

Thermodynamics

Thermodynamics

It is the branch of Physics which deals with the transformation of heat into other forms of energy & vice-versa.

A few definitions

(i) System - An assembly of extremely large no. of particles having a certain value of pressure, volume & temp.
eg → a large collection of gas molecules.

(ii) Thermodynamic variables - The variables which determine the thermodynamic behaviour of a system.
eg → P, V, T , internal energy (U), entropy (S)

(iii) Thermal equilibrium

A thermodynamical system is said to be in thermal equilibrium when macroscopic variables like pressure, volume, temp. that characterise the system do not change with time.

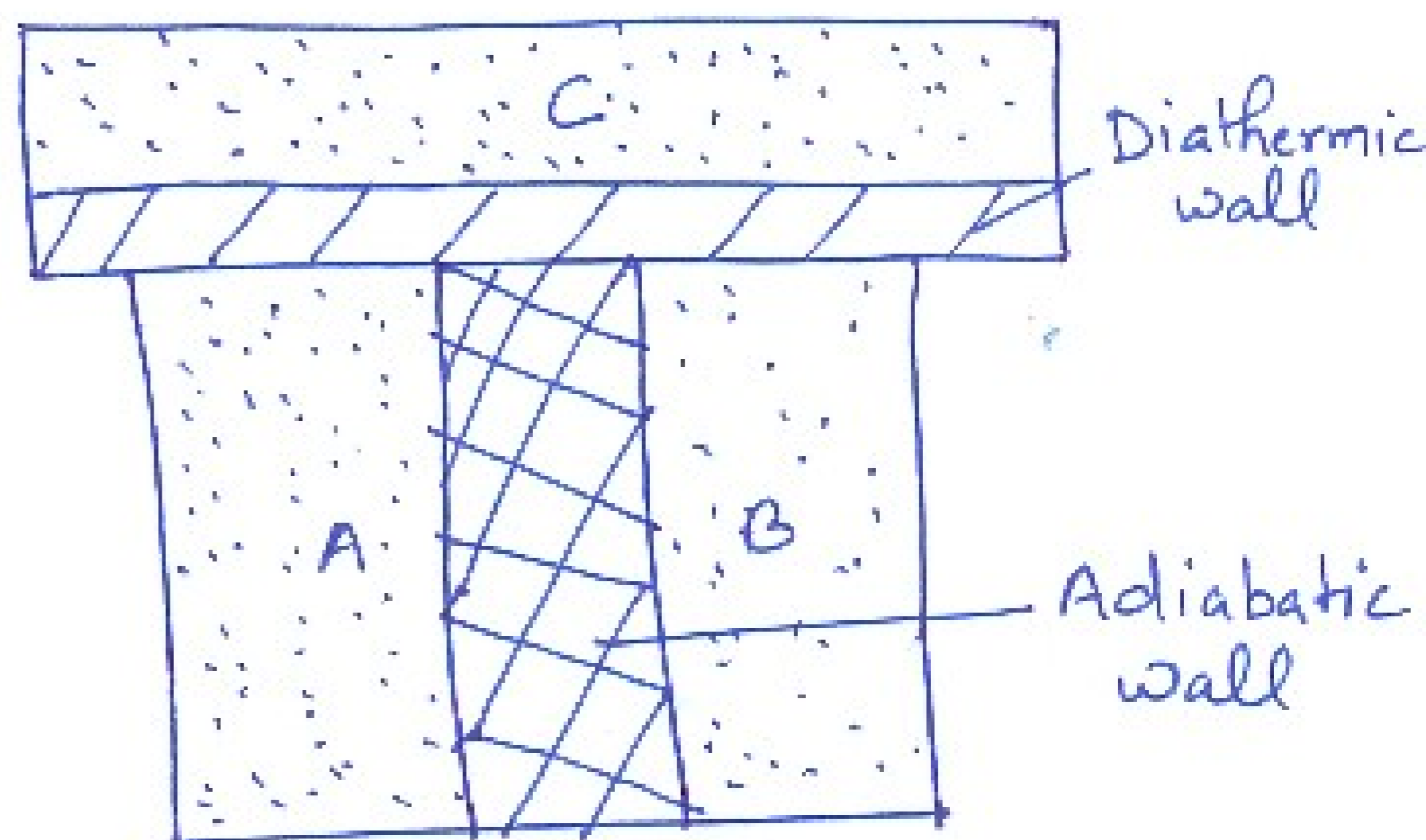
Zeroth law of Thermodynamics

If 2 systems A & B are in thermal equilibrium with a third system C, then A & B must be in thermal equilibrium with each other.

→ A & B separated by adiabatic wall so no heat transfer betⁿ them.

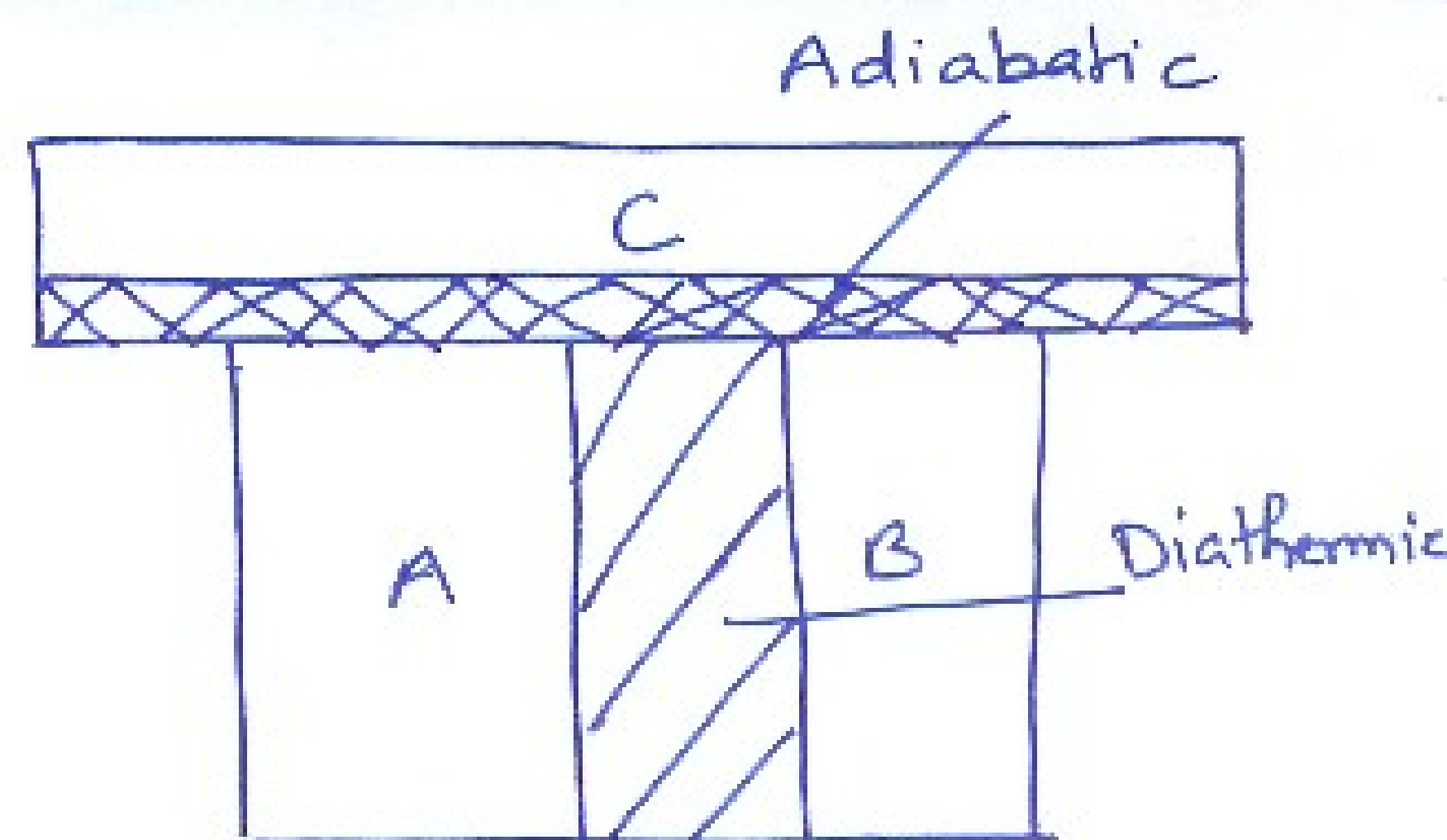
→ A & B both in contact with C through diathermic wall which allows transfer of heat.

→ The macroscopic variables of A & B will change until both A & B come to thermal equilibrium with C.



- Now, change the wall betⁿ A & B from adiabatic to diathermic & wall betⁿ A & C & B & C to adiabatic

- A & B show no change, i.e. they are in thermal equilibrium with each other.



* The physical quantity that determines whether or not a given system is in thermal equilibrium with another system is called temperature.

Quasi-static process

- A process which is infinitely slow is called quasi-static process.
- The system undergoes changes in its variables like P, V, T so slowly that it continues to be in thermal equilibrium with its surrounding throughout.

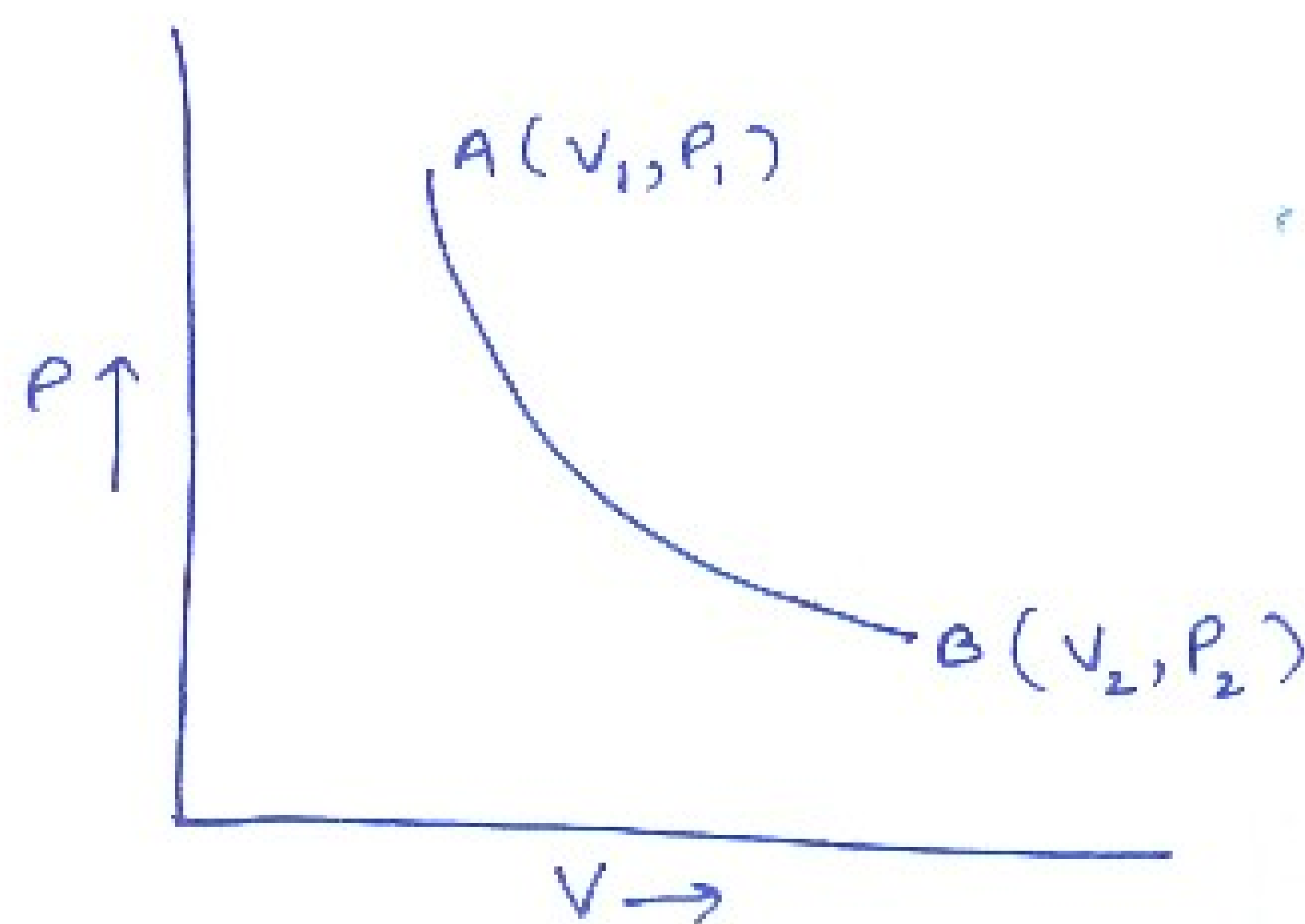
Thermodynamic processes

A thermodynamical process is said to take place when some changes occur in the state of a thermodynamic system.

| S.No. | Process | Feature |
|-------|------------|--|
| 1. | Isothermal | Tem. constant |
| 2. | Adiabatic | No heat flow bet ⁿ system & surroundy |
| 3. | Isobaric | Pressure constant |
| 4. | Isochoric | Volume constant |

Indicator Diagram

Represents variation betⁿ Volume & pressure of a system.



Isothermal change

- A change in pressure & volume of a gas without any change in its tem. is called isothermal change.
- There is a free exchange of heat betⁿ the gas & its surroundings.

eg - Melting, boiling

- For isothermal change $PV = \text{const.}$

Essential conditions for isothermal change

- ① The walls of the container must be perfectly conducting, to allow free exchange of heat between the gas & its surrounding.
- ② The process of compression or expansion should be slow so as to provide time for exchange of heat.

Adiabatic Change

- A change in pressure & volume of a gas when no heat is allowed to enter or escape from the gas is called an adiabatic change.

- Tem. also changes

eg - 1. sudden bursting of tube of bicycle tyre.
2. propagation of sound waves.

- For adiabatic change $PV^\gamma = K$

$$\gamma = \frac{C_p}{C_v}$$

Essential conditions

- ① Walls of the container must be perfectly non-conducting
- ② The process of compression or expansion should be sudden so that there is no time for exchange of heat.

Work done in an isothermal expansion

Consider 1 gm mole of an ideal gas enclosed in a cylinder with perfectly conducting walls & fitted with a perfectly frictionless & conducting piston.

Let P_1, V_1, T - initial pressure, volume & tem. of gas.

Let the gas expands to volume V_2 , when pressure reduces to P_2 & tem. remains constant T .

Let the pressure of the gas remains P during expansion at any instant.

If A is the area of cross-section of piston, then force exerted by the gas on the piston is

$$F = P \times A$$

Small work done during expansion

$$\begin{aligned} dW &= F dx \\ &= P A dx \\ &= P dV \end{aligned}$$

Total work done by the gas in expansion is

$$\begin{aligned} W &= \int_{V_1}^{V_2} P dV \\ &= \int_{V_1}^{V_2} \frac{RT}{V} dV \end{aligned}$$

$$\begin{aligned} PV &= RT \\ P &= \frac{RT}{V} \end{aligned}$$

$$= RT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$= RT [\log_e V]_{V_1}^{V_2}$$

$$= RT [\log_e V_2 - \log_e V_1]$$

$$= RT \log_e \frac{V_2}{V_1}$$

$$W = 2.303 RT \log_{10} \frac{V_2}{V_1}$$

Work done in an adiabatic expansion

Consider 1 gram mole of an ideal gas enclosed in a cylinder with perfectly non conducting walls & fitted with a perfectly frictionless, non conducting piston.

Let P_1, V_1, T_1 be the initial pressure, volume & tem. of gas.

force exerted by the gas on the piston is

$$F = P \times A$$

Small work done during expansion is

$$\begin{aligned} dW &= F dx \\ &= P A dx \\ &= P dV \end{aligned}$$

Total work done by the gas from volume V_1 to V_2 is

$$\begin{aligned} W &= \int_{V_1}^{V_2} P dV \\ &= \int_{V_1}^{V_2} K V^{-\gamma} dV \quad | \quad P V^\gamma = K \\ &= K \left[\frac{V^{1-\gamma}}{1-\gamma} \right]_{V_1}^{V_2} \\ &= \frac{K}{(1-\gamma)} [V_2^{1-\gamma} - V_1^{1-\gamma}] \\ &= \frac{1}{(1-\gamma)} [K V_2^{1-\gamma} - K V_1^{1-\gamma}] \end{aligned}$$

for adiabatic changes

$$P_2 V_2^\gamma = P_1 V_1^\gamma = K$$

$$\therefore W = \frac{1}{(1-\gamma)} [P_2 V_2^\gamma V_2^{1-\gamma} - P_1 V_1^\gamma V_1^{1-\gamma}]$$

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

If T_2 is the final temp. of the gas in adiabatic expansion, then from standard gas eqⁿ

$$P_1 V_1 = RT_1 \quad \& \quad P_2 V_2 = RT_2$$

$$\therefore W = \frac{1}{(1-\gamma)} (RT_2 - RT_1)$$

$$W = \frac{R(T_2 - T_1)}{(1-\gamma)}$$

Internal Energy (U)

It is the total energy possessed by the system due to molecular motion & molecular configuration.

$$U = U_k + U_p$$

U_k - energy due to molecular motion called internal K.E.
 U_p - " " " " configuration " " P.E.

for ideal gas

intermolecular force = 0 \rightarrow no work done $\rightarrow U_p = 0$

$\therefore U$ consists only of U_k which depends only on temp. of the gas.

for real gas

- intermolecular force not negligible

$$U = U_k + U_p$$

- U depends on both temp. & volume of gas.

First law of thermodynamics

If an amount of heat dQ is added to a system, a part of it may increase its internal energy by an amount dU , while the remaining part may be used up as external work done (dW) by the system.

$$dQ = dU + dW$$

Sign conventions

- ① Work done by the system = +ve (expansion)
" " " on " " = -ve (compression)
- ② Heat supplied to the system, $dQ = +ve$
" drawn from " " , $dQ = -ve$
- ③ Tem. of gas increases, its internal energy increases, $dU = +ve$
" " " decreases " " " decrease = -ve

Applications of First law of thermodynamics

(a) Isothermal process

If the system is an ideal gas, $dU = 0$ as tem. is constant in an isothermal process.

$$dQ = dU + dW$$

$$\boxed{dQ = dW}$$

i.e. Heat supplied in an isothermal process is used entirely to do work against the external surrounding.

(b) Adiabatic process ($dQ = 0$)

$$dQ = dU + dW$$

$$0 = dU + dW$$

$$\boxed{dU = -dW}$$

When gas expands, $dW = +ve$, so $dU = -ve$, gas cools down
" " compresses, " = -ve, " = +ve " heats

(c) Isochoric process (V const.)

$$dW = P dV = 0$$

$$\therefore \boxed{dQ = dU}$$

If heat is absorbed by a system at constant volume, its internal energy increases by the same amount.

(d) Melting process

Let m - mass of solid
 L - latent heat of solid

Amount of heat absorbed during melting, $dQ = mL$

When a substance melts, the change in its volume is very small & negligible

$$\therefore dW = PdV = 0$$

Now, $dQ = dU + dW$

$$\boxed{dU = mL}$$

(e) Boiling process

Let m - mass of liquid at its b.pt.

P - const. pressure at which boiling occurs

V_1 - volume of liquid

V_2 - " " " in vapour form

L - latent heat of vaporisation of the liquid

Work done in expansion, $dW = PdV = P(V_2 - V_1)$

Heat absorbed by liquid, $dQ = mL$

$$dQ = dU + dW$$

$$mL = dU + P(V_2 - V_1)$$

$$\boxed{dU = mL - P(V_2 - V_1)}$$

(f) Relation betⁿ C_p & C_v of a gas (Mayer's formula)

Consider 1 gram mole of an ideal gas enclosed in a cylinder with frictionless piston.

Let P, V, T be the initial pressure, volume & tem. of gas.

Let the gas be heated at const. volume through a small range of tem. dT .

\therefore Amount of heat supplied to gas, $dQ = C_v \cdot 1 \cdot dT$

As volume remains constant, $dV = 0$ & so, $dW = 0$

$$dQ = dU + dW$$

$$dU = C_v dT$$

Let the gas be heated at const. pressure through the same range of tem. dT , when its volume decreases by dV .

Amount of heat supplied to gas, $dQ' = C_p \cdot 1 \cdot dT$

$$dW' = PdV$$

Now, $dQ' = dU' + dW'$

$$C_p dT = dU' + PdV \quad \text{--- (1)}$$

As rise in tem. of the gas in the 2 cases is same so, increase in its internal energy must be same

$$dU' = dU$$

So, eqⁿ (1) becomes

$$C_p dT = C_v dT + PdV$$

$$(C_p - C_v) dT = PdV \quad \text{--- (2)}$$

Now, $PV = RT$

$$PdV = R dT$$

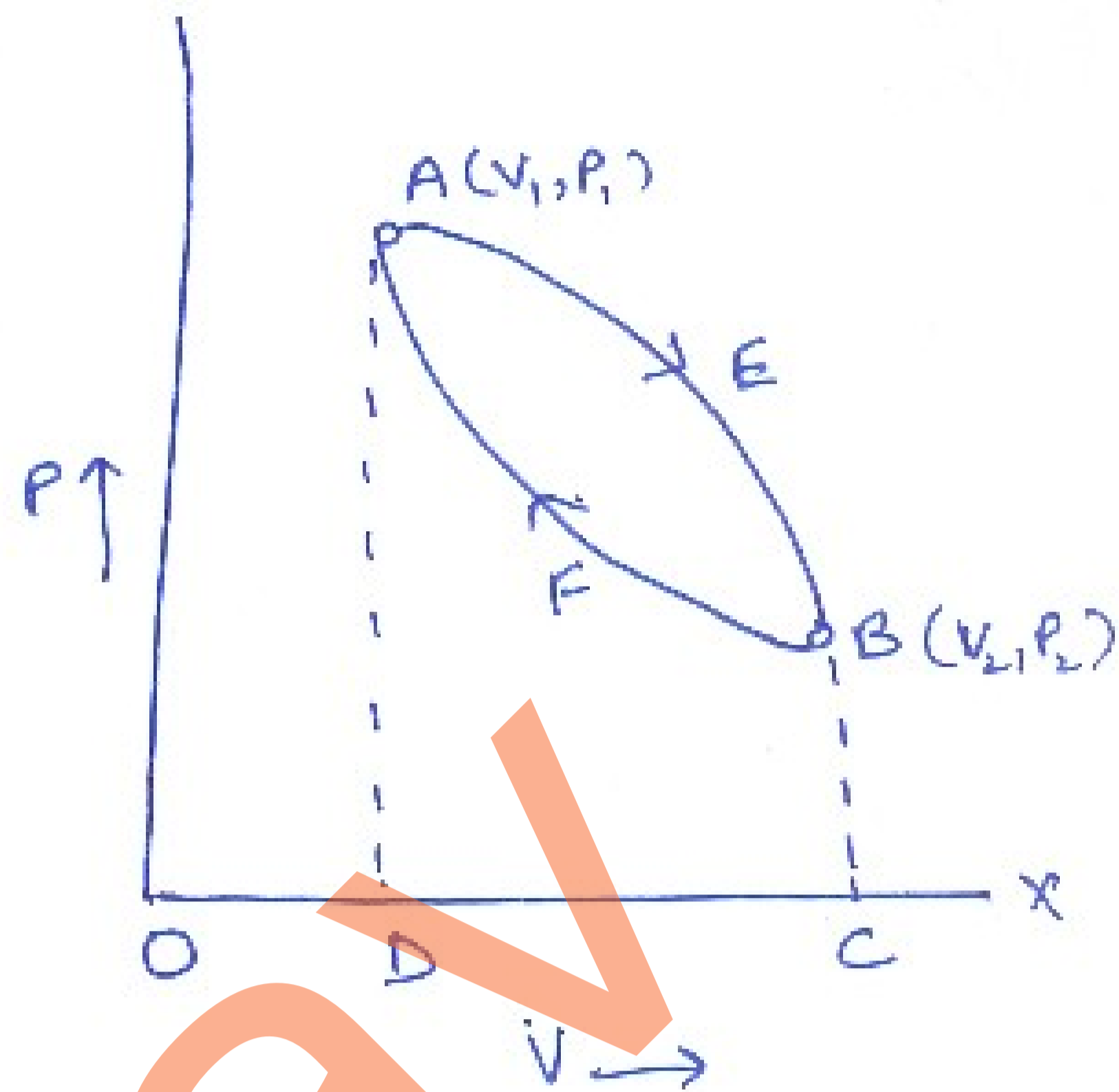
$\therefore (C_p - C_v) dT = R dT$

$$\boxed{C_p - C_v = R}$$

Work done during a cyclic process

Let $A (V_1, P_1)$ represents the initial state of a gas.

Let the gas is subjected to a no. of changes in volume & pressure such that it acquires final state $B (V_2, P_2)$ via path AEB



\therefore Work done by the gas in going from A to B is

$$W_1 = \text{area AEBCDA}$$

Let the system be now subjected to another succession of changes in volume & pressure, which return the system back to $A (V_1, P_1)$ along the path BFA

\therefore Work done on the gas in going from B to A via BFA is

$$W_2 = -\text{area BFADCB}$$

Net work done by the gas in cyclic process is

$$W = W_1 + W_2$$

$$= \text{area of AEBCDA} - \text{area BFADCB}$$

$$= \text{area AEBFA}$$

\therefore Work done per cycle is numerically equal to the area enclosed by the loop representing the cycle.

Second law of thermodynamics

Heat flows spontaneously from a substance at higher tem. to another at lower temperature. Heat does not flow spontaneously in the reverse direction.

Kelvin Planck Statement

It is impossible to construct a heat engine which would absorb heat from a reservoir and convert 100% of the heat absorbed into work.

Clausius Statement

It is impossible to design a self acting machine unaided by any external agency, which would transfer heat from a body at a lower tem. to another body at a higher tem.

Reversible & Irreversible processes

Reversible process

A thermodynamical process taking a system from initial state to final state is reversible if the process can be turned back such that both, the system & surrounding return to their original states, with no other change anywhere else in the universe.

Conditions for reversible change

- ① The process should take place ^{very} slowly so that the system is always in mechanical, thermal & chemical equilibrium.
- ② The system should be free from dissipative forces like friction, viscosity, elasticity etc.

Examples:

- ① An ideal gas allowed to expand slowly & compressed slowly so as to return to its initial state.
- ② All thermal processes taking place at infinitely slow rate.

Irreversible process

Any process which can't be made to proceed in reverse direction is called an irreversible process.

Examples:

- ① Diffusion of gases
- ② Exchange of heat betⁿ 2 bodies
- ③ Adiabatic expansion or compression of a gas.

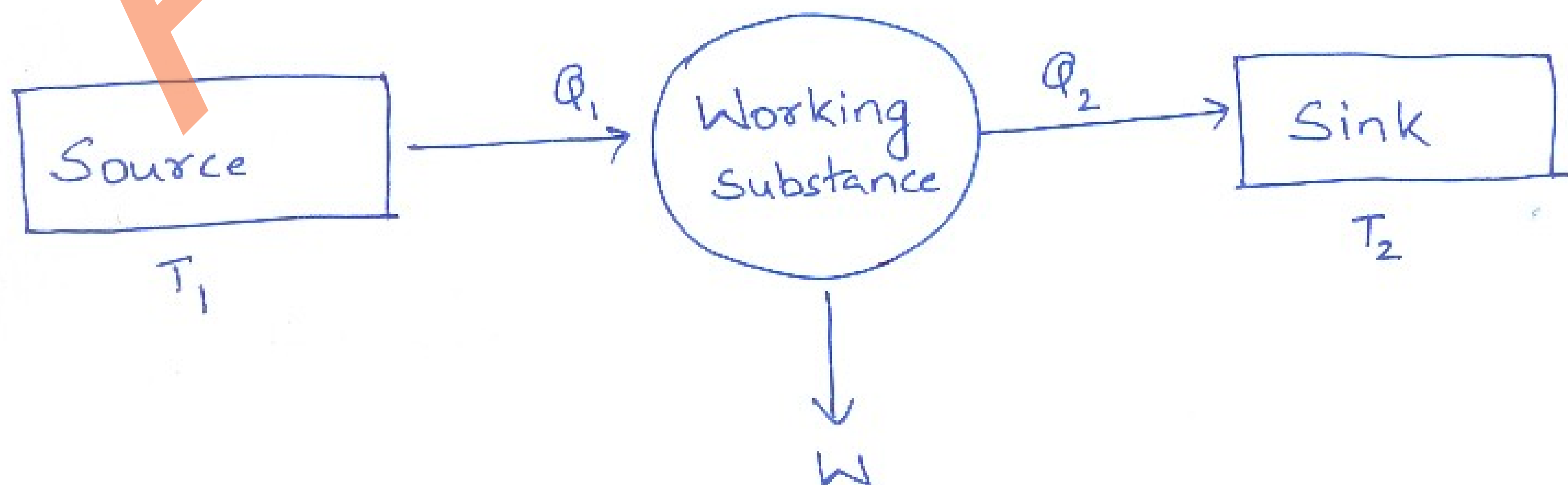
Heat Engine

It is a device which converts heat energy into mechanical energy.

It consists of 3 parts:

- (i) Source of heat (at higher tem.)
- (ii) Working substance
- (iii) Sink of heat (at lower tem.)

→ The working substance absorbs heat from the source, undergoes a cyclic change consisting of several processes & reject some heat to the sink.



Let Q_1 - amount of heat absorbed in one complete cycle

Q_2 - " " " " rejected " " " "

W - net amount of external work done by the working substance on environment

Net heat absorbed in one cycle, $dQ = Q_1 - Q_2$

As the working substance returns to its initial state
 $dU = 0$

Acc. to 1st law of thermodynamics

$$dQ = dU + dW$$

$$dQ = dW$$

$$Q_1 - Q_2 = W$$

Thermal efficiency

Thermal efficiency of a heat engine is defined as the ratio of net work done per cycle by the engine to the total amount of heat absorbed per cycle by the working substance from source

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

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

* $Q_2 \neq 0$, $\eta \neq 1$ or 100%.

| | |
|----------|-------------------------------|
| * Engine | Working Substance |
| Steam | steam |
| Diesel | mixture of fuel vapours & air |

Carnot Cycle

- Ideal cycle of operation for a heat engine devised by Sadi Carnot.

Construction

① Source

- It is a hot body of infinitely large thermal capacity.
- The working substance draws heat from the source again & again but its tem. remains const. (T_1).

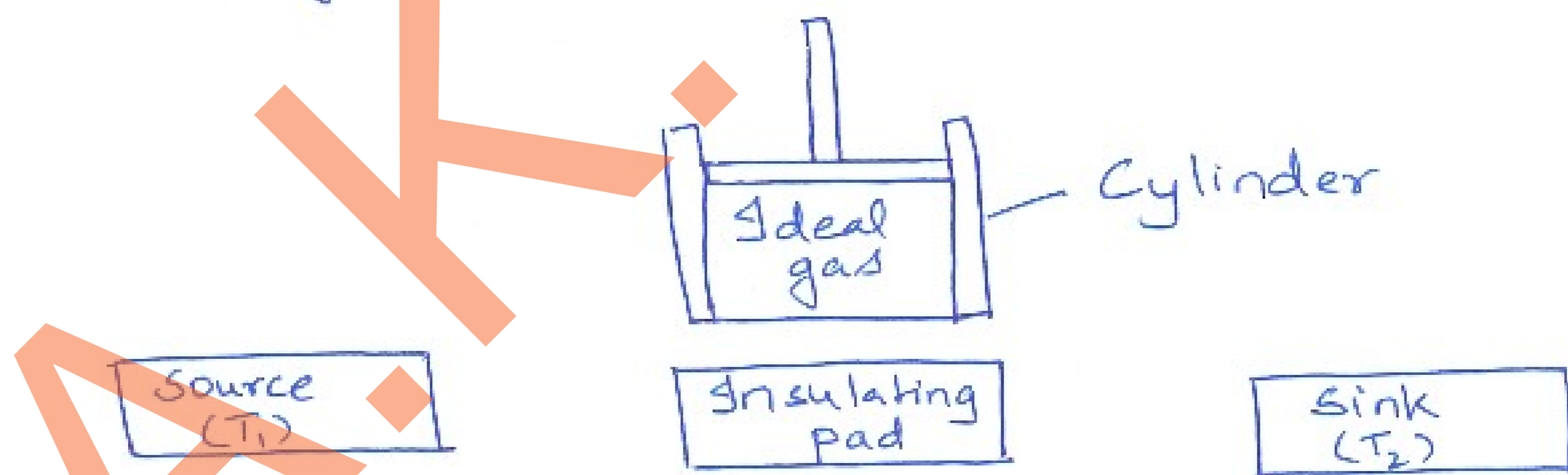
② Sink

- It is a body at some lower tem. having infinite thermal capacity.
- The working substance rejects heat to sink but its tem. remains const. (T_2).

③ Working substance

- An ideal gas acts as a working substance.
- It is contained in a cylinder with non-conducting sides but perfectly conducting base.

④ Insulating pad - on which cylinder is placed.



Theory

Consider 1 gram mole of an ideal gas enclosed in a cylinder.

Let V_1, P_1, T_1 be the initial volume, pressure & tem. of the gas (represented by pt. A on P-V graph)

We assume that all the processes in the cycle are quasi-static & non-dissipative (conditions of reversibility)

Isothermal expansion (curve AB)

- Let the cylinder be placed on the source and the gas be allowed to expand.
- Since it absorbs the required amount of heat from source through the conducting base of cylinder, so, temp. of gas remains constant.

Let Q_1 - amount of heat absorbed in the process

W_1 - amount of work done by the gas in expanding isothermally from $A(V_1, P_1)$ to $B(V_2, P_2)$

$$\therefore Q_1 = W_1 = \int_{V_1}^{V_2} P \cdot dV = RT_1 \log_e \frac{V_2}{V_1} = \text{area ABMKA}$$

Adiabatic expansion (curve BC)

- Cylinder is removed from source & is placed on the insulating pad.
- The gas is allowed to expand further from $B(V_2, P_2)$ to $C(V_3, P_3)$.
- Since, the gas is thermally insulated from all sides, temp. of gas falls to T_2 & so the expansion is adiabatic.

The work done by the gas in expanding adiabatically from $B(V_2, P_2)$ to $C(V_3, P_3)$ is

$$W_2 = \int_{V_2}^{V_3} P \cdot dV = \frac{R(T_2 - T_1)}{1 - \gamma} = \text{area BCNMB}$$

Isothermal compression

- Cylinder is removed from the insulating pad & is placed on the sink.
- The piston is moved inwards slowly so that the gas is compressed until its pressure is P_4 & volume V_4 .
- Since the base of cylinder is conducting, heat produced in compression will pass to sink so that the temp. of gas remains at T_2 .

Let Q_2 - amount of heat rejected to sink

W_3 - work done on the gas in compressing it isothermally from $C(V_3, P_3)$ to $D(V_4, P_4)$

$$\therefore Q_2 = W_3 = \int_{V_3}^{V_4} -P dV = -RT_2 \log_e \frac{V_4}{V_3} = RT_2 \log_e \frac{V_3}{V_4} = \text{area CDLNC}$$

④ Adiabatic compression (curve DA)

- Cylinder is again placed on the insulating pad.
- Piston is further moved downwards so that gas is further compressed to its initial volume V_1 & pressure P_1 .
- As the gas is insulated from all sides, heat produced raises the temp. of the gas to T_1 .

Work done on the gas in compressing it adiabatically from $D(V_4, P_4)$ to $A(V_1, P_1)$.

$$\therefore W_4 = \int_{V_4}^{V_1} -P dV = \frac{-R(T_2 - T_1)}{1-\gamma} = -\text{area DAKLD}$$

Net work done by the gas in a complete cycle is

$$W = W_1 + W_2 + (-W_3) + (-W_4)$$

$$= W_1 + W_2 - W_3 - W_4$$

$$= W_1 - W_3$$

$$\therefore W_4 = W_2$$

$$W = Q_1 - Q_2$$

Also, $W = \text{area ABMKA} + \text{area BCNMB} - \text{area CDLNC} - \text{area DAKLD}$

$$W = \text{area ABCDA}$$

Hence, in Carnot heat engine, net work done by the gas per cycle is numerically equal to the area of the loop representing the cycle.

Efficiency of Carnot engine (η)

It is defined as the ratio of net mechanical work done per cycle by the gas (W) to the amount of heat energy absorbed per cycle from the source (Q_1).

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad \text{--- (1)}$$

Since A & B lie on the same isothermal, $P_1 V_1 = P_2 V_2$ --- (2)

" B & C " " " " " adiabatic, $P_2 V_2^\gamma = P_3 V_3^\gamma$ --- (3)

" C & D " " " " " isothermal, $P_3 V_3 = P_4 V_4$ --- (4)

" D & A " " " " " adiabatic, $P_4 V_4^\gamma = P_1 V_1^\gamma$ --- (5)

$$\text{(2)} \times \text{(3)} \times \text{(4)} \times \text{(5)}$$

$$P_1 V_1 \times P_2 V_2^\gamma \times P_3 V_3 \times P_4 V_4^\gamma = P_2 V_2 \times P_3 V_3^\gamma \times P_4 V_4 \times P_1 V_1^\gamma$$

$$V_1 V_2^\gamma V_3 V_4^\gamma = V_2 V_3^\gamma V_4 V_1^\gamma$$

$$V_2^{\gamma-1} V_4^{\gamma-1} = V_1^{\gamma-1} V_3^{\gamma-1}$$

$$(V_2 V_4)^{\gamma-1} = (V_1 V_3)^{\gamma-1}$$

$$V_2 V_4 = V_1 V_3$$

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\text{So, } \log \frac{V_2}{V_1} = \log \frac{V_3}{V_4}$$

$$\text{Now, } \frac{Q_2}{Q_1} = \frac{RT_2 \log_e V_3/V_4}{RT_1 \log_e V_2/V_1} = \frac{T_2}{T_1}$$

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

∴ eqn ① becomes

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

Conclusion

① η depends only on T_1 & T_2 .

② η is independent of nature of working substance.

③ $\eta = 1$ if $T_1 = \infty$ or $T_2 = 0\text{K}$.

As neither T_1 can be made infinite nor T_2 can be made 0K , it means that the efficiency of Carnot's heat engine can't be 100%.

④ If $T_2 = T_1$, $\eta = 0$

It means that the conversion of heat energy into mechanical work is impossible without having the source & sink at different temperatures.

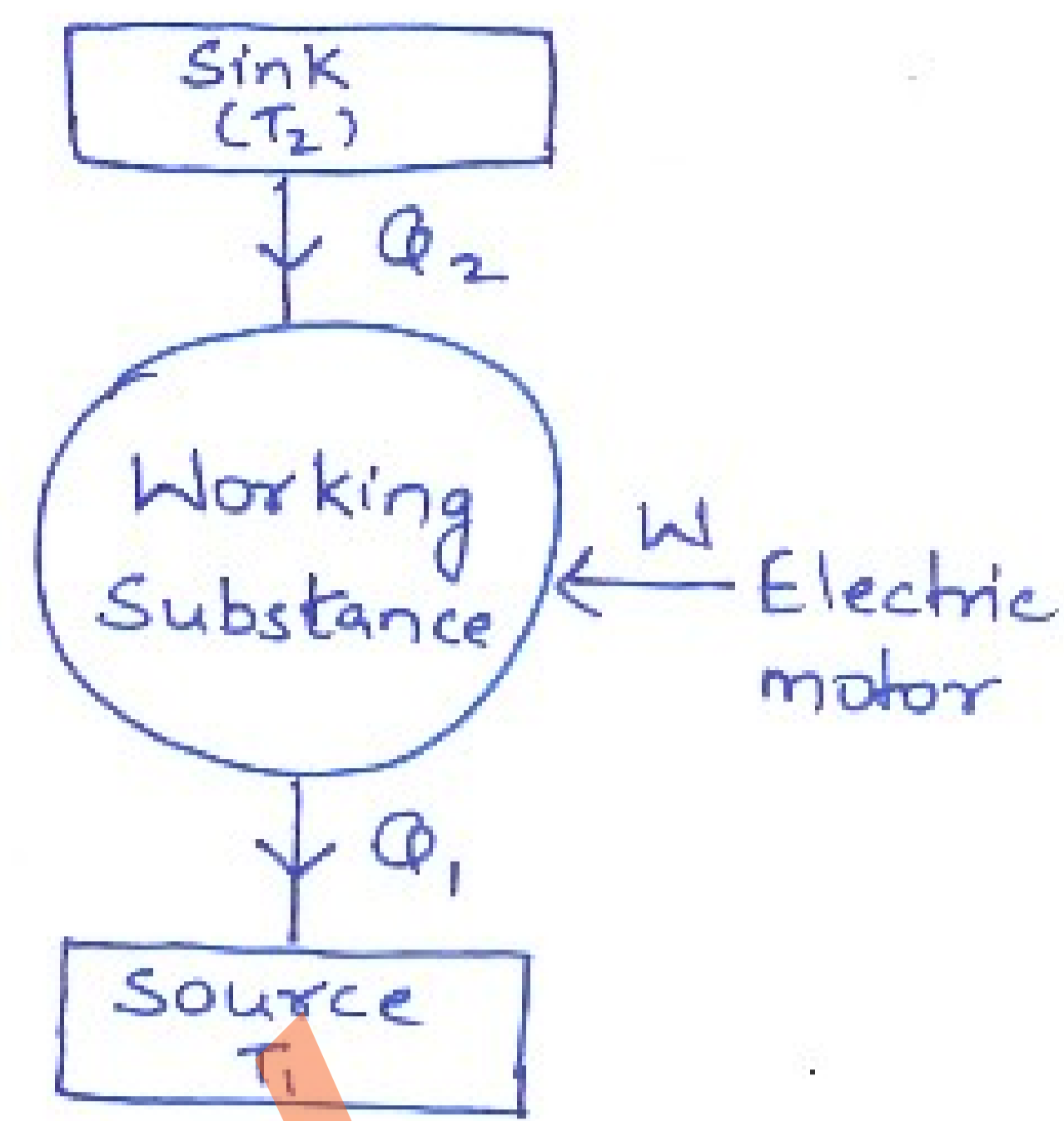
$$\text{⑤ } \frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

if $T_2 = 0$, then $Q_2 = 0$

Since $T_2 = 0$ is not possible, it implies that in a heat engine $Q_2 = 0$ is also not possible. i.e. it is not possible to convert whole of heat energy absorbed from the source completely into mechanical work continuously, without rejecting a part of it to sink.

Principle of a refrigerator (Heat pump)

- An ideal refrigerator is a heat engine working in reverse direction.
- The working substance absorbs heat Q_2 from the sink (contents of refrigerator) at lower temp. T_2 & rejects a large amount of heat Q_1 to source (atmosphere) at a higher temp. (T_1) with the help of compressor.



In the cycle of changes, as the working substance returns to its initial state, so $dU = 0$

If Q_2 - heat extracted from sink
 Q_1 - " released to source, then

$$dQ = Q_2 - Q_1$$

Work done on the system, $dW = -W$

Acc. to 1st law of thermodynamics

$$dQ = dU + dW$$

$$Q_2 - Q_1 = 0 - W$$

$$W = Q_1 - Q_2$$

Coefficient of performance (β)

It is defined as the ratio of quantity of heat removed per cycle from the contents of the refrigerator (Q_2) to the energy spent per cycle (W) to remove this heat.

$$\beta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

Also,

$$\beta = \frac{1 - \eta}{\eta}$$

Conclusion

- ① Higher the value of β , more efficient is the refrigerator.
- ② Smaller is the difference in temperatures of atmosphere & food stuff to be cooled i.e. $(T_1 - T_2)$, more efficient will be the refrigerator (i.e. higher value of β).

Q. Why is the defrosting necessary for better working of the refrigerator?

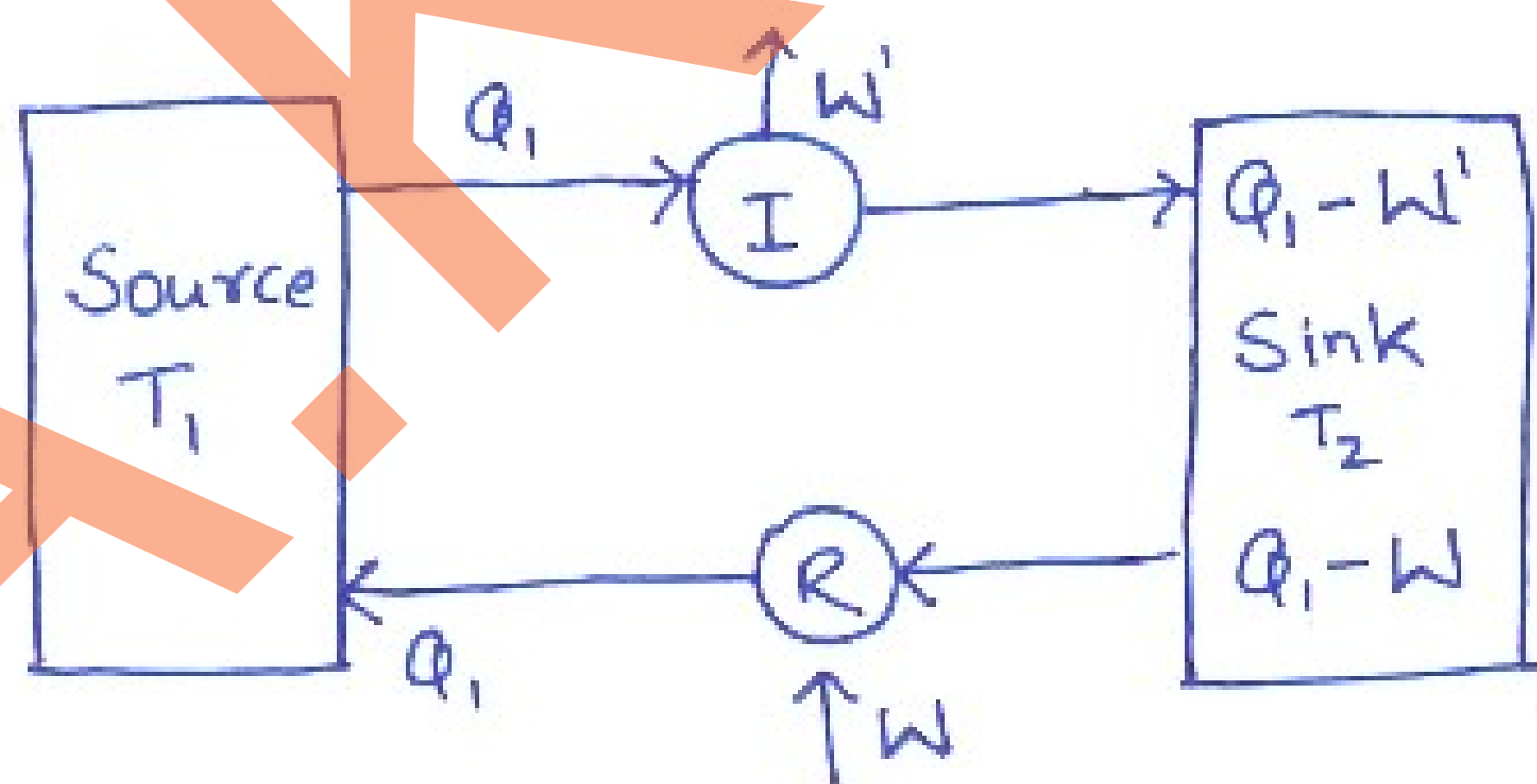
Ans: As the refrigerator works, T_2 goes on decreasing due to formation of ice & T_1 remains almost constant & so β decreases.

When the refrigerator is defrosted, T_2 increases & hence β increases. & so the refrigerator performs better.

Carnot Theorem

"It states that no engine working betⁿ 2 temperatures can be more efficient than a Carnot's reversible engine working betⁿ the same 2 temperatures"

Proof: Imagine a reversible Carnot engine R & an irreversible heat engine I, working betⁿ T_1 & T_2 .



Suppose the 2 engines are coupled in such a way that irreversible engine I acts like heat engine reversible engine R " " refrigerator.

Let, engine I absorb Q_1 heat from source, delivers work W' & release $(Q_1 - W')$ to sink in one full cycle.

We arrange engine R such that it returns same heat Q_1 to source when work W is done on it in one full cycle & hence it takes heat $Q_1 - W$ from sink.

Suppose $\eta_R < \eta_I$

\therefore for given Q_1 , $W < W'$

$$Q_1 - W > Q_1 - W'$$

Thus, the coupled I-R system extracts heat $(Q_1 - W) - (Q_1 - W')$ $= (W' - W)$ from sink & delivers the same amount of work $(W' - W)$ to the source in one full cycle.

This is against 2nd law of thermodynamics.

Hence, the assumption $\eta_R < \eta_I$ is wrong.

\therefore Working betⁿ a given temperatures, no engine can have efficiency greater than the efficiency of reversible Carnot engine.