰昇華 $l_{13} = l_{12} + l_{23}$

$$= 80 + 538$$

latent heat of fusion = 80

$$= 618 \text{ kcal/kg}$$

TABLE 4.1 Latent heats of vaporization and fusion for various substances.

| Latent Heat of Vaporization at Steam Point, 1 atm | | Latent Heat of Fusion at Melting Point, 1 atm | |
|--|-------------|--|------------|
| Water | 538 kcal/kg | Water | 80 kcal/kg |
| Mercury | 63 | Mercury | 3 |
| Alcohol | 207 | Lead | 5 |
| Gasoline | 95 | Aluminum | 77 |

4.4 Relationships involving Enthalpy

Enthalpy 是針對相變設計出來的 ($dh=l$), 本節要研究無相變 ideal gas 的

$$\boxed{P \ v \ T} \quad Pv = RT$$

在 section 4.2 中 $u=u(v, T)$, 其中 v, T 是任意變的。之後將會發現這種選擇是自然的。

同樣的, 自然會選 $h=h(T, P)$

用 $h(T, P)$ 來研究 ideal gas 的 c_p . (在無相變狀況下)

已知 $\left[\begin{array}{l} \sigma \delta = du + Pdv \end{array} \right. \quad (4.20)$

定義 $\left[\begin{array}{l} h = u + Pv \end{array} \right. \quad (4.21)$ 要將 $\sigma \delta$ 換成以 h 為函數
T, P 為獨立變

$$\text{因 } h=h(T, P) \Rightarrow dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP \quad (4.22)$$

$$\begin{aligned} \text{由 (4.21)} \Rightarrow & \left[\begin{array}{l} dh = du + Pdv + vdp \\ du + Pdv = dh - vdp \end{array} \right. \quad (4.23) \end{aligned}$$

$$\text{代入 (4.20)} \Rightarrow \sigma \delta = dh - vdp$$

$$(4.22) \text{ 代入上式} \Rightarrow \sigma \delta = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP - vdp \quad (4.25)$$

$$\Rightarrow c_p \equiv \left(\frac{\sigma \delta}{dT}\right)_P = \left(\frac{\partial h}{\partial T}\right)_P \quad (4.26)$$

$$\sigma \delta = c_p dT + \left[\left(\frac{\partial h}{\partial P}\right)_T - v \right] dp$$

For an ideal gas $h = h(T)$ only, $\Rightarrow \left(\frac{\partial h}{\partial p}\right)_T = 0$. (ch5 會再說明)

$$(4.25) \Rightarrow \delta q = c_p dT - v dp \quad (4.28)$$

也因 $c_p = \left(\frac{\partial h}{\partial T}\right)_p = \frac{dh}{dT}$

$$\Rightarrow dh = c_p dT$$

$$h = h_0 + c_p(T - T_0) \quad (4.29)$$

4.5 Comparison of u and h

| | Internal energy u | Enthalpy h |
|--------------------|---|---|
| Reversible Process | $du = \delta q - p dv$ $c_v = \left(\frac{\partial u}{\partial T}\right)_v$ | $dh = \delta q + v dp$ $c_p = \left(\frac{\partial h}{\partial T}\right)_p$ |
| Ideal gas | $\delta q = c_v dT + p dv$ $\left(\frac{\partial u}{\partial v}\right)_T = 0$ $u - u_0 = \int_{T_0}^T c_v dT$ | $\delta q = c_p dT - v dp$ $\left(\frac{\partial h}{\partial p}\right)_T = 0$ $h - h_0 = \int_{T_0}^T c_p dT$ |

4.6 Work done in an Adiabatic Process for an ideal gas.

Specific work w done in an isobaric process is: $P(v_2 - v_1)$

in an isothermal process is: $RT \ln\left(\frac{v_2}{v_1}\right)$

$$P_1 v_1 = P_2 v_2 = RT$$

To find the specific work done in an adiabatic process for an ideal gas.

$$\text{由 } d\zeta = c_p dT - v dp = 0 \Rightarrow c_p dT = v dp \quad (4.31)$$

$$\text{由 } d\zeta = c_v dT + p dv = 0 \Rightarrow c_v dT = -p dv \quad (4.32)$$

$$\Rightarrow \frac{v dp}{p dv} = \frac{-c_p}{c_v} = -\gamma, \quad (\gamma > 1).$$

$$\Rightarrow \frac{dp}{p} = -\gamma \frac{dv}{v}$$

$$\ln \frac{P_f}{P_i} = -\gamma \ln \frac{v_f}{v_i}$$

$$\ln \frac{P_f}{P_i} + \ln \left(\frac{v_f}{v_i}\right)^\gamma = 0$$

$$\ln \frac{P_f v_f^\gamma}{P_i v_i^\gamma} = 0$$

绝热 ideal gas.

$$P_f v_f^\gamma = P_i v_i^\gamma \Rightarrow P v^\gamma = K = \text{常数} \quad (4.34)$$

The work done in an adiabatic process for an ideal gas is

$$\begin{aligned}
 w &= \int p \, dv = K \int_{v_1}^{v_2} v^{-\gamma} \, dv = \frac{1}{1-\gamma} (K v^{1-\gamma}) \Big|_{v_1}^{v_2} \\
 &= \frac{K}{1-\gamma} (v_2^{1-\gamma} - v_1^{1-\gamma}) \\
 &= \frac{1}{1-\gamma} (P_2 v_2 - P_1 v_1) \quad (4.35) \\
 &= \frac{R}{\gamma-1} (T_1 - T_2)
 \end{aligned}$$

前面曾得到 $w = u_2 - u_1 = C_v(T_2 - T_1)$ for an ideal gas (4.16)

在 an adiabatic process

Ideal monatomic gas: $C_v = \frac{3}{2}R$, $C_p = \frac{5}{2}R$, $\gamma = \frac{5}{3}$.

例: 初始 $P_1 = 8 \text{ atm}$, $V_1 = 4 \text{ m}^3$, $T_1 = 400 \text{ K}$.

绝热膨胀到 $P_2 = 1 \text{ atm}$.

求 V_2 , T_2 , W , and ΔU

For an adiabatic process: $P_1 V_1^\gamma = P_2 V_2^\gamma \Rightarrow V_2 = V_1 \left(\frac{P_1}{P_2} \right)^{1/\gamma} = 13.9 \text{ m}^3$

For an ideal gas $\begin{cases} P_1 V_1 = n R T_1 \\ P_2 V_2 = n R T_2 \end{cases} \Rightarrow T_2 = \frac{P_2 V_2}{P_1 V_1} T_1 = \frac{1}{8} \frac{13.9}{4} 400 = 174$

$$\begin{aligned}
 W &= \frac{1}{1-\gamma} (P_2 V_2 - P_1 V_1) = \frac{1}{1-1.67} [(1.013)(13.9) - (8)(1.013)(4)] \times 10^5 \\
 &= 2.74 \times 10^6 \text{ J}
 \end{aligned}$$

因 $Q=0$, $\Delta U = -W = -2.74 \times 10^6 \text{ J}$

$$\begin{aligned}
 \text{由 } \Delta U &= C_v(T_2 - T_1) = n \left(\frac{3R}{2} \right) (T_2 - T_1) = \frac{P_1 V_1}{R T_1} \left(\frac{3R}{2} \right) (T_2 - T_1) \\
 &= -2.74 \times 10^6 \text{ J}
 \end{aligned}$$