Ch 6 The Second Law of Thermodynamics

6.1 Introduction

The first law does not constitute a complete theory because certain process that it permits do not occur in nature
例:熱全部轉成功不出現於自然界.

問題1: The first law $dU = đQ - PdV$, 其中 $đQ$ 是 inexact differential,
$đQ$ 可否像 $đW$ 那樣換成 state variables 表示. yes!

問題2: 可逆與不可逆過程在 the first law 中無法區分,
是否有 state variable 來區分它們. yes!

問題3: 符合 the first law 的某些 process 在自然界不能發生,
1^{st} law 的敘述顯然不足, 需要 a second fundamental law

6.2 The Mathematical Concept of Entropy

1^{st} law: $dU = đQ - đW$，其中 $đQ$ 和 $đW$ 均為 inexact differe

For a reversible process, the work is configuration work alone,

$$đW_r = P\,dV$$

$$\Rightarrow \frac{đW_r}{P} = dV \text{ is exact}$$，可見 $\frac{1}{P}$ is integrating factor.

$đW_r$, dV are extensive, P is intensive.

上述方法是否可用在 $đQ$ 上呢？

Ideal gas 的 3 個 state variables (P, V, T) 已用掉 2 個，剩下 T.

設：

$$\frac{đQ_r}{T} = dS \quad \text{is exact and extensive.} \qquad (6.3)$$

(6.3) 為 Clausius definition of the entropy S.

$$\Rightarrow 1^{st} \text{ law}: \quad dU = T\,dS - P\,dV \quad \text{for reversible proc} \qquad (6.4$$

尚未討論.

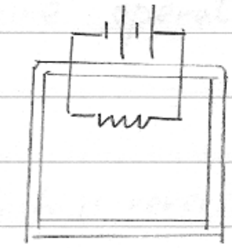
注意 1. 尚未證明 dS is exact.

注意 2. (6.4) 式只成立於 reversible process.

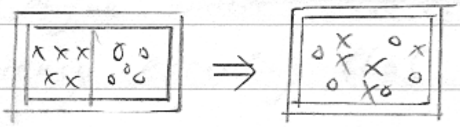
6.3 Irreversible Processes

考慮4種 irreversible proccesses：

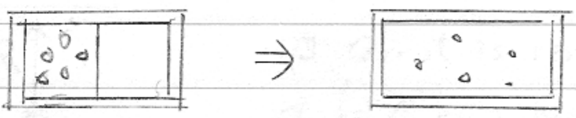
1. Dissipative work：電能加熱，Fig 6.1



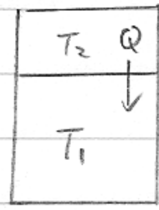
2. Two different gases mixing，Fig 6.2



3. Free expansion. Fig 6.3



4. Heat flows from high T to low T. Fig 6.4



Two famous statement of the 2nd law:

① Clausius statement: It is impossible to construct a device that operates in a cycle and whose sole effect is to transfer heat from a cooler body to a hotter body. Fig 6.5

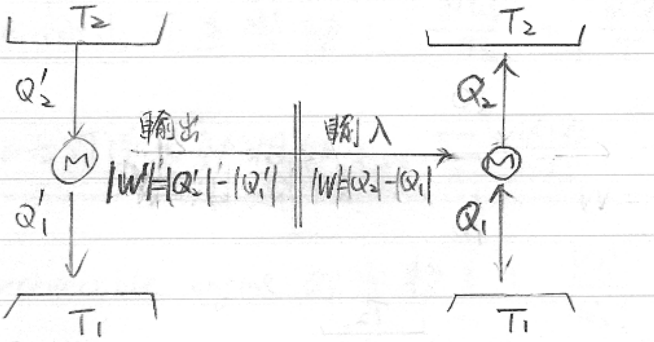
② Kelvin-Planck statement: It is impossible to construct a device that operates in a cycle and produce no other effect than the performence of work and the exchange of heat with a single reservoir. Fig 6.6

6.4 Carnot's Theorem

Carnot theorem: No engine operating between two reservoirs can be more efficient than a Carnot engine operating between those same two reservoirs.

Proof: 考慮2個 engines: ① Carnot engine which is reversible.

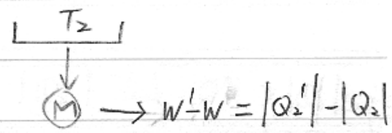
② hypothetical engine ~~which is also reversible~~ with efficiency exceeding that of the Carnot engine.



因 Carnot is reversible. 可組合此2 engines.

因 Hypothetical engine 效率較好:

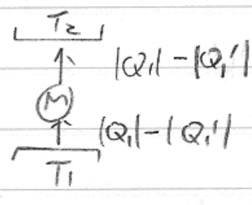
① 當 $|Q_1'| = |Q_1|$ 時, $|Q_2'| > |Q_2|$ ⇒ 淨效應



不成立.

② 當 $|W'|=|W|$ 時, $|Q_2'|-|Q_1'| = |Q_2|-|Q_1|$ ⇒ 淨效應

但因 H Engine 效率較好: $\frac{|Q_2'|}{|Q_1'|} = \frac{|Q_1'|+W}{|Q_1'|} > \frac{|Q_2|}{|Q_1|} = \frac{|Q_1|+W}{|Q_1|}$



左右各減1 ⇒ $\frac{W}{|Q_1'|} > \frac{W}{|Q_1|}$

⇒ $|Q_1| > |Q_1'|$ → 淨效應

不成立.

$\Rightarrow$ All reversible engines operating between the same reservoir have the same efficiency $\eta = 1 - \frac{T_1}{T_2}$, $(T_2 > T_1)$, Irreversible engines will have a lesser efficiency.

6.5 The Clausius Inequality and the Second Law

由 (5.20) $\frac{Q_1}{Q_2} = \frac{-T_1}{T_2}$ for Carnot engine. $\Rightarrow \frac{Q_2}{T_2} + \frac{Q_1}{T_1} = 0$

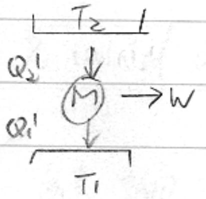
where $\frac{Q}{T}$ is Carnot ratio.

$\boxed{\text{Q以流入為正}}$

取極小可逆變動： $\frac{\bar{d}Q_2}{T_2} + \frac{\bar{d}Q_1}{T_1} = 0$

很多可逆變動相加成迴路 $\sum_i \frac{\bar{d}Q_i}{T_i} \rightarrow \oint \frac{\bar{d}Q_r}{T} = 0$ 可逆

Irreversible engine 效率較差： $\frac{|Q_1'|}{|Q_2'|} > \frac{|Q_1|}{|Q_2|}$



$$\frac{Q_1'}{Q_2'} < \frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

$\Rightarrow \frac{Q_2'}{T_2} + \frac{Q_1'}{T_1} < 0$

$\boxed{\text{若 } |Q_2'| = |Q_2| \text{ 則 } |Q_1'| > |Q_1|.}$

$\Rightarrow \frac{\bar{d}Q_2'}{T_2} + \frac{\bar{d}Q_1'}{T_1} < 0 \quad \Rightarrow \oint \frac{\bar{d}Q'}{T} < 0$

結論

$$\boxed{\text{Clausius inequality : } \oint \frac{\bar{d}Q}{T} \leq 0} \qquad (6.14)$$

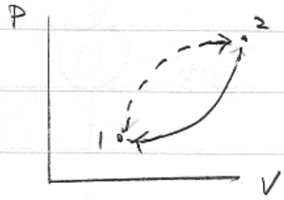
(6.14) is sometimes taken as a statement of the 2nd law.

回頭看 Clausius definition of S

定義 $\frac{đQ_r}{T} = dS$, S : entropy.

可逆時 $\oint \frac{dQ_r}{T} = \oint dS = 0 \Rightarrow dS$ is an exact differential.

S is state variable.



考慮一cycle, $1 \rightarrow 2$ 不可逆,

$2 \rightarrow 1$ 可逆

$$\oint \frac{đQ}{T} = \underbrace{\int_1^2 \frac{đQ}{T}}_{irr} + \underbrace{\int_2^1 \frac{dQ_r}{T}}_{r} < 0$$

$$\Rightarrow \int_{1\,不可}^2 \frac{đQ}{T} < \int_{1\,可}^2 \frac{đQ_r}{T} \equiv S_2 - S_1 = \Delta S$$

$$\Rightarrow dS \underset{\uparrow}{\geq} \frac{đQ}{T} \qquad (6.15)$$

等号在可逆時成立.

若 isolated $đQ = 0$, 則 $dS \geq 0$.

結論: Principle of increasing entropy: The entropy of an isolated system increase in any irreversible process and is unaltered in any reversible process.

(unaltered: 不變)

各别部份的 Entropy 可增.可減, 但宇宙總 Entropy 則只可增加或不變

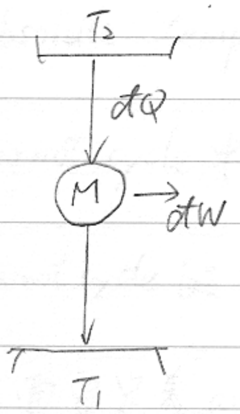
$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} \geq 0$.

It provides a direction for the sequence of natural events.

"The arrow of time": 有些自然現象的時間反轉是不成立的.

6.6 Entropy and Available Energy

除了用 Entropy，亦可用 Available Energy 來敘述熱力學 2nd law.



T_2 送出熱 dQ 到熱机 M，不可能完全轉為功.
能轉為功的只有：

$$dQ\left(1-\frac{T_1}{T_2}\right).$$

這些可轉為功的能量稱作 "Available Energy".

對應於 "The entropy always increases in a spontaneous process"

$\Rightarrow$ "The available energy always decrease in an irreversible cycle"

There exists no process that can increase the available energy in the universe.

6.7 Absolute Temperature

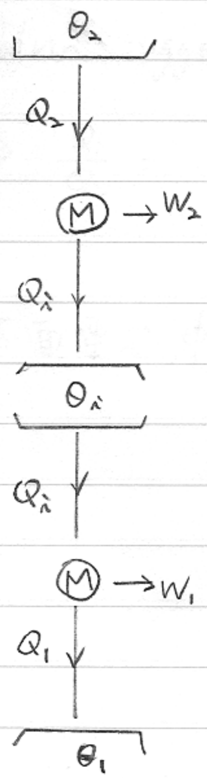
Carnot's theorem can serve as the basis for defining an absolute temperature scale.

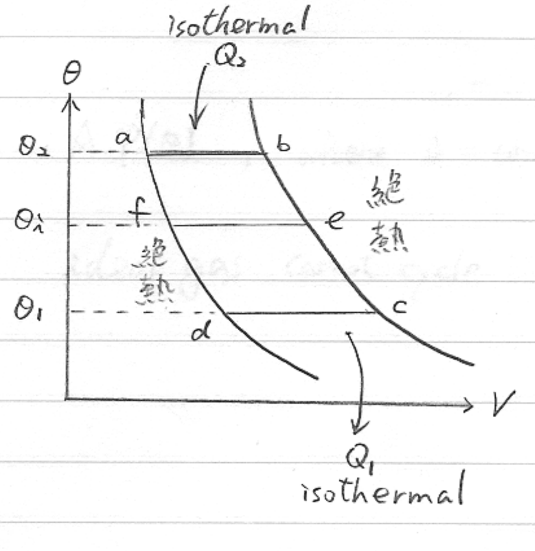
Carnot cycle 中 $\frac{Q_1}{Q_2} = \frac{-T_1}{T_2}$ 的結果 for all reversible cycle 都一樣

Carnot cycle 的物質是 ideal gas，事實上對任何物質都一樣.

下面要定義 an absolute scale of temperature.

設 θ 是某經驗溫度.
原 Carnot cycle : $a \to b \to c \to d \to a$
將 Carnot cycle 分成 2 段：





廣義的設 $\frac{Q_1}{Q_2} = \frac{-|Q_1|}{|Q_2|} = f(\theta_2, \theta_1)$

要求 $f(\theta_1, \theta_2)$

由 cycle $a \to b \to e \to f \to a$: $\dfrac{-|Q_i|}{|Q_2|} = f(\theta_2, \theta_i)$

由 cycle $f \to e \to c \to d \to f$: $\dfrac{-|Q_1|}{|Q_i|} = f(\theta_i, \theta_1)$.

$$\Rightarrow \quad \frac{|Q_1|}{|Q_i|}\frac{|Q_i|}{|Q_2|} = \frac{|Q_1|}{|Q_2|}$$

$$\Rightarrow \quad f(\theta_i, \theta_1)\, f(\theta_2, \theta_i) = -f(\theta_2, \theta_1)$$

因右邊與 θ_i 無關，則左邊 θ_i 必須消掉。故 $f(\theta_i, \theta_1)$ 的形式必為

$$f(\theta_i, \theta_1) = \frac{-\phi(\theta_1)}{\phi(\theta_i)} \quad ; \quad f(\theta_2, \theta_i) = \frac{-\phi(\theta_i)}{\phi(\theta_2)}$$

$$\Rightarrow \quad \frac{Q_1}{Q_2} = f(\theta_2, \theta_1) = \frac{-\phi(\theta_1)}{\phi(\theta_2)}$$; where $\phi(\theta)$ 尚未得知。

Kelvin suggested: $T = A\,\phi(\theta)$, where A = constant.

$$\Rightarrow \quad \frac{Q_1}{Q_2} = \frac{-T_1}{T_2}$$ ideal gas carnot cycle 的結果

下面要求 $\phi(\theta)$.

$\boxed{T, v, P}$ $\boxed{T, v, u}$

可逆 因 $T ds = \bar{d}Q = du + p\,dv \Rightarrow ds = \frac{1}{T}(du + P\,dv)$ (6.20)

取 T, v 為獨立變數：$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$ (6.21)

(6.21) 代入 (6.20) $\Rightarrow$ $ds = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v dT + \frac{1}{T}\left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] dv$ (6.22)

因 $s = s(T, v) \Rightarrow ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$ (6.23)

比較 (6.22) 與 (6.23) $\Rightarrow$

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v \qquad (6.24)$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{1}{T}\left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] \qquad (6.25)$$

因 $\left[\frac{\partial}{\partial v}\left(\frac{\partial s}{\partial T}\right)_v\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial v}\right)_T\right]_v$

$$\Rightarrow \frac{\partial}{\partial v}\left[\frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v\right] = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial u}{\partial v}\right)_T + \frac{P}{T}\right]$$

$$\Rightarrow \frac{1}{T}\frac{\partial^2 u}{\partial v\,\partial T} = \frac{-1}{T^2}\left(\frac{\partial u}{\partial v}\right)_T + \frac{1}{T}\frac{\partial^2 u}{\partial T\,\partial v} - \frac{P}{T^2} + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_v$$

$$\Rightarrow \underline{\underline{\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P}} \quad \textit{important relation} \qquad (6.26)$$

因 (6.18)： $T = A\phi(\theta) \Rightarrow T$ 與 θ 是一對一函數

$$\Rightarrow \begin{bmatrix} \left(\frac{\partial u}{\partial v}\right)_T = \left(\frac{\partial u}{\partial v}\right)_\theta \\ \left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial P}{\partial \theta}\right)_v \left(\frac{d\theta}{dT}\right) \end{bmatrix} \tag{6.27}$$

(6.27) 代入 (6.26) $\Rightarrow \quad \left(\frac{\partial u}{\partial v}\right)_\theta = T\left(\frac{\partial P}{\partial \theta}\right)_v \left(\frac{d\theta}{dT}\right) - P$

$$\Rightarrow \quad \frac{dT}{T} = \frac{\left(\frac{\partial P}{\partial \theta}\right)_v d\theta}{\left(\frac{\partial u}{\partial v}\right)_\theta + P} \tag{6.28}$$

For an ideal gas, $P = \frac{K\theta}{v}$, $u = u(\theta)$

$$\Rightarrow \begin{bmatrix} \left(\frac{\partial P}{\partial \theta}\right)_v = \frac{K}{v} = \frac{P}{\theta} \\ \left(\frac{\partial u}{\partial v}\right)_\theta = 0 \end{bmatrix}$$

結果代入 (6.28) $\Rightarrow \quad \frac{dT}{T} = \frac{\frac{P}{\theta} d\theta}{P} = \frac{d\theta}{\theta}$

$$\Rightarrow \quad T = A'\theta \tag{6.29}$$

The Kelvin scale 是在 $\frac{T}{T_1} = \frac{|Q|}{|Q_1|}$ 中定 $T_1 = 273.16\,K$ (水的三相點)

$$\Rightarrow \quad T = (273.16^\circ K)\frac{|Q|}{|Q_1|}$$

6.8 Combined 1st and 2nd Laws.

1st law for reversible process : $dU = \bar{d}Q_r - \bar{d}W_r = Tds - PdV.$

1st law for irreversible process : $dU = \bar{d}Q - \bar{d}W$

由 2nd law : $Tds = \bar{d}Q_r > \bar{d}Q$. $\Rightarrow \left[\begin{array}{l} \text{設 } \bar{d}Q_r = \bar{d}Q + \varepsilon \\ \Rightarrow \bar{d}W_r = \bar{d}W + \varepsilon \end{array} \right.$

$$\Rightarrow \overbrace{\bar{d}W}^{\text{real work}} = \underbrace{\bar{d}W_r}_{\text{configuration work}} + \underbrace{(-\varepsilon)}_{\text{dissipative work}}$$

dissipative work 外界對系統作功, 故為負

此功進入系統後轉為熱能.

$$\begin{aligned} dU = \bar{d}Q - \bar{d}W &= \bar{d}Q_r - \varepsilon - (\bar{d}W_r - \varepsilon) \\ &= \bar{d}Q_r - \bar{d}W_r \\ &= Tds - PdV \qquad (6.37) \end{aligned}$$

Tds = 總吸熱 $= \underbrace{\bar{d}Q}_{\text{實際吸熱}} + \underbrace{\varepsilon}_{\text{功轉換成熱}}$.

(6.37) 不只對 reversible process, 對 irreversible process 依然成立.