Chapter 5

Applications of Statistical Thermodynamics

5.1 Entropy S

M. C. E.

$\downarrow$

Macroscopic parameters: $E,\ \{x_i\}$

$\downarrow$

$$S = S(E,\ \{x_i\}) \tag{5.1}$$

$$= k_B \ln \Omega(E,\ \{x_i\}) \tag{5.2}$$

$$dS = \left(\frac{\partial S}{\partial E}\right)_{\{x_i\}} dE + \sum_i \left(\frac{\partial S}{\partial x_i}\right)_{E,\ \{x_i\}'} \cdot dx_i \tag{5.3}$$

$$= \frac{1}{T} dE + \sum_i \frac{\overline{X_i}}{T} dx_i \tag{5.4}$$

$\therefore$ one can obtain the other macroscopic quantities T & $\{\overline{X_i}\}$ from its derivatives.

e. g. 1 Gas system

$$x = V,\ \overline{X} = P \tag{5.5}$$

$$S = S(E,\ V),\ \frac{\partial S}{\partial E} = \frac{1}{T},\ \frac{\partial S}{\partial V} = \frac{P}{T} \tag{5.6}$$

e. g. 2 Magnetic system

$$x = B \text{ (external magnetic field)} \tag{5.7}$$

$$\overline{X} = M \text{ (magnetization)} \tag{5.8}$$

$$S = S(E,\ B) \tag{5.9}$$

$$\frac{\partial S}{\partial E} = \frac{1}{T},\ \frac{\partial S}{\partial B} = \frac{M}{T} \tag{5.10}$$

e. g. 1 & e. g. 2 $\longrightarrow$ $^{\exists}$four macroscopic quantities

$$\{(E,\ T),\ (V,\ P)\},\ \{(E,\ T),\ (B\ M)\} \tag{5.11}$$

$$\downarrow$$

Only two of the four quantities are indep.

$\because$ $^{\exists}$two conditions

$$\left(\frac{\partial S}{\partial E}\right)_x = \frac{1}{T},\ \left(\frac{\partial S}{\partial x}\right)_E = \frac{\overline{X}}{T} \tag{5.12}$$

$$\downarrow \qquad\qquad \downarrow$$

$$E = E(T,\ x) \qquad \overline{X} = \overline{X}(T,\ x) \tag{5.13}$$

5.2 Thermodynamic Potentials and Maxwell's relations

A thermodynamic function whose dimension is energy is called a "thermodynamic potential."

5.2.1 Internal Energy U

$$U = U(S,\ x) \tag{5.14}$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_x dS + \left(\frac{\partial U}{\partial x}\right)_S \cdot dx \tag{5.15}$$

$$dS = \frac{1}{T}dU + \frac{\overline{X}}{T}dx \longrightarrow dU = T\ dS - \overline{X} \cdot dx \tag{5.16}$$

$$\therefore \left(\frac{\partial U}{\partial S}\right)_x = T,\ \left(\frac{\partial U}{\partial x}\right)_S = -\overline{X} \tag{5.17}$$

$$\{(S,\ T)\ (x,\ \overline{X})\} \tag{5.18}$$

$$\frac{\partial^2 U}{\partial x\,\partial S} = \frac{\partial^2 U}{\partial S\,\partial x} \quad \longrightarrow \quad \left(\frac{\partial T}{\partial x}\right)_S = -\left(\frac{\partial \overline{X}}{\partial S}\right)_x \tag{5.19}$$

Maxwell's relation

$^\exists$four thermodynamic variables

↓

Only two of the four variables: indep.

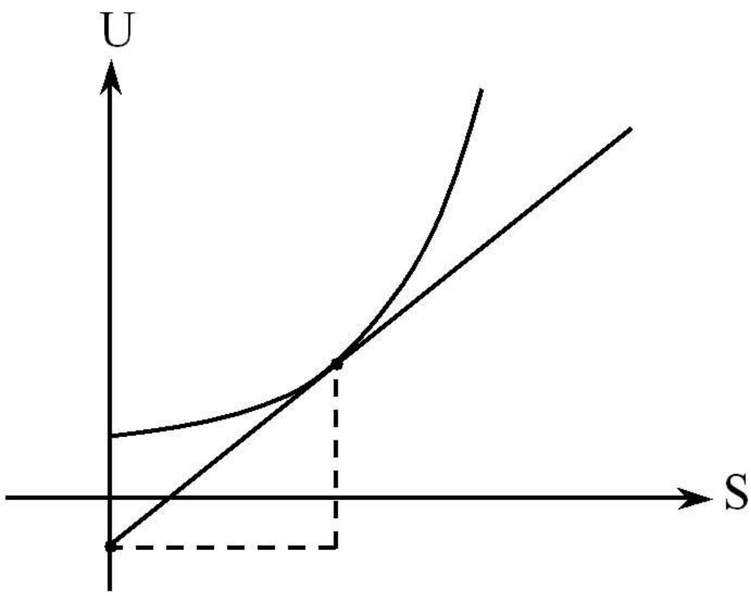
↓

The other two quantities can be obtained from the partial derivatives of the thermodynamic potential with respect to the chosen indep. thermodynamic variables

5.2.2 Helmholtz Free Energy

$$F = F(T,\ x) \longleftarrow U = U(S,\ x) \tag{5.20}$$

Legendry transformation



$$\text{Slope of the tangent:} \quad T \rightarrow \frac{\partial U}{\partial S} = T \tag{5.21}$$

$$\text{Intercept of the tangent:} \quad F \tag{5.22}$$

$$\longrightarrow \quad T = \frac{U - F}{S} \tag{5.23}$$

$$\therefore F(T,\ x) = U(S,\ x) - TS,\ \left(\frac{\partial U}{\partial S}\right)_x = T \tag{5.24}$$

$$S = S(T,\ x)$$

$$dF = dU - T\,dS - S\,dT \tag{5.25}$$

$$= -S\,dT - \overline{X} \cdot dx \tag{5.26}$$

$$\therefore \left(\frac{\partial F}{\partial T}\right)_x = -S,\ \left(\frac{\partial F}{\partial x}\right)_T = -\overline{X}. \tag{5.27}$$

$$\text{Maxwell's relation:} \quad \left(\frac{\partial S}{\partial x}\right)_T = \left(\frac{\partial \overline{X}}{\partial T}\right)_x$$

5.2.3 Enthalphy H

$$U = U(S,\ x) \quad \longrightarrow \quad H = H(S,\ \overline{X}) \tag{5.28}$$

$$\left(\frac{\partial U}{\partial x}\right)_S = \frac{U - H}{x} = -\overline{X} \tag{5.29}$$

$$\therefore H = U - \left(\frac{\partial U}{\partial x}\right)_S \cdot x \tag{5.30}$$

$$= U + \overline{X} \cdot x,\ \overline{X} = -\left(\frac{\partial U}{\partial x}\right)_S \tag{5.31}$$

$$\downarrow$$

$$x = x(S,\ \overline{X})$$

$$dH = dU + \overline{X} \cdot dx + x \cdot d\overline{X} \tag{5.32}$$

$$= T \cdot dS + x \cdot d\overline{X} \tag{5.33}$$

$$\therefore \left(\frac{\partial H}{\partial S}\right) = T, \ \left(\frac{\partial H}{\partial \overline{X}}\right) = x. \tag{5.34}$$

$$\text{Maxwell's relation: } \left(\frac{\partial T}{\partial \overline{X}}\right)_S = \left(\frac{\partial x}{\partial S}\right)_{\overline{X}}$$

5.2.4 Gibbs Free Energy G

$$F = F(T,\ x) \quad \longrightarrow \quad G = G(T,\ \overline{X}) \tag{5.35}$$

$$\left(\frac{\partial F}{\partial x}\right)_T = \frac{F - G}{x} = -\overline{X} \tag{5.36}$$

$$\therefore G = F - \left(\frac{\partial F}{\partial x}\right)_T \cdot x = F + \overline{X} \cdot x \tag{5.37}$$

$$dG = dF + \overline{X} \cdot dx + x \cdot d\overline{X} \tag{5.38}$$

$$= -S\, dT + x \cdot d\overline{X} \tag{5.39}$$

$$\therefore \left(\frac{\partial G}{\partial T}\right)_x = -S, \ \left(\frac{\partial G}{\partial \overline{X}}\right)_T = x. \tag{5.40}$$

$$\text{Maxwell's relation: } -\left(\frac{\partial S}{\partial \overline{X}}\right)_T = \left(\frac{\partial x}{\partial T}\right)_{\overline{X}}$$

5.3 Extensive and Intensive Parameters

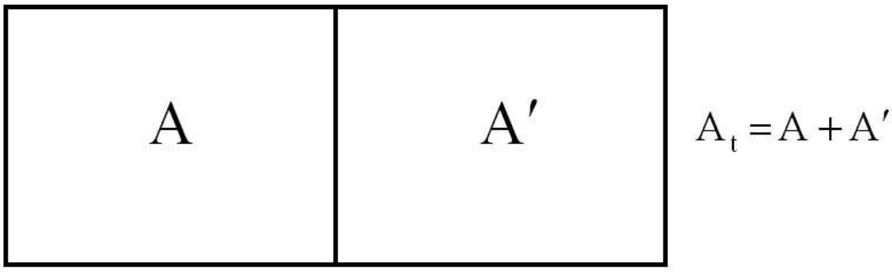
Let us consider a system A_t whose macrostate is specified by macroscopic parameters $(E,\ \{x_i\},\ N)$.

$$\downarrow$$

$$S$$

$$\downarrow$$

$$T,\ \{\overline{X_i}\}$$



$$N_t = N + N', \quad E_t = E + E', \quad S_t = S + S', \tag{5.41}$$

$$V_t = V + V', \quad M_t = M + M', \tag{5.42}$$

$$T_t = T = T', \quad P_t = P = P', \quad B_t = B + B' \tag{5.43}$$

y : a macroscopic parameter

$y_t = y + y' \implies y$: extensive parameter

$y_t = y = y' \implies y$: intensive parameter

extensive parameter $\longrightarrow$ intensive parameter

$$\text{int.} \;=\frac{\text{ext.}}{\text{ext.}} \tag{5.44}$$

$$\text{e. g. } e = \frac{E}{N}, \; m = \frac{M}{N}, \; \ldots \tag{5.45}$$

5.4 Relations between partial derivatives of several variables

There are three variables $(x, \; y, \; z)$.

But, only two variables are independent.

$$\text{e. g. } (x, \; y) : \text{ indep., } z = z(x, \; y) \tag{5.46}$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{5.47}$$

$$\left(\frac{\partial y}{\partial x}\right)_z \quad ? \tag{5.48}$$

$$\left(\frac{\partial y}{\partial x}\right)_z = -\frac{\left(\frac{\partial z}{\partial x}\right)_y}{\left(\frac{\partial z}{\partial y}\right)_x} : \text{ Euler's relation} \tag{5.49}$$

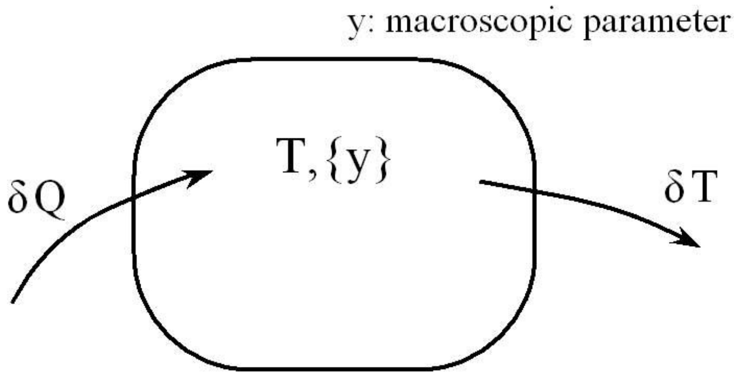
$$F = F(x,\ y(x,\ z)),\ y = y(x,\ z) \tag{5.50}$$

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy \tag{5.51}$$

$$\left(\frac{\partial F}{\partial x}\right)_z = \left(\frac{\partial F}{\partial x}\right)_y + \left(\frac{\partial F}{\partial y}\right)_x \cdot \left(\frac{\partial y}{\partial x}\right)_z \tag{5.52}$$

$$\left(\frac{\partial F}{\partial z}\right)_x = \left(\frac{\partial F}{\partial y}\right)_x \cdot \left(\frac{\partial y}{\partial z}\right)_x \tag{5.53}$$

5.5 Specific Heat and Susceptibility



$$\delta Q = C_y \cdot \delta T \tag{5.54}$$

Def. Heat Capacity

$$C_y \equiv \left(\frac{\delta Q}{\delta T}\right)_y \tag{5.55}$$

$$\longrightarrow C_y = C_y(T,\ y) : \text{ ext. parameter} \tag{5.56}$$

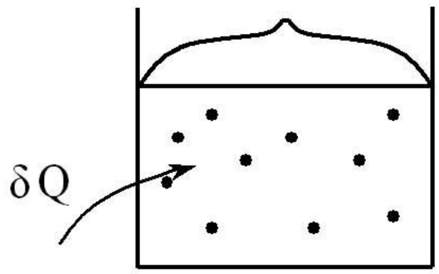
Ext.$\longrightarrow$ Int.

$$\frac{C_y}{N},\ \frac{C_y}{M},\ \frac{C_y}{\nu} : \text{ specific heat per ptl., mass, mole} \tag{5.57}$$

e. g. 1 Gas system

$$y = V,\ P \tag{5.58}$$

(1) C_V



$$dU = \delta Q - \delta W = T\ dS - P\ dV \tag{5.59}$$

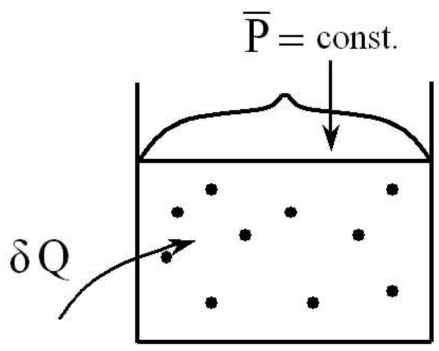
$$\downarrow V = \text{const}$$

$$dU = \delta Q \tag{5.60}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T \cdot \left(\frac{\partial S}{\partial T}\right)_V \tag{5.61}$$

$$= -T \cdot \left(\frac{\partial^2 F}{\partial T^2}\right)_V \tag{5.62}$$

(2) C_P



$$\delta Q = dU + P \cdot dV = dH \tag{5.63}$$

$$dH = T \cdot dS + V \cdot dP \tag{5.64}$$

One can expect that $C_P > C_V$

$$C_P = \left(\frac{\delta Q}{\delta T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P = T \cdot \left(\frac{\partial S}{\partial T}\right)_P \tag{5.65}$$

$$= T \cdot \left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P\right] \tag{5.66}$$

$$= C_V + T \cdot \left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P \tag{5.67}$$

$$\therefore\ C_P - C_V = T \cdot \left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P \tag{5.68}$$

$$V = V(T,\ P) \tag{5.69}$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P \cdot dT + \left(\frac{\partial V}{\partial P}\right)_T \cdot dP = 0 \tag{5.70}$$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} : \text{ Euler's relation} \tag{5.71}$$

$$\therefore\ C_P - C_V = -T \cdot \frac{\left[\left(\frac{\partial V}{\partial T}\right)_P\right]^2}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{5.72}$$

Def. Coefficient of Volume Expansion

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{5.73}$$

Def. Isothermal Compressibility

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{5.74}$$

$$\therefore\ C_P - C_V = T \cdot V \cdot \frac{\alpha^2}{\kappa} > 0 \tag{5.75}$$

(3) Limiting Behavior of C_y ($T \to 0$)

$$T \longrightarrow 0^+,\ E = E_0 \tag{5.76}$$

$$S = k_B \ln \Omega(E_0) \tag{5.77}$$

$$= S_0 : \text{ indep. of all parameters} \tag{5.78}$$

$$C_y = T \cdot \left(\frac{\partial S}{\partial T}\right)_y \to \left(\frac{\partial S}{\partial T}\right)_y = \frac{C_y}{T} \; ; \; y = V \& P \tag{5.79}$$

$$\therefore S(T) - S(0) = \int_0^T \frac{C_y(T')}{T'} \cdot dT' \tag{5.80}$$

$$\therefore \text{ As } T \to 0, \; C_y(T) \to 0. \tag{5.81}$$

$$(\because \text{ to guarantee the proper convergence of the integral}) \tag{5.82}$$

e. g. 2 Magnetic system

$$dU = T\,dS - M\,dB \tag{5.83}$$

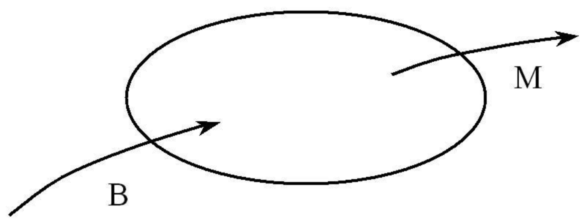
$$dF = -S\,dT - M\,dB, \; S = -\left(\frac{\partial F}{\partial T}\right)_B \;\&\; M = -\left(\frac{\partial F}{\partial B}\right)_T \tag{5.84}$$

- Specific heat

$$C_B = \left(\frac{\partial U}{\partial T}\right)_B = T \cdot \left(\frac{\partial S}{\partial T}\right)_B = -\left(\frac{\partial^2 F}{\partial T^2}\right)_B \tag{5.85}$$

- Magnetic Susceptibility

$$\chi = \left(\frac{\partial M}{\partial B}\right)_T = \left(\frac{\partial^2 F}{\partial B^2}\right)_T \tag{5.86}$$



e. g. 1 Ideal Gas

$$S = N\,k_B \left[\ln V + \frac{3}{2} \ln U\right] + S_0 \tag{5.87}$$

$$\downarrow$$

$$U(S,\; V) = e^{\frac{2(S-S_0)}{3Nk_B}} \cdot V^{-\frac{2}{3}} \tag{5.88}$$

$$\frac{\partial U}{\partial S} = \frac{2}{3N\ k_B} \cdot U = T \longrightarrow U = \frac{3}{2} N\ k_B T \tag{5.89}$$

$$\frac{\partial U}{\partial V} = -\frac{2}{3} U = -P \longrightarrow P\ V = N\ k_B T \tag{5.90}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} N\ k_B \longrightarrow \frac{C_V}{N} = \frac{3}{2} k_B \tag{5.91}$$

$$H(S,\ P) = U(S,\ V) + P \cdot V \tag{5.92}$$

$$\downarrow$$

$$H = \frac{5}{2} N\ k_B T \tag{5.93}$$

$$\therefore\ C_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{5}{2} N\ k_B \longrightarrow \frac{C_P}{N} = \frac{5}{2} k_B \tag{5.94}$$

$$\therefore\ C_P - C_V = N\ k_B \tag{5.95}$$

- Coefficient of volume expansion:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{T} \tag{5.96}$$

- Isothermal compressibility

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{P} \tag{5.97}$$

e. g. 2 Magnetic System

$$S(U,\ B) = -N\ k_B [p_+ \ln p_+ + p_- \ln p_-] \tag{5.98}$$

$$p_+ = \frac{1}{2}\left[1 + \frac{U}{N\varepsilon}\right],\ p_- = \frac{1}{2}\left[1 - \frac{U}{N\varepsilon}\right] \tag{5.99}$$

$$\varepsilon = -\mu B \tag{5.100}$$

$$\frac{\partial S}{\partial U} = \frac{1}{T} \longrightarrow U(T,\ B) = -N \cdot \varepsilon \cdot \tanh \frac{\varepsilon}{k_B T} \tag{5.101}$$

$$C_B = \left(\frac{\partial U}{\partial T}\right)_B = \frac{N\varepsilon^2}{k_B T^2} \cdot \mathrm{sech}^2 \frac{\varepsilon}{k_B T} \tag{5.102}$$

$$\frac{\partial S}{\partial B} = \frac{M}{T} \longrightarrow M = N\mu \cdot \tanh(\frac{\mu B}{k_B T}) \tag{5.103}$$

$$\chi_T = \left(\frac{\partial M}{\partial B}\right)_T = \frac{N\mu^2}{k_B T}\,\text{sech}^2\left(\frac{\mu B}{k_B T}\right) \propto \frac{1}{T} \tag{5.104}$$

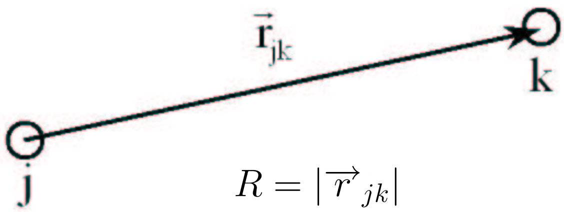
5.6 Van der Walls Gas

Non-ideal gas $\longrightarrow$ interacting gas

$$H = T + U,\ T = \sum_{i=1}^{N} \frac{\overrightarrow{P_i^2}}{2m} \tag{5.105}$$

U?

"pair interaction" u_{jk}



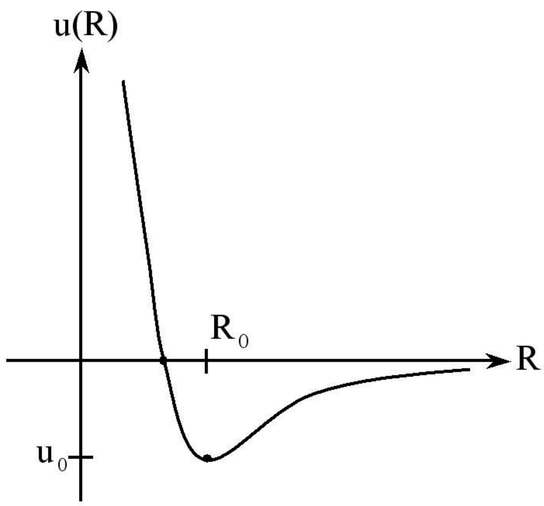
$$R = |\overrightarrow{r}_{jk}| \tag{5.106}$$

"Lennard-Jones potential" (semi-empirical pot.)

$$u(R) = u_0 \left[\left(\frac{R_0}{R}\right)^{12} - 2\left(\frac{R_0}{R}\right)^{6}\right] \tag{5.107}$$

u_0 & R_0 (empirical parameters):

constants depending on the molecules or atoms under consideration



long-range attractive part

+

short-range repulsive part

$$U = \frac{1}{2} \sum_{j,\, k=1 (j \neq k)}^{N} u_{jk} \tag{5.108}$$

- (Empirical) Eq. of State

$$(p + \underline{a \cdot \frac{N^2}{V^2}}) \cdot (V - \underline{b \cdot N}) = N \cdot k_B T \tag{5.109}$$

long-range attraction   short-range repulsion

a, b: empirical positive parameters depending on the molecules or atoms

- Virial expansion

$$p + an^2 = nk_B T (1 - bn)^{-1} \tag{5.110}$$

$$\downarrow$$

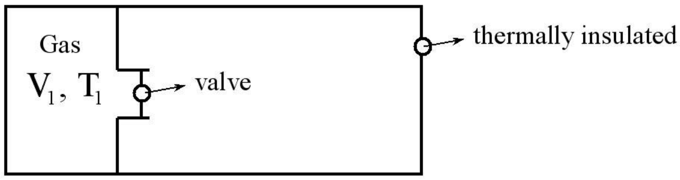
$$\begin{aligned} p &= nk_B T [1 + bn + b^2 n^2 + \cdots] - an^2 & (5.111) \\ &= nk_B T \left[1 + \left(b - \frac{a}{k_B T} \right) n + \cdots \right] & (5.112) \end{aligned}$$

Generally, $p = k_B T [n + B_2(T) \cdot n^2 + B_3(T) \cdot n^3 + \cdots]$

$$B_2,\ B_3,\ \cdots:\ \text{virial coefficients} \tag{5.113}$$

$$\text{Van der Waals} \longrightarrow B_2(T) = b - \frac{a}{k_B T} \tag{5.114}$$

5.7 Free Expansion



$$\text{Initial state: } V_1,\ T_1 \tag{5.115}$$

$$\downarrow \qquad \text{valve: open}$$

$$\text{Final state: } V_2,\ T_2(?) \tag{5.116}$$

$$Q = 0,\ W = 0 \longrightarrow U = \text{const.} \tag{5.117}$$

$$\left(\frac{\partial T}{\partial V}\right)_U ? \tag{5.118}$$

$$U = U(T,\ V) \rightarrow dU = \left(\frac{\partial U}{\partial V}\right)_T \cdot dV + \left(\frac{\partial U}{\partial T}\right)_V \cdot dT \tag{5.119}$$

$$= 0 \tag{5.120}$$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V} = -\frac{1}{C_V} \cdot \left(\frac{\partial U}{\partial V}\right)_T \tag{5.121}$$

$$U = U(S,\ V) \tag{5.122}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_S + \left(\frac{\partial U}{\partial S}\right)_V \cdot \left(\frac{\partial S}{\partial V}\right)_T \tag{5.123}$$

$$= -p + T \cdot \left(\frac{\partial p}{\partial T}\right)_V \tag{5.124}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = \frac{\alpha_p}{\kappa_T} \tag{5.125}$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = -p + \frac{T \cdot \alpha_p}{\kappa_T} \tag{5.126}$$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}[p - T \cdot \frac{\alpha_p}{\kappa_T}] \tag{5.127}$$

e. g. 1 Ideal Gas

$$\left(\frac{\partial T}{\partial V}\right)_U = 0 \qquad T_2 = T_1 \tag{5.128}$$

e. g. 2 Van der Waals Gas

$$p \simeq k_B T[n + B_2(T)n^2] = nk_B T(1 + B_2 \cdot n) \tag{5.129}$$

$$B_2(T) = b - \frac{a}{k_B T} \tag{5.130}$$

$$V \simeq \frac{Nk_B T}{p}(1 + B_2 \cdot n) \tag{5.131}$$

$$= N(\frac{k_B T}{p} + B_2 \cdot \frac{nk_B T}{p}) \tag{5.132}$$

$$\simeq N \cdot (\frac{k_B T}{p} + B_2) \tag{5.133}$$

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \simeq \frac{N}{V}\left(\frac{k_B}{p} + \frac{\partial B_2}{\partial T}\right) \tag{5.134}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \simeq \frac{N}{V} \cdot \frac{k_B T}{p^2} \tag{5.135}$$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left(-\frac{p^2}{k_B}\right)\frac{\partial B_2}{\partial T} \tag{5.136}$$

$$\frac{\partial B_2}{\partial T} = \frac{a}{k_B T^2} > 0 \tag{5.137}$$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_U < 0 \tag{5.138}$$

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V} \cdot a \cdot \left(\frac{p}{k_B T}\right)^2 \tag{5.139}$$

$$\simeq -\frac{a}{C_V} \cdot n^2 < 0 \tag{5.140}$$

$$T_2 < T_1 \tag{5.141}$$

5.8 Adiabatic Expansion

Quasi-static adiabatic process: $\triangle S = 0$

$$\left(\frac{\partial T}{\partial V}\right)_S ? \tag{5.142}$$

$$S = S(T,\ V) \tag{5.143}$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V \cdot dT + \left(\frac{\partial S}{\partial V}\right)_T \cdot dV = 0 \tag{5.144}$$

$$\begin{aligned}
\therefore \left(\frac{\partial T}{\partial V}\right)_S &= -\frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} && (5.145)\\
&= -\frac{T}{C_V}\cdot\left(\frac{\partial P}{\partial T}\right)_V && (5.146)\\
&= -\frac{T}{C_V}\cdot\frac{\alpha_P}{\kappa_T} && (5.147)
\end{aligned}$$

e. g. Ideal Gas

$$\begin{aligned}
\left(\frac{\partial T}{\partial V}\right)_S &= -\frac{T}{C_V}\cdot\left(\frac{\partial P}{\partial T}\right)_V,\ P\cdot V = Nk_BT,\ C_V = \frac{3}{2}Nk_B && (5.148)\\
&= -\frac{T}{C_V}\cdot\frac{Nk_B}{V} && (5.149)\\
&= -\frac{3}{2}\cdot\frac{T}{V} && (5.150)
\end{aligned}$$

$$\therefore \frac{1}{T}dT = -\frac{2}{3}\cdot\frac{1}{V}dV \tag{5.151}$$

$$\downarrow$$

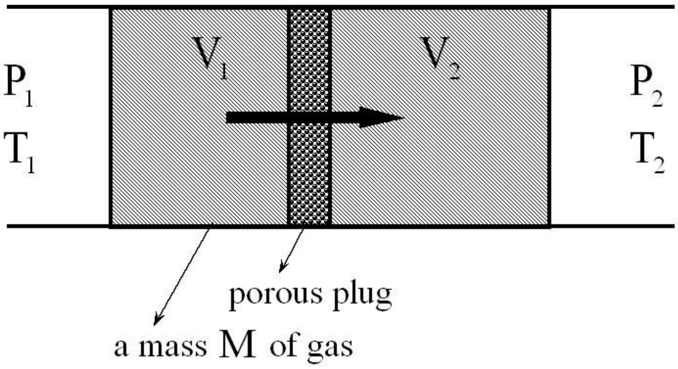
$$T_f\cdot V_f^{\frac{2}{3}} = T_i\cdot V_i^{\frac{2}{3}} \tag{5.152}$$

$$\gamma \equiv \frac{C_P}{C_V} = \frac{5}{3} \longrightarrow T\cdot V^{\gamma-1} = \text{const.} \tag{5.153}$$

$$\downarrow$$

$$P\cdot V^{\gamma} = \text{const.} \tag{5.154}$$

5.9 Throttling Process (Joule-Thomson process)



thermally insulated P_1 & P_2: const. $P_1 > P_2$

The gas to the left of the mass M $\rightarrow$ mass $M = P_1 \cdot V_1$

Mass M $\rightarrow$ the gas to the right of it $= P_2 \cdot V_2$

$$Q = 0, \tag{5.155}$$

$$W = P_2 \cdot V_2 - P_1 \cdot V_1 \tag{5.156}$$

$$\therefore \ \triangle U = -W = P_1 \cdot V_1 - P_2 \cdot V_2 \tag{5.157}$$

$$\therefore \ U_1 + P_1 \cdot V_1 = U_2 + P_2 V_2 \tag{5.158}$$

$$\therefore \ H_1 = H_2 \longrightarrow H = \text{const} \tag{5.159}$$

$$H(T_1,\ P_1) = H(T_2,\ P_2) \tag{5.160}$$

$$\text{J. T. coefficient} \quad \mu \equiv \left(\frac{\partial T}{\partial P}\right)_H \tag{5.161}$$

$$H = H(T,\ P) \longrightarrow dH = \left(\frac{\partial H}{\partial T}\right)_P \cdot dT + \left(\frac{\partial H}{\partial P}\right)_T \cdot dP = 0 \tag{5.162}$$

$$\therefore \ \mu = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\frac{1}{C_P} \cdot \left(\frac{\partial H}{\partial P}\right)_T \tag{5.163}$$

$$H = H(S,\ P) \longrightarrow dH = T\ dS + V\ dP \tag{5.164}$$

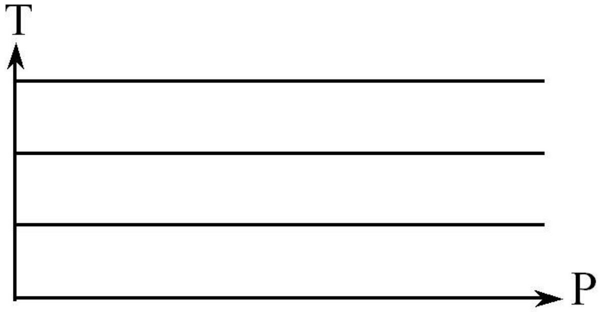
$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_S + \left(\frac{\partial H}{\partial S}\right)_P \cdot \left(\frac{\partial S}{\partial P}\right)_T \tag{5.165}$$

$$= V - T \cdot \left(\frac{\partial V}{\partial T}\right)_P \tag{5.166}$$

$$\therefore \ \mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(T \cdot \alpha_P - 1) \tag{5.167}$$

e. g. 1 Ideal Gas

$$\alpha_P = \frac{1}{T} \longrightarrow \mu = 0 \text{ (no temp. change)} \tag{5.168}$$



$$H = \frac{5}{2}k_B T \qquad \left(\frac{\partial T}{\partial P}\right)_H = 0 \tag{5.169}$$

e. g. 2 Van der Waals Gas

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{Nk_B}{P \cdot V} + \frac{N}{V}\frac{\partial B_2}{\partial T} \tag{5.170}$$

$$T \cdot \alpha_P - 1 = \frac{Nk_B T}{P \cdot V} + \frac{NT}{V}\frac{\partial B_2}{\partial T} - 1 \tag{5.171}$$

$$\frac{Nk_B T}{P \cdot V} = (1 + B_2 \cdot n)^{-1} \simeq 1 - B_2 \cdot n \tag{5.172}$$

$$\therefore \ T \cdot \alpha_P - 1 \simeq (T \cdot \frac{\partial B_2}{\partial T} - B_2) \cdot n \tag{5.173}$$

$$\frac{\partial B_2}{\partial T} = \frac{a}{k_B T^2} \tag{5.174}$$

$$\therefore \ \mu \cong \frac{N}{C_P}(T \cdot \frac{\partial B_2}{\partial T} - B_2) = \frac{N}{C_P}(\frac{2a}{k_B T} - b) \tag{5.175}$$

For sufficiently low temp., $\frac{a}{k_B T}$ (attractive int.)

$$> b \text{ (repulsive int.)}$$

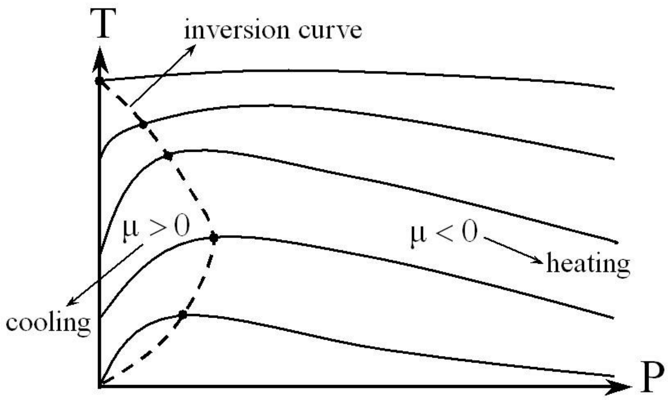
$$\therefore\ \mu > 0 \text{ (cooling)} \tag{5.176}$$

For sufficiently high temp., $\frac{a}{k_B T} < b$

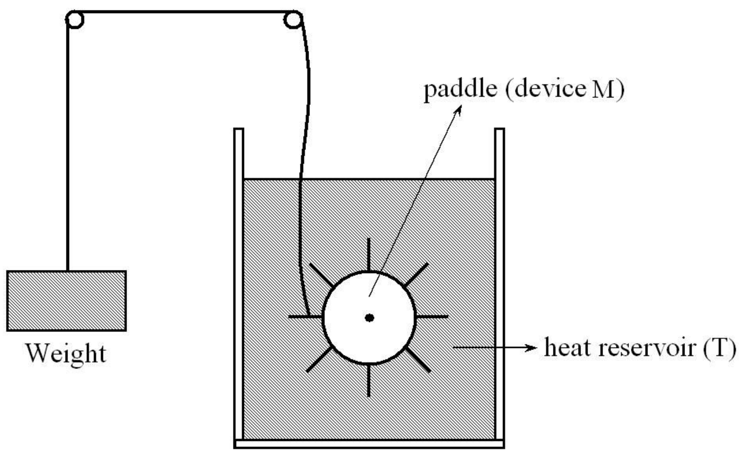
$$\therefore\ \mu < 0 \text{ (heating)} \tag{5.177}$$

For some intermediate temp., $\frac{a}{k_B T} = b$

$$\mu = 0 \tag{5.178}$$



5.10 Heat Engine

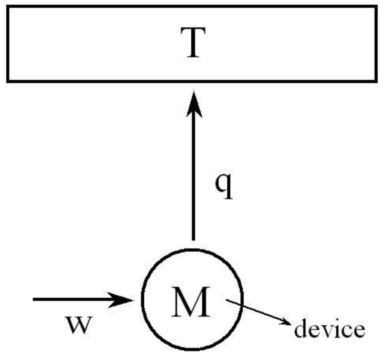


- Falling a weight

  Conversion of mechanical work into heat

$\Updownarrow$

Transformation of order into randomness



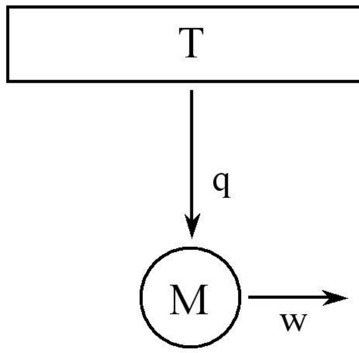
many degrees of freedom (random motion)

$\triangle S = \frac{q}{T} > 0$

(a single degree of freedom): ordered motion

- Lifting a weight

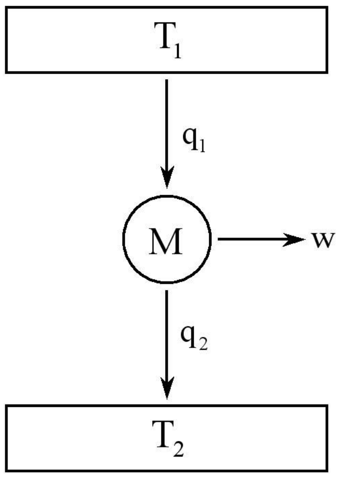
Conversion of heat into work (reverse process)



$\triangle S = -\frac{q}{T} < 0$

Perfect Engine for one cycle

Real Engine



$T_1 > T_2$

$$q_1 = W + q_2,\ \triangle S = -\frac{q_1}{T_1} + \frac{q_2}{T_2} \geq 0 \tag{5.179}$$

$$-\frac{q_1}{T_1} + \frac{q_1 - W}{T_2} \geq 0 \longrightarrow \frac{W}{T_2} \leq q_1 \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5.180}$$

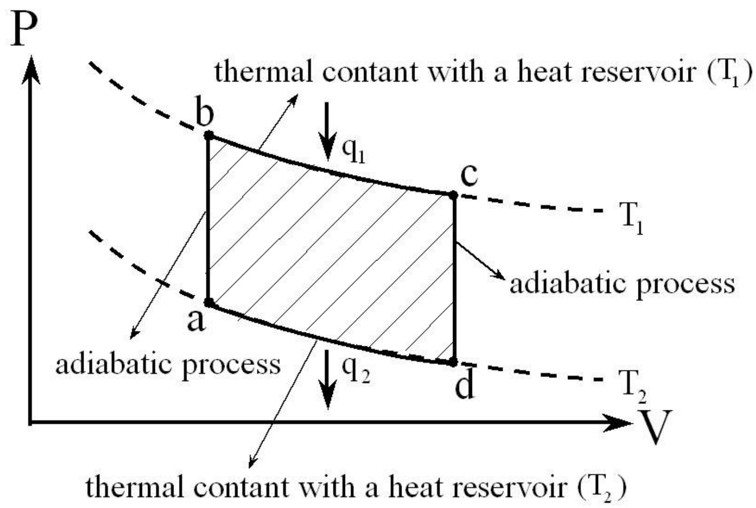
$$\therefore\ T_2 < T_1 \tag{5.181}$$

$$\text{Efficiency} \quad \eta \equiv \frac{W}{q_1} \leq 1 - \frac{T_1}{T_2} = \frac{T_1 - T_2}{T_1} \tag{5.182}$$

$=$: quasi-static process (max. work)

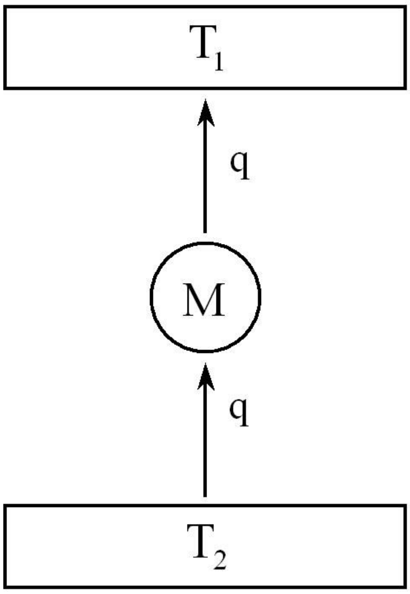
↓

e. g. Carnot Engine



5.11 Refrigerators

- a perfect refrigerator

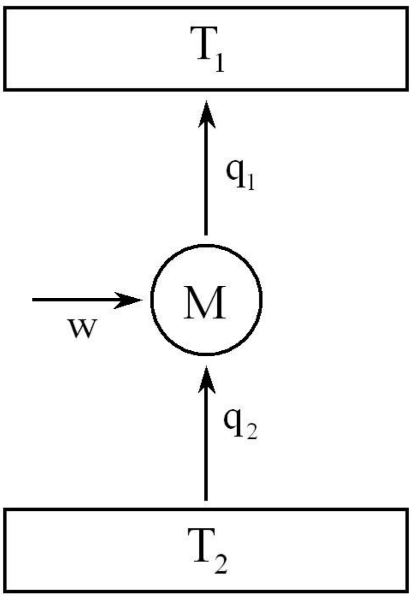


$$T_1 > T_2$$
$$q > 0$$

$$\triangle S = q\left(\frac{1}{T_1} - \frac{1}{T_2}\right) < 0 \qquad (5.183)$$

$\therefore$ impossible

- a real refrigerator



$$T_1 > T_2$$

$$\triangle S = \frac{q_1}{T_1} - \frac{q_2}{T_2} \geq 0 \quad \longrightarrow \quad \frac{q_2}{q_1} \leq \frac{T_2}{T_1} \tag{5.184}$$

$$\frac{q_2}{q_2 + W} \leq \frac{T_2}{T_1} \tag{5.185}$$

$$\downarrow$$

$$q_2 \leq W \left(\frac{T_2}{T_1 - T_2} \right) \tag{5.186}$$

Coefficient of performance of a refrigerate

$$K \equiv \frac{q_2}{W} \leq \frac{T_2}{T_1 - T_2} \tag{5.187}$$