



SHORT NOTES

C H A P T E R

Laws of Thermodynamics

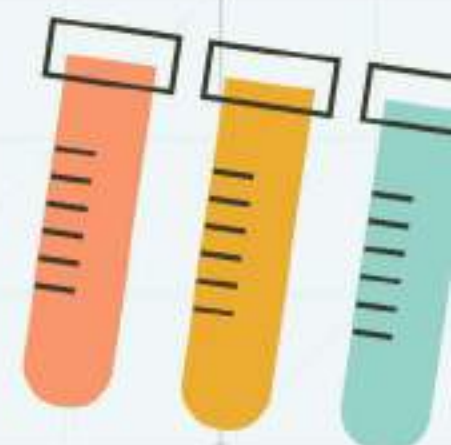
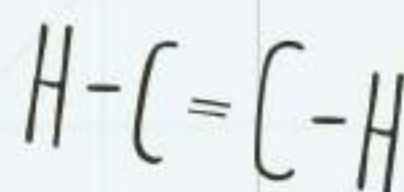
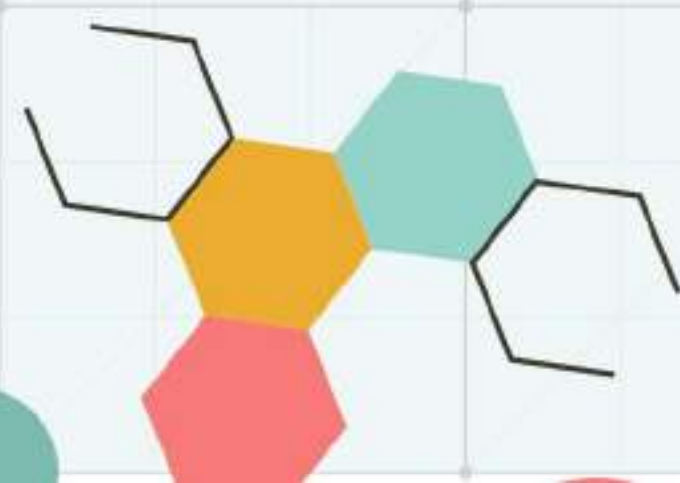
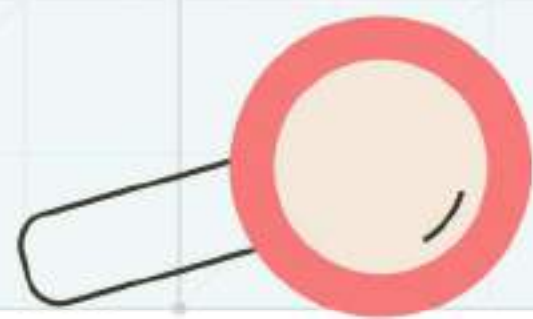
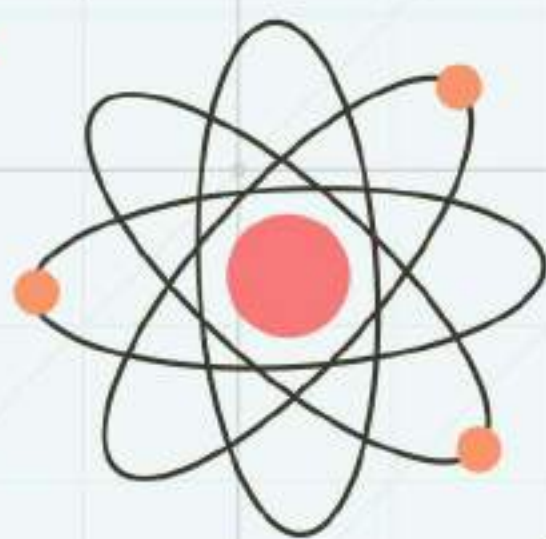
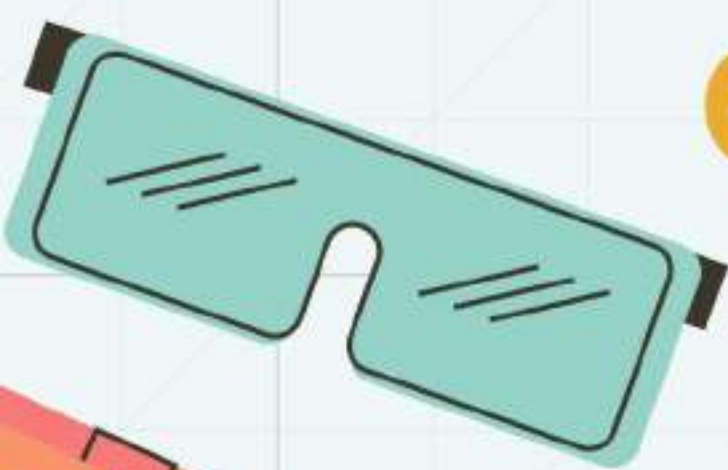
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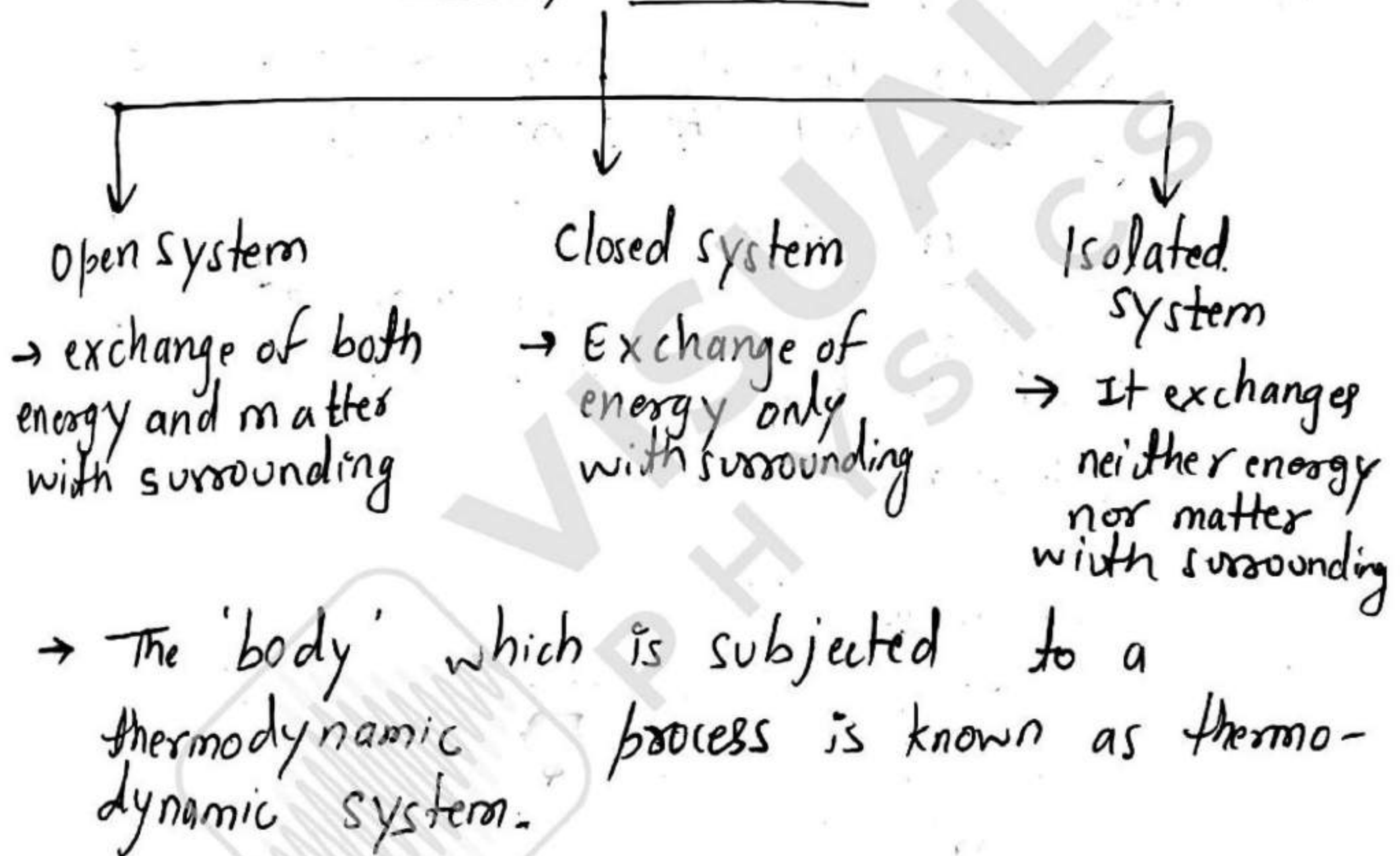
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Thermodynamics

→ Branch of science which deals with exchange of heat energy between bodies and conversion of the heat energy into mechanical energy & vice versa.

Thermodynamic System



Thermodynamic Variables and Equation of state:

A thermodynamic system is described by

Specifying

- pressure
- volume
- temperature
- Internal energy & number of moles.

→ Relationship between thermodynamics variables is called equation of states.

Thermodynamic Equilibrium:

→ when variables attain a steady value i.e. they are independent of time.

(i) Mechanical equilibrium:

No unbalanced force between the system and its surrounding.

(ii) Thermal equilibrium:

There is a uniform temperature in all parts of system and same that of surrounding.

(iii) chemical equilibrium:

This is a uniform chemical composition throughout the system and the surrounding.

Thermodynamic Process:

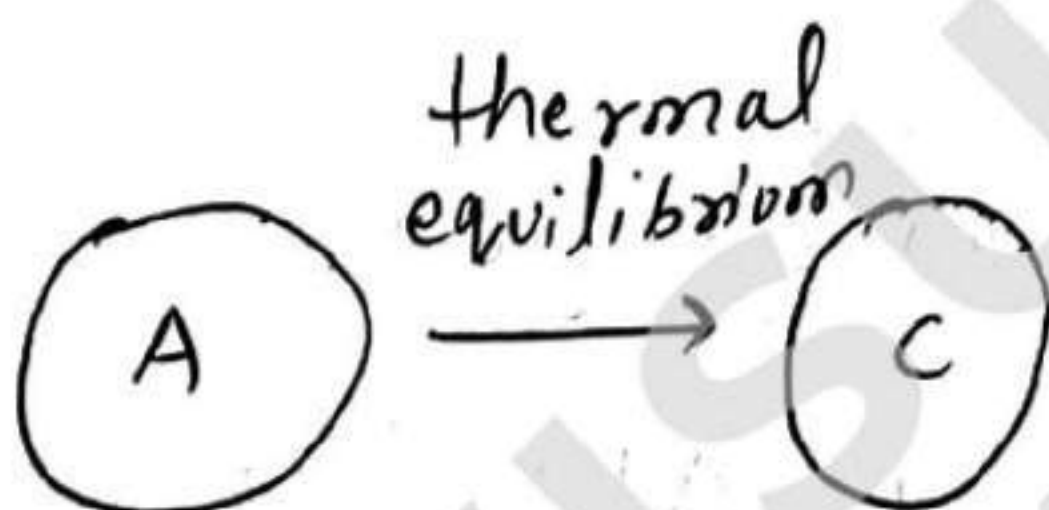
through thermodynamic process state of a system involves change of thermodynamic variables such as pressure, P , volume V and temperature T of system

Some Important processes:

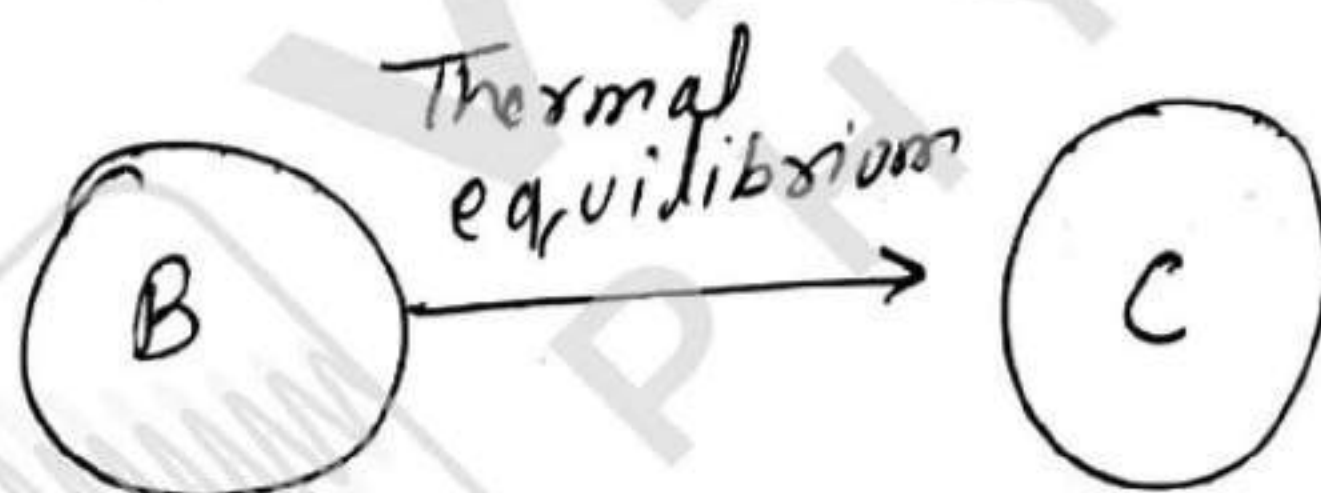
- Isothermal process
- adiabatic process
- Isobaric process
- Isochoric
- Cyclic and non-cyclic process
- reversible & irreversible process.

Zeroth Law of Thermodynamics:

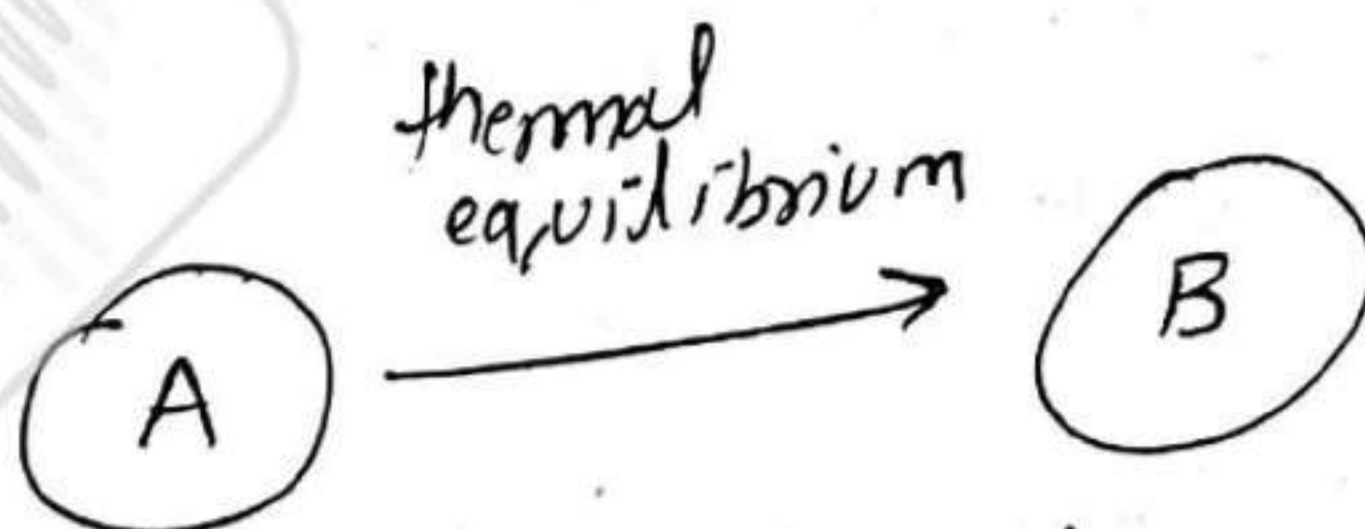
if



&



then



if A & C are in thermal equilibrium

if B & C are in thermal equilibrium

then A & B are in thermal equilibrium also.

First law of thermodynamics:

Internal energy (U):

- Energy contained within the system due to the relative positioning and motion, i.e. due to molecular motion and molecular configuration.
- Sum all the energy possessed inside the system is internal energy

$\Delta \rightarrow$ means change

$$\boxed{\Delta U = \Delta Q + \Delta W} \rightarrow \text{first law of thermodynamics}$$

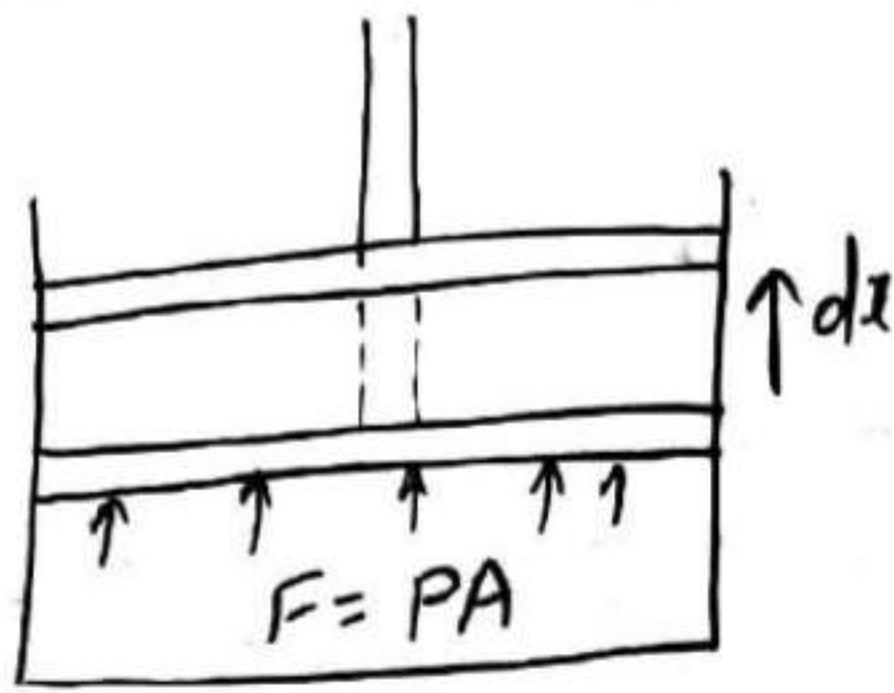
* In Easiest form: Energy of the universe is conserve.

$\Delta Q \rightarrow$ positive $\rightarrow$ Heat given to the system
 $\rightarrow$ negative $\rightarrow$ Heat is extracted from the system

$\Delta W \rightarrow$ positive $\rightarrow$ Work done on the system
 $\rightarrow$ Negative $\rightarrow$ Work done by system

heat and work are path function
means they depend on path itself.

Work done by a gas:



Now small work
 $dW = F dx$

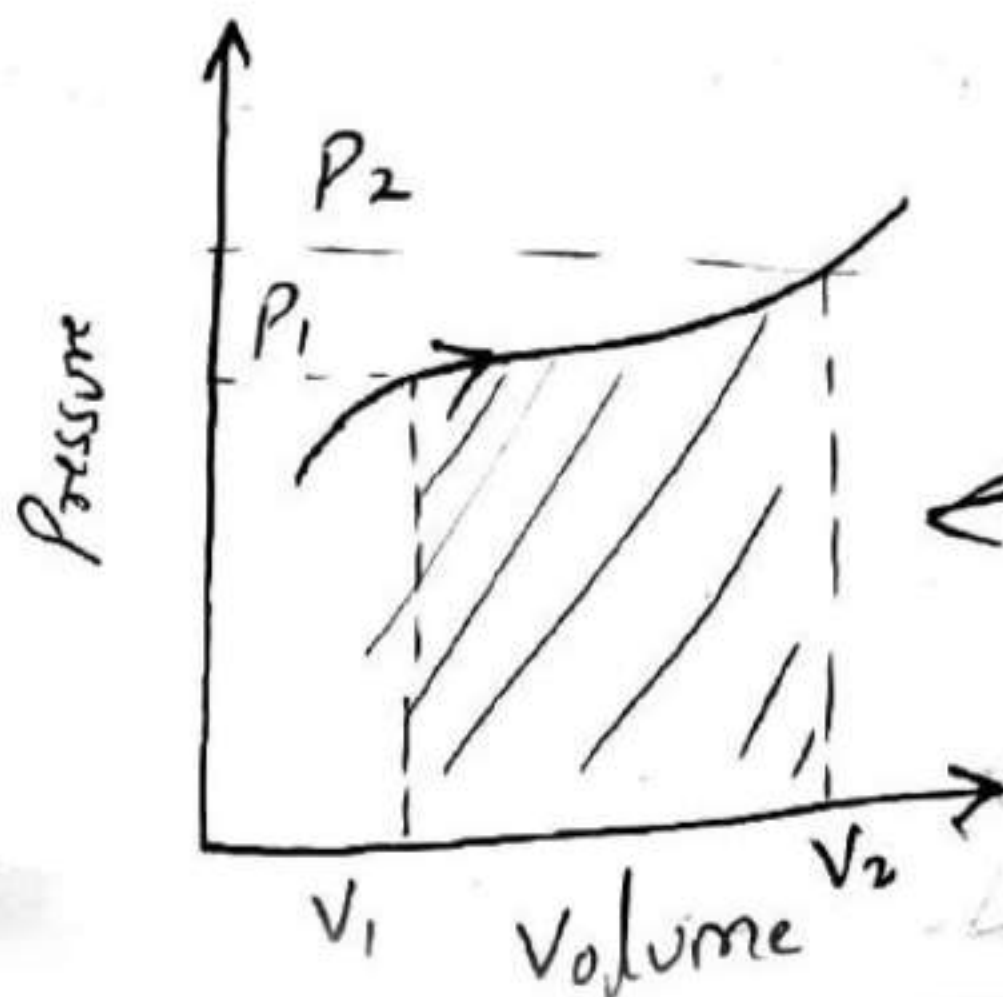
$$\Rightarrow dW = PA dx$$

now total work from one state to state 2

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

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

* Area of Pressure to volume graph will give work



now work from
state 1 to state 2
is shaded area

Important points on Internal Energy (U)

As energy due to molecular motion is called Internal kinetic energy U_k

And energy due to molecular configuration is called Internal potential energy U_p

So,
$$U = U_k + U_p$$

total internal energy

(i) For an ideal gas, $U_p = 0$
& $U_k = \left(\frac{f}{2}\right) \mu RT$ [$\mu \rightarrow$ no. of moles]
 $f \rightarrow$ degree of freedom.

(ii) Now change in internal energy

$$\Delta U = \mu C_v \Delta T$$

as
$$C_v = \frac{f}{2} R$$

(iii) change in internal energy does not depend on the path of process.

(iv) change in internal energy in a cyclic process is always zero.

Thermodynamic properties

Extensive
properties that do not
depend on quantity
of matter.
e.g. - pressure and
temperature

Intensive
properties depends
on mass of system
e.g. - volume,
, energy

Joule's law:

Whenever heat is converted into mechanical work mechanical work is converted into heat, ratio of work done to heat produced remain constant.

i.e. $\frac{W}{Q} = J$ $\rightarrow$ mechanical equivalent

$$J = 4.186 \text{ kJ/kcal}$$

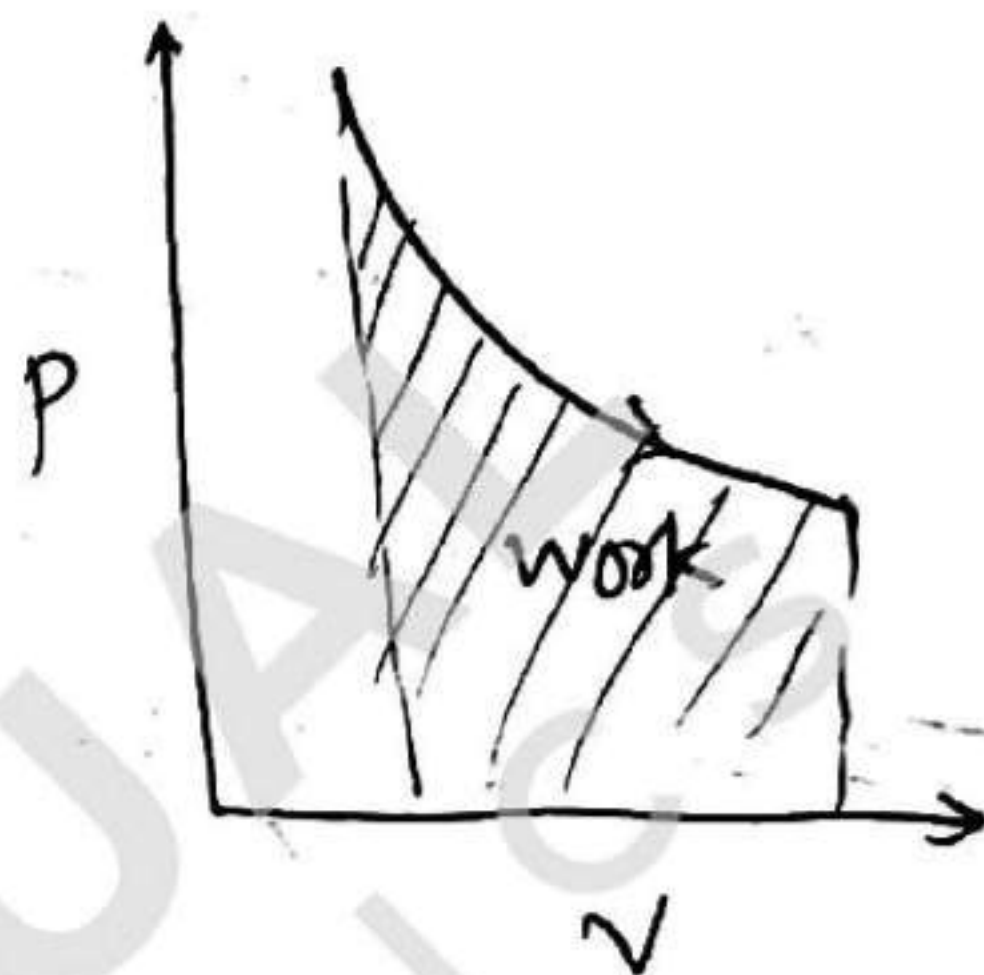
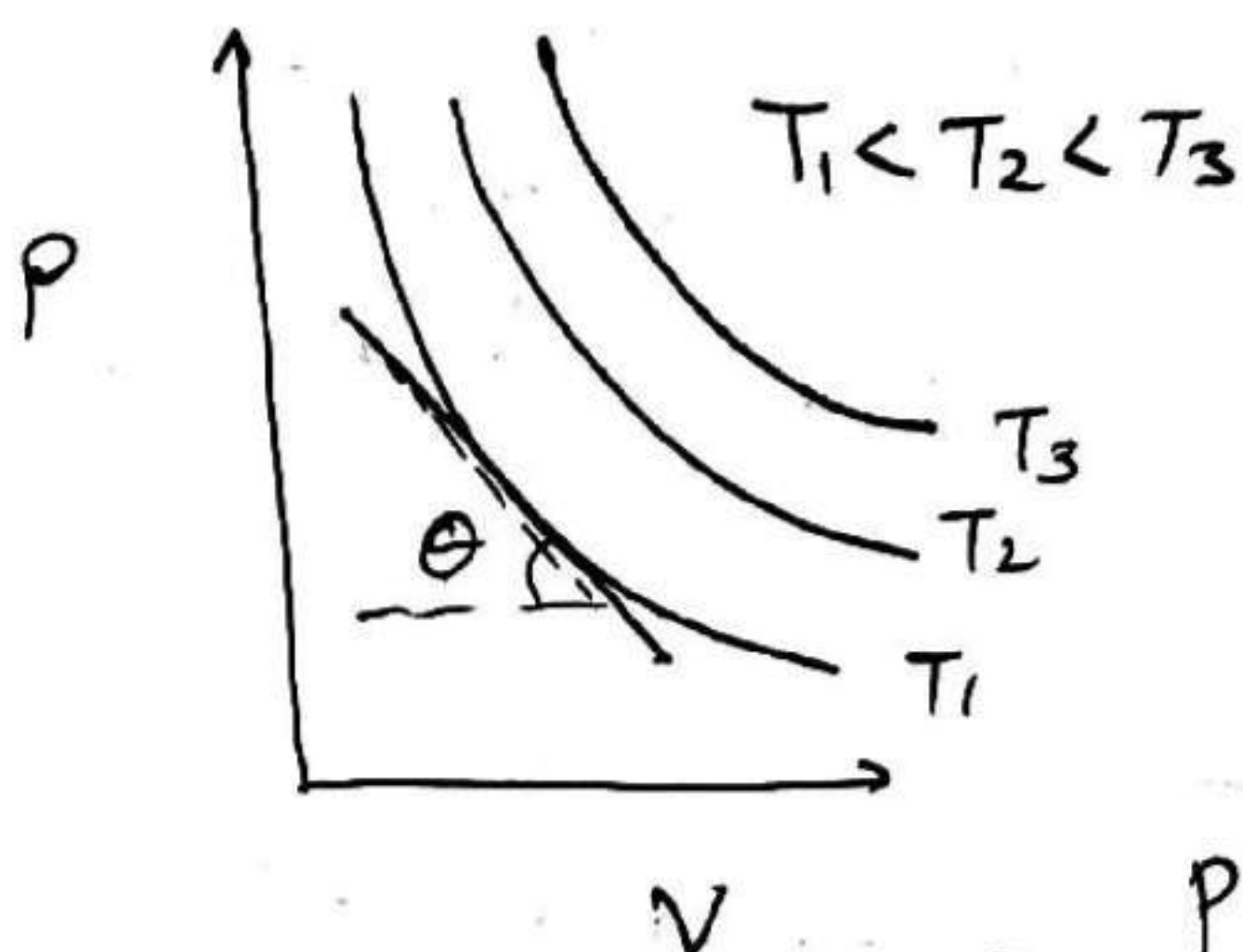
Isothermal process:

$\rightarrow$ if temperature remains constant throughout the process is known as Isothermal.

Equation of state:

$$PV = \text{constant}$$

Melting & Boiling process are example of isothermal process.



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

as $C = \frac{Q}{m\Delta T} \Rightarrow \boxed{C \rightarrow \infty}$

specific heat

work done:

$$W = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{\mu R T}{V} dV$$

$$PV = \mu R T$$

$\mu \rightarrow$ no. of moles (also 'n')

$$W = nRT \ln\left(\frac{V_2}{V_1}\right)$$

as $\Delta U = \Delta Q + \Delta W$

now $\Delta U \propto \Delta T$

hence $\Delta U = 0$

$\Rightarrow \Delta Q = -\Delta W$

heat
given to
system

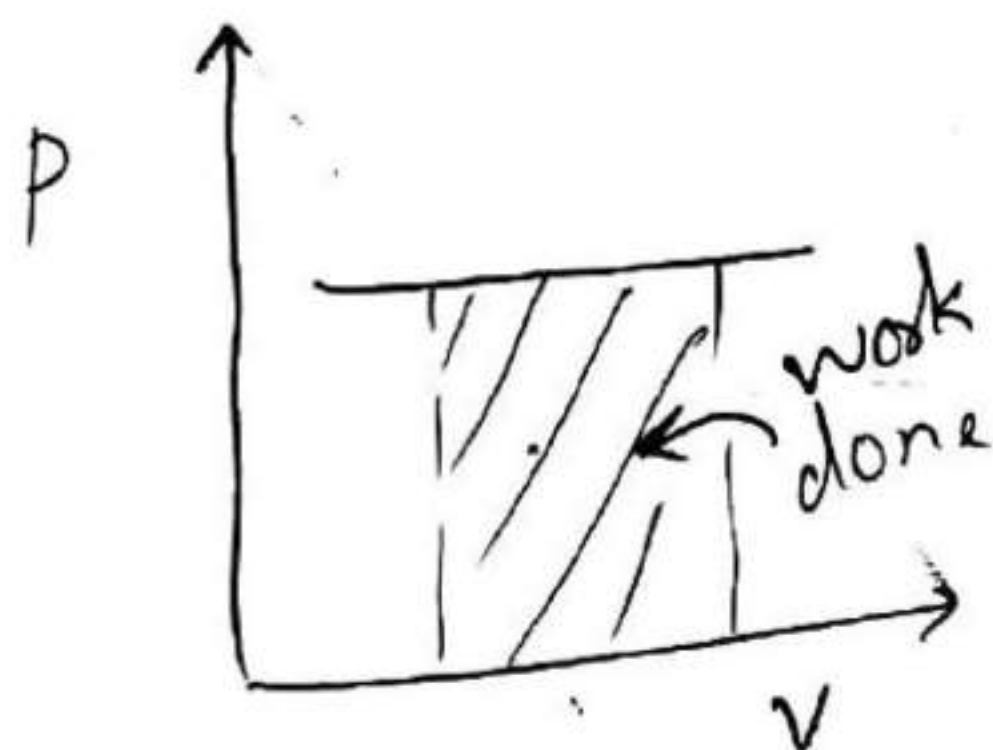
work done
by the system
or vice-versa

Isobaric Process:

Pressure constant throughout the process

As $PV = nRT$

$\Rightarrow V/T = \text{constant}$



Now $C_p = \left(\frac{f}{2} + 1\right) R$

Specific heat
at constant pressure

Work done:

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

$$\boxed{\Delta W = P(V_2 - V_1)}$$

as $\Delta W = \mu R(T_2 - T_1)$

as, $\Delta U = \mu C_v \Delta T = \frac{\mu R}{(\gamma - 1)} \Delta T$

by System

← $\Delta W = \mu R \Delta T$

so, $\Delta Q = \Delta U + \Delta W$

$$= \frac{\mu R}{(\gamma - 1)} \Delta T + \mu R \Delta T$$

$$\boxed{\Delta Q = \mu C_p \Delta T}$$

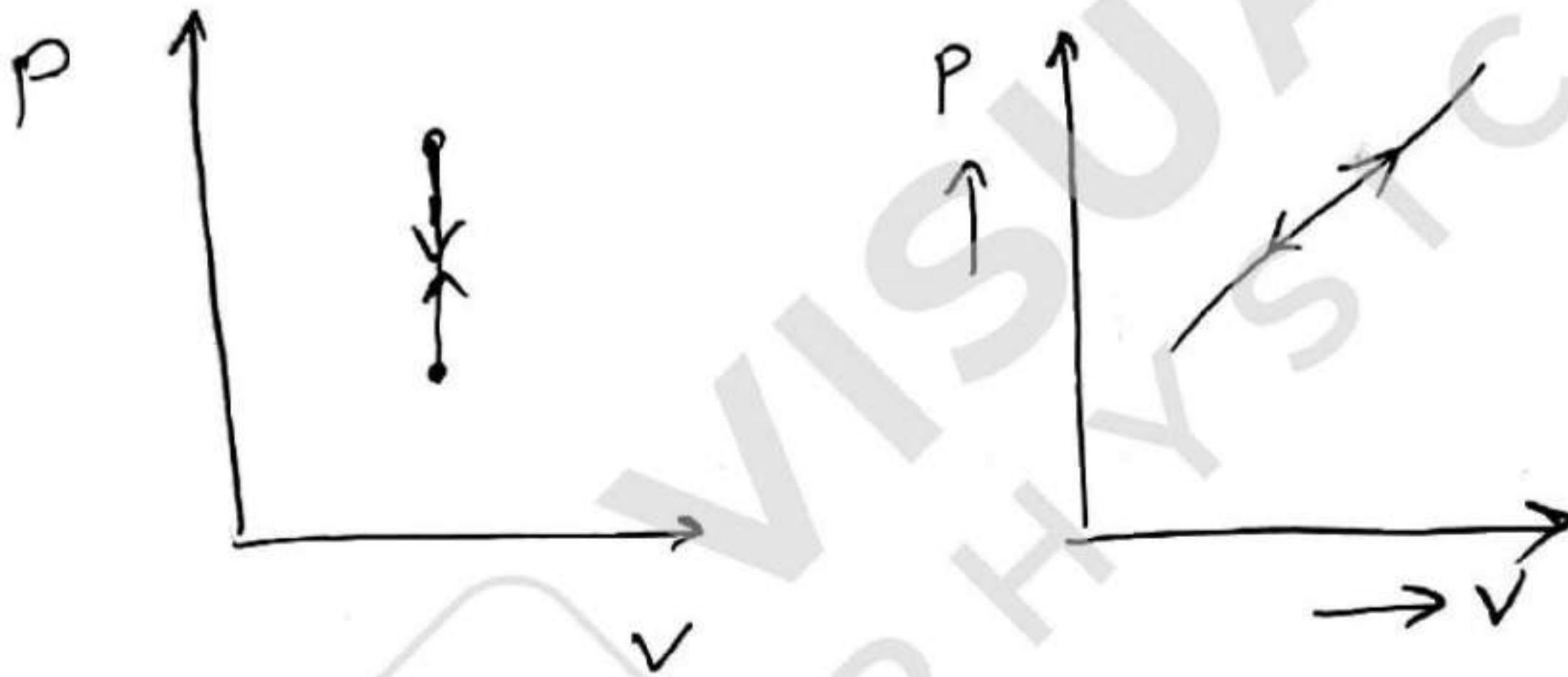
Isochoric or Isometric process:

→ process in which volume remains constant.

$$P \propto T$$

$$\text{as } PV = nRT$$

$$\Rightarrow \boxed{P \propto T}$$



So for specific heat:

$$C_v = (f/2) R$$

specific
heat at constant
volume.

Now for constant volume

$$\boxed{\Delta W = 0} \text{ as } \Delta W \propto \Delta V$$

$$\Delta Q = \Delta U$$

$$\Delta Q = \mu C_v \Delta T$$

$$\boxed{\Delta Q = \frac{\mu R}{\gamma - 1} \Delta T}$$

Adiabatic process:

→ process in which no exchange of heat take place between system and surrounding

as $\Delta U + \Delta W = 0$

now $dU = \mu C_v dT$ & $dW = PdV$

$$\mu C_v dT + PdV = 0$$

$$PV = \mu RT, \quad PdV + VdP = \mu R dT$$

$$\frac{\mu C_v (PdV + VdP)}{\mu R} + PdV = 0$$

$$\frac{PdV + VdP}{\gamma - 1} + PdV = 0$$

$$C_v = \frac{R}{(\gamma - 1)}$$

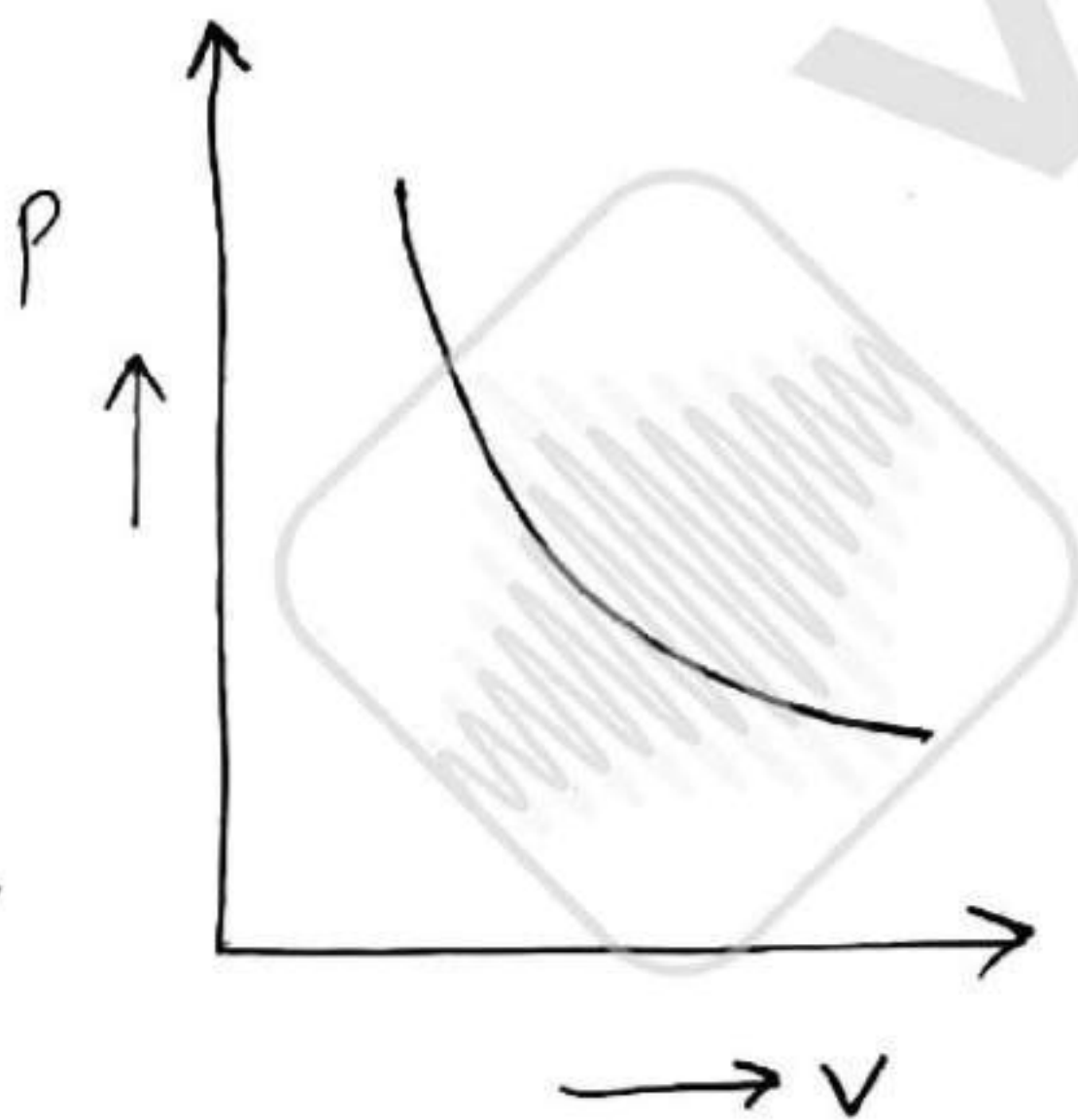
$$\gamma P dV + V dP = 0$$

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

$$\text{from } PV = \mu RT$$

$$TV^{\gamma-1} = \text{Constant}$$

$$\text{And also } \frac{T^\gamma}{P^{\gamma-1}} = \text{Constant}$$



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

Work done:

$$W = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{k}{V^\gamma} dV$$

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

as $P = \frac{k}{V^\gamma}$

$$W = \frac{-nR\Delta T}{(\gamma-1)}$$

$$\rightarrow W = \frac{P_1 V_1 - P_2 V_2}{(\gamma-1)}$$

★ Free expansion is an adiabatic process

★ Sudden compression is an adiabatic process

Now as for free expansion:

$$\Delta U = \Delta W + \Delta Q$$

$$\Delta Q \rightarrow 0 \quad \& \quad \Delta W \rightarrow 0$$

no exchange of heat

no work is done

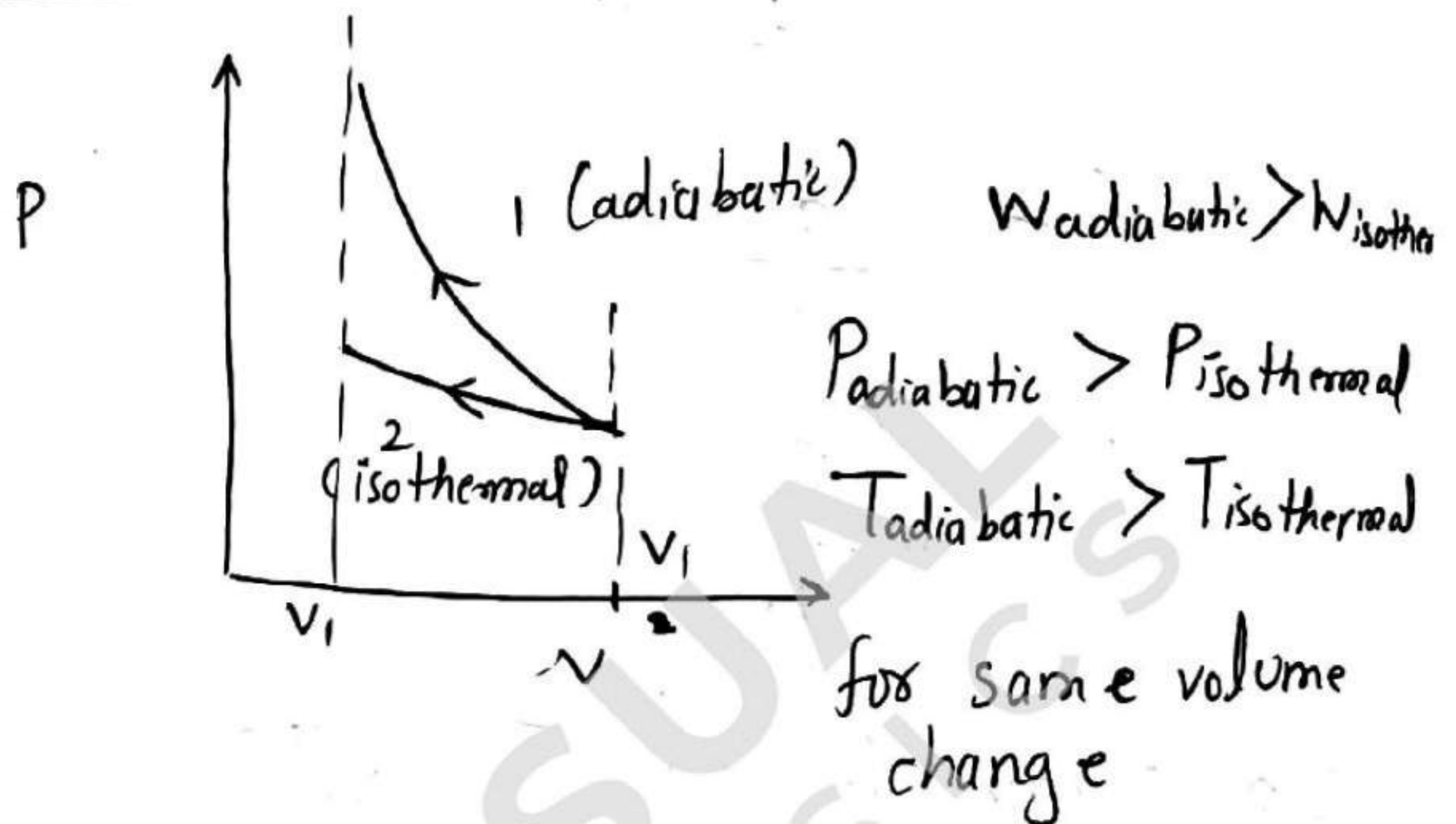
$$\rightarrow \Delta U = 0$$

$$\text{or } U_f = U_i$$

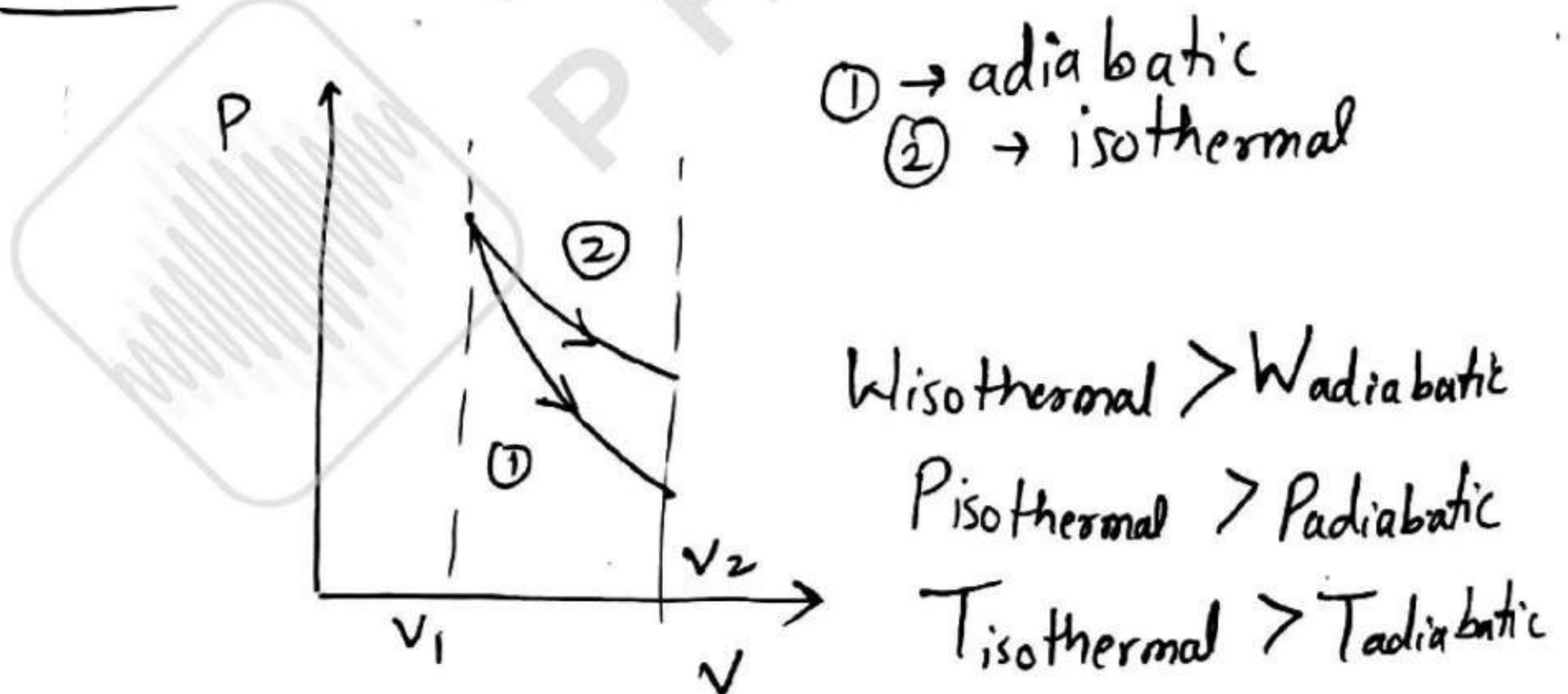
★ this implies no change in Temperature as well.

Comparison between Isothermal and adiabatic

Compression:



Expansion:



Polytropic process

$$PV^\gamma = \text{constant} \quad (\text{adiabatic})$$

In general process follows:

$$PV^n = \text{constant}$$

$$n \neq 1 \text{ or } \gamma$$

Work done:

$$W = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{k}{V^n} dV$$

$$W = \frac{P_1 V_1 - P_2 V_2}{(n-1)}$$

$$W = \frac{-R(\mu \Delta T)}{(n-1)}$$

$$\boxed{W = -\frac{\mu R \Delta T}{(n-1)}}$$

Specific heat:

$$Q = \Delta U + W$$

Now

for $\mu = 1$

$$C \Delta T = C_v \Delta T - \frac{R \Delta T}{(n-1)}$$

$$\left[C = C_v - \frac{R}{(n-1)} = \frac{R}{(\gamma-1)} - \frac{R}{(n-1)} \right]$$

Reversible and Irreversible process:

Reversible process → which can be reversed in such a way that all changes occurring in the direct process are exactly repeated in opposite order with no change in universe.

For this:

- No dissipative forces like friction, viscosity etc
- The process should take place infinitely slow
- Temperature difference between system and surrounding should not differ appreciably.

Irreversible process:

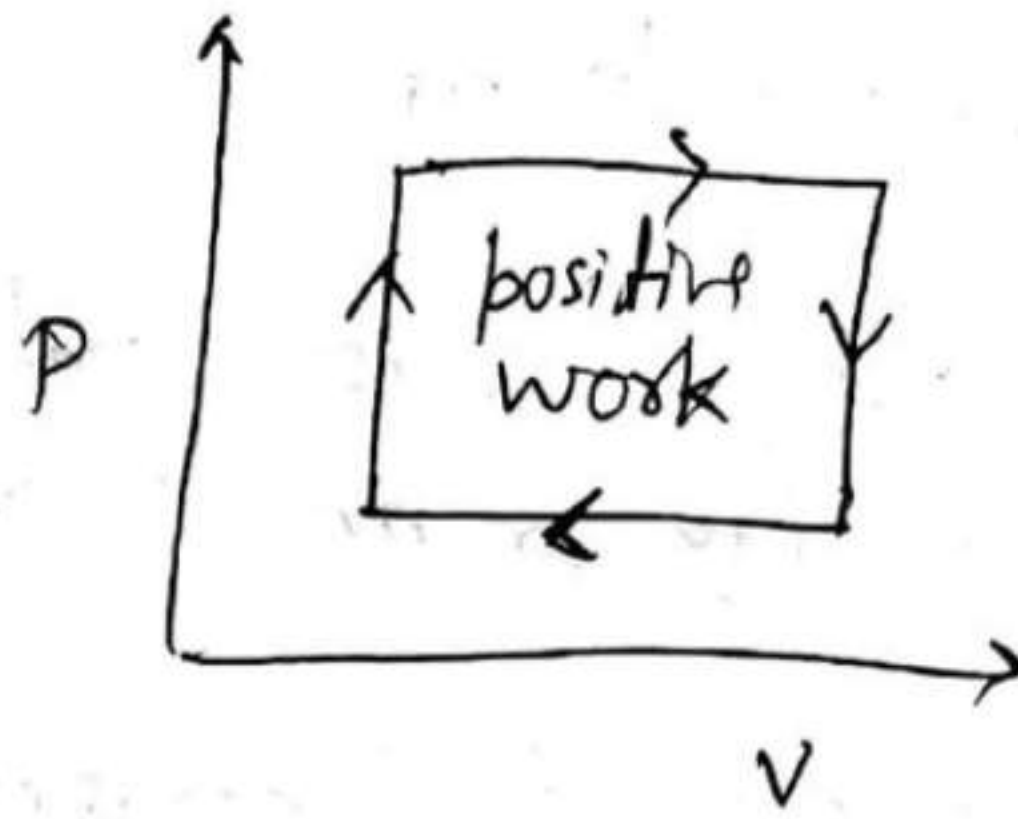
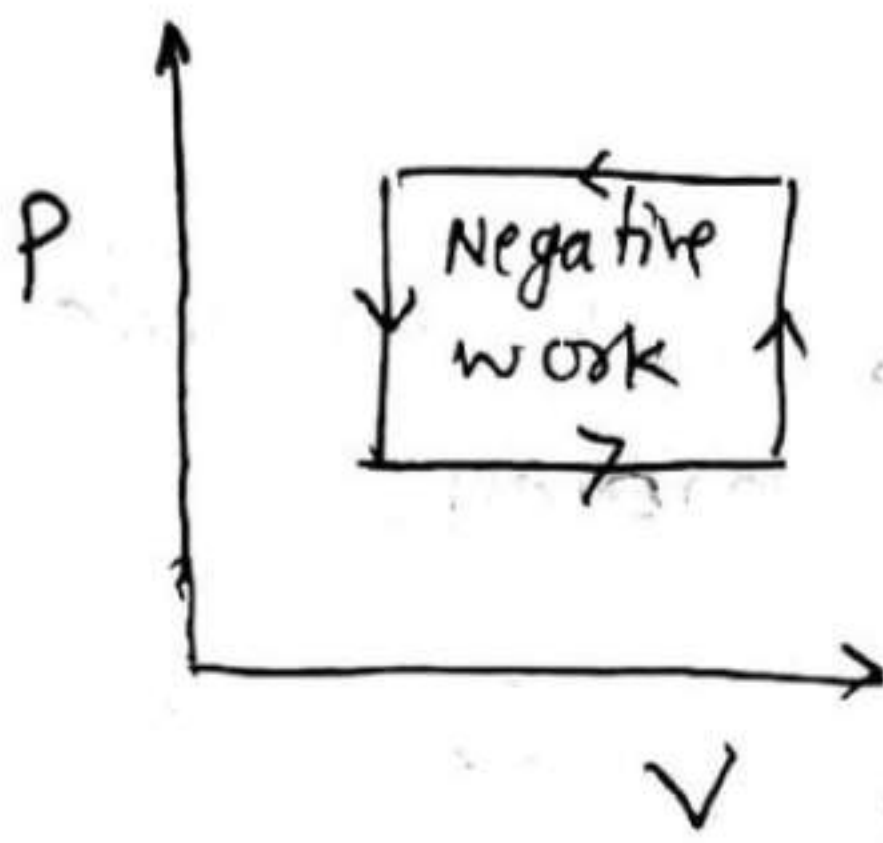
→ Any process which is not reversible exactly is an irreversible process.

- * All practical processes such as free expansion, Joule-Thomson expansion, electrical heating of a wire are also irreversible.

Cyclic and Non-Cyclic process:

→ cyclic process consists of a series of changes that returns the system back to its initial state.

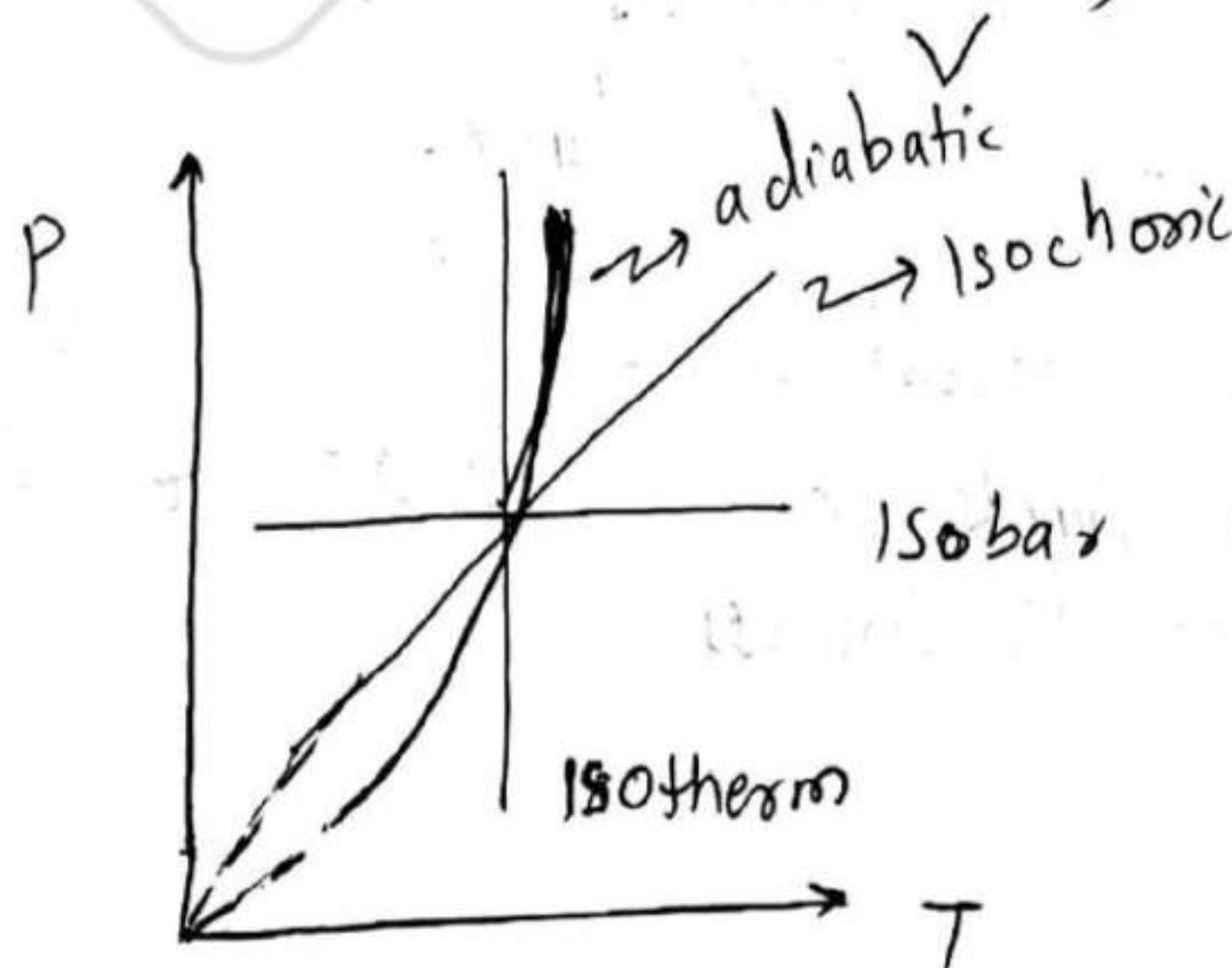
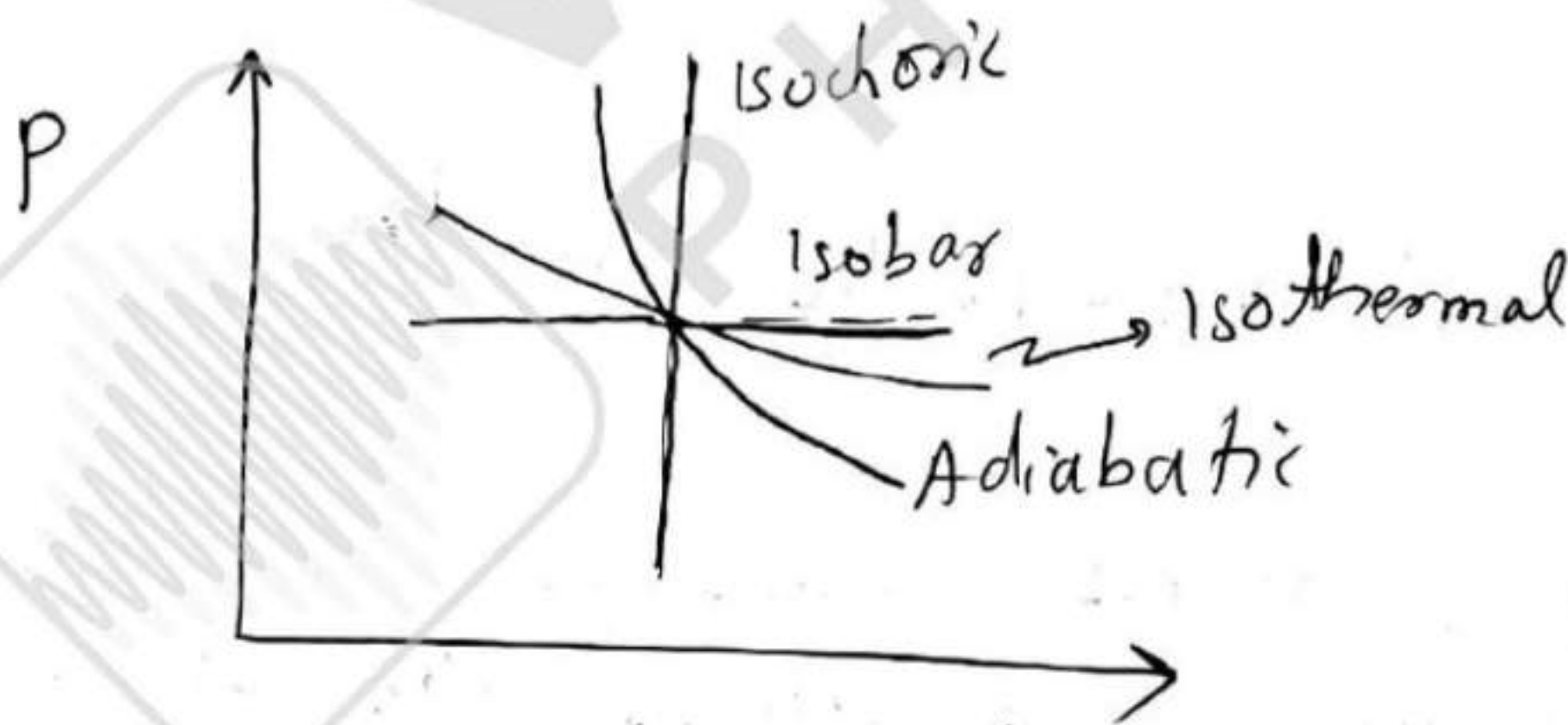
→ Series of process which do not bring system back to initial state is non-cyclic process.

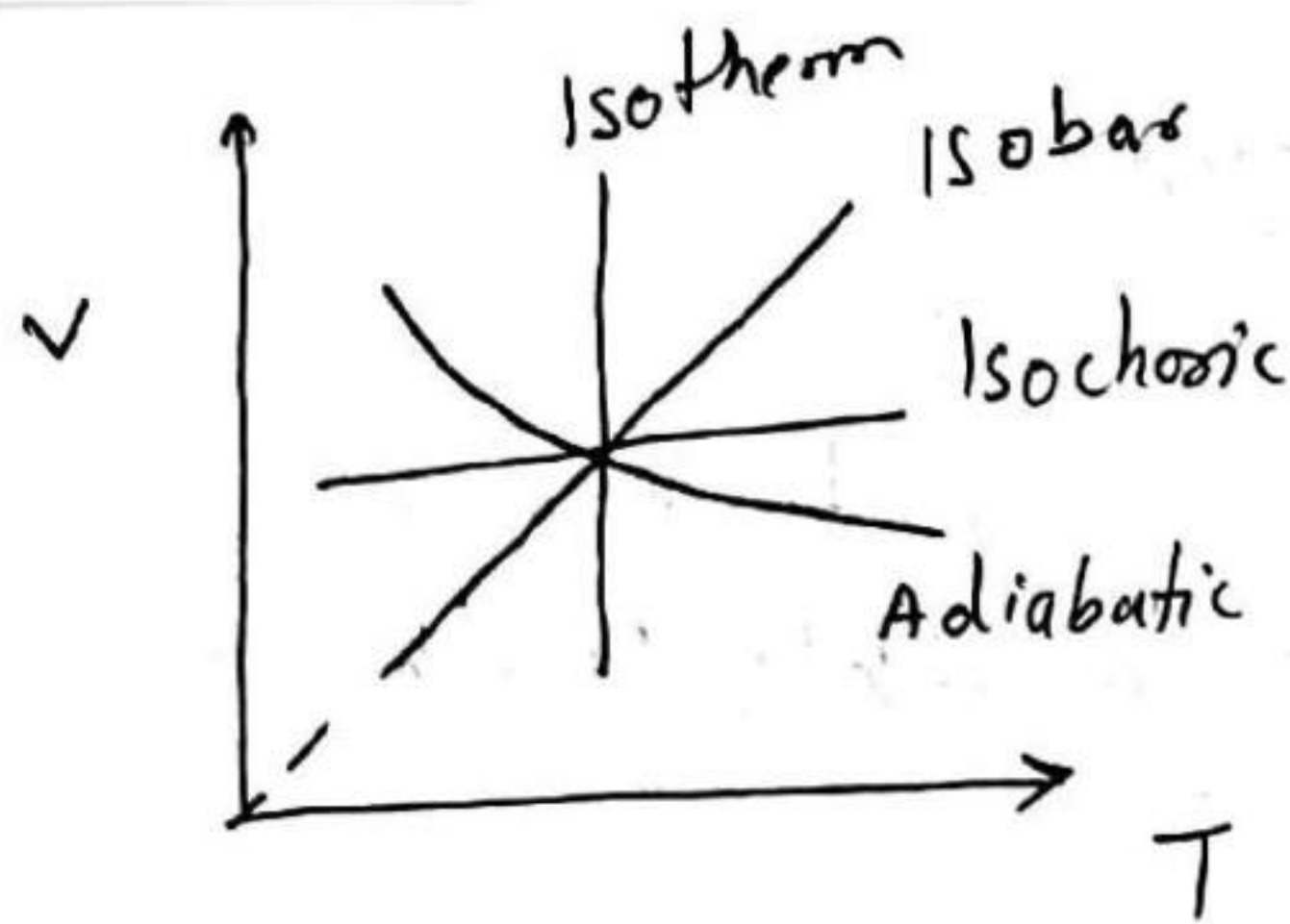


efficiency of a cyclic process :

$$\eta = \frac{\text{Work done per cycle}}{\text{Gross heat supplied per cycle}}$$

General representation of various processes:





Entropy & 2nd law:

Entropy (S): It is an extensive property of a thermodynamic system, it quantifies the number of microscopic configurations that are consistent with macroscopic quantities that characterize the system.

→ In more common terms the randomness or measure of randomness of the system and/or surrounding.

* Second law of thermodynamics states that state of entropy of entire universe (system + surrounding) as isolated system, will always increase over time.

→ It also states $\Delta S \rightarrow$ never be zero
change of entropy

Kelvin - Planck statement:

No process is possible whose sole result is the absorption of heat from a reservoir and the complete conversion of heat into work.

Clausius statement:

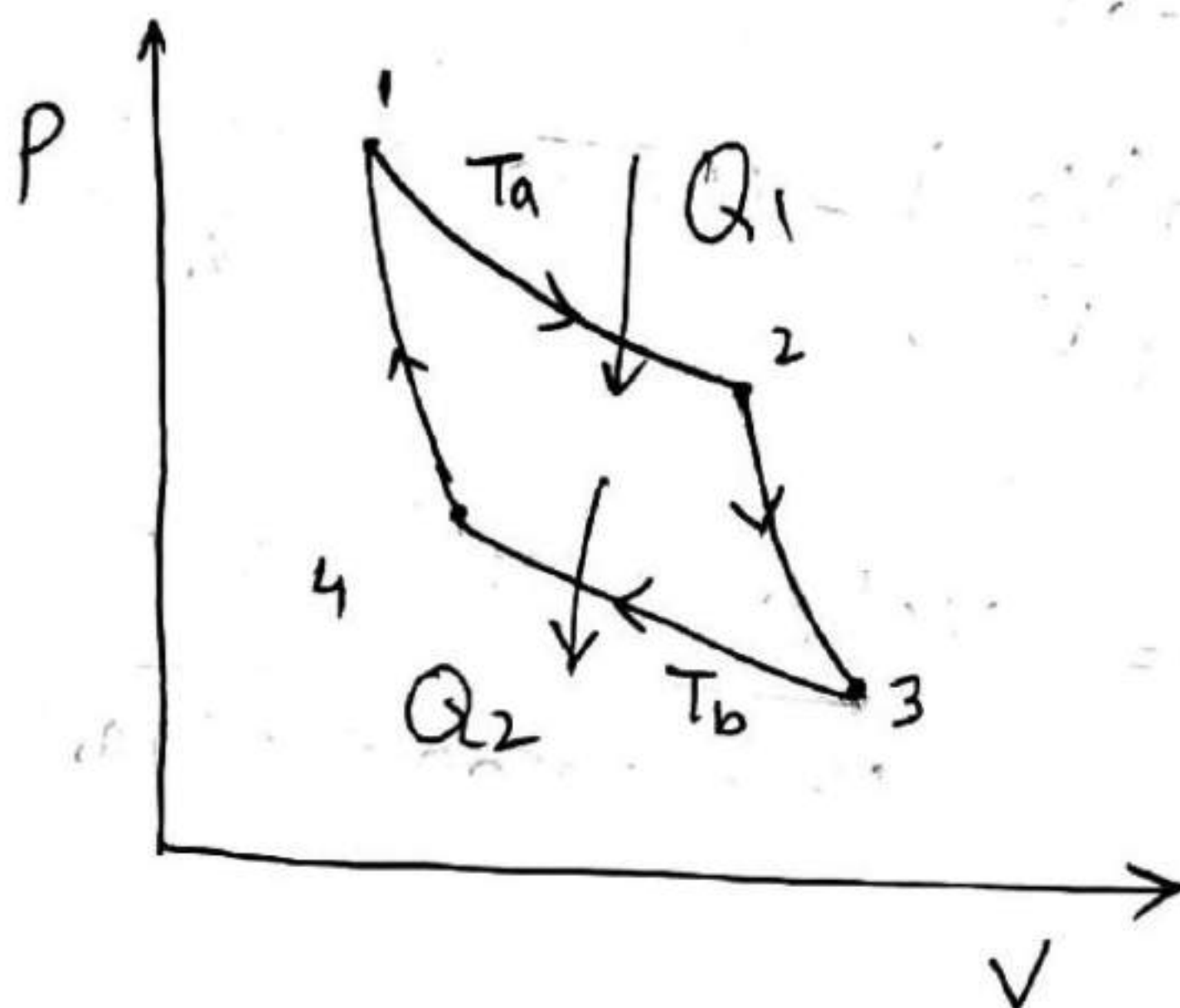
No process is possible whose result is the transfer of heat from a colder object to a hotter object.

- ★ It can be proved that the two statements above are completely equivalent.

Carnot Theorem:

Any system working between two given temperatures T_1 (hot reservoir) and T_2 (cold reservoir) can never have efficiency more than Carnot engine working between same reservoirs.

Carnot cycle:



1 → 2 isothermal expansion

2 → 3 adiabatic expansion

3 → 4 isothermal compression

4 → 1 adiabatic compression

$$T_a = T_1 = T_2$$

$$T_b = T_3 = T_4$$

now 1 → 2 Isothermal process

$$Q_1 = W_{1 \rightarrow 2} = \mu R T_a \ln \left(\frac{V_2}{V_1} \right)$$

2 → 3 adiabatic process

$$W_{2 \rightarrow 3} = \frac{\mu R}{\gamma - 1} (T_a - T_b)$$

3 → 4 isothermal process

$$W_{3 \rightarrow 4} = -\mu R T_b \ln \left(\frac{V_3}{V_4} \right) = Q_2$$

4 → 1 adiabatic process

$$W_{4 \rightarrow 1} = \frac{-\mu R}{\gamma - 1} (T_a - T_b)$$

Now net work

$$W = W_{1 \rightarrow 2} + W_{2 \rightarrow 3} + W_{3 \rightarrow 4} + W_{4 \rightarrow 1}$$

$$W = \mu R T_1 \ln\left(\frac{V_2}{V_1}\right) - \mu R T_2 \ln\left(\frac{V_3}{V_4}\right)$$

$$\text{Net efficiency} = \frac{\text{Net workdone by gas}}{\text{Heat absorbed by gas}}$$

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

$$\eta = 1 - \frac{Q_2}{Q_1}$$

$$\eta = 1 - \frac{\mu R T_2 \ln\left(\frac{V_3}{V_4}\right)}{\mu R T_1 \ln\left(\frac{V_2}{V_1}\right)}$$

as,

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

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

Similarly for the process $4 \rightarrow 1$

$$\frac{V_1}{V_2} = \left(\frac{T_2}{T_1} \right)^{1/\gamma - 1}$$

$$\text{So, } \eta = 1 - \frac{T_2}{T_1} \frac{\ln \left[\left(\frac{T_2}{T_1} \right)^{1/\gamma - 1} \right]}{\ln \left[\left(\frac{T_2}{T_1} \right)^{1/\gamma - 1} \right]}$$

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

