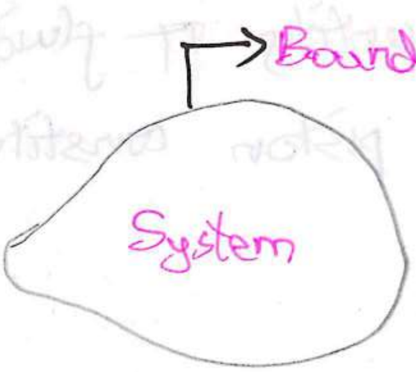
UNIT-1

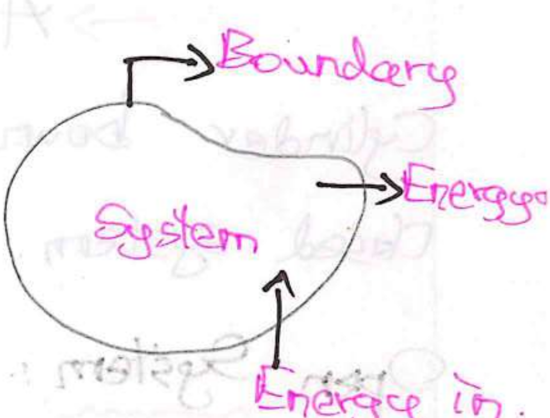
BASICS, ZEROTH AND FIRST LAW

Thermodynamic System:

→ Thermodynamic System is defined a a quantity of matter or a region in space upon which attention is concentrated in the analysis of a problem. Everything external to the system is called **surrounding** or environmen A system and its surroundings together comprise a **universe**.



a) Thermodynamic System



b) Closed System.

Types of Systems:

There are three classes of systems which are as follows.

- ★ Closed System
- ★ Open System
- ★ Isolated System

Closed System:

→ System consists of a fixed mass.

→ There is no mass transfer across the system boundary.

→ There may be energy transfer into or out of the system.

→ A certain quantity of fluid in a cylinder bounded by a piston constitutes a closed system.

Open System:

→ Open System is one in which matter crosses the system boundary.

→ There may be energy transfer also.

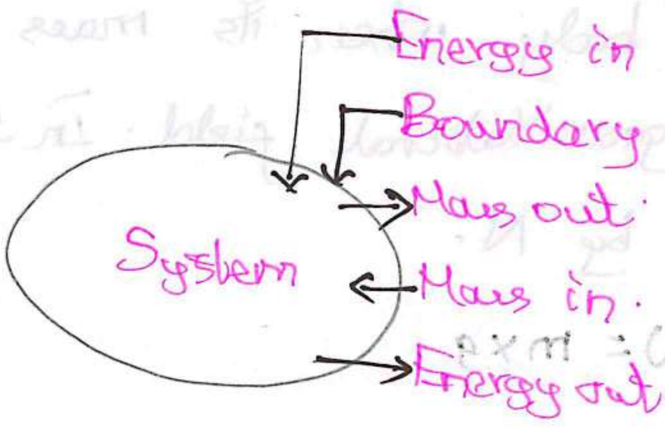
→ Most of the engineering devices are generally open system.

Eg: An air compressor in which air enters at low pressure and leaves at high pressure and there are energy transfer across the system boundary.

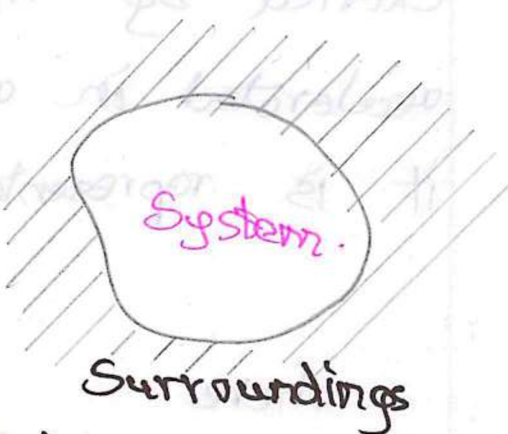
Isolated System:

→ Isolated system is one in which there is no interaction between the system and surrounding.

→ It is of fixed mass and energy, and there is no mass or energy transfer across the system boundary.



a) Open System



b) Isolated System

Thermodynamic Properties and Processes:.

→ Thermodynamic properties describe the measurable characteristics of a substance.

→ The knowledge of these properties is essential to the understanding of thermodynamics.

→ The following are the properties of Thermodynamics.

i) Mass (m) and Weight (w)

→ Mass of a body is the measure of the amount of material present in the same body. In S.I unit it is represented by kg

→ Weight of a body is the force created by the body when its mass is accelerated in a gravitational field. In S.I unit it is represented by N.

$$W = m \times g$$

where

m is the mass of body.

g is the gravitational acceleration.

ii) Density (ρ) :

→ Defined as the mass per unit volume. It is denoted by ρ (rho). In S.I unit it is represented by kg/m³.

$$\text{Density } \rho = \frac{\text{Mass}}{\text{Total Volume}} = \frac{m}{V}.$$

→ It is also denoted by specific mass or mass density.

iii) Specific Volume (v):

→ It is defined as the volume occupied by unit mass of the substances. It is the reciprocal of density. In S.I unit it is represented by m³/kg.

$$\text{Specific Volume } v = \frac{\text{Total Volume}}{\text{Mass}} = \frac{V}{m}.$$

iv) Specific Weight (w) :

→ It is defined as the weight per unit volume.

→ In SI unit it is expressed by N/m^3 or kN/m^3.

$$\text{Specific weight} = \frac{\text{Total Weight}}{\text{Total Volume}} = \frac{W}{V}.$$

v) Specific Gravity (s) :

Ratio of density of a substance to the density of some standard at a specific temperature.

$$\text{Specific gravity} = \frac{\text{Density (or) } w \text{ of given substance.}}{\text{Density (or) } w \text{ of standard substance}}$$

vi) Pressure (p) :

Force exerted per unit mass. The pressure is considered as a property when a gas or liquid is dealt.

$$\text{Pressure } p = \frac{\text{Force}}{\text{Area}} = F/A.$$

1 Pascal = $1\ N/m^2$

1 Bar = $10^5\ N/m^2 = 100\ kN/m^2$

1 Torr = 1 mm of mercury (Hg) = $133.3\ N/m^2$

1 mm of water (H_2O) = $9.80665\ N/m^2$.

THERMODYNAMIC EQUILIBRIUM :-

→ A system is said to exist in a state of thermodynamic equilibrium when no change in any macroscopic property is registered if the system is isolated from its surroundings

→ An isolated system always reaches in course of time a state of thermodynamic equilibrium and can never depart for it spontaneously

→ Therefore, there can be no quick changes in any macroscopic property if the system exists in an equilibrium state.

→ Thermodynamic study mainly the properties of physical systems that are found in equilibrium states.

→ A system will be in a state of thermodynamic equilibrium if the conditions for the following three types of equilibrium are satisfied.

- Mechanical equilibrium
- Chemical equilibrium
- Thermal equilibrium.

* Mechanical equilibrium :-

→ There are no unbalanced forces withi the system or between the surroundings.

→ The pressure in system is same at all points and does not change with respect to time.

* Chemical equilibrium :-

→ No chemical reaction takes place in the system and the chemical compositi, which is same throughout the system does n very with time.

* Thermal equilibrium

The temperature of system does no change with time and has same value at al points of the system.

→ When the conditions for any one of the three types of equilibrium are not satisfied a system is said to be in a non equilibrium state.

→ There is no single pressure that refers to the system as a whole.

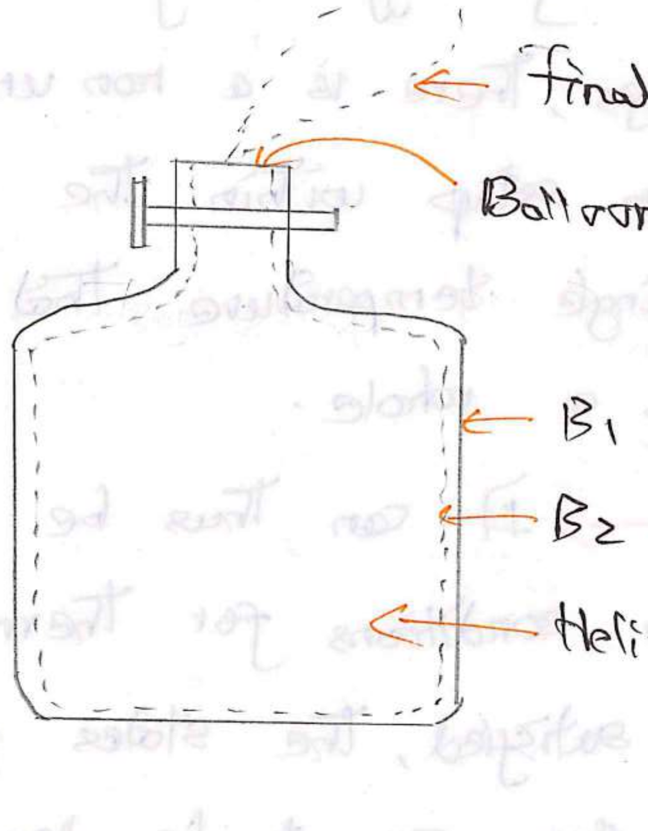
→ Similarly, if the non equilibrium is because of the temperature of the system being different from that of its surroundings, there is a non uniform temperature distribution setup within the system and there is no single temperature that stands for the system as a whole.

→ It can thus be inferred that when the conditions for thermodynamic equilibrium are not satisfied, the states passed through by a system cannot be described by the thermodynamic property which represents the system as a whole.

DISPLACEMENT WORK :

Gas from a Cylinder of compressed helium is used to inflate an inelastic flexible balloon, originally folded completely flat, to a volume 0.6 m^2. If the barometer reads 760 mm Hg, what is the amount of work done upon the atmosphere by the balloon? Sketch the system before and after the process.

Solution:-



The firm line B_1 shows the boundar of the system before the process, and dotted li B_2 shows the boundary after the process.

Displacement work

$$W_d = \int_{\text{cylinder}} pdV + \int_{\text{balloon}} pdV$$

$$= 0 + \int_{\text{balloon}} pdV. \qquad [\because dV = 0.6\,m^3]$$

$$= 101.325 \times 0.6$$

$$\boxed{W_d = 60.795\ kJ}$$

→ This is a positive work, because the work is done by the system.

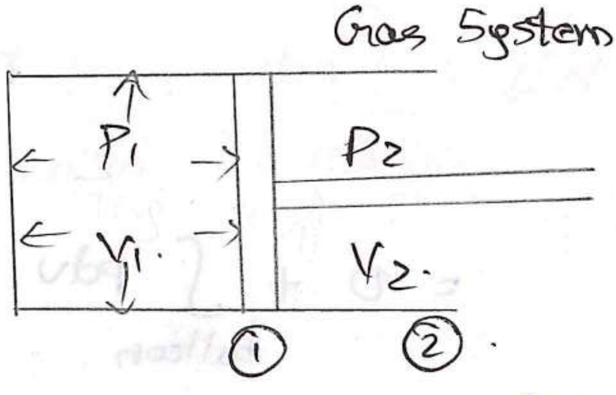
→ Work done by the atmosphere is −60.795 kJ.

→ It is assumed that the pressure in the balloon is atmospheric at all times, since the balloon fabric is light, inelastic and unstressed.

→ If the system includes both the gas and the balloon, the displacement work should be 60.795 kJ, as estimated above.

PV DIAGRAM :-

Gas System.



→ Let the gas in the cylinder be a system having initially the pressure p_1 and volume v_1.

→ let the piston move out to a new final position 2, which is also a Thermodynam equilibrium state specified by pressure P_2 and volume V_2.

→ When the piston moves an dis n dl, and if 'a' be the area of the piston, the force F acting on the piston F = p.a and the infinitesimal amount of work done by gas on pist

$$dW = F \cdot dl = padl = pdv.$$

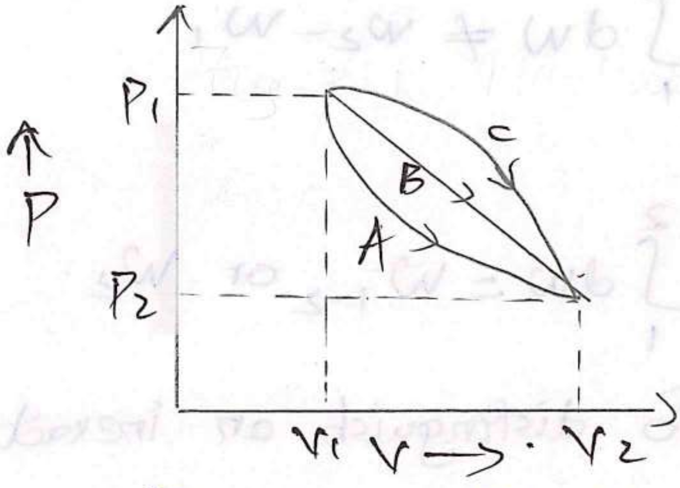
where

$dv = adl$ = infinitesimal displacement volum

→ When the piston moves out from position 1 to position 2 with the volume changing from V_1 to V_2, the amount of work done by the system will be:

$$W_{1-2} = \int_{V_1}^{V_2} p\,dv$$

Path and Point function:



→ It is possible to take a system from state 1 to state 2 along many quasi static paths, such as A, B or C.

→ For this reason work is called a path function, and dW is an inexact or imperfect differential.

→ The differential of point functions

are exact or perfect differentials and the integration is simply.

$$\int_{V_1}^{V_2} dV = V_2 - V_1 .$$

→ On the other hand, workdone in a quasi static process between two given states depar on the path followed.

$$\int_1^2 dW \neq W_2 - W_1 .$$

Rather,

$$\int_1^2 dW = W_{1-2} \text{ or } W_2 .$$

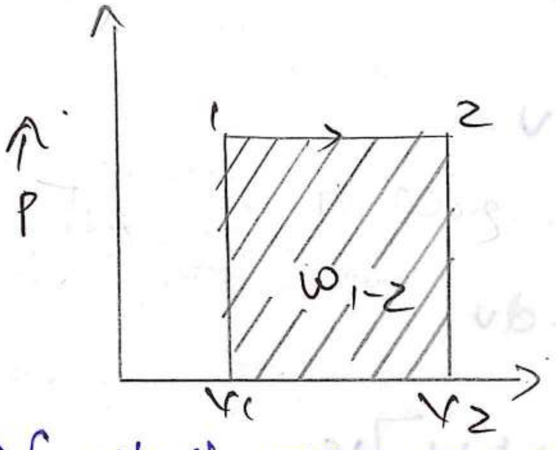
→ To distinguish an inexact differential di from an exact differential dV or dp the differential sign is being cut by a line at its fe

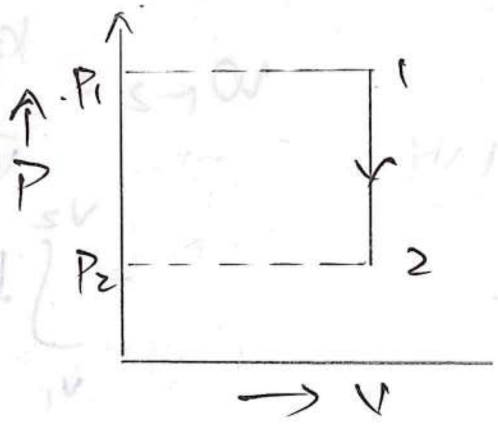
$$dV = \frac{1}{p} dW$$

→ For a cyclic process, the initial and final states of the system are the same & hen

$$\oint dV = 0 , \oint dp = 0 , \oint dT = 0 .$$

pdV work in Various quasi static processes :-





(a) Constant pressure process

$$W_{1-2} = \int_{V_1}^{V_2} p\,dV = p(V_2 - V_1)$$

(b) Constant Volume process.

$$W_{1-2} = \int p\,dV = 0.$$

(c) Process in which $pV = C$.

$$W_{1-2} = \int_{V_1}^{V_2} p\,dV \quad , pV = p_1V_1 = C.$$

$$p = \frac{(P_1V_1)}{V}$$

$$W_{1-2} = p_1V_1 \int_{V_1}^{V} \frac{dV}{V} = p_1V_1 \ln \frac{V_2}{V_1}$$

$$= P_1V_1 \ln \frac{P_1}{P_2}$$

(d) Process in which $pV^n = C$, where n is a constant.

$$pV^n = p_1V_1^n = P_2V_2^n = C.$$

$$p = \frac{(p_1 v_1^n)}{v^n}$$

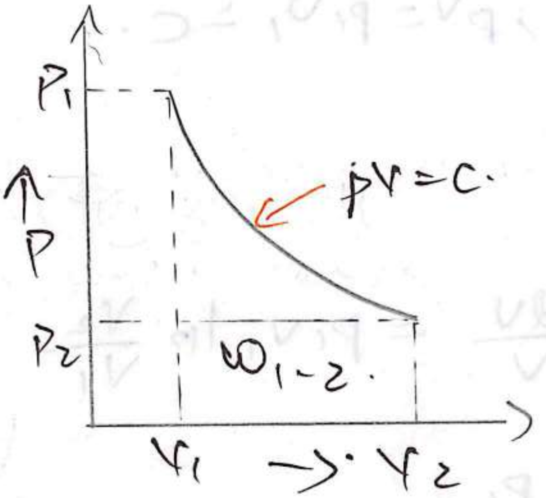
$$W_{1-2} = \int_{V_1}^{V_2} p\,dV.$$

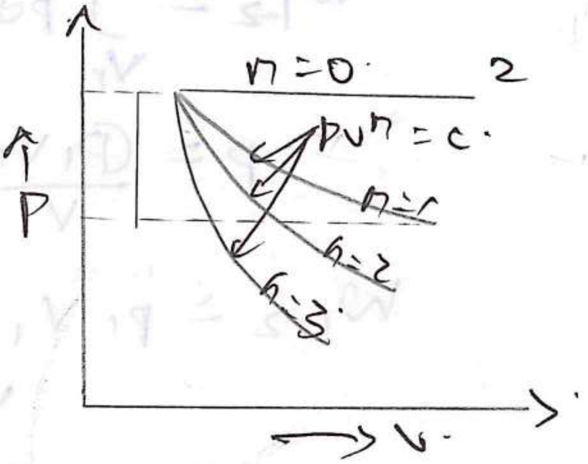
$$= \int_{v_1}^{v_2} \frac{p_1 v_1^n}{v^n}\,dv$$

$$= (p_1 v_1^n)\left[\frac{v^{-n+1}}{-n+1}\right]_{v_1}^{v_2}$$

$$= \frac{p_1 v_1^n}{1-n}\left(V_2^{1-n} - V_1^{1-n}\right)$$

$$= \frac{p_2 v_2^n \times v_2^{1-n} - p_1 V_2^n \times V_1^{1-n}}{1-n}.$$





$$= \frac{p_1 V_1 - p_2 V_2}{n-1}$$

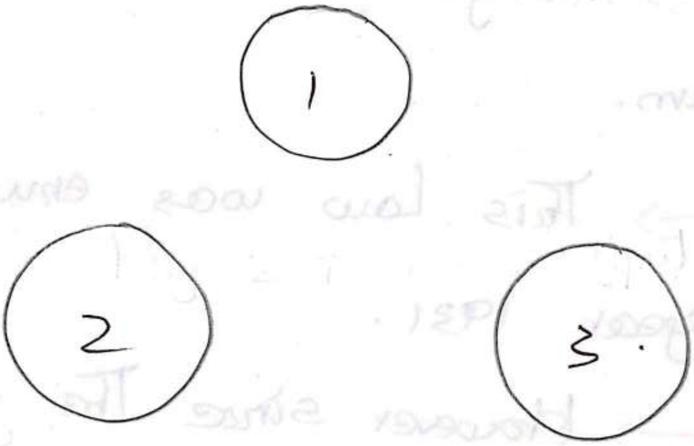
$$W_{1-2} = \frac{p_1 V_1}{n-1}\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}\right]$$

ZEROTH LAW OF THERMODYNAMICS:

→ Zeroth law deals with thermal equilibrium and establishes a concept of temperatu

→ Zeroth law states that

"If two systems are each equal in temperatu to a third, they are equal in temperature fr each other"



→ System 1 may consist of a mass of gas enclosed in a rigid vessel fitted with a pressure gauge.

→ If there is no change of pressur when this system is brought into contact wit system 2 a block of iron, then the two system are equal in temperature.

→ Experiment reveals that if system 1 is brought into contact with system 3 again with no change of properties then system 2 & 3 will show no change in their properties whe brought into contact provided they do not react with each other chemically or electrically

→ Therefore 2 and 3 must be in equilibrium.

→ This law was enuciated by R.H.Fou in the year 1931.

→ However since the first and second laws already existed at that time, it was designated as Zeroth Law so that it procede with first and second laws to form a logical sequence.

CONCEPT OF TEMPERATURE AND TEMPERATURE SCALES.

→ The Zeroth law of Thermodynamics provides the basis for the measurement of temperature.

→ There are other methods of temperature measurement which utilize various other properties of materials, that are functions of temperature, as Thermometric properties.

Thermometer	Thermometric propert
Constant Volume gas	Pressure (p)
Constant Pressure gas	Volume (v)
Alcohol or mercury in glass	Length (L)
Electric resistance.	Resistance (R)
Thermocouple	Electromotive force (E
Radiation	Intensity (I or J

Temperature measuring instruments:

These instruments may be classified into two broad categories.

* Non electrical methods:

→ By using change in volume of a liquid when its temperature is changed.

→ By using change in pressure of a gas when its temperature is changed.

→ By using changes in vapour pressure when the temperature is changed.

* Electrical methods:

→ By Thermocouples.

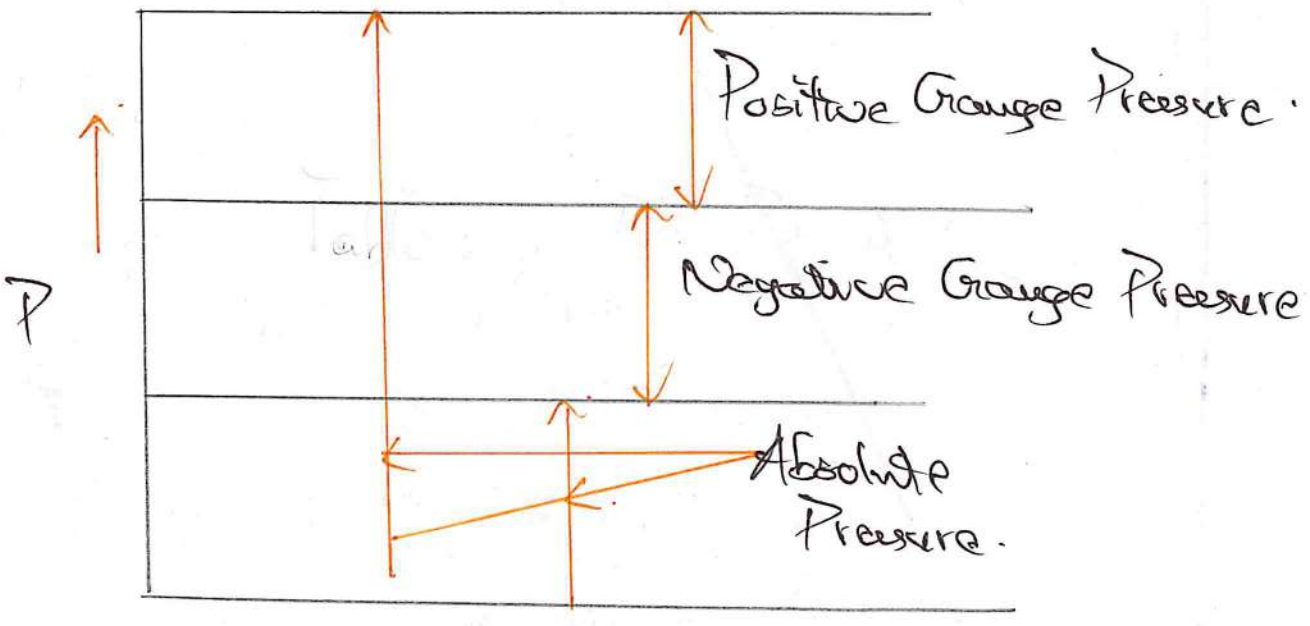
→ By change in resistance of materia with change in temperature.

→ By comparing the colours of fila and the object whose temperature is to be found out.

→ By ascertaining the energy received by radiation.

The thermometers may also be classified as follows.

* Expansion Thermometer.
    - Liquid in glass Thermometers.
    - Bimetallic
* Pressure Thermometer.
    - Vapour Pressure Thermometer.
    - Liquid filled
    - Gas filled.
* Thermocouple Thermometer
* Resistance Thermometer
* Radiation pyrometer.
* Optical pyrometer.



→ Based on the available method of measurement the whole temperature scale maybe divided into four ranges.

* From $-259.34^\circ C$ to $0^\circ C$:-

$$R_t = R_0(1 + At + Bt^2 + Ct^3).$$

* From $0^\circ C$ to $630.74^\circ C$:-

→ It is based on platinum resistance thermometer.

→ The diameter of platinum wire must lie between 0.05 and 0.2 mm.

* From $630.74^\circ C$ to $1064.43^\circ C$

$$E = a + bt + ct^2$$

* Above $1064.43^\circ C$:-

$$\frac{J_T}{J_{Au}} = \frac{\exp\left(\frac{C_2}{\lambda T_{AU}}\right) - 1}{\exp\left(\frac{C_2}{\lambda T}\right) - 1}.$$

where

$C_2 = 0.01438^\circ C$.

λ = wavelength.

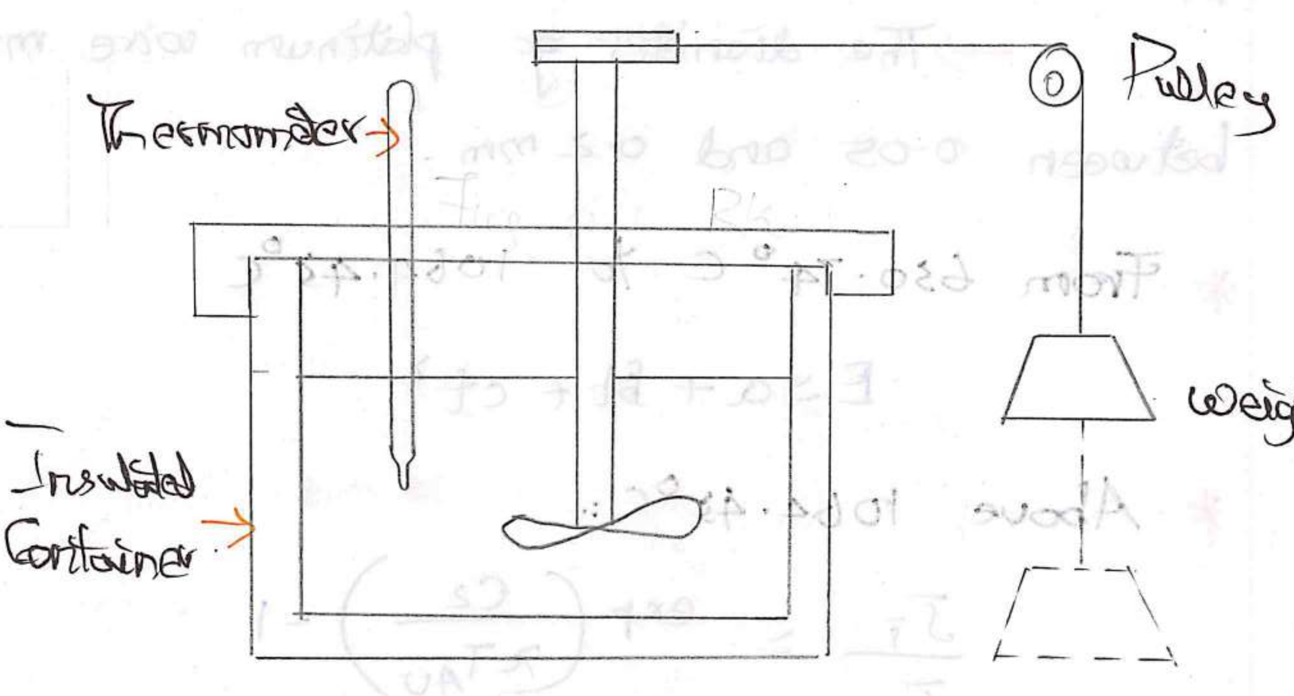
FIRST LAW OF THERMODYNAMICS:

"When a system undergoes a Thermodynamic Cycle then the net heat supplied to the system from surroundings is equal to net work done by system on its surroundings."

$$\oint dQ = \oint dw.$$

where

$\oint$ = sum for complete cycle.



→ It can be stated as an invariable experience that whenever a physical System pauses through a complete cycle the algebric sum of the work transfers during cycle.

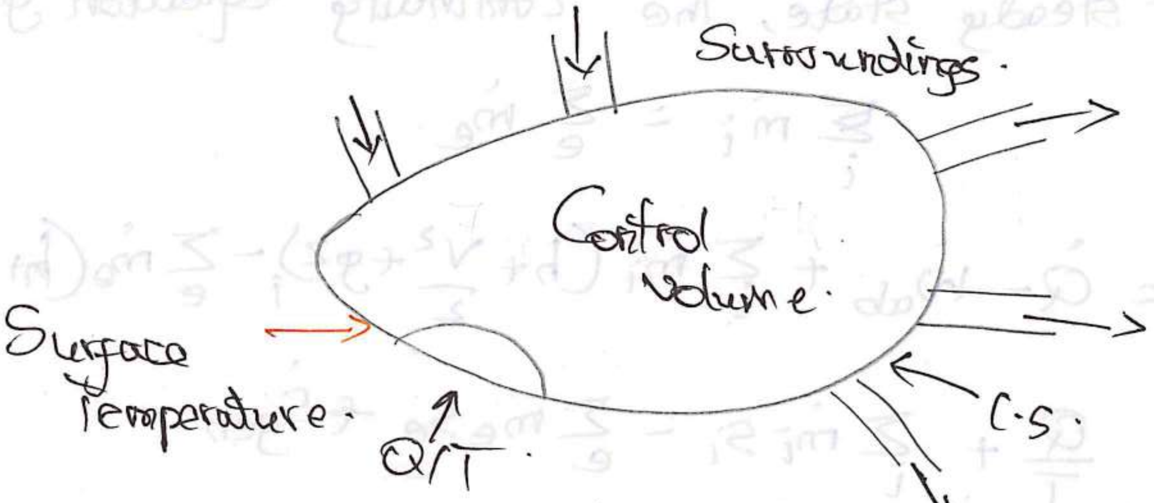
$$\oint dw = J \oint dQ$$

where

J = proportionality constant.

Application of First Law to open system:

→ In open system there is transfer of three quantities : mass, energy and entropy.



The continuity equation gives

$$\underbrace{\sum_i m_i - \sum_e m_e}_{\text{net mass transfer rate}} = \underbrace{\frac{\partial M}{\partial \tau}}_{\text{rate of mass accumulation in CV.}}$$

The energy equation gives

$$\sum_i m_i\left(h + \frac{v^2}{2} + gz\right)_i - \sum_e \dot{m}_e\left(h + \frac{v^2}{2} + gz\right)_e + \dot{Q} - \dot{w}_{sh} = \frac{\partial E}{\partial \tau}.$$

The second law inequality principle gives

$$\sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e + \frac{Q}{T} \leq \frac{\partial s}{\partial \tau}.$$

The difference is the entropy generated within the control volume due to irreversibility. Hence the entropy generation is given by.

$$\dot{S}_{gen} = \frac{dS}{d\tau} - \sum_i \dot{m}_i s_i + \sum_e \dot{m}_e s_e - \frac{\dot{Q}}{T}$$

$$\dot{S}_{gen} \geq 0.$$

At steady state, the continuity equation gives.

$$\sum_i \dot{m}_i = \sum_e \dot{m}_e.$$

$$0 = \dot{Q} - \dot{W}_{ab} + \sum_i \dot{m}_i \left(h + \frac{V^2}{2} + gz\right)_i - \sum_e \dot{m}_e \left(h + \frac{V^2}{2} + gz\right)_e$$

$$0 = \frac{\dot{Q}}{T} + \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e + \dot{S}_{gen}$$

$$0 = \frac{\dot{Q}}{T} + \dot{m}(s_1 - s_2) + \dot{S}_{gen}$$

$$s_2 - s_1 = \frac{1}{\dot{m}}\left(\frac{\dot{Q}}{T}\right) + \frac{\dot{S}_{gen}}{\dot{m}}$$

Application of First law to Closed system:

→ The entropy of any closed system can increase in two ways.

$$dS = d_eS + d_iS$$
$$= \frac{dQ}{T} + d_iS.$$

$$ds \geq \frac{dQ}{T}$$

$$d_iS \geq 0$$

For an infinitesimal reversible process by a closed system

$$dQ_R = dU_R + pdV.$$

If process is irreversible

$$dQ_I = dU_I + dW.$$

$$dU_R = dU_I$$

$$dQ_R - pdV = dQ_I - dW.$$

$$\left(\frac{dQ}{T}\right)_R = \left(\frac{dQ}{T}\right)_I + \frac{pdV - dW}{T}.$$

$$ds = d_eS + d_iS.$$

$$\int_1^2 dQ - \int_1^2 dW = E_2 - E_1$$

$$Q_{1-2} = E_2 - E_1 + W_{1-2}$$

By second Law

$$S_2 - S_1 \geq \int_1^2 \frac{dQ}{T} = S_{gen}.$$

$$S_{gen} \geq 0.$$

$$dS_{gen} = dS - dQ/T$$

$$(S_{gen})_A > (S_{gen})_B.$$

Problems:: Steady and Unsteady flow processes..

During a flow process 5 kW paddle wheel work is supplied while the internal energy of the system increases in one minute as 200 kJ. Find the heat transfer when there is no other forms of energy transfer.

Given:.

$$W = -5\ kW,\ \Delta U = 200\ kJ/min = \frac{200}{60} = 3.33\ kJ/$$

To find:

Q.

Soln:-

$$Q = W + \Delta U$$

$$= -5 + 3.33$$

$$Q = -1.67\ kW.$$

A liquid of mass 18 kg is heated from 25°C to 85°C. How much heat transfer is required? Assum Cp for water is 4.2 kJ/kg.K.

Given:

$m = 18\ kg$

$T_1 = 25^\circ C = 25 + 273 = 298\ K$

$T_2 = 85^\circ C = 85 + 273 = 358\ K.$

To find :

$Q = ?$

Soln:

$$Q = mC_p(T_2 - T_1)$$

$$= 18 \times 4.2 \times (358 - 298)$$

$$Q = 4536 \text{ kJ}.$$

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25 people attended a farewell party in a small roo of size 10 m × 8 m and has a 5 m ceiling. Each person gives up about 350 kJ of heat / hour. Assumin that the room is completely sealed off and insulated Calculate the air temperature rise occuring within 10 minutes. Assume C_v of air 0.718 kJ/kgk and $R = 0.287$ kJ/kgk and each person occupies a volum of 0.05 m^3.

<u>Given</u> :

No of persons = 25

Room size = 10 × 8 m.

Ceiling height = 5 m.

Heat / person = 350 kJ/hr.

Time t = 10 min.

$C_v = 0.718$ kJ/kgk

$R = 0.287$ kJ/kgk, $v_p = 0.05 m^3$.

To find::

Δt.

Solution::

$$V_r = 10 \times 8 \times 5 = 400 \, m^3.$$

$$V_a = V_r - V_p \times n = 400 - 0.05 \times 25$$

$$= 398.75 \, m^3.$$

$$m = \frac{PV_a}{RT} = \frac{1.013 \times 100 \times 398.75}{0.287 \times 293} = 472.29 \, kg$$

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

Assume heat addition at constant volume process

$\therefore W = 0.$

$Q = \Delta U$ = Heat / Person × No of persons.

$= 350 \times 25 = 8750$ kJ/hr.

Heat loss for 10 minutes $Q = \frac{8750}{60} \times 10$

$= 1458.33$ kJ

Heat gained by air $Q = m C_v \Delta T$

$$1458.33 = 472.29 \times 0.718 \times \Delta T$$

$$\Delta T = 4.22°C.$$

Mass of 15 kg of air in a piston cylinder device is heated from 25°C to 90°C by passing current through a resistance heater inside the cylinder. The pressure inside the cylinder is held constant at 300 kPa during the process and a heat loss of 60 kJ occurs. Determine the electric energy supplied in kw-hr and change in inter energy.

Given data:

$m = 15\ kg$

$T_1 = 25^\circ C = 25 + 273 = 298\ K.$

$T_2 = 90^\circ C = 90 + 273 = 363\ K$

$P_1 = P_2 = 300\ kPa = 300\ kN/m^2$

$Q = -60\ kJ.$

To find:

(i) Electrical energy supplied

(ii) Change in internal energy.

Solution:

$W = mR(T_2 - T_1).$

$= 15 \times 0.287 (363 - 298)$

$= 279.825$ kJ.

$W = 279.825 \times 3600$

$W = 1007.37 \times 10^3$ kW-hr.

$\Delta U = Q - W$

$= -60 - 279.825$

$\Delta U = -339.825$ kJ.

A boiler produces steam from water at 35°C. The enthalpy of steam is 2675 kJ/kg. Calculate the heat transferred per kg. The specific heat capacity of water is 4.19 kJ/kg. Neglect potential and kinetic energy.

Given:

$T_w = 35°C = 35 + 273 = 308$ K.

$h = 2675$ kJ/kg., $C_{pw} = 4.19$ kJ/kgK.

Soln:

$h_1 = C_{pw} T_w = 4.19 \times 308 = 1290.52$ kJ/kg

$Q = h_1 - h_2 = 2675 - 1290.52 = 1384.48$ kJ/kg.

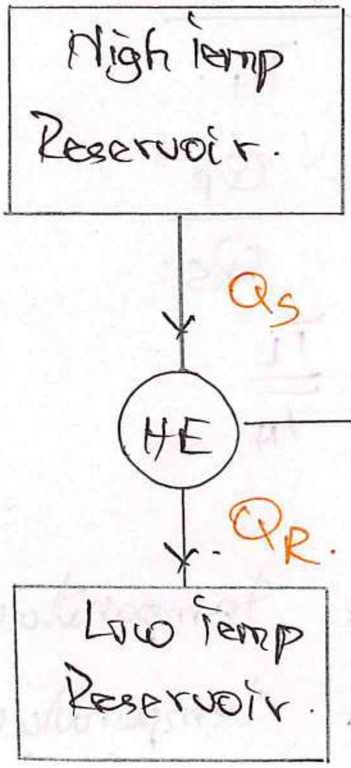
UNIT-II SECOND LAW AND ENTROPY

Heat Engine:

→ Heat engine is a device which operates in a Thermodynamic cycle and produces work by supplying heat from hot reservoir.

→ Performance of any engine is measure by the term 'efficieny'.

→ It is defined as the ratio of the network produced by an engine to the amount of heat supplied to the engine.



①

$$\text{Efficiency } \eta = \frac{W}{Q_S}$$

where

W = workdone.

Q_S - heat supplied from hot reservoir at temperature T_S.

we know that

$$W = Q_S - Q_R.$$

where

Q_R - heat rejected

Substituting we get.

$$\eta = \frac{Q_S - Q_R}{Q_S}$$

$$= \frac{T_H - T_L}{T_H}$$

$$= 1 - \frac{Q_R}{Q_S}$$

$$\eta = 1 - \frac{T_L}{T_H}.$$

where

T_H - Higher temperature.

T_L - Lower temperature.

Problems:

A heat engine operating between two reservoirs at 1000 k and 300 k is used to drive heat pump which extracts heat from reservoir at 300 k at a rate twice that at which the engine rejects heat. If η of engine is 40% & COP of heat pump is 50%., w is the temperature of reservoir? What is the rate of heat rejection if the rate of heat supply is 50 kW.

Solution:-

$$\eta_{actual} = 0.4\left(1 - \frac{300}{1000}\right) = 0.28.$$

$$W = 0.28\, Q_1.$$

$$Q_2 = Q_1 - W = 0.72\, Q_1.$$

$$Q_3 = 2Q_2 + W = 1.72\, Q_1.$$

$$(COP)_{actual} = \frac{1.72\, Q_1}{0.28\, Q_1}$$

$$= \frac{T}{T-300} \times (0.5).$$

$$\text{or } 6.143\,T = 300 \times 6.143 = T \times 0.5$$

$$T = 326.58 \text{ K}.$$

$$Q_3 = 1.72 \times 50 \text{ kW} \Rightarrow \boxed{Q_3 = 86 \text{ kW}}$$

Show that if two bodies of thermal capacities C_1 and C_2 at temperatures T_1 and T_2 are brought to same temperature T by means of reversible heat engine, then

$$\ln T = \frac{C_1 \ln T_1 + C_2 \ln T_2}{C_1 + C_2}.$$

Solution:-

$$(\Delta S)_1 = \int_{T_1}^{T} C_1 \frac{dT}{T} = C_1 \ln\left(\frac{T}{T_1}\right)$$

$$(\Delta S)_2 = \int_{T_2}^{T} C_2 \frac{dT}{T} = C_2 \ln\left(\frac{T}{T_2}\right)$$

$$(\Delta S)_{univ} = (\Delta S)_1 + (\Delta S)_2.$$

For reversible process

$$0 = C_1 \ln\left(\frac{T}{T_1}\right) + C_2 \ln\left(T/T_2\right)$$

$$\left(\frac{T}{T_1}\right)^{C_1}\left(\frac{T}{T_2}\right)^{C_2} = 1.$$

$$T^{C_1 + C_2} = T_1^{C_1} T_2^{C_2}.$$

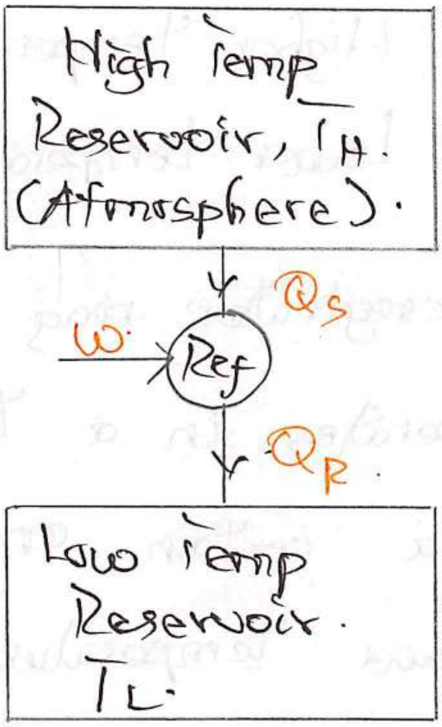
$$(C_1 + C_2)\ln T = C_1 \ln T_1 + C_2 \ln T_2$$

$$\ln T = \frac{C_1 \ln T_1 + C_2 \ln T_2}{C_1 + C_2} //.$$

Refrigerator :

→ Refrigerator is a device which is used to remove heat from a cold system.

→ In other words it is used to maintai the temperature of the body lower than the surroundings.



→ Performance of a refregirator or a heat pump is measured with a term called 'Coefficient of Performance'

→ It is the ratio of heat extracte

to The work input.

COP of a refregirator is given by.

$$C.O.P_{ref} = \frac{Q_R}{W}$$

$$= \frac{Q_R}{Q_S - Q_L}$$

$$\boxed{(C.O.P)_{ref} = \frac{T_L}{T_H - T_L}}$$

where T_H = Higher temperature.
T_L = Lower temperature.

→ A refregirator may be defined as a device That operates in a Thermodynamic Cycl and transfers a certain amount of heat from a body at lower temperature to a body at a higher temperature by consuming certain amou of external work.

→ Examples :- Domestic refrigerator
Room Air Conditioners.

Problem:

A reversible heat engine operating between reser
at 900 K and 200K drives a reversible refrigerator operating between reservoirs at 300 K & 250K. The heat engine receives 1800 KJ heat from 900 K reser
The net output from the combined engine refregirat
is 360 KJ. Find the heat transferred to the refregerator & net heat rejected to reservoir at 300

Given:

$T_2 = 900\,K$

$T_1 = 300\,K$

$T_3 = 250\,K$

$Q_{S1} = 1800\,KJ.$

To Find:

$Q_{S2} = ?,\ Q_{R1} + Q_{R2} = ?.$

Solution:

$$\eta_{max} = \frac{T_H - T_L}{T_H} = \frac{T_2 - T_1}{T_2}.$$

$$= \frac{900 - 300}{900} = 0.66 = 66.6\%$$

$$\eta_{max} = \frac{W_1}{Q_{S1}}$$

$W_1 = Q_{S1} \times \eta_{max} = 1800 \times 0.66 = 1200$ kJ.

$W_1 = Q_{S1} - Q_{R1} \Rightarrow Q_{R1} = Q_{S1} - W_1 = 1800 - 1200$.

$\boxed{Q_{R1} = 600 \text{ kJ}}$

$$COP_{ref} = \frac{T_L}{T_H - T_L} = \frac{T_3}{T_1 - T_3}$$

$$= \frac{250}{300 - 250} = 5$$

$$COP_{ref} = \frac{Q_{R2}}{Q_{S2} - Q_{R2}} \Rightarrow \frac{Q_{R2}}{W_2} = 5$$

$W_1 - W_2 = 360$ kJ.

$W_2 = W_1 - 360 = 1200 - 360$.

$\boxed{W_2 = 840 \text{ kJ}}$

$$\frac{Q_{R2}}{840} = 5 \Rightarrow Q_{R2} = 5 \times 840 = 4200 \text{ kJ}.$$

$W_2 = Q_{S2} - Q_{R2}$.

$840 = Q_{S2} - 4200$.

$Q_{S2} = 840 + 4200 \Rightarrow \boxed{Q_{S2} = 5040 \text{ kJ}}$

Net heat transferred to reservoir at 300 K.

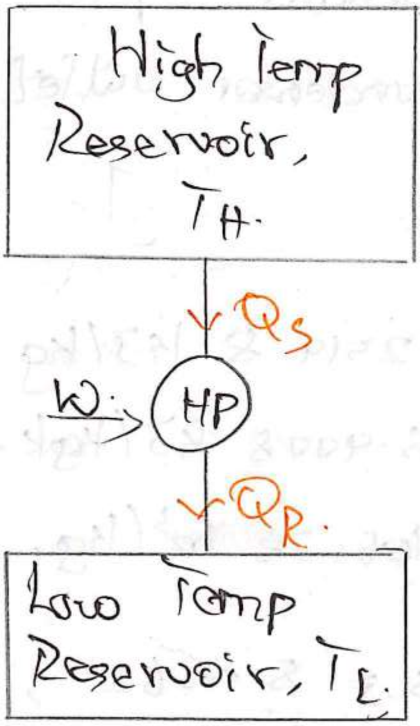
$= Q_{R1} + Q_{S2} = 600 + 5040$.

$\boxed{= 5640 \text{ kJ}}$

HEAT PUMP:

→ Heat pump is a device which is used to supply heat to a hotter system.

→ In other words, it is used to maintain the temperature of the body higher than the surroundings.



COP of heat pump is given by.

$$(C.O.P)_{HP} = \frac{Q_S}{W}$$

$$= \frac{Q_S}{Q_S - Q_R}$$

$$\boxed{(C.O.P)_{HP} = \frac{T_H}{T_H - T_L}}$$

Problems :

A heat pump installation is proposed for a home heating unit with an output rated at 30 kW. The evaporator temperature is 10°C and the condenser pressure is 0.5 bar. Using ideal vapour compression cycle, estimate the power required to drive the compressor if water mixture is used as working fluid. Assume saturated vapour at compressor inlet and liquid at condenser outlet.

Solution :

$h_1 = 2519.8$ kJ/kg.

$S_1 = 8.9008$ kJ/kgk.

$v_1 = 106.38$ m^3/kg.

400°C 50 kPa $s = 8.8862$, $h = 3278.9$.

500°C 50 kPa $s = 9.1546$, $h = 3488.7$.

$$h_2 = (3488.7 - 3278.9) \times \left(\frac{8.9008 - 8.8642}{9.1546 - 8.8642} \right) + 3278.9.$$

$$\boxed{h_2 = 3305.3 \text{ kJ/kg.}}$$

$$\text{Heating } (Q) = h_2 - h_3$$

$$= (3305.3 - 340.5)$$

$$\boxed{Q = 2964.8 \text{ kJ/kg.}}$$

$$\dot{m} \times Q = 30.$$

$$\dot{m} = \frac{30}{2964.8} \Rightarrow \boxed{\dot{m} = 0.0101 \text{ kg/s.}}$$

$$COP = \frac{2964.8}{785.5} \Rightarrow \boxed{COP = 3.77}$$

Compressor power $= \dot{m}W = 7.95$ kW.

Using an engine of 30% thermal efficiency to drive a refrigerator having a COP of 5, what is the heat pump into the engine for each MJ removed from the cold body by the refrigerator? If this system is used as heat pump, how many MJ of heat would be available for heating for each MJ of heat input to the engine?

Solution:

COP of refrigerator is 5.

So for each MJ removed from cold body we need work.

$= \frac{1 \text{ MJ}}{5}$

$= 200$ MJ.

For 200 KJ work output of heat engine

$\eta = 30\%$

We have to supply heat $= \frac{200}{0.3}$.

$= 666.67$ KJ.

Now

COP of H.P = COP of ref + 1.

$= 5 + 1$

$\boxed{(COP)_{HP} = 6.}$

Heat input to H.E = 1 MJ.

Work output (W) = 1 × 0.3 MJ.

$\boxed{W = 300 \text{ KJ}.}$

That will be the input of H.P.

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

$Q_1 = (COP)_{HP} \times W$

$\boxed{Q_1 = 1.8 \text{ MJ}.}$

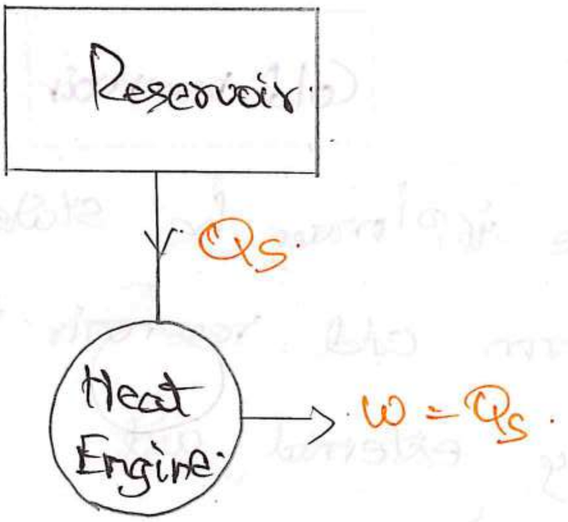
STATEMENT OF SECOND LAW:

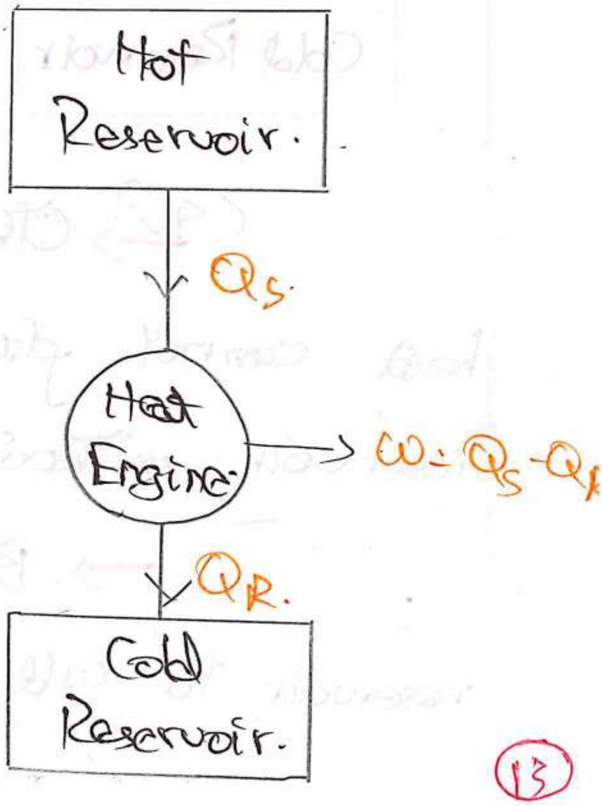
→ The second law of Thermodynamics is stated in two ways.

- Kelvin - Planck statement.
- Clausius Statement.

* Kelvin - Planck Statement :

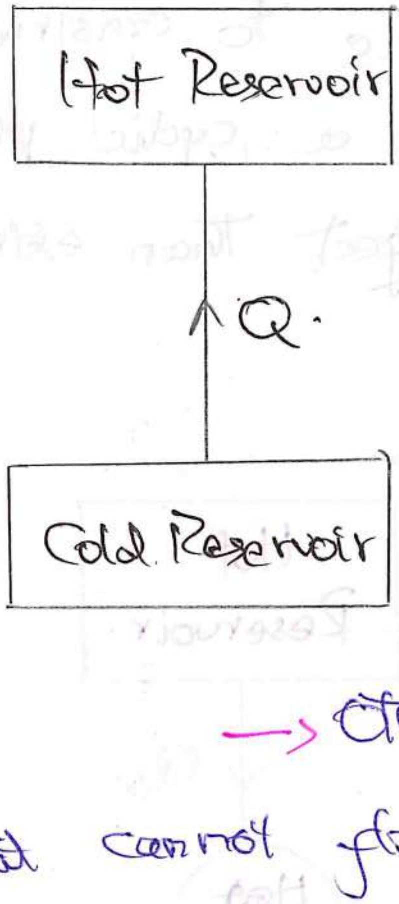
It is impossible to construct an operating device working on a cyclic process which produces no other effect than extraction e energy.

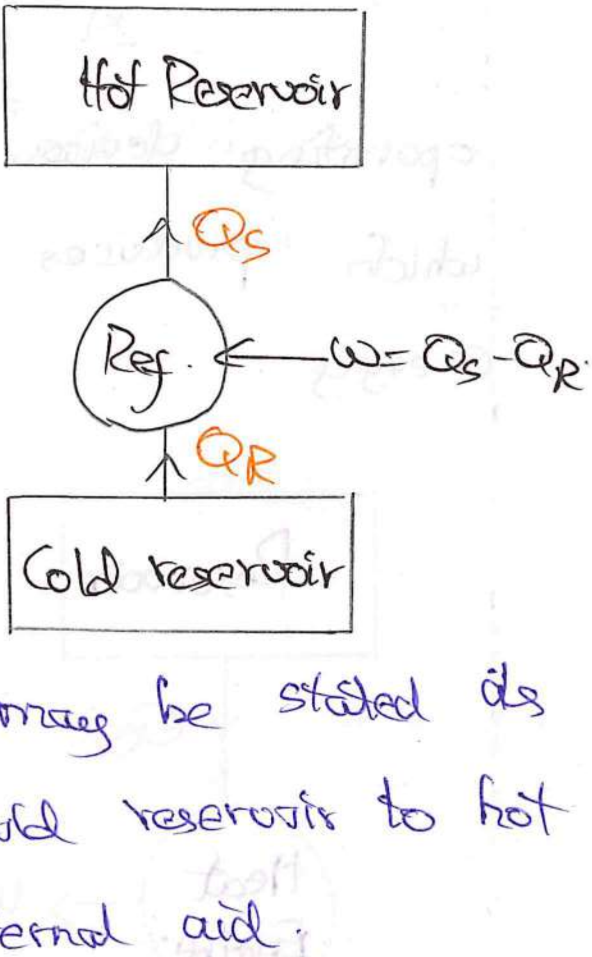




* Clausius Statement

→ It is impossible to construct an operating device working on a cyclic process which produces no other effect than the transfer of energy as heat from a low temperature body to high temperature body.





→ Otherwise it may be stated as heat cannot flow from cold reservoir to hot reservoir without any external aid.

→ But heat can flow from hot reservoir to cold reservoir without external aid.

COROLLARIES OF SECOND LAW AND EQUIVALENCE:-

The statements which can be proved by the help of reversible cycle are called as corollaries of second law of Thermodynamics.

Corollary 1:-

It is impossible to construct a system which will operate in a cycle and transfer heat from a cooler to hotter body without supplying work on the system by surroundings.

Corollary -2:-

An engine operating between two heat reservoirs cannot have higher efficiency than that of a reversible engine operating between the same heat reservoirs.

Corollary -3:-

All reversible engines operating between same two reservoirs have same efficiency.

Corollary 4:

The efficiency of any reversible engi operating between more than two reservoirs must be less than that of reversible engine operating between two reservoirs which have temperatures equal to the highest and lowest temperature of fluid in original engine.

Corollary 5:

Whenever a system undergoes a cycle $\oint dQ/T$ will be zero if the cycle is reversible and it is negative if the cycle is irreversib ie in general. $\oint dQ/T \leq 0$.

Corollary 6:

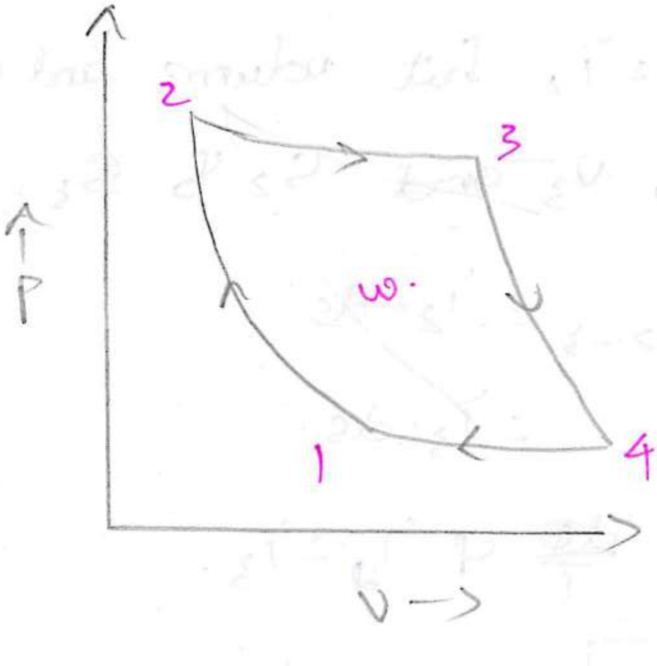
The entropy of any closed system which is thermally isolated from the surroun remains constant. The process undergone by the system is reversible.

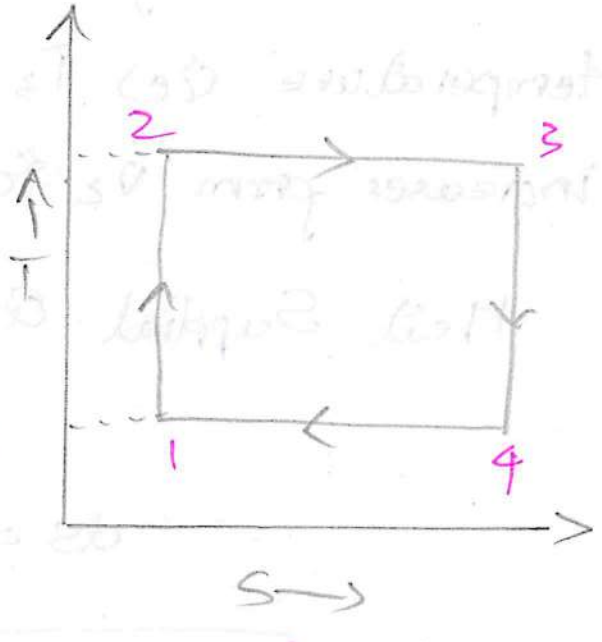
CARNOT CYCLE:

→ It is also called as constant temp cycle.

→ It consists of four processes such as two isentropic and two isothermal process.

→ The p-v and T-s diagram for Carnot cycle are as follows.





Process 1-2:

→ Air is compressed isentropically from stage 1 to 2.

→ During This process both the pressure and temperature increases from p_1 To p_2 and

T_1 to T_2 respectively.

→ Volume decreases from V_1 to V_2 and so no heat added or rejected during this proce

Process 2-3:

→ During this process, heat is supplied to the fluid at constant temperature.

→ Therefore there is no change in temperature (ie) $T_3 = T_2$ but volume and entrop increases from V_2 to V_3 and S_2 to S_3.

$$\text{Heat Supplied } Q_{2-3} = T_2 \cdot ds$$

$$= T_3 \cdot ds.$$

$$\because ds = \frac{dQ}{T} \text{ \& } T_2 = T_3.$$

$$\boxed{dQ = T \cdot ds.}$$

Process 3-4:

→ Air is expanded isentropically from 3-4.

→ During this process pressure and.

decreases from p_3 to p_4 and T_3 to T_4 respectively

→ But entropy remains constant $(S_3 = S_4)$

Process 4-1 :

→ During this process, heat is rejected isothermally from the fluid and attains its initial position.

→ Thus the fluid completes one full cycle.

Heat rejected $Q_{R4-1} = T_1 \cdot ds$. $[\because T_1 = T_4]$.
$= T_4 \cdot ds$.

⟹ Workdone during the cycle,

$W =$ Heat supplied − Heat rejected.

$W = T_2 \cdot ds - T_1 \cdot ds$.

$W = (T_2 - T_1) ds$.

Efficiency of carnot Cycle $\eta = W/Q_s$.

$$= \frac{(T_2 - T_1) ds}{T_2 \cdot ds}$$

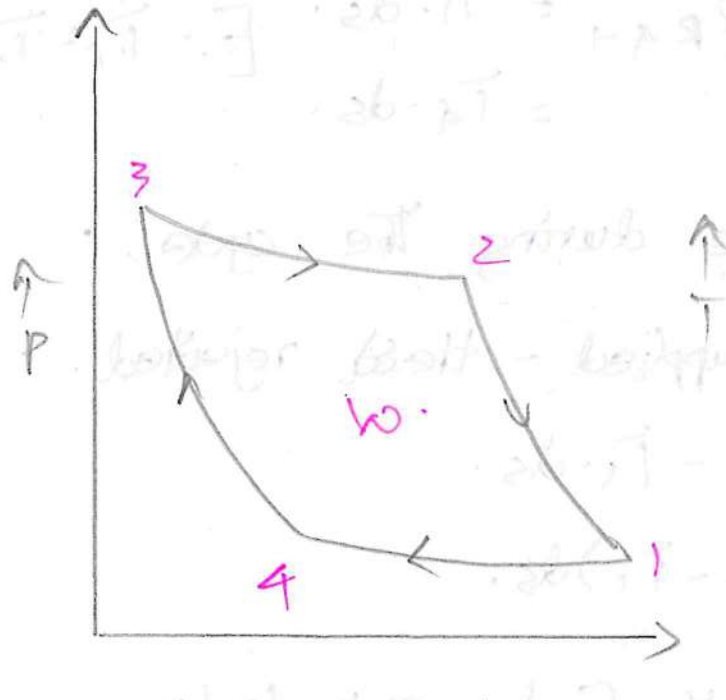
$$\boxed{\eta_{Carnot} = \frac{T_H - T_L}{T_H}}$$

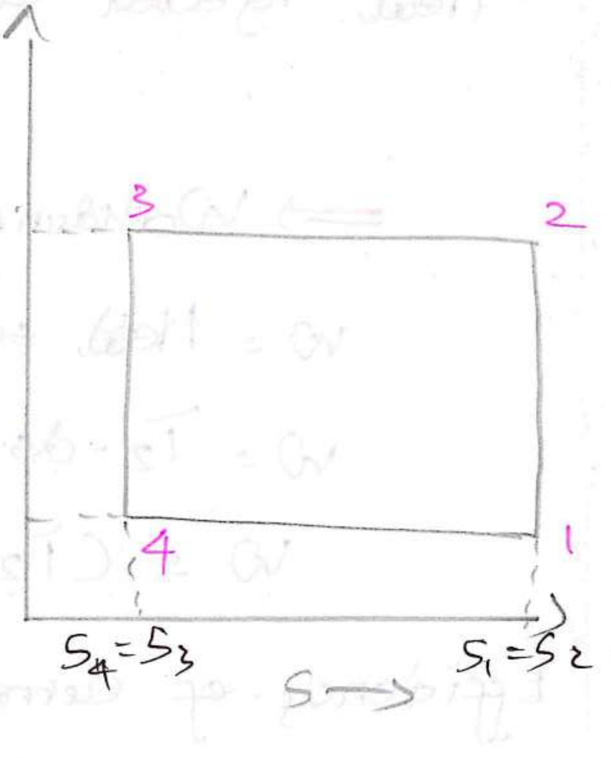
REVERSED CARNOT CYCLE:

→ This cycle consists of two isothermal and two isentropic process.

→ But This cycle is used to extract heat from cold body and rejects it into hot body.

→ Therefore The same cycle is performed in The reverse direction.





Process 1-2 : Isentropic Compression.

Process 2-3 : Isothermal Heat rejection.

Process 3-4: Isentropic expansion.

Process 4-1: Isothermal Heat Extraction.

Heat extraction during 2-3:

Heat extraction $E = T_1 ds = T_4 ds$.

Heat rejected during process 4-1:

$Q_R = T_2 \cdot ds = T_3 \cdot ds$.

Work input, $W = Q_R - E$

$T_2 \cdot ds - T_1 \cdot ds = (T_2 - T_1) ds$.

→ This machine is used to produce cooling effect.

→ Therefore here we are using the term "Coefficient of Performance" called COP.

→ It is defined as the ratio of heat extracted to work input.

$$COP = \frac{\text{Heat Extraction}}{\text{Work input}} = \frac{E}{W}$$

$$\boxed{COP = \frac{T_L}{T_H - T_L}}$$

→ Here, where T_1 & T_2 are minimum and maximum temperatures respectively.

$$T_2 = T_H \text{ and } T_1 = T_L.$$

→ The above equation is used for refrigerator.

→ If the same cycle is operated as a heat pump, heat is extracted from hot body and supplied to it into higher temperature for the purpose of heating.

→ In this case

$$COP = \frac{\text{Heat Rejected}}{\text{Work input}}$$

$$= \frac{T_2 \cdot ds}{(T_2 - T_1) ds}.$$

$$COP \text{ for HP} = \frac{T_2}{T_2 - T_1}$$

$$= \frac{T_H}{T_H - T_L}.$$

Here $T_2 = T_H$ and $T_1 = T_L$.

PERFORMANCE :-

→ A temperature scale That is independent of The properties of the substances That are used to measure temperature is called performance.

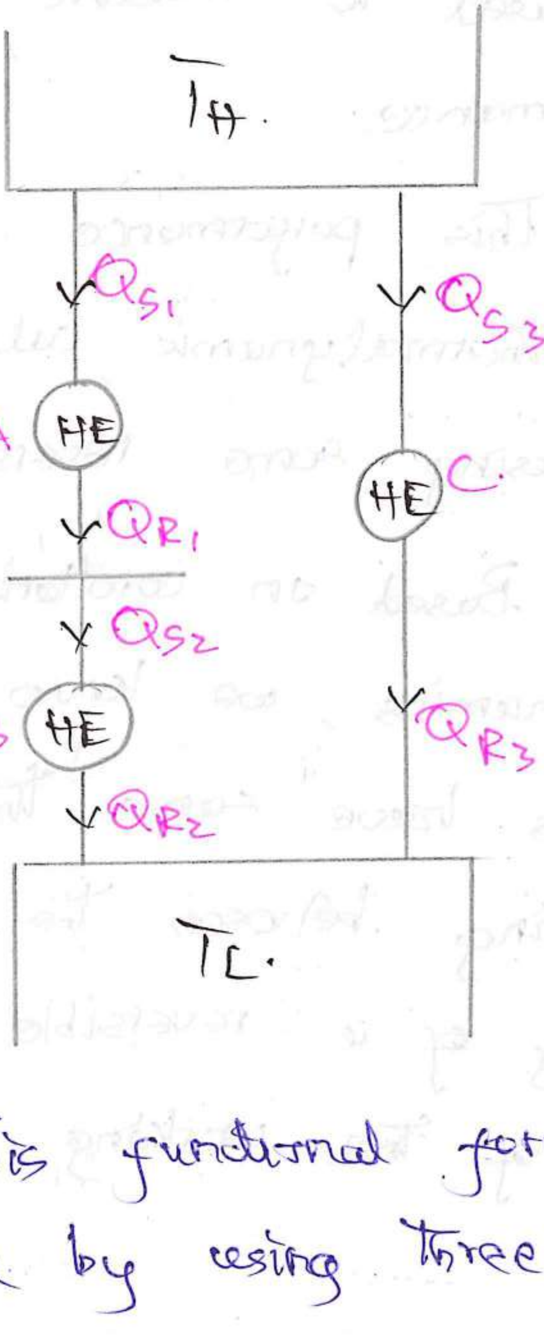
→ This performance should be much useful in Thermodynamic calculations and its derivation using some reversible heat engine.

→ Based on corollaries of second law of Thermodynamics, we know all reversible heat engines have same thermal efficiency when operating between The same two reservoi the efficiency of a reversible heat engine is independent of The working fluid and its properties.

→ Since the reservoirs are differentiate by Their temperature either it is cold reservoi or hot reservoir.

$$\boxed{\eta_{th\,rev} = g(T_H, T_L)}$$

$$\frac{Q_H}{Q_L} = f(T_H, T_L) \quad \left[\because \eta_{th} = 1 - \frac{Q_L}{Q_H}\right]$$



→ This functional form of (T_H, T_L) can be developed by using three reversible heat engines.

→ Engine A and C draws heat from T_H reservoir.

→ Then A rejects heat to the engine B.

→ The engine B receives heat from A and rejects to low temperature reservoir T_L.

→ But, engine C directly rejects heat to the low temperature reservoir, T_L.

→ The intermediate temperature between engine A and B is T.

$$\frac{Q_{S1}}{Q_{R1}} = f(T_H, T)$$

$$\frac{Q_{S2}}{Q_{R2}} = f(T, T_L)$$

$$\frac{Q_{S3}}{Q_{R3}} = f(T_H, T_L).$$

Here $Q_{S1} = Q_{S3}$ & $Q_{R1} = Q_{S2}$.

So we can write the equations as.

$$\frac{Q_{R1}}{Q_{R2}} = f(T, T_L).$$

$$\frac{Q_{S1}}{Q_{R2}} = f(T_H, T_L).$$

$$\frac{Q_{S1}}{Q_{R2}} = \frac{Q_{S1}}{Q_{R1}} \cdot \frac{Q_{R1}}{Q_{R2}}$$

Then $f(T_H, T_L) = f(T_H \cdot T) \cdot f(T, T_L)$.

→ The above equation is a function of T_H and T_L only, and independent of T on left hand side.

→ The right hand side is also a function of T_H and T_L, only not T.

So $f(T_H, T) = \frac{\phi(T_H)}{\phi(T)}$ and.

$$f(T, T_L) = \frac{\phi(T)}{\phi(T_L)}$$

The product above yields

$$f(T_H, T_L) = \frac{\phi(T_H)}{\phi(T_L)}$$

→ This obeys The kelvin Planck statement of second law of Thermodynamics

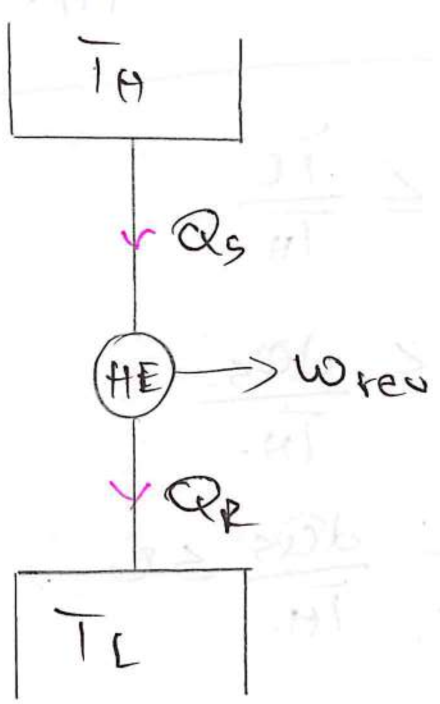
CLAUSIUS INEQUALITY :

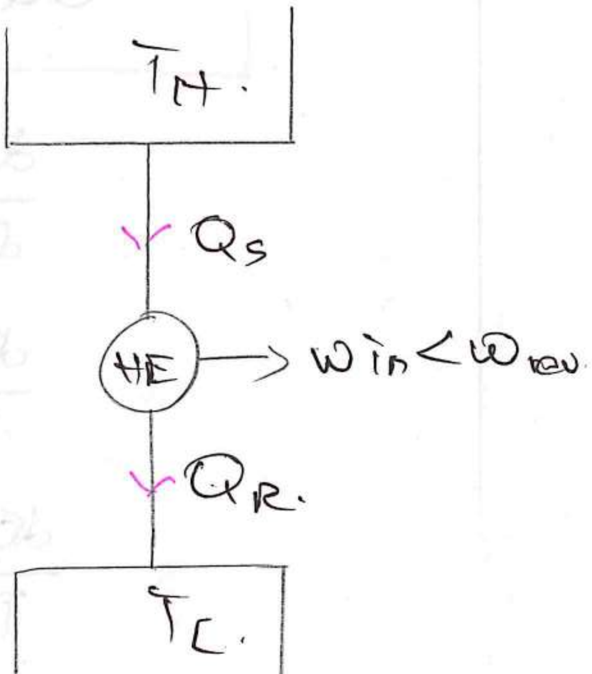
→ Clausius inequality states that when a system undergoes a cyclic process, the summation of dQ/T around a closed cycle is less than or equal to zero.

→ Consider an engine operating between two fixed temperature reservoirs T_H and T_L.

→ Let dQ_s unit of heat be supplied at temperature T_H and dQ_R units of heat be rejected at temperature T_L during a cycle.

$$\boxed{\text{Thermal } \eta = \frac{dQ_s - dQ_R}{dQ_s}.}$$





→ Thermal efficiency of any reversible engine working on the same temperature limit is given by.

$$(\text{Thermal efficiency})_{rev} = \frac{T_H - T_L}{T_H}.$$

→ The efficiency of an actual engine cycle must be less than that of a reversible cycle.

→ Since no engine can be more efficie that of a reversible engine, Hence.

$$\boxed{\frac{dQ_S < dQ_R}{dQ_S} \leq \frac{T_H - T_L}{T_H}.}$$

$$\frac{dQ_R}{dQ_S} \leq \frac{T_L}{T_H}.$$

$$\frac{dQ_R}{T_L} \leq \frac{dQ_S}{T_H}.$$

$$\frac{dQ_R}{T_L} - \frac{dQ_S}{T_H} \leq 0.$$

For entire Cycle $\oint \frac{dQ}{T} \leq 0$.

→ This equation is known as Clausius inequality.

→ It provides the criterion of the reversibility of a cycle.

* If $\oint \frac{dQ}{T} = 0$, reversible cycle.

* If $\oint \frac{dQ}{T} < 0$, irreversible & possible cycle.

* If $\oint \frac{dQ}{T} > 0$, impossible cycle.

→ Since the cycle integral $\oint \frac{dQ}{T}$ is less than zero in a cycle, the cycle violates the second law of thermodynamics.

→ So the cycle is impossible.

→ We can apply the equality to the Carnot Cycle since it is a reversible cycle.

→ The equation becomes.

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

CONCEPT OF ENTROPY :-

→ Entropy is an index of unavailability or degradation of energy.

→ Heat always flow from hot body to cold body and thus becomes lesser value available.

→ This unavailability of energy is measured by entropy.

→ It is an important Thermodynamic property of the working substance.

→ It increases with the addition of heat and decreases with removal of heat.

→ It is the function of quantity of heat with respect to temperature.

→ We are usually interested in change in entropy.

→ The change in entropy for a

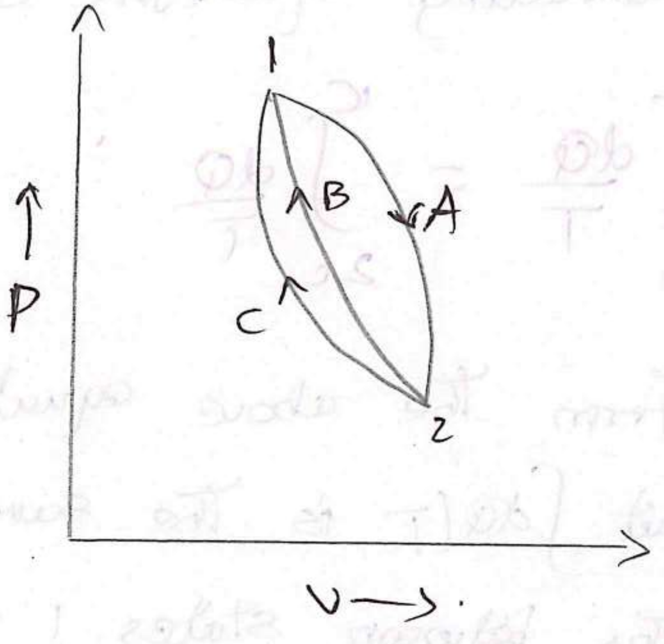
reversible process is mathematically given by.

$$\text{Change in entropy } ds = \frac{\text{Change of Heat transfer}}{\text{Absolute temperature}}.$$

$$\boxed{ds = \frac{dQ}{T}}$$

→ Unit of entropy is kJ/k or J/k.

→ Let a Thermodynamic system undergoes a change of state from 1 to 2 by a reversible process 1-A-2 and return to its original state 1 by another reversible process 2-B-1 and completing a cycle 1-2-1.



→ For this cyclic reversible process, the entropy equation is:

$$\oint_{rev} \frac{dQ}{T} = 0.$$

$$= \int_{1A}^{2A} \frac{dQ}{T} + \int_{2B}^{1B} \frac{dQ}{T} \quad \text{—} ①$$

→ Now let us consider the cycle 1-2-

is completed by another reversible process 2-C-

Then:

$$\oint_{rev} \frac{dQ}{T} = 0 = \int_{1A}^{2A} \frac{dQ}{T} + \int_{2C}^{1C} \frac{dQ}{T} \quad \text{—} ②$$

→ Subtracting equations ② from ①.

$$\int_{2B}^{1B} \frac{dQ}{T} = \int_{2C}^{1C} \frac{dQ}{T}.$$

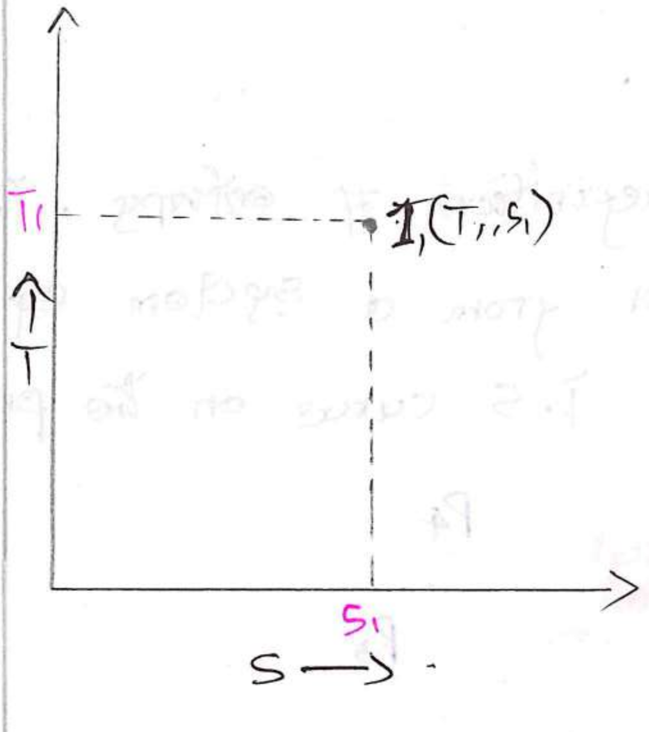
→ From the above equation we conclude that $\int dQ/T$ is the same for all reversible paths between states 1 and 2.

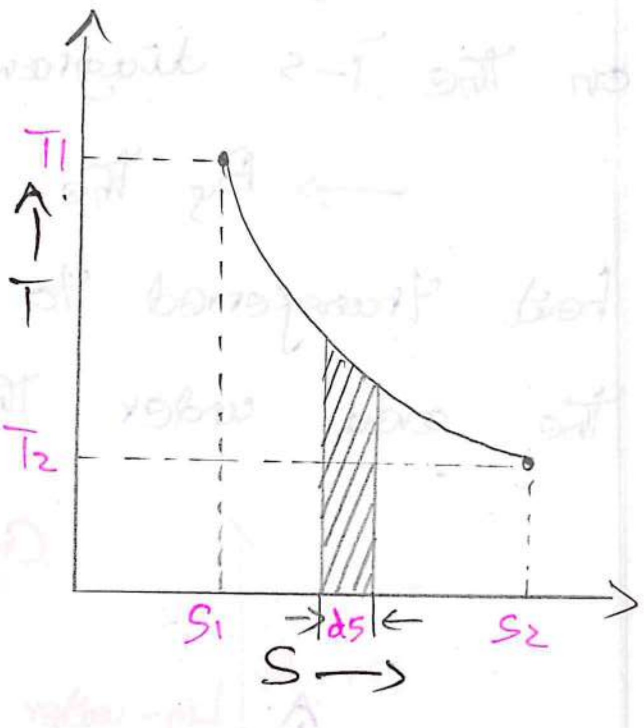
→ Hence entropy is a property of system

T-S DIAGRAM :-

→ A T-S diagram is the type of diagram most frequently used to analyze energy transfer system cycles.

→ We can represent a state of system by selecting properties (ie) temperature (T) and entropy (S) as coordinates.





$$dQ = Tds.$$

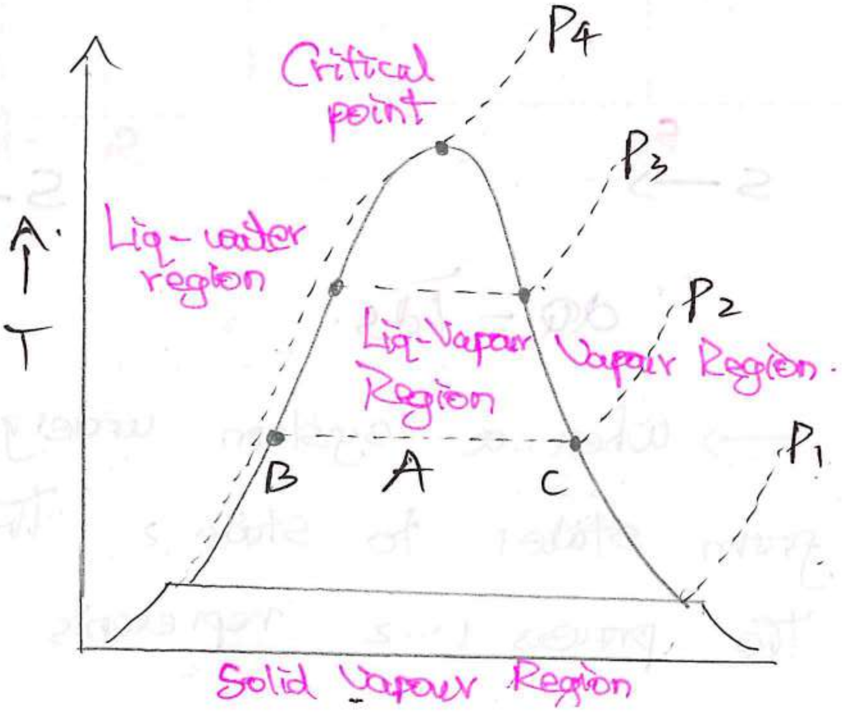
→ When a system undergoes a change of state from state1 to state 2 then the area under the process 1-2 represents heat transfer from state 1 to state 2.

$$(Q_{1-2})_{rev} = \int_{1}^{2} T\,ds$$

→ The quantity of heat transfer $(Q_{1-2})_{re}$ is represented by the area under the T-S diagram [(ie) Area $1-2-s_2-s_1$]

→ This is because the work done by a on the system and the heat added to or removed from the system can be visualized on the T-S diagram.

→ By the definition of entropy, the heat transferred to or from a system equals the area under the T-S curve on the process



→ Figure represents the T-S diagram for pure water.

→ A T-S diagram can be constructed for any pure substance.

→ It exhibits the same features as P-u diagram.

→ In the liq-vapour region water and steam exist together.

→ For example, at point A, water with an entropy given by point B exists together with steam with an entropy given by point C.

$$s = x s_g + (1-x) s_f .$$

$$x = \frac{s - s_f}{s_{fg}} .$$

where

s = specific entropy.

x = quality of mixture.

s_g = specific entropy of standard vapour.

s_f = specific entropy of standard liquid.

s_{fg} = specific entropy of change of vaporization.

TdS Equation:

→ The Three tds equations have been known to generations of students as the "tedious equations" - Though they are not all tedious to a true lover of Thermodynamics.

→ Because among other things, they enable us to calculate the change of entropy during various reversible proces in terms of either dv and dT, or dP and dT or dV and dP, even in terms of directly measurable quantities such as the coefficient of expansion and bulk modulus.

i) We can express entropy in terms of any two of PVT. Let us first express entropy as a functio of V and T.

$$ds = \left(\frac{\partial s}{\partial v}\right)_T dv + \left(\frac{\partial s}{\partial T}\right)_v dT$$

Therefore the above equation can be expressed as.

$$Tds = T\left(\frac{\partial s}{\partial v}\right)_T dv + T\left(\frac{\partial s}{\partial T}\right)_v dT.$$

From a Maxwell relation $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$

→ Also in a constant volume process,

$Tds = du$ so that, $T\left(\frac{\partial s}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v = C_v.$

Therefore

$$Tds = T\left(\frac{\partial P}{\partial T}\right)_v dv + C_v dT.$$

→ This is the first Tds Equation.

ii) This time let us express entropy as a function of P and T.

$$ds = \left(\frac{\partial s}{\partial P}\right)_T dP + \left(\frac{\partial s}{\partial T}\right)_P dT.$$

Therefore

$$Tds = T\left(\frac{\partial s}{\partial P}\right)_T dP + T\left(\frac{\partial s}{\partial T}\right)_P dT.$$

From a Maxwell relation $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P.$

→ Also in a constant pressure process.

$$Tds = dH.$$

so That $T\left(\frac{\partial s}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P = C_p.$

Therefore

$$Tds = -T\left(\frac{\partial v}{\partial T}\right)_P dP + C_p\, dT.$$

→ This is The second Tds equation.

iii) If we express entropy as a function of P and v, we have.

$$ds = \left(\frac{\partial s}{\partial P}\right)_v dP + \left(\frac{\partial s}{\partial v}\right)_P dv.$$

Therefore

$$Tds = T\left(\frac{\partial s}{\partial P}\right)_v dP + T\left(\frac{\partial s}{\partial v}\right)_P dv.$$

→ In a constant volume process, $Tds = C_v d$

So That.

$$T\left(\frac{\partial s}{\partial P}\right)_v = C_v\left(\frac{\partial T}{\partial P}\right)_v.$$

→ In a constant pressure process, $Tds = C_P dT$

so That.

$$T\left(\frac{\partial s}{\partial v}\right)_p = C_p\left(\frac{\partial T}{\partial v}\right)_p .$$

Therefore

$$T\,ds = C_v\left(\frac{\partial T}{\partial P}\right)_v dP + C_p\left(\frac{\partial T}{\partial v}\right) dv .$$

→ This is the third Tds equation.

→ In summary then these are the three Tds Equations.

i) $T\,ds = T\left(\frac{\partial P}{\partial T}\right)_v dv + C_v\,dT .$

ii) $T\,ds = -T\left(\frac{\partial v}{\partial T}\right)_p dP + C_p\,dT .$

iii) $T\,ds = C_v\left(\frac{\partial T}{\partial P}\right)_v dP + C_p\left(\frac{\partial T}{\partial v}\right)_p dv .$

→ These equations can be used, for exampl by integration the change of entropy between one state and another provided that the equati of state is known in order that we can evaluate the partial derivatives.

ENTROPY CHANGE FOR A PURE SUBSTANCE:

→ Entropy is a Thermodynamic property, i.e entropy only depends on the state of the system

Example: given T & P, entropy, S, can be obtaine from thermodynamic table just like v, u, h.

→ If the state corresponds to a liquid/vapour mixture, entropy can be determined as.

$$\boxed{s = s_f + xs_{fg}}$$

where x is the quality and s_f and s_{fg} are saturated values listed in saturation table

→ For an incompressible liquid, the entropy can be approximated by the entropy of the saturated liquid at a given temperature sin it is not a function of pressure.

→ The entropy concept can be understood from the following problem.

Problem:

A rigid tank contains 5 kg of refrigerant -134a initially at 20°c and 140 kPa. The refrigerant is cooled until its pressure drops to 100 kPa. Determine the entropy change of the refrigerant during this process.

Solution:

Constant volume process $v_1 = v_2$.

Initial State:-

$P_1 = 140\,kPa\ ,\ T_1 = 20°C$

$S_1 = 1.0532\,(kJ/kgk)\ ,\ v_1 = 0.1652\,(m^3/kg)$

Final State:-

$P_2 = 100\,kPa$ and $v_2 = v_1 = 0.1652\,(m^3/kg)$

$v_f = 0.0007258\,(m^3/kg)\ ,\ v_g = 0.1917\,m^3/kg$

Since $v_f < v_2 < v_g$ we have two phase mixture

where $x_2 = (v_2 - v_f)/v_{fg}$

$= (0.1652 - 0.0007258)/0.191$

$= 0.865$

From table A-9, $S_f = 0.0678$, $S_g = 0.9395$

$$\boxed{S_2 = S_f + x_2(S_g - S_f)}$$

$$= 0.0678 + 0.865(0.9395 - 0.0678)$$

$$= 0.822.$$

$$\boxed{\Delta S = m(S_2 - S_1)}$$

$$= 5 \times (-0.231).$$

$$\boxed{\Delta S = -1.157 \text{ kJ/kgK}}$$

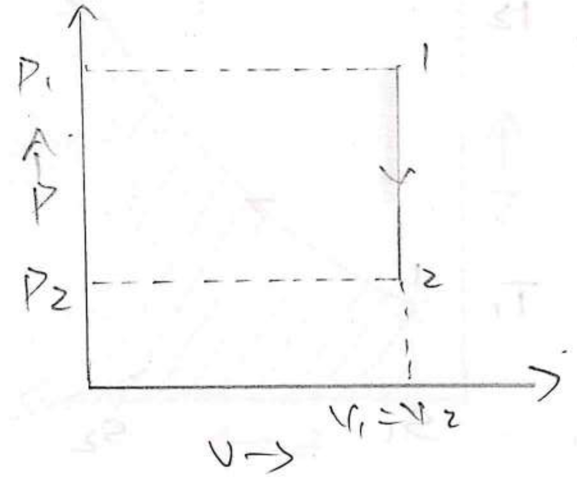
UNIT - III

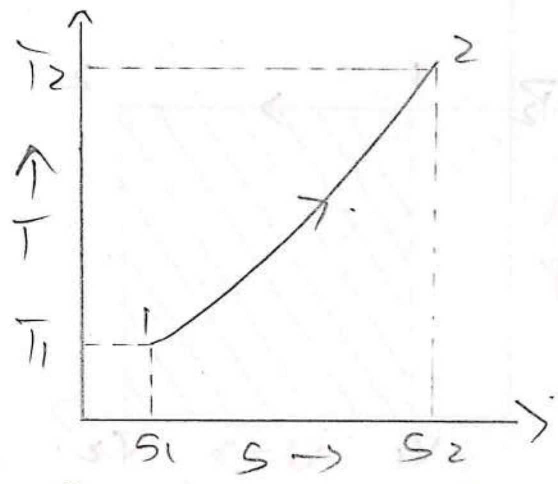
AVAILABILITY AND APPLICATION OF II LAW

① Ideal Gases Undergoing Different Processes.

* Constant Volume Process

A system undergoing change of state from 1 to 2 at constant volume process is shown in P-V and T-S diagram.





$$ds = mR\ln\left(\frac{V_2}{V_1}\right) + mC_v\ln\left(\frac{T_2}{T_1}\right)$$

But in constant volume process.

$$V_1 = V_2, \quad \therefore \ln\left(\frac{V_2}{V_1}\right) = 0.$$

$$\boxed{ds = mC_v\ln\left(\frac{T_2}{T_1}\right)}$$

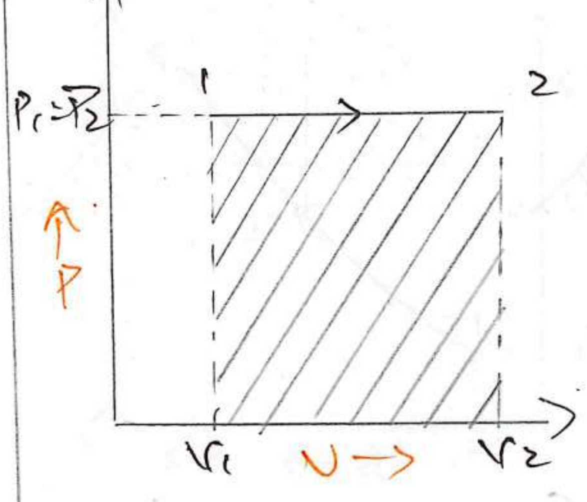
For constant volume process

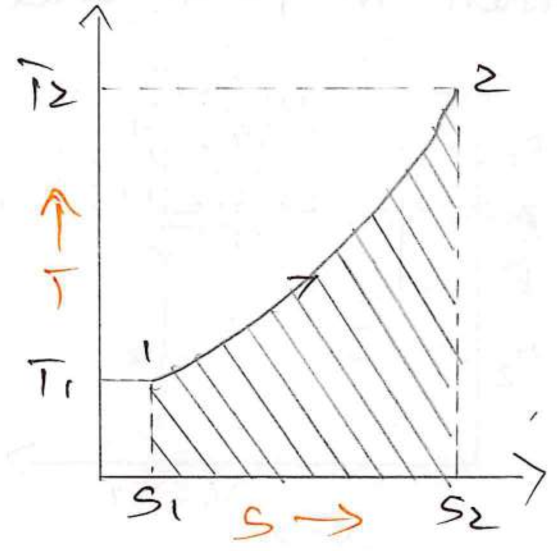
$$\boxed{ds = mC_v \ln\left(\frac{P_2}{P_1}\right) \text{ kJ/K}}$$

* Constant Pressure Process.

A system undergoing a change of state from 1 to 2 at constant pressure process is shown in P-V and T-S diagram.

$$ds = mR \ln\left(\frac{V_2}{V_1}\right) + mC_v \ln\left(\frac{T_2}{T_1}\right).$$





For constant pressure process

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

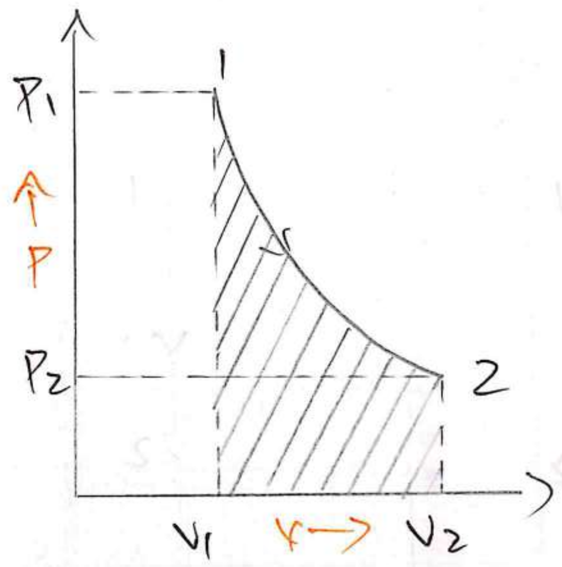
$$ds = mR \ln\left(\frac{V_2}{V_1}\right) + mC_v \ln\left(\frac{V_2}{V_1}\right)$$

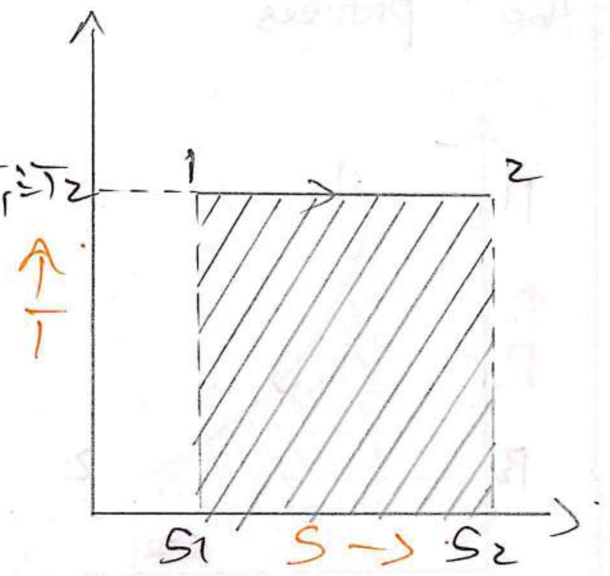
$$ds = m(C_p - C_v) \ln\left(\frac{V_2}{V_1}\right) + mC_v \ln\left(\frac{V_2}{V_1}\right)$$

$$ds = mC_p \ln\left(\frac{V_2}{V_1}\right) \text{ (or) } \boxed{ds = mC_p \ln \frac{T_2}{T_1}}$$

* Constant Temperature Process:

A system undergoing a change of state from 1 to 2 at constant temperature process is shown in P-v and T-s diagram.





$$ds = mR\ln\left(\frac{V_2}{V_1}\right) + mC_v\ln\left(\frac{T_2}{T_1}\right)$$

$$T_1 = T_2 \quad \therefore \ln\left(\frac{T_2}{T_1}\right) = 0$$

$$ds = mR\ln\left(\frac{V_2}{V_1}\right) \text{ kJ/K}$$

Multiplying & dividing by T.

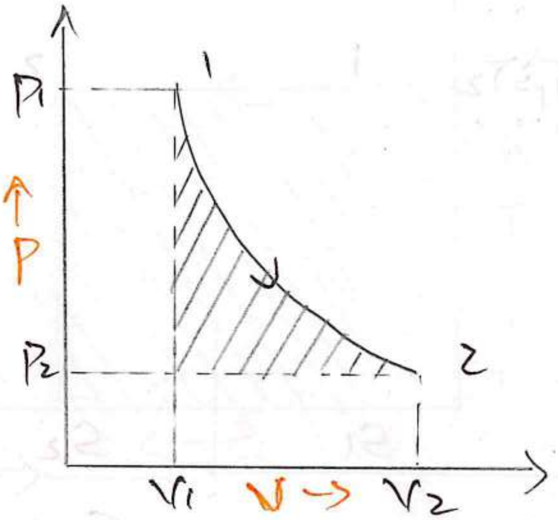
$$ds = \frac{mRT\ln\left(\frac{V_2}{V_1}\right)}{T}$$

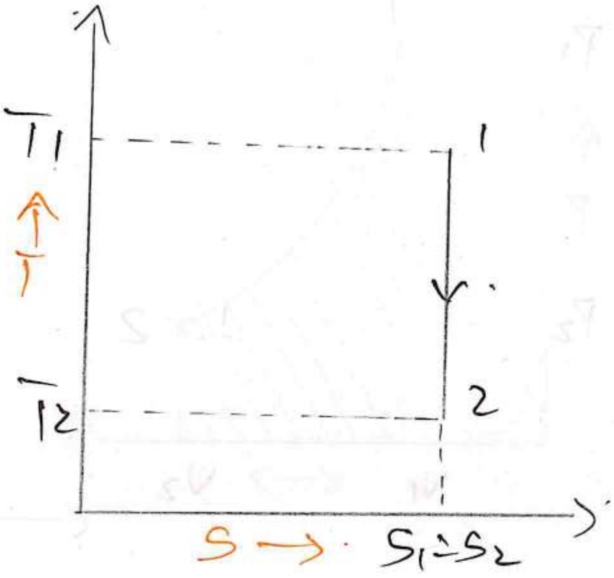
$$\boxed{ds = \frac{Q}{T}} \qquad \therefore \left[Q = mRT\ln\left(\frac{V_2}{V_1}\right)\right]$$

* Reversible adiabatic or isentropic process

→ Adiabatic process is the process in which the heat is neither received nor rejected

→ Simply there is no transfer during the process.





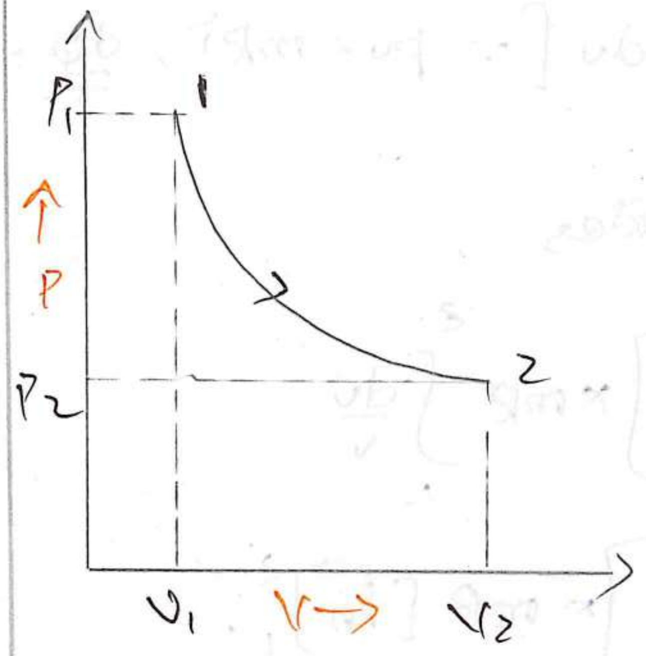
→ Since there is no heat transfer duri the process, change in entropy is zero.

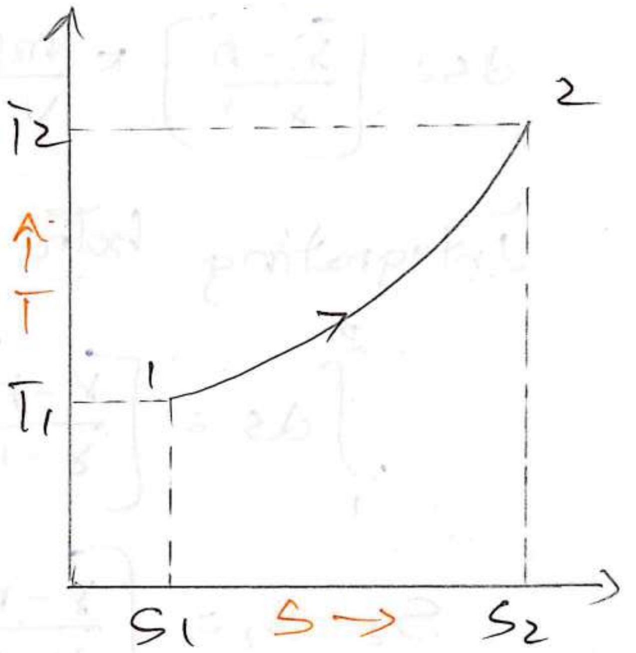
* Polytropic Process.

→ During the polytropic process, there being heat transfer between a system and its surroundings.

→ Change in entropy is calculated by

$$ds = mR \ln\left(\frac{V_2}{V_1}\right) + mC_v \ln\left(\frac{T_2}{T_1}\right) \text{ kJ/k}.$$





Another expression may be derived as follows

Heat transfer during polytropic process is given by.

$$dQ = \left[\frac{\gamma - n}{\gamma - 1}\right] \times w.$$

where.

γ = Adiabatic index
n = Polytropic index.
w = Workdone.

$$dQ = \left[\frac{\gamma - n}{\gamma - 1}\right] \times p\,dv.$$

Dividing both sides by T.

$$\frac{dQ}{T} = \left[\frac{\gamma - n}{\gamma - 1}\right] \times \frac{P}{T} \times dv.$$

$$ds = \left[\frac{\gamma - n}{\gamma - 1}\right] \times \frac{mR}{V} dv \left[\because pv = mRT, \ \frac{dQ}{T} = ds\right]$$

Integrating both sides.

$$\int_1^2 ds = \left[\frac{\gamma - n}{\gamma - 1}\right] \times mR \int_1^2 \frac{dv}{V}.$$

$$S_2 - S_1 = \left[\frac{\gamma - n}{\gamma - 1}\right] \times mR \left[\ln\right]_1^2.$$

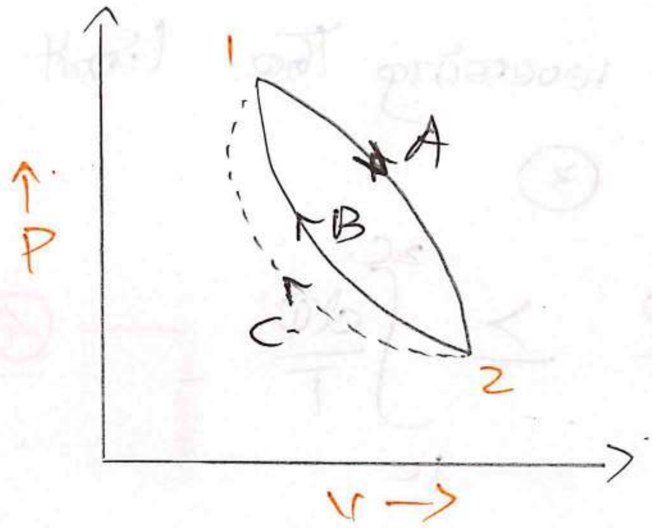
$$\boxed{ds = \left[\frac{\gamma - n}{\gamma - 1}\right] \times mR \ln\left[\frac{v_2}{v_1}\right]}$$

② Principle of Increase in Entropy :-

→ We know that The change of entropy for reversible process is given by expression $ds = \frac{dQ}{T}$.

→ Now, we will examine The entropy change for an irreversible process.

→ Let a thermodynamic system undergoes a change of state from 1 to 2 by a reversible process 1-A-2 and returns to state 1 either by internally reversible process 2-B-1 or by an irreversible process 2-C-1 as shown.



→ For the reversible cycle 1-A-2-B-1, we can write the equation same as equation

$$\int_{1-A}^{2-A} \frac{dQ}{T} + \int_{2B}^{1B} \frac{dQ}{T} = 0 \quad \text{—— } ①$$

→ For the irreversible cycle 1-A-2-C-1, we can apply clausius inequality and express it as:

$$\int_{1,A}^{2A}\frac{dQ}{T}+\int_{2C}^{1C}\frac{dQ}{T}\le 0.$$ — ②

Subtracting Eqn 1 from Eqn 2, we get

$$\int_{2C}^{1C}\frac{dQ}{T}-\int_{2B}^{1B}\frac{dQ}{T}\le 0.$$ — ③

On reversing the limit and rearranging the equation ③

$$\int_{1B}^{2B}\frac{dQ}{T}\ge\int_{1C}^{2C}\frac{dQ}{T}$$ — ④

Since the process 2-B-1 is reversible

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

Substituting this value in equation ④

$$\int_{1}^{2}ds\ge\int_{1C}^{2C}\frac{dQ}{T}\quad\text{(or)}\quad ds\ge\frac{dQ}{T}$$ — ⑤

→ when the equality sign refers to reversible process and inequality sign refers to irreversible process from equation ⑤ we note that the effect of irreversibility is always to increase the entropy of the system.

→ From this equation it can also be seen that the entropy of a system increases when the heat is supplied to the system.

→ Principle of increase of entropy state that the entropy of an isolated system never decreases $ds \geq 0$ for an isolated system.

Simply.

$ds = 0$ → Reversible process.

$ds > 0$ → Irreversible process.

$ds < 0$ → Impossible process.

→ Increase of entropy states that the entropy of an isolated system never decreases $ds \geq 0$ for an isolated system.

③ Application of II Law:

→ Entropy principle is the quantitative approach of the Second law of Thermodynamics.

→ It is due to irreversibility of the process which increases with increase in irreversibility

→ The following applications are.

- * Transfer of heat through a finite temperature difference.
- * Mixing of two fluids.
- * Mixing work obtainable from two finite bodies of temperature T_1 and T_2.
- * Maximum work obtainable from a finite body & and a TER.

→ The II Law can be applied to following characteristics like.

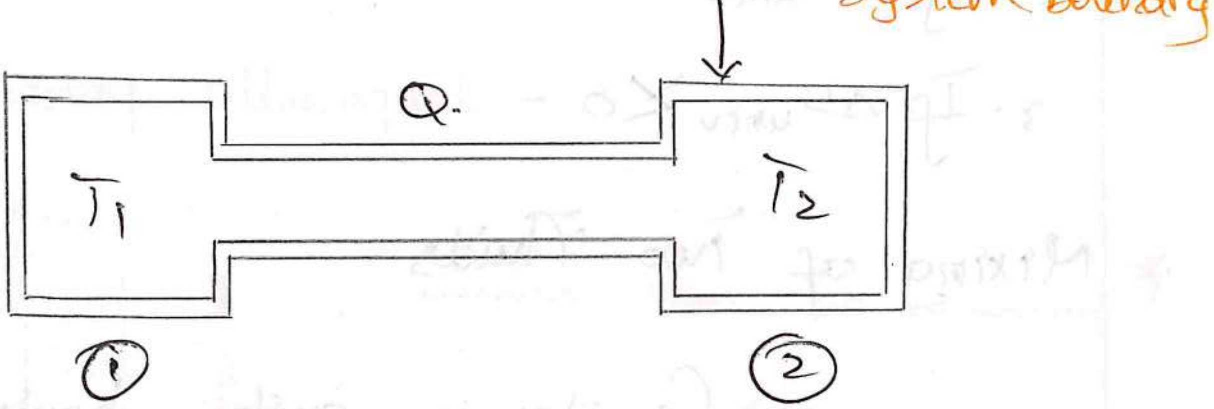
- * Transfer of heat through Finite Temperature.
- * Mixing of two fluids.

⑩

* Transfer of heat Through Finite Temperature

→ Consider two small reservoir of 1 at T_1 and 2 at T_2.

→ It exchanges heat Q from reservoir 1 and reservoir 2.



→ For reservoir 1, change in entropy

$$\Delta S_1 = \frac{-Q}{T_1}$$

→ For reservoir 2, change in entropy

$$\Delta S_2 = \frac{Q}{T}$$

→ Heat transfer from reservoir 1 and 2 to the surrending is considered as negligible

∴ The total entropy of universe.

$$\Delta S_{univ} = \Delta S_1 + \Delta S_2$$

$$= -\frac{Q}{T_1} + \frac{Q}{T_2}.$$

$$= Q\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

1. If $\Delta S_{univ} > 0$ - Possible and Irreversible proce

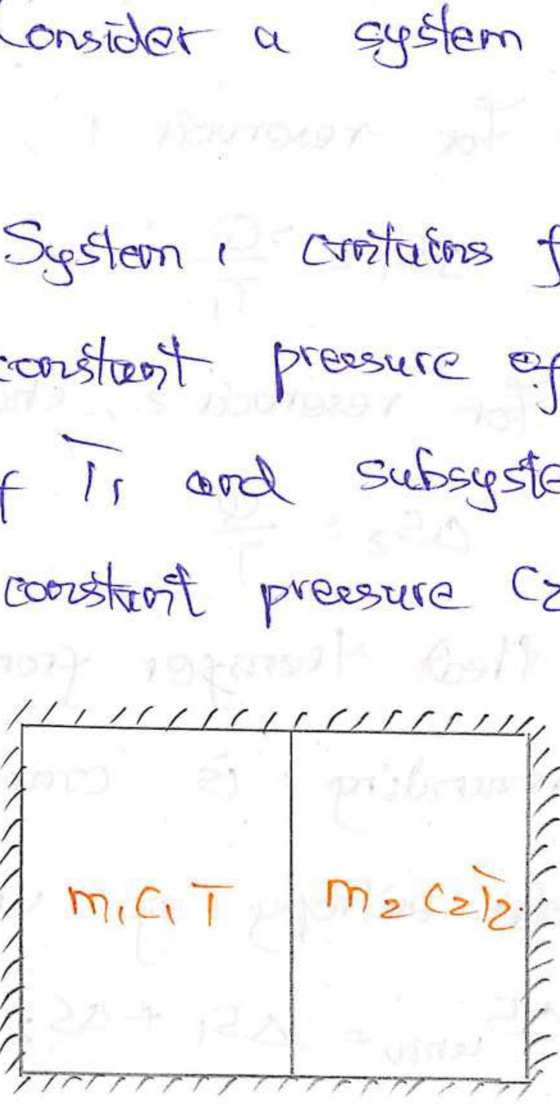
2. If $\Delta S_{univ} = 0$ - Reversible Process.

3. If $\Delta S_{univ} \not< 0$ - Impossible process.

* Mixing of Two Fluids:

→ Consider a system having two subsystems.

→ System 1 contains fluid of mass m_1, sp. heat at constant pressure of C_1, and temperature of T_1 and subsystem 2 of mass m_2 sp. heat at constant pressure C_2, and T_2.



→ T_f should always be lesser than T_1 but greater than T_2.

By energy balance,

$$m_1 C_1 (T_1 - T_f) = m_2 C_2 (T_f - T_2)$$

$$T_f = \frac{m_1 C_1 T_1 + m_2 C_2 T_2}{m_1 C_1 + m_2 C_2}.$$

Change in entropy fluid contained in ①.

$$\Delta S_1 = \int_{T_1}^{T_f} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{m_1 C_1 \, dT}{T}$$

$$= m_1 C_1 \ln \frac{T_f}{T_1}.$$

Similarly change in entropy fluid contained in.

$$\Delta S_2 = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} m_2 C_2 \frac{dT}{T}.$$

$$= m_2 C_2 \ln \frac{T_f}{T_2}$$

Total entropy $= \Delta S_1 + \Delta S_2$.

$$\boxed{\Delta S_{univ} = 2 m C_1 \ln \frac{(T_1 + T_2)/2}{\sqrt{T_1 T_2}}}$$

④ High and Low Grade Energy:-

→ Consider two identical finite bodies containing third constant heat with same mass at the temperatures T_H and T_L.

→ Then final temperature

$$\boxed{T_f = \frac{T_H + T_L}{2}}$$

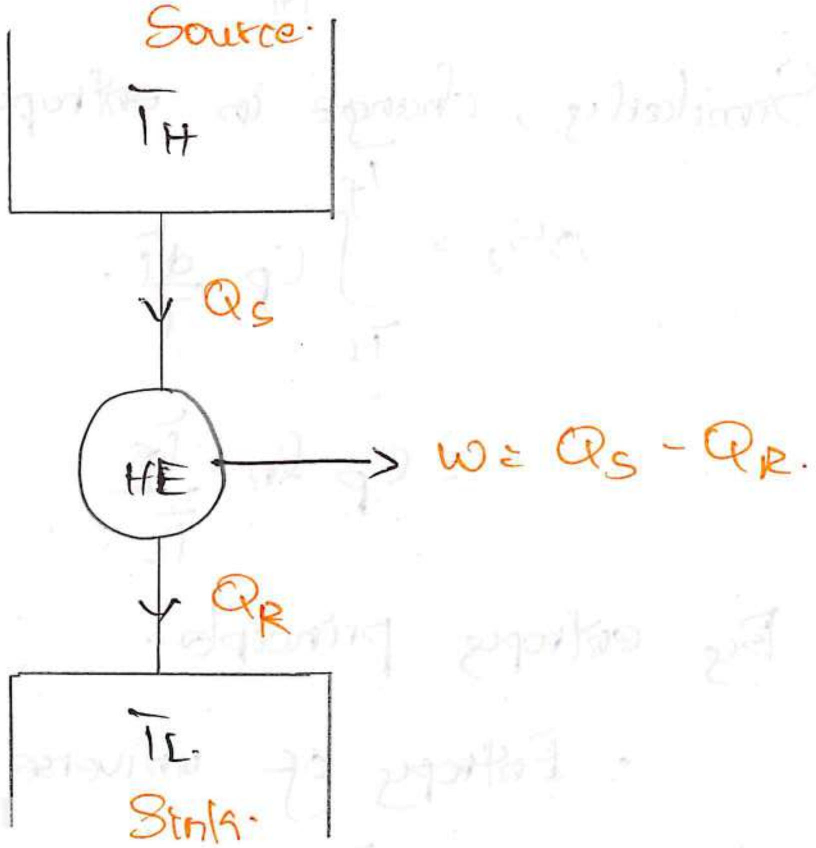
→ when the heat engine is operated between these two temperatures of T_H and T_L. The portion of body 1 is supplied to heat engine to convert into work.

→ The remaining heat is rejected to the body 2.

→ After some time both bodies will reach thermal equilibrium at a temperature of T_f.

→ At thermal equilibrium, the heat

engine stops its working.



Heat supplied to Engine.

$$Q_S = C_p(T_H - T_f).$$

Heat rejected to body. 2

$$Q_R = C_p(T_f - T_L).$$

$$W = C_p(T_H - T_f - T_f + T_L)$$

$$= C_p(T_H + T_L - 2T_f).$$

we know that, change in entropy of body 1

$$\Delta S_1 = \int_{T_H}^{T_f} C_p \, dT/T.$$

$$= C_p \ln \frac{T_f}{T_H}.$$

Similarly, change in entropy of body 2.

$$\Delta S_2 = \int_{T_L}^{T_f} C_p \frac{dT}{T}.$$

$$= C_p \ln \frac{T_f}{T_L}$$

By entropy principle.

∴ Entropy of universe, ΔS_{univ}.

$$\therefore C_p \ln \frac{T_f}{T_H} + C_p \ln \frac{T_f}{T_L} \geq 0.$$

$$C_p \ln \frac{T_f^2}{T_H T_L} \geq 0.$$

T_f to be minimum.

$C_p \ln \frac{T_f^2}{T_1 T_2}$ should be equal to zero

$$C_p \ln \frac{T_f^2}{T_1 T_2} = 0.$$

$\ln \frac{T_f^2}{T_1 T_2} = 0$ and $C_p \neq 0$.

$$\ln \frac{T_f^2}{T_1 T_2} = \ln 1.$$

$$\frac{T_f^2}{T_1 T_2} = 1.$$

$$T_f = \sqrt{T_1 T_2}$$

∴ Maximum work

$$W_{max} = C_p\left(T_1 + T_2 - 2\sqrt{T_1 T_2}\right)$$

$$= C_p\left[\left(\sqrt{T_1}\right)^2 + \left(\sqrt{T_2}\right)^2 - 2\sqrt{T_1}\sqrt{T_2}\right]$$

$$\boxed{W_{max} = C_p\left[\sqrt{T_1}\sqrt{T_2}\right]^2}$$

→ To determine absolute entropy, a zero value of entropy of system is chosen arbitary as a standard state.

→ Then the entropy change is calculated with respect to this standard.

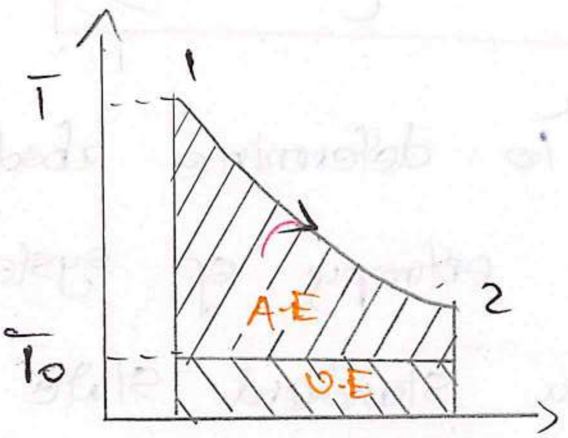
⑤ Availability and Irreversibility for Open and Closed systems :-

Availability :-

→ A Thermodynamic system undergoes a change of state through a reversible process until it comes to equilibrium with atmosphere

→ Then work done by system on the atmosphere is maximum.

→ The maximum work obtained is called as availability of a system.



Irreversibility :-

→ It is defined as the difference between max work to the actual work

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

$$\boxed{I = T_0 \Delta S}$$

Open System:

Case 1 : Constant Volume Process.

→ Consider air is heated from temperature of T_1 to T_2 at constant volume and also heat transfer with surrounding at T_0.

$$Q = m C_v (T_2 - T_1)$$

Available Energy.

$$AE = Q - T_0 \Delta S.$$

where $\Delta S = m C_v \ln \left(\frac{T_2}{T_1}\right)$

Unavailable Energy

$$U.A.E = Q - A.E.$$

$$U.A.E = m C_v (T_2 - T_1) - \left[m C_v (T_2 - T_1) - T_0 \Delta S\right]$$

$$\boxed{U.A.E = T_0 \Delta S.}$$

Case 2 : Constant Pressure Process

→ If air is heated from T_1 to T_2, with the surrounding at the temperature of T_0

Heat energy supplied

$$Q = mC_p(T_2 - T_1).$$

Available Energy.

$$A.E = Q - T_0 \Delta S.$$

$$\Delta S = mC_p \ln\left(\frac{T_2}{T_1}\right)$$

Unavailable Energy,

$$U.A.E = Q - A.E.$$

$$\boxed{U.A.E = T_0 \Delta S}$$

Case 3 : Constant Temperature Process:

$$Q = p_1 V_1 \ln\left(\frac{P_2}{P_1}\right)$$

Available Energy $A.E = Q - T_0 \Delta S$.

$$\Delta S = \frac{Q}{T_1} \text{ or } \frac{Q}{T_2}.$$

$$\boxed{U.A.E = T_0 \Delta S}$$

Closed System :-

→ We know that steady flow energy equation for any kind of closed system.

$$m\left(h_1 + \frac{C_1^2}{2} + z_1 g\right) + Q = m\left(h_2 + \frac{C_2^2}{2} + z_2 g\right) + W$$

Case 1 : Turbine

→ The following assumptions are made.

* Potential energies are negligible.

* Inlet velocity is negligible.

$$W_{act} = m(h_1 - h_2) + Q$$

$$W_{max} = (h_1 - h_2) - T_0(S_1 - S_2).$$

Irreversibility, $I = T_0 \Delta S \quad [\because \Delta S = S_1 - S_2]$.

$$\boxed{\eta_{II} = \frac{W_{max}}{W_{act}}}$$

Case 2 : Compressor

→ The following assumptions are made such as change in potential & kinetic energy

$$m(h_1) + Q = m(h_2) + w.$$

$$W = m(h_1 - h_2) + Q.$$

$$W_{act} = m(h_2 - h_1) = Q.$$

$$W_{max} = m(h_2 - h_1) - T_0(S_2 - S_1).$$

Irreversibility $I = T_0 \Delta S$.

$$\boxed{\eta_{II} = \frac{W_{max}}{W_{act}}}$$

Case 3: Heat Exchanger

Consider m_1 kg of hot fluid with a specific heat of C_1 exchanges heat with cold fluid of m_2 kg with C_2.

$$m_2 C_2 (T_4 - T_3) = m_1 C_1 (T_1 - T_2).$$

Availability of cold fluid

$$B_c = m_2 C_2 (T_4 - T_3) - T_0(S_4 - S_3).$$

$$B_h = m_1 C_1 (T_1 - T_2) - T_0(S_1 - S_2).$$

$$\boxed{\eta_{II} = \frac{\text{Availability of Cold Fluid}}{\text{Availability of Hot Fluid}}}$$

⑥ I and II Law Efficiency :-

In a steam generator, the steam generating tubes receive heat from hot gases passing over the outside surface evaporating water inside the tubes. Flue gas flow rate is 20 kg/s with an average specific heat of 1.04 kJ/kgk. The gas T decreases from 650°C to 400°C while generating steam at 300°C water enters the tubes as a saturated liquid and leaves with a quality of 90%. Assume environment temp as $T_0 = 27°C$. Determine water flow rate, availability of hot fluid and cold fluid. Irreversibility & second law efficiency.

Given:-

$m_1 = 20$ Kg/s

$C_1 = 1.04$ kJ/kgk

$T_1 = 650°C$

$T_2 = 400°C$

$T_3 = 300°C$

$x_4 = 0.9$

$T_0 = 27°C$

To Find:

$$m_2, \psi_1, \psi_2, I, \eta_{II} = ?$$

Solution:

$$h_3 = h_f = 1345 \text{ kJ/kg}$$

$$h_{fg} = 1406 \text{ kJ/kg}.$$

$$s_3 = s_f = 3.255 \text{ kJ/kgK}.$$

$$s_{fg} = 2.453 \text{ kJ/kgK}.$$

$$h_4 = h_f + x_4 h_{fg}.$$

$$= 1345 + 0.9 \times 1406.$$

$$= 2610.4 \text{ kJ/kg}.$$

$$s_4 = s_f + x_4 s_{fg}.$$

$$= 3.255 + 0.9 \times 2.453.$$

$$= 5.46 \text{ kJ/kgK}.$$

$$m_1 c_1 (T_1 - T_2) = m_2 (h_4 - h_3).$$

$$20 \times 1.04 (650 - 400) = m_2 (2610.4 - 1345).$$

$$\boxed{m_2 = 4.11 \text{ kg/s}.}$$

Availability of Hot Fluid.

$$\psi_1 = m_1 [C_p (T_1 - T_2) - T_0 (s_1 - s_2)]$$

$$= 20\left[1.04(650-40) - 300 \times \left[1.04 \ln\left(\frac{923}{613}\right)\right]\right]$$

$$\boxed{\psi_1 = 3228.88 \text{ kW}}$$

Availability of Cold Fluid.

$$\psi_2 = m_2\left[(h_4 - h_3) - T_0(s_4 - s_3)\right].$$

$$= 4.11\left[(2610.4 - 1345)\right] - 300\,(5.467 - 3.255$$

$$\boxed{\psi_2 = 2473.39 \text{ kW}}$$

Irreversibility, $I = \psi_1 - \psi_2$.

$$= 3228.88 - 2478.39.$$

$$\boxed{I = 755.49 \text{ kW}}$$

Second Law Efficiency $= \dfrac{\text{Availability of Cold Fluid}}{\text{Availability of Hot Fluid}}$.

$$= \frac{2473.39}{3228.88} \times 100.$$

$$\boxed{\eta_{II} = 76.6\%}$$

- x ——— xxx ——— x.

Steam flows in a pipeline at 1.5 MPa. After expand to 0.1 Mpa in a Throttling calorimeter, The temperat is found to be 120°C. Find the quality of steam in the pipeline and also calculate availabili irreversibility & second law η. Assume $T_0 = 25°C$.

Given:

$p_1 = 1.5$ Mpa, $p_2 = 0.1$ Mpa

$T_2 = 120°C$.

To Find:

$x_1, \psi_1, \psi_2, I = ?$

Solution:

Corresponding to $p_2 = 1$ bar & $T_2 = 120°C$ from super heated Table, read.

$h_2 = 2716.2$ kJ/kg.

$s_2 = 7.4606$ kJ/kgk.

For throttling process

$h_1 = h_2$.

$h_1 = 2716.2$ kJ/kg.

But at $p_1 = 15$ bar

$h_{fg} = 1947.3$ kJ/kg

$h_f = 844.89$ kJ/kg.

$S_f = 2.3315$ kJ/kgK.

$S_{fg} = 6.4448$ kJ/kgK.

$h_1 = h_f + x_1 h_{fg}$.

$2716.2 = 844.89 + x_1(1947.3)$.

$$\boxed{x_1 = 0.963}$$

$S_1 = S_f + x_1 S_{fg}$.

$S_1 = 2.3315 + 0.963(6.4448)$

$$\boxed{S_1 = 8.538 \text{ kJ/kgK}}$$

Availability at inlet $\psi_1 = h_1 - T_0 s_1$.

$= 2716.2 - 298 \times 8.538$.

$$\boxed{\psi_1 = 171.876 \text{ kJ/kg}}$$

Availability at outlet $\psi_2 = h_2 - T_0 s_2$.

$\psi_2 = 2716.2 - 298 \times 7.4606$.

$$\boxed{\psi_2 = 492.94 \text{ kJ/kg}}$$

Irreversibility $I = \psi_2 - \psi_1$.

$= 492.94 - 171.876$.

$$\boxed{I = 321.064 \text{ kJ/kg}}$$

$$= T_0 (s_1 - s_2)$$

$$= 298(8.538 - 7.4606)$$

$$\boxed{I = 321.065 \text{ kJ/kg}}$$

Second Law Efficiency $\eta_{II} = \frac{\psi_1}{\psi_2}$.

$$= \frac{171.876}{492.94} \times 100.$$

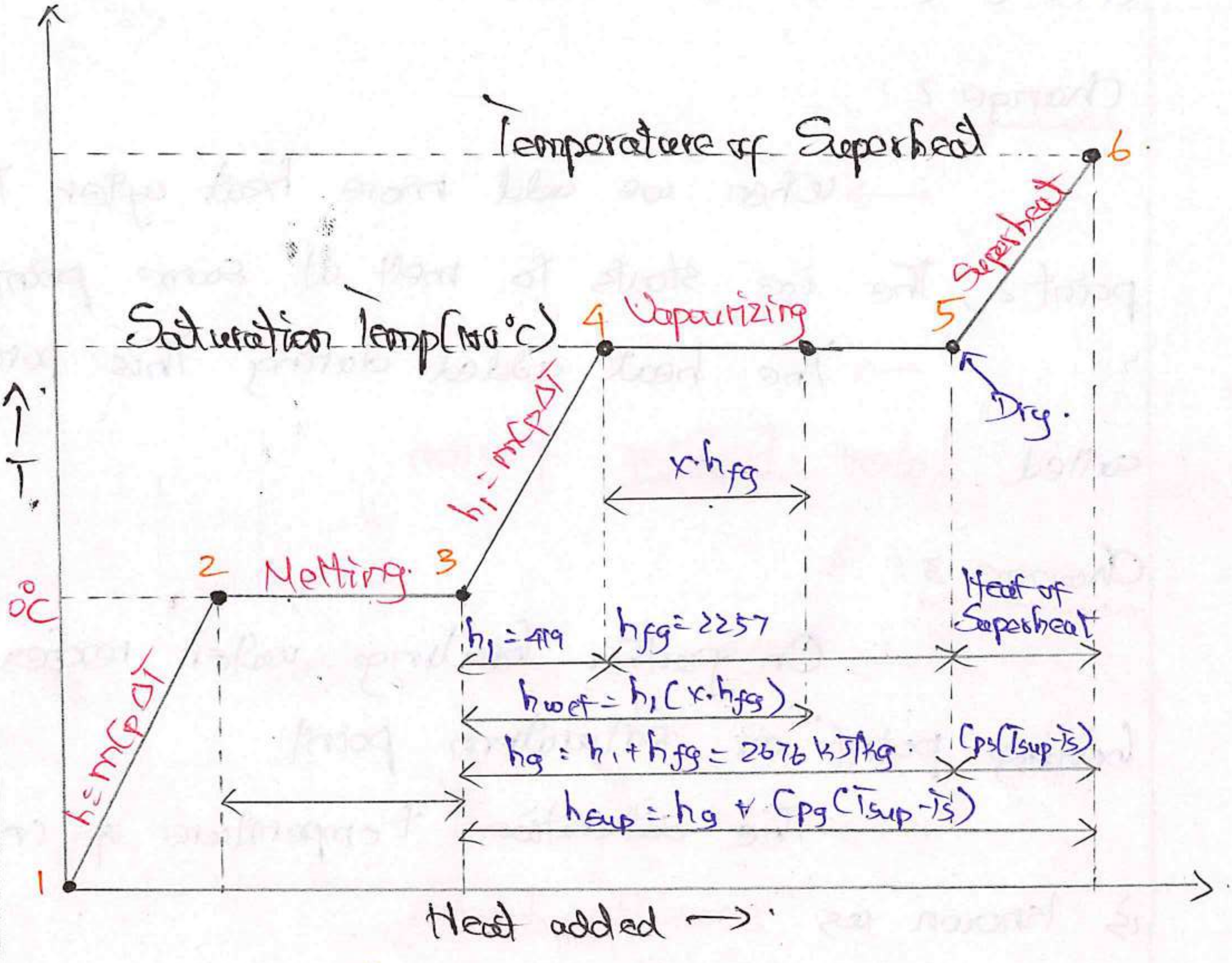
$$\boxed{\eta_{II} = 34.867\%}$$

x — x x x — x

UNIT-III

PROPERTIES OF PURE SUBSTANCES

① Steam Formation:



→ Consider 1 kg of water in a closed vessel under a pressure of p N/m² and at a temperature of -20°C.

→ If we heat the water gradually when pressure remains constant, the following occur

Change 1 :-

→ The temperature of ice will increase till it reaches the freezing temperature of water (i.e) 0° C. This is shown in line 1 - 2.

Change 2 :-

→ When we add more heat after the point 2, the ice starts to melt at same point.

→ The heat added during this period is called Latent heat of fusion.

Change 3 :-

→ On further heating water reaches its boiling point or saturation point.

→ The saturation temperature of 100°C is known as sensible heat.

Change 4 :-

→ On further heating beyond 4, the water will gradually be converted into steam.

→ At this stage the steam will have some water particles in suspension called wet steam.

Change 5:

→ If water is heated further the water particles in suspension will be converted to ste

→ The amount of heat added during this period is called Latent heat of vaporizatio

Change 6:

→ When the dry steam is further heated, the temperature rises again.

→ This process is called superheating an The steam obtained is known as Superheated Steam

Mathematically,

$$\boxed{h_{sup} = h_g + C_p (T_{sup} - T_s) \ \text{kJ/kg}}$$

where

h_{sup} - Superheated Steam.

C_p - Specific heat of water at constant temperature.

→ Based on the properties of steam formation there are various kinds which are responsible for this action.

Thermodynamic Properties:

Various properties of water at various conditions of steam are discussed below.

* Enthalpy of Steam:

→ Amount of heat added to water to from freezing point to till water becomes wet or dry or superheated steam.

For wet steam, $h_{wet} = h_f + x h_{fg} +$ kJ/kg

For dry steam, $h_{dry} = h_f + h_{fg}$ kJ/kg.

For superheated steam, $h_{sup} = h_g + C_p(T_{sup} - T_{sat})$ kJ/k

* Specific Volume

→ Defined as the volume occupied by unit mass of steam at given pressure and temperature.

For wet steam, $v_{wet} = x v_g$ m^3/kg

For dry steam, $v_{dry} = v_g$ m^3/kg.

For superheated steam, $v_{sup} = \frac{v_g T_{sup}}{T_{sat}}$ m^3/kg.

* Density :

→ Defined as the ratio of mass to the unit volume of steam at given pressure and temperature.

* Workdone :

→ During evaporation process, there is a considerable increase in volume when pressure remains constant.

→ In other words, it is the energy required for absorption of latent heat for increasing volume of steam.

For wet steam, $W_{wet} = 100 \, p \, x \, v_g$ kJ.

For dry steam, $W_{dry} = 100 \, p \, v_g$ kJ.

For superheated steam, $W_{sup} = 100 \, p \, v_{sup}$ kJ.

* Entropy

For wet steam, $S_{wet} = S_f + x \, s_{fg}$ kJ/kgK

For dry steam, $S_{dry} = S_f + S_{fg}$ kJ/kgK.

For superheated steam, $S_{sup} = S_g + C_{ps} \log_e \left(\frac{T_{sup}}{T_s} \right)$

② P-V Diagram:

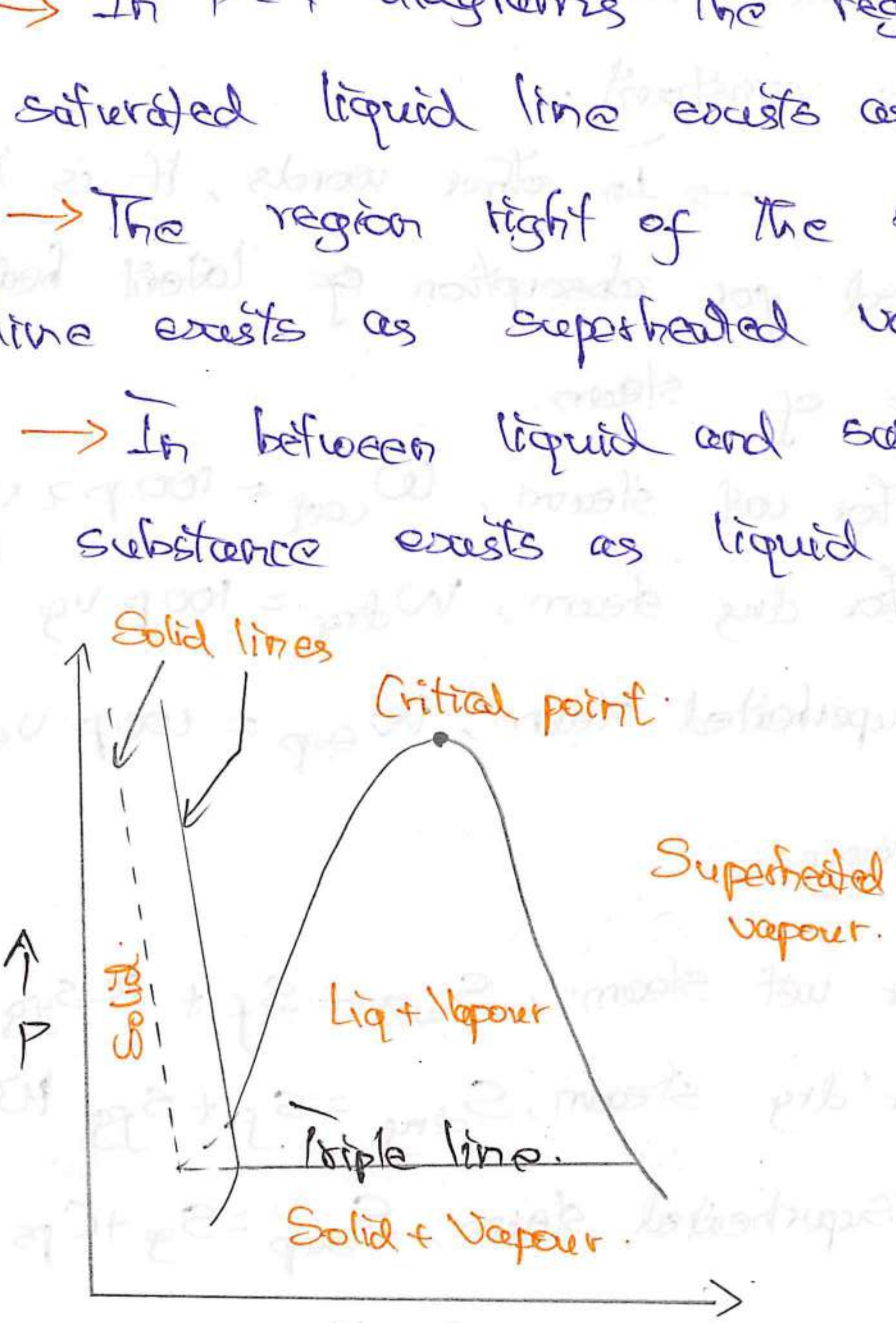
→ P-V diagram is the plot between specific volume and pressure.

→ The state changes of a pure substance when heated slowly at different constant pressure are shown.

→ In P-V diagrams the region left of the saturated liquid line exists as liquid.

→ The region right of the saturated vapour line exists as superheated vapour.

→ In between liquid and saturated vapour line the substance exists as liquid vapour mixtu



→ On P-V diagram triple phase states from a line called triple line.

→ This is the line where all three phases solid, liquid and gas exist in equilibrium

→ The states on triple line of a substance have same pressure and temperature but different specific volumes.

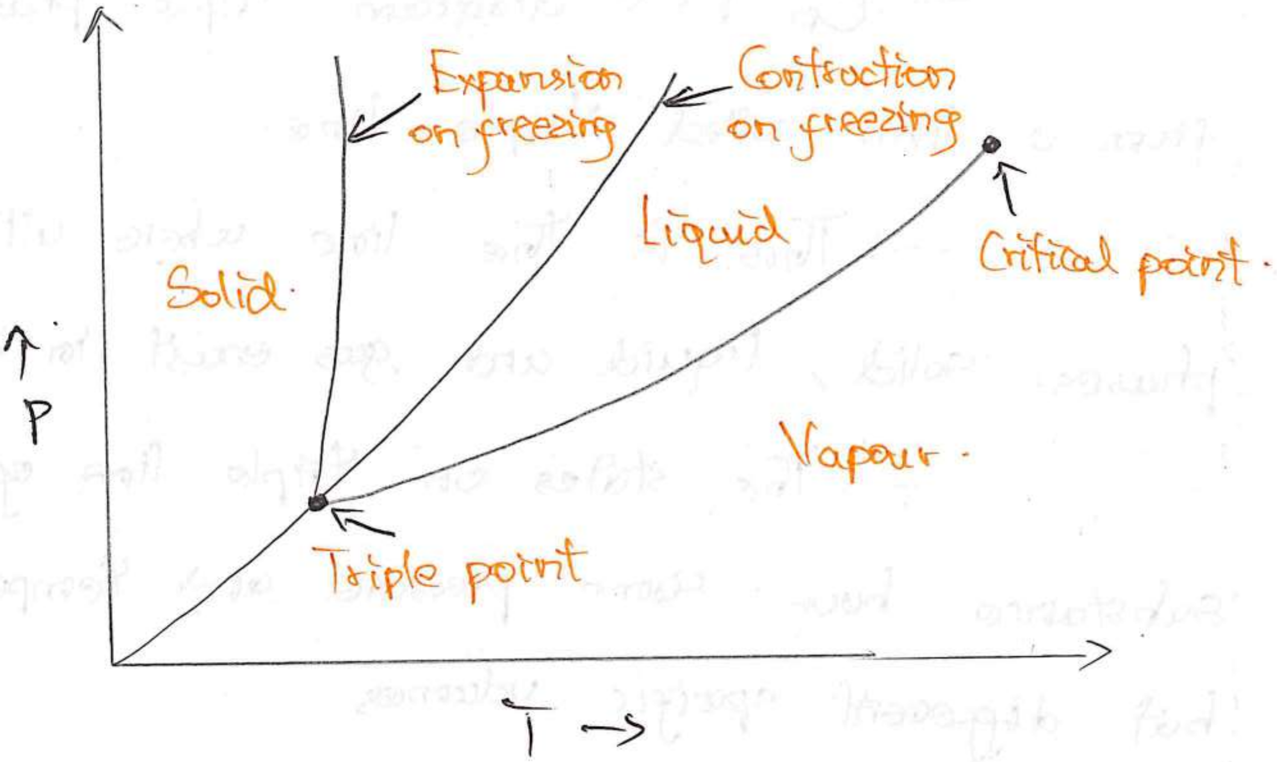
→ The triple line appears as a point on the P-T diagrams and is often called as triple point.

→ Below the triple point, the liquid i directly converted into vapour without formation o liquid vapour mixture.

P-T diagram:

→ The state changes of a pure substan when heated study of different constant pressure are plotted on P-~~T~~ coordinate.

⑦



→ The diagram is often called as phase diagram since all three phases are seperated from each other by three lines.

→ The sublimation curve seperates the solid and vapour region, The vapourization curves seperates the liquid & vapour regions, and the fusion or melting curves seperates the solid & liquid regions.

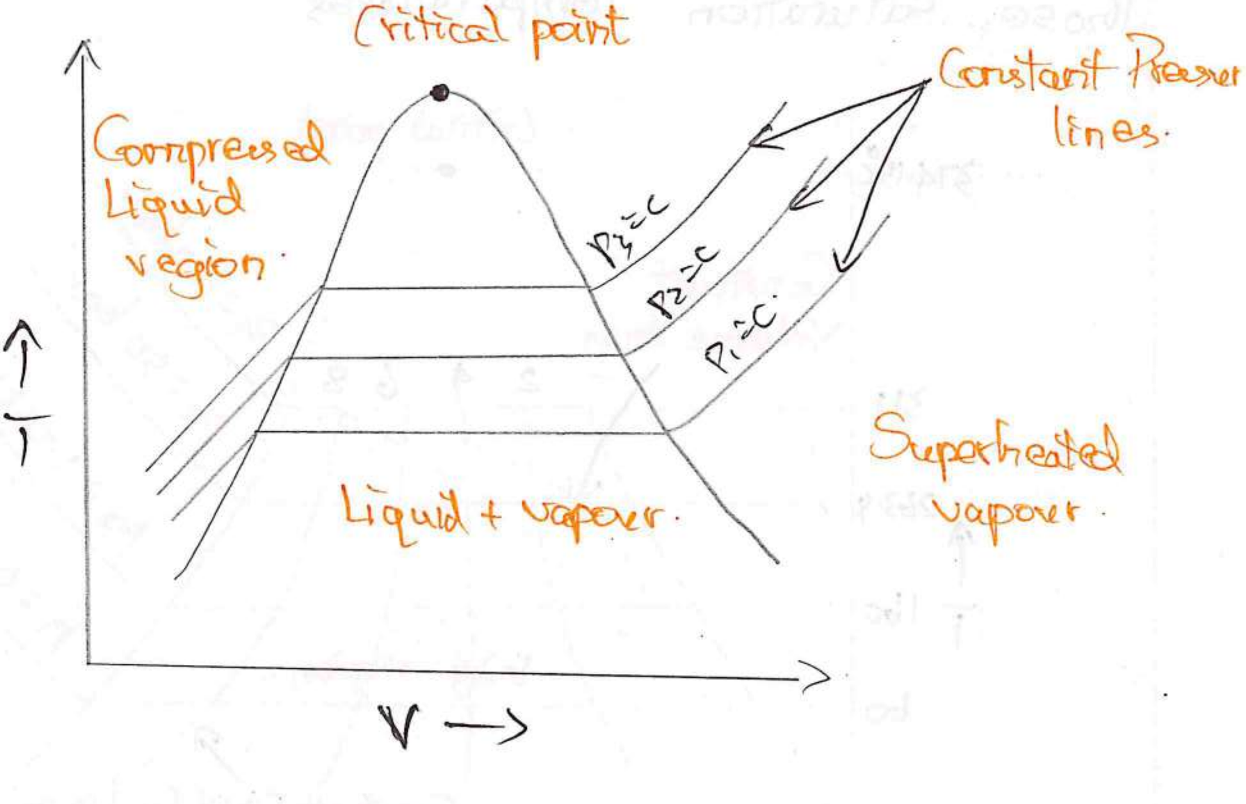
→ These three curves meet at a tripl point where all three phases coexist in equilibrium.

T-V Diagram :

→ The general shape of the T-V diagram of pure substance is very much like the p-v diagram, but the p = constant lines on this diagram have a upward trend.

→ In the T-V diagram the region left of the saturated liquid line, the substance exists as compressed liquid.

→ In the right of saturated liquid line, the substance exists as superheated vapour

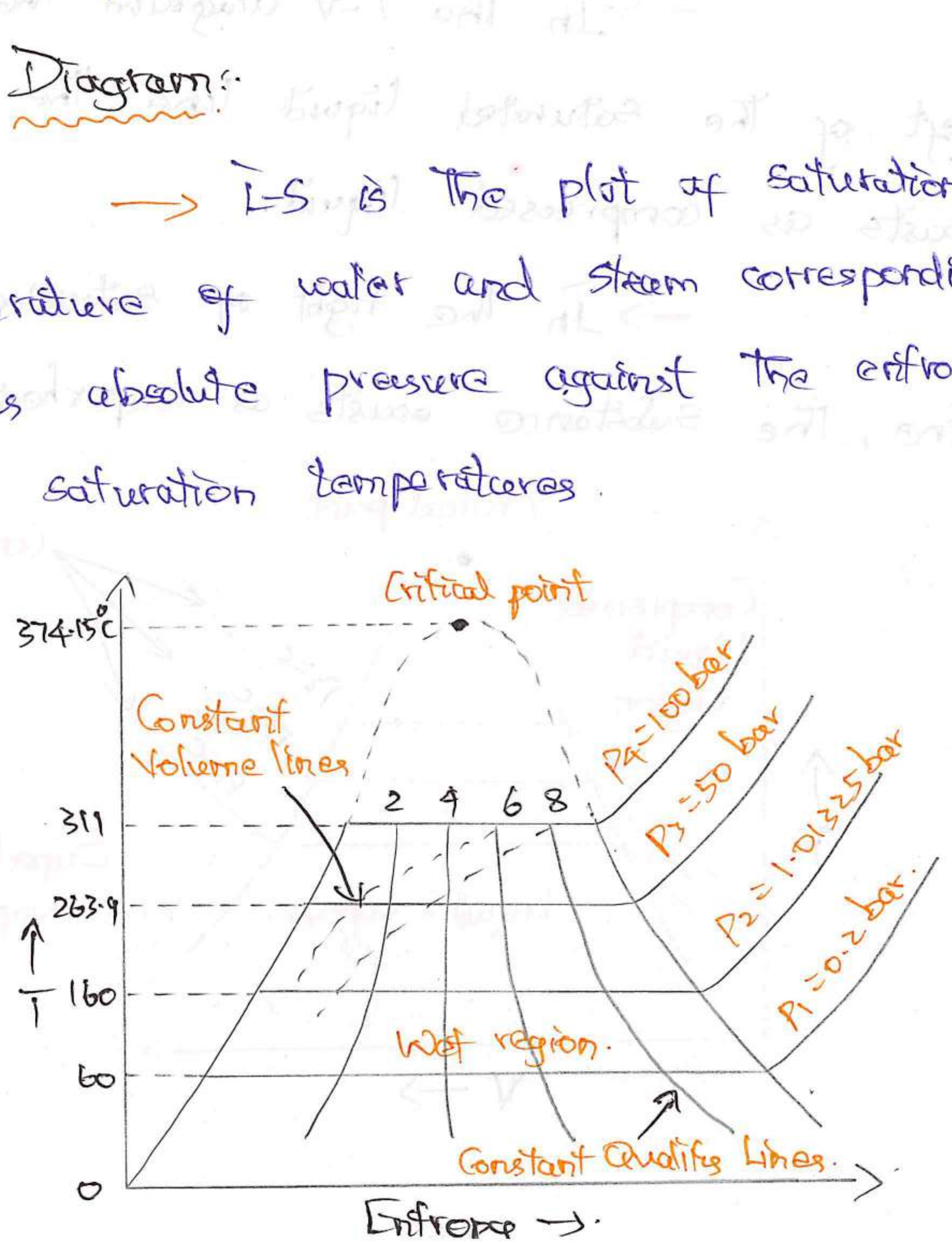


→ In between liquid and saturated vapour line, The substance exists as a liquid vapour mixture.

→ At a particular point, The liquid is directly converted into vapour without formation of liquid vapour mixture.

T-S Diagram:

→ T-S is The plot of saturation temperature of water and steam corresponding to various absolute pressure against the entropies at those saturation temperatures.



→ The region left of the water line, the water exists as liquid.

→ In the right of dry steam line, the water exists at a superheated steam.

→ In between water and dry stream line, the water exists as wet steam.

→ It can be noted that the water line and steam lines are converging with increase in temperature.

→ At a particular point the water is directly converted into dry steam with formation of wet steam.

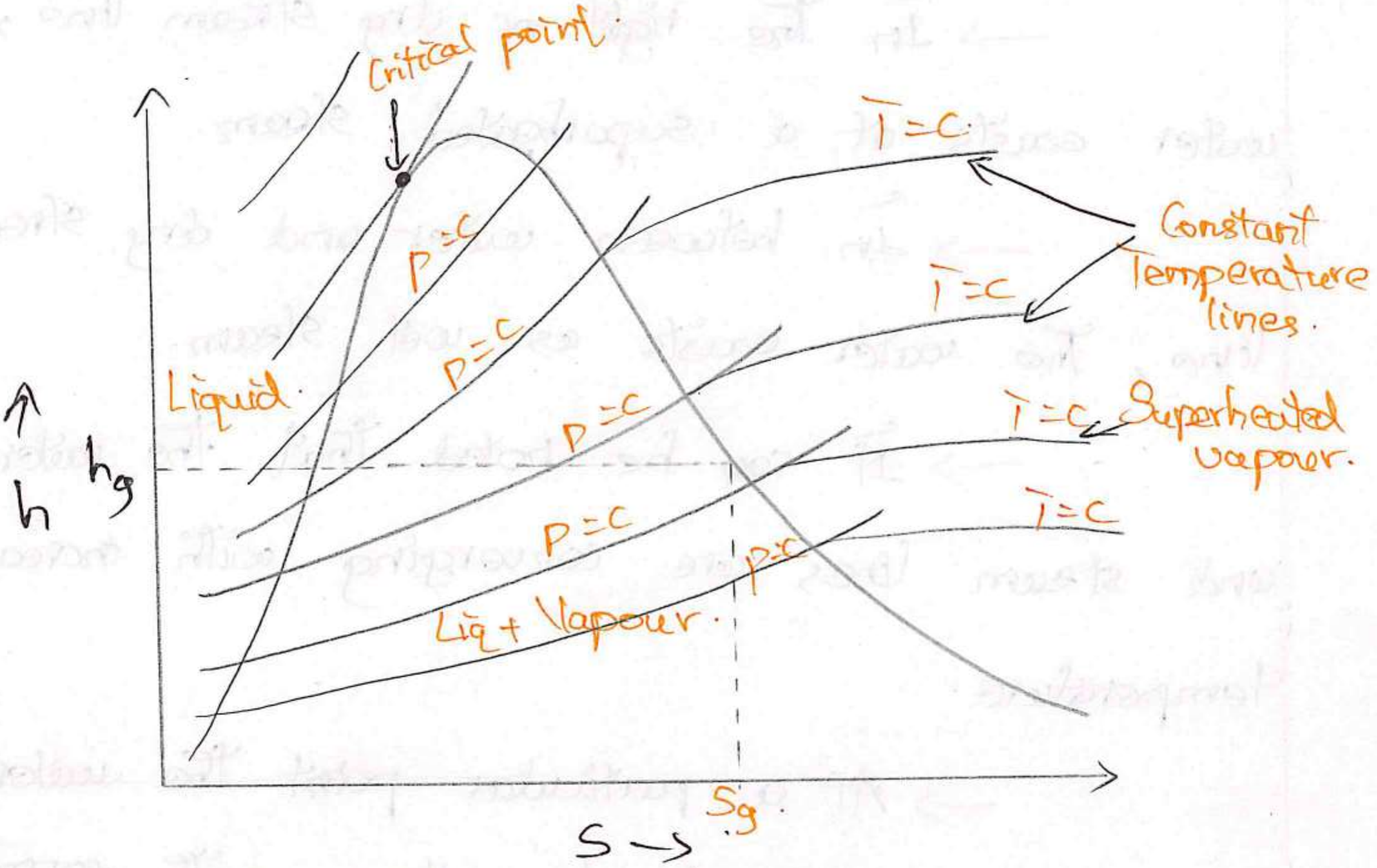
h-S Diagram:

→ It is also called Mollier chart.

→ In h-s diagram the dry steam line divides this chart into two regions.

→ The region which is below the dry steam is the wet condition of steam.

→ Here the dryness fraction lines are shown parallel to dry steam line.



→ The region above the dry steam line represents the superheated condition of steam.

→ It should be noted that the lines at constant temperature lines are straight in wet steam region but curved in superheated steam region.

→ Throttling process in which enthalpy remains constant is represented by horizontal line.

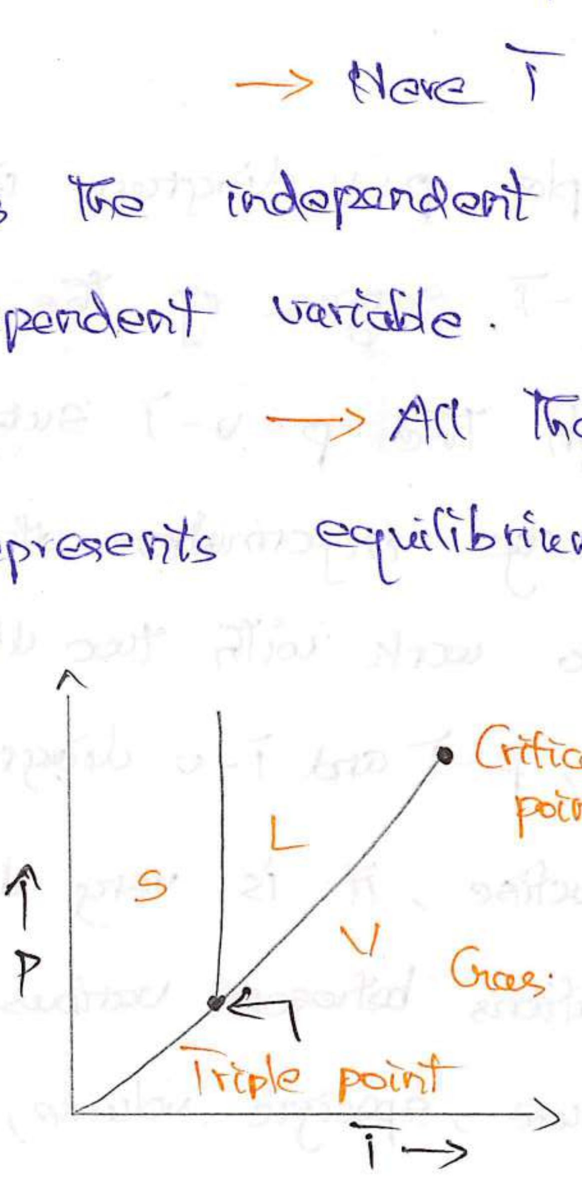
③ PVT Surface:

→ The Three important Thermodynamic properties such as pressure, sp. volume and temperature are plotted in three dimensional coordinate.

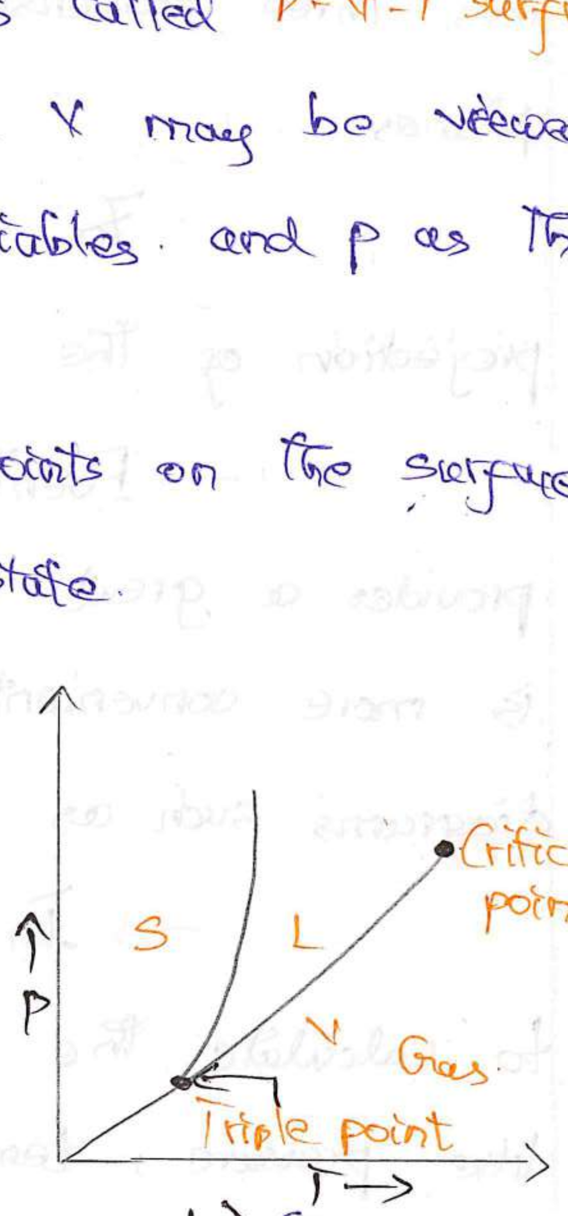
→ This plot is called P-V-T Surface.

→ Here T and V may be viewed as the independent variables and P as the dependent variable.

→ All the points on the surface represents equilibrium state.



a) Water



b) CO_2

→ The single phase region appers as

Curved surface on the p-v-T surface and the two phase regions as surfaces perpendicular to p-T plane.

→ All the two dimensional diagrams we discussed so far are merely projections of this three dimensional plot onto the appropriate planes.

→ For example p-v diagram is a projection of the p-v-T surface of the p-v plan

→ Eventhough the p-v-T surface provides a great deal of information at once, i is more convenient to work with two dimension diagrams such as p-v, p-T and T-v diagrams.

→ In practise, it is very difficult to calculate the relations between various quanti like pressure, temperature, specific volume, enthalp and entropy of steam at various stages.

→ Various quantities like sp. volume, and sp entropy for various pressures.

④ Determination of Dryness Fraction:

→ Defined as the ratio of the mass of the dry steam actually present to the mass of total steam.

→ It is denoted by 'x'.

$$\boxed{x = \frac{m_g}{m_f + m_g}}$$

where

m_g - mass of dry steam

m_f - mass of water vapours in suspension

For dry steam, $m_f = 0$.

$\therefore x = 1$.

→ The dryness fraction when expressed in percentage is called the quality of steam.

→ The dryness fraction can experimentally measured by using calorimeters which are.

- * Bucket Calorimeter
- * Throttling Calorimeter.
- * Separating Calorimeter.

Determine the state of steam at a pressure of 12 bar with its sp. volume of 0.175 m^3/kg.

Given:

$p = 12$ bar.

$v = 0.175\ m^3/kg$.

To Find:

State of steam.

Solution:

$$v_{sup} = v_g \left[\frac{T_{sup}}{T_s}\right]$$

$$T_{sup} = \frac{v_{sup}}{v_g} \times T_s$$

$$= \left(\frac{0.175}{0.16321}\right) \times 188$$

$$\boxed{T_{sup} = 201.58\,^\circ C}$$

x —— x —— x

Find the specific volume and enthalpy of steam at 9 bar when the condition of steam is (a) wet with dryness fraction 0.98 (b) dry saturated (c) super heated, the steam temperature is 240°C.

Given:

$p = 9$ bar.

$x = 0.95$, $x = 1$, $T_{sup} = 240°C$.

Solution:

From steam table at 9 bar

$T_s = 175.4°C$

$v_g = 0.21501\ m^3/kg$.

$h_f = 742.6\ kJ/kg$.

$h_{fg} = 2029.5\ kJ/kg$.

$h_g = 2772.1\ kJ/kg$.

a) Wet steam, $x = 0.95$

$v_{wet} = x v_g = 0.95 \times 0.21501$

$= 0.204\ m^3/kg$.

$h_{wet} = h_f + x h_{fg} = 742.6 + 0.95 \times 2029.5$

$$\boxed{h_{wet} = 2670.625\ kJ/kg}$$

b) Dry Steam

$v_g = 0.21501\ m^3/kg$

$h_g = 2772.1\ kJ/kg$.

c) Super Heated Steam, $T_{sup} = 240°C$.

$v_{sup} = v_g \boxed{\frac{T_{sup}}{T_s}}$

$= 0.21501 \times \left(\frac{240}{175.4}\right)$

$$\boxed{v_{sup} = 0.294 \text{ m}^3/\text{kg}}$$

Corresponding to p = 9 bar and T = 240°C, from the superheated enthalpy table.

$h_{sup} = 2923.29$ kJ/kg.

x ——— x ——— x

Determine the condition of steam at a temperature of 220°C and enthalpy of 2750 kJ/kg.

Given:

T = 220°C, h = 2750 kJ/kg

To find:

State of steam.

Solution:

From steam table of temperature at 220°C

$h_f = 943.7$ kJ/kg, $h_{fg} = 1856.2$ kJ/kg.

$h_g = 2799.9$ kJ/kg.

$$x = \frac{h_{wet} - h_f}{h_{fg}} = \frac{2750 - 943.7}{1856.2}$$

$$\boxed{x = 0.973}$$

⑤ Calculation of work done and Heat Transfer

Steam initially at 400 kPa and 0.6 dry is heated i a rigid vessel of 0.1 m^3 volume. The final conditio is 600 kPa. Find the amount of heat added and mass of steam.

Given :

$P_1 = 400$ kPa

$x_1 = 0.6$

$V_1 = 0.1\ m^3$

$P_2 = 600$ kPa.

To Find :

Q and m.

Solution :

From steam table, corresponding to 4 bar.

$h_{f1} = 604.7$ kJ/kg.

$h_{fg1} = 2132.9$ kJ/kg.

$v_{g1} = 0.4622\ m^3/kg$.

Specific Volume $v_1 = x_1 v_{g1}$

$v_1 = 0.6 \times 0.4622$.

$$\boxed{v_1 = 0.277\ m^3/kg}$$

$h_1 = h_{f1} + x_1 h_{fg1}$

$= 604.7 + 0.6 \times 2132.9..$

$$\boxed{h_1 = 1884.44 \text{ kJ/kg}}$$

Mass of steam, $m = V_1$

$m = 0.36$ kg.

For rigid vessel, $v_1 = v_2$.

$$\boxed{v_2 = 0.277 \text{ m}^3/\text{kg}}$$

From Steam table corresponding to 6 bar.

$h_{f2} = 670.4$ kJ/kg

$v_{g2} = 0.31546$ m^3/kg

$h_{fg2} = 2085.1$ kJ/kg.

$v_{g2} > v_2 \Rightarrow$ Steam is wet condition.

$v_2 = x_2 v_{g2}$

$0.277 = x_2 \times 0.31546$.

$$\boxed{x_2 = 0.88}$$

$h_2 = h_{f2} + x_2 h_{fg2}$

$= 670.4 + 0.88 \times 2085.1$

$$\boxed{h_2 = 2505.2 \text{ kJ/kg}}$$

x — x — x.

One kg of steam at a pressure of 700 kPa and 0.6 dry is heated at constant pressure until it becomes dry. Determine change in workdone and internal energy.

Given:

$m = 1\,kg$

$p = 700\,kPa = 7\,bar.$

$x_1 = 0.6$

$x_2 = 1.$

To Find:

ΔU and W.

Solution:

From steam table at 7 bar.

$h_{f1} = 697.1\,kJ/kg$

$h_{fg1} = 2064.9\,kJ/kg$

$h_{g1} = 2762\,kJ/kg$

$v_{g1} = 0.27288\,m^3/kg.$

$V_1 = m x_1 v_{g1}$

$= 1 \times 0.6 \times 0.27288.$

$$\boxed{V_1 = 0.164\,m^3}$$

$$h_1 = m(h_{f1} + x_1 h_{fg1})$$

$$= 1(697.1 + 0.6 \times 2064.9)$$

$$\boxed{h_1 = 1936.04 \ kJ}$$

$$v_2 = v_{g1} = 0.27288 \ m^3/kg$$

$$V_2 = m v_{g1} = 1 \times 0.27288$$

$$V_2 = 0.27288 \ m^3$$

$$h_2 = m h_{g1}$$

$$= 1 \times 2762.$$

$$\boxed{h_2 = 2762 \ kJ/kg}$$

Change in internal energy.

$$\Delta U = u_2 - u_1$$

$$= (h_2 - h_1) - (P_2 v_2 - P_1 v_1)$$

$$= (h_2 - h_1) - p_1(v_2 - v_1)$$

$$= (2762 - 1936.04) - 700(0.273 - 0.164)$$

$$\boxed{\Delta U = 749.66 \ kJ}$$

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

$$= 700(0.273 - 0.164)$$

$$\boxed{W = 76.3 \ kJ}$$

UNIT - V

GAS MIXTURES AND THERMODYNAMIC RELATIONS

① Properties of Ideal Gas:

→ An imaginary gas which obeys the equation of state as $pv = mRT$ at all pressure and temperature is known as ideal gas.

→ If the pressure of real gas tends to zero or temperature tends to infinity, the real gas behaves as ideal gas.

→ It means the temperature T is equivalent to $-273.15\,^{\circ}C$.

→ The properties of ideal gas are as follows.

- Specific Heat.
- Enthalpy
- Entropy

→ The temperature of these properties

are known as absolute temperature.

*Specific Heat :-

→ Ideal gases obeys the law of equation of state and have constant specific heats.

$$Q = \Delta U + W$$

$$Tds = pdv + du$$

$$Tds = du + pdv$$

$$ds = \frac{du}{T} + \frac{P}{T} dv$$

→ There are two assumptions made.

Assumption 1 :-

$$\frac{\partial^2 s}{\partial T \partial v} = \frac{1}{T}\frac{\partial^2 u}{\partial v \partial T} + \left(\frac{\partial u}{\partial v}\right)_T \times \left(-\frac{1}{T^2}\right) + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right) + P \times \left(-\frac{1}{T^2}\right)$$

$$= \frac{1}{T}\frac{\partial^2 u}{\partial v \partial T} - \frac{1}{T^2}\left(\frac{\partial u}{\partial v}\right)_T + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_v - \frac{P}{T^2}.$$

$$\therefore \frac{1}{T}\frac{\partial^2 u}{\partial T \partial u} = \frac{1}{T}\frac{\partial^2 u}{\partial v \partial T} - \frac{1}{T^2}\left(\frac{\partial u}{\partial v}\right)_T + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_v - \frac{P^2}{T}$$

$$0 = \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_v - \frac{1}{T^2}\left(\frac{\partial u}{\partial v}\right)_T - \frac{P}{T^2}.$$

$$\frac{1}{T^2}\left(\frac{\partial u}{\partial v}\right)_T + \frac{P}{T^2} = \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)$$

$$\frac{1}{T}\left(\frac{\partial u}{\partial v}\right)_T + \frac{P}{T} = \left(\frac{\partial P}{\partial T}\right)_v.$$

$$\because pv = RT$$

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + 0 \times dv.$$

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT$$

Let $C_v = \left(\frac{\partial u}{\partial T}\right)_v$.

$$\therefore \boxed{du = C_v\, dT}$$

Assumption 2:

$$\frac{\partial^2 s}{\partial p\,\partial T} = \frac{1}{T}\frac{\partial^2 u}{\partial p\,\partial T} + \left(-\frac{1}{T^2}\right)\frac{\partial u}{\partial p} - \frac{1}{T}\left(\frac{\partial v}{\partial T}\right)_p - \left(-\frac{1}{T^2}\right)$$

$$= \frac{1}{T}\frac{\partial^2 u}{\partial p\,\partial T} - \frac{1}{T^2}\left(\frac{\partial u}{\partial P}\right)_T - \frac{1}{T}\left(\frac{\partial v}{\partial T}\right)_P + \frac{v}{T^2}$$

$$\frac{1}{T}\frac{\partial^2 u}{\partial p\,\partial T} = \frac{1}{T}\frac{\partial^2 u}{\partial p\,\partial T} - \frac{1}{T^2}\left(\frac{\partial u}{\partial P}\right)_T - \frac{1}{T}\left(\frac{\partial v}{\partial T}\right)_P + \frac{v}{T^2}.$$

$$\frac{1}{T^2}\left(\frac{\partial u}{\partial P}\right)_T + \frac{1}{T}\left(\frac{\partial v}{\partial T}\right)_P = \frac{v}{T^2}$$

$$pv = RT$$

$$P\left(\frac{\partial v}{\partial T}\right)_P = R.$$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P} = \frac{v}{T} \qquad \because \left[\frac{R}{P} = \frac{v}{T}\right]$$

$$\frac{1}{T}\left(\frac{\partial u}{\partial P}\right)_T + \left(\frac{\partial v}{\partial T}\right)_P = \frac{v}{T}.$$

$$\frac{1}{T}\left(\frac{\partial u}{\partial P}\right)_T + \frac{v}{T} = \frac{v}{T}$$

$$\frac{1}{T}\left(\frac{\partial u}{\partial P}\right)_T = 0.$$

* Enthalpy :

we know that enthalpy = Internal energy + Flo

$h = u + pv$

$= u + RT$ $(\because pv = RT)$.

Then $dh = du + RdT$

$= C_v dT + RdT$ $(\because du = C_v dT)$.

$= (C_v + R) dT$

$= C_p dT$ $(\because C_p - C_v = R)$.

$$\boxed{C_p = \left(\frac{\partial h}{\partial T}\right)_P}$$

* Entropy :

From First Law of Thermodynamics.

$$Q = W + \Delta U$$

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

$$Tds = du + pdv.$$

$$ds = \frac{du}{T} + \frac{P}{T} dv.$$

$$= C_v \frac{dT}{T} + \frac{R}{V} dv.$$

Integrating both sides.

$$\int ds = \int C_v \frac{dT}{T} + R \int \frac{dv}{v}$$

$$S_2 - S_1 = C_v \ln(T)_{T_1}^{T_2} + R \ln(v)_{v_1}^{v_2}$$

$$= C_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right)$$

$$S_2 - S_1 = C_p \ln\left(\frac{T_2}{T_1}\right) - (C_p - C_v) \ln\left(\frac{P_2}{P_1}\right)$$

$$= C_p \ln\left(\frac{\frac{T_2}{T_1}}{\frac{P_2}{P_1}}\right) + C_v \ln\left(\frac{P_2}{P_1}\right)$$

$$\boxed{S_2 - S_1 = C_p \ln\left(\frac{v_2}{v_1}\right) + C_v \ln\left(\frac{P_2}{P_1}\right)}$$

② Properties of Real gas :-

→ The gas which does not obey the law of equation of state is known as real gas

→ The specific heat are constant which vary with pressure and volume.

→ The new term is introduced in equation of state called as compressibility factor

$$\boxed{pv = ZRT}$$

where Z = Compressibility Factor.

→ The properties of real gas are as follows.

- ✱ Intermolecular Forces.
- ✱ Shape Factor.

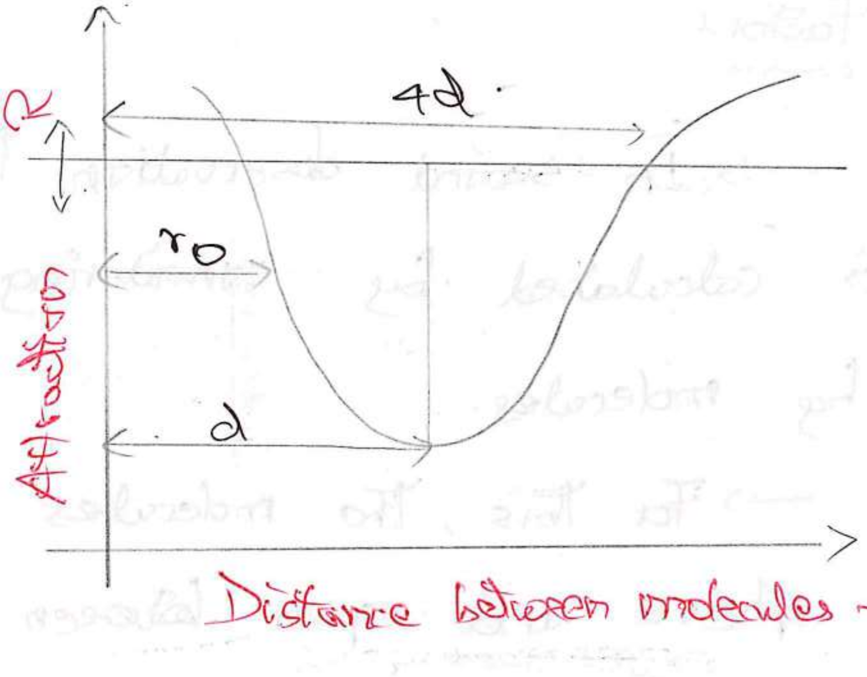
✱ Intermolecular Forces :-

→ First the molecules are attracted each other at distance r_0 when the distance between molecule increases.

→ When the distance reaches 4d or more, the attractive force almost died out.

→ where d is the diameter of the molecule.

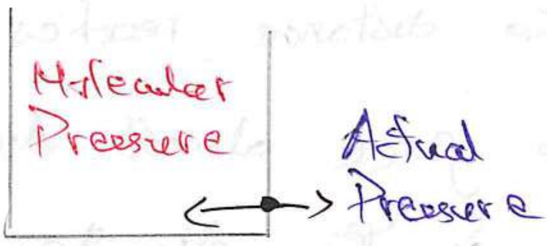
→ If the distance between molecule is less than r_0, the molecules will repulse each othe

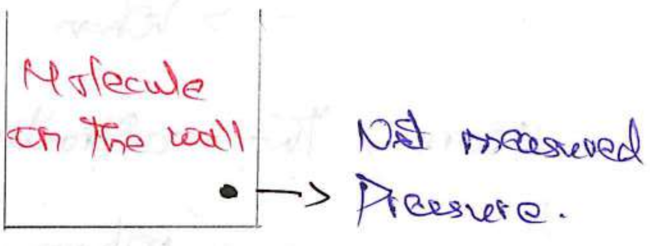


→ Let us consider a vessel having real gases.

→ In these gases, we consider the molecule exactly at the middle.

→ It means the resultant attraction force is zero.



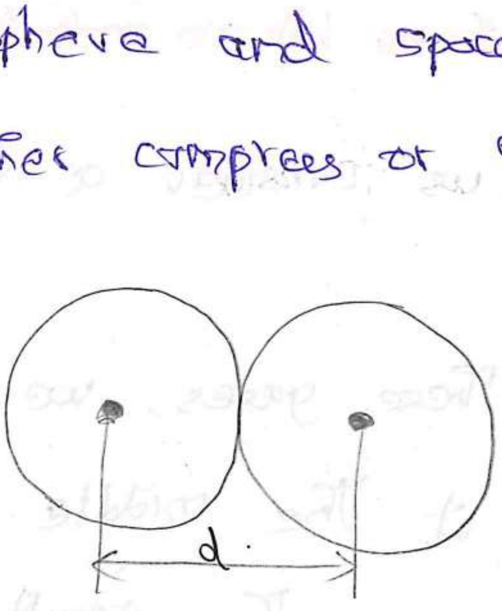


→ So the force of attraction is proportional to $\frac{1}{V^2}$ and the actual pressure of the gas exerted will increase to $\left(P+\frac{a}{V^2}\right)$

* Shape Factor:

→ In second observation the correcti factor is calculated by considering the volume occupied by molecules.

→ For this, the molecules are assume as right sphere and space between molecules i used to either compress or expand.



→ At low pressures, the volume occupie by molecules is very small.

→ But at high pressures, The volume cannot be ignored.

→ The diameter of each molecule is assumed 'd'.

→ The distance between two molecules from centre to centre is also 'd'.

→ We know That the forbidden volume of sphere

$$\boxed{V = \frac{4}{3}\pi d^3}$$

→ Eight molecules can be placed around each molecules:

→ But effective volume of molecules is

$$\boxed{\frac{4}{3}\pi \frac{d^3}{8}}$$

→ Then it is considered for four molecules around each molecules.

→ To compensate The behaviour of real gas molecules, These two corrections for pressure and volume are to be carried out.

③ Equation of State of Ideal Gas:

→ An ideal gas is a substance which obeys the law of $pv = \bar{R}T$ or $pV = \bar{R}T$.

where.
p = pressure of gas.
v = Sp. volume of gas.
V = Total volume of gas.
$\bar{R}$ = Universal gas constant
$R = \frac{\bar{R}}{M}$ for any gas.
T = Absolute Temperature in K.

→ If we consider mass of the gas m, the equation of state becomes.

$$\boxed{pv = N m \bar{R} T} \quad \text{or} \quad \boxed{pV = N m \bar{R} T}$$

→ For example, the gas constant R for air is calculated by.

$$R = \frac{\bar{R}}{M} = \frac{8.314}{28.97}$$

$$\boxed{R = 0.287 \text{ kJ/kg K}}$$

* Boyle's Law:

Boyle's Law states that "The volume of given mass of a gas varies inversely with its absolute pressure when the temperature remains constant".

$$\boxed{v \propto \frac{1}{p}} \text{ or } \boxed{pv = \text{constant}}$$

→ For example, The ideal gas at state can be written as.

$$\boxed{p_1 v_1 = c}$$

At state 2

$$\boxed{p_2 v_2 = c.}$$

$$\boxed{p_1 v_1 = p_2 v_2}$$

* Charle's Law:

Charles Law states that "The volume of given mass of a gas varies directly with its absolute temperature when the pressure remains constant.

$$\boxed{v \propto T}$$

$$\boxed{\frac{V}{T} = \text{constant}}$$

At state point 1, $\frac{V_1}{T_1} = C$

At state point 2, $\frac{V_2}{T_2} = C$

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

→ Charles Law also states that "The pressure of given mass of a gas varies directly with its absolute temperature when the volume remains constant.

$$\boxed{P \alpha T}$$

$\frac{P}{T}$ = constant.

At state point 1, $\frac{P_1}{T_1} = C$

At state point 2, $\frac{P_2}{T_2} = C$

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

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

* Joule's Law :

Joules Law states that " The internal

energy of a given quantity of a gas depends only on the temperature.

→ Already the internal energy depends only on the temperature but not on pressure and volume.

$$\boxed{\Delta U = C_v \Delta T}$$

* Regnault's Law:

→ Regnault's Law states that "The two specific heat C_p and C_v of a gas do not change with the change of temperature and pressure".

* Avogadro's Law:

→ Equal volumes of different perfect gase at the same temperature and pressure contain equal number of molecules.

* Characteristic Gas Equation:

General gas equation for ideal gas.

$$\boxed{\frac{PV}{T} = \text{constant}}$$

④ Equation of State for Real Gas:

* Vander Waal's Equation:

The equation of state for real gas is given by.

$$\boxed{\left(p + \frac{a}{v^2}\right)(v - b) = RT}$$

→ For ideal gas the constant a and b are zero.

→ The values of a and b are dependent upon the type of fluid or gases used.

→ If we consider molar volume in analyses, the equation of state becomes.

$$\boxed{\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = \bar{R}T}$$

where.

$\bar{v}$ - Molar volume.

$\bar{R}$ - Universal gas constant

→ The value of a and b is theoretically determined by.

$$a = \frac{27R^2(T_c)^2}{64 P_c}$$

$$b = \frac{RT_c}{8P_c}$$

where.

T_c - Critical temperature.

P_c - Critical pressure.

Limitations:

→ The study has not been made closely under actual conditions and it's validity has failed.

→ The values of a and b are assumed as constant but they will vary with temperature which is found experimentally.

→ At critical point, the Vander waal's equation.

$$\frac{P_c V_c}{RT_c} = \frac{3}{8} \text{ for real gases.}$$

$$\frac{P_c V_c}{RT_c} = 1 \text{ for ideal gases.}$$

* Beattie Bridegman Equation:

→ This equation is based on five experimentally determined constrains in the form of

$$\boxed{P = \frac{R_u T}{-\bar{v}^2}\left(1 - \frac{c}{\bar{v}T^3}\right)\left(\bar{v} + B\right) - \frac{A}{\bar{v}^2}}$$

where.

$$\boxed{A = A_0\left(1 - \frac{a}{\bar{v}}\right)} \text{ and } \boxed{B = B\left(1 - \frac{b}{v}\right)}$$

→ The equation is known to be a reasonably accurate for densities values upto 0.8 P_{cr}.

* Benedict Webb Rubin Equation:

→ The equation of state is expressed as

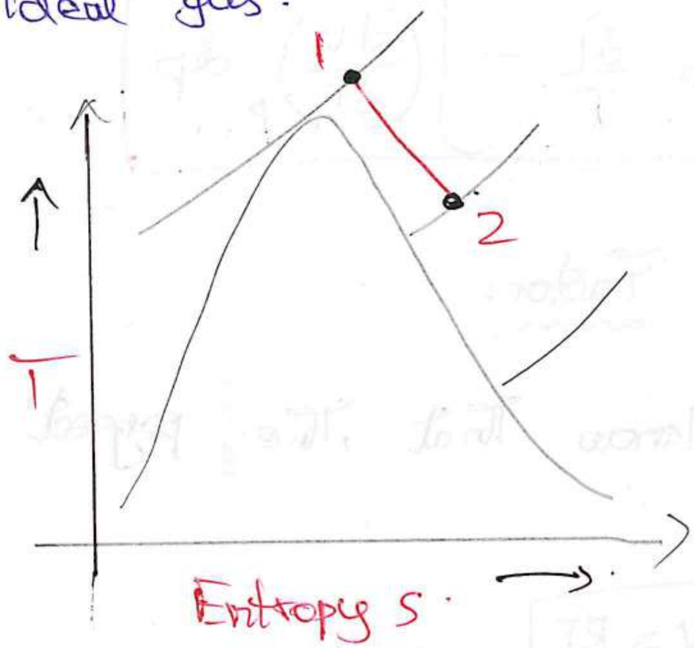
$$\boxed{P = \frac{R_u T}{\bar{v}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T^2}\right)\frac{1}{\bar{v}^2} + \frac{bR_u T - a}{v^{-3}} + \frac{aa}{v^{-6}}}$$

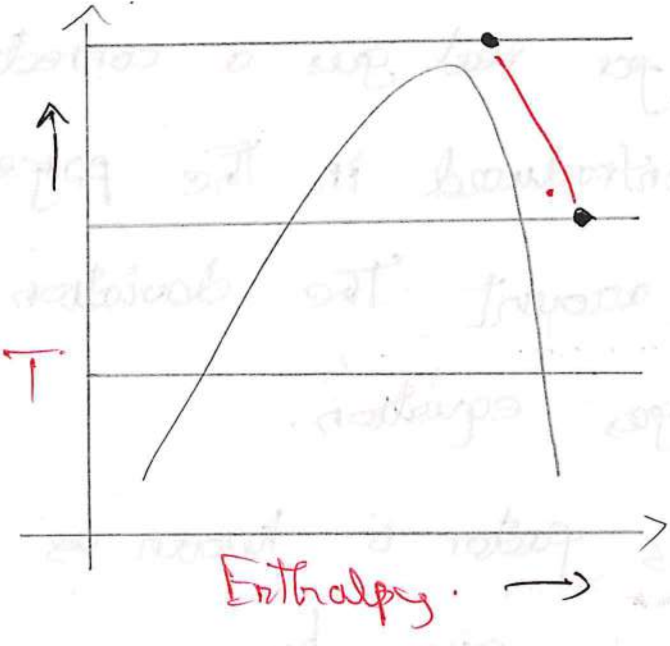
→ This can take densities upto about 2.5 P_{cr}.

⑤ Reduced Properties.

→ The generalized reduced properties are approximated to enthalpy and entropy changes.

→ The enthalpy and entropy calculations are extensions of simple Δh and Δs relations of an ideal gas.





→ The enthalpy of any real gas is determined by.

$$\boxed{\Delta h = \int C_p \, dT - \int \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right] dp}$$

→ Entropy of any real gas is given by.

$$\boxed{\Delta s = \int C_p \, \frac{dT}{T} - \int \left(\frac{\partial v}{\partial T} \right)_p dp}$$

Compressibility Factor:

→ We know that, the perfect gas equation is.

$$\boxed{pV = RT}$$

→ But for real gas a correction factor has to be introduced in the perfect gas equation to take into account the deviation of real gas from perfect gas equation.

→ This factor is known as compressibility factor and it is given by.

$$\boxed{Z = \frac{PV}{RT}}$$

→ The general compressibility chart is plotted with compressibility factor z versus reduced pressure for various values of reduced temperature.

→ This is constructed by plotting the known data of one or more gases and can be used for any gas.

→ The equation of state for real gas at any state becomes.

$$\boxed{pv = ZRT}$$

→ Similarly the equation of state for same real gas at critical point becomes.

$$\boxed{P_c v_c = Z_c R T_c}$$

Compressibility Chart :-

→ We know the perfect gas equation i

$$\boxed{pv = RT}$$

→ But for real gas, a correction factor has to be introduced in the perfect gas equation to take into account the deviation of the real gas from the perfect gas equation.

→ This factor is known as compressibility factor and is defined by.

$$\boxed{Z = \frac{pv}{RT}}$$

Compressibility Chart (Google).

→ The general compressibility chart is plotted with compressibility factor (z) versus reduced pressured (p_r) for various values of reduced temperature.

→ This is constructed by plotting the known data of one or more gases and can be used for any gas.

→ The following observations can be made from the generalized compressibility chart.

* At very low pressure ($p_r << 1$) the gases behave as an ideal gas.

* At high temperatures ($T_r > 2$) ideal gas behaviour is assumed as with good accuracy of pressures.

* The deviation of a gas from ideal gas behaviour is the greatest in the vicinity of critical point.

Problems:

A vessel of volume $0.3\ m^3$ contains 15 kg of air at 303 K. Determine the pressure exerted by the air using 1. Perfect gas equation 2. Vander Waals equation 3. Generalized Compressibility Chart [Take Critical temperature of air is 132.8 K; Critical pressure of air is 37.7 bar].

Given:

Volume $v = 0.3\ m^3$

Mass $m = 15$ kg

Temperature $T = 303$ K.

Critical Temperature $(T_c) = 132.8$ K.

Critical Pressure $(P_c) = 37.7$ bar

$= 37.7 \times 100\ kN/m^2$.

Solution:

1. Perfect Gas Equation

$$pv = mRT$$

$$p = \frac{mRT}{v}$$

$$= \frac{15 \times 0.287 \times 303}{0.3}$$

$$\boxed{P = 4348.05\ kPa}$$

2. Vander Waals Equation:-

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

Critical Pressure, $P_c = 37.7$ bar $= 3770$ kN/m².

$$a = \frac{27 \times (0.287)^2 \times (132.8)^2}{64 \times (37.7) \times (100)}.$$

$$\boxed{a = 0.162}$$

we know that.

$$b = \frac{RT}{8P_c} = \frac{0.287 \times 132.8}{8 \times 37.7 \times 100}.$$

$$\boxed{b = 1.26 \times 10^{-3}}$$

$$\text{Specific Volume} = \frac{\text{Volume}}{\text{mass}} = \frac{0.3}{1.5}.$$

$$\boxed{v = 0.02 \text{ m}^3/\text{kg}}$$

Substituting a, b and v values in Vander Waal's Equation.

$$\left[P + \frac{0.162}{(0.02)^2}\right]\left[0.02 - 1.26 \times 10^{-3}\right]$$

$$\boxed{p = 4235.4 \text{ kN/m}^2}$$

3. Generalized Compressibility Chart

Reduced Temperature

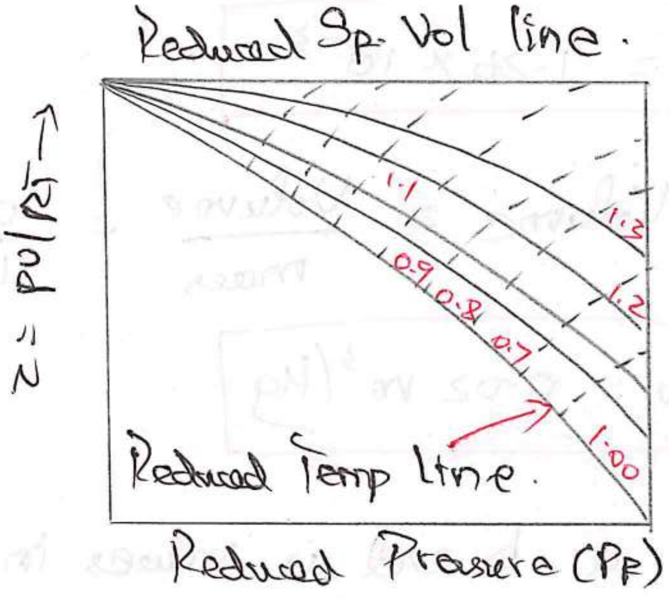
$$T_r = \frac{T}{T_c}$$

$$= \frac{303}{132.8}$$

$$\boxed{T_r = 2.28}$$

$$v_r = \frac{v}{v_c}$$

$$= \frac{v}{\frac{RT_c}{P_c}} \qquad \because P_c v_c = RT_c$$



$$= \frac{vP_c}{RT_c} = \frac{0.02 \times 37.7 \times 100}{0.287 \times 132.8}$$

$$\boxed{v_r = 1.98\ m^3/kg.}$$

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The gas neon has a molecular weight of 20.18 and its critical temperature, pressure and volume are 46 K, 2.5 MPa and 0.05 m^3/kg mol. Reading from a compressibilites chart for a reduced pressure if 2 and a reduced temperature of 1.2, the Z is 0.75. what are the corresponding specific volume, pressure, temperature and reduced volume?

Given:

Molecular weight of neon = 20.183

Critical Temperature $T_c = 46$ K.

Critical Pressure $p_c = 2.5$ MPa.

Critical Volume $v_c = 0.05$ m^3/kg mol.

$T_r = 1.2$

$p_r = 1.2$

$Z = 0.75$

Solution:

Pressure $p = p_r \times p_c$

$= 2 \times 2.5$

$$\boxed{p_r = 5 \text{ Mpa}}$$

$$\frac{T}{T_c} = 1.2$$

$$T = 1.2 \times 46.$$

$$\boxed{T = 55.2 \text{ K.}}$$

We know that, $pv = ZRT$.

$$v = \frac{ZRT}{P}$$

$$= \frac{0.7 \times \frac{8.3143}{20} \times 55.2}{5 \times 10^3}$$

$$\boxed{v = 3.213 \times 10^{-3} \text{ m}^3/\text{kg}}$$

Volume ratio, $v_r = \frac{v}{v_c}$

$$= \frac{3.213 \times 10^{-3} \times 20}{0.5}$$

$$\boxed{v_r = 0.129.}$$

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Compute the specific volume of steam at 0.9 bar and 550 K using Vander Waals Equation. Take critical temperature of steam is 647.3 K and Critical pressure is 220.9 bar.

Given:

$p = 0.9$ bar $= 0.9 \times 100 = 90$ kPa.

Temperature $T = 550\,K$.

Critical Temperature $T_c = 647.3\,K$

Critical Pressure $P_c = 220.9$ bar $= 220.9 \times 100$ kN/

Solution:

Vander Waals Equation.

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

where

$$a = \frac{27 R^2 (T_c)^2}{64 P_c}$$

where

$$R = \frac{\text{Universal Gas Constant}}{\text{Molecular Weight of Steam}}$$

$$= \frac{8.314}{18}\ \text{kJ/kgK}$$

$$\boxed{R = 0.462\ \text{kJ/kgK}}$$

$$a = \frac{27 \times (0.462)^2 \times (647.3)^2}{64 \times (220.9) \times 100}$$

$$\boxed{a = 1.7}$$

$$b = \frac{RT}{8 P_c}$$

$$= \frac{0.462 \times 647.3}{8 \times 220.9 \times 100}$$

$$\boxed{b = 1.69 \times 10^{-3}}$$

Substituting a, b and pressure & temperature values in Vander Waals Equation.

$$\left(0.75 \times 100 + \frac{1.70}{v^2}\right) \times \left(v - 1.69 \times 10^{-3}\right) = 0.462 \times 570.$$

$$\left(75 + \frac{1.70}{v^2}\right)\left(v - 1.69 \times 10^{-3}\right) = 263.34.$$

Specific Volume $\boxed{v = 0.25 \text{ m}^3/\text{kg}}$

x ——— x ——— x.

A perfect gas of 0.5 kg has a pressure of 300 kPa, a temperature of 100°C and a volume of 0.06 m³. The gas undergoes an irreversible adiabatic process to a final pressure of 400 kPa and final volume of 0.15 m³, workdone on gas is 50 kJ. Find Cp, Cv.

Given:

$m = 0.2$ kg.

$p_1 = 300$ kPa.

$T_1 = 40^\circ C + 273 = 313\ K.$

$V_1 = 0.06\ m^3$

$p_2 = 400\ kPa$

$V_2 = 0.15\ m^3$

$W = -50\ kJ.$

Solution:

$p_1 V_1 = mRT_1$

$$R = \frac{p_1 V_1}{m T_1} = \frac{300 \times 0.06}{0.2 \times 313}.$$

$$\boxed{R = 0.288\ kJ/kgK.}$$

$p_2 V_2 = mRT_2.$

$$T_2 = \frac{p_2 V_2}{mR} = \frac{400 \times 0.15}{0.2 \times 0.288}.$$

$$\boxed{T_2 = 1041.67\ K.}$$

Heat transfer, $Q = W + \Delta U.$

$= W + mC_v(T_2 - T_1)$

$Q = -50 + 0.2 \times C_v(1041.67 - 313).$

For adiabatic Process, $Q = 0.$

$0 = -50 + 0.2 \times C_v(1041.67 - 313).$

$$\boxed{C_v = 0.343\ kJ/kgK.}$$

⑥ Maxwell Relations:

→ Modelling the dependence of Gibbs and Helmholtz functions behave with varying temperature, pressure and volume is fundamentally useful.

→ But in order to do that, a little bit more development is necessary.

→ To see the power and utilities of these functions, it is useful to combine the first and Second Law into a single mathematical statement.

$$ds = \frac{dq}{T} \quad — ①$$

→ For a reversible change it follows tha

$$dq = Tds \quad — ②$$

→ And since.

$$dw = Tds - pdv \quad — ③$$

→ For a reversible expansion in which only p-v works is done.

$$dU = Tds - pdv \quad ④$$

→ The Maxwell relations relate entropy to the three directly measurable properties p, v and T for pure simple compressible substances

→ From First Law of Thermodynamics.

$$Q = W + \Delta U$$

→ Rearranging the parameters.

$$Q = \Delta U + W$$

$$Tds = du + pdv$$

$\left[\because ds = \frac{Q}{T}\right.$ by second Law of Thermodynamics$\left.\right]$

$W = pdv$ by First Law of Thermodynamics.

$$du = Tds - pdv \quad ⑤$$

We know that

$$h = u + pv$$

$$dh = du + d(pv)$$

$$= du + vdp + pdv \quad ⑥$$

Substituting value du in equation ⑥

$$dh = Tds - pdv + vdp + pdv.$$

$$dh = Tds + vdp. \quad —⑦$$

By Helmotz function.

$$a = u - Ts$$

$$da = du - d(Ts).$$

$$= du - Tds - sdT \quad —⑧$$

Substituting value of du in equation ⑧.

$$da = Tds - pdv - Tds - sdT$$

$$= -pdv - sdT.$$

By Gibbs function.

$$G = h - Ts.$$

$$dg = dh - d(Ts).$$

$$dg = dh - Tds - sdT.$$

Substituting value of dh in equation ⑥

So dg becomes

$$dg = Tds + vdp - Tds - sdT.$$

$$\boxed{dg = vdp - sdT.}$$

By inverse exact differential we can write equation (1) as:

$$du = Tds - pdv.$$

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v.$$

Similarly Equation can be written as.

$$dh = Tds + vdp.$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P.$$

Similarly equation can be written as

$$-\left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial s}{\partial v}\right)_T$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T.$$

Similarly equation can be written as.

$$dg = vdp - sdT.$$

$$\boxed{\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T}$$

⑦ Tds Equation:

→ Tds equation enable us to relate the entropy of a substance with directly measurable quantities provided its equation of state and heat capacities are known.

→ First Tds Equation.

$$Tds = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv.$$

→ Second Tds Equation.

$$Tds = C_p dT - T\left(\frac{\partial v}{\partial T}\right)_P dp.$$

First Tds Equation:

$$Tds = C_v dT + \left(\frac{\partial P}{\partial T}\right)_v dv.$$

$$S = S[T, v].$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv.$$

Multiplying by T.

$$Tds = T\left(\frac{\partial s}{\partial T}\right)_v dT + T\left(\frac{\partial s}{\partial v}\right)_T dv. \quad \text{—} ①$$

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v \quad \text{— ②}$$

Using Maxwell Relation (Second).

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \quad \text{— ③}$$

Using ② and ③ in ①

$$T\,ds = C_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_v dv.$$

ii) Second Tds Equation

$$T\,ds = C_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_p dp.$$

Let $S = S(T, P)$

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial P}\right)_T dp.$$

Multiplying by T both sides, we get.

$$T\,ds = T\left(\frac{\partial s}{\partial T}\right)_p dT + T\left(\frac{\partial s}{\partial P}\right)_T dp. \quad \text{— ④}$$

we know that.

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_p. \quad \text{— ⑤}$$

Maxwell's fourth relation.

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P \quad — ⑥$$

Using ⑤ & ⑥ in ④.

$$T\,ds = C_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_P dP.$$

→ The entropy of a pure substance can be expressed as a function of temperature (T) and pressure (P).

$$s = f(T, P).$$

We know that

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP.$$

$$C_p = T\left(\frac{\partial s}{\partial T}\right)_P.$$

$$\boxed{\left(\frac{\partial s}{\partial T}\right)_P = \frac{C_p}{T}}$$

From Maxwell equation, we know that

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P.$$

Substituting in ds equation.

$$ds = \frac{C_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp.$$

Multiplying by T on both sides of equation

$$\boxed{T ds = C_p dT - T \left(\frac{\partial v}{\partial T}\right)_p dp.}$$

→ This is known as first form of entropy equation (or) first Tds Equation.

→ By considering entropy of a pure substance as a function of Temperature and Specific volume.

$$s = f(T, v).$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv.$$

We know that $C_v = T\left(\frac{\partial s}{\partial T}\right)_v$

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{C_v}{T}$$

From Maxwell Equations we know that

$$\boxed{T ds = C_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dv}.$$

⑧ Heat Capacity Relations:

→ The total amount of energy in the form of heat needed to increase the temperature of 1 mole of any substance by 1 unit is called molar heat capacity of that substance.

→ It also significantly depends on the nature, size and composition of a substance.

$$\boxed{q = nC\Delta T}$$

→ We know that there are two specific heats of gas (ie) Cp and Cv can be measured experimentally.

→ From the definition of specific heats

$$C_p = \left[\frac{\partial h}{\partial T}\right]_p \longleftarrow ①$$

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v. \longrightarrow ②$$

$$① \Rightarrow C_p = \left(\frac{\partial h}{\partial T}\right)_p$$

$$= \left(\frac{\partial h}{\partial s}\right)_p \times \left(\frac{\partial s}{\partial T}\right)_p.$$

$$\boxed{C_p = T \times \left(\frac{\partial s}{\partial T}\right)_p}$$

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial u}{\partial s}\right)_v \times \left(\frac{\partial s}{\partial T}\right)_v$$

$$C_v = T \times \left(\frac{\partial s}{\partial T}\right)_v \quad \left[\because \left(\frac{\partial u}{\partial s}\right)_v = T\right] \text{ — } ④$$

$$C_p - C_v = T\left[\left(\frac{\partial s}{\partial T}\right)_p - T\left(\frac{\partial s}{\partial T}\right)\right]$$

$$C_p - C_v = T\left[\left(\frac{\partial s}{\partial T}\right)_p - \left(\frac{\partial s}{\partial T}\right)_v\right] \text{ — } ⑤$$

Let Entropy is a function of Temperature and Specific Volume (v).

(ie) $s = f(T, v)$.

By Equation (2)

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv.$$

Dividing by dT.

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv.$$

$$\left(\frac{\partial s}{\partial T}\right)_p - \left(\frac{\partial s}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p \text{ — ⑥}$$

Substituting ⑥ in ⑤

$$C_p - C_v = T\left[\left(\frac{\partial s}{\partial v}\right)_T \times \left(\frac{\partial v}{\partial T}\right)_p\right]$$

From Maxwell Equation we know that

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v.$$

$$C_p - C_v = T\left[\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p\right] \text{ — ⑦}$$

→ From ⑦ we can determine the difference between the two specific heats Cp and Cv in terms of measurable properties P, V and T.

we know that

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{\beta}{K}.$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \beta v.$$

where

β - Coefficient of volume expansion.

k - Isothermal Compressibility.

Substituting $\left(\frac{\partial P}{\partial T}\right)_v$ and $\left(\frac{\partial v}{\partial T}\right)_P$ values in equation ⑦.

$$C_P - C_v = T\left[\left(\frac{\beta}{k}\right)_v \times \beta v\right]$$

$$C_P - C_v = T \times \frac{\beta^2 v}{k}$$

$$\boxed{C_P - C_v = \frac{T\beta^2 v}{k}}$$

Ratio of Specific Heat Capacities:

$$C_P = T\left(\frac{\partial s}{\partial T}\right)_P \quad — ①$$

$$C_v = T\left(\frac{\partial s}{\partial T}\right)_v \quad — ②$$

Dividing equation ① by ②

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

$$\boxed{\gamma = \left(\frac{\partial s}{\partial T}\right)_P \left(\frac{\partial T}{\partial s}\right)_v}$$

⑨ Energy Equations:

→ By the first Law of Thermodynamics the change in internal energy ΔU for finite process at constant P and T is.

$$\boxed{\Delta U = \lambda - P\Delta V}$$

→ For a pVT System and from First & Second Law of Thermodynamics.

$$dQ = du + pdv.$$

$$Tds = dQ.$$

→ By combining first and second Law of Thermodynamics.

$$du = Tds - pdv.$$

(or)

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - P.$$

(or)

$$\boxed{\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P.}$$

Derivation of change in internal energy:

→ Take U as dependent variable; T and V as independent variables.

$$U = U(T, V).$$

$$\boxed{du = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial u}{\partial V}\right)_T dV.}$$

$$du = C_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

as $C_V = \left(\frac{\partial u}{\partial T}\right)_V$.

$$\boxed{\therefore du = C_V\, dT + \left[T\left(\frac{\partial P}{\partial T}\right) - P\right] dV.}$$

2nd Energy Equation.

→ For a PVT System

From 1st Law of Thermodynamics

From 2nd Law of Thermodynamics

$$dQ = du + p\,dV.$$

$$T\,ds = dQ.$$

→ By combining 1st & 2nd Laws.

$$dv = T\,ds - p\,dv.$$

(or)

$$\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial s}{\partial P}\right)_T - P\left(\frac{\partial v}{\partial P}\right)_T.$$

(or)

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

Derivation of Change in internal energy:

→ Take U as dependent variable; T and p as independent variables.

$$U = U(T, p)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right) dp.$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT - \left[T\left(\frac{\partial v}{\partial T}\right)_P + P\left(\frac{\partial v}{\partial P}\right)_T\right] dp.$$

Application of Energy Equation:

→ The entropy of pure substance can be expressed as a function of temperature.

and pressure (P).

$$S = f(T, P).$$

We know that

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial v}\right)_T dv.$$

Substituting ds value in the equation

$$du = T\left[\left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv\right] - p\,dv.$$

We know that.

$$C_v = T\left(\frac{\partial s}{\partial T}\right)_v.$$

From Maxwell Equation we know that

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v.$$

$$du = T\left(\frac{\partial s}{\partial T}\right)_v dT + T\left(\frac{\partial s}{\partial v}\right)_T dv - p\,dv.$$

$$= C_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_v dv - p\,dv.$$

$$\boxed{du = C_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_v dv - p\,dv.}$$

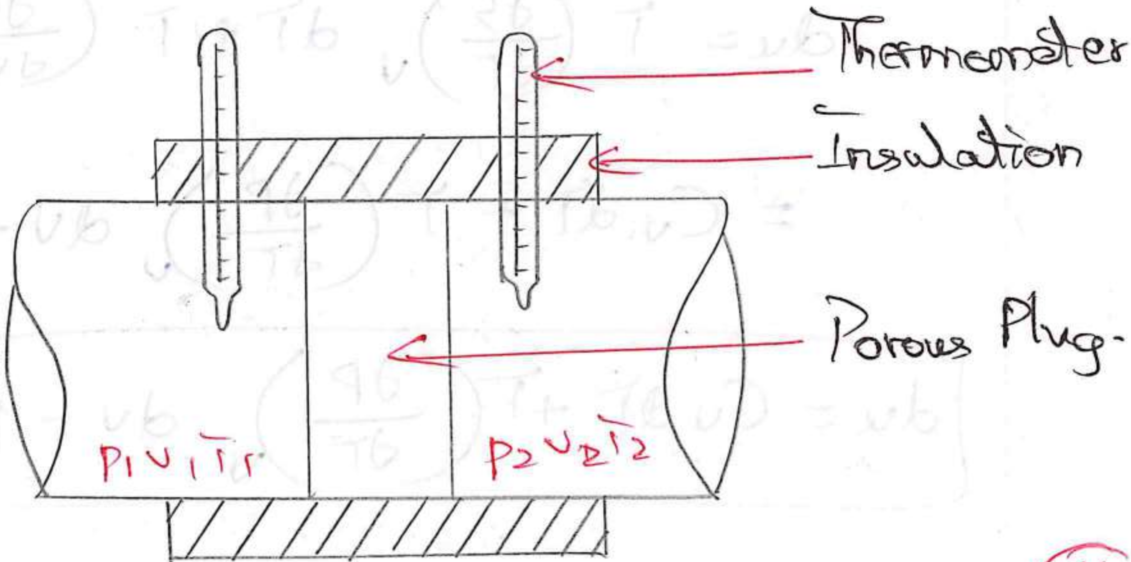
⑩ Joule Thomson Experiment:

→ Joule Thomson Coefficient is define as the change in temperature with change in pressure keeping the enthalpy remains constant.

$$\boxed{\mu = \left(\frac{\partial T}{\partial P}\right)_h}$$

→ Figure shows the arrangement of porous plug experiment.

→ In this experiment, a stream of gas at a pressure P_1 and temperature T_1 is allowed to flow continuously through a porous plug.



→ The whole apparatus is completely insulated.

→ Therefore no heat transfer takes place

$$\boxed{Q = 0}$$

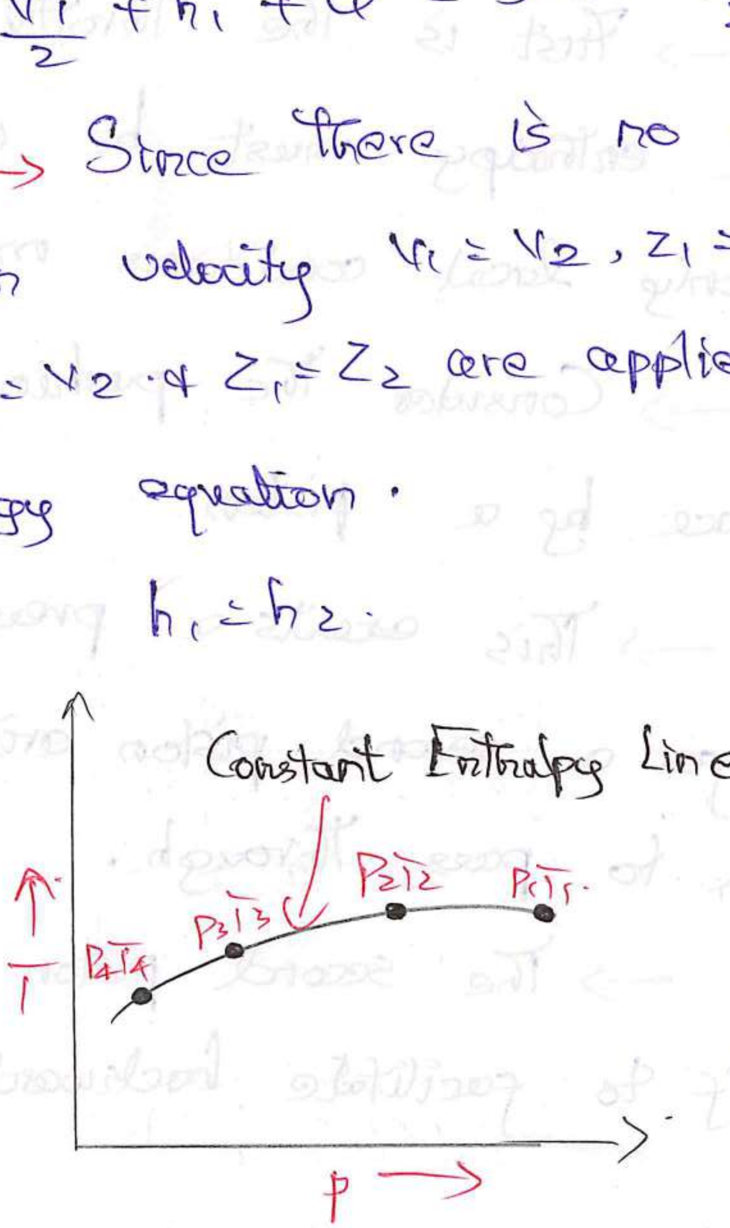
→ The system does not exchange work with the surroundings.

$$W = 0.$$

$$gz_1 + \frac{v_1^2}{2} + h_1 + Q = gz_2 + \frac{v_2^2}{2} + h_2 + W.$$

→ Since there is no considerable change in velocity $v_1 = v_2$, $z_1 = z_2$, $Q = 0$, $W = 0$, $v_1 = v_2$ & $z_1 = z_2$ are applied in steady flow energy equation.

$$h_1 = h_2.$$



→ The slope of a constant enthalpy is known as Joule Thomson Coefficient which is denoted by μ.

→ For real gas, μ may be either positive or negative depending upon the Thermodynamic state of the gas.

Derivation for Joule Thomson Coefficient

→ First is the throttling process in which the enthalpy must be constant partiall because only local conditions must be considg

→ Consider the pushing of the flui takes place by a piston.

→ This exerts a pressure Pi while a need for a second piston arises to enable the fluid to pass through.

→ The second piston will have th pressure Pf to facilitate backward movement.

→ V_i is the initial volume while V_f is the final volume.

→ Assume that no heat flow takes place, so energy change is.

$$U_f - U_i = Q + W$$ which written is.

$$U_f - U_i = 0 + W_{left} + W_{right}.$$

→ Take W_{Left} to be positive and W_{right} as negative.

$$U_f - U_i = P_iV_i - P_fV_f$$

→ Rearranging this will provide.

$$U_f + P_fV_f = U_i + P_iV_i$$

→ The third partial derivative is the inverse of isothermal Joule Thomson coefficient

$$(\partial T/\partial P)_H (\partial H/\partial T)_P (\partial P/\partial H)_T = -1.$$

$$C_P = (\partial H/\partial T)_P.$$

$$\boxed{\mu T = (\partial H/\partial T)T}$$

(11) Clausius Clapeyron Equation:

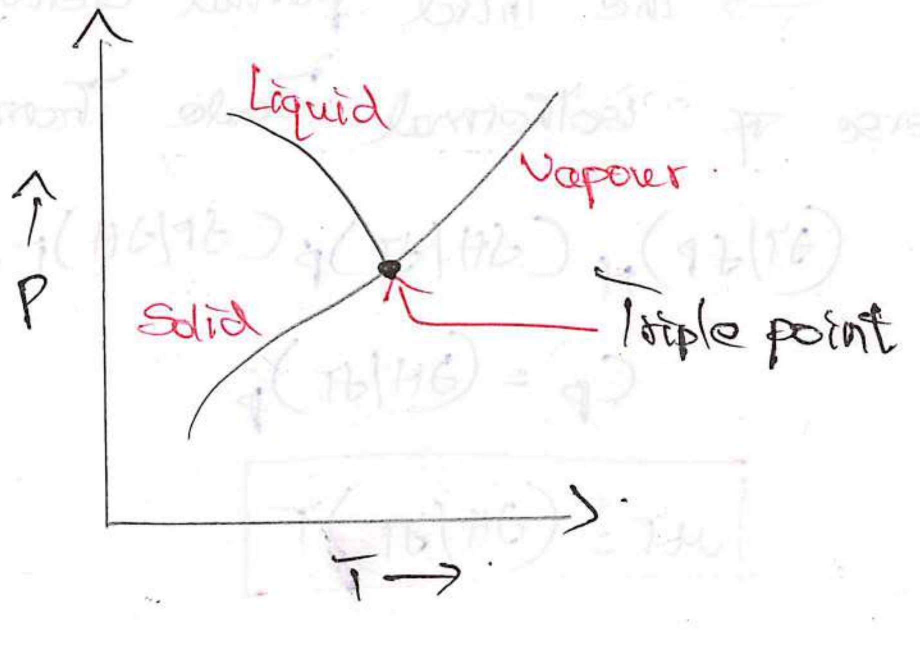
→ Clausius Clapeyron Equation which involves the relationship between saturation pressure, temperature, enthalpy of evaporation and the specific volume of two phases involved.

→ This equation provides a basis for calculation of properties in a two phase region.

→ Let Entropy is a function of T and v.

$$s = f(T, v).$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv.$$



→ when The phase is changing from saturated liquid to saturated vapour, temperature remains constant.

$$ds = \left(\frac{\partial s}{\partial v}\right)_T dv.$$

For Maxwell Equation we know that

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v.$$

$$s = \left(\frac{\partial P}{\partial T}\right)_v dv.$$

→ The term $\left(\frac{\partial P}{\partial T}\right)$ is The slope of the Saturation Curve.

→ Integrating above equation between saturated liquid and saturated vapour.

$$\int_{s_f}^{s_g} ds = \frac{dP}{dT}\int_{v_f}^{v_g} dv$$

$$S_{s_f}^{s_g} = \frac{dP}{dT}\left[v\right]_{v_f}^{v_g}.$$

$$\left[s_g - s_f\right) = \frac{dP}{dT}\left[v_g - v_f\right].$$

$$\frac{dP}{dT} = \frac{s_g - s_f}{v_g - v_f}.$$

$$\boxed{\frac{dP}{dT} = \frac{s_g - s_f}{v_g - v_f} = \frac{s_{fg}}{v_{fg}}}$$

From Second Law of Thermodynamics.

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

For constant pressure process.

$$dQ = dh.$$

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

$$s_{fg} = \frac{h_{fg}}{T}.$$

$$\frac{dP}{dT} = \frac{s_g - s_f}{v_g - v_f}$$

$$\boxed{\frac{dP}{dT} = \frac{s_{fg}}{v_{fg}} = \frac{h_{fg}}{T v_{fg}}.}$$

This is known as Clapeyron Equation.

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