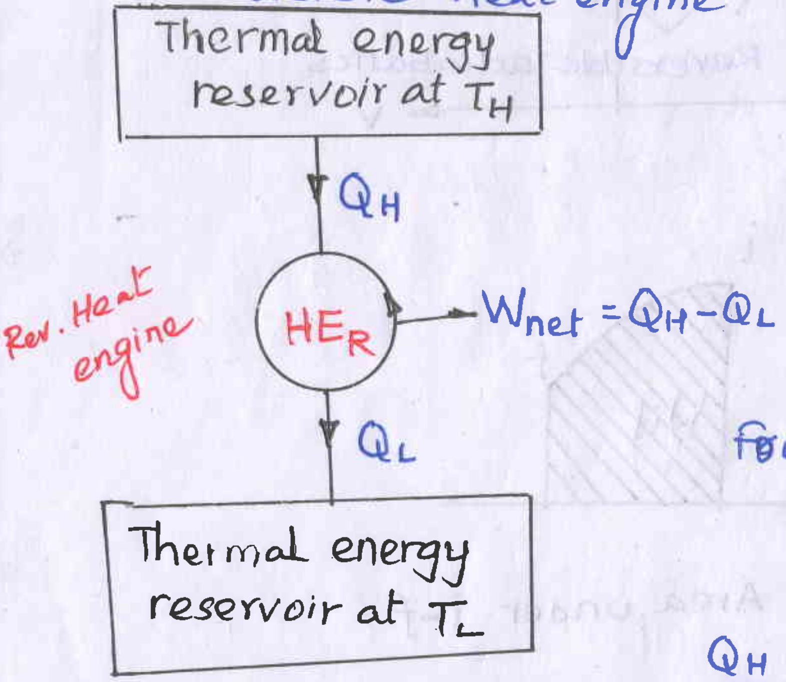
CHAPTER-4

ENTROPY

1) **Introduction:** The entropy is a thermodynamics property of a working substance and serves as a valuable tool in the second law analysis of engineering devices.

* Birth of entropy

Reversible heat engine



$$\eta_R = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_L}{Q_H}$$

$$= 1 - \frac{Q_L}{Q_H}$$

from thermodynamic temp. scale for Reve-HE

$$1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L} \Rightarrow \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

$$\frac{Q_H}{T_H} + \frac{(-Q_L)}{T_L} = 0$$

$$\sum_{\text{Cycle}} \left(\frac{\delta Q}{T}\right)_R = 0 \quad \text{OR} \quad \oint \left(\frac{\delta Q}{T}\right)_R = 0$$

$\therefore \oint \left(\frac{\delta Q}{T}\right)_R = \oint ds$ (Cycle intergration point function is zero)

For process - 1 to 2

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_R = \Delta S = S_2 - S_1$$

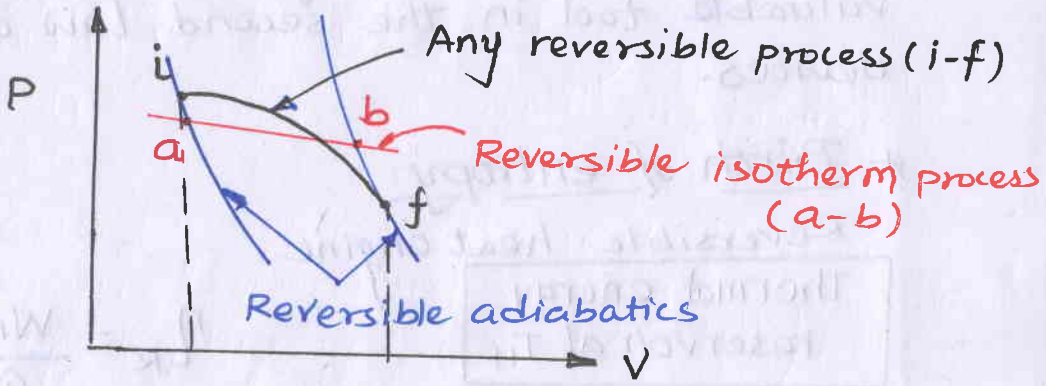
$$\boxed{S \Rightarrow \text{entropy}}$$

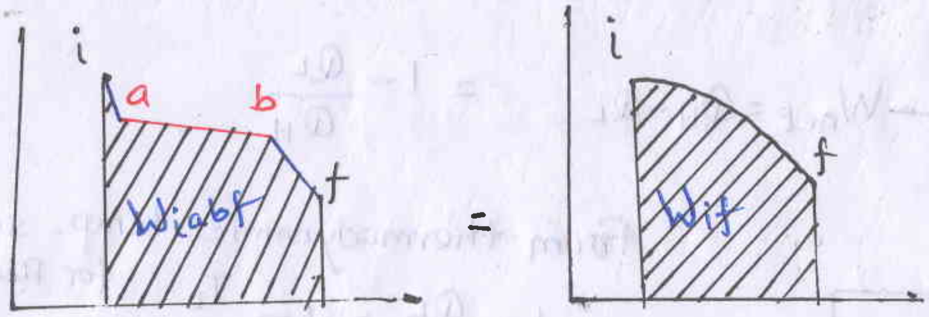
- $S\uparrow \rightarrow$ min. $\rightarrow$ high temp.
- $S\downarrow \rightarrow$ Max. $\rightarrow$ Low temp.
- Max - S $\rightarrow$ min. work-conversion
- Min - S - Max. work-conversion

2) Clausius' Theorem

* Information

→ Any reversible process can be replace by two Reversible adiabatics with one reversible isotherm betn. them.





Area under i-a-b-f = Area under i-f

Applying 1st law for

Process i-f $\quad Q_{i-f} = U_f - U_i + W_{if}$

Process-i-a-bf $\quad Q_{iabf} = U_f - U_i + W_{iabf}$

since $W_{if} = W_{iabf}$

$\therefore Q_{if} = Q_{iabf}$

$= Q_{ia} + Q_{ab} + Q_{bf}$

$Q_{if} = Q_{ab}$ $\quad$ ($\because Q_{ia} = 0, Q_{bf} = 0$ Reversible adiabatic process)

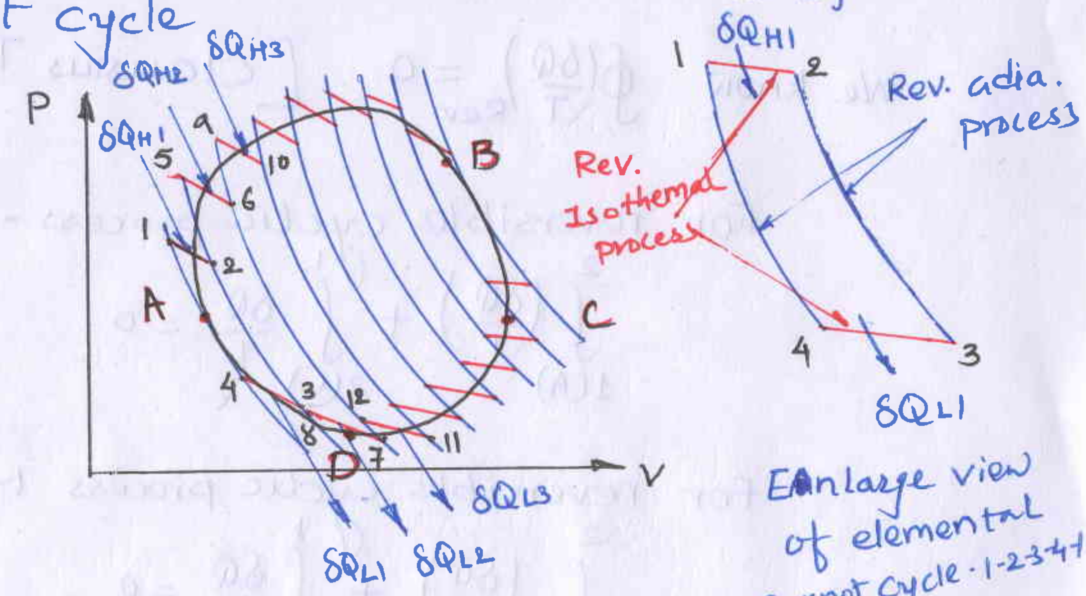
→ Heat transferred in any rev. process is equal ~~$dQ = 0$~~ to the heat transferred in the isothermal process

Clausius theorem

"The cyclic integration of $\frac{\delta Q}{T}$ is equal to zero"

To prove $\frac{\delta Q}{T} = 0$

Consider a arbitary closed curve ABCDA representing a reversible cycle and closed cycle ABCDA is divided into a number of small carnot cycle



Enlarge view of elemental Carnot cycle. 1-2-3-4

For elemental Carnot cycle 1-2-3-4

$$\frac{\delta Q_{L1}}{T_{L1}} = \frac{\delta Q_{H1}}{T_{H1}} = \cancel{\frac{\delta Q_{L1}}{\delta Q_1}} \Rightarrow \frac{\delta Q_{H1}}{T_{H1}} + \frac{(-\delta Q_{L1})}{T_{L1}} = 0$$

$(-ve \overset{\wedge}{\text{sign}}$ Heat rejected$)$

Similarly for - 5-6-7-8

$$\frac{\delta Q_{H2}}{T_{H2}} + \left(\frac{-\delta Q_{L2}}{T_{L2}}\right) = 0$$

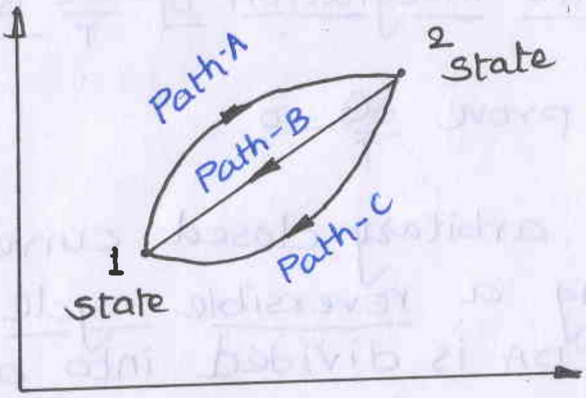
for - 9-10-11-12 $\Rightarrow \frac{\delta Q_{H3}}{T_{H3}} + \left(-\frac{\delta Q_{L3}}{T_{L3}}\right) = 0$

For All the elemental Cornot cycles

$$\left(\frac{\delta Q_{H1}}{T_{H1}} + \frac{\delta Q_{H2}}{T_{H2}} + \frac{\delta Q_{H3}}{T_{H3}} + \dots\right) + \left(\frac{\delta Q_{L1}}{T_{L1}} + \frac{\delta Q_{L2}}{T_{L2}} + \frac{\delta Q_{L3}}{T_{L3}} + \dots\right) = 0$$

$$\boxed{\oint \left(\frac{\delta Q}{T}\right)_{Rev.} = 0}$$

3) Entropy is a property



We know $\oint \left(\frac{\delta Q}{T}\right)_{Rev} = 0$ [Clausius Theorem]

For reversible cyclic process - 1-A-2-C-1

$$\int_{1(A)}^{2} \left(\frac{\delta Q}{T}\right) + \int_{2(C)}^{1} \frac{\delta Q}{T} = 0 \quad \ldots\ldots (i)$$

For reversible cyclic process 1-A-2-B-1

$$\int_{1(A)}^{2} \left(\frac{\delta Q}{T}\right) + \int_{2(B)}^{1} \frac{\delta Q}{T} = 0 \quad \ldots\ldots (ii)$$

subtracting eq^n. (i) from eq^n. (ii) we get

$$\int_{2(C)}^{1} \frac{\delta Q}{T} - \int_{2(B)}^{1} \frac{\delta Q}{T} = 0 \Rightarrow \int_{2(C)}^{1} \frac{\delta Q}{T} = \int_{2(B)}^{1} \frac{\delta Q}{T} = ds$$

From above equation, the magnitude of $\frac{\delta Q}{T}$ is same for the ~~phat~~ path B & C and it does not depend upon the path

4) Inequality of Clausius

"When a system undergoes a complete cyclic process, the integral of $\frac{\delta Q}{T}$ around the cycle is less than zero or equal to zero"

$$\oint \frac{\delta Q}{T} \le 0$$

Consider a reversible engine R and irreversible engine I working betn. same two thermal energy reservoir

$$\eta_R > \eta_I \quad (\text{Carnot Theorem})$$

$$1 - \frac{\delta Q_{LR}}{\delta Q_{HR}} > 1 - \frac{\delta Q_{LI}}{\delta Q_{HI}}$$

$$-\frac{\delta Q_{LR}}{\delta Q_{HR}} > -\frac{\delta Q_{LI}}{\delta Q_{HI}} \Rightarrow \frac{\delta Q_{LR}}{\delta Q_{HR}} < \frac{\delta Q_{LI}}{\delta Q_{HI}}$$

$$\frac{T_L}{T_H} < \frac{\delta Q_{LI}}{\delta Q_{HI}} \quad \left(\text{for reversible engine } \frac{\delta Q_{LR}}{\delta Q_{HR}} = \frac{T_L}{T_H}\right)$$

$$\frac{\delta Q_{HI}}{T_H} < \frac{\delta Q_{LI}}{T_L}$$

$$\frac{\delta Q_{HI}}{T_H} - \frac{\delta Q_{LI}}{T_L} < 0$$

$$\left(\frac{\delta Q_H}{T_H}\right)_I + \left(-\frac{\delta Q_L}{T_L}\right)_I < 0 \quad (-\text{ve sign for Heat Rejected})$$

$$\oint \left(\frac{\delta Q}{T}\right)_I < 0 \quad \text{for irreversible cycle}$$

According to Clausius theorem $\oint \frac{\delta Q}{T} = 0$ for reversible cycle

Combing results for reversible and irreversible cycle

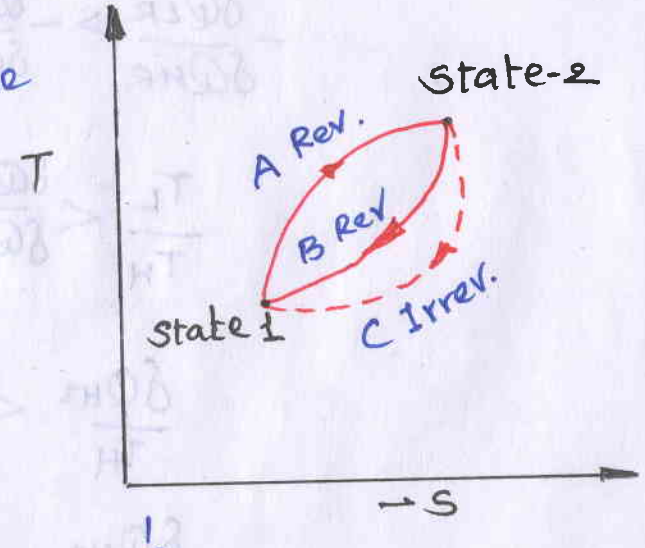
$$\oint \frac{\delta Q}{T} \leq 0$$

$\oint \frac{\delta Q}{T} = 0$ for reversible cycle

$\oint \frac{\delta Q}{T} < 0$ for irreversible cycle

$\oint \frac{\delta Q}{T} > 0$ for cycle is impossible, since it violates the second Law

5) Entropy change in an Irreversible process



For any process undergone by a system

$$\int \frac{\delta Q}{T} \leq ds$$

For the reversible cycle consisting of A & B

$$\oint \left(\frac{\delta Q}{T}\right)_R = \int_{1A}^{2} \frac{\delta Q}{T} + \int_{2B}^{1} \frac{\delta Q}{T} = 0$$

$$\int_{1_A}^{2} \frac{\delta Q}{T} = - \int_{2B}^{1} \frac{\delta Q}{T} \quad \cdots \cdots ①$$

For the irreversible cycle consisting of A and C, by the inequality of Clausius,

$$\oint \frac{\delta Q}{T} = \int_{1_A}^{2} \frac{\delta Q}{T} + \int_{2_C}^{1} \frac{\delta Q}{T} < 0 \quad \dots\dots (2)$$

From eq^n. ① & (2)

$$-\int_{2_B}^{1} \frac{\delta Q}{T} + \int_{2_C}^{1} \frac{\delta Q}{T} < 0$$

$$\int_{2_B}^{1} \frac{\delta Q}{T} > \int_{2_C}^{1} \frac{\delta Q}{T} \quad \dots (3)$$

since the path B is reversible

$$\int_{2_B}^{1} \frac{\delta Q}{T} = \int_{2_B}^{1} ds \quad \dots\dots (4)$$

Since entropy is a property entropy changes for the path B & C would be the same

$$\int_{2_B}^{1} \left(\frac{\delta Q}{T}\right) = \int_{2B}^{1} ds \Rightarrow \int_{2_B}^{1} ds = \int_{2_C}^{1} ds \quad \dots \textcircled{5}$$

from eq^n. (3) & (5)

$$\int_{2_C}^{1} ds > \int_{2_C}^{1} \frac{\delta Q}{T}$$

Thus for any irreversible process

$$ds > \frac{\delta Q}{T}$$

For the general case

$$S_2 - S_1 \geq \int_{1}^{2} \frac{\delta Q}{T}$$

6) Principle of increase of entropy

"The entropy of an isolated system during a process always increase or in the limiting case of a reversible process remains constant."

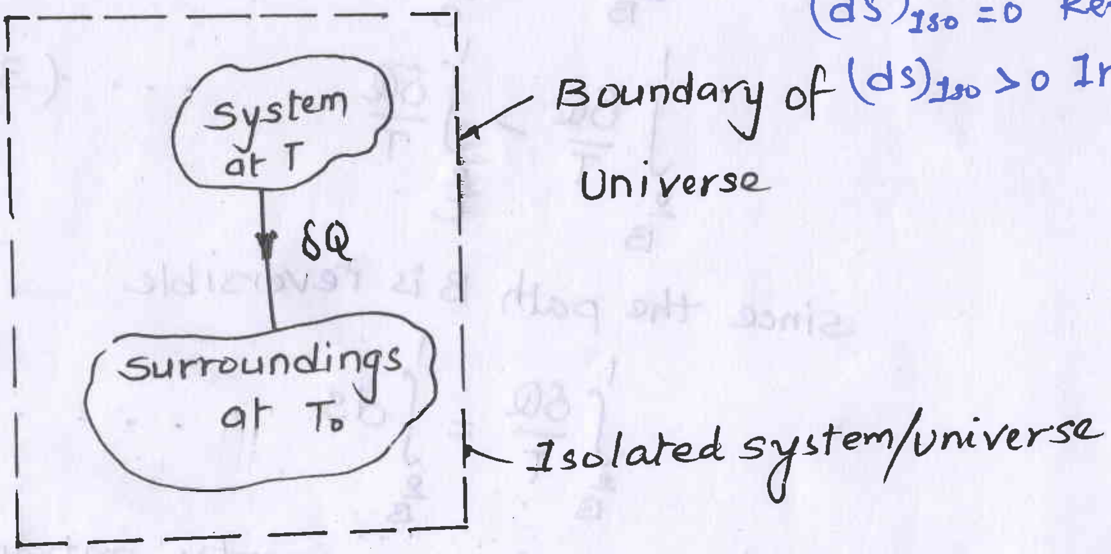
$$\boxed{\Delta S_{isolated} \geq 0}$$

For isolated system, there is no energy interaction with surroundings

$\delta W = 0$, $\delta Q = 0$

$(dS)_{Iso} = 0$ Rev.

$(dS)_{Iso} > 0$ Irrev.



System + Surrounding = Universe/Isolated

$$(\Delta S)_{system} + (\Delta S)_{surrounding} = (\Delta S)_{universe/Iso}$$

$$\therefore \quad (\Delta S)_{system} = -\frac{\delta Q}{T} \quad (-\text{ve sign} \rightarrow \text{Heat rejection})$$

$$(\Delta S)_{surrounding} = \frac{\delta Q}{T_0} \quad (+\text{ve sign} - \text{heat absorb})$$

$$(\Delta S)_{system} + (\Delta S)_{surrounding} = -\frac{\delta Q}{T} + \frac{\delta Q}{T_0}$$

$$(\Delta S)_{universe} = \delta Q\left(\frac{1}{T_0} - \frac{1}{T}\right) \quad \text{since } T > T_0$$

$$\delta Q\left(\frac{1}{T_0} - \frac{1}{T}\right) > 0$$

$$\boxed{(\Delta S)_{universe} > 0}$$

if Reversible process $T = T_0 \rightarrow (\Delta S)_{univers} = 0$

Information

$$ds > \int \frac{\delta Q}{T}$$ for irreversible process (Clausius Inequality)

$$ds = \int \frac{\delta Q}{T} + X$$ (X - some positive quantity)

$$\Delta S = \Delta S_e + \Delta S_i$$

change of entropy system = change of entropy due to external irreversibility + Change of entropy due to internal irreversibility

Case-1 for a reversible process

$$\Delta S_i = 0 \quad \therefore \quad \Delta S = \Delta S_e$$

Case-2 for reversible diabatic process

$$\Delta S = \Delta S_e = \int \frac{\delta Q}{T}$$

Case-3 For an irreversible adiabatic process

$$\Delta S_e = 0$$

$$\Delta S_i > 0$$

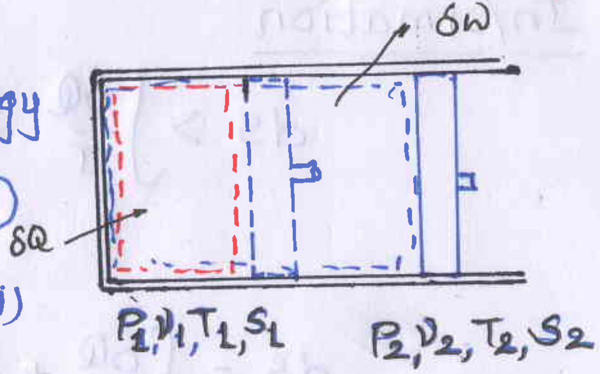
case-4 for a reversible adiabatic process

$$\Delta S_e = 0, \quad \Delta S_i = 0$$

$$\Delta S = 0 \Rightarrow S = \text{Const.}$$

A reversible adiabatic process called as Isentropic process

7) Entropy change for non-flow process (closed system)



Law of conservation of energy

$$\delta Q = du + \delta W \quad \text{...①}$$

$$\delta Q = C_v dT + p dv \quad \text{...(ii)}$$

Dividing both sides by T

$$\frac{\delta Q}{T} = C_v \frac{dT}{T} + \frac{p dv}{T} \quad \text{...(iii)}$$

We know $ds = \frac{\delta Q}{T}$, $pv = RT \Rightarrow \frac{P}{T} = \frac{R}{v}$

$$\therefore \; ds = C_v \frac{dT}{T} + R\frac{dv}{v}$$

Integrating both sides

$$\int_{S_1}^{S_2} ds = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{v_1}^{v_2} \frac{dv}{v}$$

$$S_2 - S_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \quad \text{...(iv)}$$

According to the gas eq^n.

$$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2} \Rightarrow \frac{T_2}{T_1} = \frac{P_2}{P_1} \times \frac{v_2}{v_1}$$

Substituting the value of $\frac{T_2}{T_1}$ in eq (iv)

$$S_2 - S_1 = C_v \ln \frac{P_2}{P_1} \times \frac{v_2}{v_1} + R \ln \frac{v_2}{v_1}$$

$$= C_v \ln \frac{P_2}{P_1} + C_v \ln \frac{v_2}{v_1} + R \ln \frac{v_2}{v_1}$$

$$= C_v \ln \frac{P_2}{P_1} + (C_v + R) \ln \frac{v_2}{v_1}$$

$$\boxed{S_2 - S_1 = C_v \ln \frac{P_2}{P_1} + C_p \ln \frac{v_2}{v_1}} \quad \text{...(v)}$$

Again, from gas eq^n.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 v_2}{T_2} \quad \text{or} \quad \frac{v_2}{v_1} = \frac{P_1}{P_2} \cdot \frac{T_2}{T_1}$$

Putting the value of $\frac{v_2}{v_1}$ in eq^n (iv)

$$s_2 - s_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

$$= C_v \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} + R \ln \frac{T_2}{T_1}$$

$$= (C_v + R) \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$\boxed{s_2 - s_1 = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}}$$

8) Entropy changes for an open system. (flow process)

The net change of entropy of a system due to mass transport is equal to the difference between the product of mass and its specific entropy at the inlet and at the outlet of the system.

$$ds \geq \frac{\delta Q}{T_0} + \Sigma s_i \cdot dm_i - \Sigma s_o \cdot dm_o$$

where

T_0 = Temp. of the surrounding

s_i = Specific entropy at the inlet

s_o = specific entropy at the outlet

dm_i = Mass entering the system

dm_o = Mass leaving the system

The eq^n. in general form

$$ds \geq \frac{\delta Q}{T_0} + \sum s . dm$$

Above eq^n. divided by dt

$$\frac{ds}{dt} \geq \frac{1}{T_0} \frac{\delta Q}{dt} + \sum s . \frac{dm}{dt}$$

In a steady-state, steady flow process, the rate of change of entropy of system

$$\frac{ds}{dt} = 0$$

$$0 \geq \frac{1}{T_0} \frac{\delta Q}{dt} + \sum s . \frac{dm}{dt}$$

$$\frac{1}{T_0} \dot{Q} + \sum s . \dot{m} \leq 0$$

where $\dot{Q} = \frac{\delta Q}{dt}$ and $\dot{m} = \frac{dm}{dt}$

for adiabatic steady flow process

$$\dot{Q} = 0$$

$$\sum s\dot{m} \leq 0$$

If the process is reversible adiabatic

$$\sum s\dot{m} = 0$$

9) The third Law of thermodynamics

" The entropy of all perfect crystalline solid is zero at absolute zero temperature "