

Ch 7 Applications of the Second Law.

7.1 Entropy Changes in Reversible Processes

1st Law: $dq_r = du + p dv$

$$\frac{dq_r}{T} = \frac{du}{T} + \frac{p}{T} dv = ds$$

考慮數種可逆過程的 ΔS :

1. Adiabatic process:

$dq_r = 0$, $ds = 0$, $s = \text{constant}$, isentropic process.

2. Isothermal process:

$$s_2 - s_1 = \int_1^2 \frac{dq_r}{T} = \frac{1}{T} \int_1^2 dq_r = \frac{q_r}{T} \quad (7.3)$$

3. Isothermal (and isobaric) change of phase:

$$s_2 - s_1 = \frac{l}{T}, \quad l \text{ is the latent heat.} \quad (7.4)$$

4. Isochoric process:

(4.8)

廣義定 $u = u(v, T)$, 定容下 $u = u(T)$ 如同 ideal gas: $du = dq_r = C_v dT$

$$s_2 - s_1 = \int_1^2 \frac{dq_r}{T} = \int_1^2 C_v \frac{dT}{T} = C_v \int_1^2 \frac{dT}{T} = C_v \ln \frac{T_2}{T_1} \quad (7.5)$$

5. Isobaric process:

1° $h = u + Pv$

$dh = du + Pdv + vdp$ } 將變數由 (u, v) 換成 (h, p)

2° $dq_r = du + Pdv$ } $\Rightarrow \frac{dq_r}{T} = \frac{dh}{T} - \frac{v}{T} dp = d$

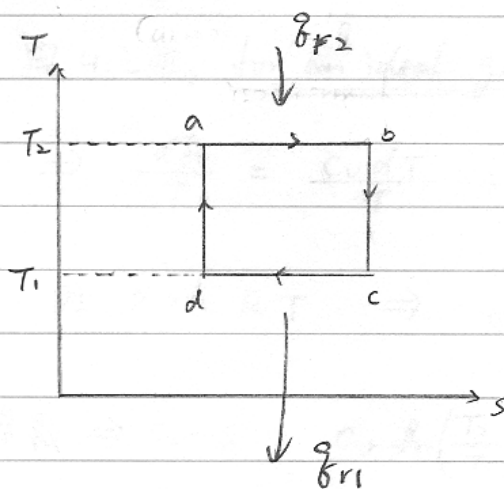
廣義設 $h = h(p, T)$, 定壓下 $h = h(T)$, $dh = dq_r = c_p dT$ (4.25)

$$s_2 - s_1 = \int_1^2 \frac{dq_r}{T} = \int_1^2 c_p \frac{dT}{T} = c_p \ln\left(\frac{T_2}{T_1}\right) \quad (7.6)$$

7.2 Temperature - Entropy Diagrams

The total quantity of heat transferred in a reversible process from state 1 to state 2:

$$q_r = \int_1^2 T ds$$



Carnot cycle

$a \rightarrow b$: isothermal expansion

$b \rightarrow c$: adiabatic expansion

$c \rightarrow d$: isothermal compression

$d \rightarrow a$: adiabatic compression

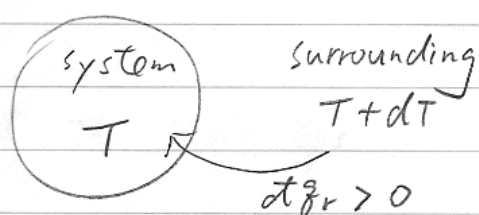
$$\oint T ds = \oint dq_r = |q_{r2}| - |q_{r1}|$$

|| $\oint du = 0$

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7.3 Entropy Change of the Surroundings for a Reversible Process

The temperatures of the system and the surroundings are essentially equal.



$$(ds)_{\text{surrounding}} = \frac{-dQ_r}{T+dT} \doteq -\frac{dQ_r}{T}$$

$$(ds)_{\text{system}} = \frac{dQ_r}{T} > \frac{dQ_r}{T+dT}$$

$$(ds)_{\text{universe}} = (ds)_{\text{surrounding}} + (ds)_{\text{system}} =$$

In any reversible process, $(\Delta S)_{\text{universe}}$ is always 0, but all natural process are irreversible and entropy is not conserved in general.

7.4 Entropy change for an Ideal Gas

由 4.2 節, for an ideal gas, (4.11) $dQ_r = C_v dT + P dv$

$$\Rightarrow \frac{dQ_r}{T} = \frac{C_v dT}{T} + \frac{P}{T} dv = ds \quad (7.7)$$

$$\text{因 } Pv = RT \Rightarrow ds = C_v \frac{dT}{T} + R \frac{dv}{v}$$

$$\text{如果 } C_v \text{ 是常數} \Rightarrow s_2 - s_1 = C_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right) \quad (7.8)$$

Consider the isentropic expansion of a gas. (reversible)

$$0 = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right)$$

$v_2 > v_1$ 必須 $T_2 < T_1$ 來補。

7.5 The Tds Eqs.

From the combined 1st and 2nd laws; $Tds = du + PdV$ (7.9), we can obtain some powerful results known as the "Tds eqs." as follows:

P, v, T 一般 ~~理想~~ 氣體有 3 個巨觀量, 任選 2 個出來算 Tds:

$$Tds = c_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv = c_v dT + \frac{TP\beta}{\kappa} dv, \quad s = s(T, v). \quad (7.10)$$

$$Tds = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp = c_p dT - Tv\beta dp, \quad s = s(T, p). \quad (7.11)$$

$$Tds = c_p\left(\frac{\partial T}{\partial v}\right)_p dv + c_v\left(\frac{\partial T}{\partial p}\right)_v dp = \frac{c_p}{\beta v} dv + \frac{c_v \kappa}{\beta} dp, \quad s = s(v, p). \quad (7.12)$$

這些 Tds eqs 有用途: ① 給出可逆過程的熱傳量。

② 可算出 entropy

③ The heat flow & entropy 都是由可測量 c_p, β, κ, T 展開

④ 可用來決定 c_v, c_p 的差。

⑤ $ds=0$ 時, 可成為 2 獨立變數的關係式。

推導 (7.10) $s = s(T, v)$ 變數換成 (T, v) , 係數換成 β, κ, c_v, c_p

$$T ds = du + p dv \quad \downarrow$$

$$= \underbrace{\left(\frac{\partial u}{\partial T}\right)_v}_{\downarrow (4.9)} dT + \underbrace{\left(\frac{\partial u}{\partial v}\right)_T}_{\downarrow (6.26)} dv + p dv$$

$$= c_v dT + T \left(\frac{\partial p}{\partial T}\right)_v dv$$

$$\boxed{\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p} \Rightarrow = c_v dT - T \left[\frac{\left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_T} \right] dv$$

$$\boxed{\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T} = c_v dT + T \frac{\beta}{\kappa} dv \quad \text{得證 (7.10)}$$

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推導 (7.11) $s = s(T, p)$

1. law: $T ds = du + p dv$

因 $h = u + p v \Rightarrow du = dh - p dv - v dp$

$$\Rightarrow T ds = dh - v dp$$

$$T ds = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp - v dp$$

$$\Rightarrow ds = \frac{1}{T} \left(\frac{\partial h}{\partial T}\right)_p dT + \frac{1}{T} \left(\frac{\partial h}{\partial p}\right)_T dp - \frac{v}{T} dp$$

$$ds \text{ is exact differential} \Rightarrow \frac{\partial}{\partial p} \left[\frac{1}{T} \left(\frac{\partial h}{\partial T}\right)_p \right] = \frac{\partial}{\partial T} \left[\frac{1}{T} \left(\frac{\partial h}{\partial p}\right)_T - \frac{v}{T} \right]$$

$$\Rightarrow \frac{1}{T} \left(\frac{\partial^2 h}{\partial p \partial T} \right) = \frac{-1}{T^2} \left(\frac{\partial h}{\partial p}\right)_T + \frac{1}{T} \left(\frac{\partial^2 h}{\partial T \partial p} \right) + \frac{v}{T^2} - \frac{1}{T} \left(\frac{\partial v}{\partial T}\right)_p$$

$$\Rightarrow \left(\frac{\partial h}{\partial p}\right)_T = -T \left(\frac{\partial v}{\partial T}\right)_p + v \quad (7.17)$$

$$\begin{aligned}
 (7.12) \text{ 代入 } (7.13) &\Rightarrow T ds = \underbrace{\left(\frac{\partial h}{\partial T}\right)_P}_{\downarrow (4.26)} dT - T \left(\frac{\partial v}{\partial T}\right)_P dP \\
 &= C_p dT - T \left(\frac{\partial v}{\partial T}\right)_P dP \\
 \left(\frac{\partial v}{\partial T}\right)_P &= v \beta \\
 &= C_p dT - T v \beta dP \quad \text{得證(7.11)}
 \end{aligned}$$

推導 (7.12)

$$\text{由 (7.10)} \quad T ds = C_v dT + T \left(\frac{\partial P}{\partial T}\right)_v dv$$

$$ds = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

$$dv=0 \text{ 時, } \xrightarrow{\text{只有1獨立變數}} ds = \frac{C_v}{T} dT \xRightarrow{\text{轉像後改寫}} ds = \frac{C_v}{T} \left(\frac{dT}{dT}\right)_v$$

$$\Rightarrow \left(\frac{\partial S}{\partial P}\right)_v = \frac{C_v}{T} \left(\frac{\partial T}{\partial P}\right)_v$$

$$\text{由 (7.11)} \quad T ds = C_p dT - T \left(\frac{\partial v}{\partial T}\right)_P dP$$

$$dP=0 \text{ 時, } \xrightarrow{\text{只有1獨立變數}} ds = \frac{C_p}{T} dT \Rightarrow ds = \frac{C_p}{T} \left(\frac{dT}{dT}\right)_P$$

$$\Rightarrow \left(\frac{\partial S}{\partial v}\right)_P = \frac{C_p}{T} \left(\frac{\partial T}{\partial v}\right)_P$$

$$\Rightarrow ds = \left(\frac{\partial S}{\partial P}\right)_v dP + \left(\frac{\partial S}{\partial v}\right)_P dv = \frac{C_v}{T} \left(\frac{\partial T}{\partial P}\right)_v dP + \frac{C_p}{T} \left(\frac{\partial T}{\partial v}\right)_P dv$$

$$\Rightarrow T ds = C_v \left(\frac{\partial T}{\partial P}\right)_v dP + C_p \left(\frac{\partial T}{\partial v}\right)_P dv = \frac{C_v \kappa}{\beta} dP + \frac{C_p}{\beta v} dv$$

P115, 例: One kilomole of an ideal gas, reversible isothermal, from P_1 to P_2 ,
find the quantity of heat transferred

isothermal.

3個 Tds eqs 中 變數 T, P . (7.11)
from P_1 to P_2 .

$$Tds = C_p dT - Tv\beta dp \xrightarrow[\beta = \frac{1}{T} \text{ for an ideal gas}]{dT=0} Tds = -vdp = -\frac{RT}{P} dp$$

$$\Rightarrow q_r = \int Tds = -RT \int_{P_1}^{P_2} \frac{dp}{P} = -RT \ln \frac{P_2}{P_1}$$

$P_2 < P_1$ 時, 吸熱, 對外作功.

$P_2 > P_1$ 時, 放熱, 外界對系統作功.

P115 例: 求 $C_p - C_v$. C_p 易由實驗得到, C_v 則由理論求得.

$$\text{由 (7.11) = (7.10)} \Rightarrow C_p dT - Tv\beta dp = C_v dT + \frac{TP}{K} dv$$

$$\Rightarrow dT = \frac{Tv\beta}{(C_p - C_v)} dp + \frac{TP}{K(C_p - C_v)} dv$$

$$\text{又 } dT = \left(\frac{\partial T}{\partial P}\right)_v dp + \left(\frac{\partial T}{\partial v}\right)_P dv$$

$$\Rightarrow \left[\begin{array}{l} \frac{1}{v\beta} \left(\frac{\partial T}{\partial v}\right)_P = \frac{TP}{K(C_p - C_v)} \\ \left(\frac{\partial T}{\partial P}\right)_v = \frac{Tv\beta}{(C_p - C_v)} \end{array} \right] \text{兩式都得到同樣結果} \Rightarrow C_p - C_v = \frac{Tv\beta^2}{K} \quad (7.19)$$

For an ideal gas, $\beta = \frac{1}{T}$, $K = \frac{1}{P}$

$$\Rightarrow C_p - C_v = \frac{Pv}{T} = R$$

P116 例, 求固体的 specific heat capacity c_v .

已知 Cu at 1000 °K, at 1 atm, 其 $c_p = 29 \times 10^3 \text{ J/kilomole} \cdot ^\circ\text{K}$.

$$\kappa = 9.5 \times 10^{-12} / \text{Pa}$$

$$\beta = 6.5 \times 10^{-5} / ^\circ\text{K}$$

$$\text{先求 } v = \frac{V}{n} = \frac{m}{n\rho} = \frac{63.6 \text{ kg/kilomole}}{8.96 \times 10^3 \text{ kg/m}^3} = 7.1 \times 10^{-3} \text{ m}^3/\text{kilomole}$$

$$\begin{aligned} \text{由 (7.19)} \Rightarrow c_v &= c_p - \frac{T v \beta^2}{\kappa} = 29 \times 10^3 - \frac{1000 \times (7.1 \times 10^{-3}) \times (6.5 \times 10^{-5})^2}{9.5 \times 10^{-12}} \\ &= 29 \times 10^3 - 3.2 \times 10^3 = 25.8 \times 10^3 \text{ J/kilomole} \cdot ^\circ\text{K} \end{aligned}$$

P117 例 可逆絕熱, $ds = 0$.

$$\text{由 (7.12)} \quad 0 = T ds = \frac{c_p}{\beta v} dv + \frac{c_v \kappa}{\beta} dp$$

$$\Rightarrow \frac{c_p}{\beta v} dv = -\frac{c_v \kappa}{\beta} dp \quad \text{等熵過程只有唯一獨立變}$$

$$\Rightarrow \underbrace{\frac{-1}{v} \left(\frac{\partial v}{\partial p} \right)_s}_{\text{Adiabatic compressibility } \kappa_s} = \kappa \frac{c_v}{c_p} = \frac{\kappa}{\gamma}$$

Adiabatic
compressibility
 κ_s

$$\kappa_s = \frac{\kappa}{\gamma}$$

$$\kappa_s < \kappa$$

絕熱壓縮率較小, 是因絕熱壓縮時溫度會上升.

已知 氣體中聲音傳播速度 (7.22) $c = \sqrt{\frac{1}{\rho \kappa_s}} = \sqrt{\frac{\gamma}{\rho \kappa}}$

由於氣體中聲波振動極快，熱來不及流動，如同絕熱過程。

Speed of sound in air: 視 Air 為 an ideal diatomic gas, $\gamma = 1.4$
 $\kappa = \frac{1}{\rho} \approx 10^{-5} / \text{Pa}$
 $\rho = 1.2 \text{ kg/m}^3$ for lat

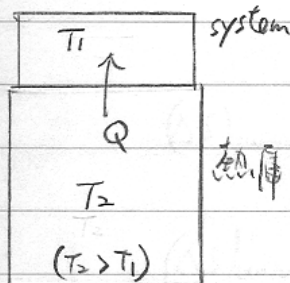
$$c = \sqrt{\frac{1.4}{1.2 \times 10^{-5}}} = 340 \text{ m/s}$$

實驗上 343 m/s at 20°C, at 1 atm

7.6 Entropy Change in Irreversible Processes

系統經由不可逆過程由 state 1 到 state 2, 其 entropy 的變化可找一可逆過程由 state 1 到 state 2 算出. That is because S is state variable

Fig 7.3



system 與熱庫接觸, 等壓過程由 $T_1 \rightarrow T_2$.

由於 $T_2 > T_1$, 熱由 T_2 流到 T_1 即為不可逆.

先由可逆過程考慮 system; for reversible isobaric process

$$d\bar{q}_r = c_p dT - \underbrace{v dp}_0 \quad (4.28) \text{ (For an ideal gas)}$$

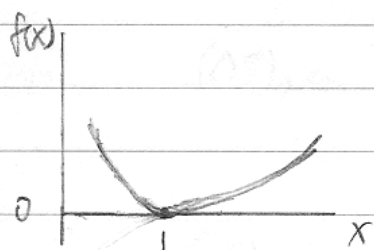
$$dS = \frac{d\bar{q}_r}{T} = c_p \frac{dT}{T}$$

$$(\Delta S)_{\text{system}} = c_p \ln\left(\frac{T_2}{T_1}\right)$$

再考慮熱庫的 $(\Delta S)_{\text{reservoir}} = \frac{-|Q|}{T_2} = -c_p \frac{(T_2 - T_1)}{T_2}$

$$\begin{aligned} \Rightarrow (\Delta S)_{\text{universe}} &= (\Delta S)_{\text{system}} + (\Delta S)_{\text{reservoir}} \\ &= c_p \ln\left(\frac{T_2}{T_1}\right) - c_p \frac{(T_2 - T_1)}{T_2} \end{aligned}$$

設 $x = \frac{T_2}{T_1} \Rightarrow (\Delta S)_{\text{universe}} = c_p \left[\ln x - \left(1 - \frac{1}{x}\right) \right] \equiv f(x)$



由 $\frac{df}{dx} = 0 \Rightarrow x=1$ (極值位置)

又 $\left. \frac{d^2f}{dx^2} \right|_{x=1} > 0 \Rightarrow x=1$ 是極小值.

故 $(\Delta S)_{\text{universe}} \geq 0$, 只有當 $T_1 = T_2$ 時 $(\Delta S)_{\text{universe}} = 0$.

P119 Example 1. 水 0.5 kg, 90°C, 放置在 20°C 環境中, 冷卻到 20°C 等壓過程。

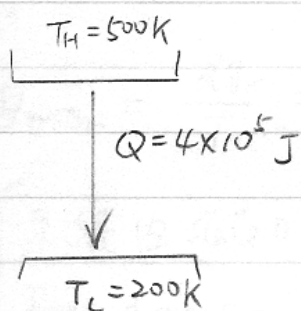
$$(\Delta S)_{\text{system}} = \int \frac{dQ_r}{T} = m c_p \int_{T_1=363\text{K}}^{T_2=293\text{K}} \frac{dT}{T} = m c_p \ln\left(\frac{T_2}{T_1}\right)$$

$$= (0.5)(4180) \ln\left(\frac{293}{363}\right) = -448 \text{ J/K}$$

$$(\Delta S)_{\text{surroundings}} = \frac{m c_p}{T_2} (T_1 - T_2) = (0.5)(4180) \frac{363 - 293}{293} = 499$$

$$(\Delta S)_{\text{universe}} = (\Delta S)_{\text{system}} + (\Delta S)_{\text{surrounding}} = 51 \text{ J/K}$$

P120 Example 2.

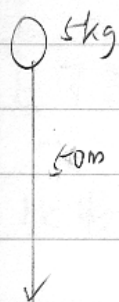


$$(\Delta S)_{\text{universe}} = (\Delta S)_{\text{system}} + (\Delta S)_{\text{surrounding}}$$

$$= \frac{-Q_r}{T_H} + \frac{Q_r}{T_C} = \frac{-4 \times 10^5}{500} + \frac{4 \times 10^5}{200}$$

$$= 1200 \text{ J/K}$$

P121 Example 3



質量 5 kg 物體, 下落 50 m 至地面後靜止, 全程等溫。

$$(\Delta S)_{\text{system}} = 0, \quad (\Delta S)_{\text{surrounding}} = \frac{W_r}{T} = \frac{mgh}{T}$$

$$= \frac{5 \times 9.8 \times 50}{293} = 8.36$$

$$(\Delta S)_{\text{universe}} = 8.36 \text{ J/K}$$

7.7 Free Expansion of an Ideal Gas

絕熱膨脹 $du=0, dq=0, dw=0$.

由 (7.10) $T ds = \underbrace{C_v dT}_{\text{絕熱}} + \frac{T\beta}{\kappa} dv$

$$\Rightarrow ds = \frac{\beta}{\kappa} dv = \frac{P}{T} dv = R \frac{dv}{v}$$

$$(\Delta S)_{\text{system}} = \int_{v_0}^{v_1} ds = R \int_{v_0}^{v_1} \frac{dv}{v} = R \ln\left(\frac{v_1}{v_0}\right)$$

$$(\Delta S)_{\text{universe}} = (\Delta S)_{\text{system}} > 0$$

For an ideal gas, $T_0 = T_1$, 因 $du=0$, 且 $u=u(T)$ only.

對於 isothermal expansion: $T=T_0=T_1$, v from v_0 to v_1 .

$$du=0 \Rightarrow dq_r = dw = \int_0^1 P dv = \int_0^1 \frac{RT_0}{v} dv = RT_0 \int_0^1 \frac{dv}{v} = RT_0 \ln\left(\frac{v_1}{v_0}\right)$$

$$(\Delta S)_{\text{system}} = \frac{dq_r}{T_0} = R \ln\left(\frac{v_1}{v_0}\right)$$

系統由 state 0 到 state 1.

Free expansion 過程中 ^{系統} entropy 增加量

與 isothermal expansion 過程 _{系統} entropy 增加量相同.

可逆的 isothermal expansion 有將熱轉成功, 而 Free expansion 沒有.

比較絕熱自由膨脹與等溫可逆膨脹, $\Rightarrow S$ 是狀態函數.

7.8 Entropy Change for a Liquid or Solid

Section 2.5 中, 由 $v(T, P)$, $dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP$

$$= \beta v dT - \kappa v dP$$

$$\doteq v_0 (\beta dT - \kappa dP)$$

$$\Rightarrow v \doteq v_0 \left[1 + \beta(T - T_0) - \kappa(P - P_0) \right] \quad \begin{matrix} (2.18) \\ (7.26) \end{matrix}$$

由 3rd Tds eq: $Tds = C_p dT - T \left(\frac{\partial v}{\partial T}\right)_P dP \quad (7.27)$

$$ds = C_p \frac{dT}{T} - v_0 \beta dP$$

$$s - s_0 = C_p \ln \frac{T}{T_0} - v_0 \beta (P - P_0) \quad (7.28)$$

$$\Rightarrow \begin{cases} T \uparrow \Rightarrow s \uparrow \\ P \uparrow \Rightarrow s \downarrow \end{cases}$$