

Module - I

Thermodynamics

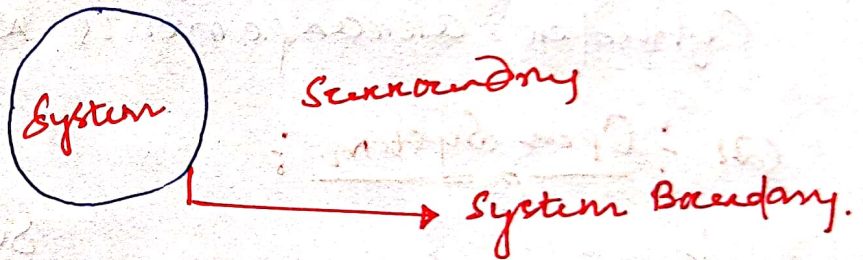
Defⁿ: It is a branch of science that deals with energies associated with heat.

Basically, it dictates the conversion of heat energy into other form of energy.

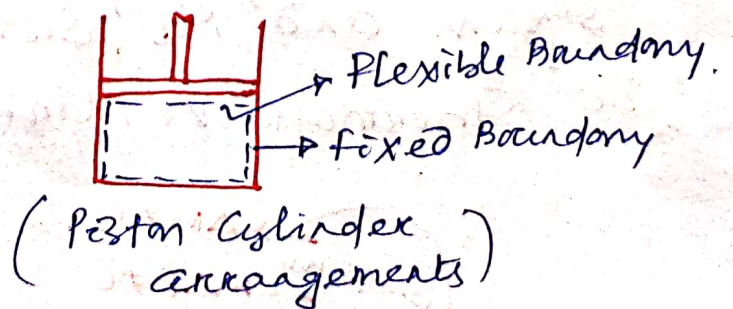
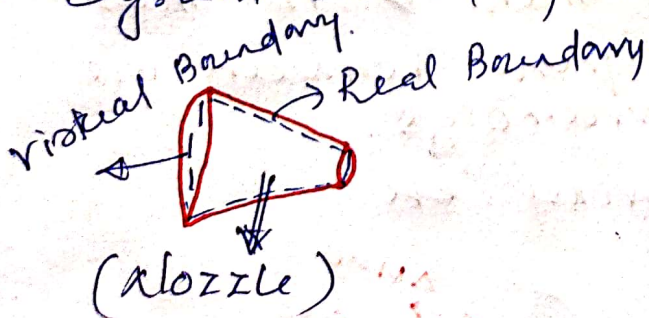
Systems:

Thermodynamic system can be defined as any part of universe under consideration for the purpose of study and analysis.

* Anything external to the system called as its surroundings.



- * System + Surroundings = Universe.
- * System is separated from surroundings by the system boundary.
- * System boundary may be real or virtual.
- * System boundary may be fixed or flexible.



Types of T.D Systems

In thermodynamics there are 3 types of systems available.

These are

- (1) Closed system
- (2) Open system
- (3) Isolated system

(1) Closed System :-

In closed systems there is no mass interaction between the system and its surroundings but energy interaction is there.

Examples

(1) Electric bulbs (2) Mobile phones (3) piston & cylinder arrangements without valves etc.

(2) Open System :-

In open systems there is both mass and energy interaction between the system and its surroundings takes place.

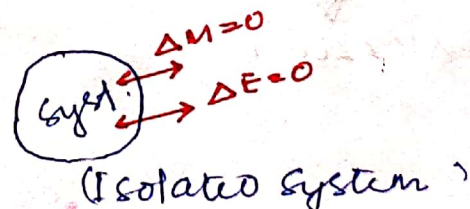
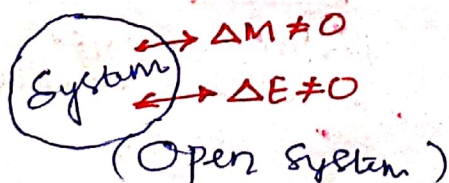
Ex-

Air compressors piston-cylinder with valves etc.

(3) Isolated Systems :-

In isolated systems there is no mass and energy interactions between the system and its surroundings.

Ex. Thermoflasks, Universe etc.



TD Properties:-

TD properties are point on state functions, since for a given state, there is a definite value for each property.

* All properties are macroscopic in nature.

Classification of TD properties:-

TD Properties

Extensive properties

* These properties are depends on mass of the system.
Ex- Mass, volume, Energy, Enthalpy, Entropy etc.

Intensive Properties

* These properties are independent of mass of the system.
Ex- pressure, Temp^r etc.

** All specific extensive properties (Per unit mass, Per unit area, Per unit vol^m) are intensive properties.

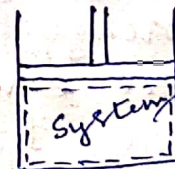
Ex- Density, Specific vol^m, specific Enthalpy, etc.

State of TD:-

A thermodynamic state of a system is its condition at specific time, that is fully identified by values of a suitable set of parameters known as properties.

Expt²

At a specific time, the system in the piston-cylinder device is assigned with x, y & z units to its properties pressure, temperature, & volume respectively, called the state of that system.



At state-1
Let

$$\begin{pmatrix} P = x \\ T = y \\ V = z \end{pmatrix}$$

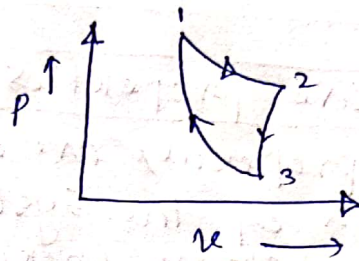
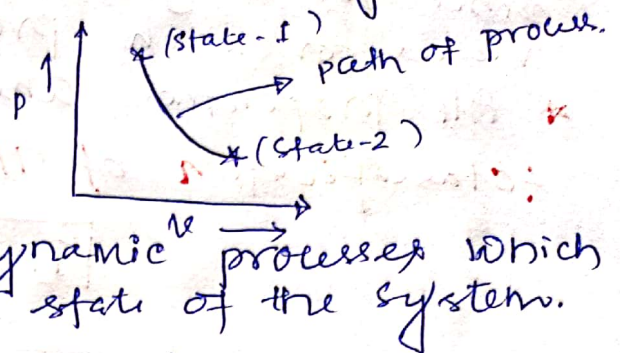
Thermodynamic process:-

When a system changes its state from one to another called a thermodynamic process.

Thermodynamic cycle:-

A thermodynamic cycle is a series of thermodynamic processes which returns to its initial state of the system.

Here, 1-2-3-1 is a thermodynamic cycle.



Energy:- (E)

Energy = Microscopic Energy + Macroscopic Energy

$$E = E_{\text{micro}} + E_{\text{macro}}$$

$$E_{\text{macro}} = \text{Kinetic Energy} + \text{Potential Energy}$$
$$= E_k + E_p$$

Internal Energy:- (U)

It is the sum of all microscopic form of energy. i.e. sum of Intermolecular kinetic energy, Intermolecular potential energy, Intermolecular rotational energy etc.

* For an ideal gas internal energy is a function of temperature.

$$U = f(T)$$

* Its SI unit = J or kJ

* It is an extensive property.

* Specific internal energy is an intensive property.

Enthalpy (H) :-

It is defined as the sum of internal energy and product of pressure and volume of a system.

$$H = U + PV$$

P = Pressure
 V = Volume
 U = Internal Energy

- * Its an extensive property.
- * Its SI unit = J or kJ
- * Specific enthalpy (h) = $\left(\frac{H}{M}\right) \rightarrow$ Enthalpy per unit mass.

$$h = u + pv$$

- * Specific enthalpy is an extensive property. $\left. \begin{array}{l} u = \frac{U}{m} \rightarrow \text{G. I. E} \\ v = \frac{V}{m} \rightarrow \text{sp. vol}^m \end{array} \right\}$
- * Its SI unit \rightarrow J/kg or kJ/kg

Laws of Thermodynamics :-

There are three different laws of thermodynamics are available.

- (1) Zeroth Law of Thermodynamics
- (2) First " " "
- (3) Second " " "

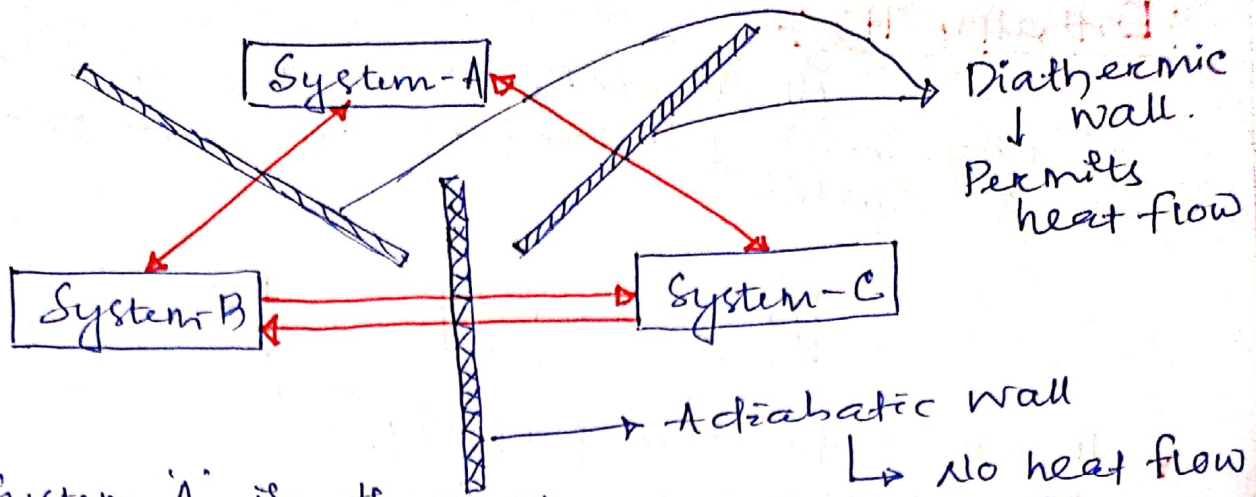
Zeroth Law of Thermodynamics :-

Statement:

It states that, "If two thermodynamic systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other."

- * Temperature is a thermodynamic property derived from the Zeroth Law of Thermodynamics.
- * Its a fundamental law of thermodynamics.

Expf:



If System 'A' is in thermal equilibrium with System 'B' then $T_A = T_B$

Again, If System 'A' is in thermal equilibrium with System 'C' then $T_A = T_C$

Then, $T_B = T_C$ as System 'B' and System 'C' are separated by an adiabatic wall.

First Law of Thermodynamics :-

First Law of thermodynamics is also known as Law of conservation of energy, states that energy can neither be created nor destroyed, energy can only be transferred from one form to another.

For a TD cycle :-

For a TD cycle, Net amount of work interactions is equal to the net amount of heat interactions

i.e

$$\boxed{\sum Q = \sum W}$$

Q - Heat transfer
 W - Work transfer

For a TD process :-

For a TD process, the difference of heat interactions and work interactions is equal to the change in energy of the system.

i.e

$$\boxed{\sum Q - \sum W = \Delta E}$$

We know

$$E = KE + PE + IE$$
$$= E_k + E_p + U$$

By considering a stationary closed system

$$E_k = 0 \quad E_p = 0$$

Also

1st Law of TD

then

$$E = U$$

By considering

$$\sum Q - \sum W = \Delta U$$

an infinitesimal amounts

$$dQ - dW = dU$$

* Properties are state variables, exact differentials and point functions i.e independent of path of the process.

i.e Internal energy is a property of system so, its differential is exact (dU).

* Heat and work transfers are not properties of the system, they are path functions and inexact differentials i.e (dW, dQ).

Energy transfers:-

These energies are not possessed by the system at a particular state. These are comes into the picture when the change of state occurs in the system. These are boundary phenomena.

Ex - Heat transfer, Work transfer.

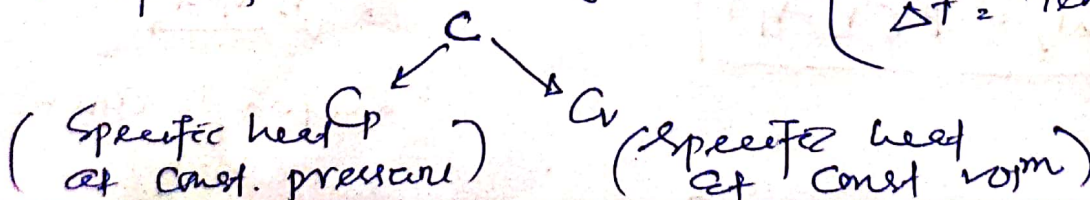
Heat transfer :- (Q)

The energy transfer takes place by virtue of temperature difference between system and surroundings called as heat transfer.

$$Q = mc \Delta T$$

Q = Total heat
 m = mass of the substance
 c = specific heat
 ΔT = temp^r gradient

* Specific heats for gases



* Specific heat for solid/liquid = (C_p/C_v) - only one.

* Unit of total heat (Q) = J or kJ

Unit of specific heat = J/kgK or kJ/kgK.

Work transfer :- (W)

Any form of energy transfer betⁿ system and surroundings other than heat transfer is called as work transfer.

These are

- (1) Displacement work (2) Flow work (3) Elastic work
- (4) Shaft work etc.

* Unit = J or kJ

Displacement work (Non-flow work)

We know.

$W = F \cdot x$

$P = F/A$
 $F = P \cdot A$

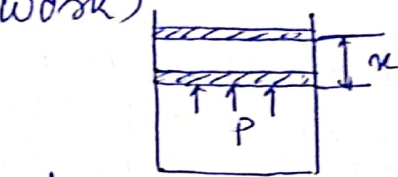
$= P \cdot A \cdot x$

$|W| = P \cdot V$

For infinitesimal work

$dw = P dv$

Let work ${}_1W_2 = \int_1^2 P dv$



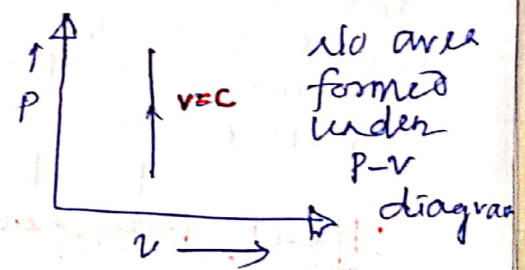
Let
 P = Internal pressure
 A = Cross-sectional area of piston.
 x = Displacement due to increase in pressure

→ for closed system only.

* (1) for Isochoric process $V = c$

$V = c$
 $dv = 0$

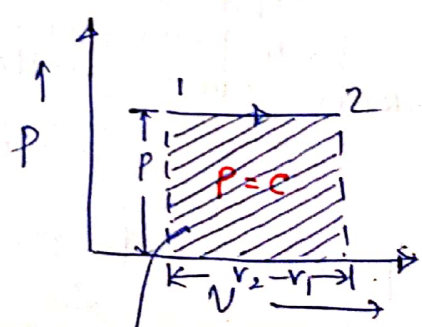
${}_1W_2 = 0$



(2) for Isobaric process ($P = c$)

${}_1W_2 = \int_1^2 P dv$
 $= P \int_1^2 dv$

${}_1W_2 = P (v_2 - v_1)$



Rectangle area = $P(v_2 - v_1)$

(3) For Bothermal process ($T=c$)

$T=c$
We know combined gas eqn

$$\frac{PV}{T} = c \quad \text{--- (1)}$$

$$P_1 V_1 = P_2 V_2 = c$$

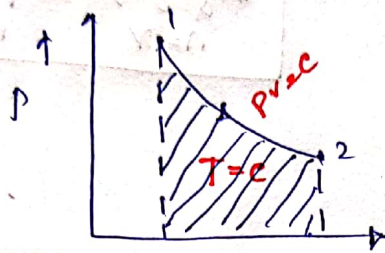
From (1) $PV=c$ as ($T=c$)

Hyperbolic function.

$$W_2 = \int_1^2 \frac{c}{v} dv = c \ln(v_2/v_1) = P_1 V_1 \ln(v_2/v_1)$$

$$= nR \theta_1 \ln(v_2/v_1)$$

$$= P_1 V_1 \ln(P_1/P_2)$$



(4) Adiabatic process ($Q=0$)

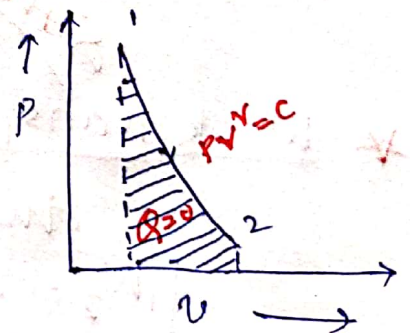
For an adiabatic process $PV^\gamma = c$

γ = adiabatic constant.
 γ = 1.33 - Triatomic gases
 γ = 1.4 - Diatomic
 γ = 1.67 - Monoatomic gases ($\gamma = \frac{C_p}{C_v}$)

$$W_2 = \int_1^2 \frac{c}{v^\gamma} dv = c \int_1^2 v^{-\gamma} dv = c \left[\frac{v^{-\gamma+1}}{-\gamma+1} \right]_1^2$$

$$= c \left[\frac{v_2^{-\gamma+1} - v_1^{-\gamma+1}}{1-\gamma} \right]$$

$$W_2 = \frac{P_2 V_2 - P_1 V_1}{1-\gamma}$$

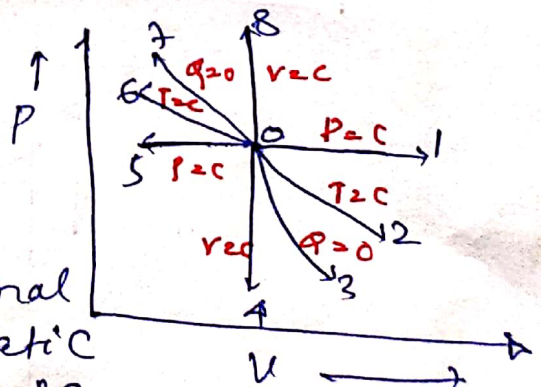


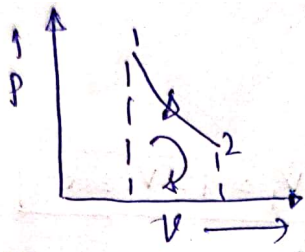
(5) For Polytropic Process

$$PV^n = c$$

$$W_2 = \frac{P_2 V_2 - P_1 V_1}{1-n}$$

For $n=0 \rightarrow P=c \rightarrow$ Isobaric
 $n=1 \rightarrow PV=c \rightarrow$ Bothermal
 $n=\gamma \rightarrow PV^\gamma=c \rightarrow$ Adiabatic
 $n=\infty \rightarrow V=c \rightarrow$ Isochoric





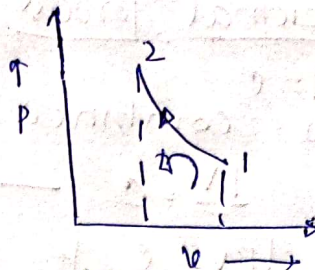
(Expansion Process)

(Clock-wise)

$$W_{\text{exp}} \propto \frac{1}{n}$$

$$W_{p=c} > W_{v=c}$$

$n=0 \qquad n=1$



(Compression Process)

(Anti-clockwise)

$$W_{\text{comp}} \propto n$$

$$W_{q=0} > W_{T=c}$$

$n=\gamma \qquad n=1$

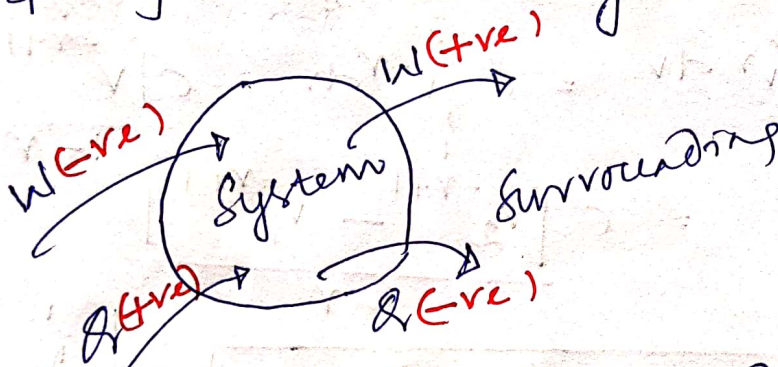
Sign Convention :-

Work transfer :-

Work done by the system on the surroundings = +ve
 Work done on the system by the surroundings = -ve

Heat transfer :-

Heat supplied to the system from the surroundings = +ve
 Heat rejected from the system to the surroundings = -ve



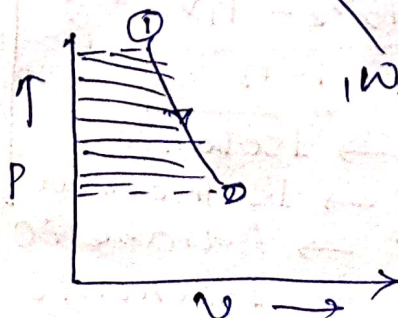
* Work transfer for Open system (Flow work)

$$dw = -v dp$$

$$W_2 = - \int v dp$$

-ve sign is to counter balance the negative pressure.
 i.e. Flow taking place in decreasing order of pressure. ($dp = -ve$)

$W_2 = \text{Area under } p-v \text{ diagram w.r.t } p \text{ pressure axis.}$



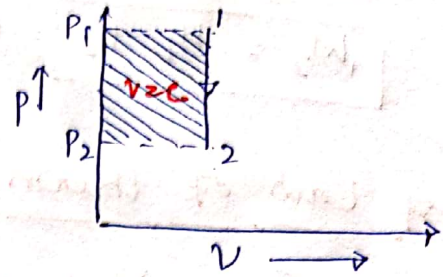
Flow work $\boxed{W_2 = -\int_1^2 v dp}$

(1) for Isochoric process ($v=c$)

$v=c$

$W_2 = -v(P_2 - P_1)$

$\boxed{W_2 = v(P_1 - P_2)}$



(2) for Isobaric process ($P=c$)

$P=c, dp=0$

$W_2 = -\int v dp$

$= 0$

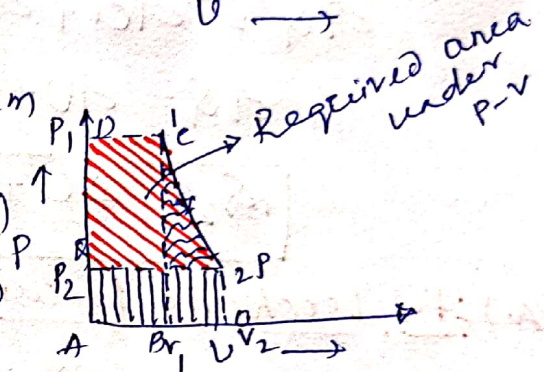
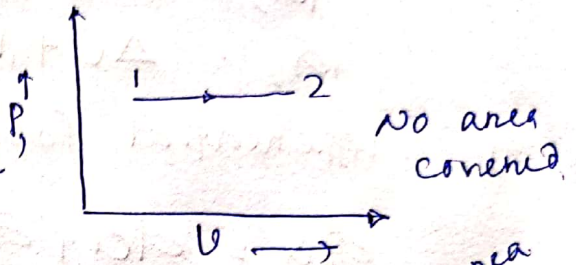
(3) for Isothermal process ($T=c$)

Area under P-v diagram with 'P' axis

= Area under P-v diagram with 'V' axis

+ Area of ABCD (□)

- Area of AOPQ (□)



$\int v dp = \int P dv + P_1 V_1 - P_2 V_2$

So $\boxed{\int v dp = \int P dv}$

But in Isothermal process

$\boxed{P_1 V_1 = P_2 V_2}$

i.e Flow work = Nm-Flow work \rightarrow for Isothermal process.

(4) for adiabatic process ($Q=0$)

$W_2 = -\int v dp \rightarrow$ Nm-Flow work expression.

$\int v dp = \int P dv + P_1 V_1 - P_2 V_2$

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

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

$= mR(T_1 - T_2) \frac{\gamma}{\gamma - 1} = m c_p (T_1 - T_2)$

for Ideal gas
 $PV = mRT$

$R = \text{Ch. gas constant}$

$$C_p = \frac{\gamma}{\gamma - 1} R \quad \text{--- (See details in prop. of Ideal gases)}$$

$${}_1W_2 = H_1 - H_2 = \text{Change in enthalpy}$$

$$\Delta H = m c_p \Delta T \quad \rightarrow \text{(Detail in Prop. of Ideal gases)}$$

∴ First Law of thermodynamics for closed system:

$${}_1Q_2 = \Delta E + {}_1W_2 \quad \text{--- (General Expression.)}$$

$${}_1Q_2 = \Delta U + {}_1W_2 \quad \text{--- (By neglecting K.E and P.E of the system)}$$

In differential form \rightarrow (Taking only Internal energy into consideration.)

$$dQ = dU + dW$$

$$dQ = dU + P dV \quad \rightarrow \text{(Taking only displaced work)}$$

$${}_1Q_2 = \Delta U + \int P dV$$

(a) ∴ For Isochoric process:

$${}_1W_2 = \int P dV = 0$$

$${}_1Q_2 = \Delta U = U_2 - U_1$$

\rightarrow Net heat interaction of an Isochoric process is equal to the change in internal energy of the system.

(b) ∴ For Isobaric process:

$${}_1W_2 = P(V_2 - V_1)$$

$$\begin{aligned} {}_1Q_2 &= (U_2 - U_1) + P(V_2 - V_1) \\ &= (U_2 + PV_2) - (U_1 + PV_1) \end{aligned}$$

$${}_1Q_2 = H_2 - H_1 = \Delta H$$

\rightarrow Net heat interaction of an Isobaric process is equal to the change in enthalpy of the system.

(c) For an Isothermal Process:

For Ideal gases Internal energy is a function of temperature only.

$$U = f(T)$$

In isothermal process $\Delta U = mRv(T_2 - T_1)$ — (Details in prop. of Ideal gases).

$$T_1 = T_2$$

Also 1st Law of TD $\Delta U = 0$
 $U_1 = U_2$

$$Q_2 = \Delta U + W_2$$

$$Q_2 = W_2 = P_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$$

Net heat interaction converted to work interaction in an Isothermal process as no change in internal energy takes place within the system.

(d) For Adiabatic Process:

$$Q = 0$$
$$Q_2 = \Delta U + W_2$$

$$W_2 = -\Delta U = U_1 - U_2$$

In an adiabatic process work is done by the system in the expense of its internal energy.

WAB: Numericals regarding 1st Law of thermodynamics solved in classrooms and also in assignments. please go through that!

Glimpses of 1st Law of thermodynamics:

* A PD property called Internal energy is derived from 1st Law of TD.

* It's a Law of Conservation of energy.

* It's a quantitative Law i.e. It only tells that quantities are conserved if the process takes place.

* It doesn't deal with the quality of energy.

* It gives no information about the feasibility of a process.

These are the limitations of 1st Law of TD.

:- First Law of TD for Open System :-

In an Open System flow takes place from system to surroundings or vice versa.

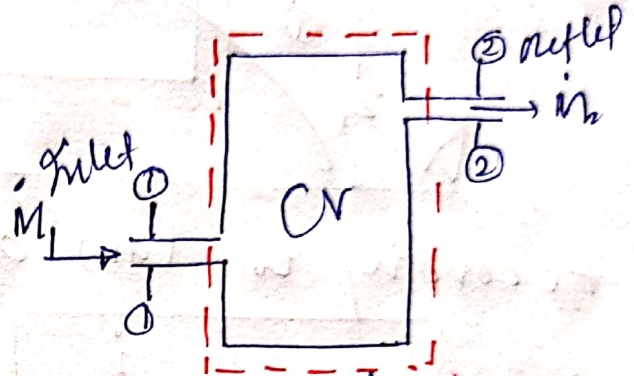
There are 2 types of flow occurs.

(1) Steady Flow :-

In a fluid flow if the fluid properties and flow properties at a particular location doesn't change with change in time it is called as a steady flow, otherwise it is called as unsteady flow.

Conservation of Mass

Let \dot{m}_1 & \dot{m}_2 are rate of mass flow at the inlet and outlet.



For steady flow

$$\dot{M}_{CV} = 0$$

→ No accumulation of mass within the control volume.

Control Surface
CV = Control Volume

So,

$$\dot{m}_1 = \dot{m}_2$$

$$\rho_1 A_1 V_1 = \rho_2 A_2 V_2$$

$$A_1 V_1 = A_2 V_2$$

A_1 & A_2 → Cross-sectional area at inlet and outlet

V_1 & V_2 → velocities of flow at 1 & 2

ρ_1 & ρ_2 → Densities at 1 & 2 respectively.

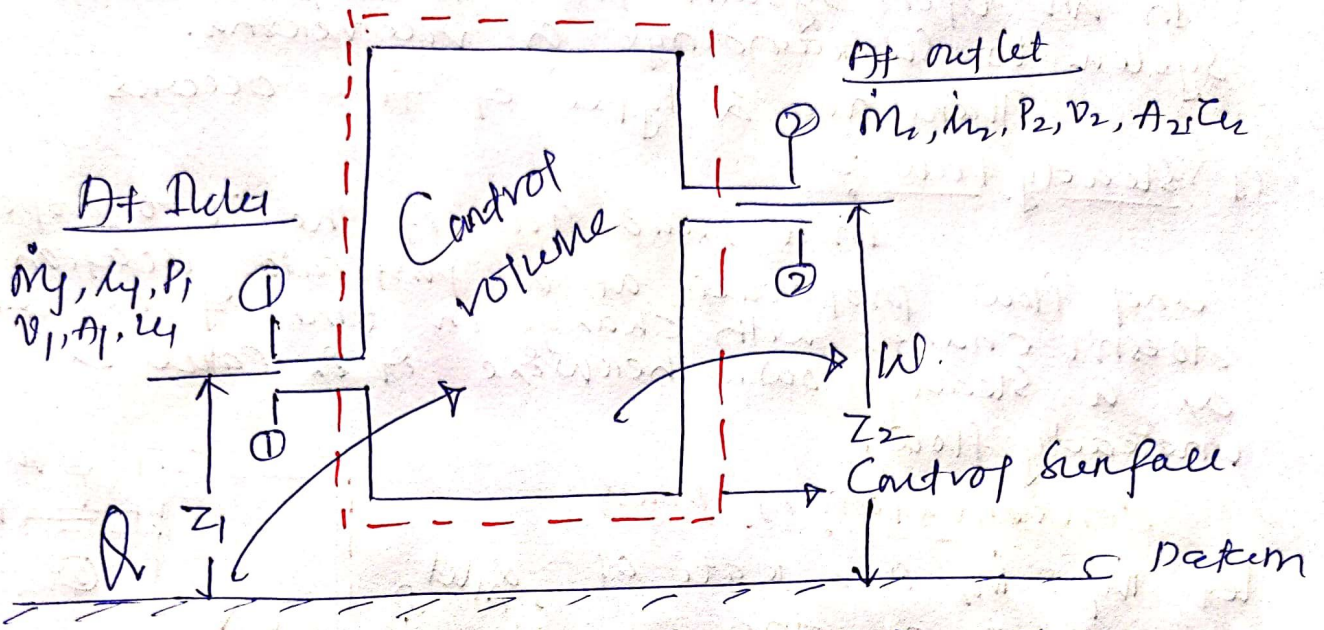
If the fluid is incompressible one

i.e. $\rho_1 = \rho_2$ → Density is constant.

then $A_1 V_1 = A_2 V_2$

→ It is called as eqn of Continuity.

Steady flow energy equation



According to Law of Conservation of energy

$$\dot{E}_{cv} = \dot{E}_1 - \dot{E}_2$$

But for steady flow $\dot{E}_{cv} = 0 \rightarrow$ No accumulation of energy within the control volume.

Now.

$$\dot{E}_1 = \dot{E}_2$$

$$\dot{m}_1 \left(h_1 + \frac{v_1^2}{2} + g z_1 \right) + \dot{Q} = \dot{m}_2 \left(h_2 + \frac{v_2^2}{2} + g z_2 \right) + \dot{W}$$

But for steady flow

$$\dot{m}_1 = \dot{m}_2$$

$$\dot{Q} - \dot{W} = \dot{m} \left[(h_2 - h_1) + \frac{v_2^2 - v_1^2}{2} + g(z_2 - z_1) \right]$$

\rightarrow **SFEE**
 \hookrightarrow steady flow energy equation.

****** Here specific enthalpy h (J/kg)
 So don't mess up with unit, Carefully convert it into (J/kg).

Second Law of Thermodynamics :-

- * It's a qualitative law of thermodynamics i.e. it deals with the quality of energy transfers.
- * A thermodynamic property called entropy derived from the 2nd Law of TD.
- * It dictates the direction of process take place.

Statements :-

(a) Kelvin-Planck statement (For Heat Engine)

It states that, "It is impossible to devise a cyclically operating heat engine, the effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work."

- * According to KP-statement, there must be a sink to reject heat of a heat engine.
- * According to KP-statement there is no heat engine in the universe which is 100% efficient.

$$\eta_{HE} \neq 100\% \quad Q_2 \neq 0$$

→ Thermal Energy Reservoir (TER)

These are the reservoir of heat energy which has a capacity of absorbing and rejecting infinite amount of heat without altering its temperature.

- * TER are of 2 types

(1) Source (High temp. TER)
(2) Sink (Low temp. TER)

Example of Source

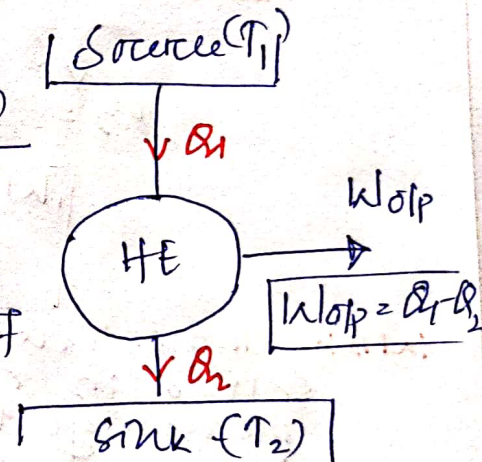
Natural :- ~~Sea~~ Sun

Man-made - furnace, Boiler etc.

Example of Sink

Natural :- Sea, Ocean, River etc.

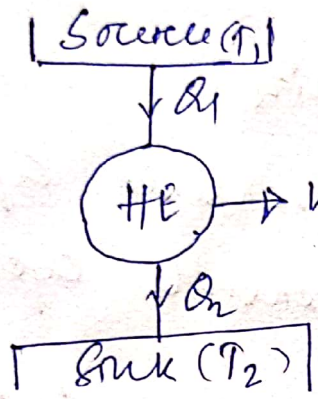
Manmade - Condenser



(b) Clausius Statement (for Heat pump and Refrigerator)

It is impossible to construct a device that operates in a cycle and whose sole effect is to transfer heat from a cooler body to a hotter body.

Heat Engine:



→ It is a thermodynamic cycle.
→ Afto 1st Law for cycle

$$Q_1 - Q_2 = W$$

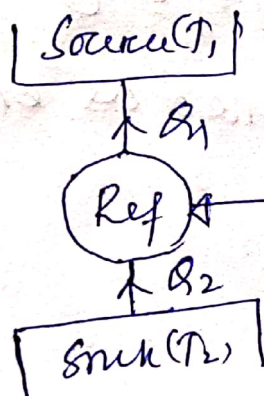
→ Thermal efficiency of HE

$$\eta = \frac{W_{op}}{Q_{sp}} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

($\eta < 1$ - always)
 $\neq 1$

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

Refrigerator:



→ Afto 1st Law of TD for a cycle

$$W_{ip} = Q_1 - Q_2$$

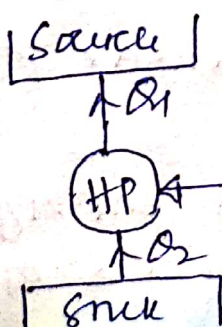
→ Co-efficient of performance COP

$$= \left(\frac{\text{Refrigerating effect}}{\text{Heat input}} \right)$$

→ $(COP)_R > 1$
 $\neq \infty$

$$(COP)_{Ref} = \frac{Q_2}{W_{ip}} = \frac{Q_2}{Q_1 - Q_2}$$

Heat Pump:



→ Afto 1st Law of TD for a cycle

$$W_{ip} = Q_1 - Q_2$$

$$(COP)_{HP} = \frac{\text{Heat pump Effect}}{W_{ip}}$$

$$(COP)_{HP} = \frac{Q_1}{Q_1 - Q_2}$$

$$\rightarrow (COP)_{HP} > 1$$

 $\neq \infty$

$$(COP)_R = \frac{Q_2}{Q_1 - Q_2}$$

Add '1' to the right side of the expression.

$$(COP)_R + 1 = \frac{Q_2 + Q_1 - Q_2}{Q_1 - Q_2} = \frac{Q_1}{Q_1 - Q_2} = (COP)_{HP}$$

So

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

∴ Clausius Inequality :-

According to Clausius inequality

$$\oint \frac{dQ}{T} < 0 \rightarrow \text{Irreversible cycle}$$

$$\oint \frac{dQ}{T} = 0 \rightarrow \text{Reversible cycle}$$

$$\oint \frac{dQ}{T} > 0 \rightarrow \text{Impossible cycle}$$

For a reversible cycle (∵ $\oint \rightarrow$ It means integration over a cycle).
We know,

$$\oint_R \frac{dQ}{T} = 0, \quad \oint [d(\text{prop})] = 0$$

Here this property is called as entropy (S)

So,

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

∴ Entropy (S) :-

Entropy is a property of thermodynamic that measures the randomness or disorderliness of the system.

* It is an extensive property of the system.

* Its SI unit = J/K or kJ/K

* Specific entropy (s) = $\frac{S}{M}$ → Intensive property

* Its unit = $\frac{J}{kg \cdot K}$ or kJ/kgK.

* We always calculate change in entropy of the system to measure the randomness of that system.

We have

$$ds = \left(\frac{dQ}{T}\right) \rightarrow \text{For reversible cycle or process}$$

→ change in entropy of a reversible process

$$\int_{s_1}^{s_2} ds = s_2 - s_1 = \int_1^2 \frac{dQ}{T}$$

$$\Delta S = s_2 - s_1 = \int_1^2 \frac{dQ}{T} \rightarrow \text{For Reversible process}$$

→ Change in entropy of an irreversible process

$$\int_{s_1}^{s_2} ds = s_2 - s_1 = \int_1^2 \frac{dQ}{T} + S_{gen}$$

$$\Delta S = \int_1^2 \frac{dQ}{T} + S_{gen}$$

(S_{gen} = Self generated entropy due to presence of internal irreversibility within the system.)

→ Entropy change of a reversible process: →
($S_{gen} > 0$ - IR process)
($= 0$ - Rev. process)

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

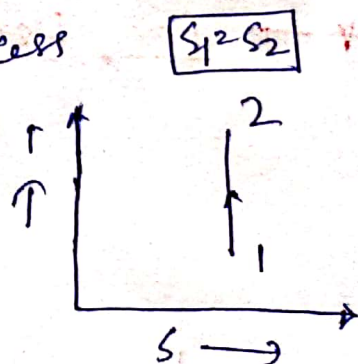
But for reversible adiabatic process

$$ds = 0$$

$$S = C$$

$$s_1 = s_2$$

$$dQ_{IR} = 0$$



★ Reversible adiabatic processes are isentropic processes, i.e. Entropy is constant.

- * Heat is a low grade energy that means the complete conversion of heat into work is not possible.
- * Heat is a dis-organised form of energy.
- * As heat is a dis-organised form of energy, Entropy transfer is associated with heat transfer only not with work transfer.
- * Work is a high grade energy that can be completely converted into heat under certain conditions.
- * Work is an organised form of energy.

$$\text{Work} \xrightarrow{\geq 100\%} \text{Heat}$$

$$\text{Heat} \xrightarrow{< 100\%} \text{Work}$$

$$\text{Entropy transfer, } ds = \frac{dQ}{T}$$

Entropy change of System :-

$(ds)_{sys} > 0 \rightarrow$ Heat added to the system
 $= 0 \rightarrow$ No heat transfer
 $< 0 \rightarrow$ Heat rejected from the system.

\rightarrow When all the processes in the system are reversible.

For Isolated system

We know

$$ds = \frac{dQ}{T} \rightarrow \text{Rev. process}$$

$$> \frac{dQ}{T} \rightarrow \text{IR}$$

But for Isolated system $dQ = 0$

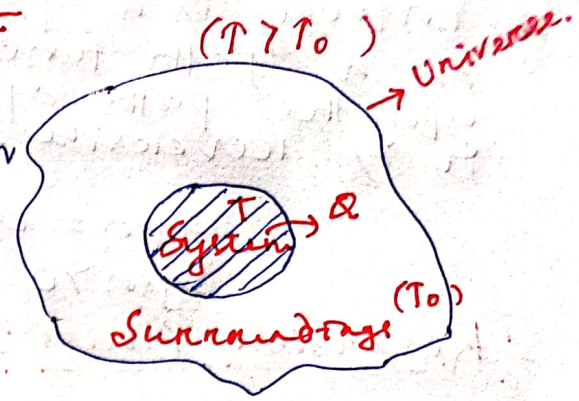
So, $(ds)_{iso} > 0$

$$\left[\begin{array}{l} ds = 0 - \text{Rev. Process} \\ > 0 - \text{IR process} \end{array} \right.$$

- * Entropy of an isolated system never decreases

∴ Entropy change of Universe:

Let. System be at tempⁿ T K and its surroundings at tempⁿ T_0 K, System rejecting ' Q ' amount of heat to the surroundings.



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

$$= -\frac{Q}{T} + \frac{Q}{T_0}$$

$$= Q \left(\frac{T - T_0}{TT_0} \right)$$

As $T > T_0$
This quantity must be greater than 0.

$$(\Delta S)_{univ} > 0$$

So

$(\Delta S)_{univ} > 0 \rightarrow$ IR process $= 0 \rightarrow$ Rev. " $< 0 \rightarrow$ Imp. "
--

* Feasibility and the direction of any TD processes can be checked & find by measuring the entropy change of the universe.

∴ Key points of Entropy:

* Area under Tempⁿ and entropy diagram represents net heat transfer with the system.

$$Q = \int T ds$$

* Energy of universe is constant but the Entropy of universe tends to maximum.

* 2nd Law of TD dictates the quality of energy i.e. quality of molecules which is compensated by increase in entropy.

- * Entropy is a point function but entropy generation is a path function because it purely depends upon the path of the process that it is reversible or irreversible.

$$S_{gen} = 0 \rightarrow \text{Rev. Process}$$

$$S_{gen} > 0 \rightarrow \text{IR Process}$$

Reversible Process:

It is a thermodynamic process in which the direction of process can be changed in opposite direction of the process occurred then the system and surroundings restored to its original state.

- Examples:- Any process which is free from friction or any other dissipative forces.
- * It is a hypothetical concept, because no process in the universe which is reversible.
- * In a TD property diagram reversible processes are represented as a solid line.
- * Integration along a path can be possible for a reversible process like $\int p dv$, $\int T ds$ etc.

Irreversible Process:

In this type of TD process, the system and its surroundings doesn't restored to its original state if the direction of process is changed in opposite direction.

- Example
 - (1) Any motion in which friction is present.
 - (2) ~~Process~~ Combustion process etc.

- * In a TD property diagram irreversible processes are represented as a dotted line.
- ** As TD properties are point functions i.e. there are independent of path of process so value of TD properties at two different states are same irrespective of Rev & IR Processes.

∴ Ideal gas :-

Any gas which obeys the ideal gas eqn is termed as ideal gas.

Condition

$$P \rightarrow 0 \quad T \rightarrow \infty$$

Ideal gas equation :

$$PV = nRT$$

$$PV = n\bar{R}T$$

$$n = \frac{m}{M} \quad R = \frac{\bar{R}}{M}$$

Where

$R \rightarrow$ Ch. gas constant

$\bar{R} \rightarrow$ Univ. gas constant

$n \rightarrow$ no. of moles

$m \rightarrow$ mass of gas

$M \rightarrow$ molecular mass of gas.

$P \rightarrow$ Pressure (Absolute)

$V \rightarrow$ volⁿ of gas

∴ Properties of Ideal gases :-

* Characteristic gas constant of ideal gases is inversely proportional to the molecular mass of the gas.

$$R = \frac{\bar{R}}{M}$$

$$\bar{R} = 8.314 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} \quad (\text{Const})$$

$$R \propto \frac{1}{M}$$

$$M_{\text{He}} = 4$$

$$M_{\text{CO}_2} = 44$$

$$R_{\text{He}} > R_{\text{CO}_2}$$

* Specific heats of ideal gases are inversely proportional to molecular mass of the gas.

We know

$$C_p - C_v = R$$

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

$$C_p = \gamma C_v$$

$C_p =$ sp. heat at const pressure.
 $C_v =$ sp. heat at const volⁿ.
 $\gamma =$ Adiabatic Const.

$$\gamma C_v - C_v = R \quad , \quad \boxed{C_v = \frac{R}{\gamma - 1}}$$

$$C_v = \frac{\bar{R}}{M(\gamma - 1)} \quad \boxed{C_v \propto \frac{1}{M}}$$

$$C_p = \gamma C_v$$

$$\boxed{C_p = \frac{\gamma \bar{R}}{M(\gamma - 1)}}$$

$$\boxed{(C_p \times C_v) \propto \frac{1}{M}}$$

$\bar{C}_p = M C_p$, $\bar{C}_v = M C_v \rightarrow$ Molar specific heats of ideal gases at constant pressure and volume respectively.

$$\boxed{\bar{C}_p - \bar{C}_v = \bar{R}}$$

Heat Capacities = $\underline{m c_p}$ & $\underline{m c_v}$. (KJ/sJ)

* Internal energy of ideal gas is a function of temperature only. $m =$ mass of gas (kg)

Heat added at constant volume

$$(Q)_{v=c} = m c_v \Delta T$$

$$(dQ)_{v=c} = m c_v dT$$

But according to 1st Law of TD for an Isochoric process $dw=0$

$$dQ = dU$$

$$m c_v dT = dU$$

$$c_v dT = \frac{dU}{m}$$

$$\boxed{c_v = \left(\frac{dU}{dT} \right)_{v=c}}$$

$$\Delta U = m c_v \Delta T$$

$$\boxed{\Delta U = f(T)} \quad (T = \text{Absolute temp.})$$

\rightarrow Change in IE is a function of temp^v only for Ideal gas.

* Enthalpy of an Ideal gas is a function of temperature only.

We know

$$H = U + PV$$

But for Ideal gas

$$PV = RT$$

$$U = f(T)$$

So,

$$H = f(T) + RT$$

$$= f(T) + g(T)$$

$H = H(T)$ → only depends on absolute temperature of the gas.

Properties of pure substance

homogeneous

A pure substance is a material with chemical composition and invariable throughout its mass.

* Pure substances may be single chemical species, like He, Ar, H₂, CO₂ etc.

* Pure substances may be a mixture with constant composition like in atmosphere

N₂ ≈ 78% → It is a homogeneous mixture of gas i.e. 1g of air contains O₂ - 21% and 1kg also contains Rest ≈ 1% the same.

* Pure substance can have multiple phases like an ice-water mixture.

Examples of pure substances

Steam, Air, Water, Ice + water, steam + water etc.

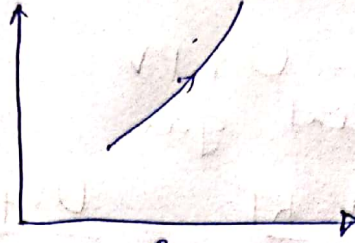
* But Air + steam is not a pure substance as it is not a homogeneous mixture.

→ In the detail study of pure substance, we take steam as the pure substance.

Steam formation

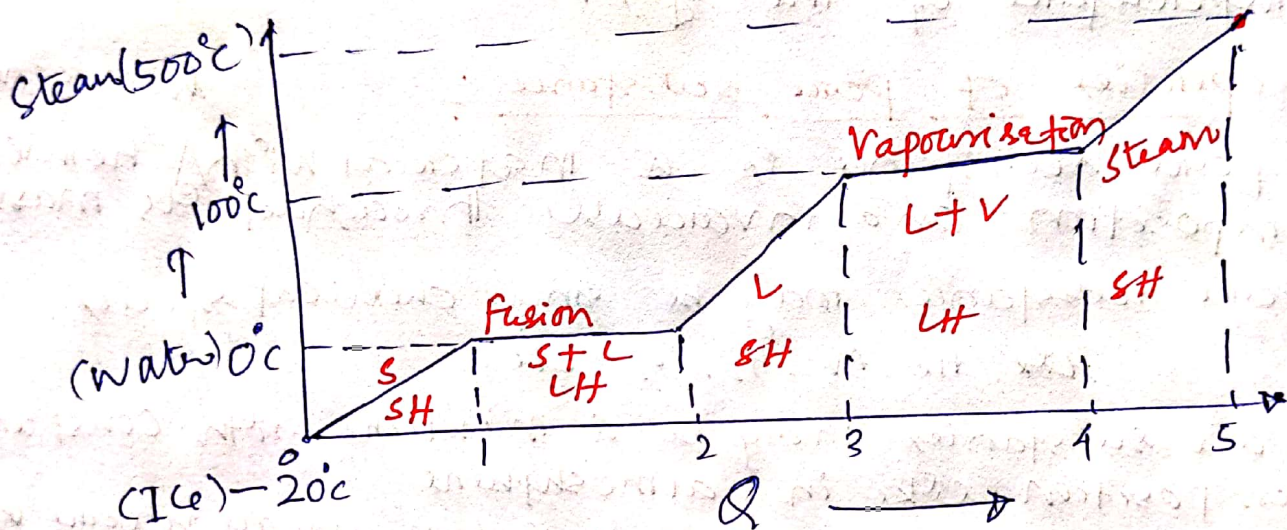
We know water boils or converts to steam at 100°C at 1 atm pressure.

- * Vapour pressure is directly proportional to saturation temp.



- .. The pressure at which liquid starts vaporizing called vapour pressure and its corresponding temperature is called as saturation temperature.

for water (ice) T-m-Q Diagram (P = 1 atm)



1. Types of Steam!

There are 2 types of steams

(1) Saturated steam or Dry separated steam

(2) Super-heated steam.

- * When saturated steam gets more heat (Degree of superheat) it becomes super-heated steam

In the above diagram.

Region - 4 represents Saturated steam

Region - 5 represents Superheated steam

and (4-5) \rightarrow Amount of heat supplied (Degree of S.H)

Quality of Steam or Dryness fraction of steam

It is defined as the ratio of mass of water vapour and the total mixture.

Mass of water vapour present in the mixture.

$$x = \frac{M_g}{M_l + M_g}$$

M_g = mass of sat. vap
 M_l = Mass of liquid
 x = Dryness fraction

Wetness fraction $(1-x)$

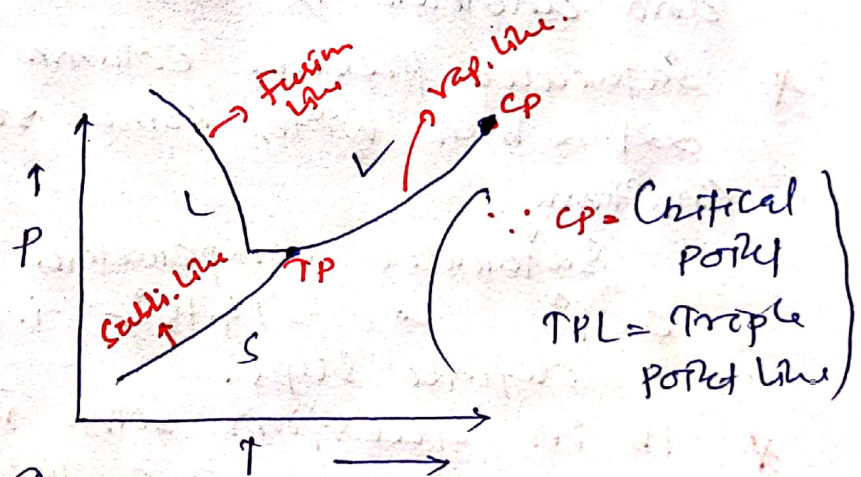
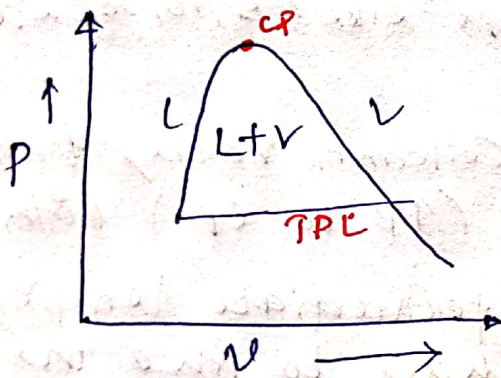
$$1-x = \frac{M_l}{M_l + M_g}$$

$x=0 \rightarrow$ For sat. liquid
 $x=1 \rightarrow$ Dry saturated vap

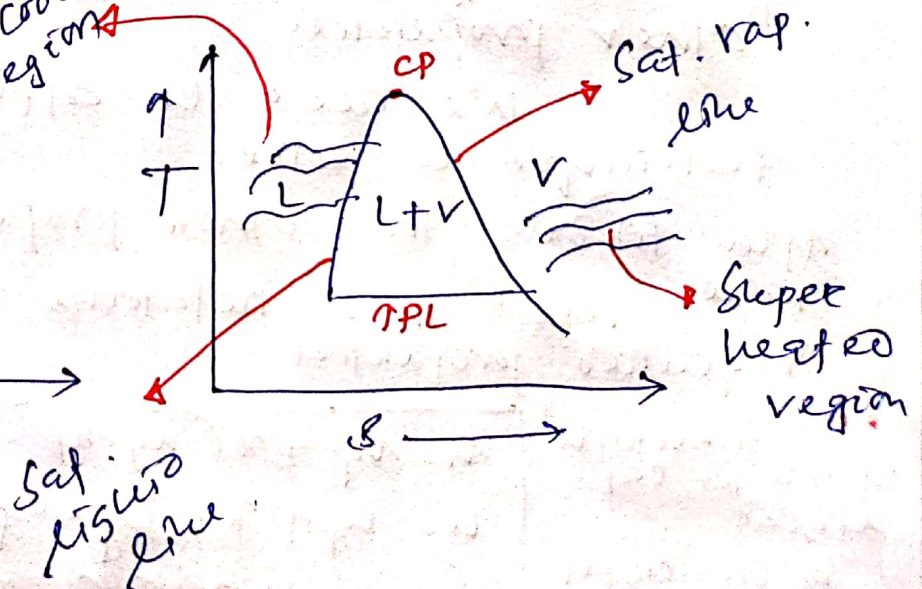
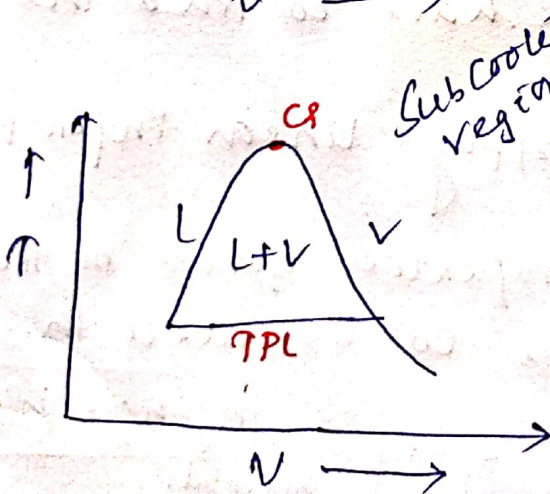
$$0 \leq x \leq 1$$

Thermodynamic Property diagrams of Pure substances.

for water-steam



\therefore CP = Critical point
 TPL = Triple point line



For Water

* Triple point :- $T = 0.01^\circ\text{C}$ to 273.16K
 $P = 611\text{Pa}$

* Critical point :- $P_c = 221.2\text{bar}$ ($\because 1\text{bar} = 10^5\text{Pa}$)
 $T_c = 374.15^\circ\text{C}$
 $v_c = 0.0037\text{m}^3/\text{kg} \rightarrow$ (specific volume)

! Use of Steam table !

$$\left(v = \frac{V}{M} = \frac{1}{\rho} \right)$$

Try to use steam table by Ramalingam.

* In steam table there are two types of tables
1 \rightarrow Saturated steam
2 \rightarrow Superheated steam

* Saturated steam table is categorized into 2 types one is based on saturated pressure and another is based on saturated temperature.

* Saturated pressure column varies from 611Pa to 221.2bar with some steps like (5, 10, 20 etc) similarly.

Saturated temperature column varies from 0.01°C to 374.15°C i.e. (TP to CP) with some definite steps.

* If in question some intermediate temperature pressure given and we have to find the other properties,

we need to apply linear interpolation technique to solve.

After finding the other properties given in the steam table, use these relations to calculate the required properties.

• 'f' subscripts stands for sat liquid
'g' subscripts stands for sat vap.

$$\begin{aligned} h &= h_f + x(h_g - h_f) \\ u &= u_f + x(u_g - u_f) \\ s &= s_f + x(s_g - s_f) \\ v &= v_f + x(v_g - v_f) \end{aligned}$$

Similarly,

$$\begin{aligned} s_g - s_f &= s_{fg} \\ v_g - v_f &= v_{fg} \\ u_g - u_f &= u_{fg} \end{aligned}$$