Chapter 3. Second and Third Laws of Thermodynamics: Entropy

3-1 The Second Law of Thermodynamics and the Carnot Engine

1. Second Law： 先說經驗上的 empirical law

例:以一杯水分成沸水及冰塊並不違反 1st law, 但不可能發生

① Clausius (Rudolf Julius Emanuel Clausius) 1822-1888 德國人, 以熱的觀點來看

It is impossible to devise a continuously cycling engine that produces no effect other than the transfer of heat from a colder to a hotter body, 即：熱不會自動由低溫物質流向高溫物質而不改變其他

② Kelvin, 以熱→功之"效率"來看

It is impossible for a system to undergo a cyclic process whose sole effects are the extraction of heat from the surrounding and the performance of an equal amount of mechanical work.

即：不可能用 cyclic process 把熱完全變成功

但 work 可以完全變爲 heat (Joule 的各種實驗即是)

③ 另有三種說法, 一種是純理論(Caratheodory), 另兩種提到 entropy, 以後再討論

2. Carnot Engine (Nicolas Leonard Sadi Carnot) 法國人 (1796-1832), 因霍亂而死

參考課本Figure 3.1

先說明 steam engine 之工作原理

再說 Carnot 之"假想" engine

heat engine 即： 用"heat" 作功

4 步驟

$\boxed{1}$ rev. isothermal expansion at T_1

$\boxed{2}$ rev. adiabatic expansion at T_1

$\boxed{3}$ rev. isothermal compression at T_3

$\boxed{4}$ rev. adiabatic compression at T_3

在 2 個溫度分別爲 T_1 及 T_3 的熱儲 (reservoir)中運作

參考課本Figure 3.2

表負值，只是爲了讓觀念清楚而”畫蛇添足”

process	w	q	ΔU	PV 關係
①	$\overline{w}_{12}=-\mathrm{R}T_1\ \ln\frac{V_2}{V_1}$	$q_{12}=\mathrm{R}T_1\ \ln\frac{V_2}{V_1}$	0	$P_1V_1=P_2V_2$
②	$\overline{w}_{23}=C_V\left(T_3-T_1\right)$	$q_{23}=0$	$C_V\left(T_3-T_1\right)$	$P_2V_2^{\gamma}=P_3V_3^{\gamma}$
③	$w_{34}=-\mathrm{R}T_3\ \ln\frac{V_4}{V_3}$	$\overline{q}_{34}=\mathrm{R}T_3\ \ln\frac{V_4}{V_3}$	0	$P_3V_3=P_4V_4$
④	$w_{41}=C_V\left(T_1-T_3\right)$	$\overline{q}_{41}=0$	$C_V\left(T_1-T_3\right)$	$P_4V_4^{\gamma}=P_1V_1^{\gamma}$
Total	$\overline{w}=\overline{w}_{12}+w_{34}$ $=-R\left(T_1-T_3\right)\ln\frac{V_2}{V_1}$	$q=q_{12}+\overline{q}_{34}$ $=R\left(T_1-T_3\right)\ln\frac{V_2}{V_1}$	0	

其中用到$\frac{V_1}{V_2}=\frac{V_4}{V_3}$

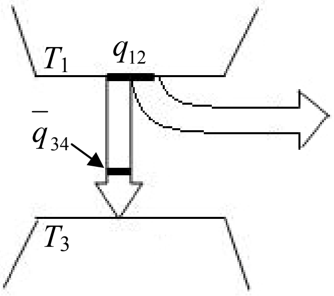
$$
\begin{aligned}
P_4V_4^{\gamma}=P_1V_1^{\gamma}&=\left(P_1V_1\right)V_1^{\gamma-1}=P_2V_2V_1^{\gamma-1}\\
&=\left(P_2V_2^{\gamma}\right)V_2^{1-\gamma}V_1^{\gamma-1}=P_3V_3^{\gamma}V_2^{1-\gamma}V_1^{\gamma-1}\\
&=\left(P_3V_3\right)V_3^{\gamma-1}V_2^{1-\gamma}V_1^{\gamma-1}=P_4V_4V_3^{\gamma-1}V_2^{1-\gamma}V_1^{\gamma-1}
\end{aligned}
$$
，故$V_4^{\gamma-1}V_2^{\gamma-1}=V_3^{\gamma-1}V_1^{\gamma-1}$

也可由 ② 中 $\frac{T_3}{T_1}=\left(\frac{V_2}{V_3}\right)^{\mathrm{R}/C_V}$，④ 中$\frac{T_3}{T_1}=\left(\frac{V_1}{V_4}\right)^{\mathrm{R}/C_V}$ 直接得到$\frac{V_1}{V_2}=\frac{V_4}{V_3}$

從"作功"的觀點，即由T_1 reservoir 取出q_{12}之熱，作了$\overline{w}$之功

efficiency e或 $\eta_{\mathrm{C}}=\frac{w_{\mathrm{surr}}}{q_{12}}=\frac{-\overline{w}}{q_{12}}=\frac{q}{q_{12}}=\frac{q_{12}+\overline{q}_{34}}{q_{12}}=1+\frac{\overline{q}_{34}}{q_{12}}$ 或$1-\left|\frac{q_{34}}{q_{12}}\right|\le 1$

對 ideal gas 而言，$\eta_{\mathrm{C}}=\frac{T_1-T_3}{T_1}=1-\frac{T_3}{T_1}$ ，因爲 $\frac{q_{12}}{T_1}=\frac{\left|q_{34}\right|}{T_3}$



☆ 任何 cyclic process 均可用 n 個 Carnot cycle 來”分解”

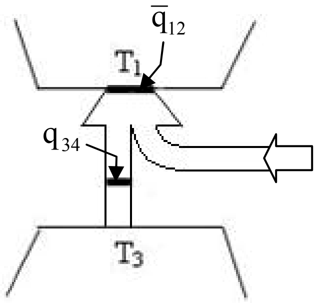
☆ $\left|\frac{q_{34}}{q_{12}}\right|$可視爲 thermodynamic temperature $\frac{\theta_3}{\theta_1}$之比例(後詳)，而$\frac{T_3}{T_1}$即爲 ideal gas temperature

☆ 由 $\frac{q_{12}}{T_1}=-\frac{\overline{q}_{34}}{T_3}$可知有一個量(即 S)可以守恆，即系統吸了$q_{12}$的熱排出$\overline{q}_{34}$，雖不相同，但如果考慮 $\frac{q_{12}}{T_1}$及$\frac{\overline{q}_{34}}{T_3}$，則爲等值負號。

3. Heat Pump (refrigerator) 即Carnot 反轉

rev. adiabatic expansion at T_3, rev. isothermal expansion at T_3

rev. adiabatic compression at T_1, rev. isothermal compression at T_1



☆ 沿用Carnot 之 notation 以免混淆

暖氣機之觀點

$$\text{efficiency } \eta_{hp} = \left|\frac{\bar{q}_{12}}{w}\right| = \underset{\text{Carnot}}{\frac{1}{\eta}} = \frac{T_1}{T_1 - T_3} = \frac{1}{1 - \frac{T_3}{T_1}}$$

coefficient of performance

實際上不常這麼用 ，通常用 EER 值

(1) 冷氣機 EER(Equivalent Energy Replacement)

$$\eta_{ref} = \frac{q_{34}}{w} = \frac{T_3}{T_1 - T_3} = \frac{1}{\frac{T_1}{T_3} - 1}$$

以前用 $\mathrm{kcal/W \cdot h}$ 一般約 2.2

現在用 $\mathrm{kJ/W \cdot h}$ 變爲 9.2, 或用 W/W ,變爲 2.56

和 η 之關係如何？

$$\frac{q_{34}}{w} = \mathrm{EER}\,\frac{1000}{3600/4.184} = 1.16\,\mathrm{EER}\ (\text{in kcal/W} \cdot \text{h})$$

$$\eta_{hp} = \left|\frac{\bar{q}_{12}}{w}\right| = 1 + \frac{q_{34}}{w} = 1 + 1.16\,\mathrm{EER}$$

例：冷氣 operate between 298 – 303 K

$$\eta = 1 - \frac{298}{303} = \frac{5}{303} \quad , \quad \eta_{hp} = \frac{303}{5} = 1 + 1.16\,\mathrm{EER}$$

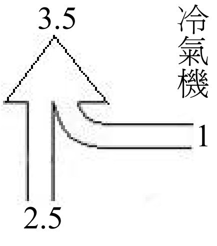
$$\text{ideal EER} = \frac{298}{5} \Big/ 1.16 = 51.4$$

cf. 實際 EER 約 2 – 4

(2) 用暖氣和電熱器比較, 電熱器最不 efficient

(3) 冷氣從整個system + surrounding 來看

爲了移q_{34}使得 surrounding 得到q_{12}



$$\left|\frac{q_{12}}{q_{34}}\right| = 1 + \frac{w}{q_{34}} = 1 + \frac{1}{1.16\,\mathrm{EER}}$$

即增加了 $\frac{100}{1.16\,\mathrm{EER}}$ % 之熱，≈ 34 % for EER = 2.5

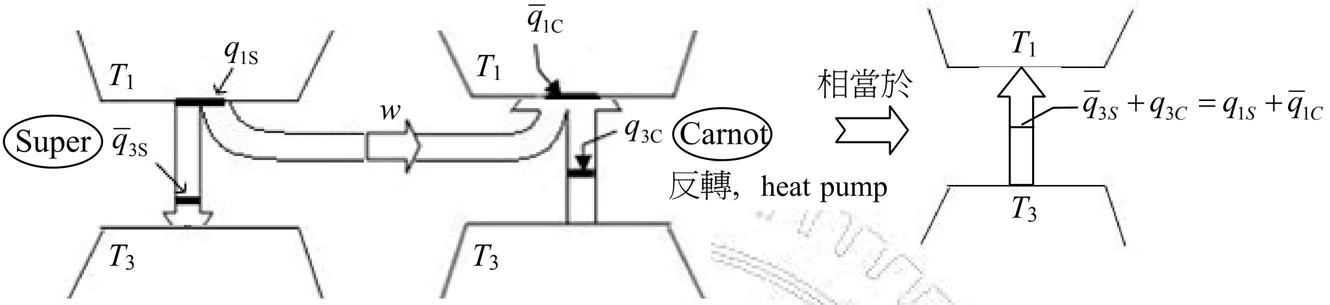
(4) ΔT 小 ，冷氣機之 efficiency 高

用電量和$(\Delta T)^2$有關 $\propto$ ΔT for heat removal之量

$\propto$ ΔT for efficiency

4. 證明Carnot engine 之 efficiency 最大 ，即証明 2nd Law

假設有一super engine $\eta_S > \eta_C$ ，將其和Carnot heat pump 連之



$$\eta_S = 1 + \frac{\quad}{q_{1S}} = \frac{\quad}{q_{1S}} \qquad \eta_C = 1 + \frac{\quad}{\bar{q}_{1C}} = \frac{\quad}{\bar{q}_{1C}}$$

$$或:\eta_S = 1 - \left|\frac{\bar{q}_{3S}}{q_{1S}}\right| = \left|\frac{\bar{w}}{q_{1S}}\right| \qquad \eta_C = 1 - \left|\frac{q_{3C}}{\bar{q}_{1C}}\right| = \left|\frac{w}{\bar{q}_{1C}}\right|$$

如果$\eta_S > \eta_C$, w 相同時，如上圖所示，則表示$|q_{1C}| > |q_{1S}|$，即熱由T_3流向T_1，和熱力學第二定律不合

(亦可假設$|q_{3S}| = |q_{3C}|$,因$\eta_S > \eta_C$ 表示$|q_{1S}| > |q_{1C}|$，即系統自 T_1 吸熱，全部拿來作功，

未傳部分熱給 T_3, 和第二定律不合)

5. Thermodynamic Temperature (有別於 ideal gas temperature) and the Zeroth Law

(1) Zeroth Law of Thermodynamics (可由第一、二定律推導，故沒有絕對必要)

If A & B are at thermal equilibrium
B & C are at thermal equilibrium } then A & C are also at thermal equilibrium.

亦即q_1/q_3 只 depend on T, 和 reservoir 的 composition 無關

(2) 定義 thermodynamic temperature θ

$$\frac{\theta_c}{\theta_h} = \left|\frac{q_3}{q_1}\right| \qquad 由前面之推導知 \frac{\theta_c}{\theta_h} = \underset{\substack{\uparrow \\ \text{ideal gas temperature scale}}}{\frac{T_c}{T_h}} \quad \text{for Carnot cycle}$$

和何種 substance 無關

亦即： θ 可以是 T 的倍數

但爲方便設計，選定其倍數爲 1，即兩個溫度 scale 是相同的

3-2 The Mathematical Statement of the Second Law: Entropy

1 較理論的考慮 (the 2nd law)：

(1) For a closed system, two reversible adiabats don’t cross.

i.e. 由某一 state 到另一 state 至多只有一條 rev. adiabatic process 可連結

<證> 反證：

參考課本Figure 3.6

①+②+③ 對 system 言是 cyclic , $\Delta U = 0$

$$q = q_1 + q_2 + q_3 = 0 + \int C_V dT + 0 = C_V(\Delta T) > 0$$

$$w_{\text{surr}} = -w = -\Delta U + q = 0 + q = q$$

即 q 全部變爲功，違反 2nd law

關鍵在 constant V 時 $w = 0$

(2) Caratheodory’s theorem

In the neighborhood of every equilibrium state of a closed system, there are states that can not be reached along any rev. adiabatic path.

<和(1)的意思是一樣的> 如果有兩個 state (2, 3) 均可由 1 reach , 則 2 rev. adiabats 就 cross 了

<推論> $\boxed{1}$ 在Carnot cycle 中 ， some heat must be exhausted to a cooler reservoir 以便從一條 rev. adiabat 到另一條 rev. adiabat

$\boxed{2}$ rev. adiabat 即爲 $dq_{\text{rev}} = 0$ 之 unique path

可定義出 $dS \propto dq_{\text{rev}}$ ，即： $dS = y(T)\,dq_{\text{rev}}$

(3) 使 dq 變爲 exact differential 的 integrating factor

以ideal gas 爲例：

$$dq_{\text{rev}} = dU - dw = C_V dT + PdV = C_V dT + \frac{RT}{V}dV \quad \text{不是 exact}$$

$$ydq_{\text{rev}} = yC_V dT + y\frac{RT}{V}dV$$ ，假設 y 只是 function of T, not function of V

ydq_{rev} 如要 exact , 則 $\left(\dfrac{\partial\, yC_V}{\partial V}\right)_T = \left(\dfrac{\partial\, y\, RT/V}{\partial T}\right)_V$

$$\Rightarrow \quad 0 = \frac{\partial y}{\partial T}\frac{RT}{V} + \frac{yR}{V}$$

$$\Rightarrow \quad \frac{dy}{dT} = \frac{-y}{T}$$

$$\Rightarrow \quad \ln y = -\ln T\ , \ \text{即} y = \frac{1}{T}$$

故 $\boxed{dS = \dfrac{dq_{\text{rev}}}{T}}$

(4) 推論：An irreversible adiabatic process 之 final state 只能落在 T-V 圖上 reversible adiabat 之右邊
i.e. high-temperature side

參考課本Figure 3.7

1→2→3

左邊：$q = 0 + C_V dT + 0 > 0$

$w = -q < 0$ ， $w_{\text{surr}} = q$

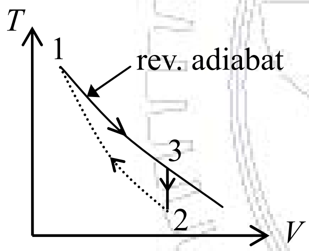
即：全部之 q 變成 w，不可

右邊：全部之 w 變成 q，可以

因 $q = 0 + C_V dT + 0 < 0$

$w > 0$

<註> 上圖反方向進行



	q	w
1→3	0	w_1
3→2	$q < 0$	0
2→1	0	w_2
		$w = -q > 0$

環境對 system 作功, system 將全部功變爲熱, 可行,
似乎表示 irreversible process 落在 rev. adiabat 的左邊也無妨

但問題是由 2 找不到可以回到 1 之 irreversible path.

ideal gas, irreversible expansion
⇒如 final state T 相同, 則 $V_{\text{rev}} < V_{\text{irr}}$ ，或 $P_{\text{rev}} > P_{\text{irr}}$
⇒如 final state 之 V 相同, 則 $T_{\text{rev}} < T_{\text{irr}}$
與 1st law 之 irreversible adiabatic expansion 例子相呼應

2. 2nd Law 之 Mathematical Statement：

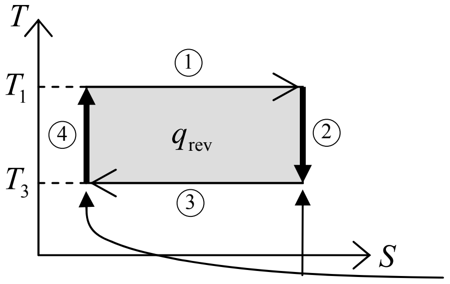
有一個 state function $dS = \dfrac{dq_{\text{rev}}}{T}$ (entropy 之定義，注意是 dq_{rev} 而非 dq)

$$\boxed{\oint \frac{dq_{\text{rev}}}{T} = 0}$$

<Note>: ΔU 可以由 $dw_{\text{adiabatic}}$ 或 dq_V (simple system) 而來

ΔS 則由 dq_{rev} 而來

Carnot cycle



灰色區域之面積：

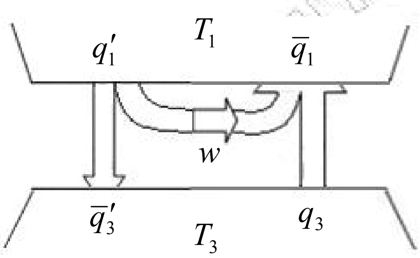
$|q_{\text{rev}}| = |w_{\text{rev}}|$

rev. adiabatic
是 constant entropy process

3. Clausius Inequality and Some Important Conclusions

$$\oint\frac{dq}{T}\le 0\qquad\begin{cases} <0 & \text{for process with any part being irreversible}\\ =0 & \text{for process with all parts being reversible}\end{cases}$$

<證 1> 連接 real engine (irreversible, 以 prime 表之) 與Carnot heat pump (reversible)



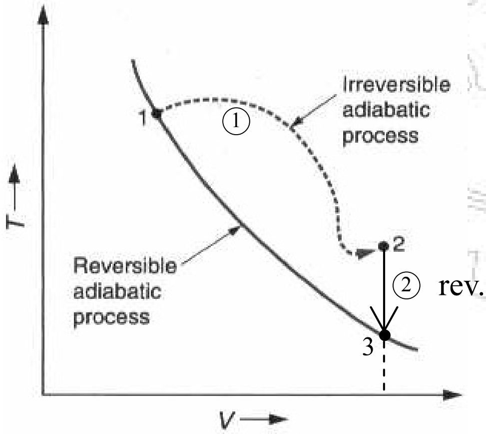
$$\eta' = \frac{-\bar{w}}{q_1'} < \eta = \frac{w}{-\bar{q}_1}$$

$$1+\frac{\bar{q}'_3}{q_1'} < 1+\frac{q_3}{\bar{q}_1} = 1-\frac{T_3}{T_1}$$

$$\frac{T_3}{T_1} < \frac{-\bar{q}'_3}{q_1'}\ ,\quad \frac{q_1'}{T_1} < \frac{-\bar{q}'_3}{T_3}$$

$$\oint\frac{dq}{T} = \frac{q_1'}{T_1}+\frac{\bar{q}'_3}{T_3}+\frac{\bar{q}_1}{T_1}+\frac{q_3}{T_3} = \frac{q_1'}{T_1}+\frac{\bar{q}'_3}{T_3} < 0$$

<證 2>



① $q_1 = 0$

② $q_2 = \int C_V dT < 0$

③ $q_3 = 0$

Clausius得證

引伸：

	ΔS	$\frac{dq}{T}$
①	ΔS_1	0
②	$\Delta S_2 = \int\frac{dq_2}{T} < 0$	ΔS_2
③	0	0

Total (cyclic步驟)之$\Delta S = \Delta S_1 + \Delta S_2 + 0$

即: $\Delta S_1 + \Delta S_2 + 0 = 0$

而因 $\oint\frac{dq}{T} = 0 + \Delta S_2 + 0 < 0$

知 $\Delta S_2 < 0$,

故 $\Delta S_1 > 0$

即 $\boxed{\Delta S_{\text{irr. adia.}} > 0}$

<推論> ① $\left.\begin{array}{l}\Delta S_{\text{irr, adiab.}} > 0\\ \Delta S_{\text{rev. adiab.}} = 0\end{array}\right\}$ $\Delta S_{\text{adiab.}} \ge 0$ ($\Delta S_{\text{isolated}} \ge 0$ 較 narrow)

② $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ for an irreversible process

③ $\boxed{T_{\text{surr}} dS \ge dq}$

$\Delta S > 0$ 吸熱, $T\Delta S$是 Δq 的 upper limit

$\Delta S < 0$ 放熱, $|T\Delta S|$ 是 $|\Delta q|$ 的minimum

<證明>: $dS + dS_{\text{surr}} \ge 0$, $dS_{surr} = \dfrac{dq_{\text{surr}}}{T_{\text{surr}}} = \dfrac{-dq}{T_{\text{surr}}}$

故 $dS \ge \dfrac{dq}{T_{\text{surr}}}$ ↑ reservoir 夠大, 可視爲 reversible process

Note: ②要考慮 system 及 surrounding, 即使是 $\Delta S_{sys} < 0$ 仍有可能發生

但③只要考慮 system 之 ΔS (即 surrounding 之 effect 已納入式中)

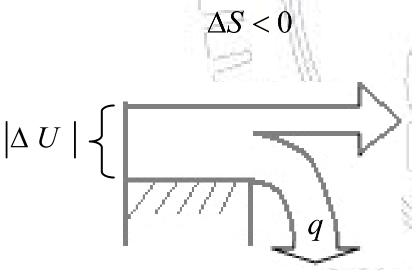
4. Entropy 之意義：

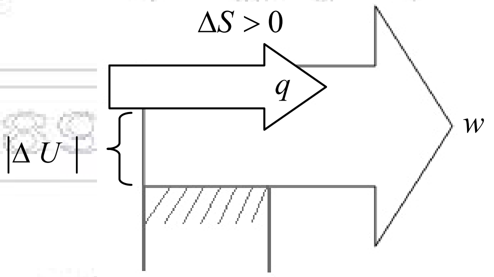
以 Rich guy $\xrightarrow{\text{donates}}$ poor guy 爲例

q 即 money , T 即其存款

$\left|\dfrac{\Delta q_{\text{rich}}}{T_{\text{rich}}}\right| < \left|\dfrac{\Delta q_{\text{poor}}}{T_{\text{poor}}}\right|$ 雖然 $-\Delta q_{\text{rich}} = +\Delta q_{\text{poor}}$, 但 $\Delta S_{\text{rich}} + \Delta S_{\text{poor}} > 0$, 會發生

ΔU 小於 0時 (即：降低能量想對外作 功時)





系統 S 變小，故 S_{surr} 要變大(系統放熱)

〝送紅包給別人〞，即可拿來作功之 ΔU 減少

有一部份要變爲給 surrounding 之 q

$|-w|$ 較 $|-\Delta U|$ 爲小

"傷害環境"

"交男/女朋友要請他的其他朋友"

系統 S 變大，故 S_{surr} 可以 afford 變小(系統吸熱)

有"外援"

surrounding 來的 q 也可作功

$|-w|$ 較 $|-\Delta U|$ 爲大

"善用環境"

"男/女朋友請客"

5. 整理第二定律的另外一些說法及推論

① Mathematical: $dS = \dfrac{dq_{\text{rev}}}{T}$, $dS > \dfrac{dq_{\text{irr}}}{T_{\text{surr}}}$

② Clausius 說過：The energy of the Universe is constant, ←1st law

the entropy of the Universe is always increasing ←2nd law

③ The entropy of an isolated (adiabatic) system will always increase in a spontaneous process.

④ Caratheodory’s theorem 也可視爲 2nd law

⑤ 在 T-V 圖中, irreversible adiabatic process 會落在 reversible adiabat 之右邊

3.3 The Calculation of Entropy Changes

$$dq = dU + P_{\text{ext}}\,dV \quad , \qquad PV\text{ - only}$$

$$\begin{aligned} dq_{\text{rev}} &= dU + PdV \\ &= C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV \\ &= C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV + PdV \\ &= C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \end{aligned}$$

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{C_V dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV$$

通式 $\boxed{dS = \frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV}$ 或 $\boxed{dS = \frac{C_P}{T}dT - \left(\frac{\partial V}{\partial T}\right)_P dP}$

即：① $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$ ， ② $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

③ $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$ ， ④ $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

§ 第一式亦可由const. V 時, $dq_v = dU$

又$TdS = dq$ for rev. process 得到 $T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$ 而導出

§ 第二、四式爲maxwell relation, 下一章會再討論

1. Ideal gas, $P = \frac{R}{V}T$, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$

故 $dS = C_V d\ln T + R d\ln V$

此式成立不一定非 ideal gas 不可

$\Delta S = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1} \Rightarrow$ constant V , $\Delta S = C_V \ln\frac{T_2}{T_1}$

constant T , $\Delta S = R\ln\frac{V_2}{V_1} = R\ln\frac{P_1}{P_2}$

constant P , $\Delta S = C_v \ln\frac{T_2}{T_1} + R\ln\frac{T_2}{T_1} = C_P \ln\frac{T_2}{T_1}$

回顧 rev. adiabatic expansion :

爲constant S 之 process， 故 $C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1} = 0$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_1}\right)^{-R/C_V}$$

或因$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$, $C_P\ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1} = 0$,

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{R/C_P}$$

2. vdW gas, $P=\dfrac{RT}{V-b}-\dfrac{a}{V^2}$, $\left(\dfrac{\partial P}{\partial T}\right)_V=\dfrac{R}{V-b}$

$$\Delta S=\int C_V\,d\ln T+\int R\ln(V-b)$$

$$=C_V\ln\frac{T_2}{T_1}+R\ln\frac{V_2-b}{V_1-b}\qquad (\text{假設 } C_V \text{ 是indep. of } T)$$

3. Change of state (phase change)

$$\Delta S=\frac{q_{\text{rev}}}{T}=\frac{\Delta H}{T}\quad \text{(reversible phase change at const. } P\text{)}$$

4. Entropy of mixing

V_1	V_2

$\left.\begin{array}{l}\text{等壓}\\\text{等溫}\end{array}\right\}$下, mixing 可視爲 constant T 之 expansion

$$\Delta S_i=n_i R\ln\frac{V}{V_i}\ ,\quad V=\sum V_i\ ,\ i\text{表第}i\text{個component}$$

$$\Delta S_{\text{total}}=\sum\Delta S_i=\sum_i n_i R\ln\frac{V}{V_i}$$

$$=R\sum n_i\ln\frac{1}{x_i}\ ,\quad x_i=\text{mole fraction}=\frac{V_i}{V}$$

$$=-R\sum_i n_i\ln x_i$$

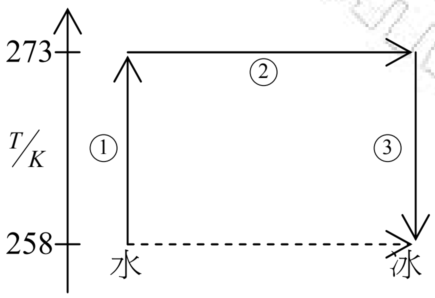
故 $\overline{\Delta S}$ (per mole) $=-R\sum_i x_i\ln x_i$

問：① mix 1 mole He with 1 mole of He at same P and T, ΔS = ? ($\Delta S=0$)

② 如果在定溫下但不等壓 時, 怎麼辦？ $\Delta S=-R\sum_i n_i\ln x_i$ 是否仍成立？

5. 舉例 (irreversible)

(1) 水在−15°C 結冰 (Chap. 2 已算過 ΔH), 可用①+②+③來計算



① $C_P=76.1\ \text{JK}^{-1}\text{mol}^{-1}$

② $C_P=-333.5\ \text{Jg}^{-1}$

③ $C_P=37.15\ \text{JK}^{-1}\text{mol}^{-1}$

對 system：

① $\Delta S=C_P\ln\dfrac{T_2}{T_1}=76.1\ln\dfrac{273.15}{258}=4.3\ \text{JK}^{-1}\text{mol}^{-1}$, $q_1=1140\,\text{J}$

② $\Delta S=-333.5\times 18/273=-22.0$, $q_2=-6010\,\text{J}$

③ $\Delta S=C_P\ln\dfrac{T_2}{T_1}=37.15\ln\dfrac{258}{273}=-2.1$, $q_3=-557\,\text{J}$

$\Delta S_{\text{sys}}=-19.8\ \text{JK}^{-1}\text{mol}^{-1}$, $q=-5427\,\text{J}$

對 surrounding：

$q=5427\,\text{J}$, $\Delta S_{\text{surr}}=5427/258=21.0\ \text{JK}^{-1}\text{mol}^{-1}$

$\Delta S_{\text{sys}}+\Delta S_{\text{surr}}=-19.8+21.0=+1.2\ \text{JK}^{-1}\text{mol}^{-1}>0$

(2)

$$\text{state } 1 \xrightarrow[①]{\text{rev}} 2 \quad , \quad \text{state } 1 \xrightarrow[②]{\text{irrev.}} 2$$

$$\Delta S_{①} = +\Delta S_{②}$$

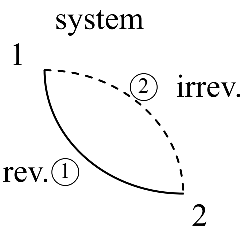
因 $\Delta S_{①} = -\Delta S_{\text{surr}①}$ ， $\Delta S_{②} + \Delta S_{\text{surr}②} > 0$

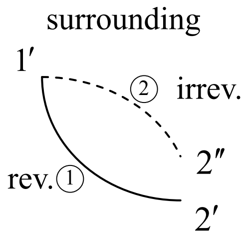
$\Delta S_{\text{surr}_{①}} > \Delta S_{\text{surr}_{②}}$，是否和〝state function〞抵觸？

Ans：並非 ΔS_{surr} 就不是 state function ,

其實 $\Delta S_{\text{surr}①} \neq \Delta S_{\text{surr}②}$,

即：因爲 surrounding 的 final state 不同





3.4 Statistical Entropy

1. 從微觀上來看

$$S = -k\ \ln\Omega + S_0 \qquad = -k\ \ln\Omega\ \ (\text{if } S_0 = 0)$$

$\uparrow$ thermodynamic probability

即與某一特定的 N, V, T 可能發生的 microstate 數目有關

因 $\Omega < 1$, 故 $S \geq 0$

由上式可以導出 $PV = n\mathrm{R}T$ 來 (if assume ideal gas behavior)

<Note>課本沒有負號係把 Ω 當成 microstate 的數目, 而非 probability

2. 由 lattice gas model 來說明 statistical entropy 和 thermodynamic entropy 是相同的

N 個 non-interacting point-mass particles 在 volume *V*,

macro state：*N*, *V*, *U*
micro state：(x, y, z)，(v_x, v_y, v_z) $\qquad \Omega = \Omega_{\text{coord}}\,\Omega_{\text{vel}}$

將 *V* 分爲 *M* 個小方塊，如課本 Fig. 3.11

則 $\dfrac{1}{\Omega_{\text{coord}}} = \dfrac{M^N}{N!}$ (因particle爲indistinguishable, 要除以*N!*)

(例一)

isothermal expansion $\qquad \Delta S = n\mathrm{R}\ln {}^{V_2}\!/_{V_1}$ (ideal gas)

統計上： $\Delta S = -k\ln\Omega_2 + k\ln\Omega_1 = -k\ln\left(\dfrac{\Omega_{\text{coord}}(2)\Omega_{\text{vel}}(2)}{\Omega_{\text{coord}}(1)\Omega_{\text{vel}}(1)}\right)$

$$= k\ln\frac{\Omega_{\text{coord}}(1)}{\Omega_{\text{coord}}(2)} = k\ln\frac{M_2{}^N}{M_1{}^N} = Nk\ln\frac{M_2}{M_1}$$

$$= Nk\ln\frac{V_2}{V_1} \qquad (Nk = \mathrm{R},\ k = 1.38\times10^{-23}\ \mathrm{JK}^{-1})$$

(例二)

entropy of mixing 也可以依樣導出

3. Interpretation of Entropy

熱力學上，*S* 是 rev. process 的 heat transfer

統計學上，*S* 是對於〝lack of information〞的度量

一般說是和〝亂度〞有關，嚴格說來是不太精確

但如果我們對混亂的資訊一無所知，當然〝亂度〞就和〝lack of information〞相當

3.5 Third Law of Thermodynamics and Absolute Entropies

1. Third Law

(1) Nernst (Walter Hermann Nernst 1864-1941，德人，1920 年 Nobel Prize)

"For certain isothermal chemical reaction of solid, the ΔS approaches zero as $\theta \to 0$."

或稱 "Nernst heat theorem"，是實驗的觀測，針對 ΔS

(2) Max Planck 1911 (1858-1947，德人，1918 Nobel)

對 individual substance, $S \to 0$ for $T \to 0$

(3) Gilbert Newton Lewis (1875-1946, 酸鹼, octet rule)

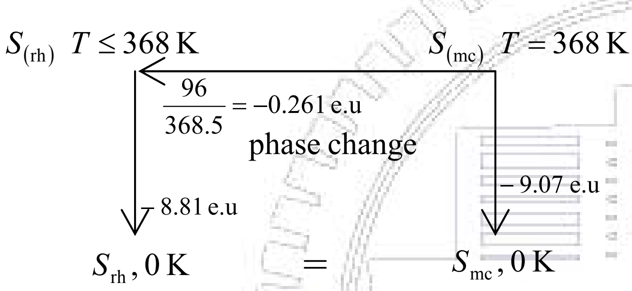
At $T = 0$, $S = 0$ for perfect crystalline substance

如不是，則 $S > 0$ 如：CO

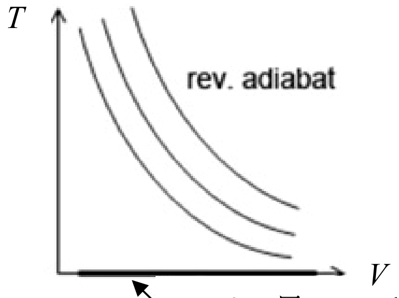
因 $C-O\cdots O-C\cdots C-O\cdots$ 不是 perfect crystalline

$\Delta S = R\ln 2 = 5.76\ \mathrm{JK^{-1}mol^{-1}}$

2. William Giaugue (1895-1982，1949 Nobel Prize) 實驗證明



3. unattainability of absolute zero

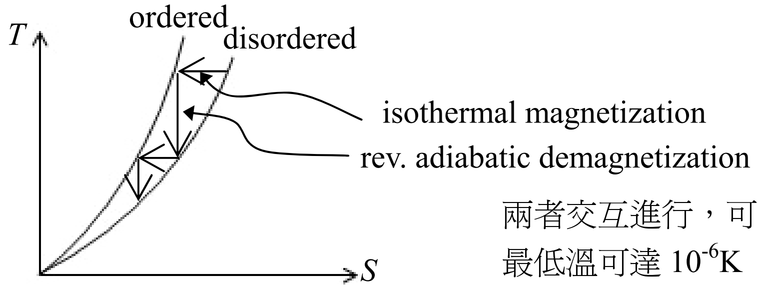


因爲 2 個 rev. adiabat 不相交

而 irrev. adiabatic process 又會往右邊跳

故無法在 finite steps 用 adiabatic process 使 $T \to 0$

$T = 0$，是 rev. adiabat，也是 rev. isotherm



兩者交互進行，可趨近絕對零度

最低溫可達 10^{-6}K

如用 laser cooling 可降至 3×10^{-9} K

4. Absolute Entropies

(1) $$S(T)=\int_0^{T_f}\underset{\uparrow}{\frac{C_P(s)}{T}}dT+\frac{\Delta H_{fus}}{T_f}+\int_{T_f}^{T_0}\frac{C_P(l)}{T}dT$$ for a liquid, T_f = freezing point

$C_V \approx C_P = aT^3 + bT$ at low T

(Debye theory)+(electron in metal)

對 0 – 15 K 很有用，因沒 data

(2) Standard State for the Entropy

solid or liq.－actual substance at P^o (1 bar)

gas－ideal gas at 1 bar (hypothetical)

(3) ΔS of chemical reactions at various T

$$\Delta S(T_2) = \Delta S(T_1) + \int_{T_1}^{T_2} \frac{\Delta C_p}{T} dT$$

(4) Trouton's rule (empirical)

For 〝normal〞 liquids，$\Delta S_{vap} \approx 10.5R \approx 88\ JK^{-1}mol^{-1}$ at the normal boiling temperature

通常不是很準