THERMODYNAMICS

↳ study of exchange of heat between Bodies!

> **SYSTEM:-**

assembly of large no. of mol. which can be described by thermodynamic variable P, V, T
Ex:- Gas enclosed in Cylinder!

> **SURROUNDING:-**

Everything around system which can have a direct effect on system!

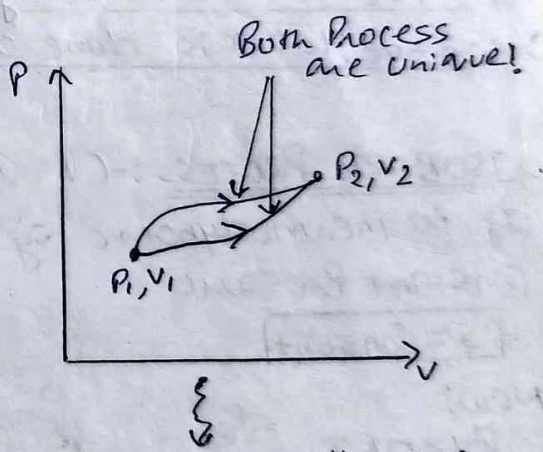
> **THERMODYNAMIC STATE:-**

If System has fix. value of P, V, T at some instant then System is in Thermodynamic state.

$PV = nRT$

> **THERMODYNAMIC PROCESS:-**

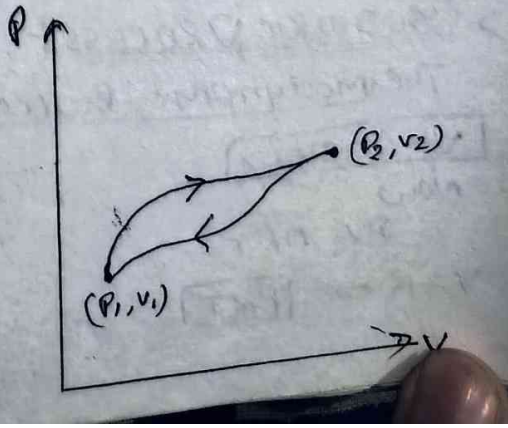
A well defined path from one Thermodynamic state to another T.D state is called Thermodynamic Process.



Indicator diagram (Representing Variation of P, V, T with each other)

> **CYCLIC PROCESS:-**

Process in which system returns to its initial thermodynamic state after undergoing a series of changes.



> WORK DONE BY GAS :-

Work done by Gas :-

$dW = F_{gas} \cdot dx$

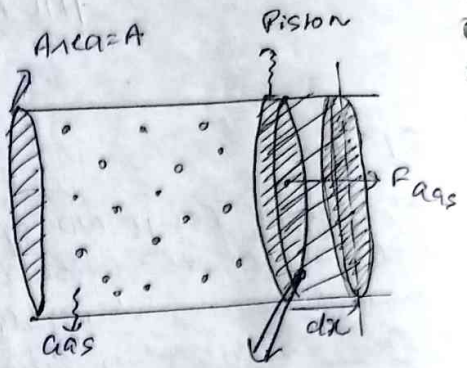
$\because \boxed{F_{gas} = PA}$ (Pressure of gas)

$dW = (PA)dx$

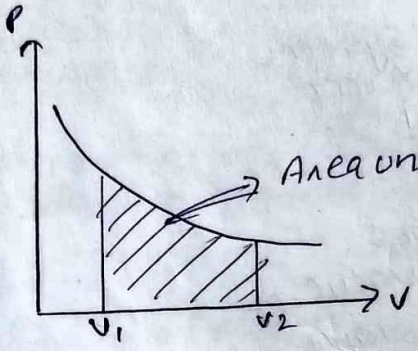
$dW = P(A\,dx)$

$dW = P(dV)$

$\boxed{W = \int P\,dV}$



> Increase in volume of Gas = $A\,dx$!



Area under curve P-V ⇒ work done by gas

> W = +ve ; work is done by the gas V(↑)

> W = -ve ; work is done ON the gas V(↓)

> ISOBARIC PROCESS :- (P = Constant)

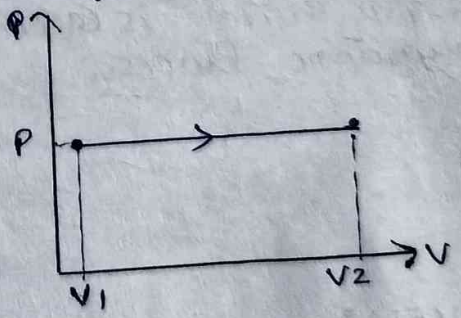
If a Thermodynamic system undergo Physical change at Constant Pressure

$\boxed{P = \text{Constant}}$

NOW;

$PV = nRT$

$P = K \Rightarrow \boxed{V \propto T}$



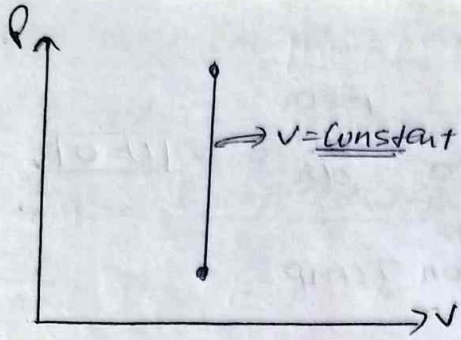
> ISOCHORIC PROCESS :-

Thermodynamic Process in which $V \rightarrow$ Constant

$\boxed{V = \text{Constant}}$

NOW

$PV = nRT$

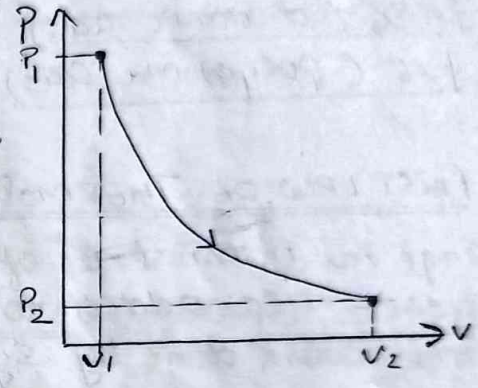


Since;
area under curve = 0
Work done = 0

> ISOTHERMAL PROCESS:-

A thermodynamical process in which T → constant.

T = Constant



Now,

$PV = nRT$

$T = K \Rightarrow PV = \text{Constant} = \boxed{P \propto \frac{1}{V}}$

$$W = \int_{V_1}^{V_2} P\,dV$$

$PV = nRT$

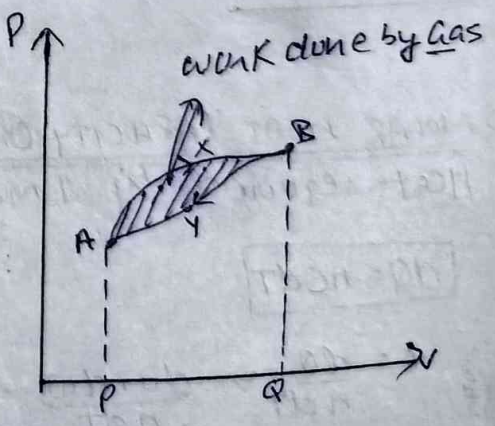
$$P = \frac{nRT}{V} \quad \text{--- (1)}$$

$$W = \int_{V_1}^{V_2} \frac{nRT}{V}\,dV$$

$$W = nRT \int_{V_1}^{V_2} V^{-1}\,dV$$

$$W = nRT[\ln V]_{V_1}^{V_2} \Rightarrow \underline{W = nRT \ln(V_2/V_1)}$$

> WORK DONE IN A CIRCULAR PATH:-



Work done by Gas:-

+ ar(AXBQP) − ar(AYBQP)

⇒ + ar(AXBYA)

#

In an Ideal Gas;

Intermolecular forces are 0.
So, Potential energy of Ideal Gas = 0

$F = 0$

$-\frac{dU}{dr} = 0 \Rightarrow \boxed{U = 0}$

Internal KE is a function of Temp.
So Internal K.E depend only upon Temp.

$\boxed{U = f/2\, nRT}$

f: degree of freedom.

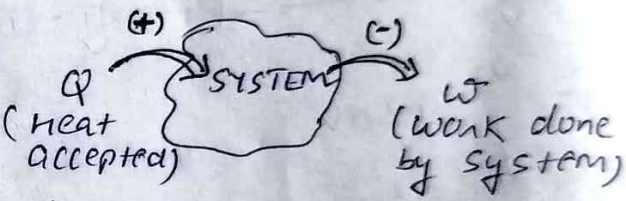
- $f = 3/2$ (Monoatomic Gas)
- $f = 5/2$ (diatomic gas)
- $f = 6$ (polyatomic gas)

∵ Isothermal Process
$\Delta T = 0$
$\boxed{\Delta U = 0}$

∵ Cyclic Process
$\Delta T = 0$
$\boxed{\Delta U = 0}$

> FIRST LAW OF THERMODYNAMICS :-

"change in Internal E of System = Heat added to System - work done by System"



$\boxed{\Delta U = Q - W}$ ∵

(Change in Internal E)

differential form:-

$\boxed{dU = dQ - dW}$

> MOLAR HEAT CAPACITY OF IDEAL GAS:-

Heat required by 1 mol of Gas for 1° rise in temperature

$\boxed{dQ = nC\,dT}$

$C = \frac{dQ}{n\,dT} \Rightarrow \frac{dU + dW}{n\,dT}$

or

$\boxed{C = \frac{dU + dW}{n\,dT}}$

> MOLAR HEAT CAPACITY At Constant Volume (C_v)

$$C = \frac{dw + du}{n\,dT}$$

In a Isobaric Process; $dw = 0$

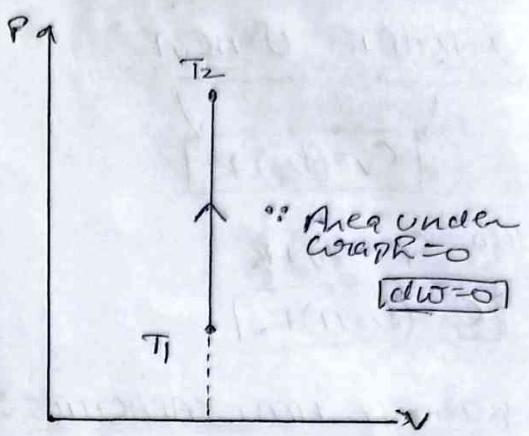
$$C_v = \frac{du}{n\,dT}$$

$$\boxed{du = nC_v\,dT}$$

$$\int_{u_1}^{u_2} du = \int_{T_1}^{T_2} nC_v\,dT$$

$$\int_{u_1}^{u_2} du = nC_v \int_{T_1}^{T_2} dT$$

$$\boxed{\Delta U = nC_v \Delta T} \text{ or } \underbrace{\boxed{U = nC_vT}}_{u_1 = 0}$$



> MOLAR HEAT CAPACITY AT CONSTANT PRESSURE (C_p)

$$C = \frac{dw + du}{n\,dT}$$

In a ISOBaric Process; $dw = Pdv$

$$C_p = \frac{Pdv + nC_v dT}{n\,dT}$$

also, $Pv = nRT$

$$Pdv = nRdT \quad \text{—①}$$

So,

$$C_p = \frac{nRdT + nC_v dT}{n\,dT}$$

$$C_p = R + C_v \quad \text{(Mayer's Relation)}$$

> WHY IS $C_p > C_v$?

$$C_v = \frac{dQ}{n\,dT} = \frac{du + \cancel{dw}^{\,0}}{n\,dT} = \frac{du}{n\,dT} \Rightarrow C_v = \frac{du}{n\,dT} \quad \text{—①}$$

$$C_p = \frac{dQ}{n\,dT} = \frac{du + dw}{n\,dT} = \frac{du}{n\,dT} + \frac{dw}{n\,dT}$$

$$C_p = C_v + \left(\frac{dw}{n\,dT}\right)_{\text{—tve}}$$

$$\boxed{C_p > C_v}$$

> HEAT CAPACITY IN TERMS OF DEGREE OF FREEDOM :-

$U = f/2\, nRT \qquad U = nC_V T$

$$\boxed{C_V = (f/2)\,R}$$

also, $C_P = C_V + R$

$$\boxed{C_P = (f/2 + 1)\,R}$$

> Ratio of HEAT CAPACITIES :-

$$\gamma = \frac{C_P}{C_V} = \frac{(f/2+1)R}{(f/2)R}$$

γ is called adiabatic index of gas

$$\gamma = \frac{f+2}{f}$$

$$f(\gamma - 1) = 2 \Rightarrow f = \left(\frac{2}{\gamma - 1}\right)$$

$$\left.\begin{aligned} > C_V &= \left(\frac{R}{\gamma - 1}\right) \\ > C_P &= \left(\frac{\gamma R}{\gamma - 1}\right) \end{aligned}\right\} \because$$

> WORK DONE IN POLYTROPIC PROCESS :-

A Process PV^n = Constant are called Polytropic Process ($\because n \neq 1$)

$$\boxed{W = \frac{nR(T_i - T_f)}{(n-1)}}$$

> MOLAR HEAT CAPACITY IN POLYTROPIC PROCESS :-

$$C = \frac{dQ}{n dT} = \frac{dU + dW}{n dT} \quad \text{— (A)}$$

$PV^{\gamma} = \text{Constant}$

$$d(PV^{\gamma}) = d(K)$$

$$1 \cdot (dP)V^{\gamma} + \gamma V^{\gamma-1} P dV = 0$$

$$dP V^{\gamma} + \frac{\gamma V^{\gamma} P dV}{V} = 0$$

$$V dP + \gamma P dV = 0$$

So,

$$V dP = -\gamma P dV \quad \text{— (1)}$$

$PV = nRT$

$$d(PV) = d(nRT)$$

$$P dV + V dP = nR dT \quad \text{— (2)}$$

from eq 1 and 2

$$P dV - \gamma P dV = nR dT$$

$$P dV(1-\gamma) = nR dT$$

$$dW = P dV = \frac{nR dT}{(1-\gamma)} \Rightarrow dW = \frac{nR dT}{(1-\gamma)}$$

Putting dW in eq. (A) :-

$$C = \frac{\left(nC_V dT + \frac{nR dT}{1-\gamma}\right)}{n dT}$$

$$\boxed{C = C_V + \frac{R}{(1-\gamma)}}$$

> MOLAR HEAT CAPACITY FOR MIX. OF NON-RCT'G GASES :-

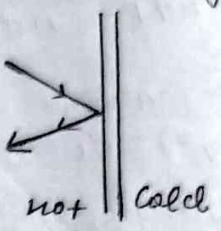
$$dU_{Mix} = dU_1 + dU_2$$

$$(n_1 + n_2) C_{V_{mix.}} T = n_1 C_{V_1} T + n_2 C_{V_2} T$$

$$\boxed{C_{Vmix} = \frac{n_1 C_{V_1} + n_2 C_{V_2}}{n_1 + n_2}}$$

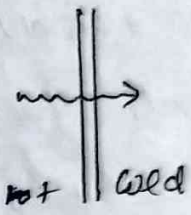
> ADIABATIC WALL :-

The wall which prevent passage of matter and energy



> DIATHERMIC WALL :-

Prevent passage of matter but allows passage of energy



> ADIABATIC PROCESS :-

In which, P, V, T of system change but there is no exchange of heat b/w system and surrounding ($\Delta Q = 0$)

In a Adiabatic Process;

> $PV^{\gamma} = \text{constant}$; $\gamma = \frac{C_P}{C_V}$

∵ According to 1st Law;

$dU = \cancel{dQ}^{0} - dW$

$dU = -dW$

$nC_V dT = -P dV$ — (1)

$nRT = -\frac{P dV}{C_V}$

also $PV = nRT$:-

$d(PV) = d(nRT)$

$P dV + V dP = nR dT$ — (2)

$P dV + V dP = -\frac{R}{C_V}(P dV)$

$V dP = -P dV\left(\frac{R + C_V}{C_V}\right)$

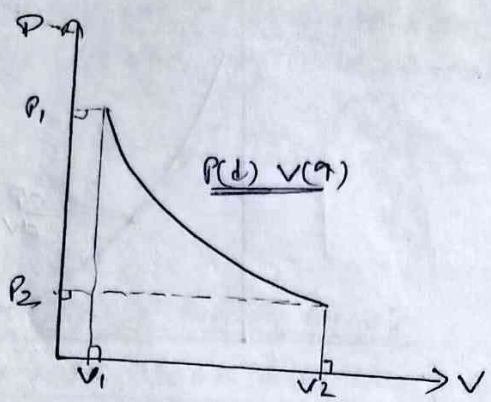
also, $C_P - C_V = R \Rightarrow (C_V + R) = C_P$

$V dP = -\left(\frac{C_P}{C_V}\right) P dV$

$V dP = -\gamma P dV$

$\left(\frac{dP}{P}\right) = -\gamma\left(\frac{dV}{V}\right)$

$\int_{P_1}^{P_2} \frac{1}{P} dP = -\gamma \int_{V_1}^{V_2} \frac{1}{V} dV$



$$[\ln P]_{P_1}^{P_2} = -\gamma [\ln V]_{V_1}^{V_2}$$

$$\ln\left(\frac{P_2}{P_1}\right) = -\gamma \ln\left(\frac{V_2}{V_1}\right)$$

$$\ln\left(\frac{P_2}{P_1}\right) = \ln\left(\frac{V_2}{V_1}\right)^{-\gamma}$$

$$\frac{P_2}{P_1} = \left(\frac{V_2}{V_1}\right)^{-\gamma}$$

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

$$P_2 V_2^{\gamma} = P_1 V_1^{\gamma}$$

$$\Rightarrow \boxed{PV^{\gamma} = \text{Constant}}$$

> WORK DONE IN ADIABATIC PROCESS :-

$$dW = F \cdot dx$$

$$dW = (PA)\,dx$$

$$dW = P(A\,dx)$$

$$dW = P\,dV$$

$$dW = KV^{-\gamma} dV$$

$$\int dW = K \int_{V_1}^{V_2} V^{-\gamma} dV$$

$$W = K\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]_{V_1}^{V_2}$$

$$W = \frac{K\left[V_2^{-\gamma} V_2 - V_1^{-\gamma} V_1\right]}{(-\gamma+1)}$$

$$\Rightarrow \left(\frac{P_2 V_2 - P_1 V_1}{1-\gamma}\right) \Rightarrow \left(\frac{P_1 V_1 - P_2 V_2}{\gamma - 1}\right) = \frac{nRC(T_1 - T_2)}{(\gamma - 1)}$$

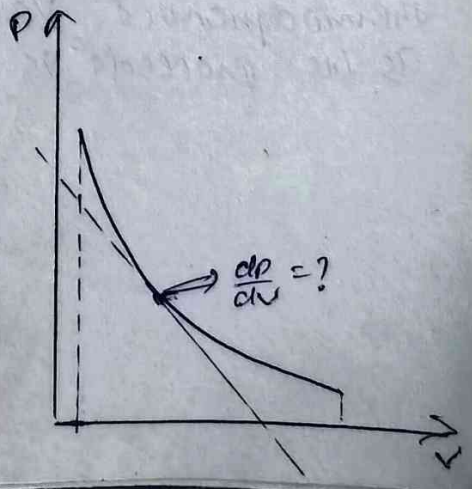
> SLOPE OF ISOTHERMAL PROCESS :-

$$PV = K$$

$$d(PV) = d(K)$$

$$P\,dV + V\,dP = 0$$

$$\boxed{\frac{dP}{dV} = -\frac{P}{V}}$$



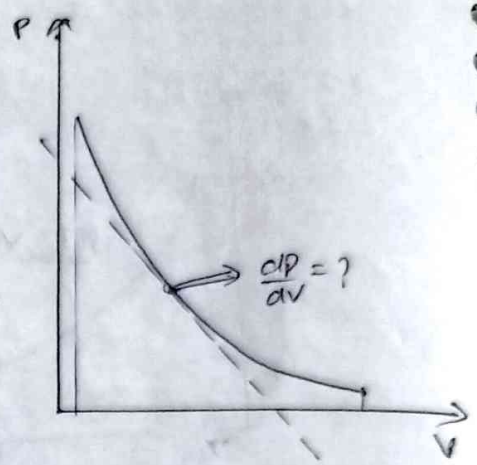
> SLOPE OF ADIABATIC PROCESS:-

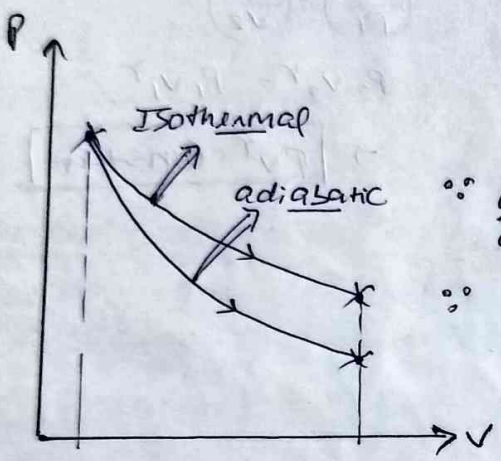
$PV^{\gamma} = K$

$d(PV^{\gamma}) = d(K)$

$(dP)V^{\gamma} + \gamma V^{\gamma-1}(dV) = 0$

$$\boxed{\frac{dP}{dV} = -\gamma\frac{P}{V}}$$





$\because \frac{dP}{dV} = -\frac{P}{V}$ (Isothermal)

$\because \frac{dP}{dV} = -\gamma\frac{P}{V}$ (adiabatic)

$M_{adiabatic} = \gamma M_{isothermal}$

Since; $\gamma > 1$

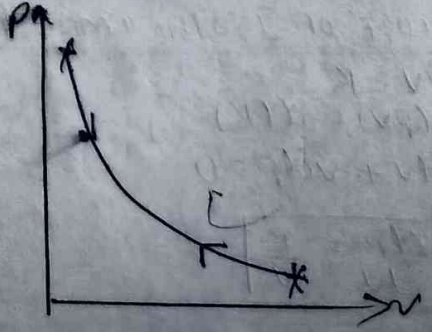
$M_{adiabatic} > M_{isothermal}$

> QUASI-STATIC PROCESS:-

∵ Process which proceeds extremely slowly such that at every instant of time, T, P, are same in all Parts of System.

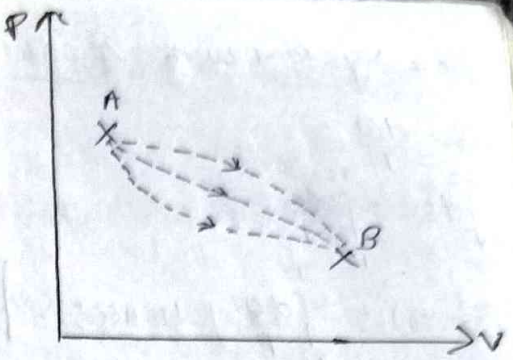
> REVERSIBLE PROCESS:-

A Process which can return to its initial state of thermodynamics variables at each stage of variation as its proceeds is called reversible process



> IRREVERSIBLE PROCESS :-

If it cannot be retraced back exastly in the opposite direction!



> DRAW BACKS OF FIRST LAW :-

(i) do not talk about direction of heat flow.

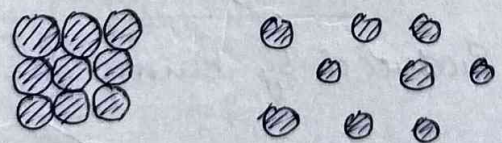
(ii) we know that;
revolving wheel catches fire due to High Kinetic Energy.
So, Ist law fails to explain why heat energy cannot be converted into K.E.

> SECOND LAW OF THERMODYNAMICS :-

It is impossible to construct a engine that can convert heat completely into work without producing any other effect.

> ENTROPY :-

∴ Entropy is thermodynamic variable of a system.
↓
related to disorder or randomless in system.



System-1 System-2

∴ entropy of system 1 is less than system 2
or
$S_1 < S_2$

∴ If System at Temp. T is supplied a small amount of heat ΔQ the change in entropy is given by

$$ds = \frac{dQ}{T} \Rightarrow \Delta S = S_f - S_i = \frac{\Delta Q}{T}$$

∵ for a system with variable temperature :-

$$ds = \frac{dQ}{T}$$

$$\int_{S_1}^{S_2} ds = \int_{T_1}^{T_2} \frac{dQ}{T}$$

$$(S_2 - S_1) = \int_{T_1}^{T_2} \frac{dQ}{T} \quad \text{Hence;} \quad \boxed{S_2 - S_1 = \int_{T_1}^{T_2} \frac{dQ}{T}}$$

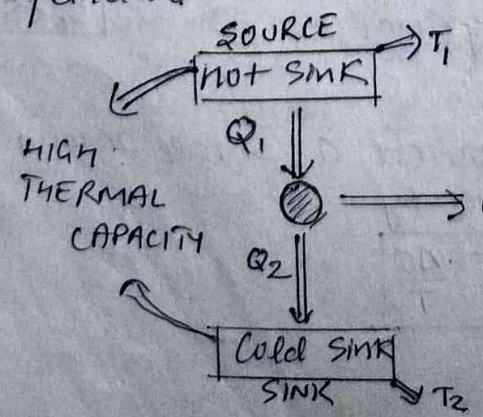
> Second law may be stated in terms of entropy :-
It is impossible to have a process in which entropy of Isolated system is decreased

∵ Entropy of universe always Increases.
∵ Entropy is not a Conserved Quantity.
∵ Entropy Can be Created but Cannot be destroyed !

> HEAT ENGINE :-
↳ device used to Convert Heat E into Mechanical E in Cyclic Process

(i) EXT. COMBUSTION ENGINE :-
Heat Needed for engine is Produced by Burning of fuel outside the Cylinder.

(ii) INT. COMBUSTION ENGINE :-
Heat Needed for engine is Produced by Burning fuel inside the Cylinder.



BY ENERGY CONS. ;
$\boxed{Q_1 = W + Q_2}$

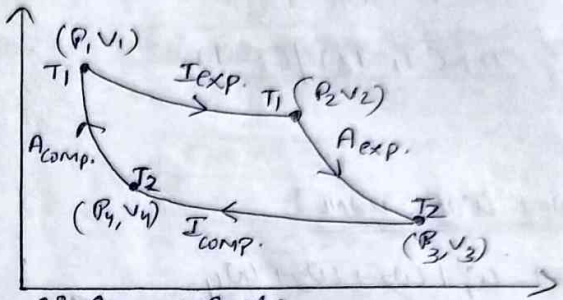
> Efficiency (η) = $\frac{\text{output}}{\text{input}} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = \boxed{1 - \frac{Q_2}{Q_1}}$

> CARNOT HEAT ENGINE :-

"It has Max. efficiency and it is an ideal heat engine."

> It is Based on four operations :-

(i) Isothermal expansion.
(ii) adiabatic expansion.
(iii) Isothermal Compression.
(iv) ~~Isothermal~~ adiabatic Compression.

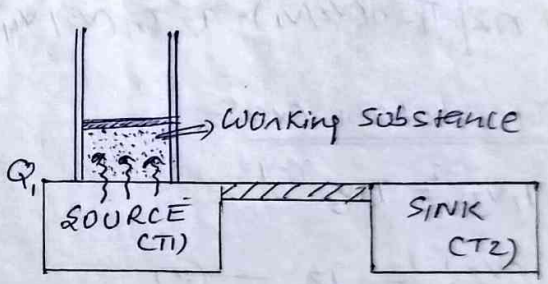


∵ Carnot cycle

Carnot cycle has 3 Main Parts

> Source (T_1)
> Sink (T_2)
> Working substance

(i) ISOTHERMAL EXPANSION :-



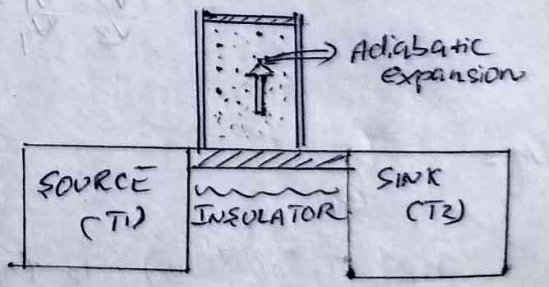
If Q_1 is heat absorbed from Source and W_1 is work done, then;

$\Delta U = 0$ (In Isothermal expansion, $\Delta T = 0$)

$\Delta U = Q - W_1$

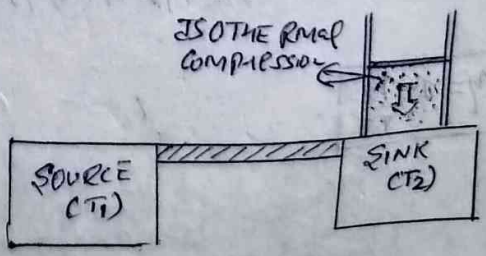
$\Delta U = 0 \Rightarrow \boxed{Q_1 = W_1} = nRT_1 \ln(V_2/V_1)$

(ii) ADIABATIC EXPANSION :-



Work done (W_2) = $nR(T_1 - T_2)/(\gamma - 1)$

(iii) ISOTHERMAL COMPRESSION :-



If Q_2 is heat rejected to sink.
Work done (W_3)

$\Delta U = Q_2 - W_3 = 0 \Rightarrow Q_2 = W_3$

$Q_2 = W_3 = nRT_2 \ln(V_4/V_3)$

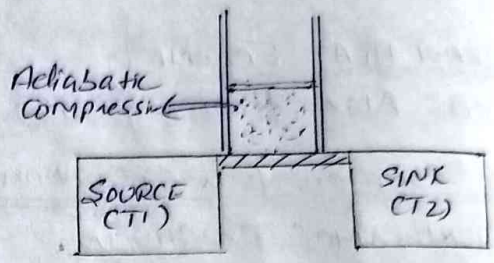
(iv) Adiabatic COMPRESSION :-

∴ Work done (W_4)

$\Rightarrow nRC(T_1 - T_4)/(\gamma - 1)$

$\Rightarrow nR(T_2 - T_1)/(\gamma - 1)$

$\Rightarrow \underline{-nRC(T_1 - T_2)/(\gamma - 1)}$



> Net WORK DONE :-

$W = W_1 + W_2 + W_3 + W_4$

$\Rightarrow nRT_1 \ln(V_2/V_1) + nRC(T_1 - T_2)/(\gamma - 1)$
$-nRT_2 \ln(V_3/V_4) - nRC(T_1 - T_2)/(\gamma - 1)$

$\Rightarrow nR[T_1 \ln(V_2/V_1) - T_2 \ln(V_3/V_4)]$ — (1)

> In Adiabatic exp :-

$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$

$\left(\frac{V_2}{V_3}\right)^{\gamma-1} = \frac{T_2}{T_1}$ — (2)

> In Adiabatic Compression :-

$T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1}$

$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)$ — (3)

$\because \frac{V_2}{V_3} = \frac{V_1}{V_4} \Rightarrow \boxed{V_1 V_3 = V_2 V_4}$

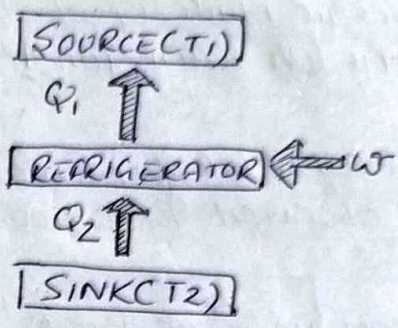
$\eta = \frac{W}{Q_1}$

$\Rightarrow \frac{nR[T_1 \ln(V_2/V_1) - T_2 \ln(V_3/V_4)]}{nRT_1 \ln(V_2/V_1)} \Rightarrow \frac{T_1 - T_2}{T_1}$

$\boxed{\eta = 1 - \frac{T_2}{T_1}}$

> REFRIGERATOR OR HEAT PUMP :-

$Q_1 = Q_2 + W$
(Energy conservation)



> Coeff of Performance of Refrigerator :-

$\beta = \frac{\text{heat absorbed from sink}}{\text{work done}}$

$\beta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} \Rightarrow \frac{1}{\left(\frac{Q_1}{Q_2} - 1\right)}$

$B = \frac{1}{\left(\frac{T_1}{T_2} - 1\right)} = \frac{1-\eta}{\eta} \Rightarrow \boxed{B = \frac{1-\eta}{\eta}}$

$Q_1 \propto W$ or $Q_1 = W$

$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

$\frac{1 - \left(\frac{Q}{W}\right)}{\left(\frac{Q}{W}\right)} = \frac{W - Q_1}{Q_1} =$