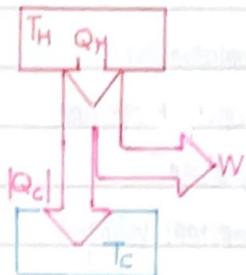


## The Second Law of Thermodynamics

### Heat Engines



cyclic process

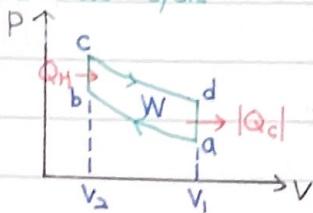
$$Q = Q_H + Q_C = |Q_H| - |Q_C|$$

$$W = Q = Q_H + Q_C$$

$$\text{thermal efficiency } e = \frac{W}{Q_H} = \frac{|Q_H - Q_C|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|} = 1 + \frac{Q_C}{Q_H}$$

### Internal-Combustion Engines

#### the Otto cycle



$$b \rightarrow c \quad Q_H = C_V(T_c - T_b)$$

$$d \rightarrow a \quad |Q_C| = C_V(T_d - T_a)$$

$$W = Q_H + Q_C$$

$$= C_V [(T_c - T_b) - (T_d - T_c)]$$

$$\textcircled{2} \text{ heating at constant volume: } b \rightarrow c \quad e = \frac{W}{Q_H} = 1 - \frac{T_d - T_a}{T_c - T_b}$$

\textcircled{3} adiabatic expansion: c \rightarrow d

$$\textcircled{4} \text{ cooling at constant volume: } d \rightarrow a \quad \text{and } a \rightarrow b \quad T_a V_a^{r-1} = T_b V_b^{r-1}$$

$$c \rightarrow d \quad T_c V_c^{r-1} = T_d V_d^{r-1}$$

$$V_a = V_d = V_1 \quad V_b = V_c = V_2$$

$$(T_d - T_a) V_d^{r-1} = (T_c - T_b) V_c^{r-1}$$

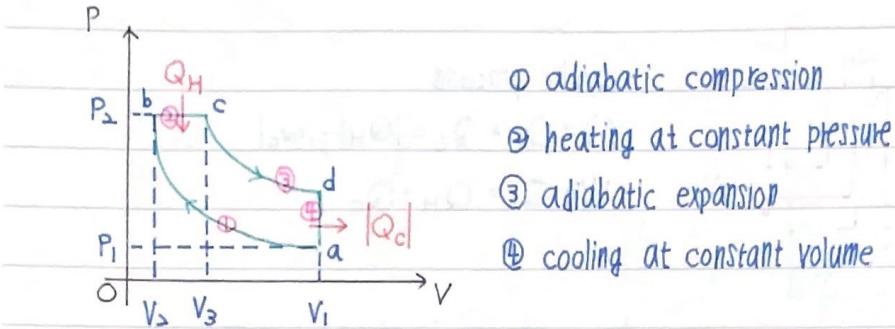
$$\frac{T_d - T_a}{T_c - T_b} = \left(\frac{V_c}{V_d}\right)^{r-1} = \left(\frac{V_2}{V_1}\right)^{r-1}$$

$$\Rightarrow e = 1 - \left(\frac{V_2}{V_1}\right)^{r-1}$$

$$\text{if } V_1 = r V_2, \text{ then } e = 1 - \frac{1}{r^{r-1}}$$

$$\text{for } r=8 \text{ and } r=1.4 \text{ (the value of air), } e=56\%$$

## the Diesel cycle



① adiabatic compression

② heating at constant pressure

③ adiabatic expansion

④ cooling at constant volume

$$\textcircled{2} \quad Q_H = C_p(T_c - T_b)$$

$$\textcircled{4} \quad |Q_C| = C_v(T_d - T_a)$$

$$\text{so } e = \frac{W}{Q_H} = 1 - \frac{C_v}{C_p} \frac{T_d - T_a}{T_c - T_b} = 1 - \frac{1}{r} \frac{T_d - T_a}{T_c - T_b}$$

$$\text{and } b \rightarrow c \quad \frac{T_b}{V_b} = \frac{T_c}{V_c} \text{ due to constant pressure}$$

$$T_c = \frac{V_c}{V_b} T_b = \frac{V_3}{V_2} T_b$$

$$a \rightarrow b \quad T_a V_a^{r-1} = T_b V_b^{r-1} \quad T_a = T_b \left( \frac{V_b}{V_a} \right)^{r-1} = T_b \left( \frac{V_2}{V_1} \right)^{r-1}$$

$$c \rightarrow d \quad T_c V_c^{r-1} = T_d V_d^{r-1} \quad T_d = T_c \left( \frac{V_c}{V_d} \right)^{r-1} = \frac{V_3}{V_2} T_b \left( \frac{V_3}{V_1} \right)^{r-1}$$

$$e = 1 - \frac{1}{r} \frac{\frac{V_3}{V_2} T_b \left( \frac{V_3}{V_1} \right)^{r-1} - T_b \left( \frac{V_2}{V_1} \right)^{r-1}}{\frac{V_3}{V_2} T_b - T_b} = 1 - \frac{1}{r} \frac{\frac{V_3}{V_2} \left( \frac{V_3}{V_1} \right)^{r-1} - \left( \frac{V_2}{V_1} \right)^{r-1}}{\frac{V_3}{V_2} - 1}$$

$$= 1 - \frac{1}{r} \frac{\frac{V_3}{V_2} \frac{V_1}{V_3} \left( \frac{V_3}{V_1} \right)^r - \frac{V_1}{V_2} \left( \frac{V_2}{V_1} \right)^r}{\frac{V_3}{V_2} - 1} = 1 - \frac{1}{r} \frac{\frac{V_1}{V_2} \left[ \left( \frac{V_3}{V_1} \right)^r - \left( \frac{V_2}{V_1} \right)^r \right]}{\frac{V_3}{V_2} - 1}$$

$$= 1 - \frac{1}{r} \frac{\left( \frac{V_3}{V_1} \right)^r - \left( \frac{V_2}{V_1} \right)^r}{\frac{V_3}{V_1} - \frac{V_2}{V_1}}$$

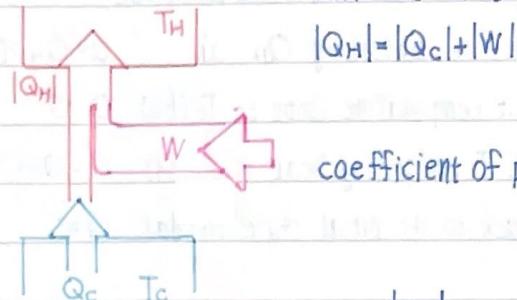
$$= 1 - \frac{1}{r} \frac{\left( \frac{V_3}{V_1} \right)^r - \left( \frac{V_2}{V_1} \right)^r}{\frac{V_3}{V_1} - \frac{V_2}{V_1}}$$

if  $V_1 = rV_2$ , and  $r = 15 \sim 20$   $r = 1.4$  then  $e = 0.65 \sim 0.70$

## Refrigerators

$$|W| = -W \quad |Q_H| = -Q_H$$

$$Q_H + Q_C - W = 0, \quad -Q_H = Q_C - W$$



$$\text{coefficient of performance } K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H - Q_C|}$$

$$= \frac{Ht}{Pt} = \frac{H}{P}$$

$$H = \frac{|Q_C|}{t} \quad \text{if heat } |Q_C| \text{ is removed in time } t$$

## The Second Law of Thermodynamics

### Kelvin-Planck statement, "engine" statement

it is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into mechanical work, with the system ending in the same state in which it began

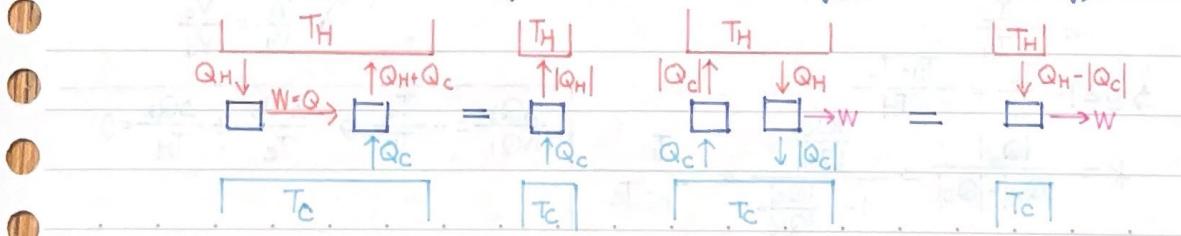
### Clausius statement, "refrigerator" statement

it is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter body

Kelvin-Planck statement and Clausius statement are equivalent

proof:

(1) if K.P. is wrong, then C is wrong, too      (2) if C. is wrong, then K.P. is wrong, too

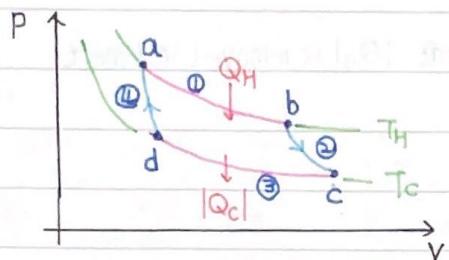


## The Carnot Cycle

to maximize the efficiency of engine  $\rightarrow$  must avoid all irreversible process: heat flow

$\rightarrow$  must have finite temperature difference  $\rightarrow$  isothermal and adiabatic

- ① the gas expands isothermally at  $T_H$ , absorbing  $Q_H$  (ab)  $Q = Q_H > 0 \quad W > 0$
- ② it expands adiabatically until its temperature drops to  $T_c$  (bc)  $Q = 0 \quad W > 0$
- ③ it is compressed isothermally at  $T_c$ , rejecting heat  $|Q_c|$  (cd)  $Q = -Q_c < 0 \quad W < 0$
- ④ it is compressed adiabatically back to its initial state  $T_H$  (da)  $Q = 0 \quad W < 0$



$$\textcircled{1} \Delta U_1 = 0 \quad \text{and} \quad \Delta U_1 = \Delta Q_1 - \Delta W_1 \quad \textcircled{2} \Delta Q_2 = 0$$

$$\Rightarrow \Delta Q_1 = \Delta W_1 = nR T_H \ln \frac{V_b}{V_a} \quad \Delta U_2 = \Delta W_2 = nC_V(T_L - T_H)$$

$$\textcircled{3} \Delta Q_3 = nR T_L \ln \frac{V_d}{V_c} = \Delta W_3 \quad \textcircled{4} \Delta U_4 = nC_V(T_H - T_L) = -\Delta W_4$$

$$\Delta W = \Delta W_1 + \Delta W_2 + \Delta W_3 + \Delta W_4 = \Delta W_1 + \Delta W_3 = \Delta Q_1 + \Delta Q_3$$

$$\Delta U = \Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4 = 0$$

$$\Delta Q = \Delta Q_1 + \Delta Q_2 + \Delta Q_3 + \Delta Q_4 = \Delta Q_1 + \Delta Q_3$$

$$e = \frac{\Delta W}{\Delta Q_1} = \frac{\Delta Q_1 + \Delta Q_3}{\Delta Q_1} = 1 + \frac{\Delta Q_3}{\Delta Q_1}$$

$$\frac{\Delta Q_3}{\Delta Q_1} = \frac{Q_c}{Q_H} = \frac{-nR T_c \ln \frac{V_c}{V_d}}{nR T_H \ln \frac{V_b}{V_a}} = -\frac{T_c}{T_H} \ln \frac{V_c}{V_d} \ln \frac{V_b}{V_a}$$

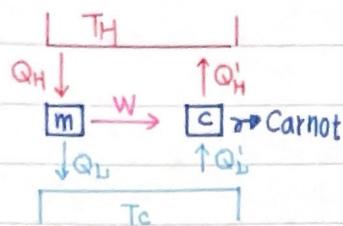
$$\text{and} \quad \begin{cases} T_H V_b^{r-1} = T_c V_c^{r-1} \\ T_H V_a^{r-1} = T_c V_d^{r-1} \end{cases} \Rightarrow \frac{V_b^{r-1}}{V_a^{r-1}} = \frac{V_c^{r-1}}{V_d^{r-1}} \Rightarrow \frac{V_b}{V_a} = \frac{V_c}{V_d}$$

$$\Rightarrow e = 1 - \frac{T_c}{T_H} = \frac{T_H - T_c}{T_H}$$

$$K = \frac{|Q_c|}{|Q_H| - |Q_c|} = \frac{|Q_c|}{1 - \frac{|Q_c|}{|Q_H|}} = \frac{T_c}{T_H - T_c}$$

$$\frac{\Delta Q_3}{\Delta Q_1} = -\frac{T_c}{T_H} \Rightarrow \frac{\Delta Q_3}{T_c} + \frac{\Delta Q_1}{T_H} = 0$$

Proof: all heat engines between two heat reservoirs are less efficient than a Carnot heat engine operating between the same reservoirs



$$e_m = \frac{W_m}{Q_H}$$

$$e_c = \frac{W_c}{Q'_H} \quad \text{and } W = W_m = W_c$$

$\Delta Q = Q_L - Q'_L = Q_H - Q'_H$  by the second law of thermodynamics, we know  $\Delta Q > 0$ .

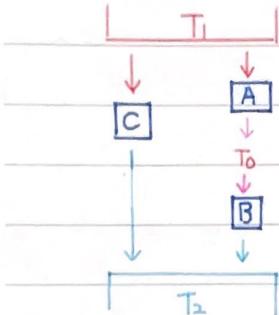
$$\text{so } \Delta Q > 0 \Rightarrow Q_H > Q'_H, e_c = \frac{W}{Q'_H} > \frac{W}{Q_H} = e_m$$

if m mechanic is also a Carnot heat engine, then mC mechanic is a reversible mechanic

$$\text{so } \Delta Q = 0 \Rightarrow Q_H = Q'_H \Rightarrow e_m = e_c$$

$$* e_m = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \leq 1 - \frac{T_L}{T_H} = e_c \Rightarrow \frac{T_L}{T_H} \leq \frac{Q_L}{Q_H}, \frac{Q_H}{T_H} \leq \frac{Q_L}{T_L}, \frac{Q_H}{T_H} - \frac{Q_L}{T_L} \leq 0$$

proof: define absolute temperature by Carnot heat engine



$$e_c = 1 - \frac{Q_2}{Q_1} = e_c(T_1, T_2), \quad \frac{Q_2}{Q_1} = 1 - e_c(T_1, T_2) = f(T_1, T_2)$$

$$\text{and } \frac{Q_2}{Q_1} = f(T_1, T_2) \quad \frac{Q_0}{Q_1} = f(\theta_1, \theta_0) \quad \frac{Q_2}{Q_0} = f(\theta_0, \theta_2)$$

$$\Rightarrow \frac{Q_2}{Q_1} = f(T_1, T_2) = f(T_1, T_0) f(T_0, T_2) \quad \text{let } T_1 = T_2, \text{ then } Q_1 = Q_2$$

$$\Rightarrow 1 = f(T_1, T_0) f(T_0, T_1), \quad f(T_1, T_0) = \frac{1}{f(T_0, T_1)}$$

$$\Rightarrow \frac{Q_2}{Q_1} = f(T_1, T_0) f(T_0, T_2) = \frac{f(T_0, T_2)}{f(T_0, T_1)}$$

$$\text{because } T_0 \text{ is arbitrary value, } \frac{Q_2}{Q_1} = \frac{f(T_0, T_2)}{f(T_0, T_1)} = \frac{\phi(T_2)}{\phi(T_1)}$$

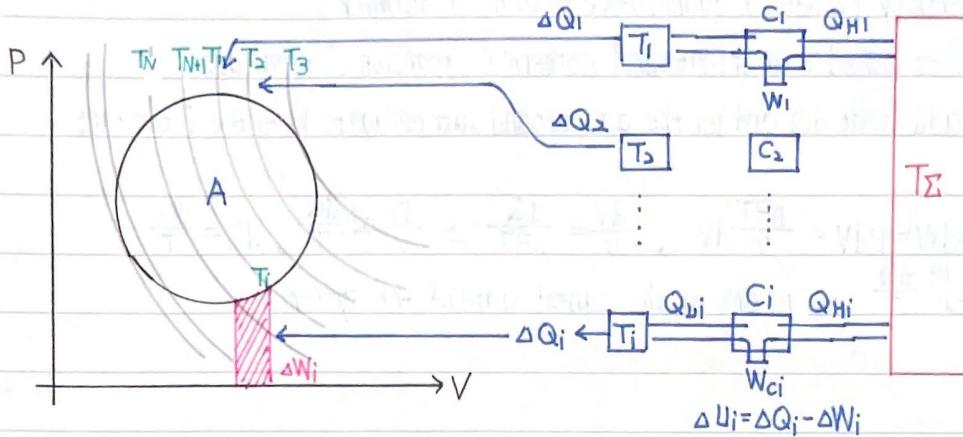
$\phi$  is a unknown function and only dependent temperature

so we define  $\phi(T) = cT(T)$   $c$  is constant  $T$  is absolute temperature

the freezing point of water is  $T_w = 273.16\text{K}$

$$\frac{Q_2}{Q_1} = \frac{\phi(T_2)}{\phi(T_1)} = \frac{T_2}{T_1}, \quad \frac{Q}{Q_w} = \frac{T}{T_w}, \quad T = T_w \frac{Q}{Q_w}$$

## Clausius Inequality



$$\Delta Q_i = Q_{Li} \quad \sum_{i=1}^{N+1} \Delta U_i = 0 = \sum_{i=1}^{N+1} (\Delta Q_i - \Delta W_i) = \sum_{i=1}^{N+1} \Delta Q_i - \sum_{i=1}^{N+1} \Delta W_i$$

$$W_A = \sum_{i=1}^{N+1} \Delta W_i = \sum_{i=1}^{N+1} \Delta Q_i \quad (\text{this doesn't mean } \Delta W_i = \Delta Q_i)$$

$$W_A + \underbrace{\sum_{i=1}^{N+1} W_{C,i}}_{\text{Work done by Carnot}} = \sum_{i=1}^{N+1} \Delta Q_i + \sum_{i=1}^{N+1} (Q_{Hi} - Q_{Li}) \quad \frac{\Delta Q_i}{T_i} = \frac{Q_{Li}}{T_i} = \frac{Q_{Hi}}{T_\Sigma} \text{ in Carnot}$$

Work done by Carnot

$$= \sum_{i=1}^{N+1} Q_{Hi} = T_\Sigma \sum_{i=1}^{N+1} \frac{\Delta Q_i}{T_i}$$

according to the second law of thermodynamics,  $W_A + \sum_i W_{Ci}$  must  $\leq 0$

$$\Rightarrow \sum_{i=1}^{N+1} \frac{\Delta Q_i}{T_i} \leq 0 \quad \sum_{i=1}^{N+1} \frac{-\Delta Q_i}{T_i} \geq 0 \quad \dots \text{---(1)}$$

if A cycle is reversible,  $\Delta U_i \rightarrow -\Delta U_i$ , the reverse cycle of A  $\sum_{i=1}^{N+1} \frac{-\Delta Q_i}{T_i} \leq 0 \quad \dots \text{---(2)}$

$$\Delta W_i \rightarrow -\Delta W_i$$

$$\Delta Q_i \rightarrow -\Delta Q_i$$

if A cycle is reversible, then by (1)(2)  $\sum_{i=1}^{N+1} \frac{\Delta Q_i}{T_i} = 0$

if  $N+1 \rightarrow \infty$  and  $|T_{i+1} - T_i| \rightarrow 0$ ,  $\lim_{N \rightarrow \infty} \sum_{i=1}^{N+1} \frac{\Delta Q_i}{T_i} = \oint \frac{dQ}{T} \leq 0$

If A is reversible,  $\oint \frac{dQ}{T} = 0$

define  $\int_a^b \frac{dQ}{T} = S(b) - S(a)$

## Entropy

\* entropy provides a quantitative measure of disorder

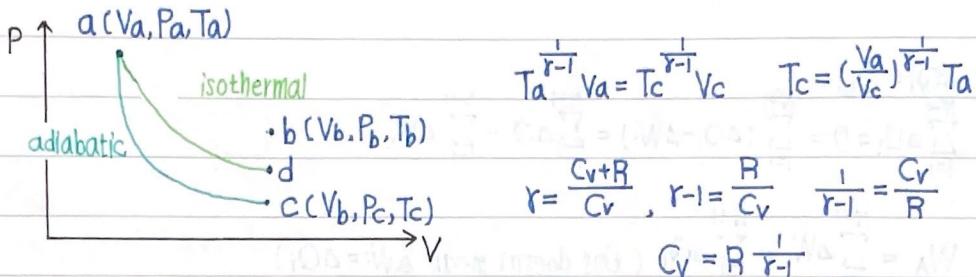
\* let's consider an infinitesimal isothermal expansion of ideal gas

add heat  $dQ$  and let the gas expand just enough to keep the  $T$  constant

$$dQ = dW = PdV = \frac{nRT}{V} dV, \quad \frac{dV}{V} = \frac{dQ}{nRT} \Rightarrow \frac{dV}{V} \propto \frac{dQ}{T}, \quad dS = \frac{dQ}{T}$$

$\Delta S = \int_1^2 \frac{dQ}{T}$  depend only on the current state of the system

### case I



$$S(b) - S(a) = S(b) - S(c) + S(c) - S(a), \quad = S(b) - S(c)$$

$$= \int_{T_c}^{T_b} \frac{n C_v dT}{T}$$

$$= n C_v \ln \frac{T_b}{T_c} = n C_v \ln \frac{T_b V_b^{\frac{1}{r-1}}}{T_a V_a^{\frac{1}{r-1}}} = n \frac{1}{r-1} \left[ (r-1) \ln \frac{V_b}{V_a} + \ln \frac{T_b}{T_a} \right]$$

$$= n R \left( \ln \frac{V_b}{V_a} + \ln \frac{T_b^{\frac{1}{r-1}}}{T_a^{\frac{1}{r-1}}} \right) = n R \frac{V_b T_b^{\frac{1}{r-1}}}{V_a T_a^{\frac{1}{r-1}}}$$

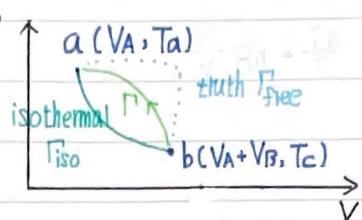
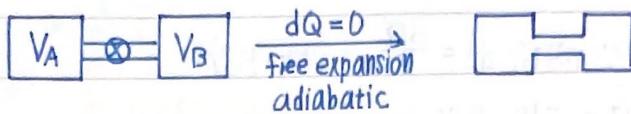
$$S(b) - S(a) = S(b) - S(d) + S(d) - S(a)$$

$$= \int_{T_a}^{T_b} \frac{n C_v dT}{T} + \int_a^d \frac{n R T_a}{T_a} \frac{dV}{V} = n C_v \ln \frac{T_b}{T_a} + n R \ln \frac{V_d}{V_a}$$

$$= n \frac{R}{r-1} \ln \frac{T_b}{T_a} + n R \ln \frac{V_d}{V_a} = n R \frac{V_b T_b^{\frac{1}{r-1}}}{V_a T_a^{\frac{1}{r-1}}}$$

$\Rightarrow S$  not depend on the path

## case II



$$S(b) - S(a) = nR \ln \frac{V_A + V_B}{V_A} = NR \ln \frac{V_A + V_B}{V_A}$$

notice: can't use  $\int \frac{dQ}{T}$  because this is irreversible

the cycle of free expansion and adiabatic plus isothermal process  $b \rightarrow a$

$$\oint \frac{dQ}{T} < 0$$

$$\oint \frac{dQ}{dT} = \int_{P_{\text{free}}}^P \frac{dQ}{T} + \int_b^a \frac{dQ}{T} = 0 + [S(a) - S(b)] < 0 \Rightarrow S(a) < S(b)$$

$\Rightarrow$  entropy increase at spontaneous process in isolated system

the mean of the different of entropy

$$e^{-\frac{S(a)-S(b)}{k}} = \frac{\left(\frac{V_c}{V_a+V_b}\right)^N}{\left(\frac{V_a}{V_a+V_b}\right)^N} = \frac{P_A}{P_{A+B}} = \frac{\Omega_A}{\Omega_{A+B}}$$

$$S(a) = k \ln P_a = k \ln \Omega_A \quad \text{Boltzmann formula}$$

$\Omega$  represent the number of possible microscopic state for a given macroscopic state

$$\Delta S = k \ln \Omega_2 - k \ln \Omega_1 = k \ln \frac{\Omega_2}{\Omega_1}$$

## case III the entropy of ideal gas

(a)  $S = S(V, T)$

We know  $dU = C_V dT$ ,  $PV = nRT$ ,  $dS = \frac{dQ}{T}$ ,  $dW = -PdV$

$$dU = dQ + dW \Rightarrow C_V dT = T dS - PdV$$

$$dS = \frac{C_V dT}{T} + \frac{PdV}{T} = C_V \frac{dT}{T} + nR \frac{dV}{V}$$

let  $C_V$  is a constant

$$\text{integration} \rightarrow S - S_0 = \int_{T_0}^T C_V \frac{dT}{T} + \int_{V_0}^V nR \frac{dV}{V}$$

$$\begin{aligned} S &= C_V \ln T + nR \ln V + (S_0 - C_V \ln T_0 - nR \ln V_0) \\ &= C_V \ln T + nR \ln V + S'_0 \end{aligned}$$

(b)  $S = S(P, T)$

We know  $C_P - C_V = nR$ ,  $PV = nRT$  and  $VdP + PdV = nRdT$

$$dS = \frac{C_V dT}{T} + \frac{PdV}{T}$$

$$= (C_P - nR) \frac{dT}{T} + \frac{nRdT - VdP}{T}$$

$$= C_P \frac{dT}{T} - V \frac{dP}{T} = C_P \frac{dT}{T} - nR \frac{dP}{P}$$

let  $C_P$  is a constant and integration

$$S - S_0 = \int_{T_0}^T C_P \frac{dT}{T} - \int_{P_0}^P nR \frac{dP}{P}$$

$$\begin{aligned} S &= C_P \ln T - nR \ln P + (S_0 - C_P \ln T_0 + nR \ln P_0) \\ &= C_P \ln T - nR \ln P + S'_0 \end{aligned}$$

case IV  A  $T_1$   B  $T_2$  and  $T_1 \neq T_2$

after two object touch,  $\Delta S$ ?

let P do not change and the final temperature is  $\frac{T_1+T_2}{2}$

$$dU = dQ + dW, dU = TdS - PdV, dS = \frac{dU + PdV}{T}$$

at the constant pressure,  $H = U + PV$ ,  $dH = dU + PdV$

$$dS = \frac{dH}{T} = C_p \frac{dT}{T}$$

$$\Delta S_A = \int_{T_1}^{\frac{T_1+T_2}{2}} C_p \frac{dT}{T} = C_p \ln \frac{T_1+T_2}{2T_1} \quad \Delta S_B = \int_{T_2}^{\frac{T_1+T_2}{2}} C_p \frac{dT}{T} = C_p \ln \frac{T_1+T_2}{2T_2}$$

$$\Delta S = \Delta S_A + \Delta S_B = C_p \ln \frac{(T_1+T_2)^2}{4T_1 T_2} > 0 \rightarrow \text{irreversible process}$$