

Module - 3

Thermal Energy Reservoir (TER)

→ Hypothetical body with a large thermal energy capacity that can supply or absorb finite amount of heat without undergoing any temp. change.

(1) SOURCE

It is a TER which supplies thermal energy (heat)

(2) SINK

TER which absorbs large amount of thermal energy.

High grade energy

→ Organised form of energy, Eg - Work

Low grade energy

→ Unorganised form of energy, Eg - heat

Second Law of Thermodynamics

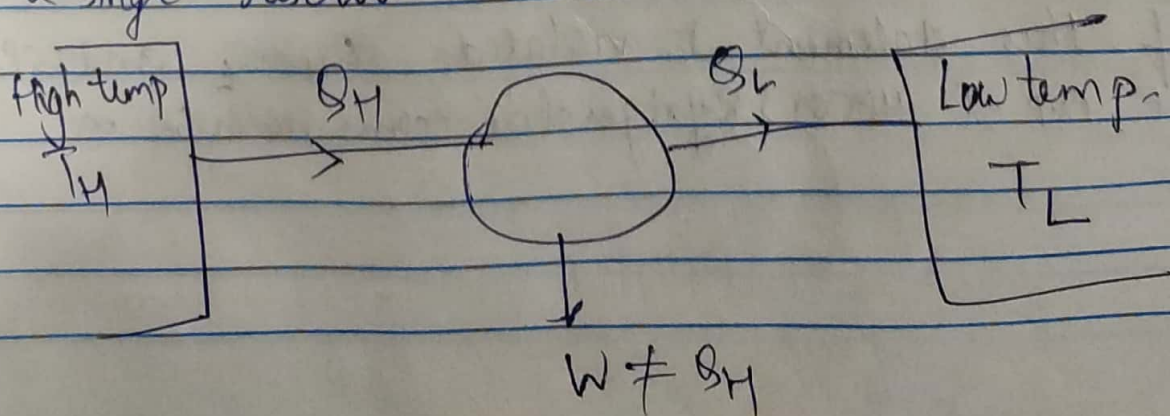
- It is impossible for a cyclic device to convert low grade energy into high grade energy totally.

Statements:-

Heat engines

KELVIN-PLANCK STATEMENT of 2nd law

- It is impossible to develop a device operating on a cycle that develops work by exchanging heat with a single reservoir.



If this statement is violated

$$W = Q_H$$

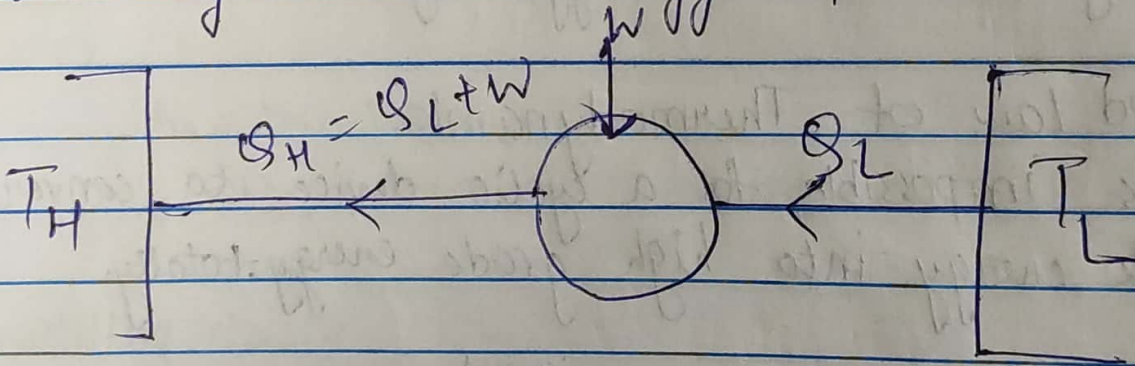
$$\eta = \frac{W}{Q_H} = 1$$

But η of any thermal energy can never be 100%.

The machine which violates Kelvin-Planck statement is known as PMM2.

→ heat pumps & refrigerators
CLAUSIUS STATEMENT

It is impossible to develop a cyclic device which transfers heat from low temp. to high temp. without any work or energy input.



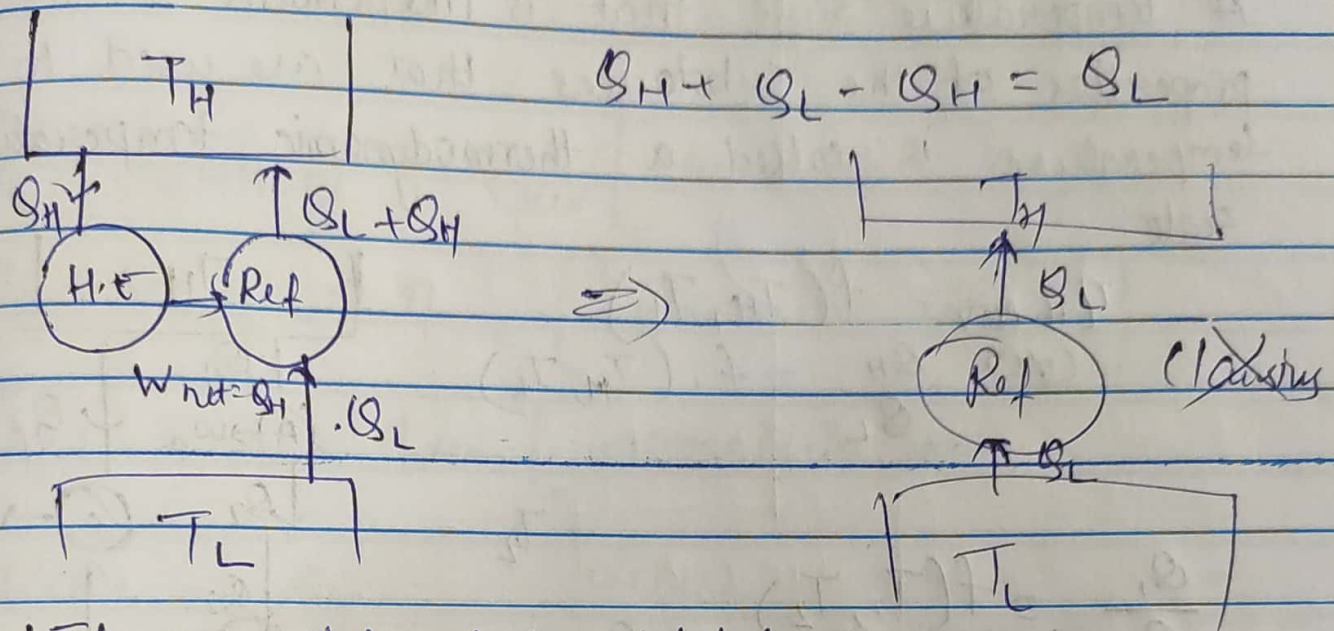
$$(COP)_{Ref} = \frac{Q_L}{Q_H - Q_L}$$

$$(COP)_{HP} = \frac{Q_H}{Q_H - Q_L}$$

$$(COP)_{HP} = 1 + (COP)_{Ref}$$

If this statement is violated, $Q_H = Q_L$ and $COP \rightarrow \infty$.
But, COP of HP (or) Refrigerator can never be ∞ .

EQUIVALENCE OF KELVIN PLANCK AND CLAUSIUS STATEMENT



∴ If one statement is violated, the other is automatically violated.

CARNOT PRINCIPLES

- (1) The efficiency of an irreversible heat engine cannot exceed the efficiency of reversible heat engine operating between the same two reservoirs.
- (2) The efficiency of all reversible heat engines operating between same two reservoirs are same.

Perpetual Motion Machine of Third Kind (PMM III)

A device which works continuously without exchanging heat or work from the surroundings is called PMM III.

It is possible only in the absence of friction which is practically impossible.

THERMODYNAMIC TEMPERATURE SCALE

A temperature scale that is independent of the properties of the substances that are used to measure temperature is called a thermodynamic temperature scale.

$$\eta_{\text{th rev}} = f(T_H, T_L)$$

$$\text{or } \frac{Q_H}{Q_L} = f_1(T_H, T_L)$$

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

$$\frac{Q_1}{Q_3} = f(T_1, T_3)$$

$$\frac{Q_2}{Q_3} = f(T_2, T_3)$$

$$\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2} \times \frac{Q_2}{Q_3}$$

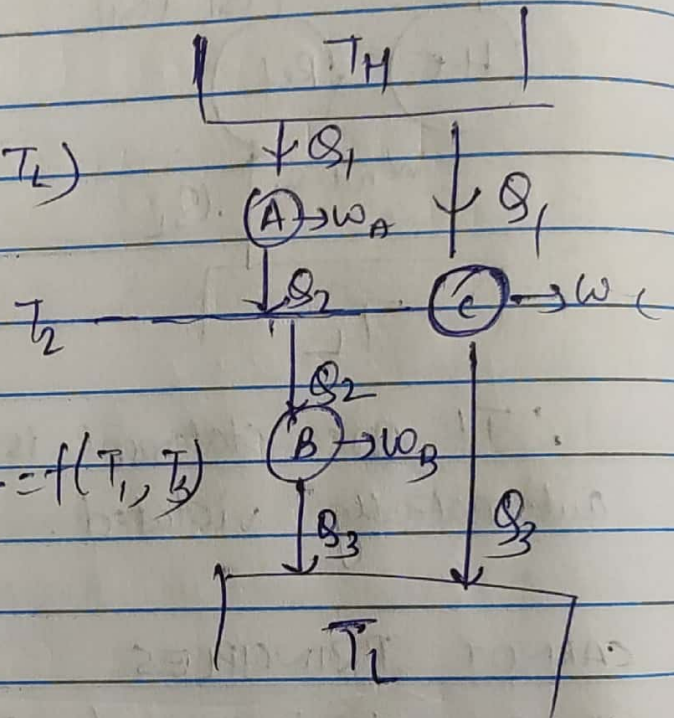
$$f(T_1, T_3) = f(T_1, T_2) \times f(T_2, T_3)$$

$$f(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2)} ; f(T_2, T_3) = \frac{\phi(T_2)}{\phi(T_3)}$$

$$\therefore f(T_1, T_3) = \frac{\phi(T_1)}{\phi(T_3)}$$

Lord Kelvin; $\left(\frac{Q_2}{Q_1}\right)_{\text{rev}} = \frac{T_2}{T_1}$

absolute scale
no -ve values.



$$\frac{Q_H}{T_H} = \frac{Q_{Lrev}}{T_L} - \frac{Q_{Lrev}}{T_L} - \frac{Q_{Lirr}}{T_L} < 0$$

$$\therefore Q_{Lirr} > Q_{Lrev}$$

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

If $\eta_{arbitrary} = \eta_{rev}$ [reversible engine]

If $\eta_{arb} < \eta_{rev}$ [irreversible engine]

If $\eta_{arb} > \eta_{rev}$ [impossible]

Refrigerator

$$(COP)_R = \frac{Q_L}{Q_H - Q_L} = \frac{Q_L/Q_H}{1 - Q_L/Q_H} = \frac{T_L/T_H}{1 - T_L/T_H} = \frac{T_L}{T_H - T_L}$$

Heat pump

$$(COP)_{H.P.} = \frac{Q_H}{Q_H - Q_L} = \frac{T_H}{T_H - T_L}$$

CLAUSIUS INEQUALITY

The cyclic integral of $\delta Q/T$ is always less than or equal to zero.

This inequality is valid for all cycles, reversible or irreversible.

115. $\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_{Lirr}}{T_L} < 0$

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

$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$

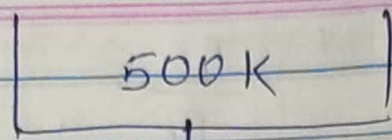
Second law efficiency :-

It is the ratio of actual efficiency to the reversible efficiency.

$$\eta_{second\ law} = \frac{\eta_{actual}}{\eta_{rev}}$$

COP \rightarrow Coefficient of Performance.

Eg:-



$$\eta_{\text{actual}} = \frac{W}{Q}$$

$$= \frac{9.5}{100} = 9.5\%$$

$$\eta_{\text{rev}} = 1 - \frac{T_L}{T_H}$$

$$= 1 - \frac{450}{500}$$

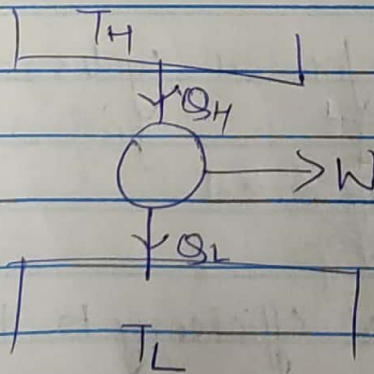
$$= 10\%$$

$$\eta_{\text{second law}} = \frac{9.5}{10} = 95\%$$

$$\eta_{\text{second law}} = \frac{(\text{COP})_{\text{actual}}}{(\text{COP})_{\text{rev}}}$$

Effect of source and sink temperature on the efficiency of a reversible engine, COP of heat pump & refrigerators

(I) ENGINE



$$\eta_{\text{Heat engine}} = 1 - \frac{T_L}{T_H}$$

Case-i) T_L decreases by ΔT

$$\eta_{\text{rev H.E}} = \frac{T_H}{T_H - (T_L - \Delta T)}$$

$$= \frac{T_H}{(T_H - T_L) + \Delta T}$$

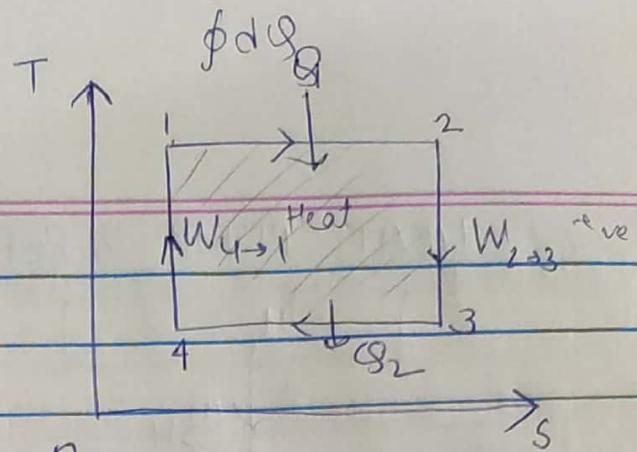
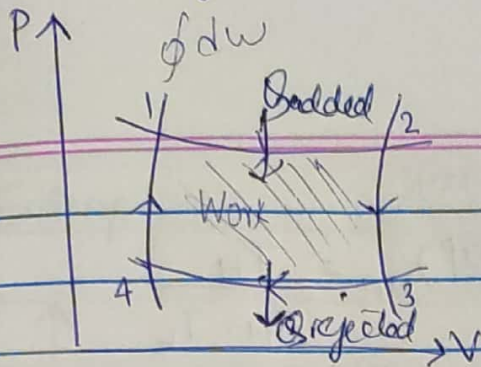
more preferable

Case-ii) Increase T_H by ΔT

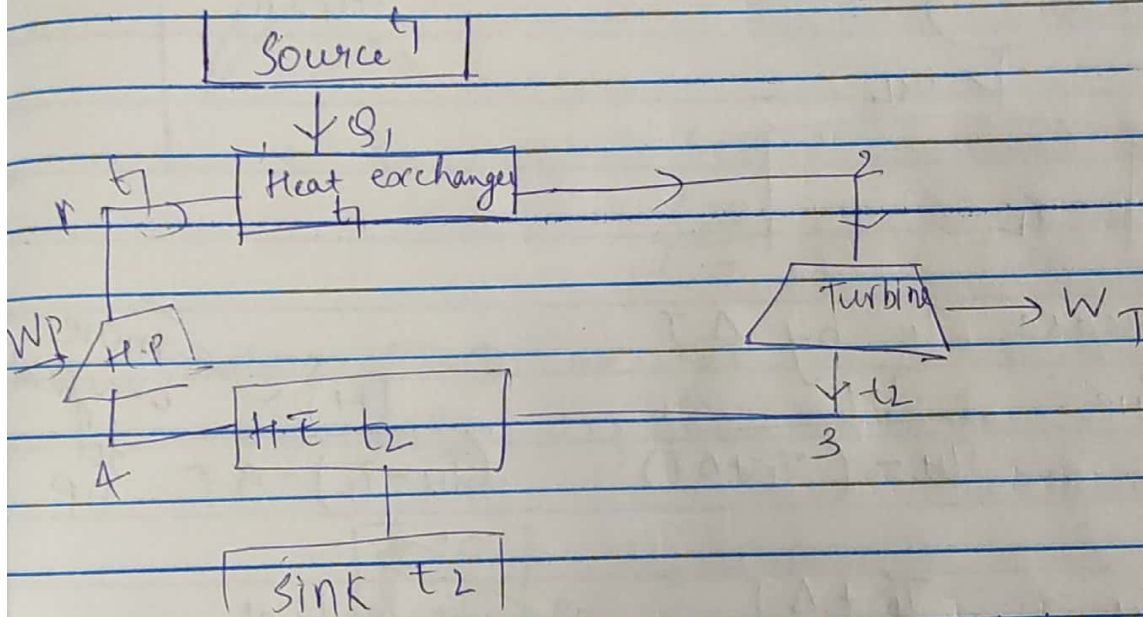
$$\eta_{\text{rev}} = \frac{(T_H + \Delta T) - T_L}{T_H + \Delta T}$$

$$\eta_{\text{rev}} = \frac{(T_H - T_L) + \Delta T}{T_H + \Delta T}$$

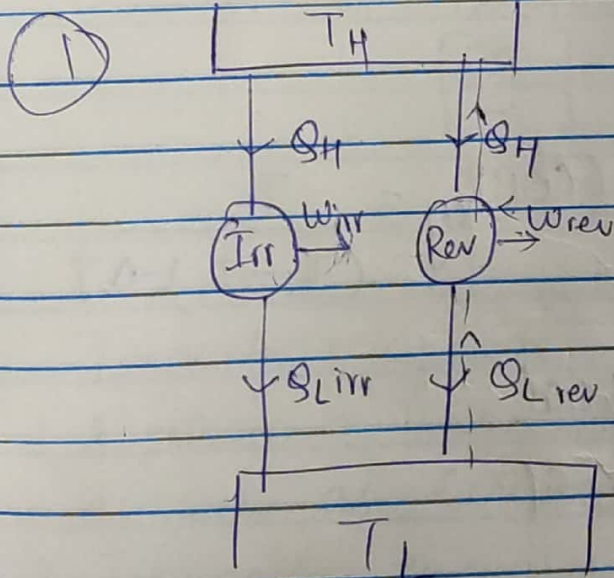
Carnot cycle



$$W_{net} = W_{12} + W_{23} - W_{41} = Q_1 - Q_2$$



Proof of Carnot principles

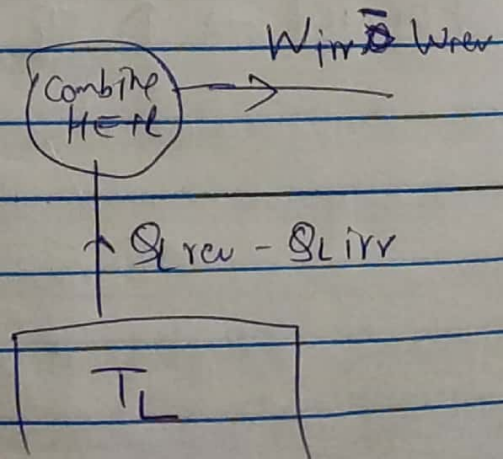


Assume

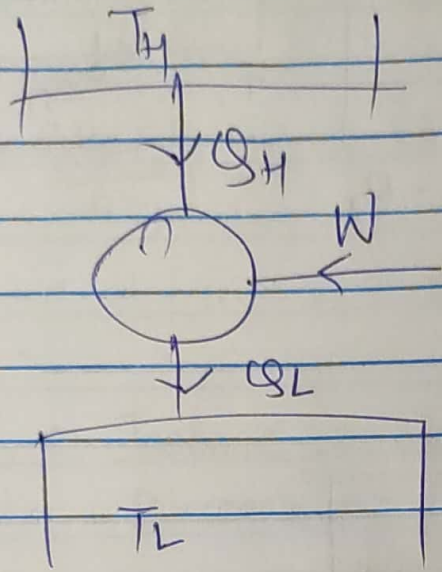
$$\eta_{irr} > \eta_{rev}$$

$$\frac{W_{irr}}{Q_H} > \frac{W_{rev}}{Q_H}$$

$$W_{irr} > W_{rev}$$



② (2) HEAT PUMP & REFRIGERATOR



$$(COP)_{HP} = \frac{T_H}{T_H - T_L}$$

$$(COP)_{ref} = \frac{T_L}{T_H - T_L}$$

i) Increase T_L by ΔT

$$(COP)_{HP} = \frac{T_H}{T_H - (T_L + \Delta T)} = \frac{T_H}{(T_H - T_L) - \Delta T} \quad \checkmark \text{ more beneficial for HP}$$

$$(COP)_{ref} = \frac{T_L + \Delta T}{(T_H - T_L) - \Delta T} \quad \checkmark \text{ more beneficial for ref}$$

ii) Decrease T_H by ΔT

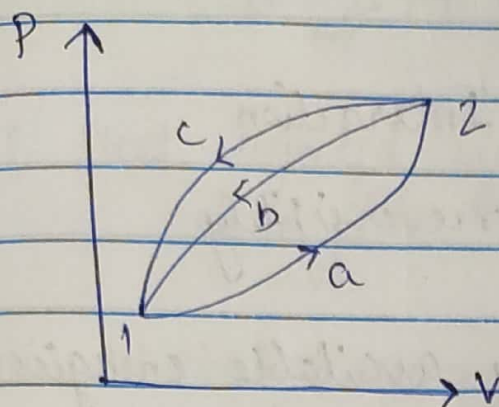
$$(COP)_{HP} = \frac{T_H - \Delta T}{(T_H - T_L) - \Delta T}$$

$$(COP)_{ref} = \frac{T_L}{(T_H - T_L) - \Delta T}$$

For HP $\rightarrow \uparrow T_L$ is beneficial

For ref $\rightarrow \uparrow T_L$ is beneficial.

Entropy



1-a-2-b-1 (Rev.)

According to Clausius inequality

$$\oint \frac{\delta Q}{T} = 0 \Rightarrow \oint \frac{\delta Q}{T} = 0 \quad \text{--- (1)}$$

1-a-2-c-1 (Rev.)

$$\oint \frac{\delta Q}{T} = 0 \quad \text{--- (2)}$$

Equating (1) & (2) we get

$$\oint \frac{\delta Q}{T_{2b1}} = \oint \frac{\delta Q}{T_{2c1}} \quad \therefore \text{Entropy is a point function.}$$

$$\left[\frac{\delta Q}{T} \right]_{\text{Rev}} = \text{Entropy}$$

For an irreversible process

$$\left[\frac{\delta Q}{T} \right] < dS (\text{Entropy})$$

$$\therefore \boxed{dS \geq \frac{\delta Q}{T}}$$

Important points:-

1. A process is reversible if it is both internally as well as externally reversible.
2. Internally reversible means no entropy is generated within the system whereas externally means no entropy is generated outside the system.
3. Entropy is the measure of unavailable energy.
4. Though entropy is a property but entropy generation is not a property and is a path function.

Entropy of a system can change in the following three ways

1. Heat interaction
 2. Mass interaction
 3. Entropy Generation \rightarrow Internal irreversibility
- } \rightarrow External Interaction

Work, K.E and P.E are totally available energies and hence no entropy is associated with energy interactions in these forms.

ENTROPY ANALYSIS OF CLOSED SYSTEM

$$dS = \frac{\delta Q}{T} + (SS)_{\text{generation}}$$

Case-i) :- Internally reversible

$$(SS)_{\text{generation}} = 0$$

$$\therefore dS = \frac{\delta Q}{T}$$

i) Heat added to the system $\delta Q \rightarrow +ve$
 $dS \rightarrow +ve$

ii) Heat rejected by the system $\delta Q \rightarrow -ve$
 $dS = \frac{\delta Q}{T} \rightarrow -ve$

iii) Adiabatic system $\delta Q = 0$
 $\therefore dS = 0$

Case-ii) Internally irreversible $(SS)_{\text{gen}} \neq 0$
 $dS = \frac{\delta Q}{T} + (SS)_{\text{gen}}$

i) Heat added to the system $\delta Q \rightarrow +ve$
 $ds = \frac{\delta Q}{T} + (\delta S)_{gen} \rightarrow +ve$

ii) Heat rejected by the system $\delta Q \rightarrow -ve$
 $ds = \frac{\delta Q}{T} + (\delta S)_{gen} \rightarrow \text{can be } +ve / -ve / 0$

iii) Adiabatic system $\delta Q = 0$
 $ds = (\delta S)_{gen} \rightarrow +ve$

Entropy change of the universe

$$ds = \delta Q/T + (\delta S)_{gen}$$

Universe is an isolated system, $\delta Q = 0$

$$ds = (\delta S)_{gen} \geq 0$$

According to second law of thermodynamics, all those processes are possible for which the entropy change of universe is greater than or equal to zero.

This is known as INCREASE OF ENTROPY PRINCIPLE

T-S Diagram

$$ds = \delta Q/T + (\delta S)_{gen}$$

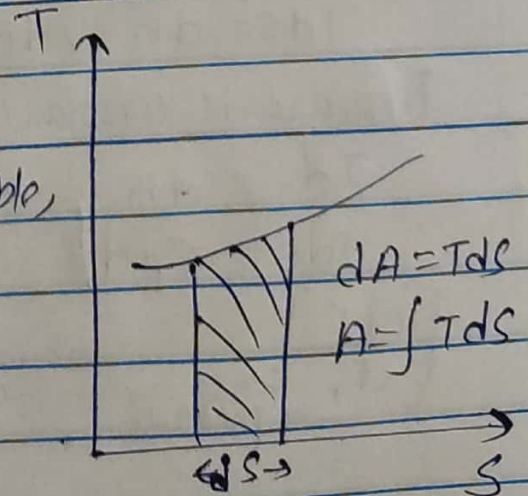
If the process is internally reversible,

then $\delta S = 0$

$$ds = \delta Q/T$$

$$dT = dQ$$

$$Q = \int T ds$$



$$TdS = dU + PdV \rightarrow \text{1st T-ds equation}$$

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

$$dH = TdS + VdP$$

$$\text{or } TdS = dH - VdP \rightarrow \text{2nd T-ds equation}$$

T-ds equations are valid for

1. Internally reversible and irreversible processes
2. Closed and open system.

Representation of constant volume and constant pressure curve on T-S diagram.

Constant volume

$$TdS = dU + PdV$$

Volume is constant, so $dV = 0$

$$TdS = dU = C_v dT$$

$$\left[\frac{dT}{dS} \right]_{\text{constant volume}} = \frac{T}{C_v}$$

Constant pressure

$$TdS = dH - VdP$$

Pressure is constant, $dP = 0$

$$TdS = dH$$

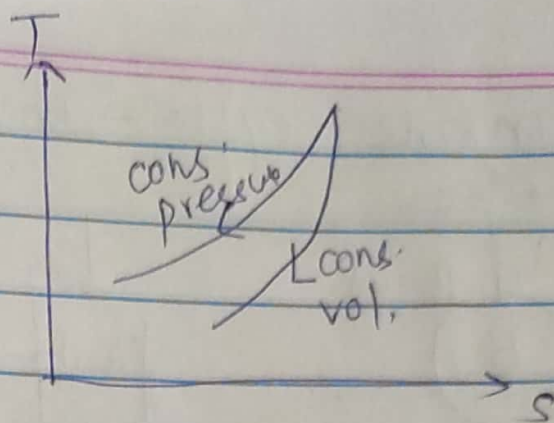
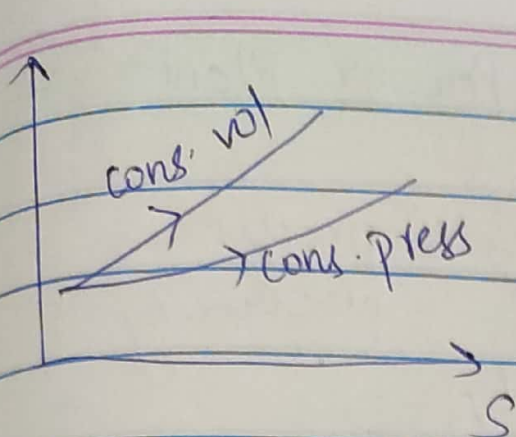
$$TdS = C_p dT$$

$$\left[\frac{dT}{dS} \right]_{\text{constant pressure}} = \frac{T}{C_p}$$

$$C_p > C_v$$

$$\frac{1}{C_v} > \frac{1}{C_p}$$

$$\left[\frac{T}{C_v} > \frac{T}{C_p} \right]$$



Entropy change for ideal gas

$$Tds = du + PdV$$

If a substance is ideal, then $du = C_v dT$, $PV = RT$

$$ds = \frac{du}{T} + \frac{PdV}{T}$$

$$= \frac{du}{T} + \frac{R}{V} dV = \frac{C_v dT}{T} + \frac{R dV}{V}$$

C_v is constant

$$s_2 - s_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$$Tds = dh - VdP$$

If substance is ideal gas, $dh = C_p dT$ and $PV = RT$

$$ds = \frac{dh}{T} - \frac{VdP}{T} = \frac{C_p dT}{T} - \frac{R dP}{P}$$

C_p is constant

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