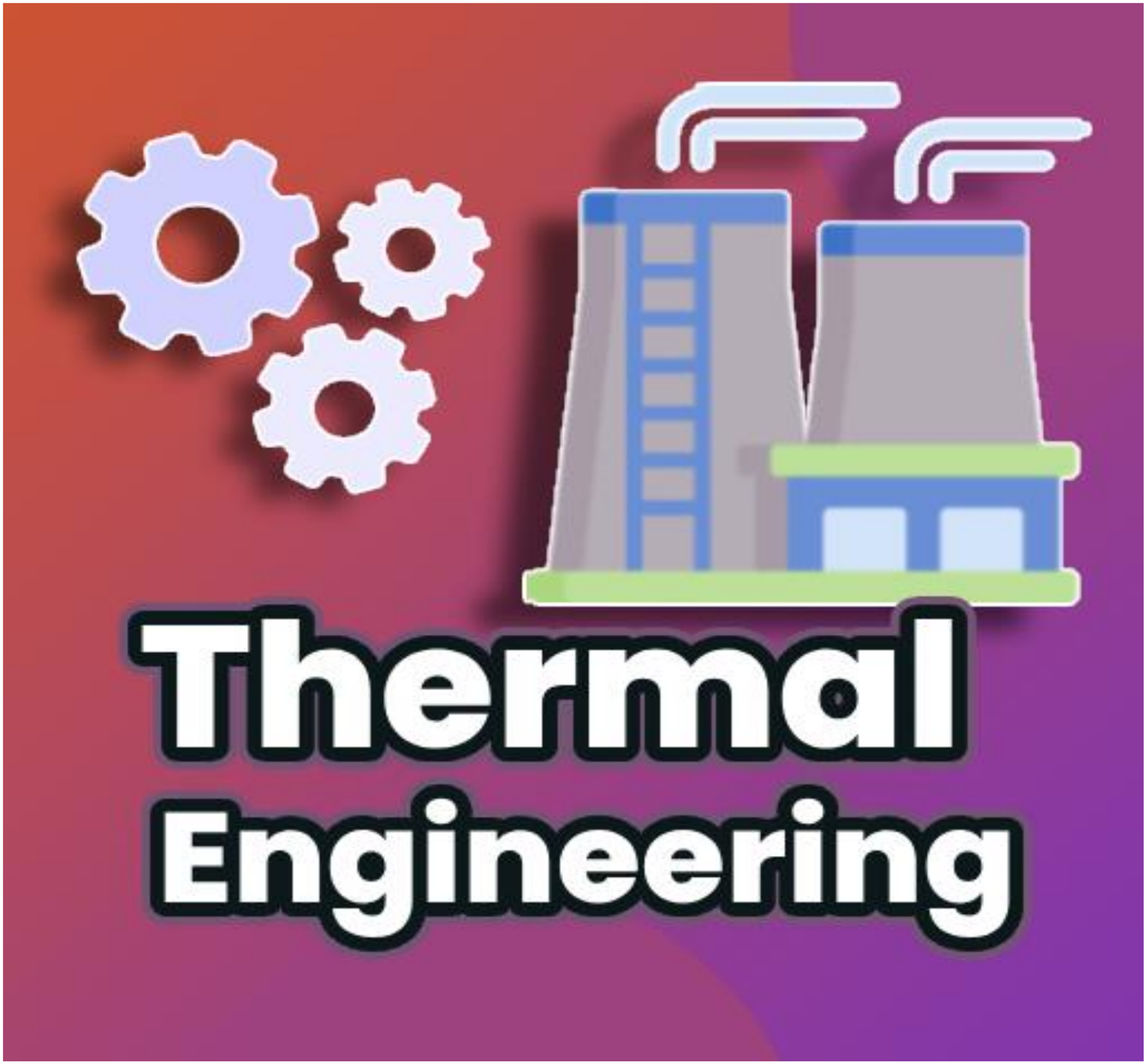


*For 3rd Semester Mechanical Engineering*

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# Thermodynamics

Therme (Heat) Dynamics (Force/motion)

* TD is a branch of Science which deals with energy and energy interaction.

* The main aim of TD is to convert non-organised form of energy into organised form of energy.

* TD is based on energy conservation and mass conservation.

* Most importantly TD tells us what things are not possible.

Example – A m/c with 100% efficiency is not possible. (2nd law of TD)

## Thermodynamic Approach :

### ① Microscopic Approach :

* our attention is focused on each & every molecules of the system.

* Individual behaviour of molecules are considered

* It is also know as statical thermodynamics.

* It is useful for low pressure gas.

Ex – Exploration of space.

## (2) Macroscopic Approach :

* Our attention is focused on certain quantity of matter.

* Average behaviour of molecules are considered.

* It is also known as classical thermodynamics, In our TD we use this approach.

* Classical TD help us to create a relation between measurable & non-measurable property.

  measurable → P, T, V

  non-measurable → Entopy, Enthalpy

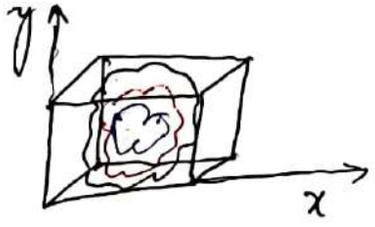
## Concept of continum :

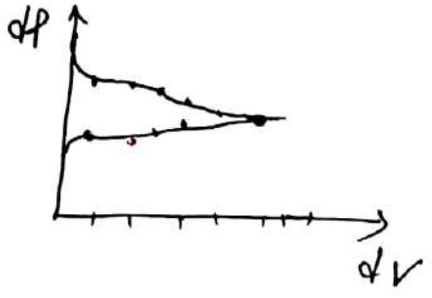
* Concept of continum gives the criteria to apply macroscopic view point.

* It gives minimum volume so that the system should be continuous and averaging is meaningfull.

* In the case of solid & liquid COC always valid.

* In case of gases we need to check whether concept of continum valid or not.



* To check weather continum is valid or not we use "Knudson Number" (Kn)

$$Kn = \frac{\text{mean free path } (\lambda)}{\text{Characterstic Dimension } (l)}$$

* If $Kn < 0.01$ the continum is valid.

* The average distance travelled by molecules after successive collision is know as mean free path.

* In milimeter(mm) device COC is always valid.

* In micrometer device COC may or may not valid.

* In Nano-device COC never valid.

* COC is not applicable in highly rarefied gases.

* Rarefied gas having extremely low pressure gases having low density gases.

<u>System</u>: The system is defined as quantity of matter or region in space where our attention is focused.

System
- Control mass system
- Control volume system

<u>Control mass system</u>: Mass of the working fluid is fixed by quantity & by identity. Also called closed system. Energy transfer possible but no mass transfer.

**Control volume system**: Here volume is fixed but mass can vary also called open system.

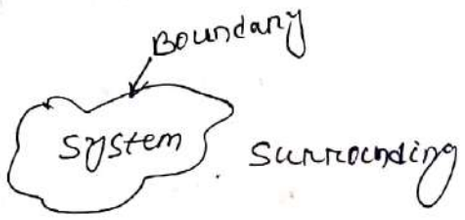
* Both mass & Energy transfer possible.
Ex- pump, Turbine, Throttle valve.

**Isolated system**:

Neither mass nor energy transfer through it. Ex - Thermoflas, Universe.

**Surrounding**: Anything external to the system is known as surrounding.

**Boundary**: A system separated from surrounding by it's boundary.




**Thermodynamic properties**:

Thermodynamic properties are the charcterstic of the system by which system identified.

TD Properties

| Intensive | Extensive |
| --- | --- |
| * It is independent of mass & size. | * Depend on mass & size of the system. |
| * pressure, Temp, Density, viscosity, thermal conductivity, etc. specific energy, sp. entropy. | * Energy, Enthalpy, Entropy, mass, volume |

* properties are independent of past history and are state or point function.

* properties are independent of path of the process & exact differential.

**State** : * A system is said to be in a state if all the properties of the system have fixed and definite value.

* State represent the condition of system and condition is specified by properties.

**Gibb's Phase Rule :**

To find the minimum number of independent properties require to fix the state of the system.

Gibb's phase rule, $P + F = C + 2$

where, $P$ = No. of phase.

$F$ = DOF/min. no. of independent properties.

$C$ = No. of component.

| $H_2O$ | $H_2O$ + steam | $H_2O$ + steam + ice |
|---|---|---|
| $P = 1$ | $P = 2$ | $P = 3$ |
| $C = 1$ | $C = 1$ | $C = 1$ |
| $F = 2$ | $F = 1$ | $F = 0$. Triple point of water |
| | | $T_{tp} = 0.01\,°C$ |
| | | $P_{tp} = 0.611\,kPa$ |

**TD process :**

Change of state is known as process.

A series of equilibrium state through which a system passes through a process called path of process.

TD process

- Reversible process
- Irreversible process

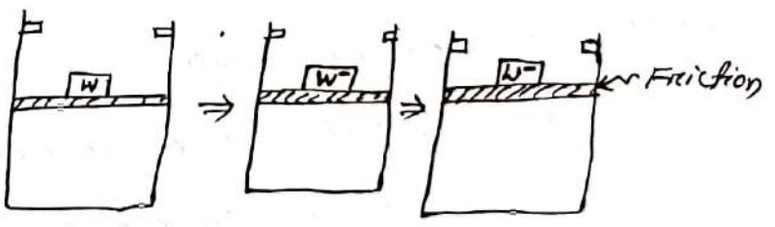
* A process is said to be reversible if it reverse & follow the same path without affecting the system & surrounding.

* All the process are irreversible.

* Friction is the main cause of irreversibility.

## Quasi-static process : (Almost static process)

* Quasi-static process is the initially slow, such that each & every state of the system is in equilibrium.




* Quasi-static + Frictionless process = Reversible process

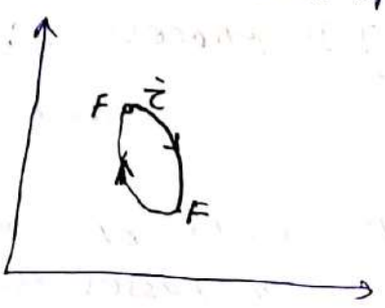
* All reversible process are quasi-static process.

* Frictionless quasi-static process are reversible.

## TD cycle

* In a TD cycle, initial & final state of system is same.

* To get TD, minimum two process is require.



**TD equillibrium condition** : A system is said to be an equillibrium, if there is no external potential & driving force within the system.

TD Equillibrium

- Thermal Equillibrium
- Chemical Equillibrium
- Mechanical Equillibrium

**Matter** : Anything that hass mass and occupy space is called matter. Matter are of two types Solid, Fluid.

**Ideal gas** : A gas which follows ideal gas equation.

$$PV = mRT \Rightarrow PV = nMRT \Rightarrow PV = n\bar{R}T$$

$$\text{No. of moles } (n) = \frac{\text{mass } (m)}{\text{molecular weight } (M)}$$

According to avegedro hypothesis, At same P, T & V every gas has same no. of moles.

$$M \cdot R = \bar{R} \quad , \quad \bar{R} = 8.314 \text{ kJ/kmol-K}$$

R = Gas constant (kJ/kg-K) $\bar{R}$ = universal gas constant (kJ/kmol-K)

* Ideal solid has infinitely large intermolecular force of attraction.

* Ideal gas has negligible (almost zero) intermolecular force of attraction.

* Any gas can behave like an ideal gas under very low pressure and high temperature.

* we derived ideal gas equation in kinetic theory of gases by taking two assumptions.

① Intermolecular force of attraction is negligible.

② The volume of the molecules is negligible.

// Clusius suggested that the free volume available for the movement of the molecules is less the volume of the container.

$$\boxed{P(V-b) = n\bar{R}T}$$

where, b = correction factor for volume occupied by gas molecules.

// Vander wall suggeseted that, we have to consider the intermolecular force of attraction.

$$P = \frac{n\bar{R}T}{(V-b)} - \frac{a}{V^2}$$

$$\Rightarrow \boxed{\left[P + \frac{a}{V^2}\right](V-b) = n\bar{R}T}$$

where, a = correction faction for intermolecular force of attraction.

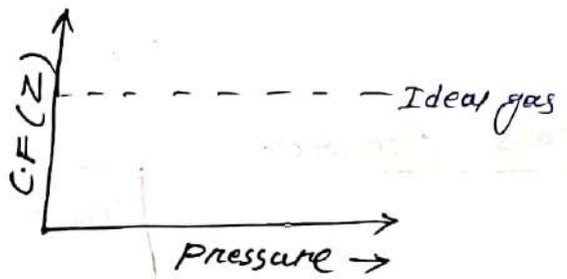
The above equation is called vander wall equation and it is used for real gas.

**Compressibility factor (Z)** : It gives idea about the deviation of real gas from the ideal gas. It also know as deviation factor.

$$PV = mRT \text{ (Ideal gas)} \Rightarrow \text{so, } \frac{PV}{mRT} = 1$$

$$PV \neq mRT \text{ (Real gas)} \Rightarrow \text{so } \frac{PV}{mRT} \neq 1$$

* Compressibility Chart.




**Mixture of Ideal gases** :

Total pressure of mixture = Sum of partial pressure of gas.

$\Rightarrow$ $\boxed{P = P_1 + P_2 + P_3 + \cdots P_n}$, This is know as ~~partial~~ Dalton's law of partial pressure.

$$\boxed{\Sigma n = n_1 + n_2 + n_3 + \cdots n_n}$$

**Mole fraction ($x_i$)** : It is defined as the ratio of no. of moles of $i$th gas to the total number of moles of the mixture.

$$\boxed{x_i = \frac{n_i}{\Sigma n}} \quad , \quad \boxed{P_i = P \cdot x_i}$$

## Gas constant of mixture :

$$R_{eq} = \frac{m_1R_1 + m_2R_2 + \cdots}{\Sigma m}$$

## Equivalent molecular weight.

$$m_{eq} = \frac{n_1m_1 + n_2m_2 + \cdots n_nm_n}{\Sigma n}$$

$$\Rightarrow m_{eq} = x_1m_1 + x_2m_2 + \cdots x_nm_n$$

## Mass fraction :

$$\boxed{MF_i = \frac{m_i}{\Sigma m}}$$

## Relation between MF & x :

$$\boxed{MF_i = x_i \times \frac{m_i}{m_{eq}}}$$

$$\boxed{MF_i = x_i \times \frac{R_{eq}}{R_i}}$$

**Q4-1** An ideal gas consist of 2kmol of $N_2$ and 6kmol of $CO_2$. The mass fraction of $CO_2$ in the mixture is.

| 1 | 2 |
|---|---|
| $N_2$ | $CO_2$ |
| $n_1 = 2$ kmol, | $n_2 = 6$ |
| $M_1 = 28$ | $M_2 = 44$ |

$$MF_{CO_2} = x_{CO_2} \times \frac{M_{CO_2}}{m_{eq}}$$

where, $$m_{eq} = \frac{n_1m_1 + n_2m_2}{\Sigma n} = \frac{2\times28 + 6\times44}{8} = 40$$

$$MF_{CO_2} = \frac{6}{8} \times \frac{44}{40} = \boxed{0.825 = MF_{CO_2}}$$

Qu-2 A rigid tank is divided into two component by a partition one component contains 7kmol of $CO_2$ at 200 kpa & other component contain 3 kmol of $N_2$ at 600kpa. Now partion removed and two homogenous mixture at 300 kpa. Find the partial pressure of $N_2$ in the mixture.

Solution:

| $CO_2$ | $N_2$ |
|---|---|
| $n_1 = 7$ kmol | $n_2 = 3$ kmol |
| $P_1 = 200$ kpa | $P_2 = 600$ kpa |

$N_2 + CO_2$

$P = 300$ kpa

we know, $P_{N_2} = X_{N_2} \times P \Rightarrow P_{N_2} = \frac{3}{10} \times 300 = 90$ kpa

Hence, partial pressure of $N_2$ is $\boxed{90 \text{ kpa}}$.

Qu-3 A 4 $m^3$ reservoir contains 10 kg of real gas at 200K. If this gas follow the vandercwall equation of state with $a = 0.0687$ $m^6 \cdot kpa/kg^2$, $b = 0.00657$ $m^3/kg$, $R = 0.187$ kJ/kg.K. Then the reservoir pressure.

Solution

we know,

$$\left(P + \frac{a}{V^2}\right)(V-b) = mRT$$

$$\Rightarrow \left(P + \frac{0.0687}{4^2}\right)(4 - 0.00657) = 10 \times 0.187 \times 200$$

$$\Rightarrow \boxed{P = 94.6 \text{ kpa}}$$

**Qu-4** An 80L rigid tank contains an ideal gas mixture of 5g of $N_2$ and 5g of $CO_2$ at specified temp & pressure. If $N_2$ were separated from a mixture at same P and T. It's volume would be?

**Solution:** we know, ideal gas equation of mixture.

$$PV = (n_{N_2} + n_{(CO_2)})RT \quad \text{---} \quad (1)$$

only for $N_2$, $PV_1 = n_{N_2}RT$ ——— (2)

Dividing equation (2) by (1).

$$\frac{PV_1}{PV} = \frac{n_{N_2}RT}{(n_{N_2} + n_{(CO_2)})RT} \Rightarrow \frac{V_1}{V} = \frac{n_{N_2}}{n_{N_2} + n_{CO_2}}$$

$$\Rightarrow V_1 = 80 \times \frac{5/28}{5/28 + 5/44} \Rightarrow \boxed{V_1 = 48\ L}$$

**Qu-5** one kg of ideal gas $M = x$ occupies a certain volume V at temp. T and pressure $P_1$. 4kg of another ideal gas $M = 2x$ is added to the first gas keeping the volume V and temp. T as before. The final pressure is?

**Solution**

| | |
|---|---|
| $m_1 = 1kg$ | $m_2 = 4kg$ |
| $M_1 = x$ | $M_2 = 2x$ |
| $P_1 = P_1$ | $P_2 = ?$ |
| $T_1 = T$ | $T_2 = T$ |

we know,

$$P_T = P_1 + P_2$$

(1) $P_1V = n_1\bar{R}T \Rightarrow P_1 = \frac{\bar{R}T}{xV}$

(2) $P_2V = n_2\bar{R}T$

$$\Rightarrow P_2 = \frac{4\bar{R}T}{2x \times V} \quad \because P_2 = 2P_1$$

Hence, $P_T = P_1 + 2P_1 = \boxed{3P_1 = \text{Final pressure}}$

Qu-6 Calculate the compresibility factor of a real gas at 500K and 250 mpa if the gas occupies a volume of $0.2\ m^3/mol$. what would be the factor if gas is ideal.

Solution: we know, $Z = \frac{PV}{n\bar{R}T} = 1$ (For ideal gas)

$$\Rightarrow Z = \frac{250 \times 10^3 \times 0.2}{8.314 \times 10^{-6} \times 500} = 10^5/8.314$$

Hence, Factor is $\frac{10^5}{8.314}$ and 1.

## Concept of temperature & zeroth law of TD:

**Temperature:** (1) macroscopic view point:

Temp. is a property by virtue difference of this property heat flows.

(2) microscopic view point: Temp. is defind as average kinetic energy of the molecules.

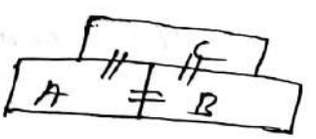
**Zeroth law of T.D:** * If two bodies (A & B) are in thermal equilibrium with a third body (C) the body A and B also thermalo equilibrium with each other.

* Temp. is defined by zeroth law of TD.

$T_A = T_C$

$T_B = T_C$

$\therefore T_A = T_B$




* Thermometry is based on zeroth law of TD.

## Types of thermometers

| | Thermometric property |
|---|---|
| ① mercury in glass thermometer | → Length |
| ② constant volume gas thermometer | → Pressure |
| ③ constant pressure gas thermometer | → Volume. |
| ④ Resistance thermometer (Wheat stone bridge) | → Resistance |
| ⑤ Thermo couple thermometer (See-back effect) | → emf |
| ⑥ Pyrometer | → Wavelength |

$$\boxed{\frac{C}{5} = \frac{F-32}{9} = \frac{K-273}{5}}$$

* At (−40) the value in °C & F scale same.

* Kelvin scale is absolute temp. scale.

**Q4** A new temp. scale say °P the boiling & freezing point of water at 1 atm is 100°P & 300°P. Correlate this scale with °C scale. The reading at 0°P on °C scale is.

**Solution:**

$$t = a + Pb$$

At ice point, $0 = a + 300b$ ---①

At steam point, $100 = a + 100b$ ---②

$\Rightarrow -200b = 100 \Rightarrow b = -1/2,\ a = 150$

putting values, $t = 150 + -1/2 \times 0$, (P=0 as reading at 0°C)

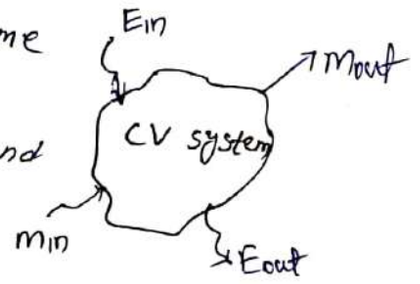
$\Rightarrow \boxed{t = 150°C}$

* The defination of 1K as per the internationally accepted temp. scale is $\Rightarrow \frac{1}{273.16}$ th of the triple point of water.

* <u>Control volume system (open system)</u> :

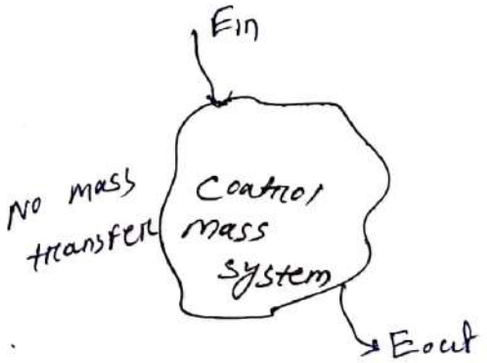
* It is a system of fixed volume

* CV system involves both fixed and moving boundaries as well as real & imaginary boundaries.




* <u>Control ~~volume~~ mass system (Closed system)</u>

* It is a system of fixed mass with a fixed identity.




* When a system undergoes a TD cycle.

$$\oint Q = \oint W$$

$$\Rightarrow \boxed{Q_{1-2} + Q_{2-1} = W_{1-2} + W_{2-1}}$$

* An imaginary device that would produce work continuously without absorbing any energy from it's surrounding is called PMMFK.

# Work and Heat

**Energy** : Energy can exist in various form like mech. thermal, chemical, kinetic energy, potential energy etc.

- Total Energy
  - Microscopic Energy
    - Internal Energy
      - Other form
        - * Nuclear
        - * Chemical
        - * Hydraulic
      - Thermal Energy
        - Sensible Energy
        - Latent Energy
  - Macroscopic Energy
    - Mechanical Energy
      - K.E
      - P.E

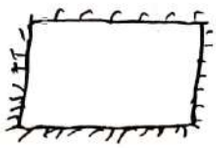
* In case of solid temp. represent intensity of molecular vibration.

* In case of fluid temp. represent the speed of molecular. Higher the temp. higher will be molecular movement.

* Group of sensible energy and latent energy is called thermal energy.

* Internal energy is a function of "P & T" but change in internal energy is a function of "T" only.

Isolated system.



$V =$ constant (All boundary fixed)

So $W = 0$

$\delta Q = dU$

* The energy associated with mass and speed of the molecules is called K.E.

* The energy associated with weight and location is called P.E.

* Any closed system can interact with the surround by two way.


① Heat transfer (Temp. Difference).

② Work transfer (other than temp. difference)

## Work transfer :

Work transfer is a transfer of energy across the boundary of the system other than temp. difference.

* TD work is a boundary phenomenon.

* Workdone on the system "−ve". Workdone by the system is given by "+ve". It depends upon path history.

## Types of work transfer :

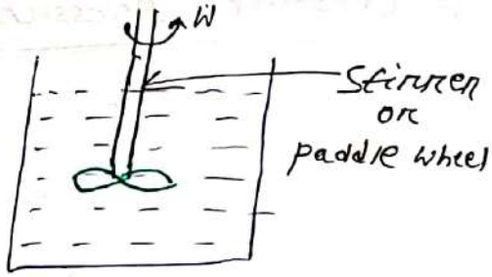
① Displacement work (Area under the curve, $W = \int_1^2 P \cdot dV$)

condition for displacement work.

* System should be closed.
* Quasi-static + frictionless/the
* system must be reversible.

* Also know as non-flow work.

## ② Paddle work

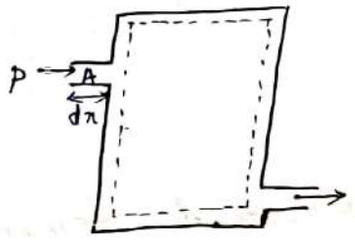



When paddle wheel rotate, friction will develop and this will lead to work transfer.

## ③ Flow work :

$$\text{Flow work} = P \cdot V = P \cdot A \cdot dx$$

$$\text{Flow work/mass} = P \cdot v$$

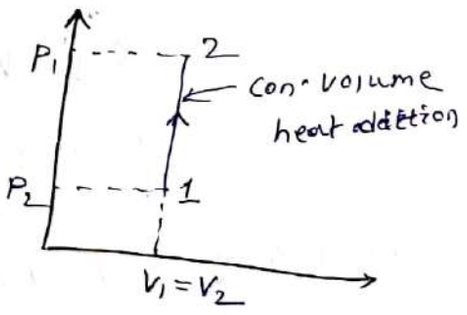



## ④ Shaft work :

When fluid passes it rotate shaft and the the work done is shaft work.

## Work transfer for various process :

### ① Constant volume process :




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

As, $V$ = constant

$\uparrow\uparrow P \propto T \uparrow\uparrow \Rightarrow P = KT$ → $P_1 = KT_1$, $P_2 = KT_2$

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

This is called Gay-Lussac's law

$$\text{Work done} = \int_1^2 P \cdot \cancel{dV}^{\,0} = 0$$

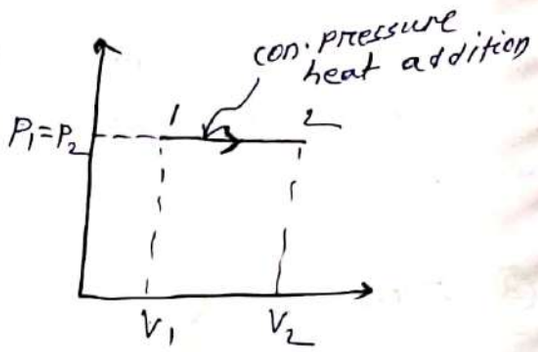
## ② Constant pressure process :

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

$$P = C \text{ (Charles law)}$$

$$V \propto T \Rightarrow V = KT$$

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



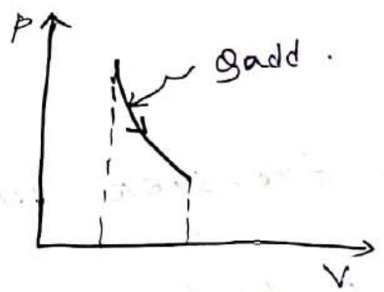

$$\text{work done} = \int_1^2 P \cdot dV = P(V_2 - V_1)$$ , Charle's law.

## ③ Constant temperature process :

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

As, $T$ = constant

$$PV = C \Rightarrow P = \frac{C}{V}$$




$$\text{workdone} = \int_1^2 P \cdot dV = \int_1^2 \frac{C}{V} \cdot dV$$

$$= C(\ln V_2 - \ln V_1)$$

$$= C \ln\left(\frac{V_2}{V_1}\right) = P_1V_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$\therefore \text{workdone} = P_1V_1 \ln\left(\frac{V_2}{V_1}\right) = P_2V_2 \ln\left(\frac{V_2}{V_1}\right) = mRT \left(\ln\left(\frac{V_2}{V_1}\right)\right)$$

* As $P \propto \frac{1}{V}$, The diagram is Rectangular hyperbola.

* Con. Temp expansion is possible when heat added the system.

* Con. temp. compression process is possible when heat rejected from system.

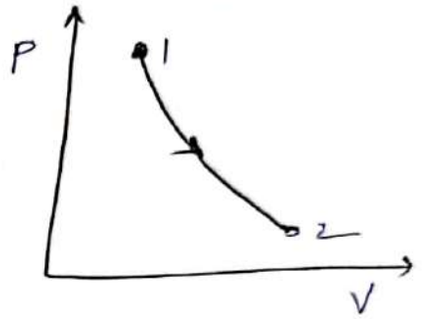
## ④ Adiabatic process :

For adiabatic process - $\boxed{PV^{\gamma} = c}$ $\boxed{\delta Q = 0}$

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

$$\text{Workdone} = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

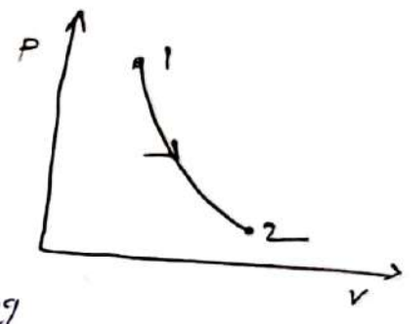
$\gamma$ = Adiabatic index.




## ⑤ polytropic process :

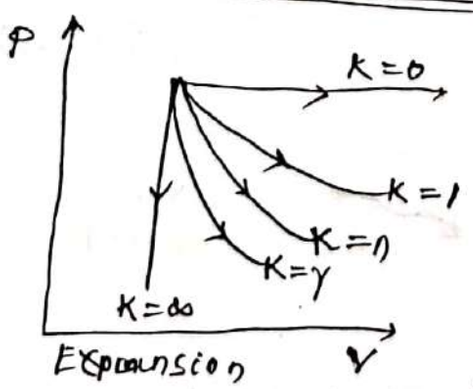
$$PV^{n} = c \;,\; P_1V_1^{n} = P_2V_2^{n}$$

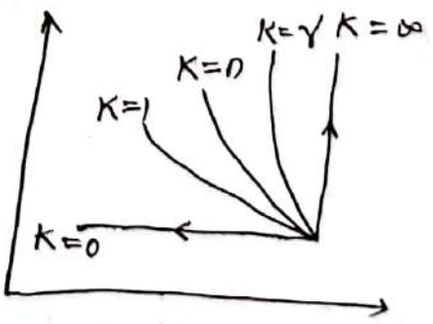
$$\text{Workdone} = \frac{P_1V_1 - P_2V_2}{n - 1}$$




* Heat transfer takes place along with work transfer

## PV diagram for various process :




$PV^{K}$ = constant

① Constant volume = $K = \infty$

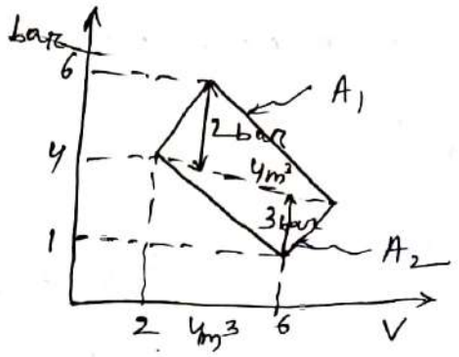
② Constant Pressure = $K = 0$

③ constant temperature = $K = 1$ $\quad 1 < n < \gamma$

④ Adiabatic process = $K = \gamma$

⑤ polytropic process = $K = n$.

Qu calculate the net work done for the closed system.




$$\text{work} = A_1 + A_2$$
$$= \frac{1}{2} \times 4 \times 2 \times 10^5 + \frac{1}{2} \times 4 \times 3 \times 10^5$$
$$= 10 \times 10^5 \text{ joule}$$

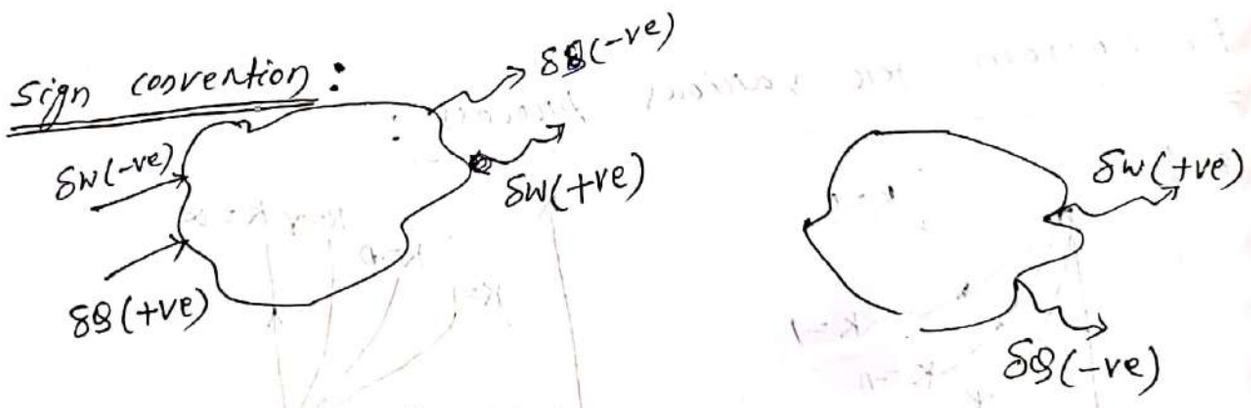
## Heat :

Heat is a transient form of energy the heat transfer takes place because of temp. Difference.

$$Q \propto m.\Delta T \Rightarrow Q = mc\Delta T$$

* Specific heat is the amount of heat which is required to change the temp. of 1kg substance by 1°c.

* Sign convention :




* Specific heat is constant in case of solid & liquid.

$$C_p = C_v = \text{constant}$$

* Mass × Specific heat = (m.c) = Heat capacity.

$V = \text{constant} \rightarrow C_V$ *When, $T = \text{constant}$, $\Delta T = 0$

$P = \text{constant} \rightarrow C_P$

$$C = \frac{Q}{m \cdot \Delta T} = \boxed{\infty}$$

Isothermal Process

For, Adiabatic process.

$Q = \text{constant}$, $\delta Q = 0$, $\boxed{C = 0}$

* $C_P > C_V$. As $V = \text{constant}$. $dQ = du + \cancel{dw} \rightarrow 0$

$\Rightarrow dQ = du$ ---- (1)

But, $P = \text{constant}$ $dQ = du + dw$

$\Rightarrow dQ = du + P(dV)$ --- (2)

Here, equation (2) is greather than (1) so $C_P > C_V$.

* Adiabatic Index : $\boxed{\gamma = \frac{C_P}{C_V} = 1 + \frac{2}{n}}$ $n = \text{DOF}$, $\gamma > 1$

* Gases

| | DOF (n) | $\gamma = 1 + \frac{2}{n}$ |
|---|---|---|
| (1) Monoatomic gases<br>He, Ar, Neon, H etc. | $n = 3$ | $\gamma = 1.667$ |
| (2) Di-atomic gases<br>$N_2, O_2$, Air, $Cl_2$, $H_2$, CO etc. | $n = 5$ | $\gamma = 1.4$ |
| (3) Poly-atomic gases<br>$O_3$, $CO_2$, $NH_3$, $SO_2$ etc. | $n = 6$ | $\gamma = 1.33$ |

FOR **Ideal gas** $C_p$, $C_v$ and $\gamma$ are constant w.r.t temperature.

**Real gas**: $C_p$ and $C_v$ increase w.r.t temp. but "$\gamma$" decrease w.r.t temperature.

**Solid and Liquid**: $C_p$ and $C_v$ both constant.

**Ques**

1 kg of fluid is contained in a cylinder at an initial pressure of 20 bar and an initial volume of $0.05 m^3$. The fluid is allowed to expand reversibly behind the piston according to the law $PV^2 = C$ untill the volume is doubled. The fluid is then cooled at constant pressure until the piston regain it's initial position. Heat is then supplied reversibly with the piston firmly locked in a position until the pressure rises to the original value 20 bar. Calculate W.D.

**Solution**:

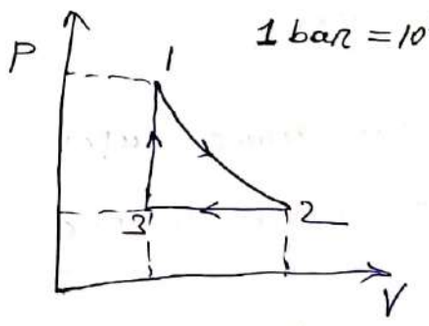
Given that, $m = 1 kg$

$P_1 = 20 bar$

$V_1 = 0.05 m^3$

$V_2 = 2 \times V_1 = 0.1 m^3$

$n = 2$




$1 bar = 10^5 pa$

Net workdone $= W_{1-2} + W_{2-3} + W_{3-1}$

$$= \frac{P_1V_1 - P_2V_2}{n-1} + P_1(V_1 - V_2) + 0$$

$$= \frac{20 \times 10^2 \times 0.05 - 5 \times 10^2 \times 0.1}{2-1} + 20(0.05 - 0.1)$$

$P_1V_1^n = P_2V_2^n$

$\Rightarrow 20 \times (0.05)^2 = P_2 \times (0.1)^2$

$\Rightarrow P_2 = 5 bar$

$$= 50 - 25 = \boxed{25 kJ}$$

* Temp. of gas is produced due to kinetic energy of molecules.

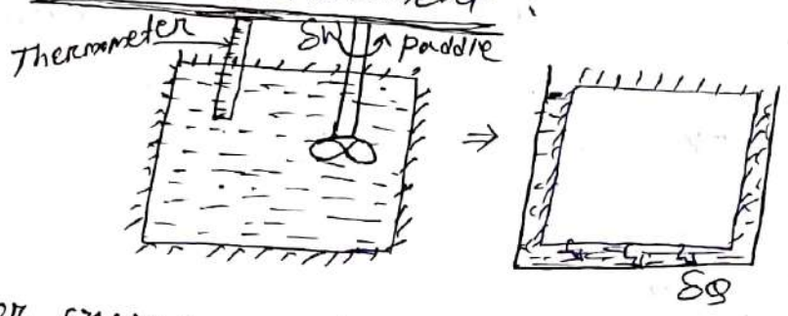
* The integrating factor of quasi-static displacement work is $\boxed{\frac{1}{P}}$

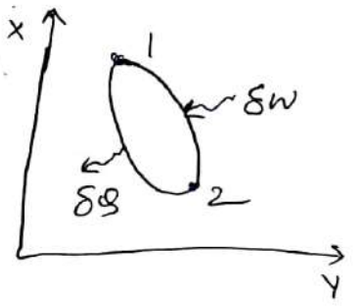
As. $\delta W = P \cdot dV \Rightarrow \boxed{dV' = \frac{1}{P} \cdot \delta W}$

## First law of Thermodynamic

Dt: 28/07/23

* **Jowe's Experiment :**




For cycle:

$$\sum W = \sum Q$$

$$\oint \delta W = \oint \delta Q \Rightarrow \boxed{\oint \delta W - \delta Q = 0}$$

$$E_{in} = E_{out}$$

* First law of thermodynamic is based on law of energy conservation. Heat and work are two different form of entity called energy which is always conserve.

For process :

* Heat transfer is a path function.

* The difference the heat transfer and work transfer is point function i.e $(\delta Q - \delta W)$. This is a property and known as total energy of the system.

i.e $\delta Q - \delta W = dE$

$\Rightarrow \boxed{\delta Q = dE + \delta W} \rightarrow$ 1st law of TD for process.

As, $dE = KE + PE + dU$ , If neglect KE and PE.

$\Rightarrow dE = dU$.

$\boxed{\delta Q = dU + \delta W}$ $\Rightarrow$ For a process of Reversible and closed system

* Internal energy (U) of the system is a point function.

$$U = f(T).$$

<u>Enthalpy</u>: In TD the term $(U + PV)$ seen frequently for our convience this term taken as enthalpy.

$$H = U + PV$$

$$\Rightarrow \frac{H}{m} = \frac{U}{m} + \frac{PV}{m}$$

$\Rightarrow \boxed{h = u + Pv}$ $\Rightarrow$ specific enthalpy.

<u>For Ideal gas</u>:

$$dU = mC_v dT$$

$$dH = mC_p dT$$

## : Heat transfer for various process :

① <u>Constant Volume</u>:

From 1st law of TD

$$\delta Q = dU + \cancel{\delta W}^{\,0}$$

$V =$ constant

$$\Rightarrow \delta Q = dU$$

$$Q = mC_v \Delta T = U$$

② <u>Constant process</u>:

$$\delta Q = dU + \delta W \Rightarrow \delta Q = dH - \cancel{PdV} - \cancel{VdP}^{(P=C)0} + \cancel{PdV}$$

$$\Rightarrow \delta Q = dH = mC_p \Delta T$$

③ constant temperature:

From 1st law of TD.

$$\delta Q = \cancel{dU}^{0} + \delta W$$

$$\Rightarrow \delta Q = \delta W$$

$$\Rightarrow \boxed{\delta Q = P_1 V_1 \ln\left(\frac{V_2}{V_1}\right)}$$

$dU = 0$, As $\Delta T = 0$

$\delta W = P_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$

④ Adiabatic process:

Heat transfer is '0'. $\boxed{Q = 0}$

⑤ polytropic process:

From 1st law of TD.

$$\delta Q = dU + \delta W$$

$$\Rightarrow \delta Q = m c_v \Delta T + \frac{P_1 V_1 - P_2 V_2}{n-1}$$

$$\Rightarrow \delta Q = \frac{\gamma - n}{\gamma - 1} \cdot \left[\frac{P_1 V_1 - P_2 V_2}{n-1}\right]$$

$$\Rightarrow \boxed{\delta Q = \frac{\gamma - n}{\gamma - 1} \cdot \delta W_{poly}}$$

* Specific heat for polytropic process (-ve) $\boxed{C_{poly} = \frac{n-\gamma}{n-1} \cdot C_v}$

* This polytropic specific heat is (-ve) because of decrease in temp. In such process the work transfer is more than the heat input as the extra work getting by conversion of internal energy into work transfer.

Proof: $C_p - C_v = R$ :

we know, $H = U + PV$

$$dH = dU + d(P.V)$$

$$\Rightarrow mC_p\Delta T = mC_v\Delta T + d(mRT)$$

$$\Rightarrow \cancel{m}^{0}C_p\cancel{\Delta T}^{0} = \cancel{m}^{0}C_v\cancel{\Delta T}^{0} + \cancel{m}^{0}R\cancel{\Delta T}^{0}$$

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

(*)

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

$$C_p - C_v = R$$

$$\Rightarrow \gamma C_v - C_v = R$$

$$\Rightarrow C_v(\gamma - 1) = R$$

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

$$\Rightarrow \boxed{C_v = \frac{\bar{R}}{m(\gamma - 1)}}$$

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

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

(*)

$$\boxed{P_1V_1^{\gamma} = P_2V_2^{\gamma}}$$

$$\Rightarrow P_1V_1V_1^{\gamma-1} = P_2V_2V_2^{\gamma-1}$$

$$\Rightarrow \cancel{mR}T_1V_1^{\gamma-1} = \cancel{mR}T_2V_2^{\gamma-1}$$

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

$$\Rightarrow \boxed{\frac{T_1}{T_2} = \left(\frac{P_1}{P_2}\right)^{\frac{\gamma-1}{\gamma}}}$$

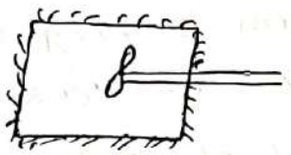
$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

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

## Special case-1

$V = \text{constant}$

$P \cdot dV = 0$

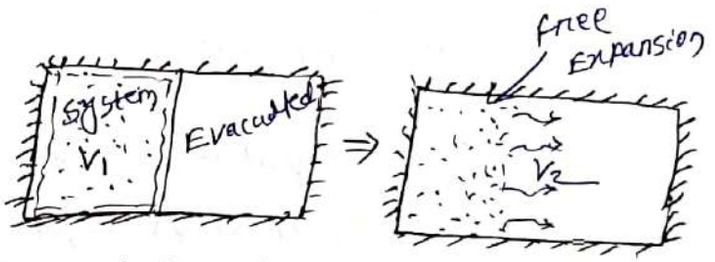


Here, PdV work will be (-ve) work transfer.

## Case-2 :

Here, $V = \text{constant}$

$PdV = 0$.




* The expansion against evacuated chamber is called free expansion.

* Free expansion work is always zero because there is no resistance offered by the surrounding.

From 1st law of TD.

$$\cancel{\delta Q}^{0} = dU + \cancel{\delta W}^{0}$$

$$\Rightarrow dU = 0 \Rightarrow \boxed{U = \text{constant}}$$

Also, $dT = 0 \Rightarrow \boxed{T = \text{constant}}$

We know. $dH = mC_p\Delta T$

$$\Rightarrow dH = 0 \Rightarrow \boxed{H = \text{constant}} \Rightarrow \text{Is called Isenthalpic.}$$

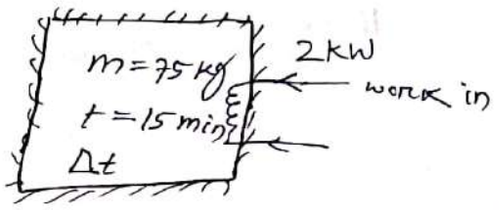
* Free expansion is the highly irreversibible process.

**Ques:** A 2W baseboard electric resistance heater in a vacant room is turned on and kept on for 15min the mass of air in the room is 75kg and the room is tightly sealed so that no air can leak in or out. The temp. rise of air at the end of 15 min is — ?

**Solution:**

From 1st law of TD.

$$\cancel{\delta Q}^{0} = dU + \delta W$$




$$\Rightarrow 0 = mC_v\Delta T - 2\times15\times60$$

$$\Rightarrow 0 = 75\times0.717\times\Delta T - 1800$$

$$\Rightarrow \Delta T = 33.47^\circ C$$

**Ques:** The integrating factor of reversible heat transfer is $\frac{1}{T}$.

As $\Delta S = \frac{\delta Q}{T}$

Here, $IF = \frac{1}{T}$

**Ques** A non-flow quasi-static (reversible process) occur for which $P = (-3V+16)$ bar, where V is changes from 2 to $6\ m^3$. Calculate work done.

**Solution:** We know, work done $= \int_2^6 (-3V+16)\,dV$

$$= \left[\frac{-3V^2}{2} + 16V\right]_2^6$$

$$= \left[\frac{-3(6^2-2^2)}{2} + 16(6-2)\right]\times10^5\ Pa$$

$$= 16\times10^5\ J$$

**Ques** 3 moles of an ideal gas is compressed to half the initial volume at a constant temp. of 300 K. The work done in the process is.

**Solution:** For constant temp. process,

$$\text{Work done} = nRT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$= 3 \times 8.314 \times 10^{-3} \times 300 \times \ln\left(\frac{1}{2}\right)$$

$$= -5186 \times 10^{-3} \text{ kJ} = -5186 \text{ J}$$

**Ques** A piston-cylinder device with air at an initial temp. of 28°C undergoes an expansion process for which pressure and volume are related as given below.

| P (kPa) | 100 | 50 | 40 | 27 | 15 |
|---|---|---|---|---|---|
| V ($m^3$) | 0.1 | 0.15 | 0.2 | 0.25 | 0.4 |

$P \neq$ constant
$V \neq$ constant
$T \neq$ constant

What is the work done by the system?

**Solution**

$$\text{Work done by the system} = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

$$= \frac{100 \times 0.1 - 15 \times 0.4}{1.4 - 1}$$

$$= \boxed{10 \text{ kJ}}$$

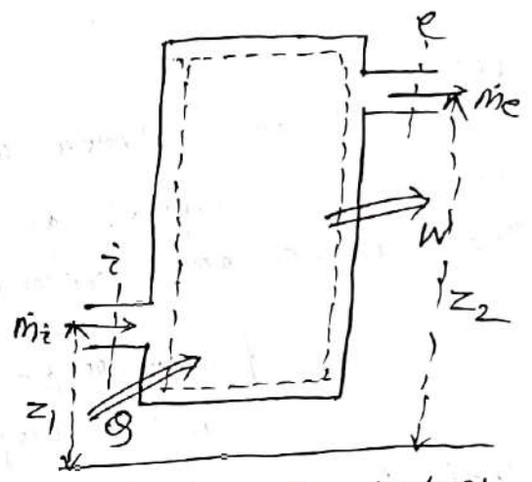
# First law of TD for open system

* In open system mass and energy transfer takes place.

* If mass flow rate is same at entry and exit of the system is called steady flow open system otherwise it is unsteady open system.

* In closed system we talk about fixed mass but in open system mass flow rate.

## Steady flow open system:




### Mass conservation:

$$\frac{dm}{dt} = \dot{m}_i - \dot{m}_e$$

* The rate of mass accumulated inside the control volume is equal to the rate of mass transfer across the control volume.

When no mass accumulation, $m_1 = m_2$

$$\frac{dm}{dt} = 0$$

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

$$\boxed{\rho_i A_i V_i = \rho_e V_e A_e}$$

**Energy conservation:** Total energy accumulated with in the control volume is equal to the net rate of energy transfer across the control volume.

$$\frac{dE}{dt} = \dot{E}_i - \dot{E}_e, \text{ steady flow } \boxed{\dot{E}_i = \dot{E}_e}$$

$$\boxed{\dot{m}\left(h_i + \frac{C_i^2}{2000} + \frac{gz_1}{1000}\right) + \dot{q} = \dot{m}\left(h_e + \frac{C_e^2}{2000} + \frac{gz_e}{1000}\right) + \dot{W}_{c.v}}$$

Unit KJ/sec

$$\boxed{h_i + \frac{C_i^2}{2000} + \frac{gz_1}{1000} + q = h_e + \frac{C_e^2}{2000} + \frac{gz_2}{1000} + W_{cv}}$$

KJ/kg

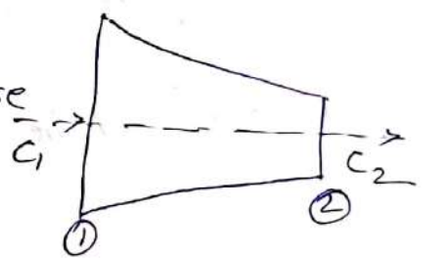
The above equation is called steady flow energy equation. First law of TD for open system.

If we neglect K.E and P.E.

$$\boxed{h_i + q = h_e + W_{c.v}}$$

## Example of steady flow open system:

**Nozzle:** It is a device which increase velocity of fluid in expense of pressure.




$\dot{q} = 0$ , $z_1 = z_2$

$\dot{W}_{cv} = 0$

From 1st law of thermodynamic.

$$h_i + \frac{C_i^2}{2000} = h_e + \frac{C_e^2}{2000}$$

$$\Rightarrow h_i = h_e + \frac{C_e^2}{2000} \qquad (C_i << C_e)$$

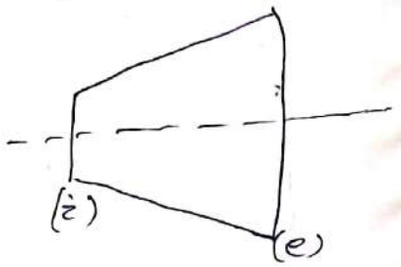
$$\Rightarrow C_e = \sqrt{2000(h_i - h_e)} \text{ m/sec.}$$

**Turbine :** Turbine is a power producing device.

$\dot{Q} = 0$ , $z_1 = z_2$

$\Downarrow$

As process is very fast.




From 1st law of TD.

$$\dot{m}_i h_i = \dot{m}_e h_e + W_T$$

$$\Rightarrow \boxed{W_T = \dot{m}(h_i - h_e)} \Rightarrow \boxed{W_T = h_i - h_e} \text{ kJ/kg}$$

**Compressor :** Compressor is a power consuming device.

$Q = 0$ . $z_1 = z_2$ , $C_i \cong C_e$

From 1st law of TD.

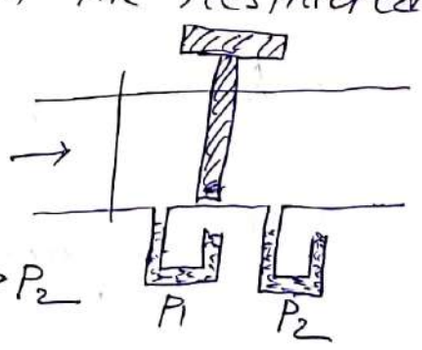
$$\dot{m}\left[h_i + \cancel{\frac{C_i^2}{2000}} + \cancel{\frac{gz_1}{1000}}\right] + \cancel{Q}^{0} = \dot{m}\left[h_e + \cancel{\frac{C_e}{2000}} + \cancel{\frac{gz_2}{1000}}\right] + \dot{W}_{cv}$$

$$\Rightarrow \dot{m}h_i + \cancel{Q}^{0} = \dot{m}h_e + \dot{W}_{cv} \Rightarrow \boxed{W_c = \dot{m}(h_e - h_i)} \text{ kJ/sec}$$

$$\Rightarrow \boxed{W_c = h_e - h_i} \text{ kJ/kg}$$

**Joule-Thomson Experiment :**

**Throttling process :** Flow through the restricted passage.




From 1st law of TD

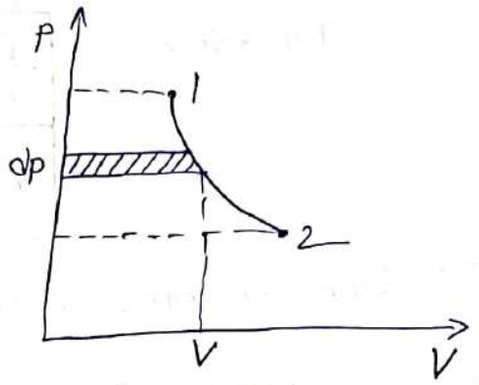
$$\dot{m}h_i + \cancel{Q}^{0} = \dot{m}h_e + W$$

$\Rightarrow \boxed{h_i = h_e} \Rightarrow$ Throttling process is the isenthalpic process.

Also highly irreversible process.

## Open system Reversible work :

$$\text{Work done} = -\int_1^2 V \cdot dP$$




* It is equal to area under the curve when projected on pressure axis on P-V diagram.

## Open system reversible work for various process :

### ① Isobaric process :

$$P = \text{constant} \Rightarrow dP = 0$$

$$\text{Work done} = -\int_1^2 V \cdot dP = 0$$

Ex – Heat exchanger, Boiler, combustion chamber, condenser etc.

### ② Isochoric process :

$$V = \text{constant} \Rightarrow dV = 0$$

$$\text{Work done} = -\int_1^2 V \cdot dP = -V(P)_1^2$$

$$= -V(P_2 - P_1)$$

$$\Rightarrow \text{Work done} = V(P_1 - P_2)$$

Ex – Pump

### ③ Isothermal process :

$$T = \text{constant} \Rightarrow dT = 0$$

Ideal gas, $PV = nRT \Rightarrow PV = \text{constant}$

$$\text{Work done} = -\int_1^2 V \cdot dP = -\int_1^2 \frac{c}{P} \cdot dP = -c(\ln P)_1^2$$

$$\Rightarrow \boxed{\text{Work done} = c(\ln P_1 - P_2) = P_1 V_1 \ln\left(\frac{P_1}{P_2}\right)} \quad \boxed{W_{open} = W_{close}}$$

④ Adiabatic process :

$$Q = 0$$

$$\text{Workdone} = \boxed{\frac{\gamma}{\gamma-1}\left[P_1V_1 - P_2V_2\right]}$$

$$= \boxed{\gamma \times W_{closed}}$$

Ex- Turbine, compressor etc.

⑤ Polytropic process :

$$\text{Workdone} = \frac{n}{n-1}\left[P_1V_1 - P_2V_2\right]$$

PMM-I : * perpetual motion machine of 1st kind is a hypothetic machine which gives output without any input

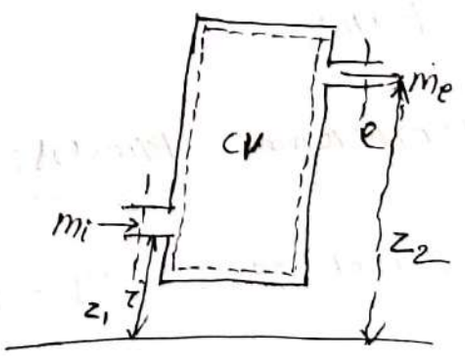
* PMM-I violates 1st law of thermodynamics.

* If two liquid at different temp are mixed, then the final temp. of the mixture of liquid can be obtained by using First law of TD.

## Unsteady flow open system :

### mass conservation :

$$\frac{dm}{dt} = \dot{m}_i - \dot{m}_e$$




Here, $\boxed{m_1 \neq m_2}$ $\boxed{\dot{m}_i = \dot{m}_e}$

## Energy Conservation :

$$\frac{dE}{dt} = \dot{E}_i - \dot{E}_e$$

$$\frac{dE}{dt} = \left[\dot{m}\left[h_i + \frac{C_i^2}{2000} + \frac{gz_1}{1000}\right] + \dot{Q}\right] - \left[\dot{m}_e\left[h_e + \frac{C_e^2}{2000} + \frac{gz_e}{1000}\right] + \dot{W}_{cv}\right]$$

$$dE = dK.E + dP.E + dU$$

If we neglecting K.E and P.E .

$$\boxed{\frac{du}{dt} = \dot{m}_i h_i + \dot{Q} - \dot{m}_e h_e - \dot{W}_{cv}}$$

Ex. of unsteady flow - Filling of tank .

* Mass flow rate $\Rightarrow \boxed{\rho_1 A_1 C_1 = \rho_2 A_2 C_2}$

$\Rightarrow \boxed{\frac{A_1 C_1}{v_1} = \frac{A_2 C_2}{v_2}}$

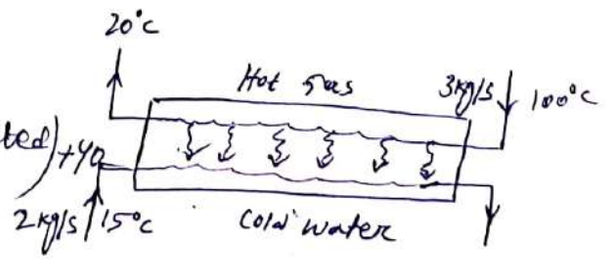
$C_1 = C_2$ = velocity at entry & exit.

$v_1 = v_2$ = Specific volume

**Qu** A heat exchanger is used to cold hot water at 15°c entering at a rate of 2kg/sec by hot air at 100°c entering at a rate of 3 kg/s . The heat exchanger is not insulated and is loosing heat at a rate of 40 Ki/sec . If the exit temp. of hot air is 20°c . The exit temp. of cold water ___ .

**Solution :**

$$\begin{pmatrix}\text{Energy rejected}\\ \text{by gas}\end{pmatrix} = \begin{pmatrix}\text{Energy received}\\ \text{by cold gas}\end{pmatrix} + 40$$




$\Rightarrow mC_p\Delta T = mC_p\Delta T + 40$

$\Rightarrow 3 \times 1.004 \times (100-20) = 2 \times 4.18 \times (T_2 - 15) + 40$

$\Rightarrow T_2 = 39°c$ .

($C_p$ used as heat exchanger is $P$ = constant)

$C_{p,Air} = 1.004$ kJ/kg.K

$C_{p,water} = 4.18$ Ki/kg.K

* For steady flow process
⇒ The rate of flow of mass energy across the control surface is constant.
⇒ Any thermodynamic property will have a fixed value at particular location & will not alter with time.

* According 1st law of TD, (Energy of system + Energy of surrounding is zero.

* Work output from a system is at the expense of internal energy in a non-flow processes carried at Adiabatically

Qu A system execute a cyclic process (two).

$_1Q_2 = 460$ kJ
$_2Q_1 = -100$ kJ
$_1W_2 = 210$ kJ


Solution: For 1-2:

$$\delta Q_{1-2} = U_2 - U_1 + \delta W_2$$

$$\Rightarrow 460 = U_2 - U_1 + 210 \Rightarrow U_2 - U_1 = +250 \text{ kJ}$$

For 2-1

$$\delta Q_{2-1} = U_1 - U_2 + \delta_2 W_1$$

$$\Rightarrow -100 = -250 + {}_2W_1 \Rightarrow \boxed{{}_2W_1 = 150 \text{ kJ}}$$

# Second law of Thermodynamic

* First law of TD simply says energy is conserved during a cycle or process and energy balance holds good. But it does not give any information whether the system is possible or not.

* It is a 2nd law of TD, which gives the criteria for the possible of the system and it gives the direction of the process with the entropy. It is also known as "Directional law".

Note - All the natural process in nature are spontaneous (occur in one direction) High potential to low potential

## TD Reservoir :

A thermal energy reservoir is a hypothetical body with a large heat capacity, that can supply or absorbe finite amount of heat without undergoing any temp. change.

TD Reservoir
- Source
- Sink

**Source** : It is a type of reservoir which can supply large amount of heat without undergoing any temp. change.
Ex - Sun

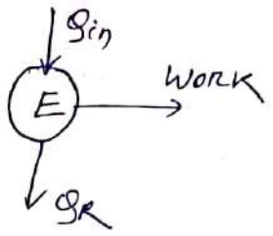
**Sink** : Sink is a type of reservoir which can absorb large amount of heat without undergoing any temp. change
Ex - Ocean, surrounding.

## Joule's Statement:

Joule demonstrate that work can be completely converted into heat but heat complete conversion into work is not possible.

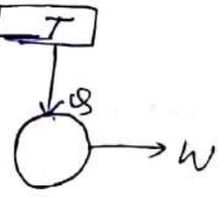
Work = High grade energy

Heat = low grade energy




## Kelvin Plank's Statement:

It is impossible to construct a device which produce work continuously while exchanging heat heat with a single reservoir.




From 1st law thermodynamic

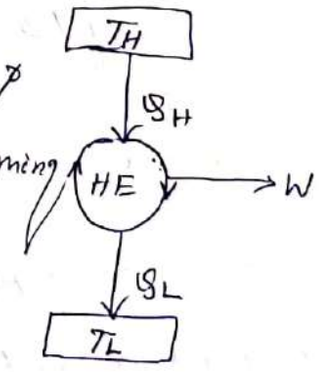
$E_{in} = E_{out}$.

$\Rightarrow Q = W$ $\qquad \eta = \frac{\text{output}}{\text{Input}} = \frac{W}{Q} = 100\%$

But $\eta \neq 100\%$.

So the above is impossible.

* Clockwise cycle are power producing & Anti-clockwise cycle are power consuming cycle.




* From 1st law of TD.

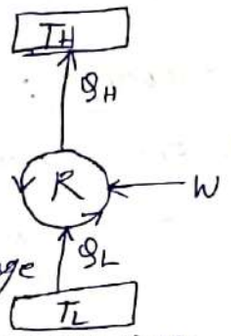
$\sum Q_{in} = \sum W_{out}$

$\Rightarrow Q_H - Q_L = W$, $\qquad \eta_{HE} = \frac{W_{out}}{\text{Heat Input}} = \frac{Q_H - Q_L}{Q_H}$

$$\Rightarrow \boxed{\eta_{HE} = 1 - \frac{Q_L}{Q_H}}$$ This is valid for both reversible & irreversible cycle.

**Clausius Statement :** Clausius suggested that it is impossible to construct a device which transfer heat from low temp. body to high temp. body without any external interaction.

$$COP = \frac{R.E}{W} = \frac{\text{Desire effect}}{\text{work done}} = \frac{Q_L}{Q_H - Q_L}$$



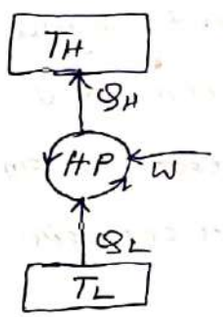

**Refrigeration effect :** It is the amount of heat which is to be extracted from storage space to maintain lower temp. from surrounding.

**Heat pump :**

$$COP = \frac{Q_H}{Q_H - Q_L}$$

$$(COP)_{H.P} = (COP)_R + 1 \; , \; (COP)_{H.P} = \frac{1}{\eta_{H.E}}$$

$$(COP)_{H.P} = \frac{1}{(COP)_{H.E}}$$



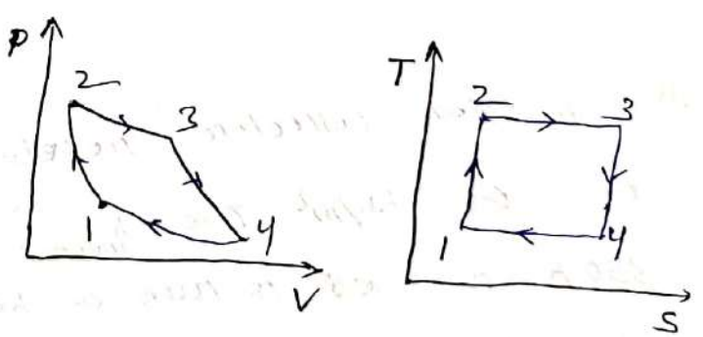

**Carnot cycle :**

1-2 :- Reversible adiabatic compression.

2-3 : Isothermal expansion (Heat addition)

3-4 : Reversible adiabatic expansion.

4-1 : Isothermal compression (Heat rejected)




* In a carnot cycle, reversible adiabatic process is very fast process and isothermal process is very slow process

and the combination of these two process is not possible.

* That's why carnot cycle is not practical cycle but it gives maximum efficiency that is why, we use carnot cycle for comparision of other practical cycles.

## Carnot theorem:

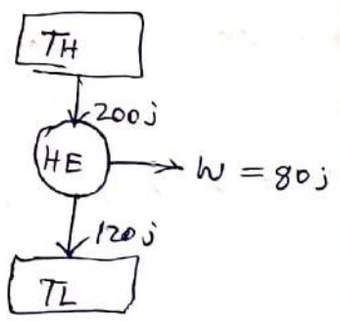
⊛ For various cycles working between same temp. limit non has efficiency greather than reversible cycle efficiency.

⊛ The efficiency of reversible cycle only depends on temp. limit does not depend on type of working fluid.

**Qu** A heat engine operate b/w a cold reservoir at temp. $T_2 = 300K$ and hot reservoir at temp. $T_1$. It take 200j of heat from hot reservoir and deliver 120j of heat to cold reservoir. Find $\eta$ of cycle.

**Solution**

$$\eta = \frac{200-120}{200} = \frac{80}{200} = 40\%$$

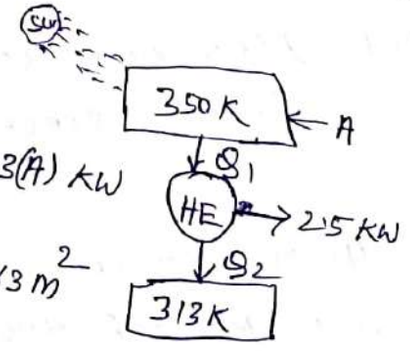



**Qu** A solar collector receiving solar radiation, at a rate of 0.6 $kW/m^2$. The $\eta_{overal} = 50\%$ the fluid heated to 350 K is used to run a heat engine which reject heat at 313 K. If heat engine produce 2.5 kW of power. Find minimum area of solar collector.

**Solution**

$$\eta_0 = \frac{Q_1}{0.6} = 0.5 \Rightarrow Q_1 = 0.3\ kW/m^2 = 0.3(A)\ kW$$

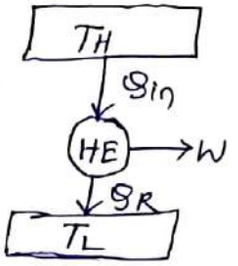
$$\eta = \frac{W}{Q_1} = \frac{2.5}{0.3A} = 1 - \frac{313}{350} \Rightarrow A = 78.83\ m^2$$



Q4 A cycle HE does 50 kJ of work per cycle if $\eta_{HE} = 75$. The heat rejected per cycle is .

Given that : $W = 50$ kJ

$\eta = 0.75$



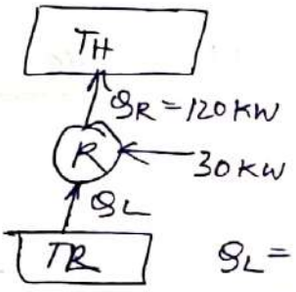

$$\eta = \frac{W}{Q_{in}} = 0.75 = \frac{50}{Q_{in}}$$

$\Rightarrow Q_{in} = 66.67$ kJ , $W = Q_{in} - Q_R \Rightarrow Q_R = 16.67$ kJ

Q4 A condenser of refrigeration system reject heat at a rate of 120 kW. While is compressor consumes a power of 30 kW. Find COP.

Solution :

$$COP = \frac{90}{30} = 3$$

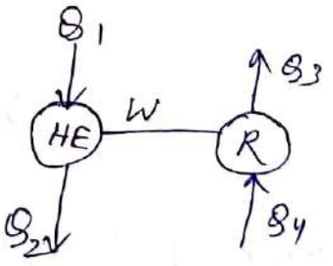



$Q_L = 120 - 30$
$= 90$ kW

Q4 In a fig. E is a heat engine with efficiency 0.4 & R is the refrigerator. Given $Q_2 + Q_4 = 3Q_1$. Find $(COP)_R$.

Solution

$$(COP)_R = \frac{Q_4}{W} = \frac{Q_4}{Q_1 - Q_2} = \frac{Q_4}{Q_3 - Q_4}$$




$$\eta = \frac{W}{Q_1} \Rightarrow 0.4Q_1 = W = Q_1 - Q_2$$

$$\Rightarrow 0.6Q_1 = Q_2$$

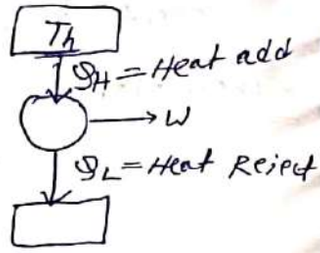
$$Q_2 + Q_4 = 3Q_1 \Rightarrow Q_4 = 3Q_1 - Q_2 = 2.4Q_1$$

Now, $(COP)_R = \dfrac{2.4Q_1}{0.4Q_1} = 6$

* For steady flow through an insulated horizontal constant diameter pipe, so Enthalpy property remains constant

* Air is being forced by a pump, slow downwards more of piston experience isothermal process, as it is slow process

## Clausius inequality :




### For Reversible cycle :

First law of TD : $E_{in} = E_{out}$

$$\Rightarrow Q_H = W + Q_L$$

$$\Rightarrow W = Q_H - Q_L$$

Already known, $\dfrac{Q_h}{T_h} = \dfrac{Q_L}{T_L}$

$$\Rightarrow \frac{Q_h}{T_h} - \frac{Q_L}{T_L} = 0 \Rightarrow \frac{Q_H}{T_h} + \left(-\frac{Q_L}{T_L}\right) = 0$$

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

### For irreversible cycle :

$$\eta_{rev} > \eta_{irrev}$$

$$\Rightarrow 1 - \frac{T_L}{T_h} > 1 - \frac{Q_L}{Q_h} \Rightarrow -\frac{T_L}{T_h} > -\frac{Q_L}{Q_h}$$

Applying (-ve) both side :> sign change to < .

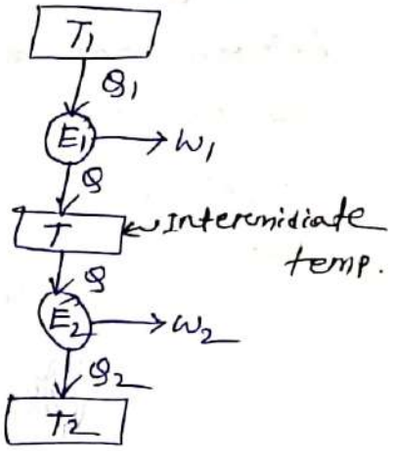
$$\frac{T_L}{T_h} < \frac{Q_L}{Q_H} \Rightarrow \frac{Q_h}{T_h} < \frac{Q_L}{T_L}$$

$$\Rightarrow \frac{Q_h}{T_h} - \frac{Q_L}{T_L} < 0 \Rightarrow \boxed{\oint \frac{\delta Q}{T} < 0}$$

Hence, $\boxed{\oint \frac{\delta Q}{T} \leq 0}$ ⇐ 2nd law of TD for a cycle.

When, $\boxed{\oint \frac{\delta Q}{T} > 0}$ ⇐ cycle is Impossible .

## Coupled Engine :




**Case-1** when $(W_1 = W_2)$.

$$W_1 = Q_1 - Q = W_2 = Q - Q_2$$

$$\Rightarrow \frac{Q_1}{Q} - 1 = 1 - \frac{Q_2}{Q} \qquad \left( \frac{Q_1}{Q} = \frac{T_1}{T} \quad \frac{Q_2}{Q} = \frac{T_2}{T} \right)$$

$$\Rightarrow \frac{T_1}{T} - 1 = 1 - \frac{T_2}{T}$$

$$\Rightarrow \frac{T_1}{T} = 2 - \frac{T_2}{T} \Rightarrow \frac{T_1 + T_2}{T} = 2 \Rightarrow \boxed{T = \frac{T_1 + T_2}{2}}$$

**Case-2** when $(W_1 = 2W_2)$, $\boxed{T = \frac{T_1 + 2T_2}{3}}$

**Case-3** when $(\eta_1 = \eta_2)$.

$$\eta_1 - \eta_2 = 1 - \frac{T}{T_1} = 1 - \frac{T_2}{T}$$

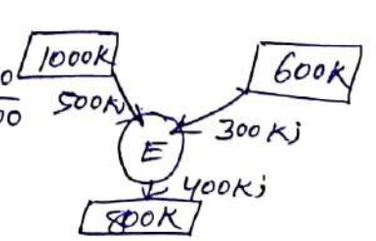
$$\Rightarrow T^2 = T_1 T_2 \Rightarrow \boxed{T = \sqrt{T_1 T_2}}$$

* combine efficiency, $\boxed{\eta = \eta_1 + \eta_2 - \frac{\eta_1 \eta_2}{100}}$

* $\eta = 1 - \frac{T}{T_1}$, To get higher efficiency it is better to $\boxed{\text{Decrease } T \text{ by keeping } T_1 \text{ constant}}$

**Qu** An inventor claims that his engine can absorbe 500 kJ & 300 kJ of heat from two thermal reservoir at 1000 K & 600 K resp. It can do 400 kJ work while rejecting at 800 K to sink.

**Solution** 2nd law of TD, $\oint \frac{\delta Q}{T} = \frac{500}{1000} + \frac{300}{600} - \frac{400}{800}$

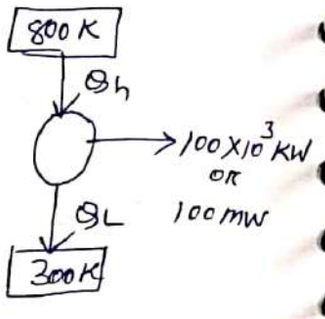



$$\Rightarrow \frac{1}{2} + \frac{1}{2} - \frac{1}{2} \Rightarrow \frac{1}{2} > 0$$

It is impossible engine.

Q4 The following HE produces are power $100 \times 10^3$ KW. The HE operates between 800K & 300K. $\eta_{then}$ equal to 50% of $\eta_{carnot}$ for the same temp. The rate at which heat is absorbed from the hot reservoir is —.

Solution:




$$\eta_{then} = 0.5\, \eta_{carnot}$$

$$\Rightarrow \frac{W}{Q_h} = 0.5\left(1 - \frac{300}{800}\right)$$

$$\Rightarrow Q_h = 0.5\left(\frac{8-3}{8}\right) \times \frac{1}{100}$$

$$\Rightarrow Q_h = \frac{1}{0.5} \times \frac{8}{5} \times 100 = \boxed{320\ mW = Q_h}$$

Q4 A HE operates at 75% of the max. possible efficiency. The ratio of the heat source temp. to the sink temp. is $\frac{5}{3}$. The fraction of the heat supplied that is converted to work is.

Solution: 75% of max. possible efficiency means.

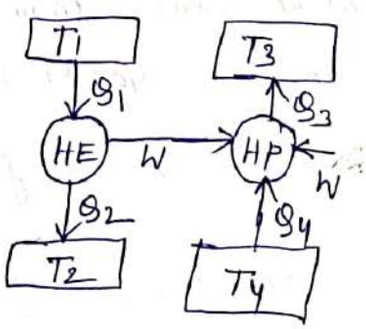
$$\eta_{then} = 0.75 \times \eta_{carnot}$$

$$\Rightarrow \frac{W}{Q_H} = 0.75 \times \left(1 - \frac{3}{5}\right) \Rightarrow \frac{W}{Q_H} = 0.3 \Rightarrow \boxed{W = 0.3\, Q_H}$$

Q4 A reversible power cycle is used to drive a reversible HP cycle. The power cycle takes in $Q_1$ unit at $T_1$ and reject $Q_2$ at $T_2$. The HP abstracts $Q_4$ from the sink at $T_4$ & discharge $Q_4$ at $T_3$. The ratio of $\frac{Q_4}{Q_1}$ in terms of 4 temp.

Solution:

$$\frac{Q_4}{Q_1} = \frac{T_4}{T_1}\left(\frac{T_1 - T_2}{T_3 - T_2}\right)$$



## 2nd law Efficiency :

$$\eta_{II} = \frac{W_{actual}}{W_{max}}$$

$$= \frac{\left(\frac{W_{actual}}{Q_{in}}\right) \leftarrow \eta_{1st\ law}}{\left(\frac{W_{max}}{Q_{in}}\right) \leftarrow \eta_{rev}}$$

$$\boxed{\eta_{II} = \frac{\eta_{1st\ law}}{\eta_{rev}}}$$

**Q4** A engine operates between temp. limit of 900K & $T_2$ and another between $T_2$ and 400K for both to be equally efficient $T_2$ will be.

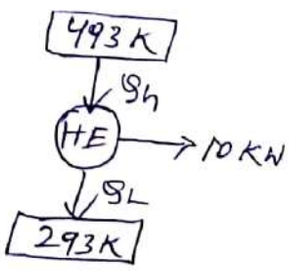
**Solution** For $\eta_1 = \eta_2$, $T_2 = \sqrt{T_1 \cdot T_3}$

$$\Rightarrow T_2 = \sqrt{900 \times 400} = 600\,K$$

* Kelvin - plank's law deals with <u>conversion of heat into work</u>.

* In a carnot engine, when working substance gives heat to the sink then, <u>temp. of sink remains same</u>.

**Q4** A carnot engine operates between reservoir at 20°c & 200°c. If 10KW of power is produced, the reject heat rate nearest to.




**Solution** we know,

$$1 - \frac{293}{493} = \frac{10}{Q_h}$$

$$\Rightarrow Q_h = 16.31\ KW$$

* A perpetual frictionless pendulum process is possible.

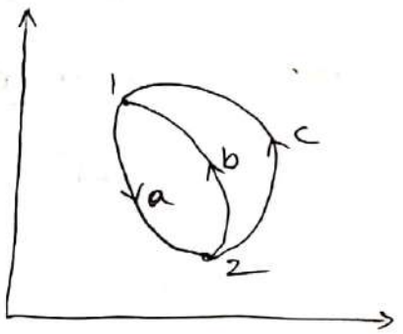
Heat transfer according to Second law of thermodynamic It occurs spontaneously from higher to lower temp. bodies but never spontaneously reverse.

# Entropy

* The process which occur without any external interaction is called a spontaneous process.
* All natural process that occur in nature are spontaneous
* Entropy is a measurable disorder.
* we can only measure the change in entropy
* Entropy is a non-measurable property.

## For Revesible cycle

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




For cycle (1a2b1)

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

For cycle (1a2c1)

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

Substract equation (1) with equation (2)

$$\boxed{\left(\frac{\delta Q}{T}\right)_{2b1} = \left(\frac{\delta Q}{T}\right)_{2c1}} \Rightarrow \text{Same for reversible process.}$$

The quantity $\left(\frac{\delta Q}{T}\right)$ for path 'b' & 'c' is same it means it does not depend on path so it is point function & This property is called entropy.

$$\Delta S = \left(\frac{\delta Q}{T}\right)_{Rev}$$

## For Irreversible process:

$$\boxed{\Delta S > \left(\frac{\delta Q}{T}\right)_{2c1}} \qquad \boxed{(\Delta S)_{Rev} > (\Delta S)_{Irrev}}$$

* Between two state infinite no. of processes are possible and out of which $\left(\frac{\delta Q}{T}\right)_{rev}$ is maximum and that is called entropy

## Entropy change for various reversible process :

**When heat added to the system :**

$$\Delta S = \left(\frac{\delta Q}{T}\right)_{rev}$$

(+ve)

Kelvin scale (+ve)

$\Rightarrow \Delta S = +ve$

$\Rightarrow$ $\boxed{S_2 > S_1, \text{ Entropy will increase}}$

**When heat is rejected from the system :**

$$\Delta S = \left(\frac{\delta Q}{T}\right)$$

−ve

+ve

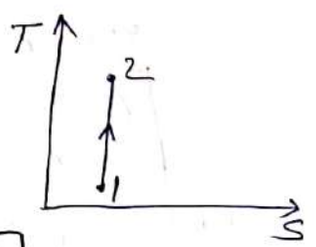
$\Rightarrow S_2 - S_1 = -ve$

$\Rightarrow$ $\boxed{S_2 < S_1, \text{ Entropy will decrease}}$

**Reversibile adiabatic process :**

$$\Delta S = \left(\frac{\delta Q}{T}\right)_{rev}$$

0




$\Rightarrow \Delta S = 0$

$\Rightarrow$ $\boxed{S_2 = S_1, \text{ Isentropic process}}$

* Reversible adiabatic process is always called Isentropic process but all Isentropic process are not Reversible adiabatic process.

## Entropy change for various irreversible process :

$$\boxed{\Delta S = \left(\frac{\delta Q}{T}\right)_{irre} + \delta S_{gen}}$$

$S_{gen}$ = Always positive & It is not a property.

**When heat is added to the system :**

$$\Delta S = \left(\frac{\delta Q}{T}\right)_{irre} + \delta S_{gen}$$

(+ve) (+ve) (+ve)

$\Rightarrow \Delta S = +ve$

$\Rightarrow S_2 > S_1$, Entropy will increase.

**When heat rejected from the system :**

$$\Delta S = \left(\frac{\delta Q}{T}\right)_{irrev} + \delta S_{gen}$$

(-ve) +ve

$\Rightarrow \Delta S = (+ve)$ or $(0)$ or $(-ve)$

**Irreversible adiabatic process :**

$$\Delta S = \left(\frac{\delta Q}{T}\right)_{irre} + \delta S_{gen}$$

0 (+ve)

$\Rightarrow S_2 - S_1 = +ve$

$\Rightarrow S_2 > S_1$

* $\boxed{\Delta S_{gas} > \Delta S_{liq} > \Delta S_{solid}}$

## Entropy principle :

$$\boxed{\Delta S_{universe} / \Delta S_{isolated} \geq 0}$$

$(\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding})$

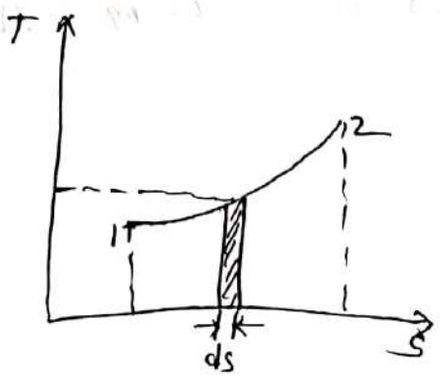
* $\Delta S_{universe} = 0 \rightarrow$ Reversible process.
* $\Delta S_{universe} > 0 \rightarrow$ Irreversible process.
* $\Delta S_{universe} < 0 \rightarrow$ Impossible process.

* Entropy of system may increase or decrease, Entropy of surrounding may increase or decrease but entropy of universe never decrease. This is known as "Entropy principle".
* All natural processess are spontaneous and irreversible.
* Entropy gives the criteria for the possibility of the process.
* A process is only possible, in the direction of increase in entropy of universe. That is why it is known as directional law.

## T-S Diagram :

$$A_{strip} = T \times ds$$

$$A_{Total} = \int_1^2 T \cdot ds \quad \text{------} (1)$$




If the process is reversible,

$$ds = \frac{\delta Q}{T}$$

$$\Rightarrow \delta Q = \int_1^2 T \cdot ds \quad \text{----} (2)$$

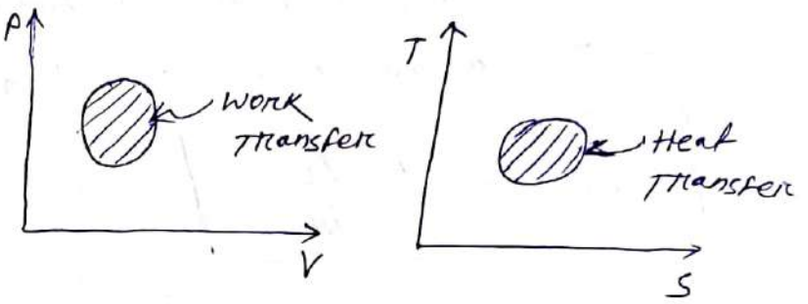
From equation ① & ②.

$$\boxed{\delta Q = A_{total}}$$

* Area under TS diagram when projected on entropy axis gives reversible heat transfer.

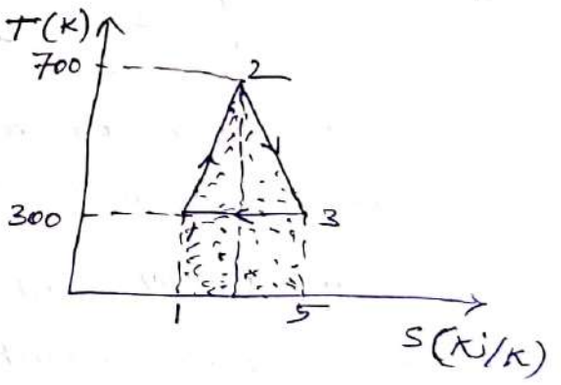
1st law of thermodynamic for a cycle.

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




* Area of cycle on PV diagram given net work transfer & Area of cycle on TS diagram gives net heat transfer. According to 1st law of TD both are same.

Q4 Calculate the thermal efficiency of the hypothetical cycle.




$$W_{net} = \frac{1}{2} bd = \frac{1}{2} \times 4 \times 400 = 800 \text{ kJ}$$

$$Q_{in} = \frac{1}{2} bd + b \times L$$

$$= \frac{1}{2} \times 4 \times 400 + 4 \times 300$$

$$= 2000 \text{ kJ}$$

$$\eta_{th} = \frac{W_{net}}{Q_{in}} = \frac{800}{2000} = 0.4 = 40\%$$

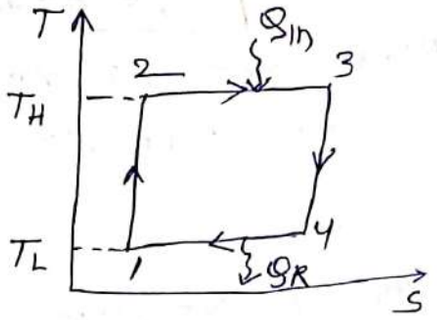
## TS diagram of carnot cycle :

1-2 : Reversible adiabatic compression

2-3 : Isothermal heat addition

3-4 : Reversible adabatic expansion

4-1 : Isothermal heat rejection




$$\boxed{\eta_{carnot} = 1 - \frac{T_L}{T_H}}$$

## Combine Ist law & 2nd law of TD :

Ist law of TD : $\delta Q = dU + \delta W$ ------ (1)

2nd law of TD : $\delta Q = T \cdot ds$ ------ (2)

From equ (1) & (2).

$$T \cdot ds = dU + \delta W$$

$$\Rightarrow \boxed{T \cdot ds = dU + PdV}$$

In above equation all are property so it's valid for both reversible and irreversible process.

As, $H = U + PV \Rightarrow dH = dU + PdV + VdP \Rightarrow dU = dH - PdV - VdP$

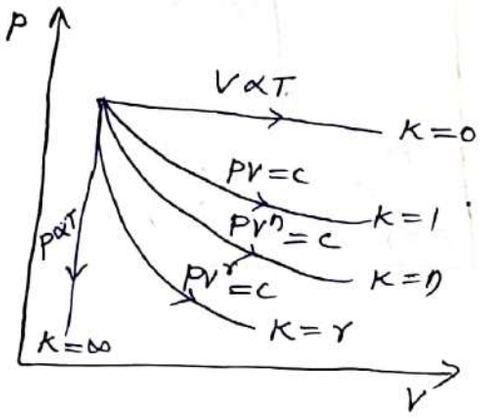
put it in final equation.

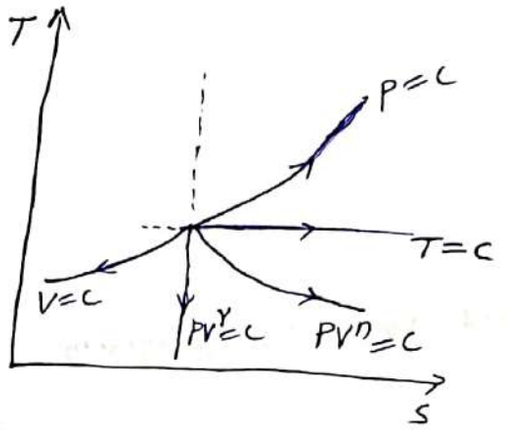
$$T \cdot ds = dH - \cancel{PdV} - VdP + \cancel{PdV}$$

$$\Rightarrow \boxed{T \cdot ds = dH - V \cdot dP}$$

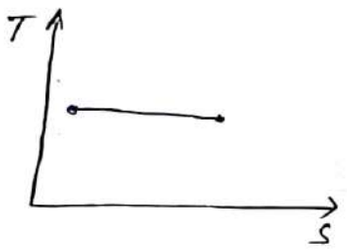
In above equation all term are property so it also used for reversible and irreversible process.

# PV diagram into TS diagram :

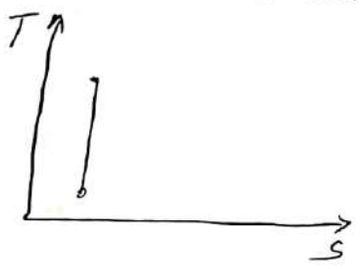



① Isothermal process




② Reversible adiabatic




③ Isobaric process

As, $T \cdot ds = dH - \cancel{V \cdot dP}^{0}$

$\Rightarrow T \cdot ds = dH \Rightarrow T \cdot ds = mC_pT$

$\Rightarrow \left.\frac{dT}{ds}\right|_p = \frac{T}{mC_p}$

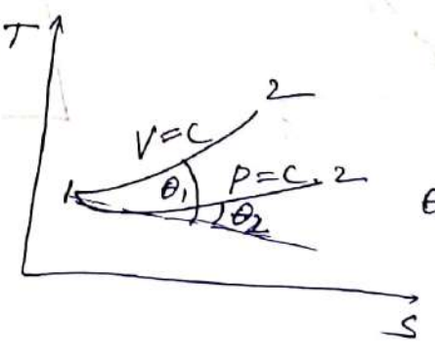
④ Isochoric process

As, $T \cdot ds = dU + \cancel{P \cdot dV}^{0}$

$\Rightarrow T \cdot ds = dU \Rightarrow T \cdot ds = mC_vT$

$\Rightarrow \left.\frac{dT}{ds}\right|_v = \frac{T}{m \cdot C_v}$

From ③ & ④ the slope of constant volume process is greather than slope of constant pressure process.




$\theta_1 > \theta_2$

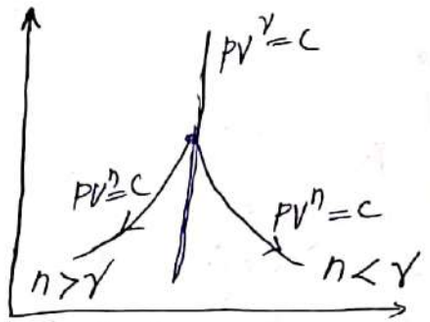
⑤ Polytropic process.

$$\delta Q_{poly} = \frac{\gamma - n}{\gamma - 1} \cdot \delta W_{poly}$$

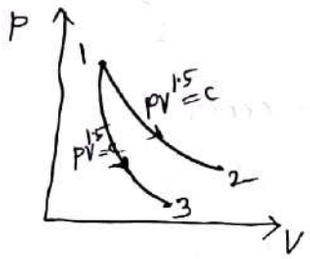
If, $n < \gamma$, $\delta Q_{poly} = +ve$, Expansion $= T\downarrow$

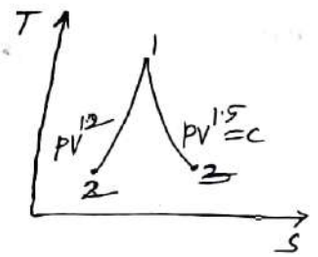
$n > \gamma$, $\delta Q_{poly} = -ve$, Compression $= T\uparrow$

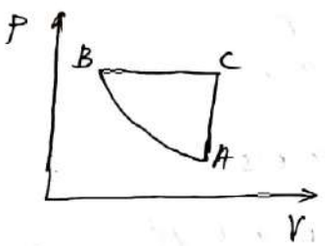
## T-S diagram for polytropic process

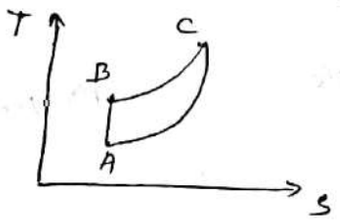


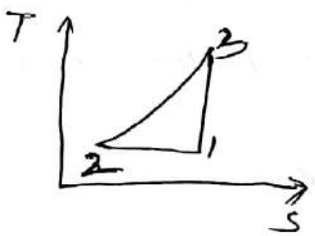

**Q4** convert PV to TS diagram

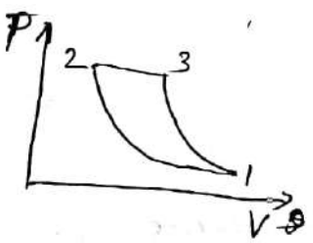


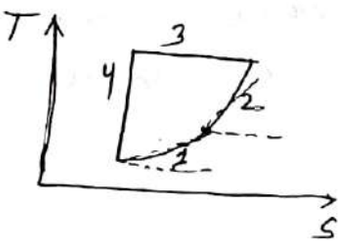



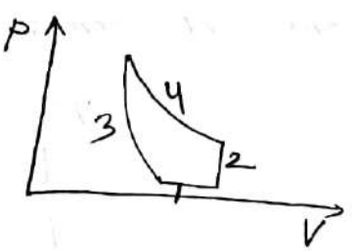



Q4 A Refrigerator unit has a COP of 4 and extracts 10 kJ of heat from the cold reservoir. If this m/c works as heat pump. How much heat it deliver to the compartment?

Solution

$COP = 4$

$Q_R = 10\ kJ$

, we know, $(COP)_R + 1 = (COP)_{H.P}$

$\Rightarrow (COP)_{HP} = 4+1 = 5$

So, $5 = \dfrac{Q_R}{Q_R - 10}$

$\Rightarrow \boxed{Q_R = 12.5\ kJ}$

* The carnot cycle is impractical because isothermal process is very slow and isentropic process is very fast.

Q4 A reversible HE rejects 80% of the heat supplied during a cycle of operation. If the engine is reversed & operates as a refrigerator, the COP is ___.

Solution:

$Q_R = 0.8\, Q_{in}$

$\eta_{H.E} = 1 - \dfrac{Q_R}{Q_{in}} = 1 - 0.8 = 0.2$

$(COP)_{H.P} = \dfrac{1}{\eta_{H.E}} = \dfrac{1}{0.2} = 5$

$(COP)_R = 5 - 1 = 4$

* When two gases mix, Entropy increase.
Ex- Free expansion.

## Statistical view of TD :

In Statistical view entropy is defined as measure of disorderness (Randomness) (uncertainity about the position of the molecules at any instant of time).

* In 1877 boltzman define entropy interms of TD probability (w) and it is defined as

$$\boxed{S = K \ln(w)}$$ , where K = Boltzman Constant $= 1.38 \times 10^{-23}$ J/K

TD probability — It is the total no. of possible microscope state available to a system at a particular condition.

## 3rd law of Thermodynamic :

The entropy of pure crystaline substance at 0K or $-273.15°c$ is zero.

**Pmm-3 :** perpetual motion machine of 3rd kind, completely eliminate friction and therefore continue motion forever due to inertia.

## Entropy Change of Ideal gas :

Case-1

$$T \cdot ds = du + pdv$$

$$\Rightarrow TS = \frac{du}{T} + \frac{pdv}{T}$$

$$\Rightarrow du = mC_v dT$$

$$\Rightarrow PV = mRT$$

$$\Rightarrow \int_1^2 ds = \int_1^2 \frac{mC_v dT}{T} + \int_1^2 \frac{mR}{T} \cdot dv$$

$$\Rightarrow \frac{P}{T} = \frac{mR}{V}$$

$$\Rightarrow [S]_1^2 = m\left[C_v \ln T + R \ln v\right]_1^2 \Rightarrow S_2 - S_1 = m\left[C_v(\ln T_2 - \ln T_1) + R(\ln V_2 - \ln V_1)\right]$$

$$\Rightarrow \boxed{S_2 - S_1 = m\left[C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}\right]}$$

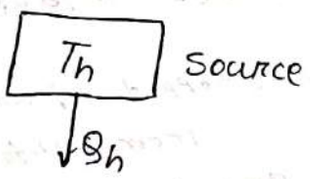
Case-II Similarly for, $T \cdot dS = dH - V \cdot dP$

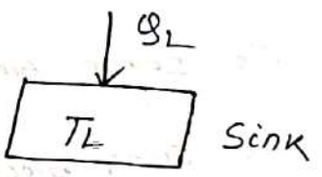
$$\boxed{S_2 - S_1 = m\left[C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)\right]}$$

Case-III

$$\boxed{S_2 - S_1 = m\left[C_p \ln\left(\frac{V_2}{V_1}\right) + C_v \ln\left(\frac{P_2}{P_1}\right)\right]}$$

## Entropy of Reservoir :



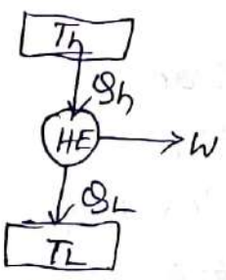

$$\Delta S = \frac{\delta Q}{T} \leftarrow (-ve)$$

$$\boxed{\Delta S = \frac{-\delta Q}{T}}$$

$$\Delta S = \frac{\delta Q}{T} \leftarrow (+ve)$$

$$\boxed{\Delta S = \frac{+\delta Q}{T}}$$

Example :




Entropy change of system heat addition

$$\Delta S = \frac{Q_h}{T_h}$$

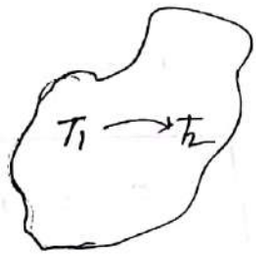
Similarly, At heat rejection side.

$$\Delta S = -\frac{Q_L}{T_L}$$

## Entropy Change of Solid and liquid due to finite temp. change:

$T_1$ = Initial temp. $T_2$ = Final temp.

we know, $dS = \frac{\delta Q}{T}$




$$\Rightarrow \int_1^2 dS = \int_1^2 \frac{mc \cdot dT}{T}$$

$$\Rightarrow (S)_1^2 = mc\,(\ln T)_1^2$$

$$\Rightarrow S_2 - S_1 = mc\,\ln(T_2) - \ln(T_1) \Rightarrow \boxed{S_2 - S_1 = mc\,\ln\left(\frac{T_2}{T_1}\right)}$$

**Q4**

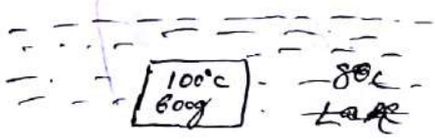
Calculate the entropy change of the universe as a result of the following.

(a) copper block of 600g mass with $C_p$ of 150 J/K at 100°C is placed in lake at 8°C.

(b) The same block at 8°C is dropped from a heigh of 100m into the lake.

(c) Two such block at 100°C and 8°C and joined together.

**Solution** (a) $m \cdot c = 150$ J/kg




$$\Delta S_{system} = mc\ln(T_2/T_2)$$

$$= 150 \times \ln\left(\frac{273+8}{373}\right)$$

$$= -42.48 \text{ J/K}.$$

$$\Delta S_{surr} = \frac{\delta Q}{T} = \frac{mc\Delta T}{273+8} = \frac{150(100-8)}{281} = 49.11 \text{ J/K}$$

$$\Delta S = \Delta S_{system} + \Delta S_{surr} = -42.48 \text{ J/K} + 49.11 \text{ J/K}$$

$$\Rightarrow \Delta S = 6.63 \text{ J/K}.$$

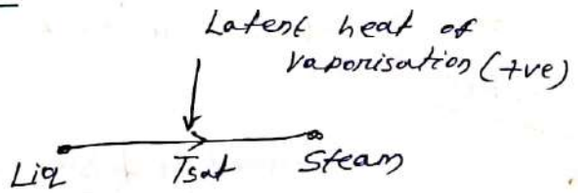
(b)

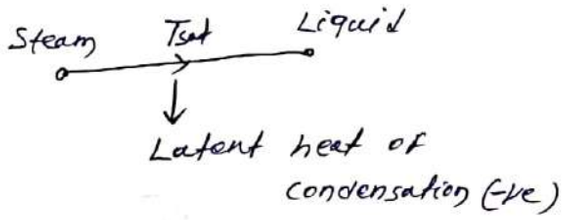
$$\Delta S_{copper} = mc\ln(T_2/T_1) = mc\ln\left(\frac{273+8}{273+8}\right) = 0$$

$$\Delta S_{lake} = \frac{\text{Energy}}{T_L} = \frac{mgh}{281} = \frac{0.6 \times 9.81 \times 100}{281} = \boxed{2.09 \text{ J/K} = \Delta S_{univ}}$$

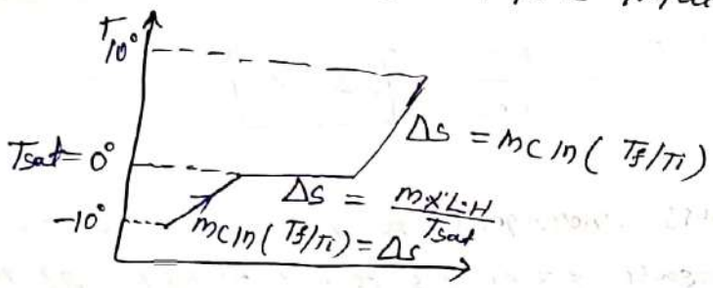
## Entropy change during phase change :

$$\boxed{\Delta S = \frac{m \times L.H}{T_{sat}}}$$



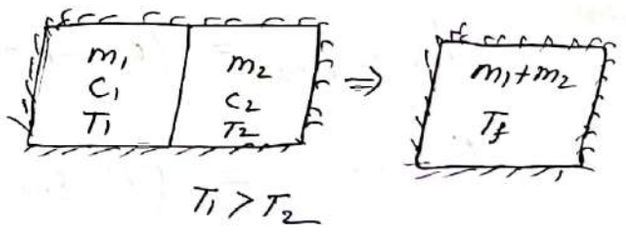




**Ex** $-10°C$ of ice $\longrightarrow$ $10°C$ liquid.




## Entropy during mixing of two liquids :

Heat lost by hot fluid = Heat gain by cold fluid




$$\Rightarrow m_1 c_1 (T_1 - T_f) = m_2 c_2 (T_f - T_2)$$

$$\Rightarrow m_1 c_1 T_1 - m_1 c_1 T_f = m_2 c_2 T_f - m_2 c_2 T_2$$

$$\Rightarrow m_1 c_1 T_1 + m_2 c_2 T_2 = m_2 c_2 T_f + m_1 c_1 T_f$$

$$\Rightarrow \boxed{T_f = \frac{(m_1 c_1 T_1 + m_2 c_2 T_2)}{(m_2 c_2 + m_1 c_1)}}$$

Entropy of universe - $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$ $\rightarrow 0$

$$\Rightarrow \Delta S_{universe} = \Delta S_{system}$$

$$\Rightarrow \Delta S_{universe} = \Delta S_{f1} + \Delta S_{f2}$$

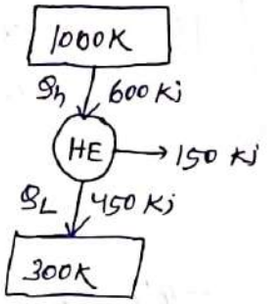
$$\Rightarrow \boxed{\Delta S_{universe} = m_1 c_1 \ln\left(\frac{T_f}{T_1}\right) + m_2 c_2 \ln\left(\frac{T_f}{T_2}\right)}$$

For same, $m_1 c_1 = m_2 c_2 = mc$

$$\boxed{\Delta S_{univer} = m \cdot c \ln\left(\frac{T_f^2}{T_1 T_2}\right)}$$

**Q4** A cyclic heat engine receives 600 kJ of heat from a 1000K & rejects 450 kJ to a 300K

**Solution**




The quantity $\oint \frac{\delta Q}{T} = \frac{Q_h}{T_h} - \frac{Q_L}{T_L}$

$= \frac{600}{1000} - \frac{450}{300}$

$= \boxed{-0.9 \text{ kJ/K}}$

$$\eta = \frac{Q_h - Q_L}{Q_h} = \frac{600-450}{600} = \frac{150}{600} = \boxed{25\%}$$

**Q4** A system of 100 kg mass undergoes a process in which it's specific entropy increase from 0.3 to 0.4 kJ/kg.K. At the same time, the entropy of surrounding decrease from 80 to 75 kJ/K. The process is <u>Irreversible</u>.

**Solution:**

$\Delta S_{system} = (0.4 - 0.3) \times 100 = 10 \text{ kJ/K}$

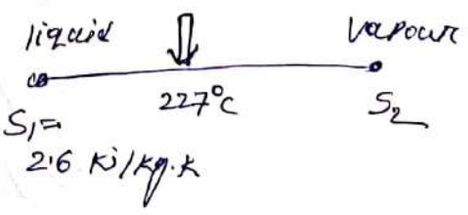
$\Delta S_{surr} = (75 - 80) \text{ kJ/K} = -5 \text{ kJ/K}$

$\Delta S_{univ} = 10 - 5 = -5 \text{ kJ/K}$

As, $\Delta S_{univer} \not> 0$. So the system is irreversible.

**Q4** Entropy of a saturated liquid at 227°C is 2.6 kJ/kgK & it's latent heat of vaporization is 1800 kJ/kg, then the entropy of saturated vapour at 227°C would be.

We know, $\delta S = \frac{m \cdot X \, L.H}{T_{sat}}$

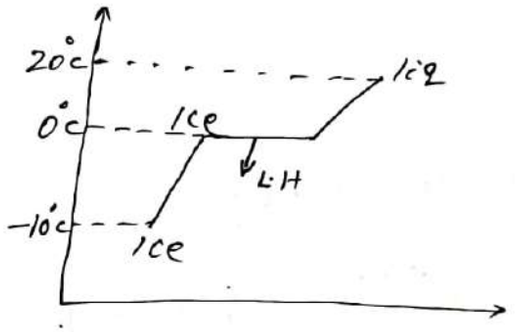



$\Rightarrow S_2 - S_1 = \frac{L.H}{T_{sat}}$

$\Rightarrow S_2 - 2.6 = \frac{1800}{500} \Rightarrow S_2 = 6.2 \text{ kJ/kg-K}$

Q4: 10 grams of water at 20°c is converted into ice at −10°c at constant atmospheric pressure. Assuming the specific heat of liquid water to remain constant at 4.2 J/gm·K and that of ice to be half of this value and taking the latent heat of fusion of ice at 0°c to be 335 J/gm. Calculate the total entropy changes of the system.

Solution:

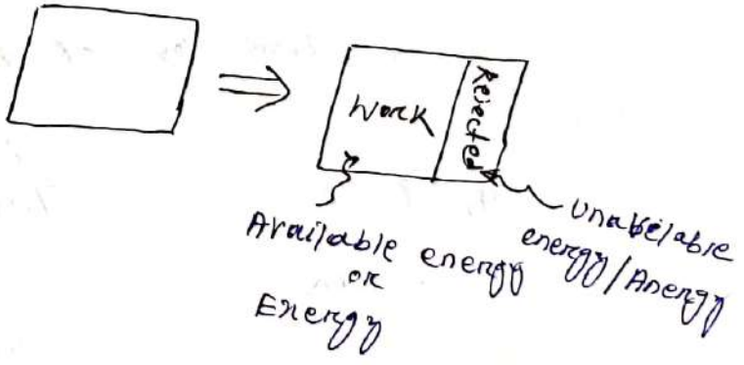



$$\Delta S = m C_w \ln\left(\frac{T_f}{T_i}\right) + \frac{m \times L.H}{T_{sat}} + m C_{ice} \ln\left(\frac{T_f}{T_i}\right)$$

$$= 10 \times 4.2 \ln\left(\frac{273}{293}\right) + \frac{10 \times -335}{273} + 10 \times 2.1 \times \ln\left(\frac{263}{273}\right)$$

$$= -16.02 \text{ J/K}$$

## Energy / Available Energy:



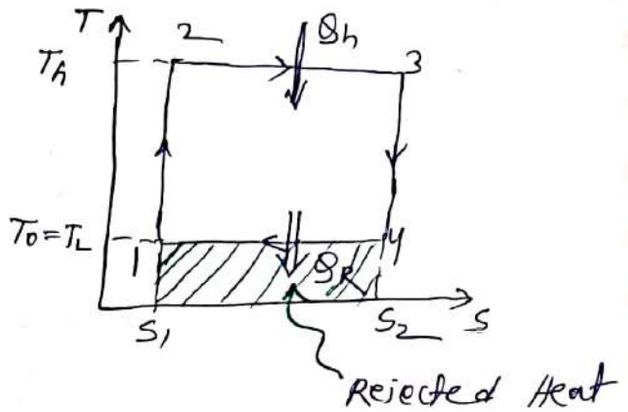

* According to 2nd law of TD complete conversion of L.E into H.E is not possible. It means only a part of energy is available for conversion. The max. part of energy which is available for conversion is called available energy and the minimum part of energy which must be rejected to surrounding is called unavailable energy.

$$\eta = \frac{W}{Q_{th}} = \left(1 - \frac{T_L}{T_H}\right) \Rightarrow \boxed{W_{max} = Q_h\left(1 - \frac{T_0}{T_h}\right)}$$, $T_0$ = surrounding temp.

Condition of available Energy : $\boxed{Q_{in} = AE + UAE}$

① cycle must be reversible.

② Heat rejected must be at ambient temp.




* Unavailable energy (UAE)

$$\boxed{UAE = T_0 \times \Delta S}$$

$$\boxed{Q_h = A.E + UAE}$$

* Loss of A.E = Increase in UAE = $\boxed{Q_{in} \cdot T_0\left(\frac{1}{T_L} - \frac{1}{T_h}\right)}$

$$\boxed{Q_{in} = AE + UAE}$$

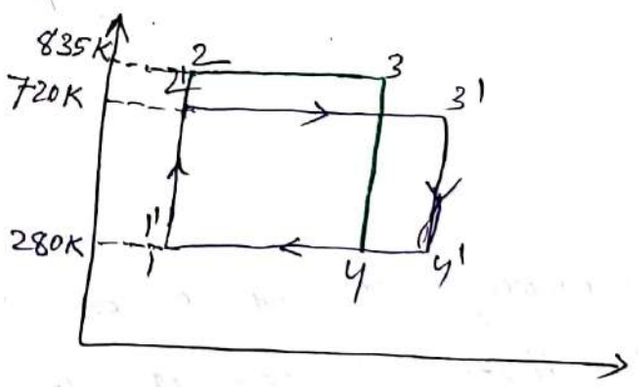
Qu 500 kJ of heat is removed from a constant temp. reservoir maintained at 835 K. The heat is received by a system at constant temp. of 720 K. The surrounding temp 280 K. Draw T-S diagram & find loss of A.E.

Solution

$T_h = 835\,K$

$T_L = 720\,K$

$T_0 = 280\,K$




Loss of AE $= Q_{in} \cdot T_0\left(\frac{1}{T_L} - \frac{1}{T_h}\right) = 500 \times 280\left(\frac{1}{720} - \frac{1}{835}\right)$

$= 26.78\,kJ$

## Availability of a closed system :

$$W_{max} = (U_1 - T_0 S_1) - (U_0 - T_0 S_0)$$

$$W_{useful} = \underbrace{(U_1 - T_0 S_1 + P_0 V_1)}_{\phi_1} - \underbrace{(U_0 - T_0 S_0 + P_0 V_0)}_{\phi_0}$$

$$\phi = U - T_0 S + P_0 V \Leftarrow \text{Availability function for Closed System.}$$

* Isentropic flow is $\begin{cases} \text{Revesible Adiabatic.} \\ \text{Irreversible heat rejection.} \end{cases}$

* Friction and continuous motion $\Rightarrow$ PMM-3

## Availability of a open system :

$$W_{rev} = (h_1 - T_0 s_1) - (h_0 - T_0 s_0) + \frac{C_1^2}{200} + \frac{g z_1}{1000}$$

Neglecting KE & PE.

$$\boxed{W_{rev} = (h_1 - T_0 s_1) - (h_0 - T_0 s_0)}$$

where, $\boxed{\psi = h - T_0 s}$ $\Rightarrow$ Availability function for open system also known as $\boxed{\text{Keenan function.}}$

## Availability (I) :

$$I = W_{rev} - W_{act}$$


* Rate of loss of availability or rate of increase in irreversibility is directly proportional to the rate of increase of entropy.

$$\boxed{\dot{I} = T \cdot d\dot{s}} \Rightarrow \text{Gouy-Stodla theorem}$$

## Energy degradation :

It is a process to convert energy from more usable form to less usable form. This will result into increase in entropy.

* In isothermal process there is increase in entropy without degradation of energy because isothermal process is a slow process so, we can make it reversible process.

* $$\boxed{ds = \frac{\delta Q}{T} + \delta S_{gen}}$$

Entropy Change $(S_2 - S_1)$ — Transfer of entropy — Entropy generation

* Entropy transfer is only associate with Heat.
* Entropy change or increase can possible by work.
* Energy not conserved.

Qu A reverse power cycle operates with temp. limits of 800K and 300K. If it takes 560 kJ of heat. Then what would be the unavailable.

Solution

$T_h = 800K$

$T_0 = 300K$

$Q_{in} = 560 kJ$

we know, $Q_{in} = AE + UAE$.

$$AE = Q_{in}\left(1 - \frac{T_0}{T_H}\right)$$

$$= 560\left(1 - \frac{300}{800}\right) = 350 kJ$$

Hence, $560 = 350 + UAE \Rightarrow UAE = 210 kJ$

Q4: A HE receives heat from a source at 1500K at a rate of 600 KW and rejects the waste heat to a medium at 350 K. If the power output from the HE is 250 KW. The irreversibility rate for the process is.

Solution:

$$W_{act} = 250 \text{ KW}$$

$$W_{rev} = AE = Q_{in}\left(1 - \frac{T_0}{T_h}\right)$$

$$= 600\left(1 - \frac{350}{1500}\right)$$

$$= 460 \text{ KW}.$$

$$I = W_{rev} - W_{act} = 460 - 250 = 210 \text{ KW}.$$

* Energy of an isolated system can never increase. But for reversible process energy energy always constant.

* Availability of a system at any given state is the max. useful work obtainable as the system goes to dead state.

* An ideal refrigerator based on reversal carnot cycle works between −23°C and +27°C what will be the required power in KW, if a cooling rate of 1.5 KW is desired?

Solution

$$COP_{Refri} = \frac{T_L}{T_H - T_L} = \frac{RE}{W}$$

$$\Rightarrow \frac{250}{300 - 250} = \frac{1.5}{W} \Rightarrow \boxed{W = 0.3 \text{ KW}}$$

# Thermodynamic Relation

## Maxwell relation :

$$\boxed{\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial P}{\partial S}\right|_V}$$

We know, Gibbs function, $\boxed{G = H - T \cdot S}$

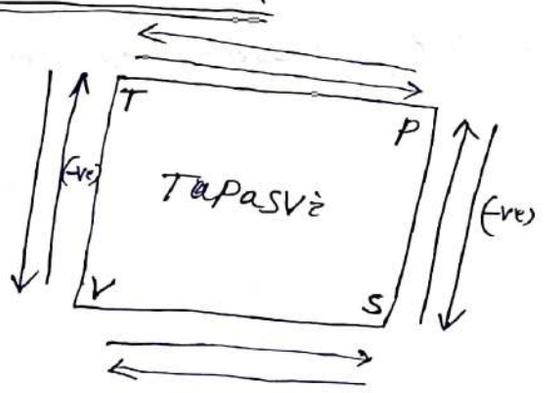
$$\boxed{\left.\frac{\partial V}{\partial T}\right|_P = -\left.\frac{\partial S}{\partial P}\right|_T}$$

Helmholtz function, $\boxed{F = U - T \cdot S}$

$$\boxed{\left.\frac{\partial P}{\partial T}\right|_V = \left.\frac{\partial S}{\partial V}\right|_T}$$

$$\boxed{\left.\frac{\partial T}{\partial P}\right|_S = \left.\frac{\partial V}{\partial S}\right|_P}$$

## Shortcut Trick




$$\left.\frac{\partial T}{\partial P}\right|_S = \left.\frac{\partial V}{\partial S}\right|_P, \quad \left.\frac{\partial P}{\partial T}\right|_V = \left.\frac{\partial S}{\partial V}\right|_T$$

$$\left.\frac{\partial V}{\partial T}\right|_P = -\left.\frac{\partial S}{\partial P}\right|_T, \quad \frac{\partial T}{\partial V} = -\frac{\partial P}{\partial S}$$

## Cyclic relation :

If, $\phi = f(x, y, z)$, $\left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial x}\right)_z \cdot \left(\frac{\partial z}{\partial x}\right)_y = -1$

If, $PV = nRT$

$$\boxed{\left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_V = -1}$$

## T·ds Equation :

$$\boxed{\begin{aligned} T\cdot ds &= C_V\cdot dT + T\cdot \left.\frac{\partial P}{\partial T}\right|_V \cdot dV \\ T\cdot ds &= C_P\cdot dT - T\left.\frac{\partial V}{\partial T}\right|_P \cdot dP \\ C_P - C_V &= T\cdot \left.\frac{\partial V}{\partial T}\right|_P \cdot \left.\frac{\partial P}{\partial T}\right|_V \end{aligned}}$$

## Thermal expansivity :

It is also know as volume expansivity. It shows the variation of volume w.r.t temp. at isobaric condition.

$$\beta = \frac{\frac{dV}{V}}{dT}$$

$$\Rightarrow \boxed{\beta = \frac{1}{V}\cdot \left.\frac{dV}{dT}\right|_P}$$

## Isothermal compressibility :

It shows the variation w.r.t pressure at constant temp.

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

$$\Rightarrow \boxed{K_T = -\frac{1}{V}\cdot \left.\frac{dV}{dP}\right|_T}$$

## Isentropic compressibility :

It shows the variation of volume w.r.t pressure at constant entropy.

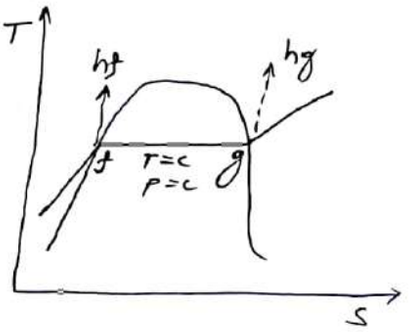
$$\boxed{\alpha = -\frac{1}{V}\cdot \left.\frac{\partial V}{\partial P}\right|_S}$$

$$\boxed{C_P - C_V = \frac{T\cdot \beta^2\cdot V}{K_T}}$$ ← Tum Bhi Yahiho jo mera Kategi

## Clausius – Clayperon Equation :

$$\frac{h_g - h_f}{T_{sat}} = \left.\frac{dP}{dT}\right|_{sat} \cdot (V_g - V_f)$$

$$s_g - s_f = \left.\frac{dP}{dT}\right|_{sat} (V_g - V_f)$$

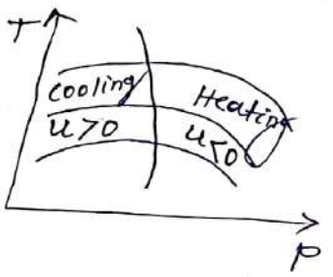



## Energy Equation :

$$du = C_v \, dT$$

$$dh = C_p \, dT$$

* For an Ideal gas the value of Joule - Thomson coefficient is $\boxed{\mu = 0}$.




* The Clausius – Clayperon equation gives the slope of curve on $\boxed{P-T}$.

# Properties of pure substance

Matter → Puresubstance (Identical particles have same size & same properties)
→ Mixture (Non-Identical particles have different size and different properties)

## Properties of pure substance :

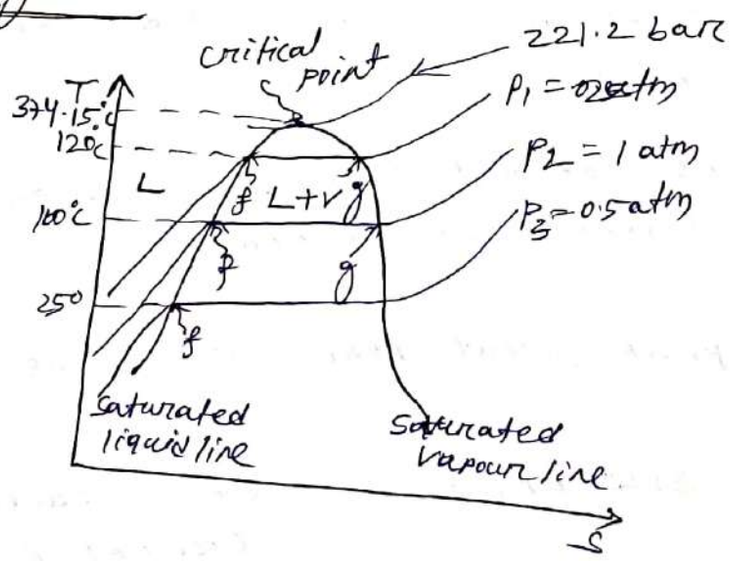
* It is a single component substance (single compound is present)
* Homogeneous and invariable chemical properties irresptive of phase change.

Ex – $H_2O$, Iron, Gold.

* As the x of mixture is same everywhere, so it treat like pure substance. Air is consider a pure substance.

Heat → Sesible Heat (Heat associated with temp. change, $Q_S = mC\Delta T$)
→ Latent Heat (Heat associated with phase change, $Q_L = m \times L.H$)

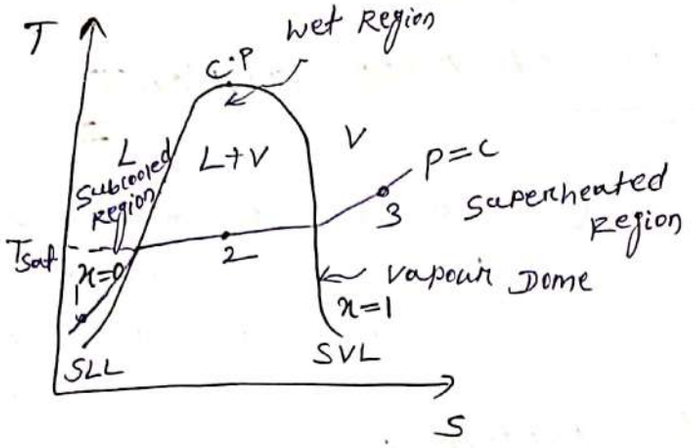
## T-S Diagram :




For water → $T_c = 374.15°C$
→ $P_c = 221.2$ bar } critical point

Saturated liquid = L

Saturated vapour = V




* Liquid below it's saturated temp. at corresponding pressure is called subcooled liquid.

* Degree of subcooling $= T_{sat} - T_1$

* The liquid which is just about to convert into vapour is called saturated liquid.

* The vapour which is just about to convert liquid by condensation is called saturated vapour.

* The vapour which is above the saturated temp. at corresponding pressure is called superheated vapour

* There is a property of a substance, that above $T_{critical}$ liquid state never exist.

* As pressure increases, saturated temp. also increases & the requirement of latent heat decreases.

* At the critical point latent heat will become zero.

* The point where SLL and SVL meet is called critical point.

* Above critical point, Latent heat still zero & flashing phenomenon continue.

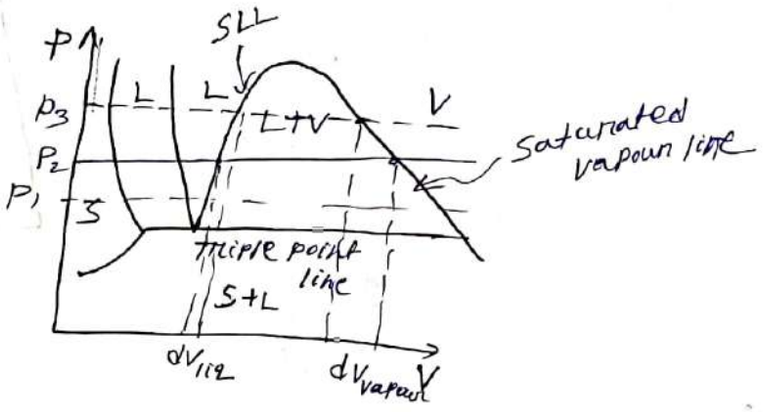
## Dryness fraction(x):

$m_f$ = mass of liquid

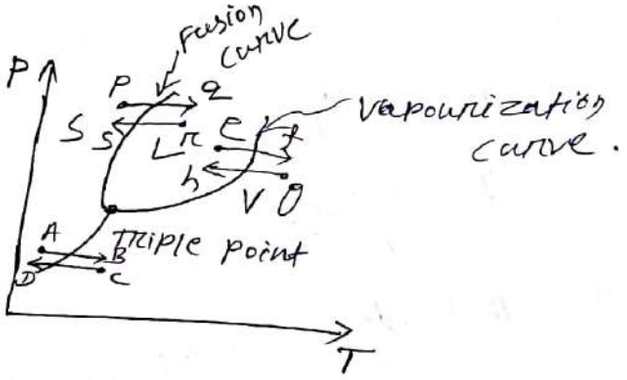
$m_g$ = mass of vapour

$$x = \frac{m_g}{m_g + m_v}$$

## P-V Diagram :




## PT Diagram :




AB = sublimation.

CD = Ablimation.

ef = vapourization.

gh = condensation.

PQ = melting.

rs = Freezing.

Triple point : The point in P-T diagram at which solid, liquid and vapour phase co-exist in equilibrium.

* sublimation curve, vapourization curve and fusion curve are (+ve) curve for pure substance.

* Only 3 substance water, Antimony and Bismuth has -ve slope of fusion curve.

* At $P = 0.611$ kpa and $T = 0.01°c$ is for triple point.

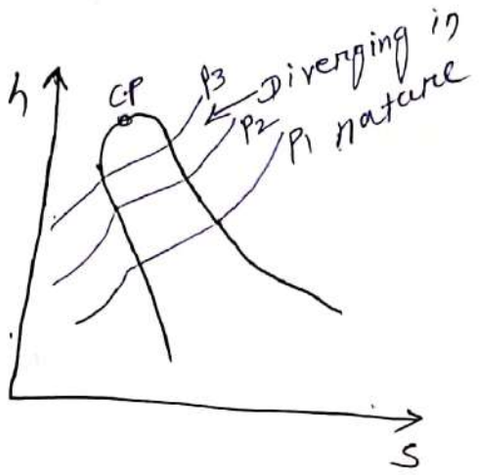
* DOF at triple point = 0

## h-s Diagram :

Consider a system at $\boxed{\begin{matrix} P = c \\ dP = 0 \end{matrix}}$

$$\delta Q = U + PdV$$

$$\Rightarrow \delta Q = h = m c_p \Delta T$$




Combine 1st and 2nd law of TD.

$$T \cdot ds = dh - V \cdot \cancel{dp}^{\,0}$$

$$\Rightarrow T \cdot ds = dh \Rightarrow \left.\frac{dh}{ds}\right|_P = T$$

* $V_1 = V_f + V_g$

$$\Rightarrow m \cdot v_1 = m_f v_f + m_g v_g$$

$$\Rightarrow v_1 = \frac{m_f}{m} v_f + \frac{m_g}{m} \cdot v_g$$

$$\Rightarrow v_1 = (1-x) v_f + x v_g$$

$$\Rightarrow \boxed{v_1 = v_f + x(v_g - v_f)} \qquad \because \frac{m_f}{m} = (1-x)$$

Similarly, $\boxed{u_1 = u_f + x(u_g - u_f) \;,\; h_1 = h_f + x(h_g - h_f)}$

* In P-V-T surface, the zone below the triple point is known as <u>sublimation zone</u>.

* At critical point the enthalpy of vaporization is <u>zero</u>.