

Chapter-2.

Basic Concepts of Thermodynamics

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* Thermodynamics :- It is the branch of energy interaction and its effect on system and surroundings.

* System :- It is a fixed mass or a region in space where an study is focused.

* Surrounding :- Everything except the system is called.

* Boundary :- A real or imaginary surface that separates the system with surrounding (Fixed and moveable)

* Type of systems :-

System	Mass	Energy	Example
(i) Closed Sys.	x	✓ interaction	Piston Cylinder without valve
(ii) Open Sys.	✓	✓	Piston cylinder
(iii) Isolated Sys.	x	x	A perfectly insulated thermal flask

* Properties of a system :- Any characteristic of the system is called property of the system.

Intensive (Intrinsic)

Extensive (Extensive)

→ Independent of mass of the system.

→ The properties which depends on mass of the system under consideration.

Ex. - Pressure, temp, density

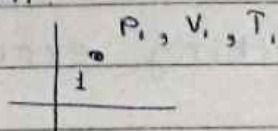
Ex. Volume, Enthalpy, Internal Energy

* All specific properties are intensive property. Ex. Spec. Vol., Spec. PE, Enthalpy

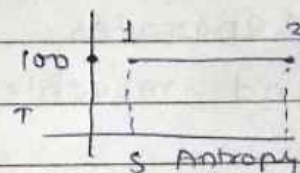
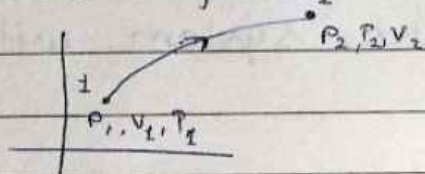
- Keypoints :-
- ① They are exact properties
 - ② They are point functions
 - ③ They are independent of past history.

* State of the system :-

- ① The condition of the system is known as state of system.



- ② The state of the system₂ is specified by its properties



- ③ The change in the state of process

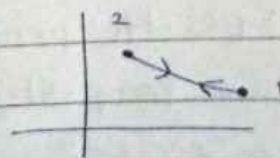
* Path :- The infinite states through which the system passes is called path.

* Quasistatic or non-quasistatic :- The process which is carried out very slowly so that the system can be assumed to be in equilibrium anywhere between initial and final state.

Non-quasistatic → which is not slowly.

* Reversible process :- A reversible process is one which can be taken from its initial state to another state without any change either to system or surround.

Ex. ① Frictionless motion



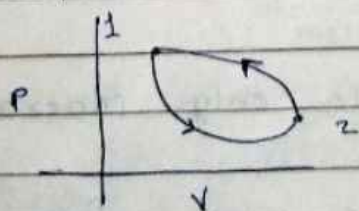
* Irreversible process:- An irreversible process is what counter in reality almost all the time. The system and environment cannot be restored to its original state at the same time.

Ex: ① When the heat flows one obj. to another.
② burning of paper.

Reversible process	Irreversible process
i) This process carried out infinite slowly	→ It is carried out rapidly.
ii) At any stage equilibrium is not disturbed.	→ Equilibrium is maintain only after completion of process
iii) It is ideal process	→ inideal
iv) Same path	→ diff. path
v) Maximum work	→ Minimum work
vi) Physical process	→ chemical process

* All reversible process are Quasistatic but all quasi-static process are not reversible.

* Cyclic process:- A process consist of a series of changes which return the system back to its initial state.



u = internal energy

w = area in the curve

① $u_f = u_i$ $\Delta u = u_f - u_i = 0$

⑤ $\Delta Q = \Delta U + \Delta W$
 $\Delta Q = \Delta W \quad \therefore \Delta U = 0$

* Non-cyclic process :- when the system doesn't return to its original state due to irreversibilities present in system (like friction) Ex - boiling water

* Thermodynamic Equilibrium :- A system is said to be in therm. equ. if following equilib. are satisfied :-

- ① Thermal Equ. $\rightarrow$ Same temp. for the system
- ② Machanical Equ. $\rightarrow$ (force) Pressure at a point shouldn't change with time.
- ③ Chemical Equ. $\rightarrow$ chemical composition shouldn't change with time
- ④ Phase equ. $\rightarrow$ The mass of each phase should remain constant with time

* Macroscopic Approach :- In macroscopic approach the individual molecular behaviour is not taken into account rather average molecular behaviour is studied.

* Macroscopic app. is valid till the continuum concept is application.

* Pressure, Density applicable only macroscopic app. is valid

It remains valid till the mean free path is much much less than system direction

* Gas Laws

- ① Pressure & temp
- ② Pressure & Volume
- ③ Pressure & amount of gas
- ④ Temp & Vol.
- ⑤ Volume & Amount gas

Boyle's law :- If temp. is constant, pressure of gas $\uparrow$, Vol $\downarrow$

$$\frac{1}{PV} = K$$

$$P_1 V_1 = P_2 V_2$$

Charles's law :- If temp. of gas $\uparrow$, vol $\uparrow$, If pressure is constant

$$\frac{V}{T} = K$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Gay Lussac's law :- As the temp. of enclosed gas $\uparrow$ pressure $\uparrow$

$$\frac{P}{T} = K$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Combined gas law :- When amount of gas is constant

$$\frac{PV}{T} = K$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

FIRST LAW OF THERMODYNAMICS :- A Thermodynamic system is a collection of objects we can regard as a unit that can exchange energy with surrounding

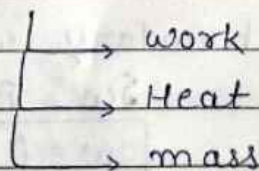
Energy transfer into and out of system can be through

- ① Energy work done (w)
- ② Heat (Q)

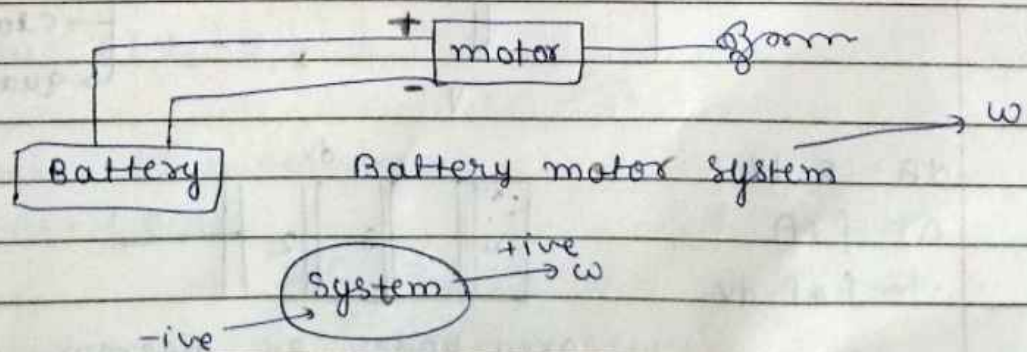
SIGN CONVENTION

For work (w)	Heat (Q)
→ Work done by system is (+ive). Ex. Turbine	$Q_{in} = (+ive)$
→ Work done on the system is (-ive) Ex. - Pump, compressor	$Q_{out} = (-ive)$

ENERGY AND ENERGY INTERACTION

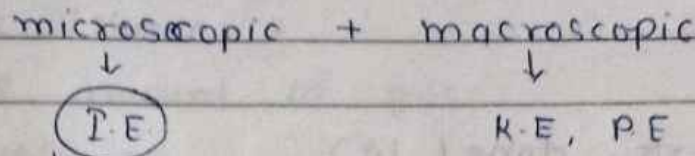


Ex: ①



Ex: ② Work is said to ~~be~~^{be} done by system, if the ~~Soul~~^{use} effect on things external to the system can be reduced to the raising of a weight.

(1) Energy



↳ Sensible energy

+ latent heat + chemical

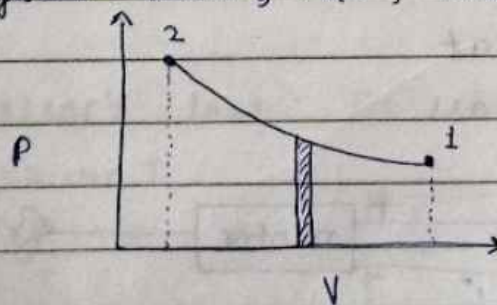
Energy + Nuclear Energy

$0^{\circ}\text{C} \rightarrow 100^{\circ}\text{C}$
Sensible

- * Macroscopic is the energy possessed by bulk molecules
- * Microscopic energy is the energy possessed by substance at molecular level

Close system Analysis

4 Close-system work, Pdv , boundary work



$$\delta W = p \cdot \overset{\text{Unit}}{\text{A}} \cdot d\alpha$$

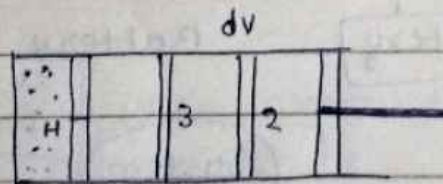
$$W = \int P \cdot dV$$

- closed
- quasistatic process

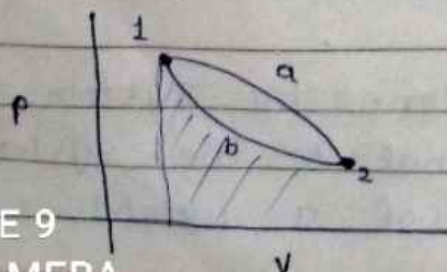
$$dA = P \cdot dV$$

$$A = \int dA$$

$$= \int P \cdot dv$$



$W = \text{Area under PV diagram}$



$$w_{1a_2} \neq w_{1b_2}$$

Path Junction

* Important point w.r.t. work.

- ① It is a path function :- Path functions are properties or quantities whose value depends on the transition of the system from initial state to final state. Heat is also a path function.
- ② It is a boundary function.
- ③ Work is not a property.
- ④ It is an inexact differential equation.

Pdv work in various processes

- ① Const. vol. process (Isochoric)

$$W = \int_1^2 P \cdot dv$$

$$= P(V_2 - V_1)$$

Volume constant

$$\boxed{W = 0}$$

- ② Isobaric ($P = \text{constant}$)

$$W = \int_1^2 P \cdot dv$$

$$W = P(V_2 - V_1)$$

- ③ Isothermal ($T = \text{constant}$)

$$W = \int P \cdot dv$$

$$W = \int_1^2 \frac{C}{V} \cdot dv$$

$$PV = nRT$$

$$P, V = \text{const.}$$

$$W = C \int \frac{1}{V} \cdot dv = C [\log V]_1^2$$

$$\boxed{W = C \ln \frac{V_2}{V_1}}$$

$$W = C \ln \frac{P_1}{P_2}$$

$$W = mRT \ln \frac{P_1}{P_2}$$

$$W = mRT \ln \frac{V_2}{V_1}$$

④ Adiabatic Process :- (Heat $\rightarrow Q = 0$)
flow

$$PV^\gamma = C$$

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

$$W = \int_1^2 P \cdot dV$$

$$\text{air} \rightarrow 1.4$$

$$= \int_1^2 \frac{C}{V^\gamma} \cdot dV$$

$$C_p - C_v = R$$

$$= C \int_1^2 \frac{1}{V^\gamma} \cdot dV$$

$$\Rightarrow C \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_1^2 = \frac{C}{1-\gamma} \left[V_2^{-\gamma+1} - V_1^{-\gamma+1} \right]$$

$$\Rightarrow W = \frac{P_2 V_2 - P_1 V_1}{-\gamma + 1}$$

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

$$PV^\gamma = C$$

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

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

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

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

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

$$\frac{P_2}{P_1} = \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}}$$

Polytropic Process :- $(PV^n = c)$

$$W = \int P \cdot dV$$

$$C_p - C_v = R$$

$$= \int \frac{c}{V^n} \cdot dV$$

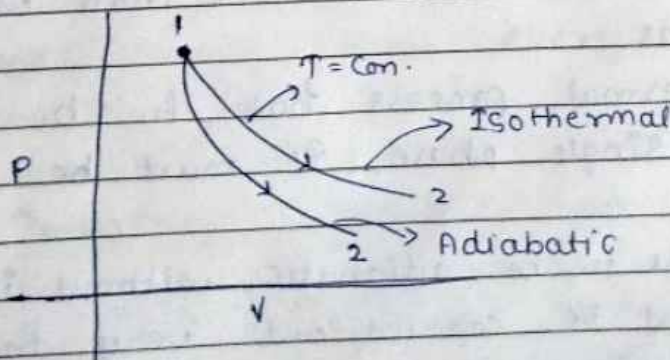
$$\frac{C_p}{C_v} = \gamma$$

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

→ For general process

n value lies b/w 1 to 1.4

Representation of isothermal & Adiabatic curves on P-V diagrams for an ideal gas.



Isothermal
 $PV = c$

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

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

Adiabatic

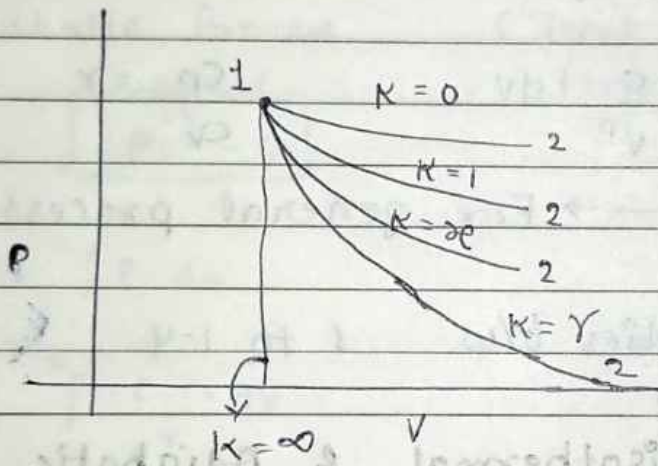
$$PV^{\gamma} = c$$

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

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

* Adiabatic curve is more steeper than isothermal curve

Isochoric	Isobaric	Isothermal	Adiabatic
$\frac{P_1}{T_1} = \frac{P_2}{T_2}$	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$	$P_1 V_1 = P_2 V_2$	$P_1 V_1^\gamma = P_2 V_2^\gamma$
			$\downarrow$ $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}}$



Practical Realisation of process :-

- ① If free piston is free to move than we can assume process
- ② If an isothermal process has to be carried out in a single phase, It must be carried out very slowly.
- ③ For a process to be adiabatic without insulation than it must be carried out very fastly. If with insulation. It can be fast or slow.

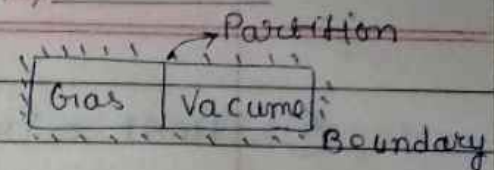
* Free expansion:- $w=0$ Work is identified at boundaries.

- ① Let the partition remove - The expansion of

Refrigerator $\xrightarrow{-w}$ [Sys] $\xrightarrow{+w}$ Ex. Turbain work give

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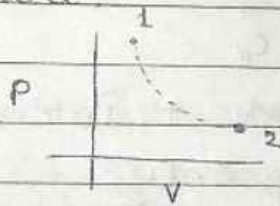
gas against vacume is known as free expansion



② $\int_1^2 dw = 0$

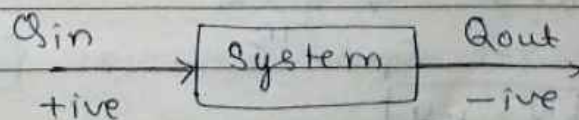
③ If only Gas is taken on system, when the partition is removed, there is change in the vol. of gas. $w = \int_1^2 P \cdot dv$

The two end states can be located at P-v and a joined by dotted line and the procession can be occure.



* However if vacum is spaces divided in large number of small vacum and partition removed slowly then every state pass by the system equ.

Heat Transferr :- Heat :- Sign convation

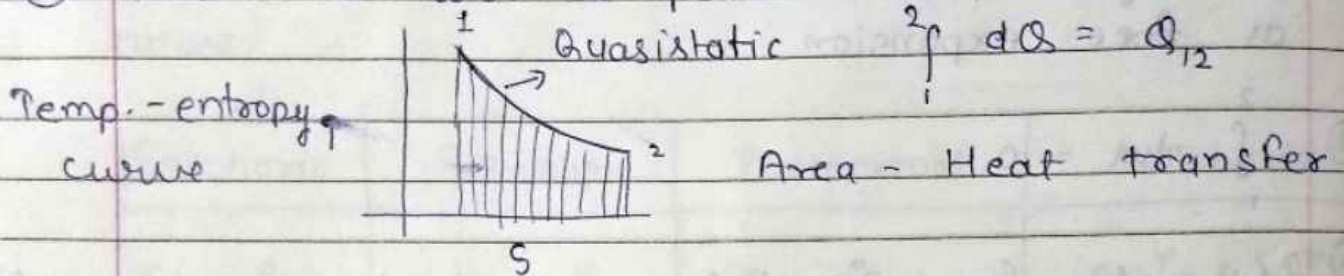


Heat is a form of energy that is transmitted across a boundary by virtue of temp. diffrens.

① It is also a (Boundary phenomenon)

② It is also not a property

③ Heat is also a path function.



Heat:-

$$Q \propto dT$$

$$Q \propto m$$

$$Q = mc dT \quad (c = \text{Specific heat})$$

$$c = \frac{Q}{m \cdot dT} \quad \left(\frac{KJ}{kg \cdot K} \right) \quad \text{or} \quad \frac{KJ}{kg \cdot C}$$

Specific heat (c) $\rightarrow \frac{C_p}{C_v} \quad C_p > C_v$

$C_p \rightarrow$ boundary work + internal energy

$C_v \rightarrow$ internal energy only

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

$$C_p - C_v = R$$

For Monoatomic gas $\Rightarrow C_v = \frac{3}{2}R$
 $C_p = R + \frac{3}{2}R = \frac{5}{2}R$

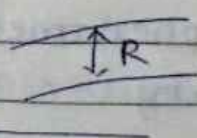
$$\boxed{\gamma = 1.67}$$

Diaatomic gas $\Rightarrow C_v = \frac{5}{2}R$
 $C_p = \frac{7}{2}R$

$$\boxed{\gamma = 1.4}$$

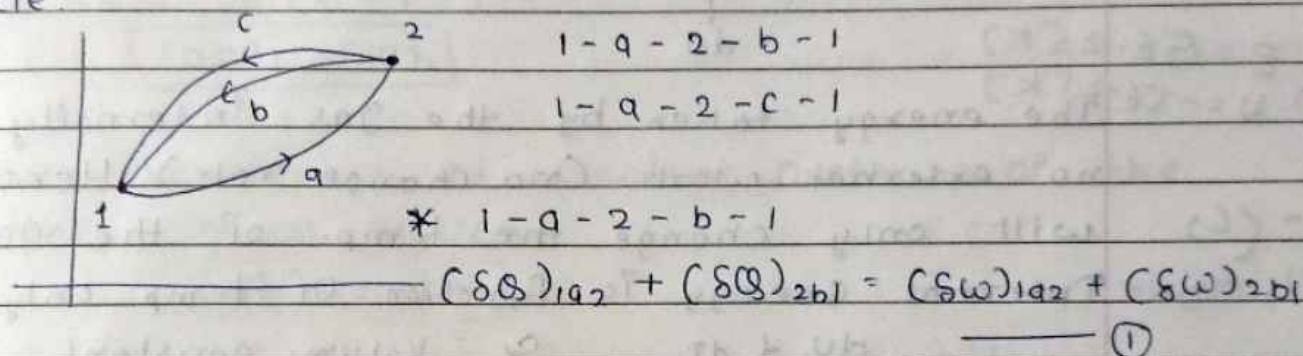
Triatomic
 $\boxed{\gamma = 1.3}$

② As the tem. $\uparrow$ both C_p and $C_v \uparrow$ by equal amount



* First law of Thermodynamic :- For a closed system (Joule's laws) undergoing a cycle net heat transfer is equal to net work transfer.

It is also called as law of consv. of energy. It is valid for both rever. as well as irreversible cycle.



* 1-a-2-c-1

$$(δQ)_{1a2} + (δQ)_{2c1} = (δW)_{1a2} + (δW)_{2c1} \text{ ——— ②}$$

$$\text{eq. ①} - \text{eq. ②}$$

$$(δQ)_{2b1} - (δQ)_{2c1} = (δW)_{2b1} - (δW)_{2c1} \text{ ——— ③}$$

from eq. ③ $(δQ)_{2b1} - (δW)_{2b1} = (δQ)_{2c1} - (δW)_{2c1}$

$$(δQ - δW)_{2b1} = (δQ - δW)_{2c1}$$

Though path ^b and c are different but the quantity (δQ - δW) is same for both the path and this must properly represent a change in property.

$$\boxed{δQ - δW = δE} \rightarrow \text{Energy}$$

It is first law of Thermo. for a process.

* First law of a process :- When a heat is transferred to a gas then a part of it is taken by the gas itself and the remaining is converted into work. This is equal to dw.

$$b = \int p dv = P_1 V_1 - P_2 V_2$$

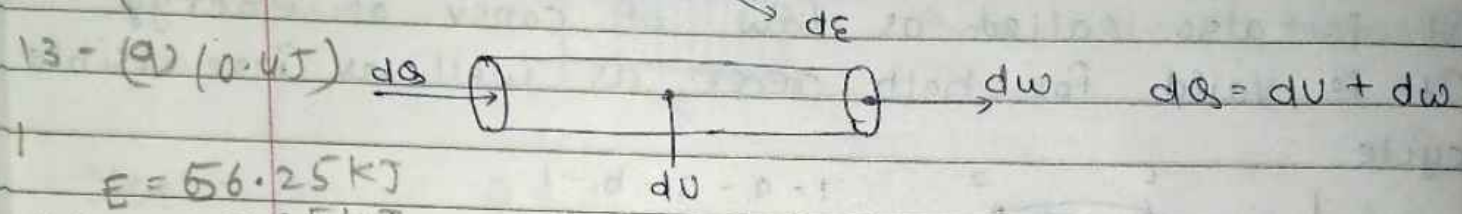
17-a
20-C A b a
18-d one
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10 KJ

The energy taken by the gas internally is known as change in internal energy (du)

4-a) $dQ = du + dw$ for a process



$E = 56.25 \text{ KJ}$

4) $W = -56.25 \text{ KJ}$
The energy taken by the gas internally has no external work (no change vol.) Hence, du will only change the temp. of the gas

12-C) Internal Energy is function of temp. only
 $du \propto dt$ $C_v = \text{Volum. constant}$

16-a $du = mc_v dt$

19-1.82 $6 = 100.52$ 11-C)

* First law for a closed system :- $\Delta Q = \Delta W$

20-C) $dw \rightarrow dw_{p.dv} + dw_{shaft} + dw_{electr.}$

17-C) $dE \rightarrow \underbrace{E_k + E_p}_{\text{macro}} + \underbrace{U}_{\text{micro}}$

50 KJ and 20+ $dQ = du + dw = dE + P.dv = du + P.dv$

14-a) Integral form
 $Q = \Delta E + \int P.dv$
 $Q = \Delta U + \int P.dv$ 7-2356.2

Enthalpy :- (h) $\rightarrow$ Specific (H - Total enthalpy)
It is thermodynamic quantity equivalent to the total heat content of the system.

$U \rightarrow mc_v dt + p.dv$
 $h = \underbrace{U}_{\text{micro}} + \underbrace{Pv}_{\text{macro}}$

(15)-b
(14)-A

c, 1.82, d, c, a, b, a, a, c, c, c, a

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H is the total heat content at constant P .
 $H \rightarrow H$ is an intensive property

$$dQ = dU + P \cdot dV$$

At constant pressure $P \cdot dV = d(PV)$

$$(dQ)_P = dU + d(PV)$$

$$(dQ)_P = d(U + PV)$$

$$(dQ)_P = dH$$

Heat transferred at constant pressure of the enthalpy of a system.

$$dH = mC_p dT$$

$$H = mC_p \int_{T_1}^{T_2} dT$$

* Energy of Isolated System :- No interaction of system with surrounding

$$dQ = 0$$

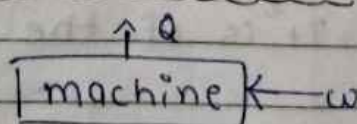
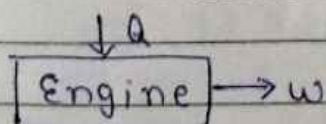
$$dW = 0$$

$$dE = 0$$

$$E = \text{constant}$$

* The Energy of an isolated system is always constant.

* Perpetual motion machine of first kind (PMM₁) :-



First law :- There can be no machine which would continuously supply mech. work without some other form of energy disappearing simultaneously.

$$\begin{aligned} \text{H} \leftarrow \text{S} & \text{ +ive} \\ \text{S} \xrightarrow{\text{H}} & \text{ -ive} \end{aligned}$$

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Such a Frictions machine is called PMM,
(The PMM, is impossible)

* Numerical Question :-

Q ① A Stationary mass of gas is compressed without friction from an initial state 0.3 m^3 and 0.105 m pascal to a final state of 0.15 m^3 and 0.105 m pascal . The pressure remaining constant during the process. There is a Heat transfer of 37.6 KJ of heat from the gas during the process. How much does the internal energy of the gas.

$$\Rightarrow \begin{aligned} V_1 &= 0.3 & P_1 &= 0.105 \\ V_2 &= 0.15 & P_2 &= 0.105 \end{aligned}$$

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

$$Q_{12} = U_2 - U_1 + W_{12}$$

$$W_{12} = \int_{V_1}^{V_2} P \cdot dV$$

$$\Rightarrow P(V_2 - V_1) = 0.105(0.15 - 0.30)$$

$$\Rightarrow -15.75 \text{ KJ}$$

$$Q_{12} = -37.6 \text{ KJ}$$

$$-37.6 = \Delta U - 15.75$$

$$\Delta U = -21.85 \text{ KJ}$$

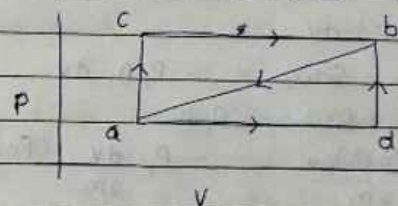
It is of the gas decrease

Q ② When a system is taken from state a to b, in fig. given along path, acb, 84 KJ of heat flows into the system and system does 32 KJ of work.

$$\text{Heat } Q = \Delta U + W$$

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- (a) How much will the heat flow into the system along path adb. If the work done is 10.5 KJ .
(b) When the system is return from b to a along the curved path the work done on the system is 21 KJ . Does the system absorbed or liberate and How much heat absorbed?
(c) If $U_a = 0$ and $U_d = 42 \text{ KJ}$ find the heat absorbed in the process ad and db



$$\Rightarrow \text{ca) } \rightarrow Q_{acb} = 84 \text{ KJ}$$

$$W_{acb} = 32 \text{ KJ}$$

$$Q_{acb} = (U_b - U_a) + W_{acb}$$

$$U_b - U_a = 52 \text{ KJ}$$

$$Q_{adb} = (U_b - U_a) + W_{adb}$$

$$Q_{adb} = 52 + 10.5 = 62.5$$

$$\text{(b) } W = -21 \text{ KJ}$$

$$Q_{ba} = U_a - U_b + W_{ba}$$

$$= -52 - (-21)$$

$$= -31 \text{ KJ liberate}$$

$$\text{(c) } U_a = 0 \quad U_d = 42$$

$$W_{adb} = W_{ad} + W_{db} = 10.5 \text{ KJ}$$

$$Q_{ad} = U_d - U_a + W_{ad}$$

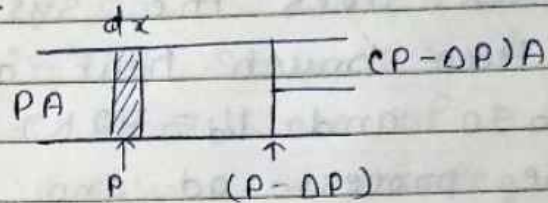
$$= 42 - 0 + 10.5 = 52.5 \text{ KJ}$$

$$Q_{adb} = 62.5 \text{ KJ} = Q_{ad} + Q_{db}$$

$$Q_{db} = 62.5 - 52.5 = 10 \text{ KJ}$$

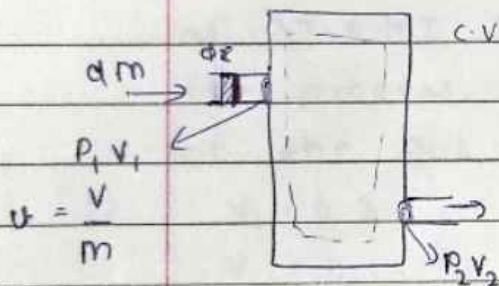
* First law for an open system :-

* Displacement work :-



$$W = P A \cdot dx = P \cdot dV$$

$$W = (P - \Delta P) A \cdot dx = (P - \Delta P) \cdot dV$$



C.V. $\Rightarrow$ Control Volume

$$\delta W_{c.v.} = -P_1 A \cdot dx$$

$$\delta W = -P_1 dV$$

$$\frac{(\delta W)_{c.v.}}{dm} = -P_1 \frac{dV}{dm} \quad (\text{Per kg basis})$$

$$= -P_1 V_1$$

$$W_{c.v.} = -P_1 V_1$$

$$W_{exit} = P_2 V_2$$

Steady Flow Energy equation (SFEE) :-

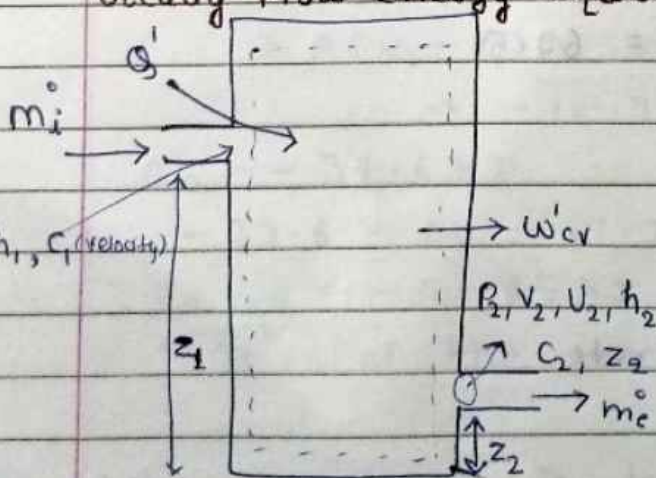
① Steady State :-

Conservation of mass

$$\dot{m}_i = \dot{m}_e = \dot{m}$$

Energy Conservation

$$\text{Energy}_{in} = \text{Energy}_{out}$$



$$\rightarrow \dot{m}_i \left(u_1 + \frac{C_1^2}{2} + gz_1 + P_1 V_1 \right) + Q = \dot{m}_e \left(u_2 + \frac{C_2^2}{2} + gz_2 + P_2 V_2 \right) + W_{cv}$$

$$\rightarrow \dot{m}_i \left(h_1 + \frac{C_1^2}{2} + gz_1 \right) + Q = \dot{m}_e \left(h_2 + \frac{C_2^2}{2} + gz_2 \right) + W_{cv}$$

ex: $q = \frac{Q}{m}$

Divided by m

$$h_1 + \frac{C_1^2}{2} + gz_1 + q = h_2 + \frac{C_2^2}{2} + gz_2 + w_{cv}$$

This is first law of thermodynamics for open system.

$$\rightarrow U_1 + P_1 V_1 + \frac{C_1^2}{2} + gz_1 + q = U_2 + P_2 V_2 + \frac{C_2^2}{2} + gz_2 + w_{cv}$$

(i) $U_1 = U_2$ Bernoulli's eq.

(ii) $q=0$ $w_{cv}=0$ $P_1 V_1 + \frac{C_1^2}{2} + gz_1 = P_2 V_2 + \frac{C_2^2}{2} + gz_2$

(iii) Incompressible

• Steady flow energy equ. applied to common engine. Devices:-

① Turbine :-

$$h_1 + \frac{C_1^2}{2} + gz_1 + q = h_2 + \frac{C_2^2}{2} + gz_2 + w_{cv}$$

$\rightarrow$ Steady State, Adiabatic $\Delta K_e = 0$ $\Delta P_e = 0$

$$h_1 = h_2 + w_{cv}$$

$$w_{cv} = h_1 - h_2$$

② Compressor :-

$$h_1 = h_2 - w_{cv}$$

$$w_{cv} = h_2 - h_1$$

Imp. Formula's

$\rightarrow \delta Q - \delta W = \delta U \rightarrow$ 1st law for a process

$\oint \delta Q = \oint \delta W \rightarrow$ 2nd law for a cycle

Enthalpy $h = U + PV$ or $mc_p \Delta T$

$$mc_p \int_{T_1}^{T_2} \Delta T \quad h = mc_p (T_2 - T_1)$$

Internal Energy - $U = mc_v \Delta T = mc_v (T_2 - T_1)$

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

$$C_p - C_v = R$$

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

$$C_p = \frac{\gamma R}{\gamma - 1}$$

Chapter: 2

Second Law of Thermodynamics

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Thermal Energy reservoir :-

Source :- It is a TER which can supply large amount of energy without undergoing any temp. change. Sum. (∞ energy receive but T constant)

Sink :- It is an TER which can receive large amount of thermal energy without undergoing any temp. change.

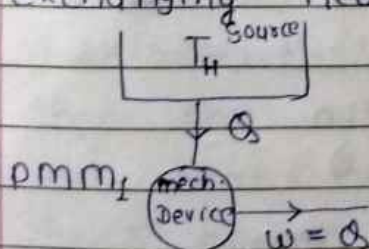
low grade Energy $\Rightarrow$ Unorganized form of energy Ex Heat

High grade Energy $\Rightarrow$ Organized form of energy $\Rightarrow$ work.

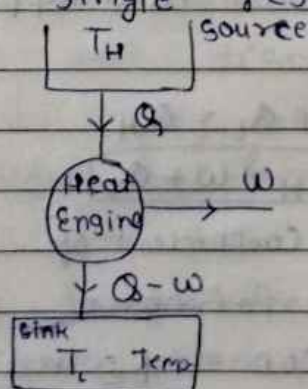
"According to second law of therm. complete conversion of low grade energy into high grade energy in a cycle is impossible without any loss."

STATEMENTS OF IInd law :-

- ① Kelvin - Planck :- It is impossible to develop a device operating on a cycle that produces work by exchanging heat with single reservoir.



(not possible)

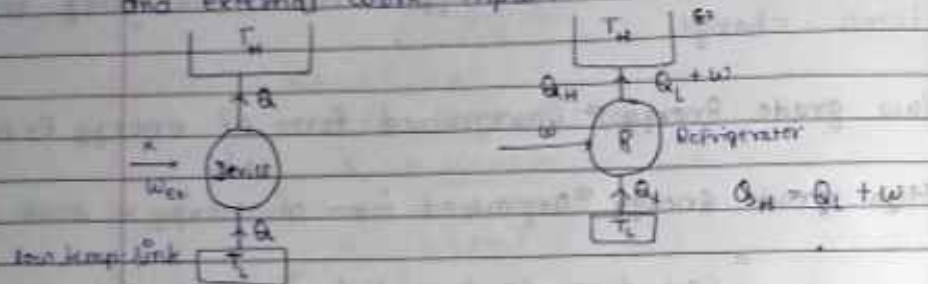


② Concept of Heat engine is derived from Kelvin-Planck^{2nd} law.

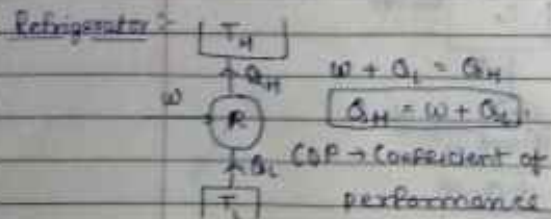
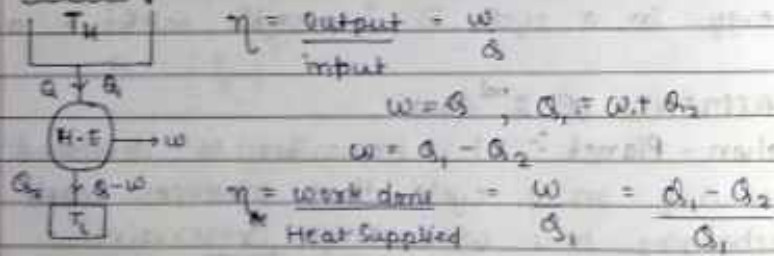
(ii) No heat engine can have η of 100%.

- PMM_2 - It is a device which violates Kelvin Planck's statement. PMM_2 is impossible.

- ② Clausius Statement :- It is impossible to develop a device which works on a cycle and transfer heat from lower temp. to higher temp. without and external work input.



* Efficiency :-



COP $\rightarrow$ Coefficient of performance

$$\text{COP} = \frac{\text{Desired Effect}}{\text{required input}} = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}$$

$$(\text{COP})_R = \frac{Q_L}{Q_H - Q_L} \quad \text{--- (1)}$$

Heat pump

$$(\text{COP})_{\text{H.P.}} = \frac{Q_H}{Q_H - Q_L} \quad \text{--- (2)}$$

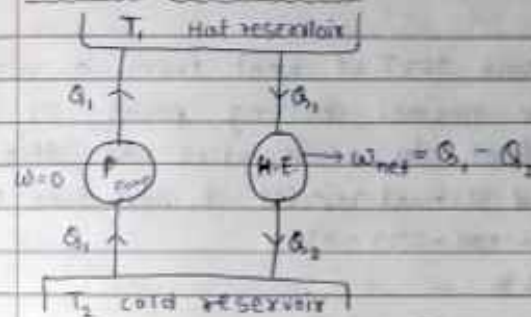
eq. (2) - (1)

$$(\text{COP})_{\text{H.P.}} - (\text{COP})_R = \frac{Q_H}{Q_H - Q_L} - \frac{Q_L}{Q_H - Q_L} = 1$$

$$(\text{COP})_{\text{H.P.}} = 1 + (\text{COP})_R$$

* Equivalence of Kelvin Planck and Clausius Statement :-

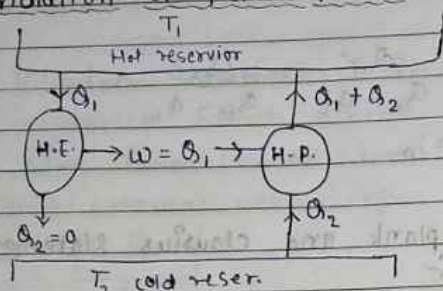
① Violation of Clausius :-



Let us assume a cyclic heat engine (E) operating between the same energy reservoir producing W_{net} in one cycle. The rate of working of H.E. is such that it draws an amount of heat Q_2 from hot reservoir equal to that discharged by heat pump. Then the hot reservoir may be eliminated and the heat Q_2 discharged by heat pump is fed to heat engine. So we see that heat pump (P) and heat engine (E) acting together constitute a heat engine operating in cycle and produces net work while exchanging heat with single reservoir. This violates Kelvin Planck.



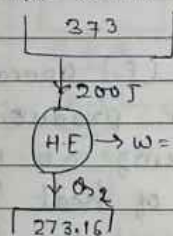
② Violation of Kelvin plank :-



Q. ① A Carnot Engine absorb 200J of heat from a reservoir at the temp. of the normal boiling point of water and rejects heat to a reservoir at the triple point of water. Find (a) Heat rejected (b) work done (c) Therm.

=> Boiling point $\rightarrow 100^\circ\text{C} = 100 + 273 = 373\text{K}$

* Triple point $\Rightarrow 273.16\text{K}$



$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

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

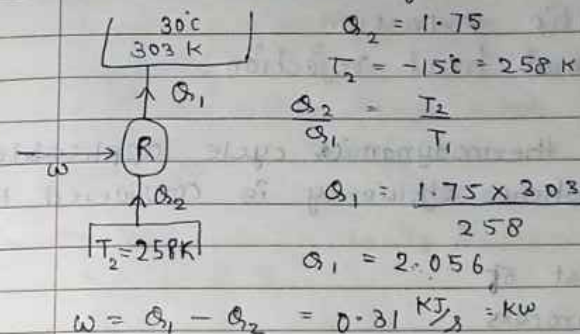
$$Q_2 = 200 \times \frac{273.16}{373} = 146.4\text{J}$$

$$W = Q_1 - Q_2 = 200 - 146.4 = 53.6\text{J}$$

$$\eta = \frac{W}{Q_1} = \frac{53.6}{200} = 26.8\%$$

Q. ② A domestic food freezer maintain a temp. of -15°C . The ambient air temp. is 30°C . If heat leaks into the freezer at continuous rate $1.75 \frac{\text{KJ}}{\text{s}}$.

What is the heat power necessary to pump this heat out continuously.



$$Q_2 = 1.75$$

$$T_2 = -15^\circ\text{C} = 258\text{K}$$

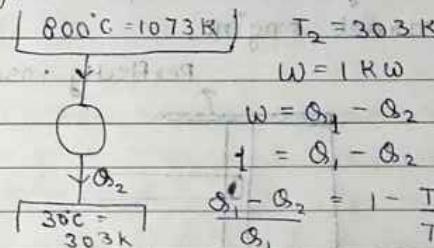
$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

$$Q_1 = \frac{1.75 \times 303}{258}$$

$$Q_1 = 2.056$$

$$W = Q_1 - Q_2 = 0.31 \frac{\text{KJ}}{\text{s}} = \text{KW}$$

Q. ③ A cyclic heat engine between a source temp. of 800°C and a sink temp. 30°C . what is the least rate of heat rejection per KW net output of the engine.



$$T_2 = 303\text{K}$$

$$W = 1\text{KW}$$

$$W = Q_1 - Q_2$$

$$1 = Q_1 - Q_2$$

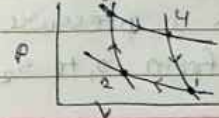
$$\frac{Q_1 - Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$\frac{1}{Q_1} = 1 - 0.282 = 0.718$$

$$Q_1 = 1.392 \frac{\text{KJ}}{\text{sec}}$$

$$Q_2 = Q_1 - 1 = 0.392 \frac{\text{KJ}}{\text{sec}}$$

* Carnot cycle :- It is a reversible cycle in which all process constituting the cycle are reversible.



Entropy $\rightarrow$ Work is done by gas.

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- (1-2) Rev. adiabatic compression
- (2-3) Rev. isothermal heat addition
- (3-4) Rev. adiabatic expansion
- (4-1) Rev. isothermal heat rejection.

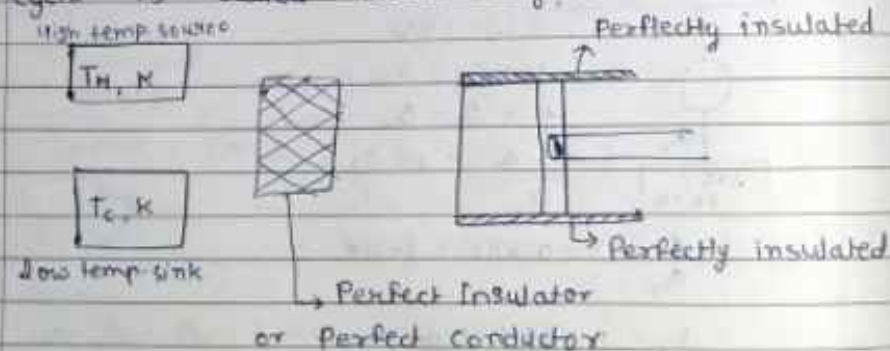
It is a thermodynamics cycle, applicable for perfect gas where efficiency is considered to be minimum.

Carnot cycle consist of

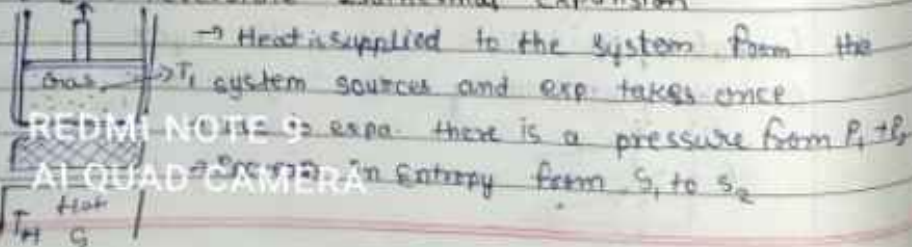
- $\rightarrow$ Two isothermal process
- $\rightarrow$ Two adiabatic process

* All 4 process are reversible and therefore it is the most efficiency cycle, as it involves no losses.

The theoretical heat engine that operates on this cycle is called Carnot engine.



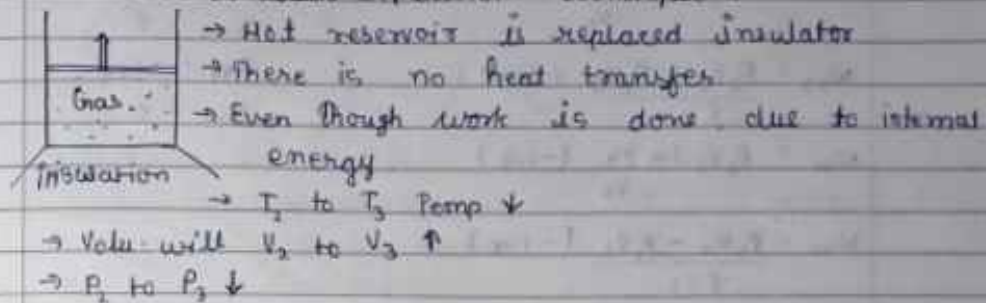
Process 1-2 $\rightarrow$ Reversible Isothermal Expansion



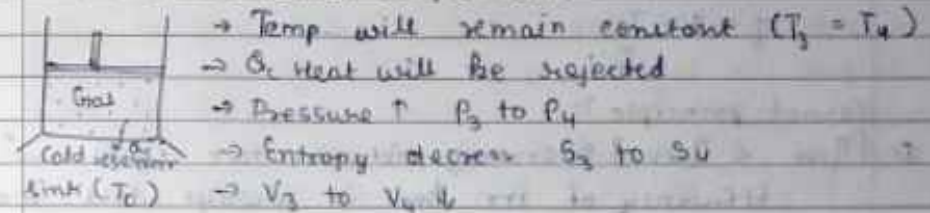
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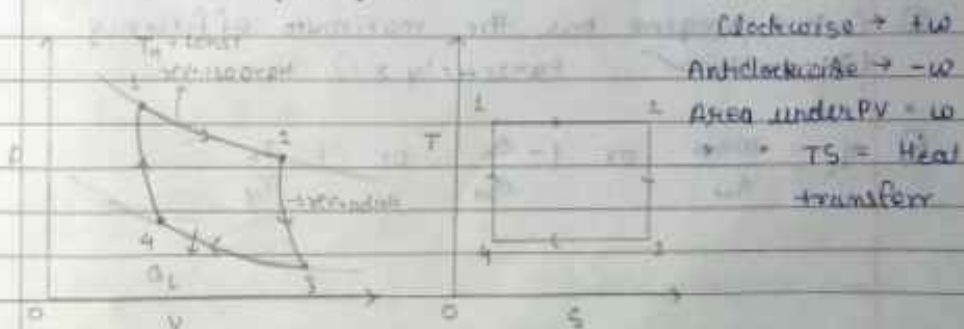
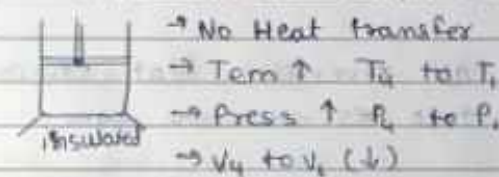
(2) 2-3 (Rev. adiabatic expansion) Isentropic :-



(3) 3-4 (Rev. Isothermal compression) :-



(4) 4-1 (Rev. adiabatic compression) :-



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Work done

$$W_{12} = P_1 V_1 \ln \frac{V_2}{V_1} \quad (+ive)$$

$$W_{23} = \frac{P_2 V_2 - P_3 V_3}{\gamma - 1} \quad (+ive)$$

$$W_{34} = P_3 V_3 \ln \frac{V_4}{V_3} \quad (-ive)$$

$$W_{41} = \frac{P_4 V_4 - P_1 V_1}{\gamma - 1} \quad (-ive)$$

$$\eta = \frac{\text{Net work done}}{\text{Heat supplied}} = \frac{W_{12} + W_{23} + W_{34} + W_{41}}{Q_{12} + Q_{34}}$$

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

Cannot principle :-

- ① $[\eta_{irr} < \eta_{rev}]$ operating between two cycle.

Efficiency of irr. heat is always less than the η of revers heat engine operating between two same reservoir.

- ② The efficiencies of all reversible heat engine operating between the same two reservoir are same.

- ③ Carnot engine has the maximum efficiency (Theoretical ✓, Practical x)

$$\eta_c = \frac{W_{net}}{Q_H} \quad \text{or} \quad 1 - \frac{Q_L}{Q_H} \quad \text{or} \quad 1 - \frac{T_L}{T_H}$$

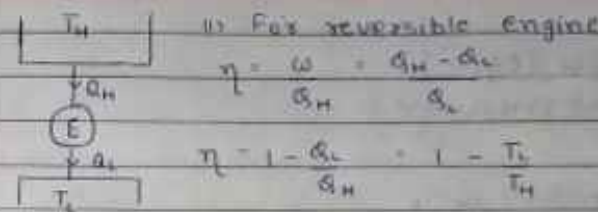
Heat transfer

$$Q_{12} = W_{12}$$

$$Q_{23} = 0$$

$$Q_{34} = W_{34}$$

$$Q_{41} = 0$$



Temp must be in Kelvin

$\eta > \eta_{rev} \rightarrow$ Impossible

$\eta = \eta_{rev} \rightarrow$ Reversible Engine

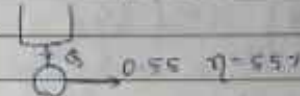
$\eta < \eta_{rev} \rightarrow$ Irreversible

- Q An inventor claims that his new concept of an engine while working between 27°C and 327°C rejects 45% of heat absorbed his new concept of engine is then equivalent to which of the following engine

- (a) Carnot (b) Otto (c) Diesel (d) Impossible (e) Otto

$$\eta_{irr} = 1 - \frac{300}{600} = 50\%$$

$\eta > \eta_{rev} =$ impossible



* Clausius inequality: $\oint \frac{dQ}{T} \leq 0$

The cyclic integral of $\frac{dQ}{T} \leq 0$

- (A) Reversible Cycle $\rightarrow$

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

For reversible eng. $\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$

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

$$\oint \frac{dQ}{T} = 0$$

For reversible engine



(B) Irreversible Engine (cycle)

$$\oint \frac{\delta Q}{T} < 0 \rightarrow \text{irreversible}$$

$$\oint \frac{\delta Q}{T} > 0 \rightarrow \text{impossible cycle}$$

* Entropy :- 1-a-2-b-1

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

$$\left(\frac{\delta Q}{T} \right)_{1a2} + \left(\frac{\delta Q}{T} \right)_{2b1} = 0 \quad \text{--- (1)}$$

1-a-2-c-1

$$\left(\frac{\delta Q}{T} \right)_{1a2} + \left(\frac{\delta Q}{T} \right)_{2c1} = 0 \quad \text{--- (2)}$$

eq. (1) - eq. (2)

$$\left(\frac{\delta Q}{T} \right)_{2b1} - \left(\frac{\delta Q}{T} \right)_{2c1} = 0$$

$$\left(\frac{\delta Q}{T} \right)_{2b1} = \left(\frac{\delta Q}{T} \right)_{2c1}$$

$\left(\frac{\delta Q}{T} = ds \right)$ Though path B and C are diff. but end points are same and the quantity $\frac{\delta Q}{T}$ is independent

of path and depends only on the end points. There $\left(\frac{\delta Q}{T} \right)_{\text{rev}}$ must represent a change in property and property is known as entropy.

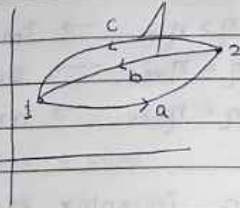
For irreversible path :-

1-a-2-c-1

$$\oint_{\text{irr.}} \frac{\delta Q}{T} < 0$$

$$\left(\frac{\delta Q}{T} \right)_{1a2} + \left(\frac{\delta Q}{T} \right)_{2c1} < 0 \quad \text{--- (1)}$$

reversible path



1-a-2-b-1

$$\oint \frac{\delta Q}{T} = 0, \quad \left(\frac{\delta Q}{T} \right)_{1a2} + \left(\frac{\delta Q}{T} \right)_{2b1} = 0$$

$$\left(\frac{\delta Q}{T} \right)_{1a2} = - \left(\frac{\delta Q}{T} \right)_{2b1} \quad \text{--- (2)}$$

Putting the value of (2) in (1)

$$- \left(\frac{\delta Q}{T} \right)_{2b1} + \left(\frac{\delta Q}{T} \right)_{2c1} < 0$$

$$\left(\frac{\delta Q}{T} \right)_{2c1} < \left(\frac{\delta Q}{T} \right)_{2b1}$$

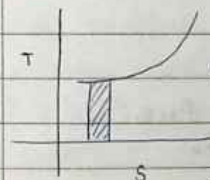
$$\left(\frac{\delta Q}{T} \right)_{\text{irr.}} < \left(\frac{\delta Q}{T} \right)_{\text{rev.}}$$

$$\boxed{\left(\frac{\delta Q}{T} \right)_{\text{irr.}} < ds}, \quad \boxed{ds > \left(\frac{\delta Q}{T} \right)_{\text{irr.}}}$$

The change in entropy for a process is greater than or equal $\left(\frac{\delta Q}{T} \right)$, the equality exists if the process is reversible.

$$\boxed{ds \geq \frac{\delta Q}{T}}$$

* Const. Volum. and Con. pressure on T-S diagram :-



① Area under T-S diagram when projected on entropy axis gives the heat interaction for a process



② Net heat interaction

$$\sum W = \sum Q \text{ (work interaction)}$$

$$\begin{aligned} \delta Q &= \delta U + \delta W \\ T \delta S &= \delta U + P \delta V \quad (\text{constant Vol.}) \\ T \delta S &= C_v dT \\ \left(\frac{dT}{dT} \right)_{\delta S} &= \frac{T}{C_v} \end{aligned}$$

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

Constant Pressure: $\delta Q = \delta U + \delta W$

$$\delta Q = dh - V \delta P$$

$$(\because h = U + PV, \quad dh = dU + P dV + V dP)$$

$$T dS = dh$$

$$T dS = C_p dT$$

$$\frac{dT}{dT} = \frac{T}{C_p}$$



* T-S relation for ideal gas:-

$$T dS = dU + P dV$$

$$\text{ideal } dU = C_v dT$$

$$T dS = C_v dT + P dV$$

$$dS = C_v \frac{dT}{T} + \frac{P}{T} dV$$

$$P V = R T \quad \frac{P}{T} = \frac{R}{V}$$

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

$$S_2 - S_1 = C_v \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right) \quad \text{Constant Press.}$$

$$R = C_p - C_v$$

$$T dS = dh - V dP$$

$$\text{ideal } dh = C_p dT$$

$$dS = C_p \frac{dT}{T} - \frac{V dP}{T}$$

$$(\because P V = R T)$$

$$\frac{V}{T} = \frac{R}{P}$$

$$S_2 - S_1 = C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right) \quad \text{constant Volume}$$

* Entropy Analysis:- The entropy of the system can change due to three reasons:-

- ① Mass interaction} external interaction
- ② Heat interaction}
- ③ Entropy Generation} Internal

→ Entropy Generation:- It is a major of the magnitude of the irreversibility present during the process $(\delta S)_{gen}$

$$\text{Total Entropy} \quad dS = \left(\frac{\delta Q}{T} \right) + (\delta S)_{gen}$$

Adiabatic process:- $\delta Q = 0$ $(\delta S) = \text{true}$

$$\text{Isolated system (Universal)} \quad dS = \frac{\delta Q}{T} + (\delta S)_{gen}$$

$$\begin{aligned} (dS)_{univ} &\geq 0 \\ \text{reversible} &= 0 \quad \rightarrow \text{irrev } dS > 0 \end{aligned}$$

- ① An adiabatic Vessel contain 2kg of water 25°C. By Paddle wheel work transfer, the temp of water is increased to 30°C. If the specific heat of water 4.187 kJ/kg°C Find the entropy change of univ.

$$m = 2 \text{ kg}$$

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$T_2 = 30 + 273 = 303 \text{ K}$$

$$dS = \left(\frac{\delta Q}{T} \right) + (\delta S)_{univ}$$

$$(\Delta S)_{univ} = (\Delta S)_{system} + (\Delta S)_{surround}$$

$$(\Delta S)_{surround} = 0$$

$$1 \text{ bar} = 10^5 \text{ Pascal}$$

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$$(\Delta S)_{\text{system}} = \int_1^F m c \frac{dT}{T}$$

$$= \int_{298}^{303} 2 \times 4.187 \frac{dT}{T}$$

$$= 2 \times 4.187 \times \ln\left(\frac{T_2}{T_1}\right) = 0.139$$