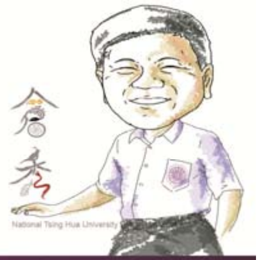
材 料 熱 力 學 一

Thermodynamics of Materials I



Chapter3 Second Law of Thermodynamics

§ 3-1 Introduction:

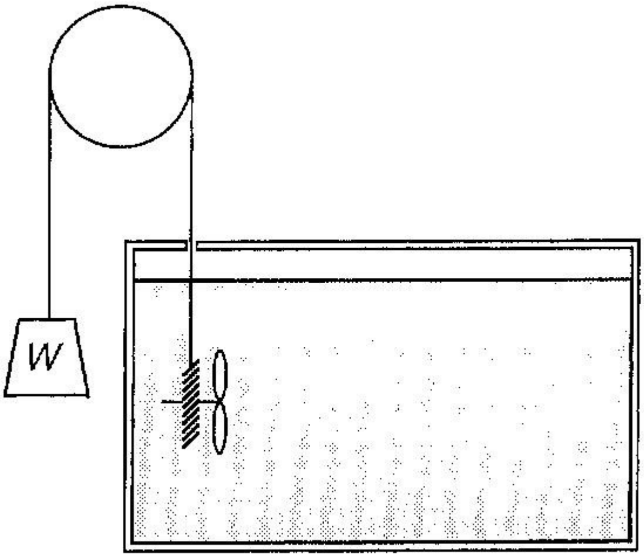
* Reversible & Irreversible processes
* Degree of irreversibility
* Entropy “S” ⟹ a state function
* Reversible heat engine → Carnot cycle (Engine)
* Criterion for Equilibrium → $S_{U,V}=S_{max}$

§ 3-2 Spontaneous (Natural) Process:

* Equilibrium state: rest state
Nonequilibrium state: spontaneous change to equilibrium
* Spontaneous process is irreversible
case 1: mixing of two gases
case 2: contact of two bodies at different temperature
* Isolated system: no mass and energy transfer with surrounding
i.e. constant U, V, m_i
Closed system: no mass transfer, but energy transfer exists
∴ constant m_i
Open system: both mass and energy transfer

§ Entropy and Degree of Irreversibility:

$$\begin{cases} (1)\ \text{conversion of work to heat} \\ (2)\ \text{heat flow down a temperature gradient} \end{cases}$$



processes:

(1) T_2, W(weight fall), Q(heat produced)

(2) Q(heat flow), $T_2 \xrightarrow{Q} T_1$

(3) T_1, W(weight fall), Q(heat produced)

$\because$ [(1)+(2) $\Leftrightarrow$ (3)]

process (3) is more irreversible than (1)

$$\text{compare } \left(\frac{Q}{T}\right) \left.\begin{matrix} \text{process (1): } \dfrac{Q}{T_2} \\ \\ \text{process (3): } \dfrac{Q}{T_1} \end{matrix}\right\}$$

$$\because T_2 > T_1 \qquad \therefore \left(\frac{Q}{T_2}\right)_{(1)} < \left(\frac{Q}{T_1}\right)_{(3)}$$

$$\text{we call} \qquad S \Rightarrow \left(\frac{Q}{T}\right)$$

$$\text{and} \qquad \triangle S = \left(\frac{Q}{T}\right)$$

$\therefore \triangle S$ is a measure of degree of irreversibility

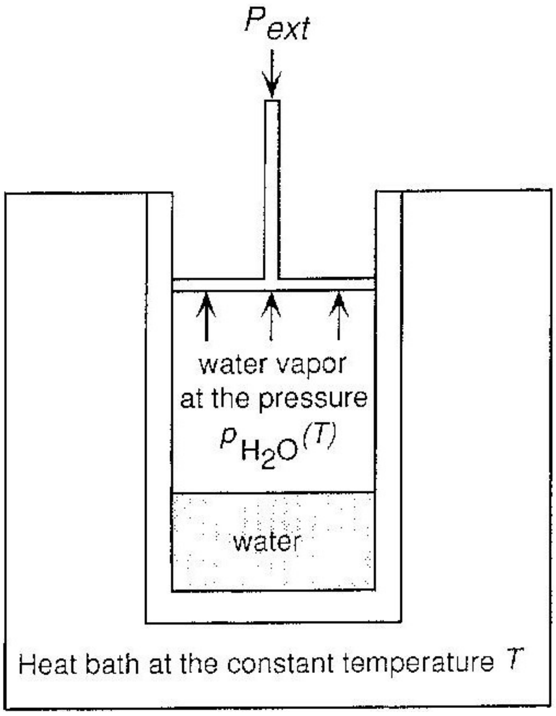
§ Reversible Processes:

- Irreversibility is zero and <u>no degradation</u>
- The process path passes through a <u>continuum of equilibrium states</u>
- It is an <u>imaginary</u> path
- Each step is under an infinitesimally small driving force

§ Example of Reversible & Irreversible Process:

Evaluation and Condensation of water

* Frictionless piston
  Heat reservoir at T
  Equilibrium: $P_{H2O}(T) = P_{ext}$



Process 1: sudden finite change of $\triangle P$

(1) decrease pressure: $(P_{ext} - \triangle P)$

spontaneous evaporation $\Longleftrightarrow$ heat absorbed, $(T_w \downarrow)$
assume: 1 mole H_2O evaporated molar volume of H_2O vapor V

$\therefore$ work done by system: $W_1 = (P_{ext} - \triangle P)V$

(2) increase pressure: $(P_{ext} - \triangle P) + \triangle P$

spontaneous condensation $\Longleftrightarrow$ exothermic $(T_w \uparrow)$

work done on system: $W_2 = -P_{ext} \cdot V$

$\therefore$(1)+(2) permanent change in external agency: $(\triangle P \cdot V)$

Process 2: infinitesimal change of pressure $\delta p \rightarrow 0$

$$(P_{ext} + \delta p) \rightarrow P_{ext}$$

then $(\delta p \cdot V) \rightarrow 0$

$$\begin{cases} W_1 = (P_{ext} - \delta p)V \sim P_{ext} \\ W_2 = -(P_{ext} + \delta p)V \sim -P_{ext} \end{cases}$$

$\therefore$ no permanent change!

$\therefore$ If the process is infinitely slow, then a complete reversibility is approached

§ Entropy and Reversible Heat:

1. Evaporation Only:

$$\begin{cases}\text{work done by system for irreversible process: } W=(P_{ext}-\triangle P)V \\ \text{work done by system for reversible process: } W_{rev}=W_{max}=P_{ext}\cdot V\end{cases}$$

$$\triangle U \quad \text{indep. of} \quad \text{path} \qquad \begin{cases}\triangle U_{rev}=Q_{rev}-W_{max} & \text{(Rev)} \\ \triangle U_{irrev}=Q-W & \text{(Irrev)}\end{cases}$$

Q_{deg} (degraded heat)$\equiv(Q_{rev}-Q)=(W_{max}-W)>0$

§ Less heat is transferred to cylinder from reservoir during irreversible process

* Reversible process:

$$\triangle S_{\text{reservoir}}=-\frac{Q_{rev}}{T}$$

$$\triangle S_{\text{cylinder}}=\frac{Q_{rev}}{T}$$

$$\therefore \triangle S_{tot}=\triangle S_{\text{reservoir}}+\triangle S_{\text{cylinder}}=0$$

* Irreversible process:

$$\triangle S_{\text{reservoir}}=-\frac{Q}{T}$$

$$\triangle S_{\text{cylinder}}=\frac{Q}{T}+\frac{Q_{deg}}{T}=\frac{Q}{T}+\frac{Q_{rev}-Q}{T}=\frac{Q_{rev}}{T}$$

$$\therefore \triangle S_{tot}=\frac{Q_{deg}}{T}=\frac{Q_{rev}-Q}{T}=\triangle S_{irr}>0 \text{ (entropy produced)}$$

$$\therefore \triangle S_{\text{cylinder}}=\frac{Q}{T}+\triangle S_{irr}$$

$$=\triangle S_{\text{trans.}}+\triangle S_{\text{produced}}$$

and $(\triangle S_{\text{cylinder}})_{\text{rev}}=(\triangle S_{\text{cylinder}})_{\text{irr}}$

2. Condensation only:

$$\begin{cases} \text{work done on system for irreversible process: } W=(P_{ext}+\triangle P)V \\ \text{work done on system for reversible process: } W_{rev}=W_{min}=P_{ext}\cdot V \end{cases}$$

$$\therefore Q_{deg}=(W-W_{min})=-(Q_{rev}-Q)>0$$

* Reversible condensation:

$$\triangle S_{reservoir}=\frac{Q_{rev}}{T}$$

$$\triangle S_{cylinder}=-\frac{Q_{rev}}{T}$$

$$\triangle S_{tot}=0$$

* Irreversible condensation:

$$\begin{cases} \triangle S_{reservoir}=\dfrac{Q}{T} \\ \triangle S_{cylinder}=-\dfrac{Q}{T}+\left(\dfrac{Q_{deg}}{T}\right)=-\dfrac{Q_{rev}}{T} \end{cases}$$

$$\therefore \triangle S_{tot}=\frac{Q_{deg}}{T}=\triangle S_{irr}>0 \quad \text{(entropy produced)}$$

$$\triangle S_{cylinder}=\triangle S_{trans}+\triangle S_{produced}$$

$$(\triangle S_{cylinder})_{rev}=(\triangle S_{cylinder})_{irr}$$

state A → state B (cylinder only)

$$\triangle S=S_B-S_A=\frac{Q_{rev}}{T}=\left(\frac{Q}{T}+\Delta S_{irr}\right)=\triangle S_{trans}+\triangle S_{produced}$$

for reversible process: $\triangle S_{irr}$ $(\triangle S_{produced})=0$

§ Summary

1. Entropy of an isolated system increases, which system undergoes an irreversible process. $\triangle S_{tot} > 0$
2. Entropy is not created ($\triangle S_p=0$) for a reversible process. $\triangle S_{tot}=0$, $\triangle S_{sys}=-\triangle S_{surrounding}$ (Entropy transferred from one part to another)
3. Entropy is a state function. $(\triangle S_{cylinder})_{rev}=(\triangle S_{cylinder})_{irr}$ (system: cylinder)

§ Reversible Isothermal Compression of one mole ideal gases

$(V_A, T) \rightarrow (V_B, T)$ $\quad V_B < V_A$

$dT=0$, $\quad \triangle U=0$, $\therefore Q=W$

$W = \int_{VA}^{VB} PdV = RT \ln\left(\frac{V_B}{V_A}\right)$ $\quad W<0$, work done "ON" system

§ Reversible Adiabatic Expansion of ideal gas

$(P_A, T_A) \xrightarrow{Rev} (P_B, T_B)$ $\qquad P_A > P_B$ (Expansion)

Adiabatic: $Q=0$

(Reversible + Adiabatic): $PV^{\gamma}=const$ $\quad Q=0$

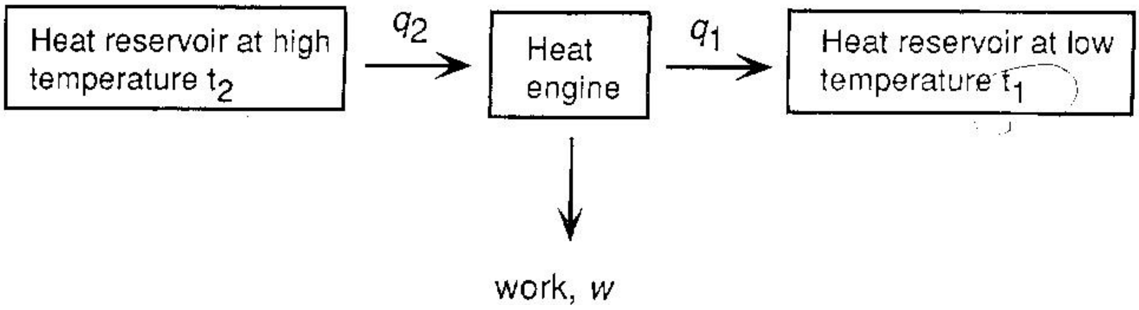
Equal Entropy (Isentropic)

$(P_A, T_A) \xrightarrow{Irrev} (P_B, T_B')$

$T_B' > T_B$ ($\because$Heat produced by degradation after irreversible adiabatic expansion remains in gas)

$\therefore$More irreversible $\Longrightarrow$ $T_B'\uparrow$ and $U_B'\uparrow$

§ Properties of Heat Engines

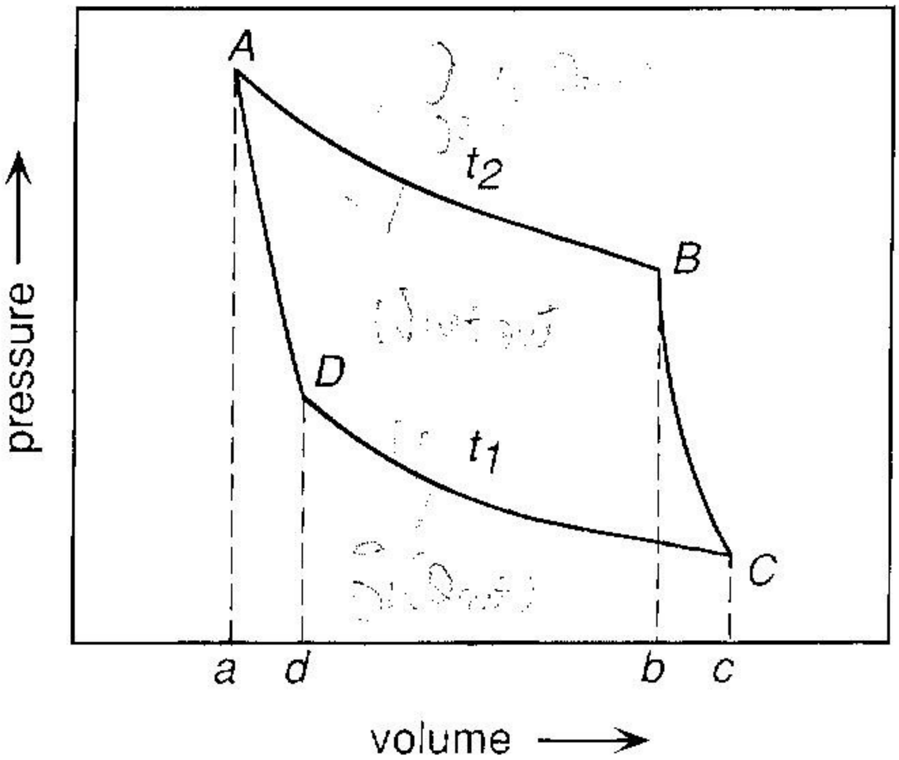


$$\eta\ \text{(Efficiency)} \equiv \frac{work\ \ done}{heat\ \ input} = \frac{w}{q_2}$$

* For a Carnot cycle process: $\begin{cases}\text{two rev. isothermal}\\ \text{two rev. adiabatic}\end{cases}$

“any thermodynamic substance”

§ Carnot Engine is an ideal engine which has the maximum efficiency



$W = W_1 + W_2 - W_3 - W_4 = (\text{area } ABCD)$

$Q = q_2 - q_1$

One cycle, $\triangle U = 0$, $\therefore W = Q = q_2 - q_1$

$\eta_c = \text{Efficiency} = \frac{w}{q_2} = \frac{q_2 - q_1}{q_2}$

($\eta' > \eta$) Greater efficiency "could be obtained" by two methods

(1) $q_2' = q_2$, if $w' > w (\eta' > \eta)$ i.e. $(q_2' - q_1') > (q_2 - q_1)$

$\therefore q_1' < q_1$

(2) $w' = w$ if $q_2' < q_2$

$\therefore q_2' - q_1' = q_2 - q_1$ then $q_1' < q_1$

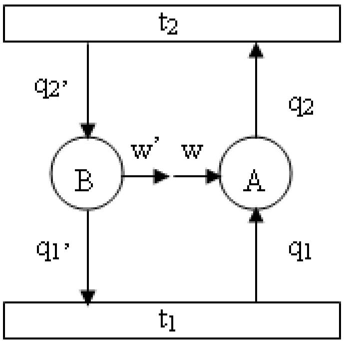
consider two engines combined together:

(1) $\boxed{\text{take } q_2' = q_2}$

$w' = q_2' - q_1' = q_2 - q_1'$

$-w = -q_2 + q_1$

$\therefore$ if $w' - w = (q_1 - q_1') > 0$



work $(w' - w) > 0$ is obtained from $(q_1 - q_1')$ heat only from one reservoir ⇨ impossible !!

$\therefore$ Preliminary statement of 2nd law:

Thomsen principle: it is impossible, by a cyclic process, to take heat from heat from a reservoir and convert it to work, without transferring heat to another cold reservoir

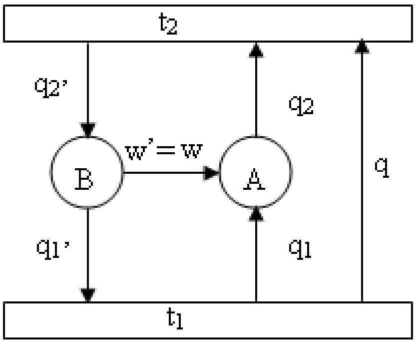
(2) engine B $w' = q_2' - q_1'$

engine A $-w = -q_2 + q_1$

$\boxed{\text{Take} \quad w' = w}$

$q_2' - q_1' = +q_2 - q_1$

if $\therefore (q_2 - q_2') = (q_1 - q_1') = q > 0$



heat q= is transferred from (low t_1) to (height t_2) ⟹ impossible!!

<u>Clausius principle</u>: It is impossible to transfer heat from a cold to a hot reservoir without converting a certain work to heat

§ Thermodynamic Temperature Scale

* All reversible Carnot cycles operating between the same upper and lower temperature must have the same (maximum) efficiency, it is "independent of working substance" and is

$$\therefore \eta_c = \frac{q_2 - q_1}{q_2} = 1 - \frac{q_1}{q_2} = f'(t_1, t_2)$$

a function only of temperatures t_1, t_2

$$\therefore \frac{q_1}{q_2} = f(t_1, t_2) = ?$$

* consider two Carnot cycles $(t_1,t_2)+(t_2,t_3)=(t_1,t_3)$

$$\therefore \quad \frac{q_1}{q_2} = f(t_1, t_2)$$

$$\frac{q_2}{q_3} = f(t_2, t_3)$$

$$\frac{q_1}{q_3} = f(t_1, t_3)$$

$$\left(\frac{q_1}{q_3}\right) \times \left(\frac{q_3}{q_2}\right) = \frac{f(t_1, t_3)}{f(t_2, t_3)} = \frac{q_1}{q_2} = f(t_1, t_2)$$

$\because f(t_1,t_2)$ indep. of t_3

$$\therefore \begin{cases} f(t_1,t_3) = F(t_1)/F(t_3) \\ f(t_2,t_3) = F(t_2)/F(t_3) \end{cases}$$

$\therefore \frac{q_1}{q_2} = \frac{F(t_1)}{F(t_2)}$

Kelvin: the simplest function!!

Define: $F(t_1) \equiv T_1$, $F(t_2) \equiv T_2$

$$\therefore \frac{q_1}{q_2} = \frac{T_1}{T_2}$$

and $\eta_c = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$

low temp(T_1) has a limiting value absolute! not relative

zero temperature of cold reservoir $T_1=0$, is $\eta=100\%$

$\therefore$Kelvin Temperature scale ≡ Ideal gas temperature scale

proof: one mole ideal gas, Carnot cycle

(1)A→B, Reversible, isothermal expansion at T_2

$$\triangle U=0,\quad Q = q_2 = w_1 = RT_2 \ln\left(\frac{V_B}{V_A}\right)$$

(2)B→C, Rev. adia. Expansion

$$Q=0,\quad w_2 = -\Delta U = -\int_{T2}^{T1} CvdT = Cv(T_2 - T_1)$$

(3)C→D, Rev. isoth. Comp. at T_1

$$\triangle U=0,\quad Q = q_1 = w_3 = RT_1 \ln\left(\frac{V_D}{V_C}\right)$$

(4)D→A, Rev. adia. Comp.

$$Q=0,\quad w_4 = -\Delta U = -\int_{T1}^{T2} CvdT = Cv(T_1 - T_2)$$

$\therefore$Total work $w = w_1 + w_2 + w_3 + w_4 = RT_2 \ln\left(\frac{V_B}{V_A}\right) + RT_1 \ln\left(\frac{V_D}{V_C}\right)$

(1),(3) $P_AV_A=P_BV_B$, $P_CV_C=P_DV_D$

(2),(4) $P_BV_B^{\gamma}=P_CV_C^{\gamma}$, $P_DV_D^{\gamma}=P_AV_A^{\gamma}$

$\therefore \frac{V_B}{V_A} = \frac{V_C}{V_D}$

$$\therefore w = RT_2 \ln\left(\frac{V_B}{V_A}\right) - RT_1 \ln\left(\frac{V_C}{V_D}\right) = R(T_2 - T_1)\ln\left(\frac{V_B}{V_A}\right)$$

$$\therefore \eta_c = \frac{w}{q_2} = \frac{R(T_2 - T_1)\ln\left(\frac{V_B}{V_A}\right)}{RT_2 \ln\left(\frac{V_B}{V_A}\right)} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$$

§ 2nd Law of Thermodynamics

$\because \eta_c = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$

$\therefore \frac{q_1}{q_2} = \frac{T_1}{T_2}$ i.e. $\frac{q_2}{T_2} - \frac{q_1}{T_1} = 0$

* Any cycle be broken down into “many” Carnot cycles

$\therefore \sum_i \frac{q_i}{T_i} = \sum \frac{Q}{T} = 0$

$\oint \frac{\delta Q}{T} = 0$ cyclic integral

令 $dS = \frac{\delta Q_{rev}}{T}$ $\therefore \oint dS = \oint \frac{\delta Q_{rev}}{T} = 0$

$\therefore$For loop ABA:

$$\oint dS = 0 = \int_A^B dS + \int_B^A dS = (S_B - S_A) + (S_A - S_B) = 0$$

$\therefore$2nd Law of Thermodynamics:

(1) Entropy function: S $\boxed{\mathrm{dS} \equiv \frac{\delta Q_{rev}}{T}}$

$$\Delta S = S_B - S_A = \int_A^B \frac{\delta Q_{rev}}{T}$$

(2) Entropy of an $\boxed{\text{isolated system}}$: $\boxed{\Delta S \geq 0}$ $\Leftrightarrow$ $\boxed{\triangle S_{U,V} \geq 0}$

Equilibrium process: $\triangle S_{U,V}=0$

Non-equilibrium process: $\triangle S_{U,V} > 0$

Entropy is increased!! or $\sum_i dS_i \geq 0$

§ Maximum Work for reversible process

state A → state B

$U_B - U_A = Q - W$

* Q and W can vary depending on path (degree of irreversibility)

$$\because dS_{system} = \frac{\delta Q_t}{T} + dS_{irr}$$

1st law $dU_{sys} = \delta Q_t - \delta W$

$$\therefore \quad \delta Q_t = dU_{sys} + \delta w$$

$$dS_{sys} = \frac{dU_{sys} + \delta w}{T} + dS_{irr}$$

$$\therefore \delta w = TdS_{sys} - dU_{sys} - TdS_{irr}$$

$$\because dS_{irr} > 0$$

$$\therefore \delta w \le (TdS_{sys} - dU_{sys})$$

A→B $w \le T(S_B - S_A) - (U_B - U_A)$

i.e. $W_{max} = T(S_B - S_A) - (U_B - U_A)$ and $dS_{irr} = 0$

Reversible process (path) has maximum work.#
If heat is absorbed (transferred) during a process

$Q_{rev} > Q$ (irreversible)

See example 1 (Ex1):

§ Criterion for Equilibrium

* spontaneous change

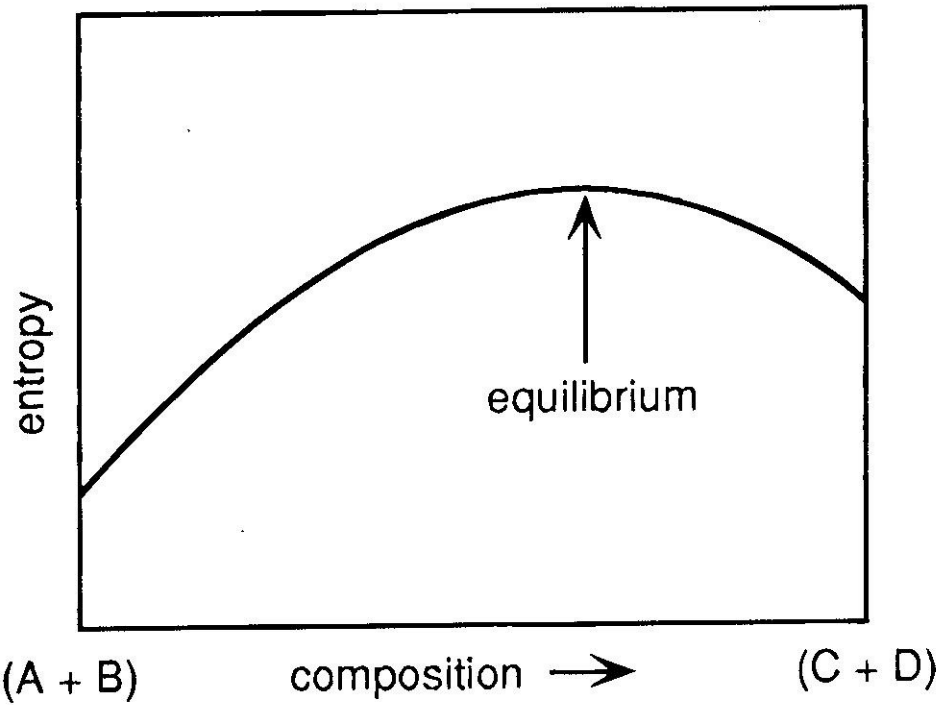
state 1 (non-equil.) $\xrightarrow{\text{Irrev.}}$ State 2 (equil.) of an isolated system

$\triangle S_{tot}=(S_2-S_1)>0$, $S_2>S_1$

entropy S↑ ⟺ reaching equil.

At equilibrium $S_{U,V}=S_{max}$

* Consider a chemical reation:



A+B = C+D

Isolated system: constant
$$\begin{cases} \text{mass (M)} \\ \text{Internal energy (U)} \\ \text{Volume (V)} \end{cases}$$

When $S_{U,V}=S_{max}$

Equil. State has a fixed composition

$$(dS)_{U,V}\geqq 0 \quad \begin{cases} >0, & \text{non-equil.} \\ =0, & \text{equil.} \end{cases}$$

§ Combined statement of 1st and 2nd Laws

1. 1st law: $dU = \delta Q - \delta w$

   2nd law: $dS = \frac{\delta Q_{rev}}{T}$

   for reversible mechanical work $\delta w_{rev} = PdV$

   $\therefore \boxed{dU = TdS - PdV}$

Application restrictions: (1)Reversible
(2)closed system (const. composition & mass)
(3)mechanical work only

In general reversible: $dU = TdS - PdV - \delta w' + \sum_i \mu_i dn_i$

2. $U = U(S,V)$

   $$dU = \left(\frac{\partial U}{\partial S}\right)_v ds + \left(\frac{\partial U}{\partial V}\right)_s dV$$

   $$\therefore \left(\frac{\partial U}{\partial S}\right)_v = T \quad , \quad \left(\frac{\partial U}{\partial V}\right)_s = -P$$

3. $S = S(U,V)$

   $$dS = \left(\frac{\partial S}{\partial U}\right)_v dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

   $$\because dS = \frac{1}{T} dU + \frac{P}{T} dV$$

   $$\therefore \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$$

4. $dU = TdS - PdV$

   $\because (dS)_{U,V} \geqq 0$ implies $(dU)_{S,V} \leqq 0$
   for a constant S,V system:
   at equil. $U_{S,V} = U_{min}$

* $dU = TdS - PdV - \delta w'$

$$\therefore dS = \frac{dU}{T} + \frac{P}{T} dV + \frac{1}{T} \delta w'$$

$dS_{U,V} \geqq 0, \quad \therefore \delta w' \geqq 0$

$\therefore dU_{S,V} = -\delta w' \leqq 0$

∴ $dU_{S,V}\downarrow$ and at equil. $U_{S,V}=U_{min}$

δw’ can be chemical work or electric work

$$\delta w' = \sum_i \mu_i dn_i = \sum_i \left(\frac{\partial U}{\partial n_i}\right)_{nj,S,V} dn_i$$

§ Ex1: (p.56) compare △S, W, Q, for one mole ideal gas

(1) Reversible, isothermal expansion, $V_A \rightarrow V_B$ ($V_B < V_A$)

(2) Free expansion (adiabatic + constant T) $V_A \rightarrow V_B$

Sol:

(1) dT=0, △U=0

$$Q_{rev} = w_{rev} = \int_{VA}^{VB} PdV = RT\ln\left(\frac{V_B}{V_A}\right) > 0 \qquad \text{吸熱}$$

$$\therefore \Delta S_{rev} = R\ln\left(\frac{V_B}{V_A}\right)$$

(2) Free expansion, dT=0, Q=W=0 (no work done)

∵ Entropy is a state function,

$$\therefore \Delta S_{irr(free.expasiojn)} = \Delta S_{rev} = S_B - S_A = \int_a^B \frac{\delta Q_{rev}}{T} = \int_A^B dS$$

$$dS = \frac{dU}{T} + \frac{P}{T}dV = \frac{P}{T}dV = \frac{R}{V}dV$$

$$\therefore \Delta S_{irr} = \int_A^B \frac{R}{V}dV = R\ln\left(\frac{V_B}{V_A}\right)$$

i.e. no heat absored, and no work done

c.p. (1),(3) $W_{rev} - W_{free\ expansion} = W_{rev} = Q_{rev}$

∴ Free expansion is the limit of irreversibility at which all “potential work” is degraded to heat and create entropy.

§ Ex2: 5 moles ideal gas, C_v=1.5R, $\gamma=\frac{5}{3}$, adiabatic expansion (P_1=50 atm→P_2=10 atm, T_1=300 K) T=?

(1) Reversible process, T_2=?

(2) Irreversible: W=4000J, T_3=?

T_2=?, T_3=?, $\triangle S_{(2)irr}$=?

Sol:

(1) $V_1 = \frac{nRT_1}{P_1} = 2.46 \ liters$

(Rev. + Adia.) $P_1V_1^\gamma = P_2V_2^\gamma$

$$\therefore V2 = \left(\frac{P_1V_1^\gamma}{P_2}\right)^{\frac{1}{\gamma}} = 6.47 \ liters$$

$$\therefore T_2 = \frac{P_2V_2}{nR} = 158 \ K$$

note: Q=0, $\Delta U = n\int_{T1}^{T2} C_v dT = nC_v(T_2 - T_1) = 5 \times \frac{3}{2}R(158 - 300) = -8854 \ J$

W=$-\triangle$U= +8854 J

$$\because dS = \frac{dU}{T} + \frac{P}{T}dV = \frac{dU}{T} + \frac{nR}{V}dV$$

$$\therefore \Delta S = \int_{T1}^{T2} \frac{nC_v dT}{T} + nR\int_{V1}^{V2} \frac{dV}{V} = nC_v \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)$$

$$\therefore \Delta S = 5 \times \frac{3R}{2} \times \ln\left(\frac{158}{300}\right) + 5 \times R \times \ln\left(\frac{6.47}{2.46}\right) = 0.025R \cong 0.2 \ (J/K) = 0$$

Reversible Adiabatic ⇒ΔS=0

(2) (Irrev. + Adia), Q=0

$\triangle U = -W = -4000$ J

$$\Delta U = n\int_{T1}^{T3} C_v dT = nC_v(T_3 - T_1) = 5 \times \frac{3R}{2} \times (T_3 - 300) = -4000$$

$\therefore T_3$=236 K

$$V_3 = \frac{nRT_3}{P_3} = 9.68 \ liters$$

state 1→state 3 $\triangle S_{rev} = \triangle S_{irr}$

Rev: $\therefore dS = \frac{dU}{T} + \frac{P}{T}dV = \frac{dU}{T} + \frac{nR}{V}dV = \frac{nC_v dT}{T} + \frac{nRdV}{V}$

$$\therefore \Delta S_{rev} = \int_{T1}^{T3} nC_v \frac{dT}{T} + \int_{V1}^{V3} nR\frac{dV}{V}$$

$$= nC_v \ln\left(\frac{T_3}{T_1}\right) + nR\ln\left(\frac{V_3}{V_1}\right)$$

$$= 5 \times \frac{3R}{2}\ln\left(\frac{236}{300}\right) + 5 \times R \times \ln\left(\frac{9.68}{2.46}\right)$$

$$= -15 + 57 = 42 \ \ (J/K)$$

$\therefore \triangle S_{irr} = \triangle S_{rev} = 42$ (J/K)

$\therefore$ **$\triangle S_{(2)} > \triangle S_{(1)}$**