

Ch 5 Consequences of the First Law.

5.1 The Gay-Lussac - Joule Experiment

十九世紀中葉，Gay-Lussac (稍後 Joule) 做一實驗。

顯示： $u = u(T)$ only. 而不是 $u(T, v)$

此結果對 ideal gas 是 exactly 正確，對一般氣體是近似正確。

T, v, u

先考慮最簡單系統。

因探討問題是 u 與 T 有關，與 v 無關，故取 T, v, u

由 the cyclical and reciprocal relation:

$$\left(\frac{\partial T}{\partial v}\right)_u = -\frac{\left(\frac{\partial u}{\partial v}\right)_T}{\left(\frac{\partial u}{\partial T}\right)_v} \quad (5.1)$$

For a reversible process (Eg. 4.9): $C_v = \left(\frac{\partial u}{\partial T}\right)_v$

$$\Rightarrow \left(\frac{\partial u}{\partial v}\right)_T = -C_v \left(\frac{\partial T}{\partial v}\right)_u \quad (5.2)$$

(5.2) 顯示：若我們能夠到固定內部下， T 對 v 的變率，即可得到 u 隨 v 的變率。若 $\left(\frac{\partial T}{\partial v}\right)_u = 0$ ，則 $u = u(T)$ only

問題是：如何能 keep u constant.

因 $du = \delta q - \delta w$ ，故必須絕熱，又不作功 $\Rightarrow du = 0$.

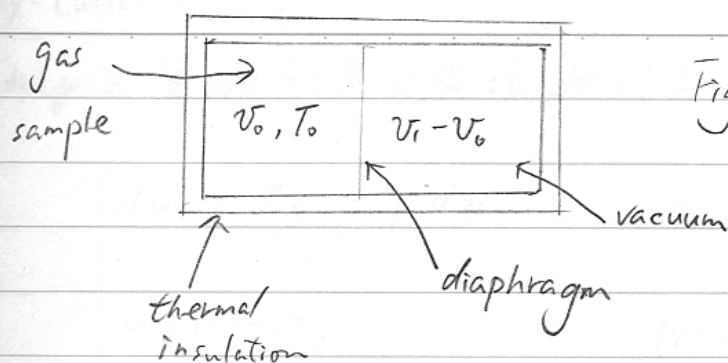


Fig 5.1 Joule 實驗裝置.

初始氣體都在左邊.

薄膜破後絕熱自由膨脹.

$$dq=0, dw=0.$$

$$\Rightarrow dU=0.$$

若 free expansion 後溫度 T_1 . $\Rightarrow T_1 = T_0 + \int_{v_0}^{v_1} \left(\frac{\partial T}{\partial v}\right)_u dv$

其中 $\left|\left(\frac{\partial T}{\partial v}\right)_u\right| \equiv |\eta|$, the Joule coefficient.

Joule 實驗結果: for air, 量不到溫度變化.

for various gas, $|\eta| < 0.001 \text{ K}^\circ \cdot \text{kilomole}/\text{m}^3$

\Rightarrow For an ideal gas $\eta = \left(\frac{\partial T}{\partial v}\right)_u = 0$, and $u = u(T)$ only.

For a van der Waals gas $\left(P + \frac{a}{v^2}\right)(v-b) = RT$

$$\eta = \frac{-a}{v^2 c_v} \neq 0. \quad \text{Problem (t-3)}$$

Gay-Lussac - Joule

for an ideal gas 的實驗結果可由理論計算得到

$$u, v, T$$

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

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

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

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

$$(4.4) \text{ 代入 } (4.5) \Rightarrow \delta q = \left(\frac{\partial u}{\partial T}\right)_v dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right] dv \quad (4.8)$$

$$\Rightarrow \frac{\delta q}{T} = \frac{1}{T} \left(\frac{\partial u}{\partial T}\right)_v dT + \frac{1}{T} \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right] dv \quad (5.4)$$

Ch 6 中會學到另一 state variable s (entropy): $\delta q = T ds$.

故 $\frac{\delta q}{T} = ds$ is an exact differential.

$$\Rightarrow (5.4) \text{ 的右邊必須 } \frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

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

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

$$\Rightarrow \left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v - p$$

$$\text{For an ideal gas } p = \frac{RT}{v} \Rightarrow T \left(\frac{\partial p}{\partial T} \right)_v = p \Rightarrow \left(\frac{\partial u}{\partial v} \right)_T = 0$$

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5.2 The Joule - Thomson Experiment Joule - Kelvin Experiment.

不同的方法得到 Joule Experiment (5.1) 的結果，

要改進實驗的原因是 Joule Experiment 中的 T 極難量測。

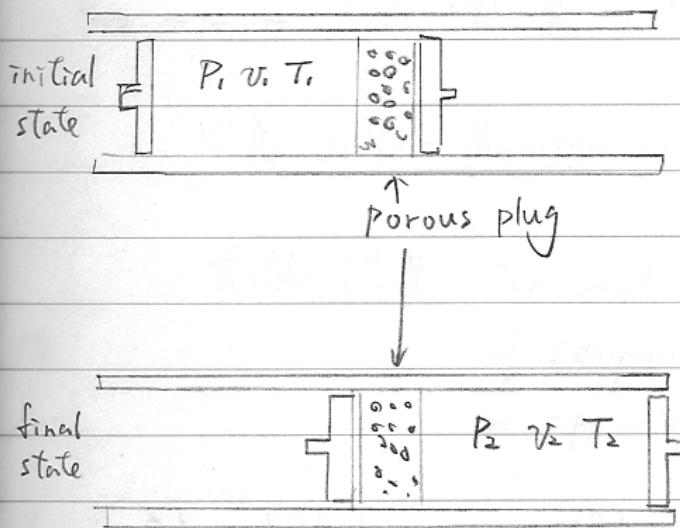


Fig 5.2 Joule - Thomson
實驗裝置.

$$P_1 \gg P_2$$

氣體保持定溫定壓 (P_1, T_1 , P_2, T_2)
從左噴到右。
絕熱過程。

Specific work 左: $w_1 = \int_{V_1}^0 P_1 dV = -P_1 V_1$

右: $w_2 = \int_0^{V_2} P_2 dV = P_2 V_2$

$$U_2 - U_1 = P_1 V_1 - P_2 V_2 = -[w_1 + w_2]$$

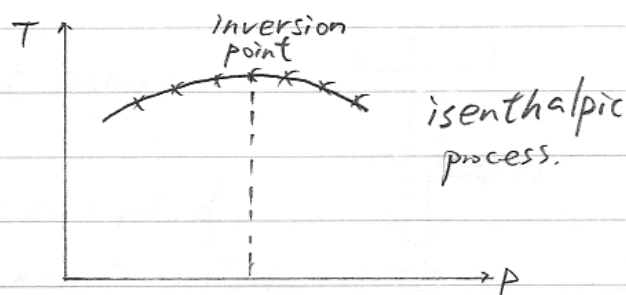
內能增加 外界對系統作的功。

$$\Rightarrow U_1 + P_1 V_1 = U_2 + P_2 V_2$$

$$\Rightarrow h_1 = h_2$$

Throttling process occurs
at constant enthalpy.

實驗結果: Fig 5.3



Free expansion 可能增溫, 可能減溫, 有 - inversion point.

定義 Joule - Thomson coefficient $\mu \equiv \left(\frac{\partial T}{\partial P}\right)_h$ 圖中斜率

實驗結果. For most gases over a reasonably wide range of temperatures and pressures, the T-P curve is approximately flat and $\mu \approx 0$.

$$\left(\frac{\partial h}{\partial P}\right)_T = -C_P \left(\frac{\partial T}{\partial P}\right)_h$$

$$\Rightarrow \left(\frac{\partial h}{\partial P}\right)_T = 0 \text{ and } h = h(T) \text{ only.}$$

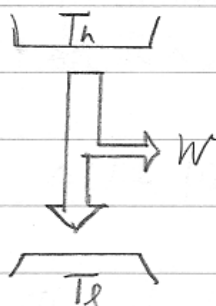
5.1 及 5.2 的實驗點是等價的.

$$\left(\frac{\partial u}{\partial v}\right)_T = \left(\frac{\partial h}{\partial P}\right)_T = 0.$$

5.3 Heat Engines and the Carnot Cycle

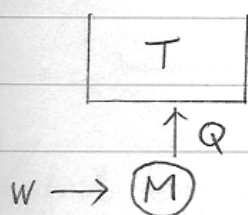
The heat engine :

It receives an input of heat at a high temperature, does mechanical work, and give off heat at a lower temperature.



先考慮 2 種極端的情況：

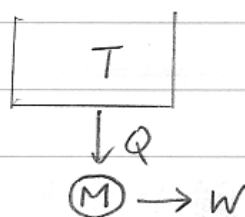
Fig 5.4 (a)



$$W = Q$$

作功完全轉成熱，
這是可能的。
電熱器，

Fig 5.4 (b)

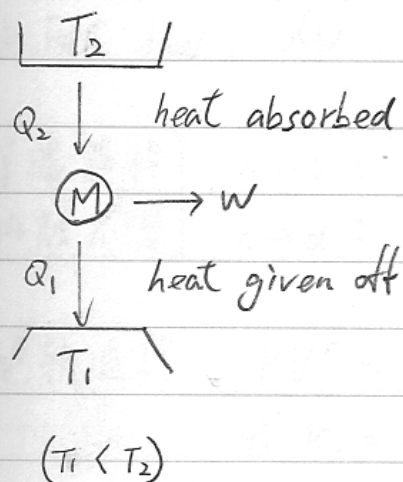


熱完全轉成功。

不可能

受 the second law 限制。

下面將就熱機效率討論



先定義符號:

以熱機 M 為系統。

熱流入為正, 向外做功為正。

$$\Delta U = |Q_2| - |Q_1| - |W| = Q_2 + Q_1 - W$$

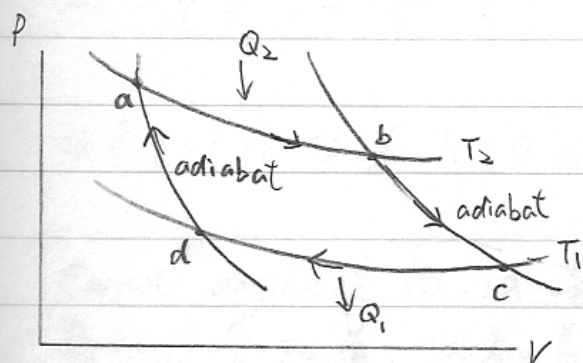
The efficiency of the engine: $\eta = \frac{|W|}{|Q_2|}$

We assume that the engine operates in a cycle: $\Delta U = 0$.

$$\Rightarrow W = |Q_2| - |Q_1| = Q_2 + Q_1$$

$$\Rightarrow \eta = 1 - \frac{|Q_1|}{|Q_2|}$$

Carnot engine: Ideal gas 系統, 包括 4 個 reversible process:



$a \rightarrow b$: isothermal exp: $Q_2 > 0, W$

$b \rightarrow c$: adiabatic exp: , W

$c \rightarrow d$: isothermal com: $Q_1 < 0, W$

$d \rightarrow a$: adiabatic com: , W

$$W = \oint P dV = |Q_2| - |Q_1| \neq 0.$$

由 First law: $dU = \delta Q - \delta W$ (5.14)

等溫過程 $a \rightarrow b$: $Q_2 = W_2 = nRT_2 \ln \frac{V_b}{V_a} > 0$ ($V_b > V_a$) (5.15)

內能不變 $c \rightarrow d$: $Q_1 = W_1 = nRT_1 \ln \frac{V_d}{V_c} < 0$ ($V_d < V_c$) (5.16)

絕熱過程: $PV^r = \text{constant}$.

因 $PV = nRT \Rightarrow P = \frac{nRT}{V} \Rightarrow \frac{nRT}{V} V^r = \text{constant}$
 $\Rightarrow TV^{r-1} = \text{constant}$.

$b \rightarrow c$: $T_2 V_b^{r-1} = T_1 V_c^{r-1}$
 $d \rightarrow a$: $T_2 V_d^{r-1} = T_1 V_a^{r-1}$ $\Rightarrow \frac{V_b}{V_a} = \frac{V_c}{V_d}$ (5.19)

$\frac{(5.16)}{(5.15)} = \frac{Q_1}{Q_2} = \frac{T_1}{T_2} \frac{\ln \frac{V_d}{V_c}}{\ln \frac{V_b}{V_a}} \xrightarrow{(5.19) \text{ 代入}} \frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$ (5.20)

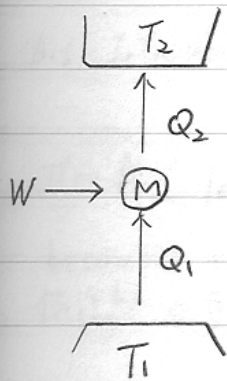
$\Rightarrow \eta = 1 - \frac{T_1}{T_2} < 1$ (5.21)

效率 $\eta = 1$ 時 必須 $T_1 = 0^\circ\text{K}$.

Carnot engine 是高, 低溫 2 個熱庫間, 可逆過程, 後面將會知道, 此為最高效率熱機.

若不是用 ideal gas, 情況當然會不同.

Carnot refrigerator: Carnot engine 的過程反過來走。



$$\text{Coefficient of performance } C = \frac{|Q_1|}{|W|} = \frac{|Q_1|}{|Q_2| - |Q_1|} = \frac{T_1}{T_2 - T_1}$$

一般 typical refrigerator 的架構是 Fig 5.9 at P80.

