

**THERMO**

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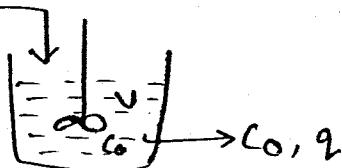
Thanks to all of You :

July 12, 14

## Process Control

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Q.7  $A \rightarrow B$  q,  $C_i$



$$-r_A = kC_A \quad (A \text{ consumed})$$

for any material balance

$$I O G C = \Delta C e$$

+ - -

Input-Output

+ Generation - Consumption = 0  
Accumulation

Material balance at unsteady state

$$qC_i - qC_0 + 0 - kC_0V = V \frac{dC_A}{dt} \quad (1)$$

no generation  
of A  
V volume.

M.B. at steady state

$$qC_{is} - qC_{os} - kC_{os}V = 0 = \frac{VdC_{os}}{dt} \quad (2)$$

Subtract above equations:-

$$q(C_i - C_{is}) - q(C_0 - C_{os}) + kV(C_0 - C_{os}) = \frac{Vd(C_0 - C_{os})}{dt} \quad (3)$$

Deviation Variables

$$\bar{C}_i = (C_i - C_{is})$$

$$\bar{C}_0 = (C_0 - C_{os})$$

$$q\bar{C}_i - q\bar{C}_0 - kV\bar{C}_0 = \frac{Vd\bar{C}_0}{dt} \quad (4)$$

Formulas of Laplace

$$\underline{f(t)}$$

$$1$$

$$\frac{dx}{dt}$$

$$\underline{F(s)}$$

$$\frac{1}{s}$$

$$s \cdot \underline{f(s)} + \underline{f(0)}$$

$$f(t) = L^{-1}\{F(s)\}$$

$$F(s) = L\{f(t)\} \quad 3$$

1

$$1/s$$

$$e^{at}$$

$$1/s-a$$

$$t^n$$

$$\frac{n!}{s^{n+1}}$$

$$\sqrt{t}$$

$$\frac{\sqrt{\pi}}{2s^{1/2}}$$

$$\sin at$$

$$\frac{a}{s^2+a^2}$$

$$\cos at$$

$$\frac{s}{s^2+a^2}$$

$$t \cos at$$

$$\frac{s^2-a^2}{(s^2+a^2)^2}$$

$$e^{at} \cos bt$$

$$\frac{s-a}{(s-a)^2+b^2}$$

$$e^{at} \sin bt$$

$$\frac{b}{(s-a)^2+b^2}$$

$$\int_0^t f(t) dt$$

$$F(s)/s$$

$$\int_0^t f(t-\tau) g(\tau) d\tau$$

$$F(s) \cdot G(s)$$

$$f(t+T) = f(t)$$

$$\int_0^T \frac{e^{-st} f(t) dt}{1-e^{sT}}$$

$$f'(t)$$

$$sF(s) - f(0)$$

$$f''(t)$$

$$s^2 F(s) - sf(0) - f'(0)$$

$$f^n(t)$$

$$s^n F(s) - s^{n-1} f(0) - s^{n-2} f'(0) - \dots - s f^{(n-1)}(0) - f^{(n)}(0)$$

$$f(t-\tau)$$

$$e^{-\tau s} F(s)$$

$$q\bar{C}_i - q\bar{C}_0 - KV\bar{C}_0 = \frac{Vd\bar{C}_0}{dt} \quad (4)$$

Taking Laplace Transform:

$$q\bar{C}_i(s) - q\bar{C}_0(s) - KV\bar{C}_0(s) = VS(s) + C_0(s) \quad \left. \begin{array}{l} \text{at } t=0, \\ C_0=0 \end{array} \right.$$

We have to find

$$G_i(s) = \frac{C_0(s)}{C_i(s)}$$

$$\begin{aligned} q_i C_i(s) &= C_0(s) [q + KV + VS] \\ &= C_0(s) (q + KV) \left[ 1 + \frac{VS}{q + KV} \right] \end{aligned}$$

$$G_i(s) = \frac{C_0(s)}{C_i(s)} = \frac{\frac{q}{q+KV} R}{1 + \frac{VS}{q+KV}} \quad \rightarrow \tau$$

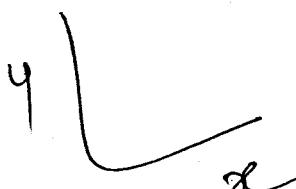
$$G_i(s) = \frac{C_0(s)}{C_i(s)} = \frac{R}{1 + \tau s} \quad \text{first order transfer function.}$$

$\tau$  = time constant.

= Resistance  $\times$  Capacitance.

$$\begin{aligned} \text{TR} &\propto \text{Cap.} \\ R &= \tau \times \frac{1}{\text{Cap.}} \end{aligned}$$

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



$\frac{dy}{dx}$  slope  
Area

$PV = \text{const}$   
 $PV = \text{const}$   
 $PV = \text{const}$

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

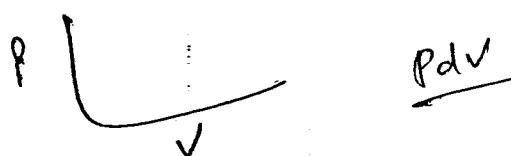
$$\gamma = \frac{C_p}{C_v}$$

$$\frac{C_p}{C_v} > 1$$

Ex Venire  
Tensive

FM

HT ✓  
Ther  
(PDC)



$PdV$

isobaric:  $P \text{ const}$

Isochoric:  $V \text{ const}$

Isothermal:  $T \text{ const}$

Adiabatic:  $Q = 0$

$$\frac{P \cdot dV}{dV_{\text{ref}}} = \frac{w_{\text{ad}}}{w_{\text{ref}}} = 0$$

\* Isenthalpic:  $h = \text{const}$   $\Leftrightarrow$  throttling

\* Isentropic:  $S = \text{const}$   $\Leftrightarrow$  adiabatic

$$PV^\gamma = \text{const}$$

$$\underline{P_1 V_1^\gamma} = \underline{P_2 V_2^\gamma}$$

## # First Law of Thermodynamics:—

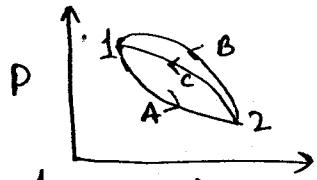
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In a closed system undergoing any thermodynamic cycle, cycle integral of work & cyclic integral of heat, are proportional to each other, when expressed in their own units & are equal to each other when expressed in the consistent units.

$$\oint \delta w \propto \oint \delta Q$$

$$\text{kJ} \quad \text{kcal}$$

$$\oint \delta w = \oint \delta Q$$



$$(1A2B1) \quad \int_1^2 (\delta w)_A + \int_2^1 (\delta w)_B = \int_1^2 (\delta Q)_A + \int_2^1 (\delta Q)_C$$

$$(1A2C) \quad \int_1^2 (\delta w)_A + \int_2^1 (\delta w)_C = \int_1^2 (\delta Q)_A + \int_2^1 (\delta Q)_C$$

$$\underline{\underline{\int_1^2 (\delta w)_A - \int_2^1 (\delta w)_C = \int_2^1 (\delta Q)_B - \int_2^1 (\delta Q)_C}}$$

$$\underline{\underline{\int_2^1 (\delta Q)_C - \int_2^1 (\delta w)_C = \int_2^1 (\delta Q)_B - \int_2^1 (\delta w)_B}}$$

$$\int_2^1 (\delta Q - \delta w)_C = \int_2^1 (\delta Q - \delta w)_B$$

$(\delta Q - \delta w) \rightarrow$  Independent of path.

point function.

↳ Thermodynamic property

all pt. functions are perfect differential

Internal energy  $\leftarrow dv = \square$

$$\boxed{\delta Q - \delta w = dv} \rightarrow \text{Process}$$

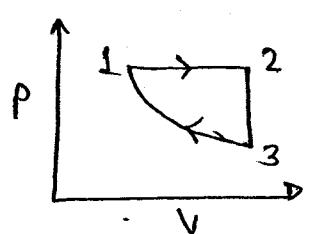
↳ Non flow energy eqn

$$1Q_2 - 1W_2 = V_2 - V_1$$

$$2Q_3 - 2W_3 = V_3 - V_2$$

$$3Q_1 - 3W_1 = V_1 - V_3$$

$$\underline{\underline{\oint dQ - \oint dw = 0}}$$



$$dV \propto dT$$

$$U_1 = C_V dT$$

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- # Process:-
- i) Isothermal
  - ii) Isochoric
  - iii) Isobaric
  - iv) Adiabatic
  - v) Polytropic
  - vi) Free expansion.

# Isothermal:- (Extremely slow process) (ideal process)

$$PV \propto C$$

$$P \propto \frac{1}{V}$$

$$P_1 V_1 = P_2 V_2$$

$$Q_2 = i w_2$$

(Boyle's Law)

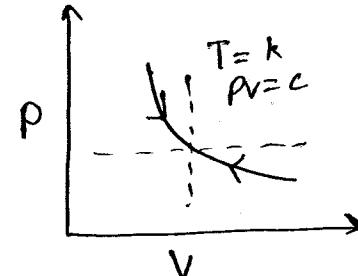
\*

$$PV = C$$

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

$$\frac{dp}{dw} = -\frac{C}{V^2} = -\frac{PV}{V^2} = -\frac{P}{V}$$

(Hyperbolic process)



\*

$$dV = C_V dT$$

$$U_2 - U_1 = C_V (T_2 - T_1)$$

$$U_2 - U_1 = 0$$

\*

Work done

$$\int_1^2 dw = \int_1^2 P dV$$

$$i w_2 \Rightarrow C \int_1^2 \frac{1}{V} dV = C \left[ \int_1^2 \ln V \right]_1^2$$

$$i w_2 = C \ln \frac{V_2}{V_1} = P V \log \frac{V_2}{V_1}$$

$$P_1 V_1 \log \frac{V_2}{V_1} = RT_1 \ln \frac{V_2}{V_1} = RT_1 \ln \frac{P_1}{P_2}$$

\*

Heat Transfer

$$dQ = dw + dV$$

$$Q_2 = i w_2$$

# Adiabatic Process :— (ideal process)

↓  
Extremely fast

Heat transfer  $\approx 0$

B

\* PVT Relation

$$\oint PdV + \oint CvdT = 0$$

$$Pv^{\frac{1}{\gamma}} = C$$

$$Tv^{\frac{1}{\gamma-1}} = C$$

$$\frac{T}{P^{\frac{1}{\gamma-1}}} = C$$

$$PdV + CvdT = 0$$

$$PV = RT$$

$$\partial P V dP + V dP = R dT$$

$$dT = \frac{Pvdp}{R} + \frac{vdP}{R}$$

$$PdV + Cv \frac{PdV + Vdp}{R} = 0$$

$$R PdV + Cv (PdV + Vdp) = 0$$

$$(C_p - Cv) PdV + Cv (PdV + Vdp) = 0$$

$$C_p PdV + Cv Vdp = 0$$

$$\frac{C_p dV}{Cv P V} + \frac{Cv Vdp}{Cv P V} = 0$$

$$\sqrt{\frac{dV}{V}} + \frac{dp}{P} = 0$$

$$\int \frac{dV}{V} + \int \frac{dp}{P} = C$$

$$\ln V + \ln P = \ln C$$

$$\ln PV^{\frac{1}{\gamma}} = \ln C$$

$$PV^{\frac{1}{\gamma}} = C$$

\* PV diagram

$$PV^{\frac{1}{\gamma}} = C$$

$$P = \frac{C}{V^Y}$$

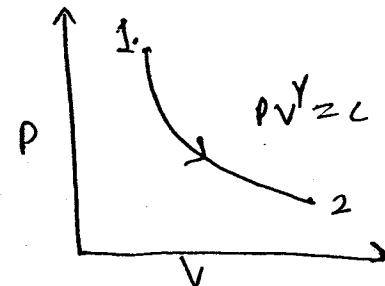
$$\frac{dP}{dV} = (C-Y)V^{-Y-1} = (PV)^Y (C-Y)(V^{-Y-1})$$

$$= -\frac{\lambda P}{V}$$

\* Change in internal energy

$$dU = C_V dT$$

$$U_2 - U_1 = C_V (T_2 - T_1)$$



\* Work done

$$\int \delta W = \int P dV$$

$$W_2 = \int \frac{C}{V^Y} dV = \int_1^2 C V^{-Y} dV$$

$$W_2 = C \left[ \frac{V^{-Y+1}}{1-Y} \right]_1^2$$

$$W_2 = \frac{C}{1-Y} [V_2^{-Y+1} - V_1^{-Y+1}]$$

$$C = PV^Y$$

$$W_2 = \frac{1}{1-Y} [P_2 V_2^Y \cdot V_2^{-Y+1} - P_1 V_1^Y \cdot V_1^{-Y+1}]$$

$$W_2 = \frac{1}{1-Y} [P_2 V_2 - P_1 V_1]$$

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

$$W_2 = \frac{R(T_1 - T_2)}{Y-1}$$

\* Heat transfer

$$\delta Q = \delta W + dV$$

$$Q_2 = W_2 + (V_2 - V_1)$$

$$1Q_2 = \frac{R(T_1 - T_2)}{\gamma - 1} + c_v(T_2 - T_1)$$

(10)

$$1Q_2 = \frac{(T_1 - T_2)(R - c_v)(\gamma - 1)}{\gamma - 1}$$

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

$$1Q_2 = (T_1 - T_2) \left[ \frac{R}{\gamma - 1} - c_v \right]$$

$1Q_2 = 0$

July 17, 14

Q) A 2kW, 40 litre water heater is switched on for 20 minutes. The heat capacity  $C_p$  for water is 4.2 kJ/kgK. Assuming all the electrical energy has gone into heating the water, increase of water temp in °C is ?

$$q = mC_p\Delta T$$

$$2 = 40 \times 4.2$$

Sol<sup>n</sup>

$$m \times C_p \times \Delta T = \text{Energy Supplied.}$$

$$40 \text{ kg} \times 4.2 \frac{\text{kJ}}{\text{kgK}} \times \Delta T \text{ K} = 2 \frac{\text{kJ}}{\text{s}} \times 60 \times 20$$

$$= \frac{2 \times 60 \times 20}{40 \times 4.2}$$

$$= 14.285 \text{ K}$$

$$= 14.285^\circ\text{C}$$

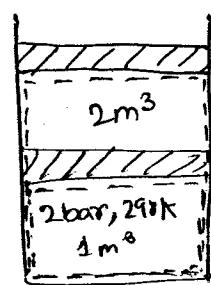
Q) Nitrogen gas (28)  $N_2$ , is enclosed in a cylinder by a piston at the initial condition of 2 bar, 298 K, 1 m<sup>3</sup> in a particular process. The gas slowly expands under isothermal condition until the volume becomes 2 m<sup>3</sup>. Heat exchange occurs with the atmosphere at 298 K during the process. Determine the work interaction for the gas  $1W_2$ ?

$$P_1 = 2 \text{ bar}$$

$$V_1 = 1 \text{ m}^3 \quad V_2 = 2 \text{ m}^3$$

$$T_1 = 298 \text{ K} = T_2$$

$$1W_2 = P_1 V_1 \ln \frac{V_2}{V_1} = m R T_1 \ln \frac{V_2}{V_1}$$



Slowly expands  
Isothermal condition

$$= (2 \times 100) \times 1 \ln \times \frac{2}{1} \\ = 138.63 \text{ kJ}$$

$$\frac{P_1 V_1}{R T_1} = m = \frac{200 \times 1}{8.314 \times 298} \\ = \frac{200 \times 1}{8.314 \times 298} \times \frac{8.314}{28} \times 298 \times \ln \frac{2}{1}$$

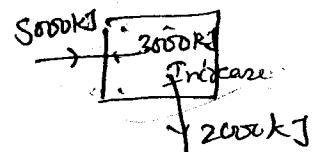
$$R = \frac{R_u}{m} = \frac{8.314 \text{ kJ/kgmol K}}{28 \text{ kg / kg mole}}$$

Q1) A gas contained in a cylinder is compressed. The work required for the compression is 5000 kJ. During the process heat interaction of 2000 kJ causes the surroundings to be heated. The change in internal energy during the process is  $(U_2 - U_1)$ ?

Soln

$$\text{Work required, } W_2 = -5000 \text{ kJ}$$

$$Q_2 = -2000 \text{ kJ}$$



$$Q_2 - W_2 = (U_2 - U_1)$$

$$-2000 + 5000 = (U_2 - U_1)$$

$$(U_2 - U_1) = 3000 \text{ kJ}$$

Q2) Nitrogen at an initial state of 10 bar, 1 m<sup>3</sup> & 300K is expanded isothermally to the volume of 2 m<sup>3</sup>. The PVT relation is given by.

$$\left(P + \frac{a}{V^2}\right)V = RT \quad a > 0$$

The final pressure will be a) < 5 bar

b) > 5 bar

c) = 5 bar

d) Can't be ascertained in the absence of value of a.

$$P_1 = 10 \text{ bar}, \quad T_1 = 300 \text{ K} \\ V_1 = 1 \text{ m}^3 \quad V_2 = 2 \text{ m}^3$$

$$\left(P_1 + \frac{a}{V_1^2}\right)V_1 = \left(P_2 + \frac{a}{V_2^2}\right)V_2$$

$$10 + a = \left(P_2 + \frac{a}{4}\right) \times 2$$

$$5 + \frac{a}{2} = P_2 + \frac{a}{4}$$

$$5 + \frac{3a}{4} = P_2$$

Q.) A monoatomic ideal gas with  $\gamma = 1.67$ ,  $M \cdot M_T = 40$ , is compressed adiabatically from 0.1 MPa, 300 K to 0.2 MPa. The work of compression of the gas in kJ/kg ( $W_2$ )?

$$\begin{aligned}
 W_2 &= \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} \\
 &= \frac{m R (T_1 - T_2)}{\gamma - 1} \\
 &= \frac{1 \times \frac{8.314}{40} \times (300 - 300 \times 2^{\frac{1.67}{1.67-1}})}{1.67 - 1} \\
 &= -29.8376
 \end{aligned}$$

$$\begin{aligned}
 \frac{T_1}{P_1^{\frac{1.67}{1.67-1}}} &= \frac{T_2}{P_2^{\frac{1.67}{1.67-1}}} \\
 300 \times 2^{\frac{1.67}{1.67-1}} &\geq T_2 / \left( \frac{P_2}{P_1} \right)^{\frac{1.67}{1.67-1}} \\
 &= T_2
 \end{aligned}$$

\*  $C_p = a + bT$  Develop relationship between  $T \leq T$  for an adiabatic process.

$$TV^{\frac{1}{\gamma-1}} = K$$

$$\begin{aligned}
 \delta q &= 0 = \delta w + dU \\
 0 &= PdV + C_v dT
 \end{aligned}$$

$$0 = \frac{PdV}{PV} + \frac{C_v dT}{RT}$$

$$\frac{dV}{V} + \frac{R}{(1-\gamma)} \frac{dT}{RT} = 0$$

Integration.

$$\ln V + \frac{1}{(1-\gamma)} \ln T = \ln C$$

$$(1-\gamma) \ln V + \ln T = (1-\gamma) \ln C$$

$$\ln V^{\frac{1}{1-\gamma}} + \ln T = \ln C$$

$$\frac{dV}{V} + \frac{(b + kT)}{(a-b)} \frac{dT}{T} = 0$$

$$(a-b) \frac{dV}{V} + b \frac{dT}{T} + k dT = 0$$

Integrating.

$$\begin{aligned}
 \frac{C_v}{R} &= \frac{1}{(1-\gamma)} ; \frac{C_p - C_v}{C_v} = \frac{R}{(1-\gamma)} ; \frac{C_p - 1}{C_v} = \frac{R}{(1-\gamma)} ; \frac{1}{1-\gamma} = R \frac{1}{C_v} ; C_v = R \frac{1}{1-\gamma}
 \end{aligned}$$

$$(a-b) \ln V + b \ln T + RT = \ln C$$

$$\ln V^{(a-b)} + \ln T^b + \ln e^{RT} = \ln C$$

$$\ln T^b V^{a-b} e^{RT} = \ln C$$

$$T^b V^{a-b} e^{RT} = \text{constant}$$

V<sub>2</sub> = 2V<sub>1</sub>

### 3) Isobaric Process :— (P = constant)

i.) P-V-T Relationship

$$P_1 = P_2$$

Charles's law

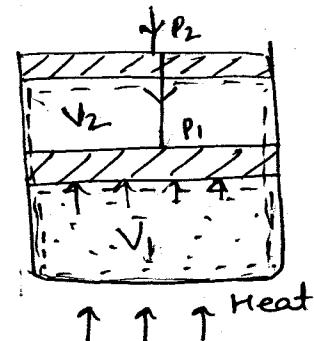
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

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

$$\frac{PV}{T} = \text{constant}$$

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

$$V \propto T$$



$$V_2 = 2V_1$$

$$T = 30^\circ\text{C}$$

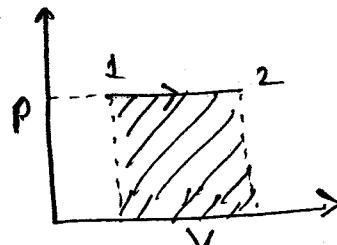
$$T_2 = 2 \times 303 \text{ K}$$

$$\approx 606 \text{ K}$$

$$\approx \frac{273}{333^\circ\text{C}}$$

### ii.) P-V diagram

$$\text{Slope} = \frac{dP}{dV} = 0$$



### iii.) Change in TE

$$dU = C_v dT$$

$$U_2 - U_1 = C_v (T_2 - T_1)$$

$$U_2 - U_1 = n C_v (T_2 - T_1) \quad \text{Molar Sp. heat}$$

$$U_2 - U_1 = m C_v (T_2 - T_1) \quad \text{Molar Sp. heat}$$

#### IV. Work done :-

$$-\int_1^2 \delta W = \int_1^2 P dV$$

$$W_2 = P(V_2 - V_1)$$

= Area under PV-diagram.

#### V. Heat Transfer :-

$$\delta Q = \delta W + \delta U$$

$$Q_2 = W_2 + (U_2 - U_1)$$

$$= P(V_2 - V_1) + mC_V(T_2 - T_1)$$

$$= mR(T_2 - T_1) + mC_V(T_2 - T_1)$$

$$= m(T_2 - T_1) + (R + C_V)$$

Suppose  
 $P_2V_2 = mRT_2$   
 $P_1V_1 = mRT_1$

$$Q_2 = mC_p(T_2 - T_1) \quad \text{const } P \Rightarrow C_p$$

$$\delta Q = mC_p dT \quad \text{in differential form}$$

$$\delta W = P dV$$

#### VI. Isochoric Process :-

##### Constant Volume Process

$$V_1 = V_2$$

Pressure increases  
 Temperature increases.

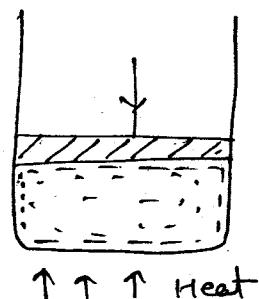
$$\frac{PV}{T} = \text{constant}$$

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

##### i) PV-T Relationship :-

$$P \propto T$$

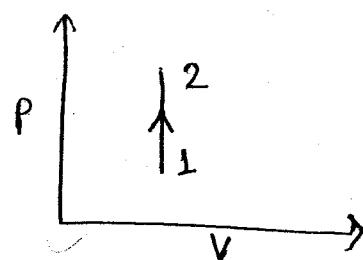
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$



##### ii) PV-diagram :-

$$\text{Slope} = \frac{dP}{dV}$$

Since constant  
 $dV = 0$   
 $\Rightarrow \infty$



iii) Change in IE :-

$$dU = mc_v dT$$

(atwz same bce of pt. function  
never depend on path or process)

$$U_2 - U_1 = mc_v (T_2 - T_1)$$

iv) Work done :-

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

$$W_2 = 0$$

v) Heat Transfer :-

$$Q_2 = \vec{W}_2 + (U_2 - U_1)$$

$$Q_2 = mc_v (T_2 - T_1)$$

const volume =  $c_v$

$$SQ = mc_v dT$$

5) Polytropic Process :-

$$PV^n = K$$

$n$  may have different values depending upon the amount of heat transfer.

i) P-V-T Relationship :-

$$a) PV^n = K$$

$$b) TV^{n-1} = K'$$

$$c) \frac{T}{P^{\frac{n-1}{n}}} = K''$$

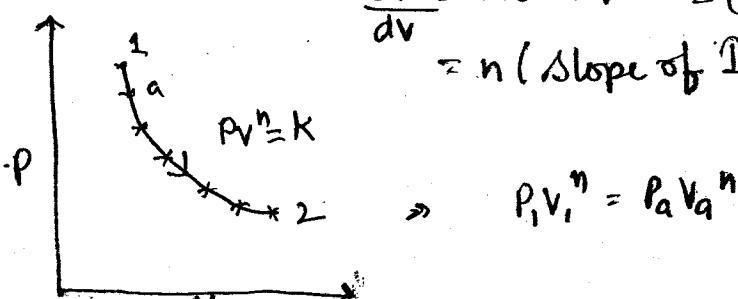
ii) P-V diagram :-

$$PV^n = K, P = KV^{-n} = (PV)^{\frac{n}{n-1}}$$

$$\frac{dP}{dV} = K(-n)V^{-n-1} = (PV^n)(-n)(V^{-n-1})$$

$$\Rightarrow -\frac{dP}{V} = n\left(\frac{-P}{V}\right)$$

=  $n$  (slope of Isothermal Curve)



$$P_1 V_1^n = P_a V_a^n$$

$$1Q_2 = \frac{\sqrt{n}}{(n-1)(\sqrt{-1})} m R (T_1 - T_2)$$

$1N_2$

$$1Q_2 = \frac{\sqrt{n}}{\sqrt{-1}} \times \frac{(P_1 V_1 - P_2 V_2)}{n-1}$$

$$1Q_2 = \frac{\sqrt{n}}{\sqrt{-1}} 1W_2$$

$$1Q_2 = \frac{\sqrt{n}}{\sqrt{-1}} \delta w$$

$U_2 - U_1$

$$1Q_2 = \frac{n-\sqrt{n}}{n-1} m \frac{R}{\sqrt{-1}} (T_2 - T_1)$$

$$= \frac{n-\sqrt{n}}{n-1} m c_v (T_2 - T_1)$$

$$1Q_2 = \frac{n-\sqrt{n}}{n-1} (U_2 - U_1)$$

$$\delta Q = \frac{n-\sqrt{n}}{n-1} dU$$

$$= m \frac{n(c_v - \cancel{c_v} c_p)}{n-1} (T_2 - T_1)$$

$$= m c_n (T_2 - T_1)$$

$$c_n = \frac{n(c_v - c_p)}{n-1}$$

Sp. heat.

$c_p$

$$P = K \quad n = 0$$

$$V = C \quad n = \infty$$

$$T = \text{const} \quad n = 1$$

$$\text{Adiabatic} \quad n = \sqrt{-1}$$

$$c_v = \frac{c_v - c_p}{1 - \gamma_n}$$

$$c_T = \infty$$

$$c_p = 0$$

$$c_n = \frac{n(c_v - c_p)}{n-1} =$$

The amount of heat required to raise the temp of  $1^\circ C$

For air  $c_p = 1.005 \text{ kJ/kgK}$

$c_v = 0.718 \text{ kJ/kgK}$

$R = 0.287 \text{ kJ/kgK}$

$\Rightarrow$  Can Sp. heat be -ve.

July 18, 14  
 Q) A perfectly insulated container of volume  $V$  is divided into two equal halves by a partition. One side is under vacuum while the other side has 1 mol of an ideal gas with constant heat capacity at 298 K. If the partition is broken, the final temp. of the gas in the container is a)  $> 298\text{ K}$   
 b)  $= 298\text{ K}$  c)  $< 298\text{ K}$  d) cannot be determined.

Free Expansion

$$T_2 = T_1$$

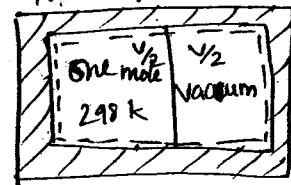
Insulate,  $Q_2 = 0$

$$W_2 = 0$$

$$Q_2 - W_2 = U_2 - U_1 = 0$$

$$C_V(T_2 - T_1) = 0$$

$$W \neq 0 \quad T_2 - T_1 \geq 0$$



Q) A path Car tyre of volume  $0.057\text{ m}^3$  is inflated to  $300\text{ kPa}$ ,  $300\text{ K}$  after the car is driven for 10 hrs. The pressure in the tyre increases to  $330\text{ kPa}$ . Assume air as an ideal gas and  $C_V = 21\text{ J/mol K}$ . The change in internal energy of air in the tyre in  $\text{J/mol}$  is ~~380~~,  $630$ ,  $760$ ,  $880$  Joule/mol

$$V_1 = 0.057\text{ m}^3 = \text{constant}$$

$$P_1 = 300\text{ kPa} \quad P_2 = 330\text{ kPa}$$

$$T_1 = 300\text{ K} \quad T_2 = ?$$

$$C_V = 21\text{ J/mol K}$$

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

$$T_2 = 330\text{ K}$$

$$U_2 - U_1 = C_V(T_2 - T_1)$$

$$= 21 \times (330 - 300)$$

$$= 630 \frac{\text{J}}{\text{mol K}}$$

Q) A gas obey  $P(V-b) = RT$ , a work done  $W_2$  from reversible isothermal expansion of 1 mol of this gas from initial  $V_1$  to final molar volume  $V_f$ :

$$P(V-b) = RT$$

$$W_2 = RT \ln \frac{V_f}{V_i}$$

$$= RT \ln \frac{V_f - b}{V_i - b}$$

$$= RT \ln \frac{V_f}{V_i - b} = RT \ln \frac{V_f - b}{V_i - b}$$

$$W_2 = \int_i^f P dV$$

$$= \int_i^f \frac{RT}{V-b} dV$$

$$= RT \int_i^f \frac{dV}{V-b}$$

$$= RT [\ln(V-b)]_i^f = RT [\ln(V_f-b) - \ln(V_i-b)]$$

$$= RT \ln \frac{V_f - b}{V_i - b}$$

Q) for the adiabatic expansion of gas from initial condition  $P_1, V_1$  to final condition  $P_2, T_2$ . Which one of the following relation is

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

$$\left(\frac{P_2}{P_1}\right)^{\frac{1}{V_1}} = \frac{T_2}{T_1}$$

$$\boxed{\left(\frac{T_2}{T_1}\right)^{\frac{1}{V_1}} = \frac{P_2}{P_1}}$$

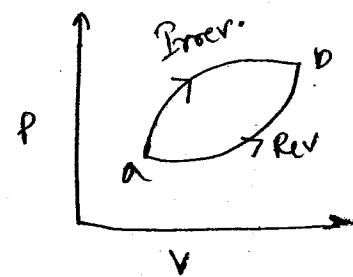
Q) For the two paths as shown in the fig. 1 reversible & one irreversible to change the state of a system from A to B.

a)  $\Delta U, Q, W$  are same.

b)  $\Delta U$  is same

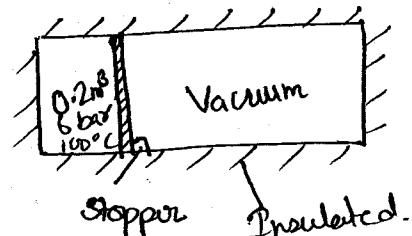
c)  $Q, W$  are same.

d)  $\Delta U, Q$  are different.



(20) Q) A perfectly insulated cylinder of volume  $0.6\text{ m}^3$  is initially divided into two parts by a frictionless piston as shown in the figure.

The smaller part of volume  $0.2\text{ m}^3$  has the ideal gas and a pressure of 6 bar &  $100^\circ\text{C}$ , and the other part is evacuated. At certain instant of time, the stopper is removed and the piston moves out freely to the other end. The final temp is  $\approx 140^\circ\text{C}$ . a)  $-33^\circ$  b)  $33^\circ$  c)  $100^\circ$



Q) The cylinder insulated is now removed and a piston is pushed back to restore the system to its initial state. If this is to be achieved only by doing work on the system (no heat addition, only heat removal allowed). What is the minimum work required?

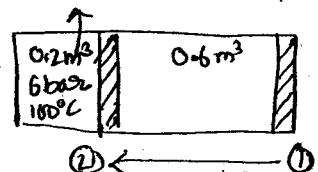
- a) 34 kJ b) 107 kJ c) 132 kJ d) 240 kJ

$$W_2 = PV \ln \frac{V_2}{V_1}$$

$$= P_1 V_1 \ln \frac{V_2}{V_1}$$

$$= 6 \times 0.2 \times \ln \frac{0.2}{0.6}$$

$$= -131.83 \text{ kJ} \quad (-ve \text{ sign indicates work will be required to be done on the system})$$



Q) 1 mol of methane is contained in a leak proof piston cylinder having 8 bar &  $200^\circ\text{C}$ . The gas undergoes isothermal expansion to 4 bar. Methane can be consider as an ideal gas. The value of the universal gas const.  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ . The H.T in kJ during the process is

- a) 11.52

~~3.76~~ 3.76

- c) 4.15

- d) 2.38

$$Q_2 = iW_2$$

$$= RT_1 \ln \frac{P_1}{P_2}$$

$$= \frac{8.314 \times 1000 \ln \frac{8}{4}}{1 \text{ mol} \times 1000 \text{ K}}$$

$$= 5.21 \text{ kJ}$$

## Open System

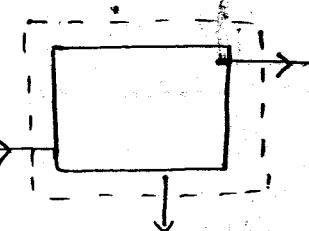
### Enthalpy

\* Sum of internal energy & flow energy.

$$\text{Flow Energy: } \frac{PV}{\text{mass}} \times m^2 \text{ kJ}$$

Steady flow  
 $m_{in} = m_{out}$

Steady flow Energy Equation.



Control volume fixed in shape, position & orientation w.r.t observer.

$$U + PV = \text{Enthalpy} \rightarrow \text{Total Energy} = \phi(T)$$

$\downarrow$        $\downarrow$   
 $f(T)$        $f(PV)$

Hence Enthalpy is total energy by virtue all 3 fundamental properties.

$$H = U + PV$$

$$U_2 - U_1 = C_v(T_2 - T_1)$$

$$H_1 = U_1 + P_1 V_1$$

$$H_2 = U_2 + P_2 V_2$$

$$H_2 - H_1 = (U_2 - U_1) + (P_2 V_2 - P_1 V_1)$$

$$= C_v(T_2 - T_1) + R(T_2 - T_1)$$

$$= (C_v + R)(T_2 - T_1)$$

$$\text{Flow } H_2 - H_1 = C_p(T_2 - T_1) \stackrel{\text{path flow}}{=} \dot{Q}_2 \text{ during } P = K$$

$$= 0$$

$$\dot{Q} = C_p dT$$

$$dH = C_p dT$$

$U \rightarrow$  only in closed system

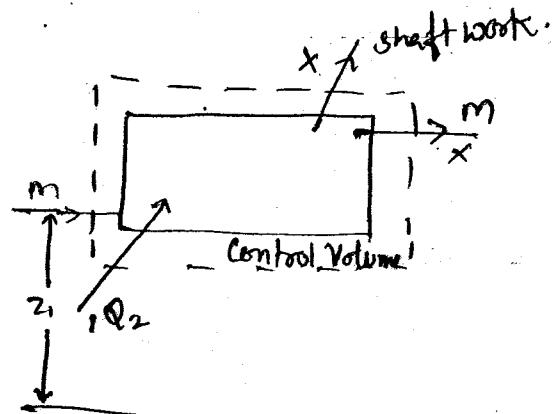
$H \rightarrow$  Open System

$$H = U + PV$$

$$\dot{Q}_2 + m \left( U_1 + P_1 V_1 + \frac{V_1^2}{2} + g z_1 \right)$$

$\downarrow \text{I.E}$     $\downarrow \text{F.E}$     $\downarrow \text{K.E}$     $\downarrow \text{P.E}$

$$= \dot{W}_{s2} + m \left( U_2 + P_2 V_2 + \frac{V_2^2}{2} + g z_2 \right)$$



$$1Q_2 + m(h_1 + \frac{V_1^2}{2} + gz_1) = 1W_{s2} + m(h_2 + \frac{V_2^2}{2} + gz_2)$$

$$1Q_2 - 1W_{s2} = m \left[ (h_2 - h_1) + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1) \right]$$

per unit mass

$$1q_2 - 1w_{s2} = (h_2 - h_1) + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1)$$

SFEE

path function

$$1q_2 - \delta w_s = dh + d\left(\frac{V^2}{2}\right) + d(gz) \quad \left. \right\} \text{point function}$$

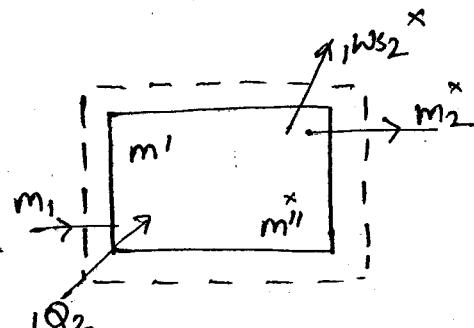
Steady Flow Energy Eqn

$$1q_2 - \delta w_s = dh + d(\text{ke}) + d(\text{pe})$$

Unsteady flow :-

Mass balance

$$m_1 + m' = m_2 + m''$$



Energy balance

$$1Q_2 + m_1(h_1 + \frac{V_1^2}{2} + gz_1) + m'(u' + \frac{V'^2}{2} + gz') = 1W_2 + m_2(h_2 + \frac{V_2^2}{2} + gz_2) + m''(u'' + \frac{V''^2}{2} + gz'')$$

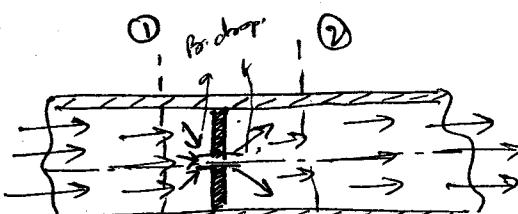
General Energy Equation

Sometime in question given that neglecting Internal Energy.

$$1Q_2 + m_1h_1 + m'u' = 1W_{s2} + m_2h_2 + m''u''$$

Throttling Process :-

Isenthalpic process.



SFEE

Partially closed Valve

Throttling is an expansion through a narrow restricted passage, without doing any external work, under adiabatic conditions.

$$\delta q - \delta w_s = dh + d(k_e) + d(p_e)$$

$$\delta q = 0, \delta w_s = 0, d(k_e) = 0, d(p_e) = 0$$

adiabatic condition

$$\delta q = 0$$

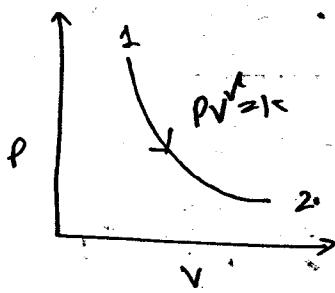
No external work

$$\delta w_s = 0$$

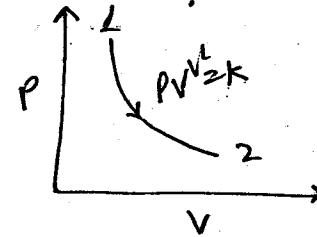
$$\therefore dh = 0$$

$h = \text{constant}$ .

Open System



Closed System

Open System:-

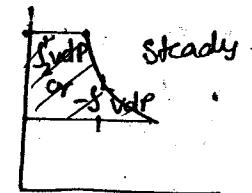
$$\delta q - \delta w_s = dh + d[k_e^0] + d[p_e^0]$$

$$(dV + PdV) = \delta w_s = d(U + PV)$$

$$(dV + PdV) - \delta w_s = dU + PdV + VdP$$

$$\int_1^2 \delta w_s = \int_1^2 -VdP$$

$$\boxed{\delta w_s = \int_1^2 -VdP}$$

Adiabatic

$$\delta w_s = \int_1^2 -VdP = \int_1^2 -\left(\frac{K}{P}\right)^{1/\gamma} dP = -K^{1/\gamma} \int_1^2 P^{-1/\gamma} dP$$

$$= -K^{1/\gamma} \left[ \frac{P^{-1/\gamma+1}}{-1/\gamma+1} \right]^{1/2}$$

$$= -K^{1/\gamma} \left[ \frac{P_2^{-1/\gamma+1}}{\frac{\gamma-1}{\gamma}} - P_1^{-1/\gamma+1} \right]$$

$$= \frac{-\gamma}{\gamma-1} \left[ K^{1/\gamma} P_2^{-1/\gamma+1} - K P_1^{-1/\gamma+1} \right]$$

$$= \frac{-\gamma}{\gamma-1} \left[ P_2^{1/\gamma} V_2 \cdot P_2^{-1/\gamma+1} - P_1^{1/\gamma} V_1 \cdot P_1^{-1/\gamma+1} \right]$$

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

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

$$\boxed{(\delta w_s)_{\text{open system}} = \gamma^{\gamma} (\delta w_s)_{\text{closed system}}}$$

As it was at rest, Actually flow is taking place wrt each other, it was felt as in rest that is non-flow system or closed system. Hence  $Q=0$  in case of adiabatic, it will be equal to  $dU + PdV$ .

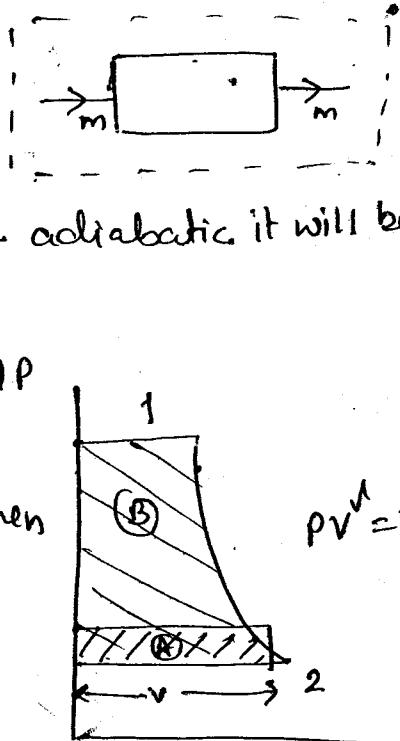
Let us consider small strip of thickness  $dP$

$$\text{Area} = Vd$$

If we are interested to find Area (B) then

$$= \int_2^1 VdP$$

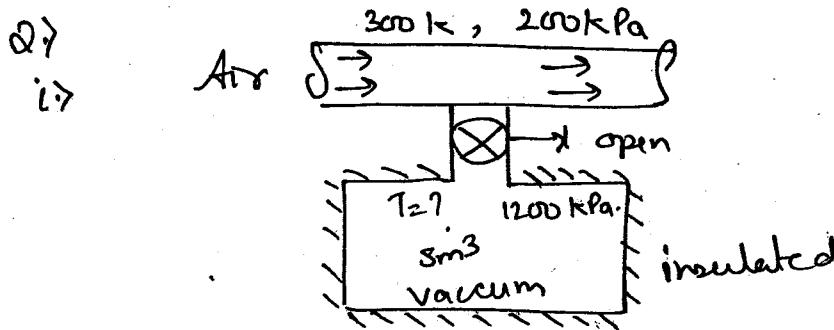
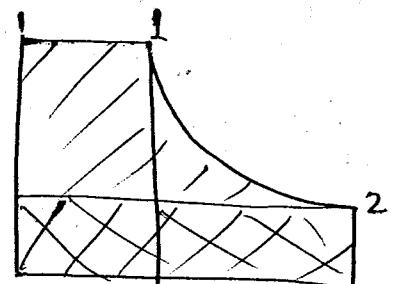
$$= - \int_1^2 VdP.$$



Relationship b/w open & closed system.

$$-\int_1^2 VdP = P_1 V_1 + \int_1^2 PdV - P_2 V_2$$

$$\underbrace{\int_1^2 VdP}_{\text{WD at open system}} = \underbrace{\int_1^2 PdV}_{\text{WD at closed system}} + \underbrace{(P_1 V_1 - P_2 V_2)}_{\text{Net flow of system.}}$$



Free expansion is only for closed system. It is an unsteady state flow and an open system.

(initially vacuum) (no energy going out)

$$1Q_2 + m_1 n_1 + m'' u' = m_1 h_2 + m_2 h_2 + m'' u''$$

(No shaft)

$$m_1 n_1 = m'' u''$$

$m_1 = m''$  (the amt of mass which enters remains there)

$$\boxed{h_1 = u''}$$

$$C_p T_1 = C_v T''$$

$$T'' = \sqrt{T_1}$$

$$= 1.4 \times 300$$

$$= 420 \text{ K}$$

$$\text{or } 147^\circ \text{ C}$$

for air  $\sqrt{1.4}$  (to remember)

ii) If system was not insulated. Final temp in system = 300 K & Pressure = 200 kPa. Then how much of the heat will be rejected.

$$1Q_2 + m_1 h_1 = m_2 h_2^0 + m'' u''$$

bcz no mass of air is going out only heat is transferred.

$$1Q_2 + m h_1 = m'' u''$$

$$1Q_2 = m'' u'' - m_1 h_1$$

$$m_1 = m'' = m \text{ (say)}$$

$$T_1 = T'' = T \text{ (say)}$$

$$1Q_2 = m (u'' - h')$$

$$= m (u_T - h_p)$$

$$1Q_2 = m T C_p (C_v - C_p)$$

$$1Q_2 = -m R T$$

$$= -P V$$

$$R = 8.314 \text{ J/Kmol K}$$

$$\text{m.wt of air} = 28.996 \text{ kg/kg mole}$$

$$R_{air} = \frac{8.314}{28.996} \frac{\text{J}}{\text{kg K}}$$

$$= 0.287 \text{ J/kg K}$$

$$C_p - C_v = R$$

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

$$C_p = \left( \frac{1}{\gamma - 1} \right)^R$$

$$= \frac{0.287}{0.4}$$

$$= 0.717 \frac{\text{kJ}}{\text{kg K}} = C_p$$

$$= 1.4 \times 0.7175$$

$$= 1.0045 \frac{\text{kJ}}{\text{kg K}}$$

Q.) A fluid flowing along a pipe line undergoes a throttling process. from 10 bar to 1 bar. i.e passing through a partially open valve. Before throttling the sp. vol of fluid is  $0.5 \text{ m}^3/\text{kg}$  & after throttling  $2 \text{ m}^3/\text{kg}$ . What is the change in sp. internal energy.

$$V_1 = 0.5 \text{ m}^3/\text{kg}$$

$$V_2 = 2 \text{ m}^3/\text{kg}$$

In Throttling process,

$$h_1 = h_2$$

$$U_1 + P_1 V_1 = U_2 + P_2 V_2$$

$$P_1 V_1 - P_2 V_2 = U_2 - U_1$$

$$10 \times 100 \times 0.5 - 100 \times 2 = U_2 - U_1$$

$$\Delta U = 200 \frac{\text{kJ}}{\text{kg}}$$

Q.) The mass flow rate of air in a compressor is  $1 \text{ kg/sec}$ . The conditions that the inlet are  $0.1 \text{ MPa}$ ,  $300 \text{ K}$ . The pressure at exit of the compressor is  $1 \text{ MPa}$ . Assuming, the compressing process to be adiabatic and air as an ideal gas the power input to compressor in  $\text{kw}$  is  $25.2, 113.2, 280, 1257.5$ .

$$m_1 = 1 \text{ kg/sec}$$

$$P_1 = 0.1 \text{ MPa}$$

Compressor  $\rightarrow$  is an open system.

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

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

$$WD = \frac{1.4}{0.4} \times 1 \times 0.287 (300 - T_2)$$

For adiabatic

$$\frac{T_1}{P_1} \frac{\gamma-1}{\gamma} = \frac{T_2}{P_2} \frac{\gamma-1}{\gamma}$$

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

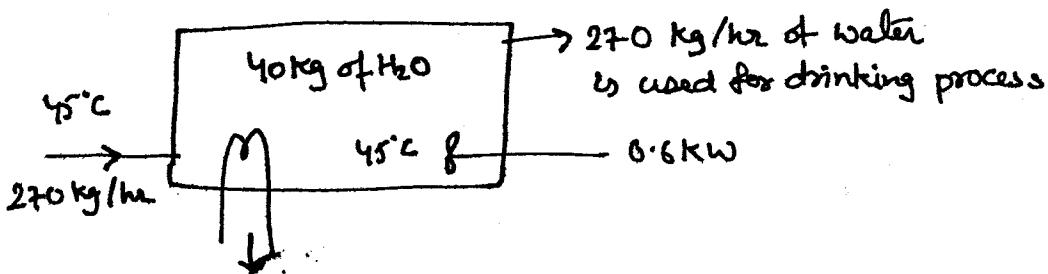
$$= 300 \times \left( \frac{1}{0.1} \right)^{\frac{0.4}{1.4}}$$

$$= 300 \times 10^{(0.4/1.4)}$$

$$WD = \frac{1.4}{0.4} \times 0.287 \left\{ 300 - 300 \times 10^{(0.4/1.4)} \right\}$$

= -280.46 kW (Work is req. to be done on system)

Q7



Water is flowing in water is flowing out & more water is entering back to back.

Develop the expression for variation in temp of  $H_2O$  wrt time.

Neglect the effect of change in KE & PE. Take  $C_{pw} = 4.2 \text{ kJ/kg}$ .

$$m_1 = m_2 = m \text{ (say)}$$

$$m' = m'' = M \text{ (say)}$$

$$Q_2 + m_1 h_1 + m' u' = m_2 s_2 + m_2 h_2 + m'' u''$$

$$Q_2 - m_2 s_2 = m(h_2 - h_1) + M(u'' - u')$$

$$[-7.6 - (0.6)] \times 3600 = 270 \times 4.2 \times (T - 318) + 45 \times 4.2 \times \frac{dT}{dt}$$

$$\frac{KJ}{Kg \cdot hr} = \frac{KJ}{Kg \cdot hr} \times \frac{KJ}{Kg \cdot K} \times K$$

$$\frac{7 \times 3600}{270 \times 4}$$

$$22 + (T - 318) + \frac{dT}{dt} = 0$$

$$(T - 296) + \frac{dT}{dt} = 0$$

$$6dz + \frac{dT}{T-296} = 0$$

Integrating,  $\ln(T-296) + 6z = C$

Initially  $z=0, T=318K$

$$\ln(318-296) = C = \ln 22$$

$$\ln(T-296) + 6z = \ln 22$$

$$\ln \frac{(T-296)}{22} = -6z$$

$$\frac{T-296}{22} = e^{-6z}$$

$$T-296 = 22e^{-6z}$$

$$T = 296 + 22e^{-6z}$$

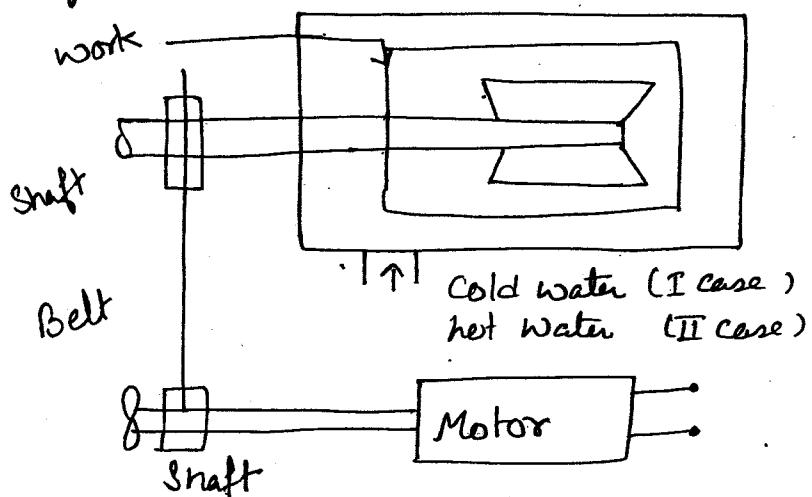
$$= (318-22) + 22e^{-6z}$$

$$= 318 - 22(1 - e^{-6z})$$

$$= 318 - 22(1 - 1)$$

$$T = 318K$$

Drawback of 1<sup>st</sup> Law of thermodynamics:-

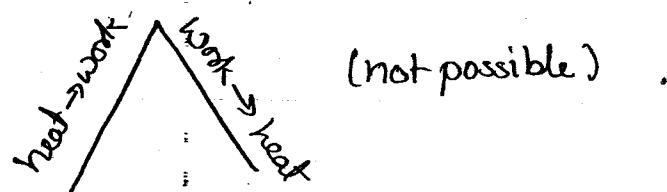


Motor  $\rightarrow$  Electrical Energy  $\rightarrow$  shaft rotates  $\rightarrow$  rotation over belt & above shaft also rotates while shaft rotation takes place, friction will be there, & heat will be generated.

It means work is converted to heat.

Now, if we supply cold water (through jacketing) then HT will take place.

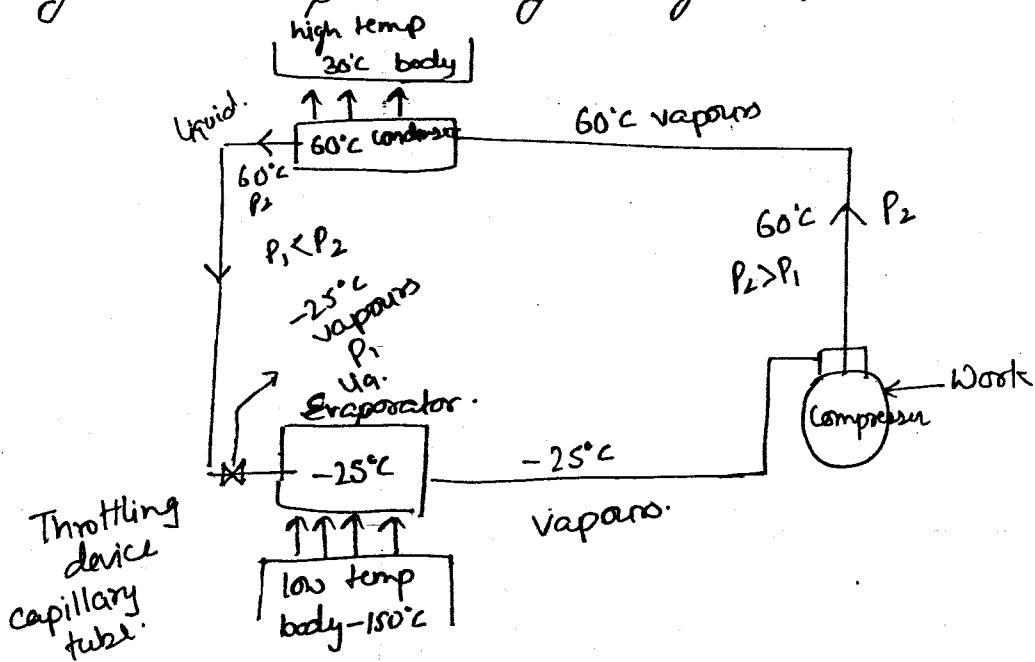
If heat is given to the system then the shaft will not rotate  
 $\therefore$  heat  $\not\rightarrow$  work.



So in 1<sup>st</sup> law of thermodynamics it is wrong to say that heat & work are interconvertible but in reality and for some cases it is not.

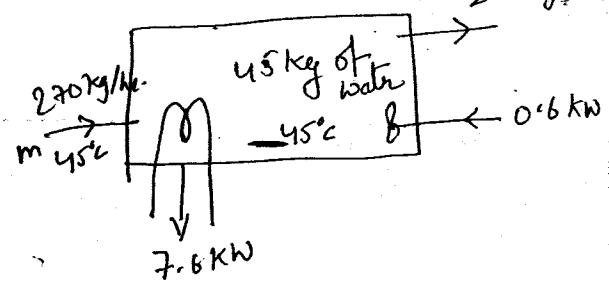
### Clausius Statement:-

"It is impossible to convert a device that operates in a thermodynamic cycle and produces no effect other than transfer of heat from a body at low temp to a body at high temp."



July 25, 19

Variation of temp w.r.t. Time

 $m_1 = m_2 = m$ , say. $m' = m'' = M$ , say.

$$Q_2 + m_1 h_1 + m' u' = w_2 + m_2 h_2 + m'' u''$$

$$Q_2 - w_2 = m(h_2 - h_1) + m(u'' - u')$$

$$[7.6(-0.6)] \times 3600 = 270 \times 4.2 \times (T-318) + 45 \times 4.2 \frac{dT}{dt}$$

$$\frac{kh}{m} \frac{kg}{hr} \times \frac{kg}{J/K} \times K + \frac{kg}{hr} \times \frac{kg}{J/K} \times K \frac{J}{kg} \times K$$

$$\frac{7 \times 3600}{270 \times 4.2} + (T-318) + \frac{45 \times 4.2}{270 \times 4.2} \frac{dT}{dt} = 0$$

$$22 + (T-318) + \frac{dT}{dt} = 0$$

$$(T-296) + \frac{dT}{dt} = 0$$

$$\frac{dT}{T-296} + 6 \frac{dt}{dt} = 0$$

Integrating,  $\ln(T-296) + 6t = C$ Initially  $C=0, T=318K$ 

$$\ln(318-296) = C$$

$$\ln(T-296) + 6t = \ln 22$$

$$\ln \frac{T-296}{22} = -6t$$

$$\frac{T-296}{22} = e^{-6t}$$

$$T-296 = 22e^{-6t}$$

$$T = 296 + 22e^{-6t}$$

$$= 318 - 22(1 - e^{-6t})$$

$$= 318 - 22(1 - (1 - 6))$$

T = 381 K.

(3)

### Halogenated hydrocarbon

↓  
 Cl, F, Br, I  
 most commonly used  
 Rarely.

HC

ASHRAE

ISHARE

C<sub>3</sub>H<sub>8</sub>  
 m<sub>23</sub>, P<sub>20</sub>  
 n<sub>26</sub>, V<sub>20</sub>

C<sub>m</sub>H<sub>n</sub>F<sub>p</sub>Cl<sub>q</sub>

$$2m+2 = n+p+q$$

$$6+2 = 8+0+0$$

$$R(m-1)(n+1)p$$

$$R 2^9 0$$

CHClF<sub>2</sub>

R 122

$$m = 1$$

$$n = 1$$

$$q = 1$$

$$p = 2$$

$$m-1 = 0$$

$$n+1 = 2$$

$$p = 2$$

$$2m+2 = n+p+q$$

$$4 = 4$$

Difluoro monochloro methane.

R12

$$m-1 = 0, \quad m = 1$$

$$n+1 = 1, \quad n = 0$$

$$p = 2, \quad p = 2$$

R134

$$m = 2$$

$$n = 2$$

$$p = 4$$

$$\begin{array}{c} F & & F \\ & \backslash & / \\ & C & - C - H \\ & / & \backslash \\ & F & H \end{array}$$

C<sub>2</sub>H<sub>2</sub>F<sub>4</sub>

CHF<sub>2</sub>:CHF<sub>2</sub>

CF<sub>3</sub>:CH<sub>2</sub>F

R134a

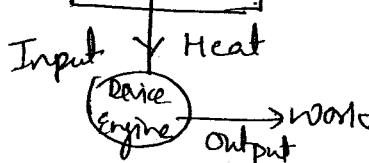
ODP = Ozone depletion potential.

GWP = Global Warming potential.

Work

thermal Reservoir

net amount of the work.

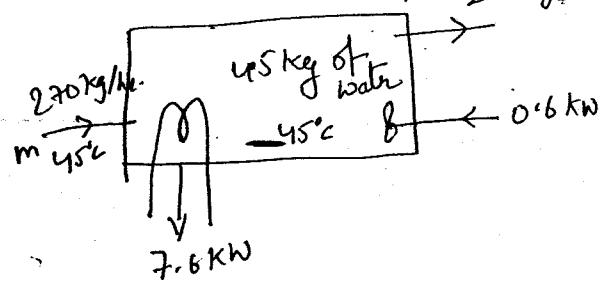


Kelvin  
Planck

An engine of 100% η is impossible.

July 25, 14

Variation of temp w.r.t Time.

 $m_1 = m_2 = m$ , say. $m' = m'' = M$ , say.

$$Q_2 + m_1 h_1 + m' u' = W_2 + m_2 h_2 + m'' u''$$

$$Q_2 - W_2 = m(h_2 - h_1) + m(u'' - u')$$

$$[7.6 - 0.6] \times 3600 = 270 \times 4.2 \times (T - 318) + 45 \times 4.2 \frac{dT}{dC}$$

$$\frac{kh}{m} = \frac{\text{kg}}{\text{hr}} \times \frac{\text{kJ}}{\text{kgK}} \times K + \frac{\text{kg}}{\text{hr}} \times \frac{\cancel{270}}{\cancel{45}} \frac{\text{kJ}}{\text{kgK}} \times K$$

$$\frac{7 \times 3600}{270 \times 4.2} + (T - 318) + \frac{45 \times 4.2}{270 \times 4.2} \frac{dT}{dC} = 0$$

$$22 + (T - 318) + \frac{dt}{dC} = 0$$

$$(T - 296) + \frac{dt}{dC} = 0$$

$$\frac{dt}{T - 296} + 6dC = 0$$

Integrating,  $\ln(T - 296) + 6C$ Initially  $C = 0, T = 318K$ 

$$\ln(318 - 296) = C$$

$$\ln(318 - 296) + 6C = \ln 22$$

$$\ln \frac{318 - 296}{22} = -6C$$

$$\frac{318 - 296}{22} = e^{-6C}$$

$$T - 296 = 22 e^{-6C}$$

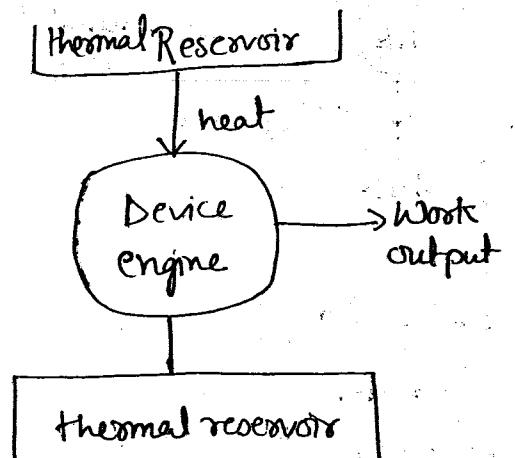
$$\begin{aligned} T &= 296 + 22 e^{-6C} \\ &= 318 - 22 + 22 e^{-6C} \\ &= 318 - 22 + 22 (1 - e^{-6C}) \end{aligned}$$

It is impossible to construct a device that operates in a closed thermodynamic cycle and produces net amount of the work giving having heat exchange with a single thermal reservoir.

July 31, 14

It is impossible to have 100%  $\eta$  of an engine.

It is hardly 30-40%.



**Thermal Reservoir:** —

Thermal Reservoir is a body from which or to which any amount of heat is transferred w/o affecting its temp.

The body from which heat is taken necessary be a body of high temp & is named as source.

The other body to which heat is rejected must be a body of low temp & is named as sink.

Source  $T_H$

↓ from  
which

Sink  $T_L$

↓ To which.

Thermal reservoir mean heat capacity is  $\infty$ .

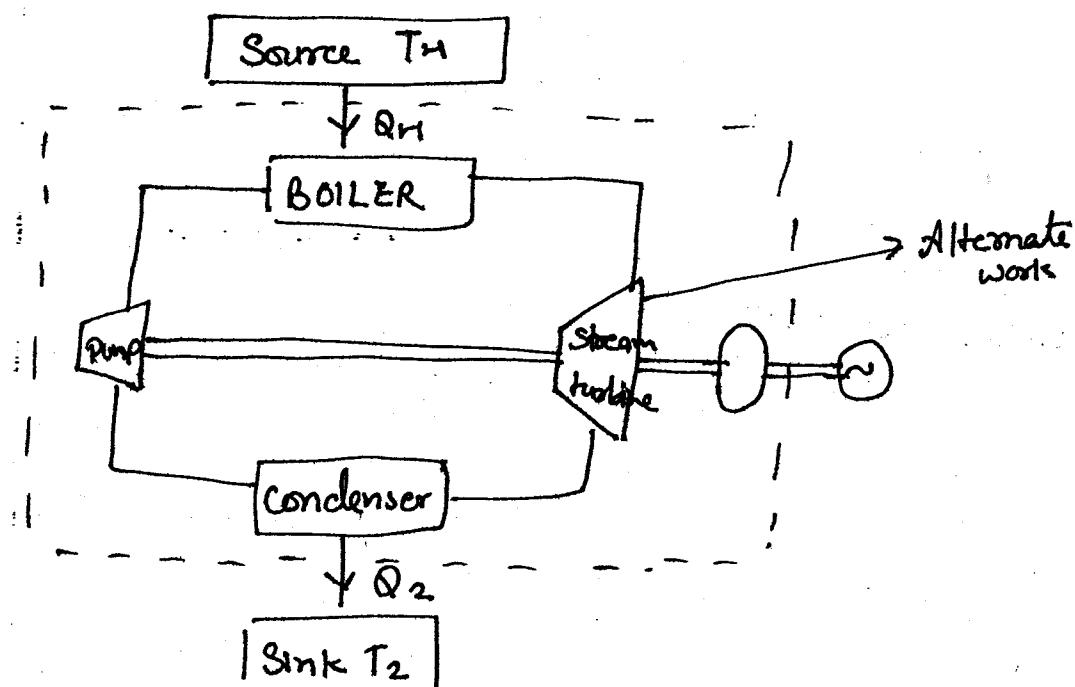
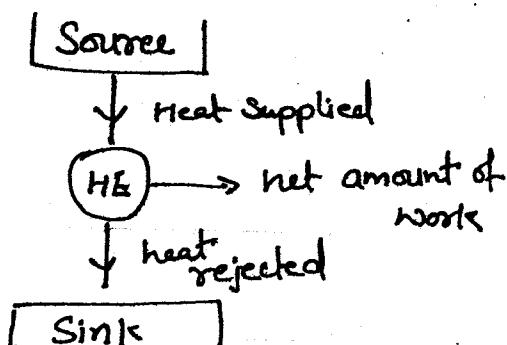
Heat capacity = Mass  $\times$  Specific heat

=  $m \times c$  =  $h \times$  molar heat capacity.

It is all at constant temp.

## Heat Engine:-

It is a device that operates in a thermodynamic cycle and produces net amount of the work having heat exchange with atleast two thermal reservoir.



Thermal efficiency of heat engine :-

$$\eta = \frac{O/P}{i/xp} = \frac{\text{energy aimed at}}{\text{energy that costs}} = \frac{\text{Net WD}}{\text{heat Supplied}}$$

$$Q_M = W_{net} + Q_L$$

$$W_{net} = Q_H - Q_L$$

$$W_{net} = W_T - W_P$$

$W_T$  = Amount of work done by Turbine.

$W_P$  = Amount of work on the pump.

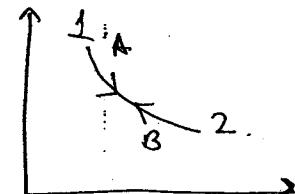
$$\eta = \frac{Q_H - Q_L}{Q_H}$$

$$\eta = 1 - \left( \frac{Q_L}{Q_H} \right)$$

Net work =  $W_T - W_P$

$Q_2 = 0 \rightarrow$  impossible.

- A) \* It is an expansion process work is obtained.  
Heat must have been supplied



- B) \* It is compression process work is required  
Heat should be rejected out.

### # Ideal Process

An ideal process is one which once having take place in 1-dim, if reversed, follows exactly the same path even no change either in the system or surrounding. Necessarily this process must be frictionless & reversible in nature.

July 31, 14

### Carnot Cycle (Used as heat engine)

[ $T_H$  source]

Reversible

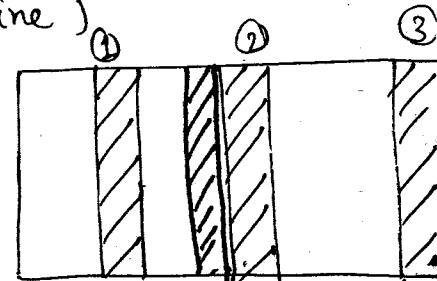
or

Ideal

or

Frictionless Process

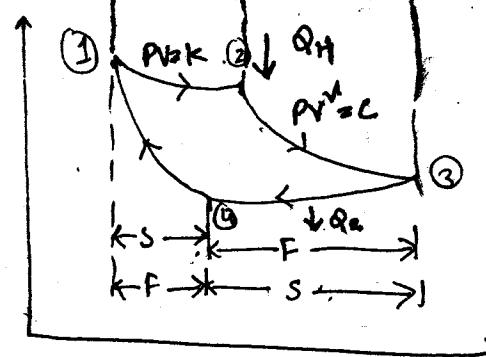
[ $T_L$  sink]



- 1-2 Rev isothermal heat supplied

$$Q_H = P_1 V_1 \ln V_2 / V_1$$

(+ve) heat supplied.



- 2-3 Rev Adiabatic process.

No heat exchange.

3-4 Reversible Isothermal heat rejection.

$$Q = P_3 V_3 \ln \frac{V_4}{V_3} \quad (-ve \because V_4 \text{ is less than } V_3)$$

∴ heat rejected.

$$= -P_3 V_3 \ln \frac{V_4}{V_3}$$

OR

$$Q = P_3 V_3 \ln \frac{V_3}{V_4}$$

4-1 Reversible Adiabatic compression. No heat exchange  
No heat transfer.

$$W_{\text{Net}} = Q_H - Q_L$$

$$W_{\text{Net}} = P_1 V_1 \ln \frac{V_2}{V_1} - P_3 V_3 \ln \frac{V_3}{V_4}$$

$$\begin{aligned} \text{Carnot } \eta &= \frac{W_{\text{Net}}}{H.S.} = \frac{Q_H - Q_L}{Q_H} \\ &= \frac{P_1 V_1 \ln \frac{V_2}{V_1} - P_3 V_3 \ln \frac{V_3}{V_4}}{P_1 V_1 \ln \frac{V_2}{V_1}} \end{aligned}$$

$$\begin{aligned} \eta_{\text{Carnot}} &= 1 - \frac{Q_L}{Q_H} = 1 - \frac{P_3 V_3 \ln \frac{V_3}{V_4}}{P_1 V_1 \ln \frac{V_2}{V_1}} \\ &\approx 1 - \frac{nRT_3 \ln \frac{V_3}{V_4}}{nRT_1 \ln \frac{V_2}{V_1}} \end{aligned}$$

IV relations 1-2 (x)

no relation.

$$\frac{2-3}{T_2 V_2^{\frac{1}{k-1}}} = T_3 V_3^{\frac{1}{k-1}}, \quad \frac{T_3}{T_2} = \left( \frac{V_2}{V_3} \right)^{\frac{1}{k-1}} = \frac{T_L}{T_H}$$

$$\boxed{\begin{aligned} \therefore T_1 &= T_2 = T_4 \\ T_3 &= T_4 = T_2 \end{aligned}}$$

3-4 (x) no relation

$$\frac{T_4 V_4^{\frac{1}{k-1}}}{T_1 V_1^{\frac{1}{k-1}}} = \left( \frac{V_1}{V_4} \right)^{\frac{1}{k-1}} = \frac{T_L}{T_H}$$

$$\frac{T_L}{T_H} = \left( \frac{V_2}{V_3} \right)^{\frac{1}{n-1}} = \left( \frac{V_1}{V_4} \right)^{\frac{1}{n-1}}$$

$$\text{i.e. } \frac{V_2}{V_3} = \frac{V_1}{V_4}$$

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

$$\eta_{\text{Carnot}} = 1 - \frac{T_3 \ln \frac{V_2}{V_1}}{T_1 \ln \frac{V_2}{V_1}}$$

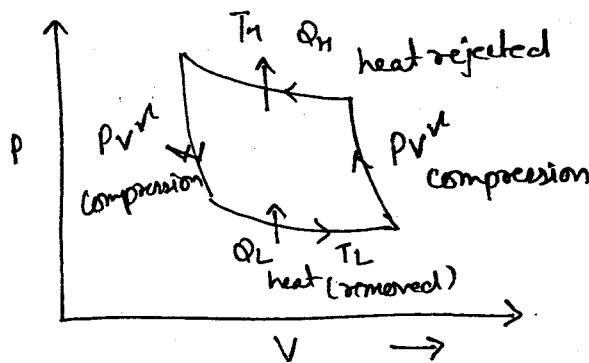
$$\eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H} = 1 - \frac{Q_L}{Q_H}$$

min (true)

$$\frac{Q_2}{Q_H} = \frac{T_L}{T_H}$$

→  $\frac{T_L}{T_H}$  should be minimum

i.e.   
 $T_L$  Sink temp should be lowest.   
 $T_H$  Source temp should be highest.



(Reversed Carnot cycle)

### Refrigerator

(objective is to remove the heat or object is to be cooled.)

$\gamma = \frac{\text{Energy aimed at}}{\text{energy that costs}}$

$$= \frac{\text{Refrigeration Cost (Q_L)}}{\text{Work done (Q_H - Q_L)}}$$

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

$$= \frac{1}{\frac{Q_H}{Q_L} - 1}$$

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

(ratios of HT = ratios of T)

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

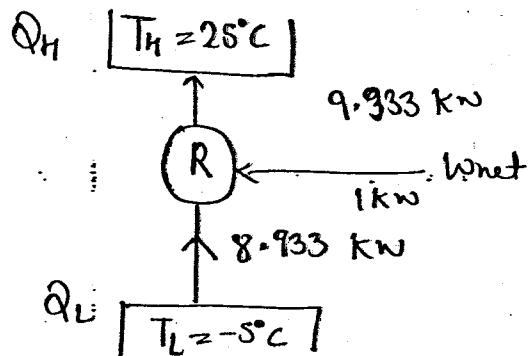
 $\eta$  is more than unity.

## COP (Coefficient of Performance)

$T_L = -5^\circ\text{C}$

$T_H = 25^\circ\text{C}$

$\eta = \frac{268}{298-268} = \frac{8.933}{1} = \frac{O/P}{I/P}$



$(Q_H - Q_L)$

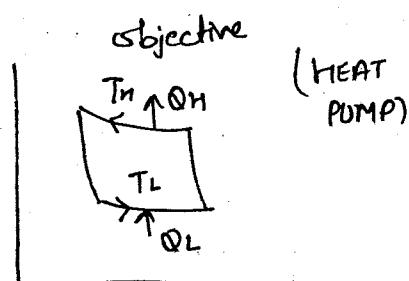
(as  $I/P$  is unity) $\therefore 9.933 \text{ kW}$  amount of heat is rejected.HEAT PUMP CYCLE :-

$\text{COP} = \frac{O/P}{I/P}$

 $= \frac{\text{energy added at } (Q_H)}{\text{energy that costs}}$  $= \frac{\text{heating effect } (Q_H)}{\text{Net work required } (Q_H - Q_L)}$ 

$\frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}}$

$= \frac{1}{1 - \frac{T_L}{T_H}} = \frac{T_H}{T_H - T_L} = \frac{298}{298 - 268} = 9.993 \text{ kW}$



Using reversible Carnot cycle as Heat Pump cycle is more beneficial than refrigerator. (8.933)  $\text{kw}$

$$\oint \delta w_1 = \oint \delta Q_H - \oint \delta Q$$

$$\frac{\delta Q_H}{\delta Q} = \frac{T_H}{T}, \delta Q_H = \frac{T_H}{T} \delta Q$$

$$\Rightarrow \oint \delta w_1 = \oint \frac{T_H \delta Q}{T} - \oint \delta Q$$

$$\oint \delta w_2 = \oint \delta Q$$

$$\oint \delta w_{\text{net}} = \oint w_1 + \oint w_2$$

$$= \left[ \oint \frac{T_H \delta Q}{T} - \oint \delta Q \right] + \oint \delta Q$$

$$\oint \delta w_{\text{net}} = \oint \frac{T_H \delta Q}{T} \quad (\text{can't be +ve})$$

$\leq 0$  required atleast Two reservoirs to get as +ve.

$T_H$  remain constant.

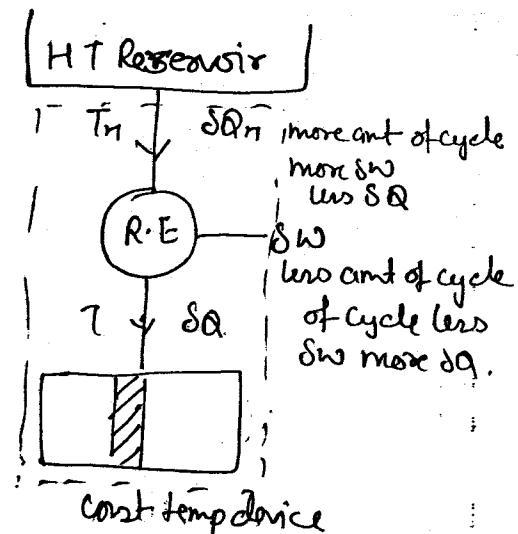
$$\oint \frac{\delta Q}{T} \leq 0$$

#

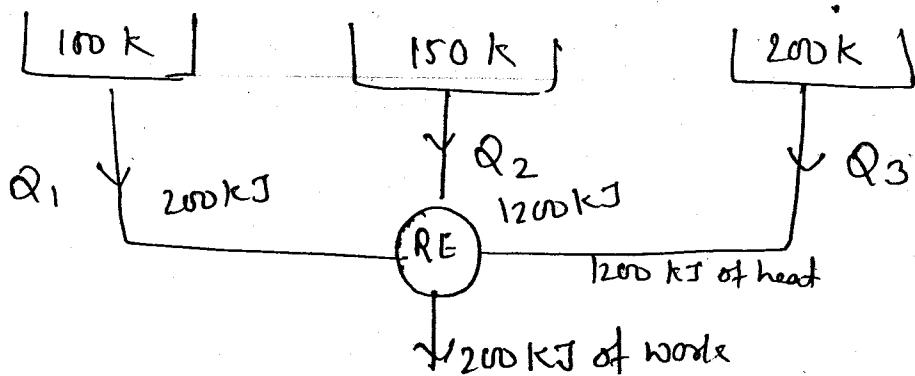
$\oint \frac{\delta Q}{T} < 0$  For actual System  
irreversible system due to friction  
Clausius Inequality.

$\oint \frac{\delta Q}{T} = 0$  For Ideal System  
i.e. Rev System or Frictionless

$\oint \frac{\delta Q}{T} > 0$  IMPOSSIBLE



Q7



Determine the direction and mag. of heat exchanged with reservoirs 100K, 150K.

Ans1<sup>st</sup> Law

$$Q_1 + Q_2 + Q_3 = \text{Work done}$$

$$Q_1 + Q_2 + 1200 = 200$$

$$Q_1 + Q_2 = -1100$$

2<sup>nd</sup> Law

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

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} = 0$$

$$\frac{Q_1}{100} + \frac{Q_2}{150} + \frac{1200}{200} = 0$$

By solving eqn

$$Q_1 = -200 \text{ kJ}$$

$$Q_2 = -1200 \text{ kJ}$$

## ENTROPY

It is the property which will increase with the increase in temp and decrease with the decrease in temp, remain constant when no heat is supplied.

Aug 01, 14

1A2 Rev Process

2B1 " "

2C1 " "

1A2B1 Rev Cycle,  $\oint \frac{dQ}{T} = 0$

1A2C1 Rev Cycle

$$\int_1^2 \left( \frac{dQ}{T} \right)_A + \int_2^1 \left( \frac{dQ}{T} \right)_B = 0 \quad \text{--- (1)}$$

1A2C1 Rev Cycle

$$\int_1^2 \left( \frac{dQ}{T} \right)_A + \int_2^1 \left( \frac{dQ}{T} \right)_C = 0 \quad \text{--- (2)}$$

Subtracting (1) - (2)

$$\int_2^1 \left( \frac{dQ}{T} \right)_B - \int_2^1 \left( \frac{dQ}{T} \right)_C = 0$$

$$\int_2^1 \left( \frac{dQ}{T} \right)_B = \int_2^1 \left( \frac{dQ}{T} \right)_C$$

$\frac{dQ}{T}$  = Independent of Path

= Point function.

= Thermodynamic Property **ENTROPY**

= Perfect differential.

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

$\frac{J}{K}$

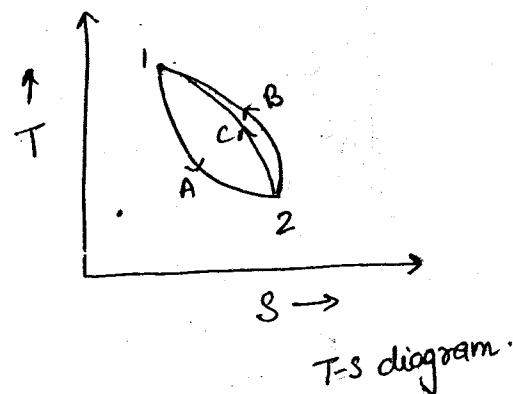
⇒ Extensive Property.

$$\frac{ds}{m} = \frac{dQ}{mT}$$

intensive

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

$\frac{J}{kg \cdot K}$  /  $\frac{J}{mol \cdot K}$



- i)  $\delta q = +ve \Rightarrow ds = +ve$
- ii)  $\delta q = -ve \Rightarrow ds = -ve$
- iii)  $\delta q = 0, \Rightarrow ds = 0$

Entropy is a thermodynamic property that increases when heat is supplied, decreases when heat is rejected and remains constant if no heat is supplied or rejected.

$$\delta q = dU + \delta w$$

$$\delta q = Cv dT + PdV$$

$$ds = \frac{\delta q}{T} = \frac{Cv dT}{T} + \frac{PdV}{T}$$

$$PV = RT$$

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

$$ds = Cv \frac{dT}{T} + \frac{R}{V} dV$$

Integrating,

$$S_2 - S_1 = Cv \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad \dots \text{ (i)}$$

i (P, T)

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

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

In eq (i)

$$\begin{aligned} S_2 - S_1 &= Cv \ln \frac{T_2}{T_1} + R \ln \frac{P_1 T_2}{P_2 T_1} \\ &= Cv \ln \frac{T_2}{T_1} + R \left( \ln \frac{P_1}{P_2} + \ln \frac{T_2}{T_1} \right) \\ &= (Cv + R) \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \end{aligned}$$

$$S_2 - S_1 = Cp \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad \dots \text{ (ii)}$$

i (P, V)

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

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

from (i)  $\delta_2 - \delta_1 = C_V \ln \frac{P_2 V_2}{P_1 V_1} + R \ln \frac{V_2}{V_1}$

$$= C_V \left( \ln \frac{P_2}{P_1} + \ln \frac{V_2}{V_1} \right) + R \ln \frac{V_2}{V_1}$$

$$= C_V \ln + (C_V + R) \ln \frac{V_2}{V_1}$$

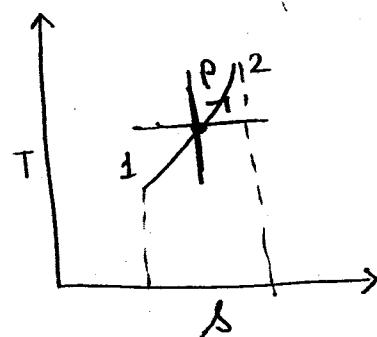
$$\boxed{\delta_2 - \delta_1 = C_V \ln \frac{P_2}{P_1} + C_P \ln \frac{V_2}{V_1}} \quad \dots \text{ (iii)}$$

### Isobaric Process

#### Constant Pressure Process

$$dS = \frac{\delta q}{T} = C_P \frac{dT}{T}$$

$$\boxed{\delta_2 - \delta_1 = C_P \ln \frac{T_2}{T_1}} = C_P \ln \frac{V_2}{V_1} \frac{V_2}{V_1}$$



$$\text{Slope} = \frac{dT}{dS} = \frac{T}{C_P} = +\text{ve}$$

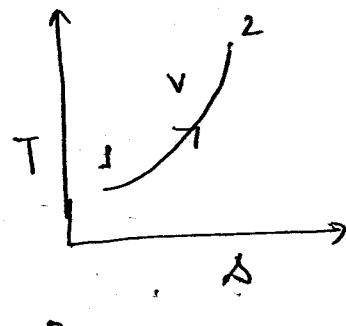
### Isochoric Process

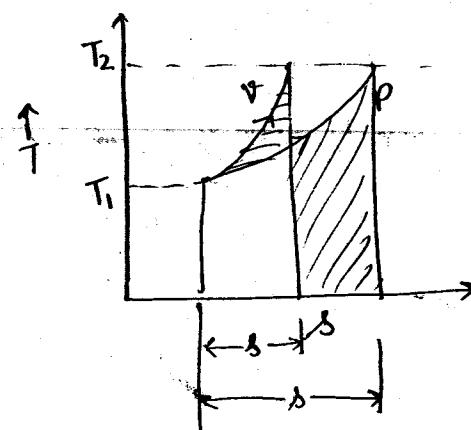
#### Constant Volume

$$dS = \frac{\delta q}{T} = C_V \frac{dT}{T}$$

$$\delta_2 - \delta_1 = C_V \ln \frac{T_2}{T_1}$$

$$\text{Slope} = \frac{dT}{dS} = \frac{T}{C_V} = +\text{ve}$$





bez of slope  
 $\frac{T}{C_V} = \text{reversible}$   
 $\frac{T}{C_P} = \text{irreversible}$

## Isothermal Process

### Constant temp. Process

$$\delta q = dU + dW$$

$$ds = \frac{\delta q}{T} = \frac{PdV}{T}$$

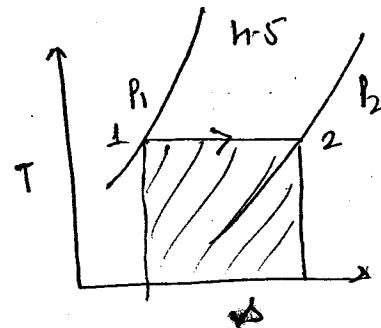
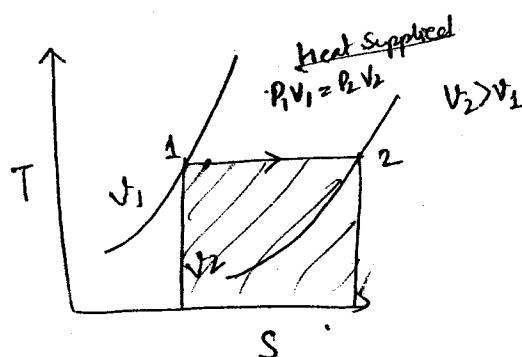
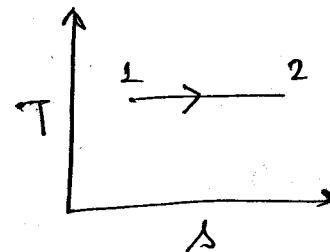
$$= \frac{R}{V} dV$$

$$\delta_2 - \delta_1 = R \ln \frac{V_2}{V_1}$$

$$\text{Slope} = \frac{dT}{ds} = 0$$

$$\delta s = \frac{\delta q}{T} = 0$$

$$s_2 - s_1 = \frac{\delta q}{T} = 0$$



## 4.) Adiabatic Process :-

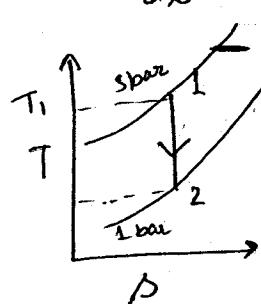
$$ds = \frac{\delta q}{T} = \frac{0}{T} = 0$$

$$\delta_2 - \delta_1 = 0$$

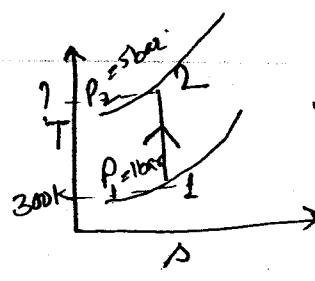
$$\delta_2 = \delta_1$$

Entropy remain constant  
 no heat supplied & rejected.

$$\text{Slope} = \frac{dT}{dS} = \frac{1}{0} = \infty$$



Adiabatic Expansion.



Adiabatic Compression

$$\frac{T_1}{P_1^{\gamma-1}} = \frac{T_2}{P_2^{\gamma-1}}$$

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

Frictionless Reversible / Isentropic process:-

Adiabatic with friction :-

Inversible Adiabatic Process

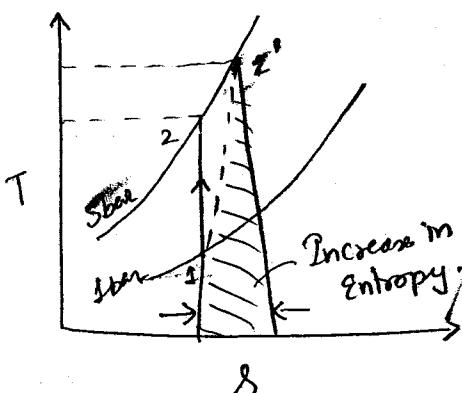
Compression

Entropy must increase

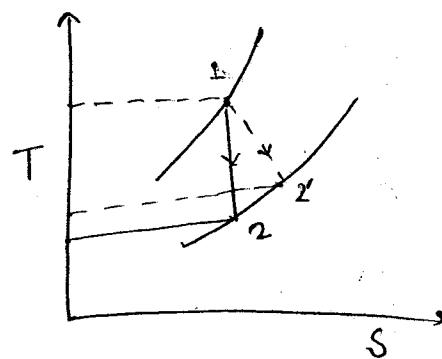
Expansion

Entropy must increase

Due to presence of friction



Ideal case



Polytropic Process

$$dq = \frac{n-1}{n-1} C_v dT$$

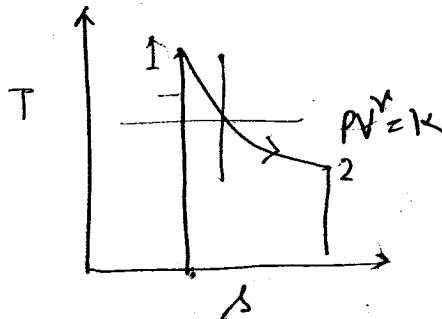
$$ds = \frac{dq}{T} = \frac{n-1}{n-1} \frac{C_v dT}{T}$$

$$S_2 - S_1 = \frac{n-1}{n-1} C_v \ln \frac{T_2}{T_1}$$

$$\text{Slope} = \frac{dT}{ds} = \frac{n-1}{n+1} \cdot \frac{T}{C_V} = -ve \quad | \text{ denominator is -ve.}$$

$\downarrow$   
 $n > 1$   
 $n < 1$

- ⇒ Entropy increase
- ⇒ Heat is supplied.
- Expansion takes place.
- Work is obtained.
- Temp. decreases.



In polytropic process, PV & TS diagram is same.

Aug 07, 14

Q: In a gas turbine, hot combustion pdt  $C_p = 0.98 \text{ kJ/kgK}$  &  $C_V = 0.7538 \text{ kJ/kgK}$  enter the turbine at 20 bar, 1500K and exist at 1 bar. The isentropic efficiency of the turbine is 0.94. The work developed by the turbine /kg of gas flow is ~~689.64 kJ/kg~~

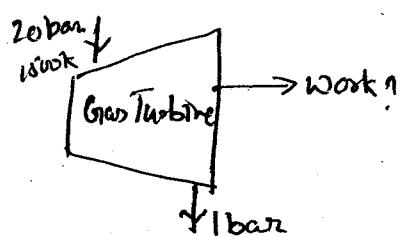
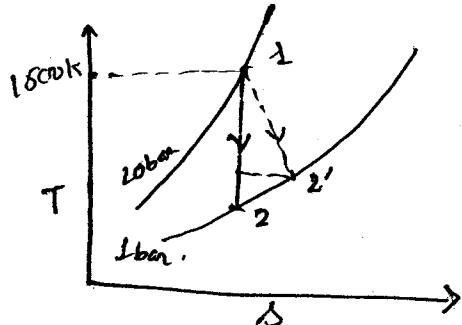
~~794.66~~

i)  $689.64 \text{ kJ/kg}$

ii)  $794.66 \text{ kJ/kg}$

iii)  $1009.72 \text{ kJ/kg}$

iv)  $1312.00 \text{ kJ/kg}$ .



$$\text{Isentropic } \eta \text{ of Turbine} = \frac{\text{Actual Work}}{\text{Ideal Work}}$$

$$\Rightarrow \frac{h_1 - h_2'}{h_1 - h_2} = \frac{C_p(T_1 - T_2')}{C_p(T_1 - T_2)}$$

$$\frac{T_1}{P_1^{\frac{1.3}{1.4}}} = \frac{T_2}{P_2^{\frac{1.3}{1.4}}} \Rightarrow T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{\frac{1.3}{1.4}}$$

$$\gamma = \frac{C_P}{C_V} = \frac{0.98}{0.7528} = 1.300$$

$$T_2 = 1500 \left( \frac{20}{20} \right)^{\frac{1.3-1}{1.3}} (20)^{\frac{1.3-1}{1.3}} \\ = 3083.29945$$

$$\text{Actual work} = \eta C_P (T_1 - T_2) \\ = 689 =$$

Q.) Hydrogen gas is contained in a cylinder by a piston at initial condition of 2 bar, 298 K and 1 m<sup>3</sup> in a particular process. The gas slowly expands under isothermal condition until the volume becomes 2 m<sup>3</sup>. Heat exchange occurs with the atmosphere at 298 K during the process. The entropy change for the universe during the process is 0.4652 kJ/K.

i) 0.4652 kJ/K

ii) 0.0067 kJ/K

iii) 0 kJ/K

iv) -0.6711 kJ/K

$$S_2 - S_1 = R \ln \frac{V_2}{V_1}$$

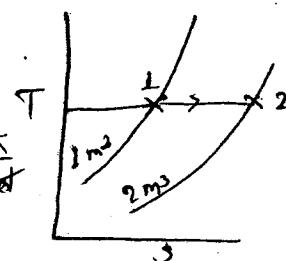
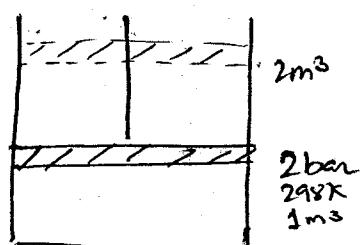
$$(\Delta S)_{\text{universe}} = (\Delta S)_{\text{system}} + (\Delta S)_{\text{surroundings}}$$

=

$$S_2 - S_1 = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$$= \frac{8.314}{28} \ln 2 = 0.2058 \frac{\text{kJ/kgmolK}}{\text{kg/kgmol}}$$

$$= 0.2058 \text{ kJ/kgK}$$



$$m = \frac{P_1 V_1}{R T_1} = \frac{(2 \times 100) \times 1}{8.314 \times 298} = 2.2602$$

$$(\Delta S)_{\text{system}} = 0.2058 \times 2.2603 = 0.4652 \text{ kJ/K}$$

$$(\Delta S)_{\text{sur}} = -m R T_1 \ln \frac{V_2}{V_1} \quad T_1$$

$$= -0.4652 \text{ kJ/K}$$

$$(\Delta S)_{\text{univ}} = 0$$

Q.2 A Solar collector receiving solar radiation at the rate of  $0.6 \text{ kW/m}^2$  transforms it to the internal energy of a fluid. Overall efficiency of 50%. The fluid is heated to 350 K.

It is used to run a heat engine which rejects heat at 315 K. If the heat engine is to deliver 2.5 kW of power. The minimum area of the solar collector required would be  $83.33 \text{ m}^2$

i)  $83.33 \text{ m}^2$

ii)  $16.66 \text{ m}^2$

iii)  $39.68 \text{ m}^2$

iv)  $79.36 \text{ m}^2$

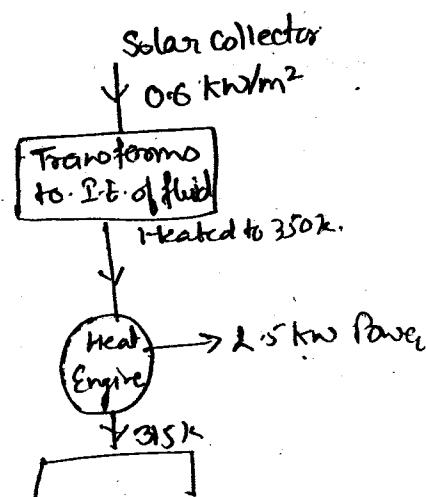
$$\eta = 1 - \frac{T_L}{T_H} = 1 - \frac{315}{350} = 0.125$$

$$0.125 = \frac{W}{Q} = 2.5$$

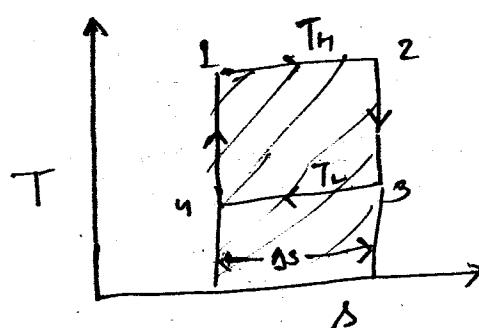
$$Q = \frac{2.5}{0.125} = 20 \text{ kW}$$

$$\text{Heat reqd} = 20 \text{ kW} = 0.6 \text{ A kW}$$

$$A = \frac{SD}{0.6} = 83.33 \text{ m}^2$$



Q.3 Draw a Carnot cycle on T-S diagram



$$1-2 \quad H \cdot S = T_H \Delta S$$

$$3-4 \quad H \cdot R = T_L \Delta S$$

$$W_{net} = T_H \Delta S - T_L \Delta S$$

$$= (T_H - T_L) \Delta S$$

$$\text{Carnot } \eta = \frac{W_{net}}{H \cdot S}$$

$$= \frac{(T_H - T_L) \Delta S}{T_H \Delta S}$$

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

Q) 2 moles of oxygen, are mixed with another 2 moles of oxygen in a mixing chamber. So that the final total pressure and temperature of the mixture becomes same as those of individual constituents at their initial states. The change in entropy due to mixing,  $\Delta S_{mix}$ , is given by.

i)  $-R \ln 2$

iii)  $R \ln 2$

;  $R$  = universal gas constant.

vii) 0

iv)  $R \ln 4$

Q) A cyclic engine exchanges heat with two reservoirs maintained at  $100^\circ\text{C}$  &  $200^\circ\text{C}$  resp. The maximum amt of work in joules that can be obtained from 1000J of heat, extracted from the hot reservoir is

vii) 349

iii) 651

iii) 667

iv) 1000

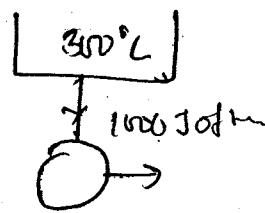
$$1 - \frac{T_L}{T_H} = 1 - \frac{100}{200} = \frac{1}{2} = \frac{W}{Q}$$

$$W = 0.349 \times 1000$$

$$= 666.666 \text{ J}$$

$$= 667 \text{ J}$$

$$= 667 \text{ J}$$



$$100^\circ\text{C}$$

Q.) Which one of the following statements is true.

- a.) Heat can be fully converted into work
- b.) Work cannot be fully converted into heat
- c.) The efficiency of a heat engine increases as the temp of the heat source is increased, while keeping the temp of the heat sink fixed.
- d.) A cyclic process can be devised whose sole effect is to transfer heat from a lower temperature to higher temperature.

Q.) A Carnot heat engine cycle is working with an ideal gas. The work performed by the gas during adiabatic expansion & compression steps are  $W_1$  &  $W_2$ .

$W_1$  (work) Exp.

$W_2$  (work) Comp

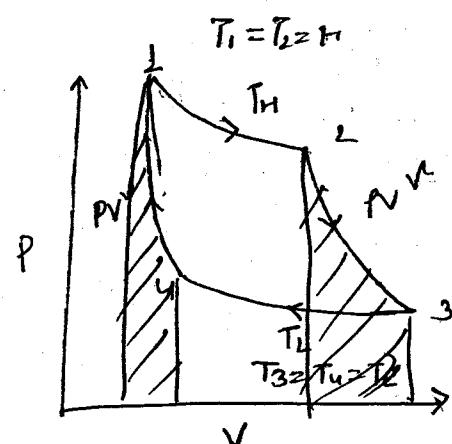
- i.)  $|W_1| > |W_2|$
- ii.)  $|W_1| < |W_2|$
- iii.)  $W_1 = W_2$
- ✓ iv.)  $W_1 = -W_2$

$$2W_3 = \frac{P_2V_2 - P_3V_3}{\sqrt{-1}}$$

$$= \frac{R(T_2 - T_3)}{\sqrt{-1}}$$

$$\text{exp: } 2W_3 = \frac{R(T_H - T_L)}{\sqrt{-1}} \Rightarrow W_1$$

$$W_1 = -W_2$$



$$4W_1 = \frac{P_4V_4 - P_1V_1}{\sqrt{-1}}$$

$$= \frac{R(T_4 - T_1)}{\sqrt{-1}}$$

$$\boxed{4W_1 = \frac{R(T_L - T_H)}{\sqrt{-1}}} \Rightarrow W_2$$

$$= -\frac{R(T_H - T_L)}{\sqrt{-1}} = -W_2$$

- Q1) A heat engine operates at 75% of maximum possible efficiency. The ratio of heat source temp to heat sink temp is.  $T_H/T_L = 5/3$ . Fraction of heat supplied that can be converted to work is \_\_\_\_\_

i) 0.2       ii) 0.3

iii) 0.4

iv) 0.6.

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

$$= 1 - \frac{3}{5} = 0.4$$

$$\text{Actual } \eta = 0.4 \times 0.75 = \frac{W}{Q}$$

$$= 0.3.$$

- Q2) For a Carnot refrigerator operating b/w 8°C and 25°C, COP

i) 1

ii) 1.67

iii) 19.88

iv) 39.74.

$$\text{COP} = \frac{T_L}{T_H - T_L} = \frac{298}{15} = 19.866$$

- Q3) In a parallel flow heat exchanger operating under steady state Hot liquid enters at a temp  $T_{hi}$  &  $T_{lo}$ , Cold liquid enters at temp  $T_{ci}$  & reaches at  $T_{co}$ . Neglect any heat loss from the heat exchanger to the surroundings and assume  $T_{hi} \gg T_{ci}$ . Then for a given time interval which 1 of the following statement is true.

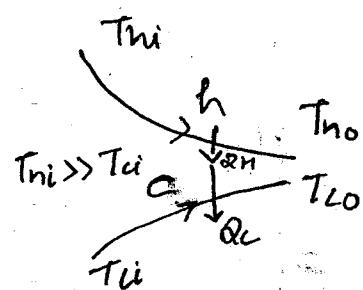
a)  $(\Delta S)_c > (\Delta S)_h$   
gain      loss

b)  $(\Delta S)_c = (\Delta S)_h$   
gain      loss

c)  $(\Delta S)_c < (\Delta S)_h$   
gain      loss

d)  $(\Delta S)_{\text{gain}} = 0$

$$\left[ \left( \frac{Q_H}{T_H} + \frac{Q_C}{T_C} \right) + (\Delta S)_{\text{sum}}^0 \right] > 0$$



$$\left( \frac{Q_H}{T_H} + \frac{Q_C}{T_C} \right) > 0$$

$$\left( \frac{Q_H}{T_H} + \frac{Q_C}{T_C} \right) > 0$$

$$\frac{Q_C}{T_C} > -\frac{Q}{T_H}$$

$$(\Delta S)_C > (\Delta S)_H$$

gain lost

Aug 07, 14

## Thermodynamic Relations :-

$x, y, z$  are also properties of perfect differentials.

$$x = x(y, z), \quad y = y(z, x)$$

$$[z = z(x, y)]$$

$$\boxed{P, V, T}$$

$$\boxed{U, H, S}$$

$$g, \text{ force}$$

8 properties  
perfect diff

$$dz = \frac{\partial z}{\partial x} \Big|_y dx + \frac{\partial z}{\partial y} \Big|_x dy$$

$$dz = M dx + N dy$$

$$M = \frac{\partial z}{\partial x} \Big|_y$$

$$N = \frac{\partial z}{\partial y} \Big|_x$$

$$\frac{\partial M}{\partial y} \Big|_x = \frac{\partial^2 z}{\partial y \partial x}$$

$$\frac{\partial N}{\partial x} \Big|_y = \frac{\partial^2 z}{\partial x \partial y}$$

$$\Rightarrow \boxed{\frac{\partial M}{\partial y} \Big|_x = \frac{\partial N}{\partial x} \Big|_y}$$

$$\delta q = dU + dS$$

$$TdS = dU + PdV$$

(close system)  $dU = TdS - PdV$

$$dz = M dx + N dy$$

$$M = T \quad N = S$$

$$N = -P \quad S = V$$

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

Maxwell's I. Relation

$$h = U + PV$$

$$dh = dU + PdV + VdP$$

$$(open\ system) dh = TdS + VdP$$

$$d_3 = Mdu + Ndy$$

$$M = T \quad n = s$$

$$N = V \quad y = P$$

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

Maxwell's II Relation

Helmholtz function (closed system)

$$a = U - TS$$

$$da = dU - TdS - SdT$$

$$da = -PdV - SdT$$

$$TdS = dU + PdV$$

$$d_3 = Mdu + Ndy$$

$$M = -P \quad n = V$$

$$N = -S \quad y = T$$

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

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

Maxwell's III Relation

Gibbs function (open system)

$$g = h - TS$$

$$dg = dh - TdS - SdT - SdT$$

$$dg = VdP - SdT$$

$$d_3 = Mdu + Ndy$$

$$M = V \quad n = P$$

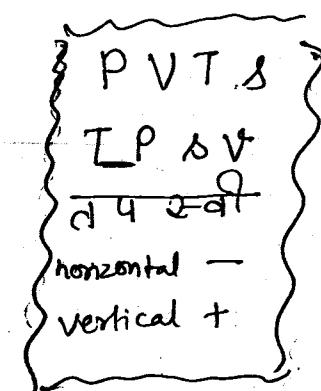
$$N = -S \quad y = T$$

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

Maxwell's IV Relation

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

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



## Tds Equations

$$\delta = \delta(T, V)$$

$$d\delta = \left. \frac{\partial \delta}{\partial T} \right|_V dT + \left. \frac{\partial \delta}{\partial V} \right|_T dV$$

$$Td\delta = \left( T \left. \frac{\partial \delta}{\partial T} \right|_V \right) dT + T \left( \left. \frac{\partial \delta}{\partial V} \right|_T \right) dV$$

or volume  
pressure

$$Td\delta = C_V dT + T \left. \frac{\partial P}{\partial T} \right|_V dV$$

$$\delta = \delta(T, P)$$

$$d\delta = \left. \frac{\partial \delta}{\partial T} \right|_P dT + \left. \frac{\partial \delta}{\partial P} \right|_T dP$$

$$Td\delta = T \left. \frac{\partial \delta}{\partial T} \right|_P dT + T \left. \frac{\partial \delta}{\partial P} \right|_T dP$$

$$Td\delta = C_P dT - T \left. \frac{\partial V}{\partial T} \right|_P dP$$

$$\begin{cases} T \left. \frac{\partial \delta}{\partial T} \right|_P = C_V \\ Td\delta = \delta q = C_V dT \\ T \left. \frac{\partial \delta}{\partial T} \right|_P = C_V \\ \left. \frac{\partial \delta}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V \end{cases}$$

$$\begin{cases} T \left. \frac{\partial \delta}{\partial T} \right|_P = C_P \\ \text{From Maxwell Relation} \\ \left. \frac{\partial \delta}{\partial P} \right|_T = -\left. \frac{\partial V}{\partial T} \right|_P \end{cases}$$

$$z = z(u, y)$$

$$dz = \left. \frac{\partial z}{\partial u} \right|_y du + \left. \frac{\partial z}{\partial y} \right|_u dy$$

$$y = y(z, x)$$

$$dy = \left. \frac{\partial y}{\partial z} \right|_x dz + \left. \frac{\partial y}{\partial x} \right|_z dx$$

$$dz = \left. \frac{\partial z}{\partial u} \right|_y du + \left. \frac{\partial z}{\partial y} \right|_u \left[ \left. \frac{\partial y}{\partial z} \right|_x dz + \left. \frac{\partial y}{\partial x} \right|_z dx \right]$$

$$= \frac{\partial^3}{\partial u \partial y} du + \frac{\partial^3}{\partial y \partial z} \Big|_x \frac{\partial y}{\partial z} \Big|_u dz + \frac{\partial^3}{\partial y \partial z} \Big|_x \frac{\partial y}{\partial u} \Big|_z du$$

$$du = \left[ \frac{\partial^3}{\partial u \partial y} + \frac{\partial^3}{\partial y \partial z} \Big|_x \frac{\partial y}{\partial z} \Big|_u \right] dz + dz$$

$$\left[ \frac{\partial^3}{\partial u \partial y} + \frac{\partial^3}{\partial y \partial z} \Big|_x \frac{\partial y}{\partial u} \Big|_z \right] du = 0$$

$$du \neq 0$$

$$\frac{\partial^3}{\partial u \partial y} + \frac{\partial^3}{\partial y \partial z} \Big|_x \frac{\partial y}{\partial u} \Big|_z = 0$$

$$\frac{\partial^3}{\partial u \partial y} = - \frac{\partial^3}{\partial y \partial z} \Big|_x \frac{\partial y}{\partial u} \Big|_z$$

$$\boxed{\frac{\partial u}{\partial y} \Big|_z \frac{\partial y}{\partial z} \Big|_x \frac{\partial^3}{\partial u \partial y} = -1}$$

tds

$$TdS = C_p dT - T \frac{\partial V}{\partial T} \Big|_P dP$$

$$TdS = C_v dT + T \frac{\partial P}{\partial T} \Big|_V dV$$

$$0 = (C_p - C_v) dT - T \left[ \frac{\partial V}{\partial T} \Big|_P dP + \frac{\partial P}{\partial T} \Big|_V dV \right]$$

$$(C_p - C_v) dT = T \frac{\partial V}{\partial T} \Big|_P dP + T \frac{\partial P}{\partial T} \Big|_V dV$$

$$dT = \frac{T \frac{\partial V}{\partial T} \Big|_P}{(C_p - C_v)} dP + \frac{T \frac{\partial P}{\partial T} \Big|_V}{(C_p - C_v)} dV$$

$$T = T(P, V)$$

$$dT = \frac{\partial T}{\partial P} \Big|_V dP + \frac{\partial T}{\partial V} \Big|_P dV$$

$$\frac{T \frac{\partial V}{\partial T} \Big|_P}{C_p - C_v} = \frac{\partial T}{\partial P} \Big|_V$$

$$C_p - C_v = T \frac{\partial V}{\partial T} \Big|_P \frac{\partial P}{\partial T} \Big|_V$$

$$\frac{T \frac{\partial P}{\partial T} \Big|_V}{C_P - C_V} = \frac{\partial T}{\partial V} \Big|_P$$

$$C_P - C_V = T \frac{\partial P}{\partial T} \Big|_V \frac{\partial V}{\partial T} \Big|_P$$

For Ideal Gas:

$$PV = RT$$

$$P = \frac{RT}{V} \quad V = \frac{RT}{P}$$

$$\frac{\partial P}{\partial T} \Big|_V = \frac{R}{V} \quad \frac{\partial V}{\partial T} \Big|_P = \frac{R}{P}$$

$$C_P - C_V = T \cdot \frac{R}{V} \cdot \frac{R}{P} \quad ; \quad PV = RT$$

$$\boxed{C_P - C_V = R}$$

$$P \ T \ V$$

$$\frac{\partial P}{\partial T} \Big|_V \frac{\partial T}{\partial V} \Big|_P \frac{\partial V}{\partial P} \Big|_T = -1$$

$$\frac{\partial P}{\partial T} \Big|_V = - \frac{\partial V}{\partial T} \Big|_P \frac{\partial P}{\partial V} \Big|_T$$

$$C_P - C_V = T \frac{\partial P}{\partial T} \Big|_V \frac{\partial V}{\partial T} \Big|_P$$

$$= T \left[ - \frac{\partial V}{\partial T} \Big|_P \frac{\partial P}{\partial V} \Big|_T \right] \frac{\partial V}{\partial T} \Big|_P$$

$$\boxed{C_P - C_V = -T \left( \frac{\partial V}{\partial T} \Big|_P \right)^2 \frac{\partial P}{\partial V} \Big|_T}$$

(tve) (tve) (tve)

Else P or V any of one  
will be -ve

$$= +ve \quad ; \quad \text{thus } C_P > C_V$$

Density of water is maxm at  $4.4^{\circ}\text{C}$

Sp Vol " " minm at  $4.4^{\circ}\text{C}$

$$\frac{\partial V}{\partial T} \Big|_P = 0$$

$$C_p - C_v = -T \left( \frac{\partial V}{\partial T} \Big|_P \right)^2 \frac{\partial P}{\partial V} \Big|_T$$

$$C_p = C_v$$

For water we use term  $C_p$  only, not  $C_v$  as  $C_p = C_v$  (value).

$$\text{as } T \rightarrow 0$$

$$C_p \rightarrow C_v$$

### Volume Expansivity or Coefficient of Thermal Expansion

$$\beta = \frac{1}{V} \frac{\partial V}{\partial T} \Big|_P$$

~~$$\kappa = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T$$~~

### Isothermal Compressibility:-

$$\kappa = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T$$

$$\frac{\partial V}{\partial T} \Big|_P = \beta V$$

$$\frac{\partial P}{\partial V} \Big|_T = -\frac{1}{\kappa V}$$

$$C_p - C_v = -T \beta^2 V^2 \left( -\frac{1}{\kappa V} \right)$$

$$C_p - C_v = \frac{T V \beta^2}{\kappa}$$

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

$$(C_p - C_v) = ?$$

$$C_p - C_v = T \frac{\partial P}{\partial T} \Big|_V \frac{\partial V}{\partial T} \Big|_P$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\frac{\partial P}{\partial T} \Big|_V = \frac{R}{V-b}$$

$$\left( P + \frac{a}{V^2} \right) \frac{\partial V}{\partial T} \Big|_P + \left( -\frac{2a}{V^3} \right) \frac{\partial V}{\partial T} \Big|_P \cdot (V-b) = R$$

$$\frac{\partial V}{\partial T} \Big|_P \left[ \left( P + \frac{a}{V^2} \right) - 2a \frac{(V-b)}{V^3} \right] = R$$

$$\frac{\partial V}{\partial T} \Big|_P \left[ \frac{RT}{V-b} - 2a \frac{(V-b)}{V^3} \right] = R$$

$$\frac{\partial V}{\partial T} \Big|_P = \frac{R}{\frac{RT}{V-b} - \frac{2a(V-b)}{V^3}}$$

$$C_p - C_v = T \frac{R}{V-b} \times \frac{R}{\frac{RT}{V-b} - \frac{2a(V-b)}{V^3}}$$

$$= \frac{RT}{V-b} \times \frac{R}{\frac{RT}{V-b} \left[ 1 - \frac{2a(V-b)}{V^3} \times \frac{(V-b)}{RT} \right]}$$

$$C_p - C_v = \frac{R}{1 - \frac{2a(V-b)^2}{RTV^3}}$$

$$x \ y \ z \ f$$

$$n = n(y, f)$$

$$y = y(z, f)$$

$$\frac{\partial x}{\partial y} \Big|_f \frac{\partial y}{\partial z} \Big|_f \frac{\partial z}{\partial x} \Big|_f = 1$$

$$S = S(P, V)$$

$$dS = \frac{\partial S}{\partial P} \Big|_V dP + \frac{\partial S}{\partial V} \Big|_P dV$$

$$TdS = T \frac{\partial S}{\partial P} \Big|_V dP + T \frac{\partial S}{\partial V} \Big|_P dV$$

$$TdS = \left( T \frac{\partial T}{\partial P} \Big|_V \frac{\partial S}{\partial T} \Big|_V \right) dP + \left( T \frac{\partial T}{\partial V} \Big|_P \frac{\partial S}{\partial T} \Big|_P \right) dV$$

$$TdS = C_V \frac{\partial T}{\partial P} \Big|_V dP + C_P \frac{\partial T}{\partial V} \Big|_P dV$$

$$S \ P \ T \ V$$

$$\frac{\partial S}{\partial P} \Big|_V \frac{\partial P}{\partial T} \Big|_V \frac{\partial T}{\partial S} \Big|_V = 1$$

$$\frac{\partial S}{\partial P} \Big|_V = \frac{\partial T}{\partial P} \Big|_V \frac{\partial S}{\partial T} \Big|_V$$

$$S \ V \ T \ P$$

$$\frac{\partial S}{\partial V} \Big|_P \frac{\partial V}{\partial T} \Big|_P \frac{\partial T}{\partial S} \Big|_P = 1$$

$$\frac{\partial S}{\partial V} \Big|_P = \frac{\partial T}{\partial V} \Big|_P \frac{\partial S}{\partial T} \Big|_P$$

$$U = U(T, V)$$

$$dU = \frac{\partial U}{\partial T} \Big|_V dT + \frac{\partial U}{\partial V} \Big|_T dV$$

$$dU = C_V dT + \frac{\partial U}{\partial V} \Big|_T dV$$

$$\rightarrow dU = T dS - P dV$$

$$= \left[ C_V dT + T \frac{\partial P}{\partial T} \Big|_V dV \right] - P dV$$

$$\rightarrow dU = C_V dT + \left( T \frac{\partial P}{\partial T} \Big|_V - P \right) dV \rightarrow \text{Compony}$$

$$\boxed{\frac{\partial U}{\partial V} \Big|_T = T \frac{\partial P}{\partial T} \Big|_V - P}$$

Energy Equation.

For an Ideal gas

$$P = \frac{RT}{V} \quad \frac{\partial P}{\partial T} \Big|_V = \frac{R}{V}$$

$$\frac{\partial U}{\partial V} \Big|_T = T \frac{R}{V} - P = 0$$

U is not a function of V

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

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\frac{\partial P}{\partial T} \Big|_V = \frac{R}{V-b}$$

$$\rightarrow \frac{\partial U}{\partial V} \Big|_T = T \underbrace{\frac{R}{V-b}}_{*} - P = P + \frac{a}{V^2} - P = \frac{a}{V^2}$$

$$\frac{\partial U}{\partial V} \Big|_T = C_V dT + \left( \frac{a}{V^2} - P \right) dV = C_V dT + \frac{a}{V^2} dV$$

$$\rightarrow 0 = \frac{\partial P}{\partial V} \Big|_T + \frac{\partial U}{\partial P} \Big|_T$$

$$\frac{\partial P}{\partial V} \Big|_T \neq 0$$

$$\therefore \frac{\partial U}{\partial P} \Big|_T = 0$$

U is not a funct<sup>h</sup> of P

u v p T

$$\frac{\partial U}{\partial V} \Big|_T \frac{\partial V}{\partial P} \Big|_T \frac{\partial P}{\partial u} \Big|_T = 1$$

$$\frac{\partial U}{\partial V} \Big|_T = \frac{\partial P}{\partial V} \Big|_T \frac{\partial u}{\partial P} \Big|_T$$

$\Rightarrow U$  is  $f(T)$  only for an Ideal Gas.

$\Rightarrow U$  is  $f(T, P, N)$  for wandewaals gas  
for an ideal gas  $B$  is function of?

$$B = \frac{1}{V} \frac{\partial V}{\partial T} \Big|_P$$

$$= \frac{1}{V} \cdot \frac{R}{P} = \frac{R}{RT}$$

$$= \frac{1}{T}$$

$$PV = RT$$

$$V = RT/P$$

$$\frac{\partial V}{\partial T} \Big|_P = R/P$$

$B$  is a function of  $T$   $\therefore$

$$k = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T$$

$$\boxed{V = RT/P}$$

$$\frac{\partial V}{\partial P} \Big|_T = -\frac{RT}{P^2}$$

$$= -\frac{1}{V} \left( -\frac{RT}{P^2} \right)$$

$$= \frac{RT}{V \cdot P}$$

$$k = \frac{1}{P}$$

$k$  is function of  $P$  =

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Enthalpy (h) :-

$$h = h(T, P)$$

$$dh = \frac{\partial h}{\partial T} \Big|_P dT + \frac{\partial h}{\partial P} \Big|_T dP$$

$$\frac{\partial h}{\partial T} \Big|_P = C_p$$

$$dh = C_p dT + \frac{\partial h}{\partial P} \Big|_T dP \quad \text{--- ---} \textcircled{*}$$

$$h = U + PV$$

$$dh = dU + PdV + VdP$$

$$dh = Tds + Vpd$$

$$dh = \left( CpdT - T \frac{\partial V}{\partial T} \Big|_p \right) + Vdp$$

$$dh = CpdT + \left( V - T \frac{\partial V}{\partial T} \Big|_p \right) dp \quad \dots \dots \dots \quad (1)$$

Comparing above (1) eqns.

$$\boxed{\frac{\partial h}{\partial p} \Big|_T = V - T \frac{\partial V}{\partial T} \Big|_p}$$

For an ideal Gas :-

$$V = RT/p$$

$$\frac{\partial V}{\partial T} \Big|_p = R/p$$

$$\frac{\partial h}{\partial p} \Big|_T = V - T \cdot \frac{R}{p} = V - V = 0$$

$h$  is not a function of  $P$ .

$h$ ,  $p$ ,  $V$ ,  $T$

$$\frac{\partial h}{\partial p} \Big|_T \frac{\partial p}{\partial V} \Big|_T \frac{\partial V}{\partial h} \Big|_T = 1$$

$$\frac{\partial h}{\partial p} \Big|_T = \frac{\partial V}{\partial p} \Big|_T \frac{\partial h}{\partial V} \Big|_T$$

$$0 = \frac{\partial V}{\partial p} \Big|_T \frac{\partial h}{\partial V} \Big|_T$$

$$\frac{\partial V}{\partial p} \Big|_T \neq 0$$

: from ideal gas eqn above

; As from Boyle's law,  $p \propto \frac{1}{V}$

$\therefore \frac{\partial h}{\partial V} \Big|_T$  must be zero.

i.e.  $h$  is not a function of  $V$ .

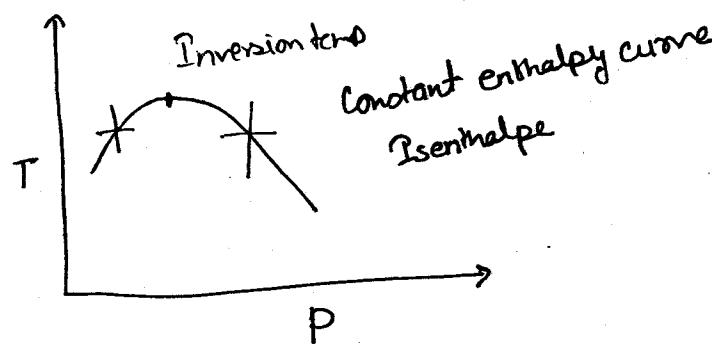
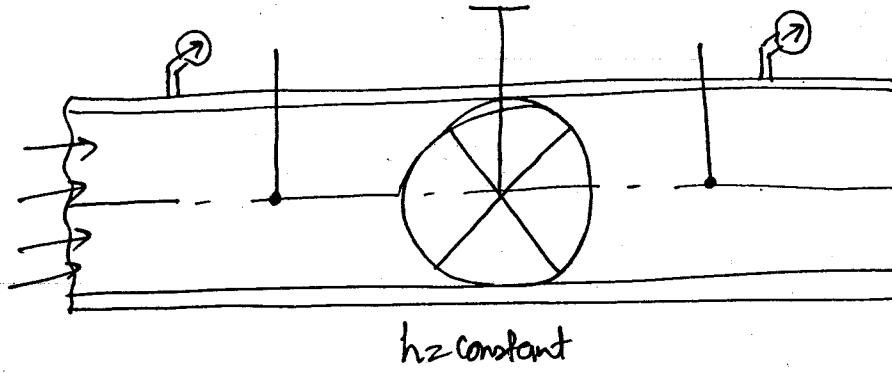
hence,  $h$  is a function of  $(T)$  only.

$$h_2 - h_1 \Big|_T = (u_2 - u_1)_T + (P_2 V_2 - P_1 V_1)_T$$

\* for ideal gas  
 $\Delta n = 0$  at const. Temp.

$$h_2 - h_1 \Big|_T = a \left( \frac{1}{V_1} - \frac{1}{V_2} \right)_T + (P_2 V_2 - P_1 V_1)_T$$

for a real gas,  $h$  is a funct<sup>n</sup> of (V) & (P) both.

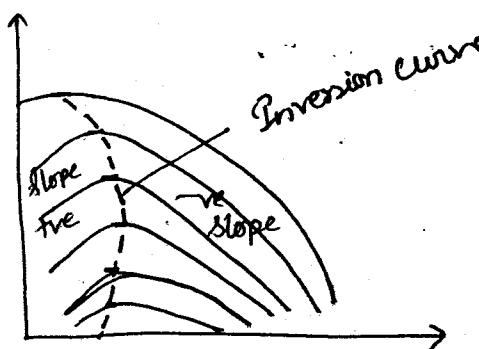


$$\frac{\partial T}{\partial P} = \text{slope} = 0$$

= -ve  
= +ve

for  $h < 0$   $\frac{\partial T}{\partial P}$  is very low,  
other  $\frac{\partial T}{\partial P}$  is same as atm temp.

$\frac{\partial T}{\partial P} = \mu = \text{Joule Kelvin co-efficient} = \text{Joule Kelvin or Joule Thomson.}$



[+slope  
temp ↓  
effect of cooling.  
-ve slope  
temp ↑  
case of heating]

$$h = u + PV$$

$$dh = dU + PdV + VdP$$

$$= TdS + VdP$$

$$= \left( C_p dT - T \frac{\partial S}{\partial T} \Big|_P \right) + VdP$$

$$dh = Cp dT - \left[ T \frac{\partial v}{\partial T} \Big|_P - v \right] dp$$

$$CpdT = \left( T \frac{\partial v}{\partial T} \Big|_P - v \right) dp$$

$$** \quad \mu = \frac{\partial T}{\partial P} \Big|_h = \frac{1}{C_p} \left[ T \frac{\partial v}{\partial T} \Big|_P - v \right]$$

If ideal gas is throttled

$$v = RT/P$$

$$\frac{\partial v}{\partial T} \Big|_P = R_P$$

$$= \frac{1}{C_p} \left[ T R_P - v \right] = \frac{1}{C_p} [v - v]$$

$$\boxed{\mu = \frac{\partial T}{\partial P} \Big|_h = 0}$$

$$\beta = \frac{1}{v} \frac{\partial v}{\partial T} \Big|_P$$

expansivity

$$= \frac{1}{C_p} (T \beta v - v)$$

$$\boxed{\mu = \frac{v}{C_p} (T \beta - 1)}$$

$$\beta = \frac{3}{4}$$

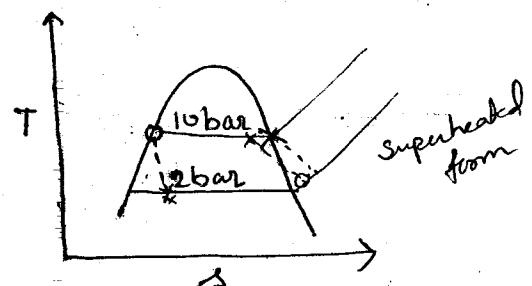
$$\frac{v}{C_p} (1 - 1) = 0$$

Mixture of air & liquid is throttled :-

NH<sub>3</sub> (90% Vapours + 10% water)

Pure NH<sub>3</sub> vapour at 10 bar throttled to a pressure of 2 bar.

Since the process is adiabatic  
So no heat is exchanged removed  
while it get added to the gas and  
changes into superheated form.



$$h = U + PV$$

$$dh = dU + PdV + VdP \\ = TdS + VdP$$

$$= CpdT - \left( T \frac{\partial V}{\partial T} \Big|_P - V \right) dP$$

$$M = \frac{\partial T}{\partial P} \Big|_h = \frac{1}{C_p} \left[ T \frac{\partial V}{\partial T} \Big|_P - V \right]$$

for van der waals eqn

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

$$\left( P + \frac{a}{V^2} \right) \frac{\partial V}{\partial T} \Big|_P + \left( -\frac{2a}{V^3} \right) \frac{\partial V}{\partial T} \Big|_P (V - b) = R$$

$$\frac{\partial V}{\partial T} \Big|_P \left[ \frac{RT}{V-b} - \frac{2a(V-b)}{V^3} \right] = R$$

$$\frac{\partial V}{\partial T} \Big|_P = \frac{R}{\frac{RT}{V-b} - \frac{2a(V-b)}{V^3}}$$

$$M = \frac{1}{C_p} \left[ \frac{RT}{\frac{RT}{V-b} - \frac{2a(V-b)}{V^3}} - V \right]$$

Gibbs functions :-

$$g = h - TS$$

$$dg = dh - TdS - SdT$$

$$= d(U + PV) - TdS - SdT$$

$$= \cancel{dU} + PdV + VdP - TdS - SdT$$

$$dg = VdP - SdT$$

$$a = U - TS$$

$$da = du - Tdg - SdT$$

$$dg = -PdV - SdT$$

$$dJ = Mdx + Ndy$$

$$\left. \frac{dP}{dT} \right|_V = \left. \frac{dS}{dT} \right|_V$$

$$\frac{dP}{dT} = \frac{dS}{dT}$$

| bec it is independent of V

Phase Change

$$\frac{dP}{dT} = \frac{h_{fg}}{V_g - V_f}$$

latent heat of vaporisation,  $h_{fg}$

$$\frac{h_{fg}}{T_s} = \text{Increase in Entropy}$$

$T_s$  = saturation temp

$$\boxed{\frac{dP}{dT} = \frac{h_{fg}}{V_g - V_f} = \frac{h_{fg}}{T_s(V_g - V_f)}}$$

Clapeyron Equation

{ to determine the latent heat of vaporisation }

$$V_g \gg V_f$$

$V_f$  may be neglected.

1 kg water take  space  
1 kg steam take  space.

$$\frac{dP}{dT} = \frac{h_{fg}}{T_s V_g}$$

Assuming vapours to behave like a gas.

$$V_g = \frac{RT_g}{P_g}$$

$$(T_g = T_s = T, \text{ say})$$

$$P_g = P$$

$$\frac{dP}{dT} = \frac{h_{fg}}{T R T_g}$$

$$* \quad \boxed{\frac{dP}{P} = \frac{h_{fg}}{R T^2} dT}$$

Clausius Clapeyron Eq<sup>n</sup>

Sat. steam

$$\int_1^2 \frac{dP}{P} = \int_1^2 \frac{h_{fg}}{R T^2} dT$$

Sat water

$$\ln P_1^2 = \frac{h_{fg}}{R} \left( -\frac{1}{T_1} \right)^2$$

$$\boxed{\ln P_2/P_1 = \frac{h_{fg}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

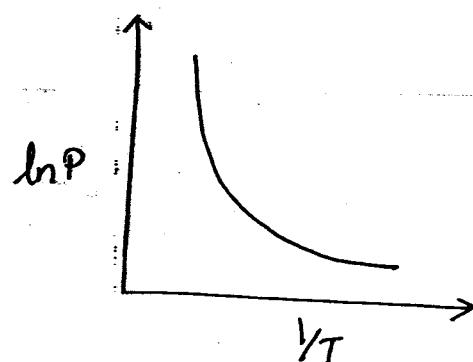
Another form of clausius  
clapeyron Eq<sup>n</sup>

$$* \frac{1}{P} dP = - \frac{h_{fg}}{R} d\left(\frac{1}{T}\right)$$

$$d(\ln P) = - \frac{h_{fg}}{R} d\left(\frac{1}{T}\right)$$

$$\boxed{\frac{d(\ln P)}{d\left(\frac{1}{T}\right)} = - \frac{h_{fg}}{R}}$$

Another form of  
Clausius-Clapeyron Eqn



$\therefore$  Slope  $= - \frac{h_{fg}}{R}$  is  $\text{+ve}$   
So slope is in II & IV  
quadrant.

Q) CCl<sub>4</sub> boils at 76°C and 101 kPa. The latent heat of vaporization for CCl<sub>4</sub> is 195 kJ/kg and characteristic gas const R = 0.0551 kJ/kgK.  
Boiling temp of CCl<sub>4</sub> at 2021 kPa is

274.54 K

✓ 374.54 K

474.54 K

574.54 K

$$\ln \frac{P_2}{P_1} = \frac{h_{fg}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$T_2 = 374.54$$

Q) Over a certain temp. interval the saturation temp  $T_{sat}$  and  
temp curve of a substance undergoing liquid-vapour phase  
change is represented by the equation  $\log P_{sat} = A - \frac{B}{T_{sat}}$  upon  
phase change the expression for  $h_{fg}$  is  $= P_{sat} \cdot V_{fg} A$

i)  $P_{sat} \cdot V_{fg} A$

✓ (ii)  $- P_{sat} V_{fg} B \frac{1}{T_{sat}}$

✓ (iii)  $\frac{P_{sat} V_{fg} B}{T_{sat}}$

iv)  $\frac{P_{sat} V_{fg} A T_{sat}}{B}$

$$\frac{dp}{dT} = \frac{h_{fg}}{T(v_g - v_f)}$$

$$\frac{1}{p} dp = \frac{B}{T^2} dT$$

$$\frac{dp}{dT} = \frac{B P}{T^2}$$

$$\frac{B P}{T^2} = \frac{h_{fg}}{T v_{fg}}$$

$$h_{fg} = \frac{B P_{sat} v_{fg}}{T_{sat}}$$

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$\alpha > \beta$  Coeff of vol. Exp  $C_p = 5 \times 10^5 \text{ K}^{-1}$

$k$  Isothermal compressibility  $= 8.6 \times 10^{-12} \text{ m}^2/\text{N}$

temp  $= 28^\circ\text{C}$

(v) Sp. Vd<sup>m</sup>  $= 0.000114 \text{ m}^3/\text{kg}$ .

Ratio of sp. heat  $= 1.024$

$C_p = 380 \text{ J/kgK}$ ,

$C_p = 380 \text{ J/kgK}$ , 421, 407, 411

Ans:

$$C_p - C_v = T V \frac{\beta^2}{K}$$

421

$$\left. \frac{T \frac{\partial S}{\partial T}}{\partial T}, -T \frac{\partial S}{\partial T} \right|_p = 0$$

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

$$= R$$

$$C_p - C_v = R$$

$$C_p \left( \frac{C_p}{C_v} - 1 \right) = T V \frac{\beta^2}{K}$$

Q.7 For a refrigerant is used for in a vapour compression refrigeration system the Joule thomson coeff. should be. (iii)

~~it is +ve~~

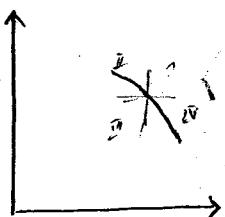
~~+ve~~ , +ve , 0 , - ,  $\infty$

$$\lambda = \left. \frac{\partial T}{\partial P} \right|_n \Rightarrow \frac{\partial T}{\partial P} = -ve$$

$$\therefore \lambda = +ve.$$

Q.8 If the temp. of a real gas is increased in the throttling process. Slope of T-P curve will be

0 , ~~+ve~~ , +ve ,  $\infty$



$$\text{Slope } \left. \frac{\partial T}{\partial P} \right|_{\text{real}} = +ve.$$

Q.9 Using Maxwell relation an ideal gas  $\left. \frac{\partial S}{\partial V} \right|_T =$

$$\frac{R}{P} , \frac{R}{V} , -\frac{R}{P} , -\frac{R}{V}$$

$$PV = RT \quad T = \frac{RT}{V}$$

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

$$PV = RT$$

$$P = RT/V$$

$$\left. \frac{\partial P}{\partial T} \right|_V = \frac{R}{V}$$

$$P + \left. \frac{\partial P}{\partial V} \right|_T = RT \quad \frac{R}{V}$$

$$P = \frac{(RT)}{(V+b)} + \frac{a}{V^2}$$

$$\left. \frac{\partial P}{\partial T} \right|_V = \frac{R}{V+b}$$

Q.10 For a real gas,  $V = RT/P - \frac{C}{T^3}$ ,  $C$  is constant. Show that

$$(h_2 - h_1)_T = \frac{4C}{T^3} (P_1 - P_2)_T \quad \& \quad (s_2 - s_1) = R \ln \frac{P_1}{P_2} + \frac{3C}{T^4} (P_1 - P_2)_T$$

$$V = RT/P - C/T^3$$

$$\text{Prove: } (h_2 - h_1)_T = \frac{4C}{T^3} (P_1 - P_2)_T$$

$$(s_2 - s_1)_T = R \ln \frac{P_1}{P_2} + \frac{3C}{T^4} (P_1 - P_2)_T$$

$$h = U + PV$$

$$dh = dU + PdV + VdP$$

$$= Tds + VdP$$

$$= CpdT - T \frac{\partial V}{\partial T} \Big|_P dP + VdP$$

$$dh = \underset{\text{constant } T}{\cancel{CpdT}} + \left( V - T \frac{\partial V}{\partial T} \Big|_P \right) dP$$

$$V = \frac{RT}{P} - \frac{C}{T^3}$$

$$\frac{\partial V}{\partial T} \Big|_P = \frac{R}{P} + \frac{3C}{T^4}$$

$$dh_T = \left[ \left( \frac{RT}{P} - \frac{C}{T^3} \right) - T \left( \frac{R}{P} + \frac{3C}{T^4} \right) \right] dP$$

$$= \left[ -C/T^3 - 3C/T^3 \right] dP$$

$$dh_T = -\frac{4C}{T^3} dP$$

integrating

$$h_{T1} = -\frac{4C}{T^3} [P_1]^2$$

$$(h_2 - h_1)_T = -\frac{4C}{T^3} [P_2 - P_1]_T$$

$$(h_2 - h_1)_T = \frac{4C}{T^3} [P_1 - P_2]_T$$

$$TdS = \cancel{CpdT} - T \frac{\partial V}{\partial T} \Big|_P dP$$

$$ds_T = -\frac{\partial S}{\partial T} \Big|_P dP$$

$$ds_T = - \left[ R/P + \frac{3C}{T^4} \right] dP_T$$

integrating

$$(s_2 - s_1)_T = -R \ln \frac{P_2}{P_1} - \frac{3C}{T^4} (P_2 - P_1)_T$$

$$= R \ln \frac{P_1}{P_2} + \frac{3C}{T^4} (P_1 - P_2)_T$$

(69)

Energy

High Grade Energy

Low " "

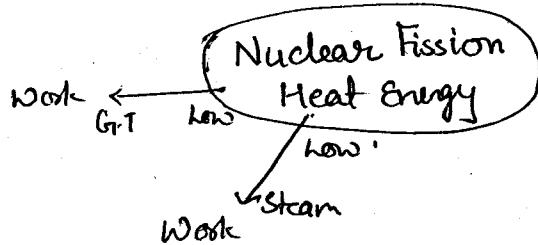
Thermal Energy — Work Energy (high grade energy)  
(low grade energy)

$\eta$  of conversion is low  $\rightarrow$  low Gr. En.

Dam

PE  $\rightarrow$  KE  $\rightarrow$  Work Energy

High Gr. En. 'H H



$$\eta \text{ of Carnot Cycle} = 1 - \frac{T_L}{T_H} \text{ lowest}$$

 $(T_L \downarrow) (T_H \uparrow)$ 

$$\eta_{rev} = 1 - \frac{T_L}{T_H}$$

$$\eta_{max} = 1 - \frac{T_0}{T_H}$$

$$= 1 - \frac{T_0}{T}$$

at which heat is rejected.

!  $T_0$  = Surrounding temp = Ambient temp.!  $T$  = temp at which heat is supplied

Available Energy :- Maximum amount of work which can be obtained from the given heat.

$$H \cdot \eta = Q$$

$$A.E = W_{max} = ?$$

$$\text{as we know } \frac{W}{Q} = \eta$$

$$W_{max} = \eta_{max} \times Q$$

$$\Rightarrow (1 - \frac{T_0}{T}) Q$$

$$\delta W = \left(1 - \frac{T_0}{T}\right) \delta Q$$

$$\int_1^2 \delta W_{\max} = \int_1^2 \left(1 - \frac{T_0}{T}\right) \delta Q$$

$$W_{\max 2} = \int_1^2 \delta Q - \int_1^2 \frac{T_0}{T} \delta Q$$

$$= 1Q_2 - T_0 (S_2 - S_1)$$

$$W_{\max 2} = AE = H \cdot S - H \cdot R \xrightarrow{UE}$$

$$AE + UE = H \cdot S$$

$$\delta W = \left(1 - \frac{T_0}{T}\right) m c_p dT$$

$$W_{\max} = m c_p \left[ (T - T_0) - T_0 \ln \frac{T}{T_0} \right]$$

$$= 1 \times 41868 \left[ 5 - 303 \ln \frac{308}{303} \right]$$

$$= 0.1758$$

$$Q = Q'$$

$$Q = T \Delta S, Q' = T' \Delta S'$$

$$Q_0 = T_0 \Delta S, Q'_0 = T_0 \Delta S'$$

$$W = T \Delta S - T_0 \Delta S, W' = Q' - Q'_0,$$

$$= Q - Q_0$$

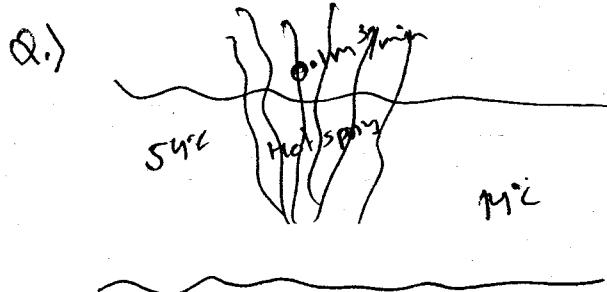
$$= (T - T_0) \Delta S = -\Delta S - T_0 \Delta S'$$

Due to finite temp. difference b/w source & working fluid temp.

$$\text{loss of work} = W - W'$$

$$= (T - T_0) \Delta S - (T \Delta S - T_0 \Delta S')$$

$$= T_0 (\Delta S' - \Delta S)$$



max<sup>m</sup> area of power.

Maximum amount of available energy is called Energy  $\frac{W_2}{m_2}$

$$\int_{T_0}^T (1 - \frac{T_0}{T}) \dot{S}Q = \int_{T_0}^T (1 - \frac{T_0}{T}) m C_p dT$$

$$= m C_p \left[ (T - T_0) - T_0 \ln \frac{T}{T_0} \right]$$

$$= \frac{100}{60} \times 4.1868 \left[ 410 - 287 \ln \frac{327}{287} \right] \text{ kW}$$

for mass  
into  $\frac{\text{kg}}{\text{s}} \times \frac{\text{kJ}}{\text{kgK}} \times \text{K}$

$$= 17.8136 \text{ kW}$$

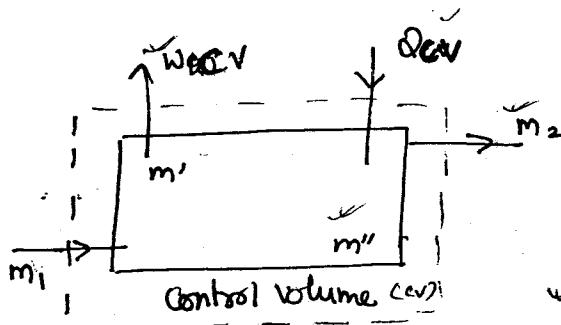
Aenergy = Unavailable Energy / Heat Rejected (UE/HR)

Energy = Available Energy

Q) Most general form of Energy =  $h$

for an actual System or

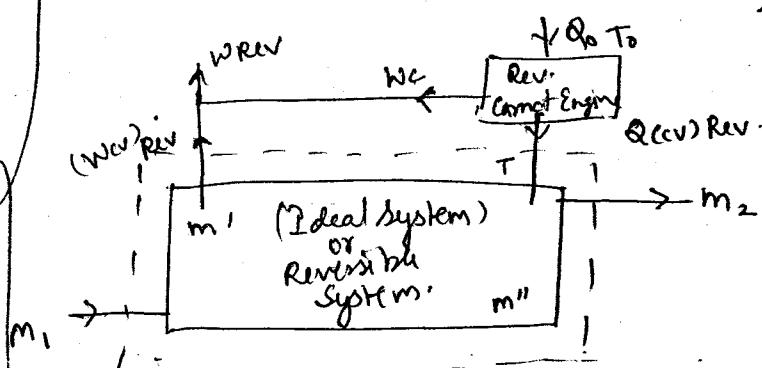
Irreversible System



✓ = in.  
✗ = out.

$$Q_{cv} + m_1 \left( h_1 + \frac{v_1^2}{2} + gz_1 \right) + m' \left( u' + \frac{v'^2}{2} + gz' \right)$$

$$= W_{cv} + m_2 \left( h_2 + \frac{v_2^2}{2} + gz_2 \right) + m'' \left( u'' + \frac{v''^2}{2} + gz'' \right)$$



$$W_{rev} - W_{cv} = \text{Irreversibility}$$

$$W_{rev} = W_c + (W_{cv})_{rev}$$

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Mass balance

$$m' + m_1 = m_2 + m''$$

Energy balance

$$Q_{cv} + m_1 (h_1 + \frac{V_1^2}{2} + gz_1) + m' (u' + \frac{V'^2}{2} + gz') \quad \text{(we neglect these terms some time)}$$

$$= W_{cv} + m_2 (h_2 + \frac{V_2^2}{2} + gz_2) + m'' (u'' + \frac{V''^2}{2} + gz'')$$

$$Q_{cv} + m_1 h_1 + m' u' = W_{cv} + m_2 h_2 + m'' u''$$

$$W_{cv} = Q_{cv} + (m_1 h_1 - m_2 h_2) + (m' u' - m'' u'')$$

Irreversibility: ~

Dif of the work obtain in reversible & irreversible system.

$$W_c = Q_0 - (Q_{cv})_{rev}$$

$$\frac{Q_0}{(Q_{cv})_{rev}} = \frac{T_0}{T}, \quad \frac{Q_0}{T_0} = \frac{(Q_{cv})_{rev}}{T} \quad \begin{matrix} \text{Ratio of h' is same} \\ \text{as ratio of} \\ \text{enthalpy.} \end{matrix}$$

$$(Q_{cv})_{rev} + m_1 h_1 + m' u' = (W_{cv})_{rev} + m_2 h_2 + m'' u'' +$$

$$\frac{(Q_{cv})_{rev}}{T} + m_1 s_1 + m' s' = m_2 s_2 + m'' s''$$

$$* \quad \frac{Q_0}{T_0} = (m_2 s_2 - m_1 s_1) + (m'' s'' - m' s')$$

$s \equiv$  specific entropy  
 $= Entropy \times mass.$   
 $S \times m = s$

$$Q_0 = T_0 [(m_2 s_2 - m_1 s_1) + (m'' s'' - m' s')]$$

$$* \quad (W_{cv})_{rev} = [(Q_{cv})_{rev} + (m_1 h_1 - m_2 h_2) + (m' u' - m'' u'')]$$

$$W_{rev} = [Q_0 - (Q_{cv})_{rev}] + (W_{cv})_{rev}$$

$$= T_0 [(m_2 s_2 - m_1 s_1) + (m'' s'' - m' s')]$$

$$- (Q_{cv})_{rev} + [(Q_{cv})_{rev} + (m_1 h_1 - m_2 h_2) + (m' u' - m'' u'')]$$

~~$m_1, T_0 \delta_1$~~

$$W_{REV} = [m_1(h_1 - T_0 \delta_1) - m_2(h_2 - T_0 \delta_2)] + [m'(u' - T_0 \delta') - m''(u'' - T_0 \delta'')]$$

If steady flow system (open)  $\{m_1 = m_2 = m; \text{say}\}$   
 $\&$   
 $\{m' = 0 = m''\}$

$$W_{REV} = [m(h_1 - T_0 \delta_1) - m(h_2 - T_0 \delta_2)] - \\ - m[(h_1 - T_0 \delta) - (h_2 - T_0 \delta_2)]$$

per unit mass,

$$W_{REV} = (h_1 - T_0 \delta_1) - (h_2 - T_0 \delta_2)$$

$$W_{REV} = g_1 - g_2$$

$\frac{W_{REV}}{m}$  at small  $W$  letter  
 gibbs energy

If non-flow system (close)  $\{m_1 = 0 = m_2\}$   
 $\&$   
 $\{m' = m'' = m; \text{say}\}$

As close system  
 nothing entering or  
 leaving

$$W_{REV} = m[(u' - T_0 \delta') - (u'' - T_0 \delta'')]$$

$$W_{REV} = (u' - T_0 \delta') - (u'' - T_0 \delta'')$$

$$W_{REV} = \alpha' - \alpha''$$

helmholtz function  
 f.g.

$$\dot{Q} = [m_1(h_1 - T_0 \delta_1) - m_2(h_2 - T_0 \delta_2)] + [m'(u' - T_0 \delta') - m''(u'' - T_0 \delta'')] - [Q_{cv} + (m_1 h_1 - m_2 h_2) + (m' u' - m'' u'')]$$

$$\dot{Q} = -m_1 T_0 \delta_1 + m_2 T_0 \delta_2 - m' T_0 \delta' + m'' T_0 \delta'' - Q_{cv}$$

$$\underline{\Gamma} = T_0 \left[ (m_2 s_2 - m_1 s_1) + (m'' s'' - m' s') + \left( -\frac{Q_{cv}}{T_0} \right) \right]$$

For steady flow System :— (Open system)  $m' = 0 = m''$   
 $m_1 = m_2 = m$ , say.

$$\underline{\Gamma} = T_0 \left[ m (s_2 - s_1) + \left( -\frac{Q_{cv}}{T_0} \right) \right]$$

$$= T_0 \left[ (s_2 - s_1) + (\Delta S)_{\text{sur.}} \right]$$

$$= T_0 \left[ (\Delta S)_{\text{system}} + (\Delta S)_{\text{sur.}} \right]$$

$$\boxed{\underline{\Gamma} = T_0 (\Delta S)_{\text{universe}}}$$

For a non-flow system i.e (closed system)  $\{m_1 = 0 = m_2\}$   
 $\{m' = m'' = m\}$  say.

$$\underline{\Gamma} = T_0 \left[ m (s'' - s') + \left( -\frac{Q_{cv}}{T_0} \right) \right]$$

$$= T_0 \left[ (\Delta S)_{\text{system}} + (\Delta S)_{\text{sur.}} \right]$$

$$\boxed{\underline{\Gamma} = T_0 (\Delta S)_{\text{universe}}}$$

### Availability :—

Max<sup>m</sup> amt of energy obtained if we were operating on universe.  
 cannot cycle.

$$\begin{aligned} \underline{\Delta Q}_{\text{Rev}} &= q_1 - q_2 \\ &= q_1 - q_0 \\ &= q - q_0 \end{aligned}$$

Atm P  
 Atm Temp  $\left( \frac{P_0}{T_0} \right)$  dead state.

$$q = u - T s$$

$$q_0 = u_0 - T_0 s_0$$

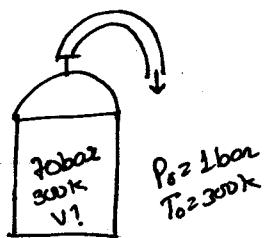
Maxm useful work obtained from a given system:

$\Rightarrow W_{\max} = \text{Work done against the atm.}$

$$= \left[ (U_1 - T_0 S_1) - \frac{(U_0 - T_0 S_0)}{\cancel{\text{atm}}} \right] - P_0 (V_0 - V_1)$$

Availability  $= (U_1 - T_0 S_1 + P_0 V_1) - (U_0 - T_0 S_0 + P_0 V_0)$

Q.1



How much amt of air should be inside to produce 5.2 mJ availability?

Soln

$$A = m \left[ (U_1 - U_0) - T_0 (S_1 - S_0) + P_0 (V_1 - V_0) \right] \quad | \quad T_1 \neq T_0$$

$$= m \left[ C_v (T_1 - T_0) - T_0 \left( C_p \ln \frac{T_1}{T_0} - R \ln \frac{P_1}{P_0} \right) + P_0 \left( \frac{R T_1}{P_1} - \frac{R T_0}{P_0} \right) \right]$$

$| \quad R = \text{Sp. gas const.}$

$$= m \left[ R T_0 \ln \frac{P_1}{P_0} + R \left( T_1 \frac{P_0}{P_1} - T_0 \right) \right]$$

$$= m \left[ R T_0 \ln \frac{P_1}{P_0} + R \left( T_1 \frac{P_0}{P_1} - T_0 \right) \right]$$

$$= m R \left( T_1 \ln \frac{P_1}{P_0} + T_1 \left( \frac{P_0}{P_1} - 1 \right) \right)$$

$$= m R T_1 \left[ \ln \frac{P_1}{P_0} + \frac{P_0}{P_1} - 1 \right]$$

$$5.2 \times 10^3 \text{ kJ} = P_1 V_1 \left[ \ln \frac{P_1}{P_0} + \frac{P_0}{P_1} - 1 \right]$$

$$5.2 \times 10^3 \text{ kJ} = \cancel{P_1} V_1 \left[ \ln \frac{70}{1} + \frac{1}{70} - 1 \right]$$

$$V_1 = 0.2278 \text{ m}^3$$

$$= 0.2278 \text{ m}^3$$

Q.) 10 kg of water 40°C is mixed with 30kg of water at 70°C. This mixing process shall be reversible. Due to mixing there will be loss of available energy. Atm temp 27°C

$$(AE)_{10\text{kg}} = ?$$

$$T_0 = 27^\circ\text{C}$$

$$(AE)_{30\text{kg}} = ?$$

$$(AE)_{40\text{kg}} = ?$$

$$AE = \dot{W}_{\text{max}} = \eta \times Q$$

$$\dot{W}_{\text{max}} = \eta \times \delta Q$$

$$\int_{T_0}^T \dot{W}_{\text{max}} = \int_{T_0}^T \left(1 - \frac{T_0}{T}\right) m C_p dT$$

$$w_{\text{max}} = m C_p \left[ \int_{T_0}^T \left( dT - \frac{T_0}{T} dT \right) \right]$$

$$AE = w_{\text{max}} = m C_p \left[ (T - T_0) - T_0 \left( \ln \frac{T}{T_0} \right) \right]$$

$$(AE)_{10\text{kg}} = 10 \times 4.1868 \left[ (13) - 300 \ln \frac{313}{300} \right]$$

$$= 11.4628$$

$$(AE)_{30\text{kg}} = 30 \times 4.1868 \left[ (43) - 300 \ln \frac{343}{300} \right]$$

$$= 353.781$$

$$(AE)_{10} + (AE)_{30} \rightarrow 40 \times 4.1868 \times T_f = 10 \times 4.1868 \times 313 + 30 \times 4.1868 \times 343$$

$$T_f = 335.5^\circ\text{C}$$

$$(AE)_{40\text{kg}} = 40 \times 4.1868 \left[ (T_f - T_0) - T_0 \ln \frac{T_f}{T_0} \right]$$

$$= 326.26$$

Aug 19, 14

## Pure Substance

- 1.) Same chemical composition whatever may be phase ..

27 Homogeneous through out

### 3.7 Single component or Multi Component

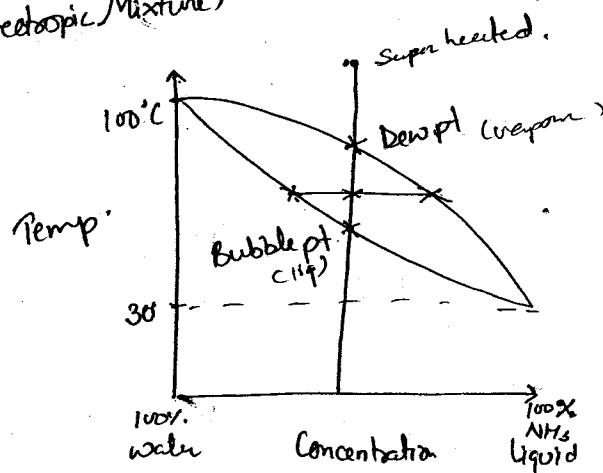
$$\text{NH}_3 + \text{H}_2\text{O}$$

Not a pure substance

$$\text{C}_6\text{H}_2\text{F}_2 + \text{CHClF}_2$$

pure substance

Binary mixture  
(Azeotropic Mixture)



Ac

( Not a pure Substance )

Chem. comp.  $O_2$ ,  $N_2$ , Traces of  $CO_2$ , Family of Noble gos (Ar, Kr...)

+  
Moisture

Air = Dry air + Moisture  
↓  
Gaseous Air.

Moisture changes continuously  
So the chem. comp of air  
also changes continuously,  
etc, Air is not pure subst.

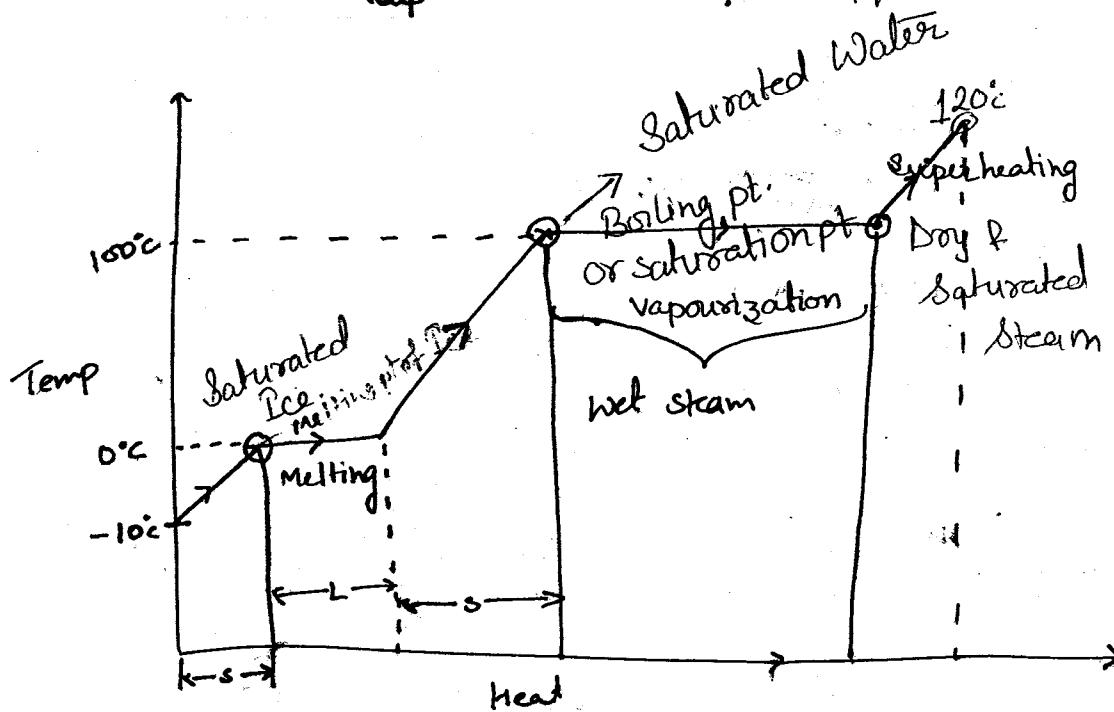
Solid  
Liquid  
Gaseous } Phases together  $\rightarrow$  Triple pt.  
0.01°C  
0.006113 bar

Any condition below critical condition, then it is vapour

" " above " " , " " " gas.

Critical condition  $\xrightarrow{\text{in vapors.}}$   $\uparrow \text{gas}$

- $-10^{\circ}\text{C}$  Ice (Solid)  $\xrightarrow{\text{Heat}}$   $0^{\circ}\text{C}$  Ice (Solid) Sensible heat of ice  
(Can be measured by thermometer)  
 $0^{\circ}\text{C}$  Ice (Solid)  $\xrightarrow{\text{Heat}}$   $0^{\circ}\text{C}$  Water (Liquid) Latent heat of Melting  
 $0^{\circ}\text{C}$  Water (Liquid)  $\xrightarrow{\text{Heat}}$   $100^{\circ}\text{C}$  Water (Liquid) Sensible heat of water  
 $100^{\circ}\text{C}$  Water (Liquid)  $\xrightarrow{\text{Heat}}$   $100^{\circ}\text{C}$  Dry & Saturated (Gaseous) Latent heat of Vapourization  
 $100^{\circ}\text{C}$  Dry & Saturated (Gaseous)  $\xrightarrow{\text{Heat}}$   $120^{\circ}\text{C}$  Superheated (Gaseous) Sensible heat of superheated steam  
or heat of superheat.  
 Steam  
 Ts



Dryness fraction, ( $X$ ) :-

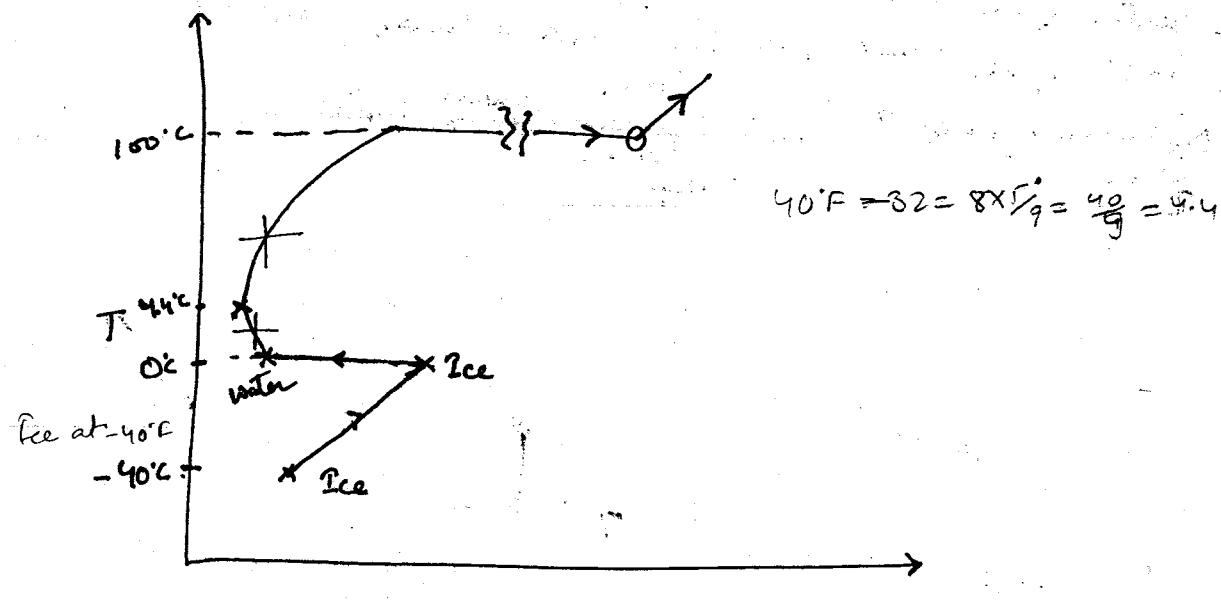
$$X = \frac{\text{Mass of dry & Sat. steam}}{\text{Mass of dry & Sat. steam} + \text{Mass of saturated water}}$$

Quality of steam  $\Rightarrow X \times 100 = n\%$

$$T_{\text{sup}} - T_s = \text{Degree of Superheat}$$

Ice - Volume  $\uparrow$  bcz S of ice is less than of water.  
 Water - " "  $\downarrow$

T-s curve (Temp & Sp. heat



$$40^{\circ}\text{F} = 32 = 8 \times \frac{5}{9} = \frac{40}{9} = 4.4$$

Steam Table: -

Sp. Enthalpy

$$h = U + PV$$

$h_{fg}$  = ~~latent heat of~~ heat of vaporization.

~~at~~ much pressure

$$h_f + h_g = h_g$$

$$h_g = \int_{273.15}^{318.15} ds = \int \frac{ds}{T} = \int \frac{C_p dT}{T}$$

$$= 4.1868 \ln \frac{318.95}{273.15}$$

$$= 0.649.$$

(in steam table also.)

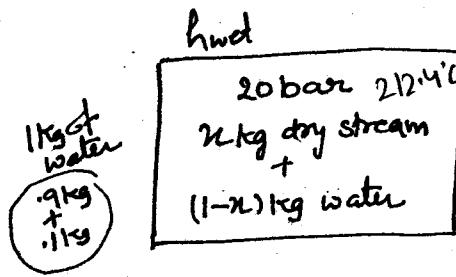
$$\delta_{fg} = \frac{h_{fg}}{T_s}$$

$$\delta_f + \delta_{fg} = \delta_g$$

or  $> 221.2$  bar only they can behave as gas.

Gas cannot be condensed at their own pressure but they can be condensed only when they are brought below the their press.

Q.)



$$h_{wet} = \eta h_g + (1-\eta) h_f$$

$$= h_f + \eta (h_g - h_f)$$

$$h_{wet} = h_f + \eta h_g$$

$$! h_f + h_{fg} = h_g$$

Q.)

512 bar  $T_s$ ?

50 bar  $T_s$

264.0°C

265.5°C

52 bar

266.5°C

25

$$\frac{2.5}{2} \times 1.2^{0.1} = 1.5$$

Method of interpolation

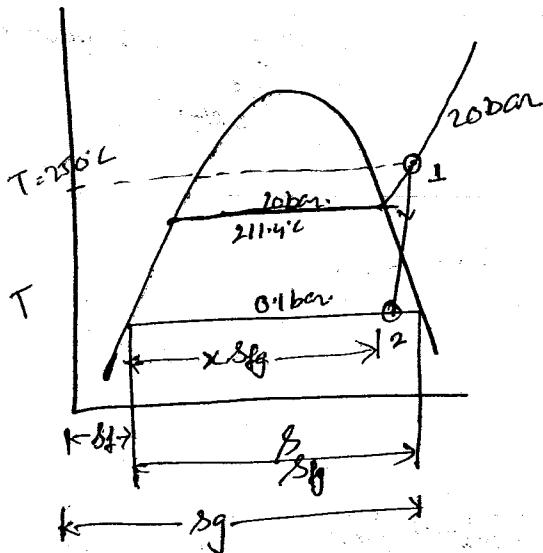
$$\ln P_{sat} = A + \frac{B}{T_{sat}} + C \ln T_{sat} + D T_{sat}^2$$

Aug 22, 14

Q &gt; 20 bar, 250°C, 5 kg/s isentropic manner to a pressure of 0.1 bar

Determine the final condition of steam and power developed?

Soln



$$\delta_1 = \delta_2$$

$$(s_{\text{sup}})_1 = (s_{\text{net}})_2$$

$$= (s_f + \Delta s_g)_2$$

$$6.545 = 0.649 + u_2 \times 7501$$

$$u_2 = 0.786$$

SFEE

$$\delta q - \delta w_s = dh + [d(\text{Re}) + d(\text{pe})]$$

$$\int_1^2 -\delta w_s = \int_1^2 dh$$

$$-w_{s2} = h_2 - h_1$$

$$w_{s2} = (h_1 - h_2) \text{ kJ/kg}$$

$$w_{s2} = m(h_1 - h_2) \text{ kg/s} \times \frac{1 \text{ kJ}}{1 \text{ kg}}$$

$$= 5(h_1 - h_2)$$

$$w_{s2} = 4149.796 \text{ kW}$$

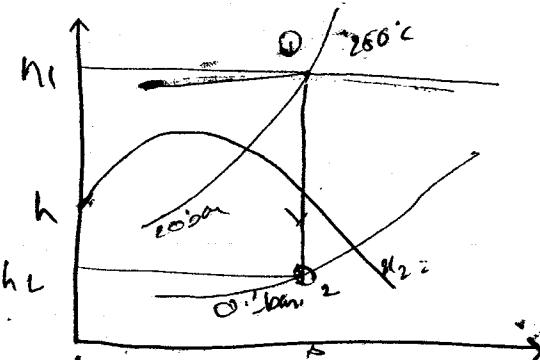
$$h_1 = (h_{\text{sup}})_1 = 2902.5 \text{ kJ/kg}$$

$$h_2 = (h_{\text{nd}})_2$$

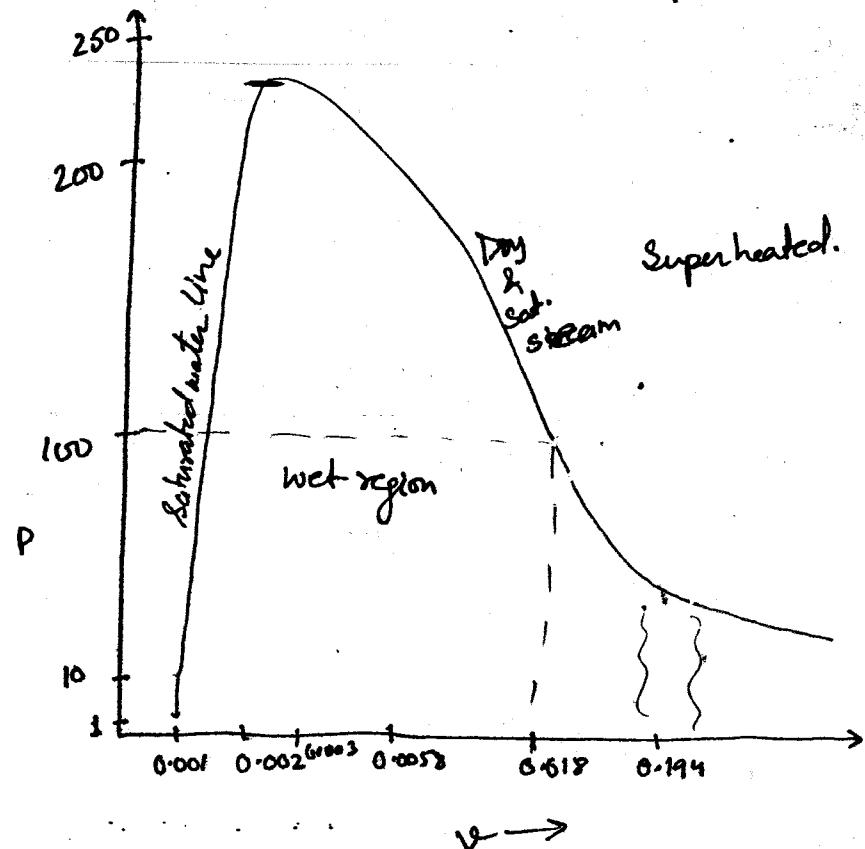
$$= (h_f + h_g)_2$$

$$= 191.8 + 0.786 \times 2392.8$$

$$= 2072.54 \text{ kJ/kg}$$



Pr	vp	vg
0.1 bar	0.001010	1.67
1	0.001043	1.694
10	0.001077	0.194
100	0.001102	0.180
200	0.001136	0.00583
21.2	0.001155	0.003155



Q.) 1kg of saturated steam at  $100^{\circ}\text{C}$ , 1.01325 bar is contained in a rigid walled vessel. It has a volume of  $1.673\text{m}^3$ . It cools to  $98^{\circ}\text{C}$ . The saturation pressure is 0.943 bar. 1kg of water vapour under these conditions have a volume of  $1.789\text{m}^3$ . The amt of water vapour condensed in 1kg is

i) 0

ii)  $0.065$

iii)  $0.1$

iv)  $1.0$

$$V_{\text{wet}} = x_1 \text{kg dry steam} + (1-x_1) \text{kg water}$$

$$V_{\text{wet}} = x_1 V_g + (1-x_1) V_g \quad | \rightarrow \text{negligibly small}$$

$$V_{\text{wet}} = x_1 V_g + V_g$$

$$= 1$$

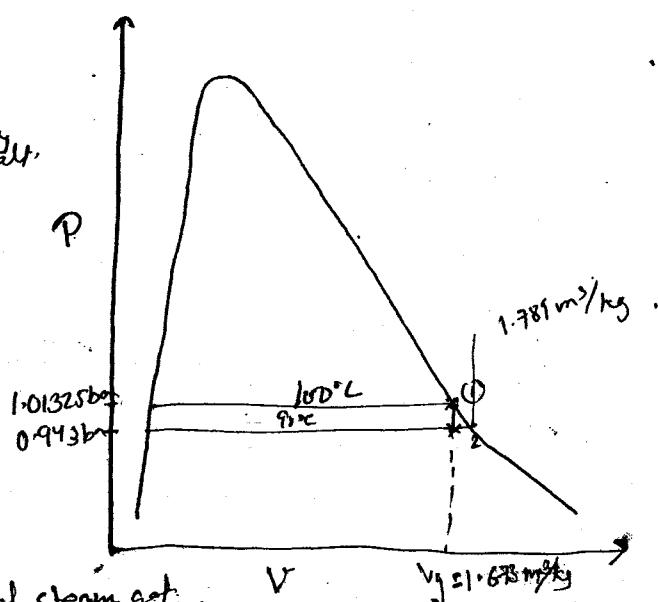
$$V_1 = V_2$$

$$(V_g)_1 = (V_{\text{wet}})_2 = (x_1 V_g)_2$$

$$1.673 = x_2 \times 1.789$$

$$x_2 = 0.935$$

$$\text{water per } 1-0.935 = 0.065 \text{ kg of steam got condensed}$$



Q.) Water has a critical specific volume of  $0.003155 \text{ m}^3/\text{kg}$ . A closed and rigid steel tank of volume  $V = 0.025 \text{ m}^3$  contains mixture of water and steam at  $0.1 \text{ MPa}$ . The mass of mixture is  $10 \text{ kg}$ ; the tank is now slowly heated. The liquid level inside the tank

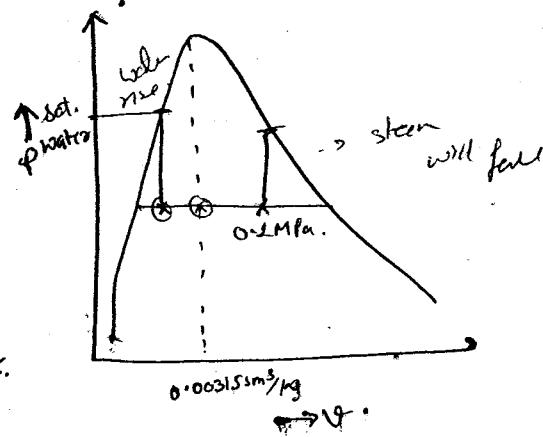
- a) will rise
- b) will fall

c) will remain constant

d) may rise or fall depending upon the amt. of heat added.



$$V_{\text{net}} = \frac{0.025}{10} \\ = 0.0025 \text{ m}^3/\text{kg}$$



Aug 23, 14

Q.) The following table of properties are printed out for saturated liquid and saturated vapours of  $\text{NH}_3$  the title for only the first two columns are available on the

All that we know that the other columns contain data from sp. properties namely internal energy, enthalpy and entropy.

① $t$ $^{\circ}\text{C}$	② $P$	③	④	⑤	⑥	⑦	⑧
-20	190.2	88.76	0.3657	89.05	5.6155	1299.5	1418.0
0	429.6	179.69	0.7114	180.36	5.3309	1318.0	1442.2
20	587.5	272.89	1.0408	274.30	5.0880	1332.2	1466.2
40	1554.9	368.74	1.3574	371.43	4.8662	1341.0	1470.2

i) h data are in columns

a) 3&7 b) 3&8 c) 5&7 ~~d) 5&8~~

ii) When saturated liquid at  $40^{\circ}\text{C}$  is throttled to  $-20^{\circ}\text{C}$ , the quality at exit will be

a) 0.189 b) 0.212 c) 0.231 d) 0.788

Smaller values are of entropy

$$\begin{array}{l|l} s_f = 4 & u_f = 3 \\ s_g = 6 & h_f = 5 \end{array}$$

$$h = u + PV$$

lower volume is for  $u_g = 7$   
& rest 1 one is  $h_g = 8$

iii) During throttling h remains constant.

$$h_1 = h_2$$

$$(h_f)_1 = (h_{\text{exit}})_2$$

$$(h_f)_1 = (h_f + n h_{fg})_2$$

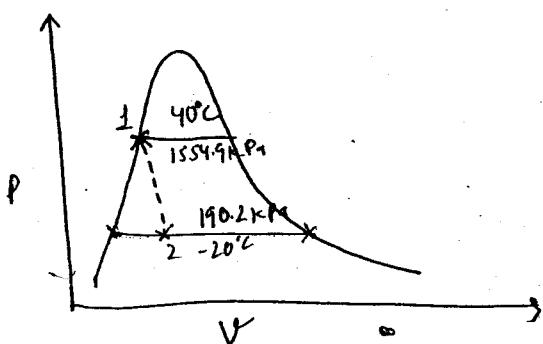
$$= [h_f + n(h_g - h_f)]_2$$

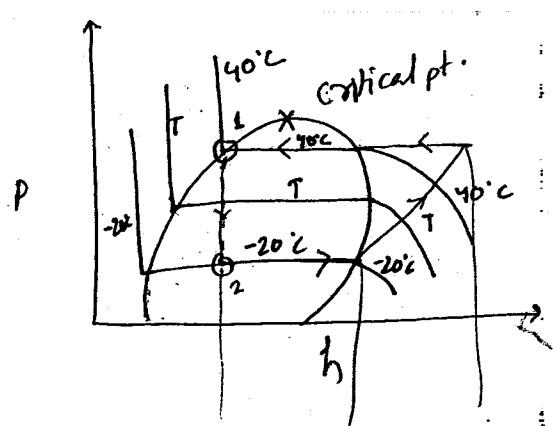
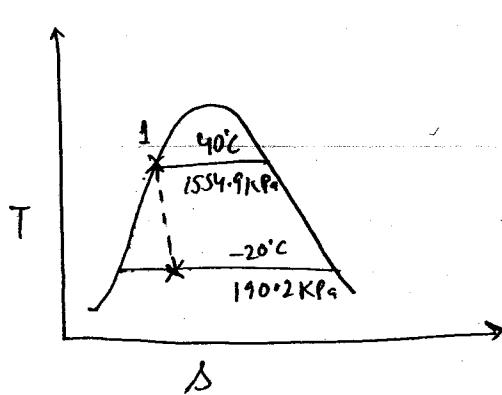
$$371.43 = [89.05 + n(1418.0 - 89.05)]$$

$$h_f + h_{fg} = h_g$$

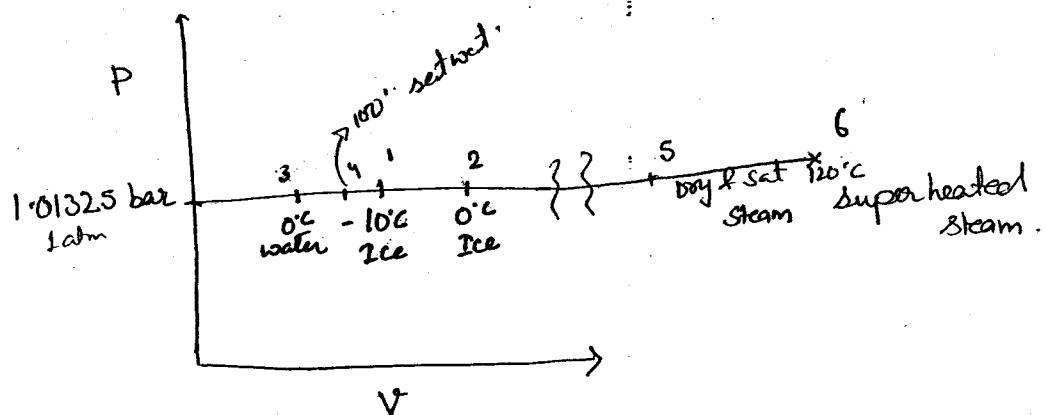
$$0.2124$$

$$n = 0.2124$$

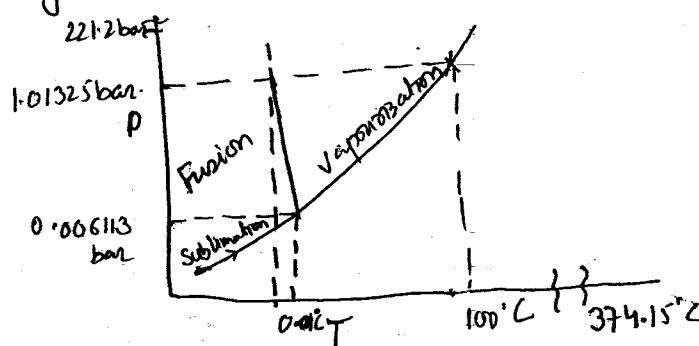


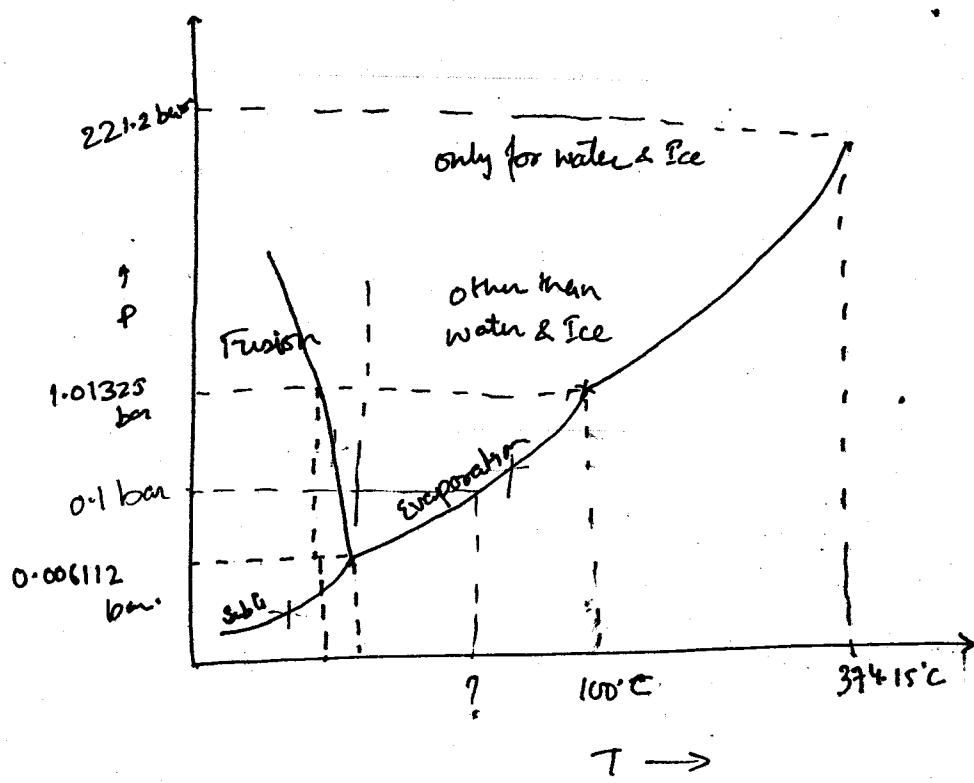


\* P-v diagram for 1 atm.



\* P-T diagram: -





- Q6) A sat. liquid at 1500 kPa, and 300 K with enthalpy of 750 kJ/kg is throttled to a liquid vapour mixture at 150 kPa. & 300 K. At exit condition enthalpy of sat. liquid is 500 kJ/kg. and enthalpy of sat. vapour is 2500 kJ/kg. % of saturated liquid which vapourises is i) 87.5 %. ii) 67.5 %. iii) 12.5 %. iv) 1 %.

$$h_f = [h_f + \eta (h_g - h_f)]$$

$$750 = 500 + \eta (2500 - 500)$$

$$\frac{250}{2000} = \eta$$

$$\eta = 12.5 \%$$

- Q7) 2 kg of steam in a piston cylinder device at 400 kPa, and 175°C undergoes a mech. reversible isothermal compression to a final pressure such that steam becomes just saturated. What is the work required for the process?

$$V = 0.503 \text{ m}^3/\text{kg}$$

$$u = 2606 \text{ kJ/kg}$$

$$\delta = 7.055 \text{ kJ/kgK}$$

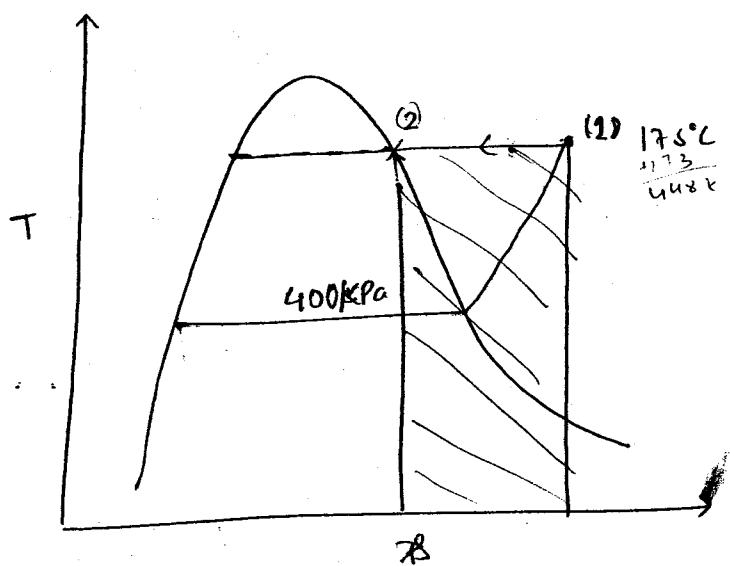
175°C sat. vapour,  $V = 0.216 \text{ m}^3/\text{kg}$ ,  $u = 2579 \text{ kJ/kg}$ ,  $\delta = 6.622 \text{ kJ/kgK}$

a) 0

b) 230 kJ

c) 334 kJ

d) 388 kJ



$$\delta q = \delta w + dU$$

$$\delta q_2 = \delta w_2 + (u_2 - u_1)$$

$$-448(7.055 - 6.622) = \delta w_2 + (2579 - 2606)$$

$$\delta w_2 = 220.98$$

1 m/s  $| \times 2$

a) Steam undergoes isentropic expansion in a turbine from 5000 kPa,

$$400^\circ\text{C} \quad \delta = 6.65 \text{ kJ/kgK}$$

$$\rightarrow 150 \text{ kPa} \quad (\delta f = 1.4336 \text{ kJ/kgK}, \delta g = 7.2234 \text{ kJ/kgK})$$

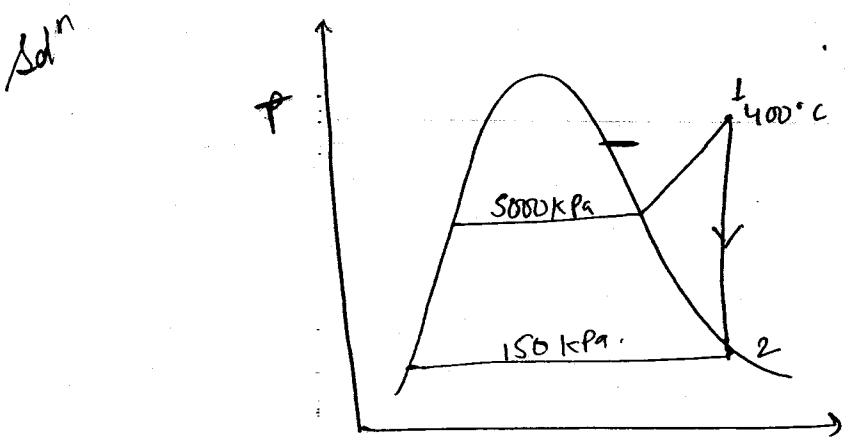
The exit condition of steam is A

a) Superheated Vapour

b) Partially Condensed Vapour w/ quality of 0.9

c) Saturated Vapour

d) Partially Condensed Vapour w/ quality 0.1



$$\Delta \quad \Delta_1 = \Delta_2$$

$$6.65 = \Delta_2 - \Delta_{\text{ref.}}$$

$$6.65 = 1.4336 + \kappa (7.2234 - 1.4336)$$

$$\kappa = 0.9$$

Aug 26, 14

# Solution Thermodynamics

Thermodynamic state of any system.

Fundamental :-  $T, P, V, C_p, C_v, U, S$ .

Derived :-  $H, G, \text{Conc, free energy}$ .

I Law  $\rightarrow$  Energy Conservation.

II Law  $\rightarrow$  Entropy of the universe always  $\uparrow$

Enthalpy :-

$$h = u + \frac{pv}{E}$$

↓  
Internal Energy.

$\square$  Rain drops

$$h = u + Pv$$

↑  
Work req.  
to create a  
system out of  
nothing at const P.

Free Energies :-

$\rightarrow$  "free" Energy available for work

$$\begin{array}{ccc} & \swarrow & \searrow \\ \text{Helmholtz} & & \text{Gibbs free Energy} \\ \text{free} & & (G) \\ \text{Energy} & & \text{const P & const T} \\ (A) & & \\ & & G = U - TS + PV \end{array}$$

Work req. to create  
a system out of nothing  
at const V & const T.

$$A = U - TS$$

$$\Delta A = \Delta U - T \Delta S$$

$$\text{from 2nd Law} \quad \Delta U = \delta Q - \delta W$$

$$\delta Q = +T \Delta S$$

$$\Delta A = -\delta W$$

max work done on the system.

A  $\rightarrow$  work funct<sup>n</sup>  
 ↳ state funct<sup>n</sup>  
 extensive

$$G_f = U + PV - TS$$

$$\Delta G = \Delta U + P\Delta V - T\Delta S$$

$$\Delta G = -W_{\text{other}}$$

$$\begin{cases} \Delta U = \delta Q - \delta W \\ \delta Q = T\Delta S \\ \delta W = \alpha(PV) = P\Delta V + V\frac{\partial P}{\partial V} \end{cases}$$

Work

Equation of State :-

→ rel<sup>n</sup> b/w T, V, P of the system.

→ Ideal gas EOS

→ Virial EOS  
 → Vanderwall EOS

Ideal gas EOS

$$PV = nRT$$

$$P\left(\frac{V}{n}\right) = RT$$

$$\boxed{PV = RT}$$

; molar volume  $\rightarrow V$

Virial eq<sup>n</sup>

$$\boxed{PV = ZRT}$$

Compressibility factor

$$Z = \frac{\text{Vol. of real gas}}{\text{Vol. of ideal gas}} = \frac{\bar{V}}{RT/P} = \frac{PV}{RT}$$

$$\boxed{PV = ZRT}$$

$$Z = \frac{PV}{RT} = 1 + \frac{B_0(T)}{V} + \frac{B_1(T)}{V^2} + \frac{B_2(T)}{V^3} + \dots$$

$B_0(T), B_1(T), B_2(T), \dots$  virial coefficients.

Neglecting the higher order terms:-

$$Z = \frac{PV}{RT} = 1 + \frac{B_0(T)}{V}$$

$$B_0 = \frac{RT_c}{P_c} (B' + \omega B'')$$

$$B' = 0.083 - \frac{0.422}{T_R^{1.6}}$$

$$B'' = 0.139 - \frac{0.172}{T_R^{4.2}}$$

$$T_R = T/T_c$$

$\omega$  = acentric factor (Molecule shape, polarity)

Q.) A 3 lit. tank contains 2 mols of nitrogen at  $-150.8^\circ\text{C}$ . Estimate the tank pressure using ideal gas law and virial eqn of state and find out the % error in pressure estimation based on virial eqn of state.

$$P_c = 33.5 \text{ atm}$$

$$T_c = 126.2 \text{ K}$$

$$\omega = 0.40$$

$$R = \frac{PV}{nT} = \frac{1 \times 22.4}{1 \times 273.15}$$

$$P = \frac{RT}{V} = \frac{V}{n} = \frac{3}{2} = 1.5 \text{ l/mol}$$

$$P_2 = \frac{8.314 \times 122.2}{1.5} = 677.31$$

$$P = \frac{0.08206 \times 122.6}{1.5} = 6.70 \text{ atm}$$

$T_c$  &  $P_c$  critical temp & Pres.

$T_R$  = Reduced temp

$$T_R = T/T_C = \frac{122.35}{126.2} = 0.969$$

$$B' = -0.3604$$

$$B'' = -0.0573$$

$$B_0 = \frac{0.08206 \times 126.2}{33.5} \left( -0.3604 + 0.40 \times (-0.0573) \right)$$

$$= -0.118 \text{ l/mol.}$$

$$\frac{P\bar{V}}{RT} = 1 + \frac{B_0(T)}{k\bar{V}^2}$$

$$P = 2.219 \text{ atm} \ 6.19$$

$$= 58.002$$

$$\gamma_r = \frac{P_{\text{ideal}} - P_{\text{actual}}}{P_{\text{actual}}} \times 100$$

$$= \frac{6.7 - 6.19}{6.19}$$

$$= 8.23 \%$$

Vander Waal Eqn of State :-

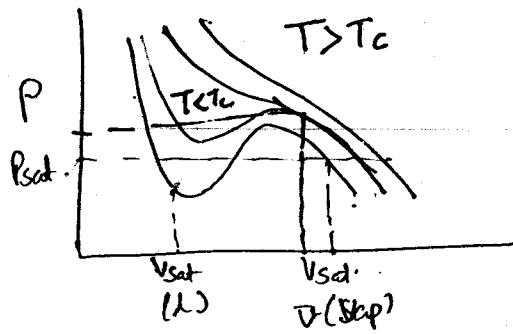
$$P = \frac{RT}{\bar{V} - b} = \frac{a}{\bar{V}^2}$$

$b \rightarrow$  finite vol. occupied by molecules.

$\frac{a}{\bar{V}^2} \rightarrow$  attractive forces btw molecules.

at critical pts

$$\left( \frac{\partial P}{\partial V} \right)_{T_C} = \left( \frac{\partial P}{\partial V} \right)_{T_C} = 0$$



$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\frac{\partial P}{\partial V} = \frac{-RT}{(V_c-b)^2} + \frac{2a}{(V_c)^3} = 0$$

$$\frac{\partial^2 P}{\partial V^2} = \frac{2RT}{(V_c-b)^3} - \frac{6a}{V_c^4} = 0$$

$$a = \frac{9}{8} R \bar{V}_c T_c$$

$$b = \frac{\bar{V}_c}{3}$$

$$P_c = \frac{RT_c}{\bar{V}_c - \frac{\bar{V}_c}{3}} - \frac{\frac{9}{8}RT_c\bar{V}_c}{\bar{V}_c^2}$$

$$= \frac{3RT_c}{2\bar{V}_c} - \frac{\frac{9}{8}RT_c}{\bar{V}_c}$$

$$= \frac{3}{8} \frac{RT_c}{\bar{V}_c}$$

$$\bar{V}_c = \frac{3}{8} \frac{RT_c}{P_c}$$

$$a = \frac{9}{8} R T_c \cdot \frac{3}{8} \frac{R T_c}{P_c}, \quad b = \frac{3}{8} \frac{R T_c}{P_c}$$

$$a = \frac{27}{64} \frac{(RT_c)^2}{P_c}$$

$$b = \frac{RT_c}{8P_c}$$

Q4

Change in entropy per unit mass is chemical potential of any system.

$$\mu_A = \frac{\partial S_f}{\partial n_A}$$

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### Solution thermodynamics —

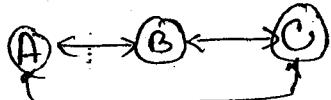
mixture (impure)  
ch. rxn, phase change.

Classical thd.

System, surrounding,  
interaction, heat & work.  
pure substance.  
T, P, Entropy, U.

↳ 0<sup>m</sup> law of thermodynamic.

if two systems are in thermal eqll with third system separately then



↳ 1<sup>st</sup> law of thermodynamic.

For any cyclic process the ~~heat syst~~ <sup>change</sup> in internal energy is equal to the heat supplied to system - work obtained by the system.

$$dU = \delta Q - \delta W$$

↳ 2<sup>nd</sup> law of thermodynamic.

The ht cannot be done from a cold region to hot region naturally, spontaneously (reversible)

reversible  
↓  
quasistatic  $\Rightarrow$  almost adiab.

### ↳ III<sup>rd</sup> Law of thermodynamics

At absolute zero temp, Abs. entropy is min<sup>n</sup> for all the system.

### Mixture

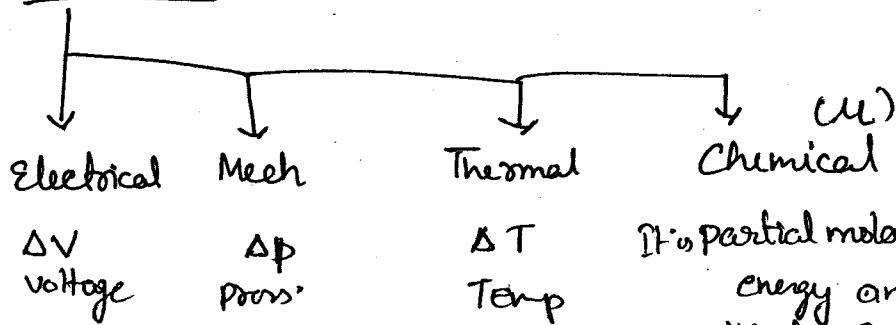
↳ Any state of material where two or more pure substances are mixed together but not chemically combined.

Any mixture is combination of two or more pure substances which are separable physically.

Types: → Homogeneous same phase ( $H_2O + \text{salt}$ ) exist

→ Heterogeneous diff. phase. ( $H_2O + \text{oil}$ ) / Colloidal sol<sup>h</sup> (milk)

### Potential

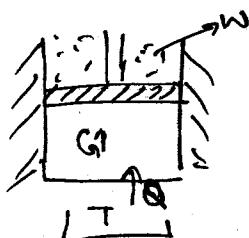


It is partial molar force

energy and equal to the change in total gibbs free energy per unit change of mole of any component

$$\mu_A = \left( \frac{\partial G_A^t}{\partial n_A} \right)_{T, P, n_A \neq A}$$

### Reversible (ideal case)



$$\Delta S_{\text{sys}} = \frac{Q}{T}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

$$\Delta S_{\text{sur}} = \frac{Q}{T}$$

$$\Delta S_{\text{sur}} = \frac{Q}{T} - \frac{Q}{T} = 0$$

$$\Delta S_{\text{sys}} - \frac{Q}{T} = 0$$

$$Q - T \Delta S_{\text{sys}} = 0$$

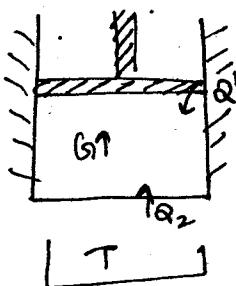
$$\Delta G_f = \boxed{H_f - H_i - Q} = 0$$

$$\Delta H = H_f - H_i$$

$$H_f = H_i + Q$$

$$\Delta H = Q$$

## Irreversible (spontaneous)



$$\Delta S_{sys} = \frac{Q_1 + Q_2}{T} = \frac{Q}{T}$$

$$\Delta S_{sur} = -\frac{Q_2}{T}$$

$$\Delta S_{univ} = \frac{Q}{T} - \frac{Q_2}{T} > 0$$

$$\Delta S_{sys} - \frac{Q_2}{T} > 0$$

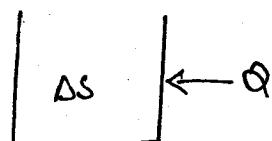
$$\frac{Q_2}{T} - \Delta S_{sys} < 0$$

$$Q_2 - T\Delta S < 0$$

$$\Delta H - T\Delta S < 0$$

$$\boxed{\Delta G < 0}$$

$$\underline{\Delta G > 0}$$



$$\Delta G > 0 \quad (\text{process is not possible})$$

$$Q - T\Delta S > 0$$

$$\frac{Q}{T} - \Delta S > 0$$

$$\frac{Q}{T} > \Delta S$$

if  $\Delta G < 0$ , process is spontaneous in forward direction.

if  $\Delta G > 0$ , process is spontaneous in backward direction.

if  $\Delta G = 0$ , process is reversible, net change in chemical potential is zero.

in (eqm)

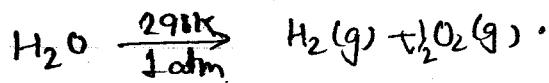
## Helmholtz free Energy :-

$$A = U - TS$$

$A \rightarrow$  Max work available

$G \rightarrow$  Max useful work available

Q) Determine the electric <sup>work</sup> required to produce 1 mol of H in the electrolysis of liquid water at a 298 K and 1 atm.



Data given :-

At 298 K  
1 atm

$$\Delta H = 286 \text{ kJ}$$

$$S_{H_2} = 131 \text{ J/K}$$

$$S_{H_2O} = 70 \text{ J/K}$$

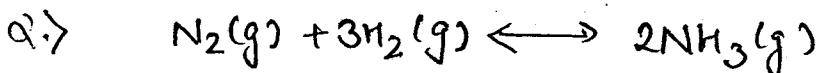
$$S_{O_2} = 205 \text{ J/K}$$

$$\Delta S = S_f - S_i$$

$$= S_{H_2} + \frac{1}{2}S_{O_2} - S_{H_2O}$$

$$\Delta H = 237.27 \text{ kJ}$$

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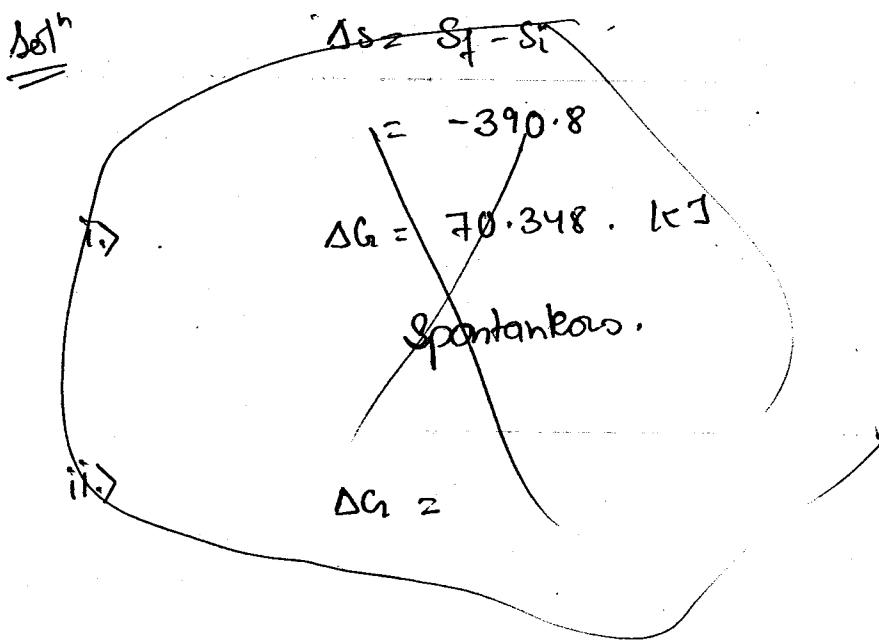
	$\Delta H^\circ$ kJ/mol	$\Delta S^\circ$ J/K/mol
$N_2$	0	191.6
$H_2$	0	130.6
$NH_3$	-46.11	192.6

std (25°C, 1 atm)

→ rxn is spontaneous or not at 25°C

→ rxn is spontaneous or not at 500°C

→ at what temp it will achieve the eqm.



$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\Delta H^\circ = \sum n H_f^\circ - \sum n H_{\text{react}}^\circ$$

$$= 2 \times (-46.11) - 0 - 0$$

$$\Delta H^\circ = -92.22 \text{ kJ}$$

$$\Delta S^\circ = \sum n S_{\text{prod}} - \sum n S_{\text{react}}$$

$$= 2 \times 192.6 - 1 \times 191.6 - 3 \times 130.6$$

$$\Delta S^\circ = -198.75 \text{ J/K}$$

i.)  $\Delta G^\circ = -92.22 - 298 \times (-198.75 \frac{\text{J}}{\text{K}}) \times 10^{-3} \text{ kJ}$

$\Delta G^\circ = -33.186 \text{ kJ}$  (spontaneous)

ii.)  $\Delta G^\circ = -92.22 - 273 \times (-198.75 \frac{\text{J}}{\text{K}}) \times 10^{-3}$

$\Delta G^\circ = 66.91 \text{ kJ}$  (not spontaneous)

(spontaneous in backward direction)

(iii)

$$\Delta G^\circ = 0$$

$$0 = -92.22 - T \left( -198.75 \frac{J}{K} \right) \times 10^{-3} \frac{kJ}{K}$$

$$T = 465.31 \text{ K}$$

## Thermodynamic Equilibrium :-

$\left[ \begin{array}{l} \text{Phase Eq}^n \\ \text{or} \\ \text{CR. Eq}^m \end{array} \right]$

$\rightarrow$  Mechanical Eq<sup>n</sup>  
 $\rightarrow$  Thermal Eq<sup>m</sup>  
 $\nwarrow$  Chemical Eq<sup>m</sup>

## Fundamental Properties Relation :-

P, V, T

S, U, A, h calculated variables.

$$dU = \delta Q - \delta W \quad | \text{ from 1st Law}$$

$$\delta Q = T dS$$

$$\delta W = P dV$$

| from 2nd Law.

$$dU = T dS - P dV \quad - (1)$$

$$U = U(S, V)$$

$$dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV \quad - (2)$$

Comparing & equating eq<sup>n</sup> (1) & (2)

$$T = \left( \frac{\partial U}{\partial S} \right)_V, \quad P = - \left( \frac{\partial U}{\partial V} \right)_S$$

## four thermodynamic Potential

U, H, A, h

$$H = U + PV$$

$$dH = dU + d(PV)$$

$$= dU + PdV + VdP$$

$$= (dU - PdV) + (PdV + VdP)$$

$$dH = TdS + VdP$$

$$dH = H(S, P)$$

$$= \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P$$

$$V = \left(\frac{\partial H}{\partial P}\right)_S$$

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

$$dA = (dU - PdV) - (TdS + SdT)$$

$$dA = -PdV - SdT$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$= TdS + VdP - TdS - SdT$$

$$\checkmark dG = VdP - SdT$$

Numeric diagram (schrodin)

		$\rightarrow -TS$
$\downarrow$	$U$	$A = U - TS$
$+PV$	$H = U + PV$	$G = U + PV - TS$

Spontaneous Process : — Irreversible + naturally

$$dG = VdP - SdT$$

for  $n$  moles,

$$d(nG) = (nV)dP - (nS)dT \quad (1)$$

single phase closed system.

\* Phase : — A system of material where its composition is uniform.

It is any space of matter which is chemically uniform, physically distinct & mechanically separable.

- Type →
- Solid
  - liquid
  - Gas
  - Plasma
  - Bose-Einstein Condensate
  - Degenerated gas
  - Super Critical fluid

for open system,

$$G = (P, T, n_A, n_B, n_C, \dots)$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n} dT + \left(\frac{\partial G}{\partial n_A}\right)_{T, P, n_i \neq A} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{T, P, n_i \neq B} dn_B + \dots$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_i \neq i} dn_i$$

$$dG = -s dT + v dP + \sum_i \mu_i dn_i$$

\*\*\*

$$d(nG) = -(ns) dT + (nv) dP + \sum_i \mu_i dn_i$$

$$dG = -s dT + v dP + \sum_i \mu_i \frac{dn_i}{n} \quad \left\{ \mu_i = \frac{n_i}{n} \right.$$

$$dG = -s dT + v dP + \sum_i \mu_i dn_i$$

⇒ for reversible process  $\Delta S_{universe} \Rightarrow \uparrow (>0)$

$$\Rightarrow G = H - TS$$

$$H = G + TS$$

$$H = G - T \left( \frac{\partial G}{\partial T} \right)_{P, n}$$

$$\Rightarrow \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P}$$

Generating function  $G = g(T, P, n_A, n_B, \dots)$

## Phase Equilibrium :-

for  $\alpha$  &  $\beta$

$$d(nG)^\alpha = (nV)^\alpha dP - (ns)^\alpha dT + \sum_i \mu_i^\alpha d\mu_i^\alpha \quad (1) \quad | \alpha \text{ is representing phase nt power}$$

$\boxed{\frac{\alpha}{\beta}}$

$$d(nG)^\beta = (nV)^\beta dP - (ns)^\beta dT + \sum_i \mu_i^\beta d\mu_i^\beta \quad (2)$$

$$\text{Eqn (1) + (2)}$$

$$d(nG) = (nV)dP - (ns)dT + \sum_i \mu_i^\alpha d\mu_i^\alpha + \sum_i \mu_i^\beta d\mu_i^\beta$$

thermodynamic

### At Equilibrium :-

$$d(nG) = 0, \quad dP = 0, \quad dT = 0$$

$$\sum_i \mu_i^\alpha d\mu_i^\alpha + \sum_i \mu_i^\beta d\mu_i^\beta = 0$$

$$n_i^t = n_i^\alpha + n_i^\beta$$

$$0 = dn_i^\alpha + dn_i^\beta$$

$$\boxed{dn_i^\alpha = -dn_i^\beta}$$

$$\sum ( \mu_i^\alpha - \mu_i^\beta ) dn_i^\alpha = 0$$

$$\mu_i^\alpha - \mu_i^\beta = 0$$

$$\boxed{\mu_i^\alpha = \mu_i^\beta}$$

|  $n_i^t$  is a constant value  
| of total no. of moles of  $i$  in  
|  $\alpha$  &  $\beta$  phase. So this diff. is  
| 0.0.

|  $dn_i^\alpha \neq 0$  bcz no. of moles  
| of any species can't be zero.

Chemical potential

## Partial Molar property :-

$$M^t = n^t \cdot M$$

$$\bar{M}_i = \left( \frac{\partial M^t}{\partial n_i} \right)_{A, B, L}$$

denotation:

Aug 29, 14

Partial Molar Properties :-Pure Substance

$$\Delta M^t = \Delta n_i \times M_i$$

change in molar property of i comp.  
mole.

Mixture

$$\Delta M^t \neq \Delta n_i \times \bar{M}_i$$

$$\Delta M^t = \Delta n_i \times \bar{M}_i$$

$$\bar{M}_i = \frac{\Delta M^t}{\Delta n_i}$$

$$\lim_{\Delta n_i \rightarrow 0}$$

$$\bar{M}_i = \left( \frac{\partial M^t}{\partial n_i} \right)_{P, T, n_i \neq i}$$

 $M_i$  = Molar prop. of i in pure substance $\bar{M}_i$  = Partial Molar prop. of i<sup>th</sup> in mixture.Denotationpure  $\rightarrow V_i, U_i, S_i, H_i, G_i$ Mixture  $\rightarrow \bar{V}_i, \bar{U}_i, \bar{S}_i, \bar{H}_i, \bar{G}_i$ Relation b/w partial molar property and Molar property of the solnPartial Molar property (PMP)  $\rightarrow$  Response funct<sup>n</sup>

measure of the response of the total M.P. w.r.t to change in moles of any component i.e.

$$M^t = M(P, T, n_A, n_B, n_C, \dots, n_i)$$

$$dM^t = \left( \frac{\partial M^t}{\partial P} \right)_{T, n} dP + \left( \frac{\partial M^t}{\partial T} \right)_{P, n} dT + \sum \left( \frac{\partial M^t}{\partial n_i} \right)_{T, P, n_A \neq i} dn_i$$

at constant T &amp; P.

1 mol  $H_2O$   
[water]

$$\rho = \frac{1g}{cc} = \frac{m \times n}{V} = \frac{18 \times 1}{V}$$

$$V = 18 \frac{cc}{mol}$$

$$V = 18 \frac{cc}{mol}, \frac{cm^3}{mol}$$

1 mol  $H_2O$   
[total]

$$V = 14 \frac{cc}{mol}$$

$$dM^t = \sum_{T, P, n_i \neq i} \left( \frac{\partial M^t}{\partial n_i} \right) dn_i$$

partial prop of M wrt i

$$dM^t = \sum_{i=1}^N \bar{M}_i \cdot dn_i$$

$$\Delta M^t = \bar{M}_1 dn_1 + \bar{M}_2 dn_2 + \bar{M}_3 dn_3 + \dots + \bar{M}_N dn_N$$

for Binary Mixtures :-

$$\Delta M^t = \bar{M}_1 dn_1 + \bar{M}_2 dn_2$$

for total property

$$M^t = \bar{M}_1 n_1 + \bar{M}_2 n_2$$

Molar prop.

$$M = \bar{M}_1 \frac{n_1}{n} + \bar{M}_2 \frac{n_2}{n} \quad \left. \begin{array}{l} M = M^t/n \end{array} \right\}$$

$$M = \bar{M}_1 x_1 + \bar{M}_2 x_2$$

$$M = \sum \bar{M}_i x_i$$

$$H = \sum \bar{H}_i x_i$$

$$U = \sum \bar{U}_i x_i$$

$$V = \sum \bar{V}_i x_i$$

$$M = \bar{M}_1 x_1 + \bar{M}_2 x_2$$

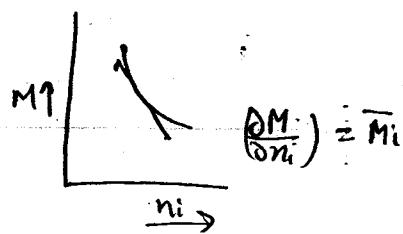
$$\frac{\partial M}{\partial x_1} = \frac{\partial}{\partial x_1} \{ \bar{M}_1 x_1 + \bar{M}_2 (1-x_1) \}$$

$$x_2 = 1-x_1$$

$$\frac{\partial M}{\partial x_1} = \bar{M}_1 - \bar{M}_2$$

$$\frac{\partial M}{\partial x_1} = x_1 \frac{\partial \bar{M}_1}{\partial x_1} + \bar{M}_1 \frac{\partial x_1}{\partial x_1} - \bar{M}_2$$

→ Graphically



→ Analytically

as we calculated above.

Sept 01, 14

Analytical Method.

$$M^t = nM$$

$$n = (n_1 + n_2)$$

$$\left( \frac{\partial M^t}{\partial n_1} \right)_{T, P, n_2} = \frac{\partial}{\partial n_1} [ (n_1 + n_2) M ]$$

$$\left( \frac{\partial M^t}{\partial n_1} \right) = M_1 = M \frac{\partial}{\partial n_1} (n_1 + n_2) + (n_1 + n_2) \frac{\partial M}{\partial n_1}$$

$$\boxed{M_1 = M + (n_1 + n_2) \frac{\partial M}{\partial n_1}}$$

$$\boxed{M_2 = M + (n_1 + n_2) \frac{\partial M}{\partial n_2}}$$

$$\chi_2 = \frac{n_2}{n_1 + n_2}$$

$$\frac{\partial \chi_2}{\partial n_1} = - \frac{n_2}{(n_1 + n_2)^2}$$

$$= - \frac{n_2}{(n_1 + n_2)}$$

$$\frac{\partial n_1}{(n_1 + n_2)} = - \frac{\partial \chi_2}{\chi_2}$$

$$\bar{M}_1 = M + \frac{\partial M}{\left(\frac{\partial x_2}{x_2}\right)}$$

$$\boxed{\bar{M}_1 = M - \bar{x}_2 \frac{\partial M}{\partial x_2}}$$

$$\bar{x}_1 + \bar{x}_2 = 1$$

$$\partial x_1 = \partial x_2$$

$$\boxed{\bar{M}_1 = M + (1-\bar{x}_1) \frac{\partial M}{\partial x_1}}$$

$$M = V, H, S, G$$

$$\boxed{\bar{M}_2 = M - \bar{x}_1 \frac{\partial M}{\partial x_1}}$$

$$\boxed{\bar{M}_2 = M + (1-\bar{x}_2) \frac{\partial M}{\partial x_2}}$$

Q) The molar vol<sup>m</sup> of binary mix is given as  $V = 220x_1 + 180x_2 + \bar{x}_1 \bar{x}_2 (90x_1 + 50x_2)$

Find out the part molar vol<sup>m</sup> of component 2 at  $x_2 = 0.3$ .

$$V = 220x_1 + 180x_2 + \bar{x}_1 \bar{x}_2 (90x_1 + 50x_2) \quad V = 212.34$$

$$= 220x_1 + 180x_2 + 9x_1^2x_2 + 50x_1x_2^2 \rightarrow$$

$$-x_1 (220 + 18x_1x_2 + 50x_2^2)$$

$$= 180x_2 + 9x_1^2x_2 + 50x_1x_2^2 - 18x_1^2x_2 \cancel{+ 50x_2^2x_1}$$

$$= 180x_2 - 9x_1^2x_2$$

$$= 180x_2$$

Q) <sup>2010</sup>  
 31)  $\delta$  of binary mix  $1+u_2$ , find out the sp. partial sp. vol<sup>m</sup> of component 2, at  $u_2=1$ .

$$\bar{V}_2|_{u_2=1} = ? \quad , \quad \bar{V}_1|_{u_2=1} = ?$$

$$V = \frac{1}{\delta}$$

$$V = \frac{1}{1+u_2}$$

$$\bar{V}_1 = V - u_2 \frac{\partial V}{\partial u_2}$$

$$= \frac{1}{1+u_2} - u_2 \left( -\frac{1}{(1+u_2)^2} \right)$$

$$= \frac{1}{1+u_2} + \frac{u_2}{(1+u_2)^2}$$

$$= \frac{1+u_2+u_2}{(1+u_2)^2} = \frac{1+2u_2}{1+u_2^2+2u_2} =$$

$$\bar{V}_1|_{u_2=1} = \frac{3}{4}$$

$$\bar{V}_2|_{u_2=1} = V - u_1 \frac{\partial V}{\partial u_1}$$

$$= \frac{1}{1+u_2} +$$

$$= \frac{1}{2}$$

Q) At 300 ~~temp~~ K, 1 bar, The volumetric data of 4g mix of  $C_6H_6$  &  $\text{C}_2H_2$  are given as  $V = 109.4 \times 10^{-6} - 16.8 \times 10^{-6}x - 2.64 \times 10^{-6}x^2$  where  $x$  is the mole fraction of  $C_6H_6$ . What is the partial molar volume of  $C_6H_6$  at  $x=0.4$

$$V_i = 109.4 \times 10^{-6} - 16.8 \times 10^{-6}x - 2.64 \times 10^{-6}x^2$$

$$V_i = V + (1-x) \frac{\partial V}{\partial x}$$

$x_1$  = mole of  $C_6H_6$

$$= 109.4 \times 10^{-6} - 16.8 \times 10^{-6}(0.4) - 2.64 \times 10^{-6}(0.4)^2$$

$$+ (1-0.4) \left( -16.8 \times 10^{-6} - 2 \times 2.64 \times 10^{-6}(0.4) \right)$$

$$= 109.4 \times 10^{-6} - 6.72 \times 10^{-6} - 0.4224 \times 10^{-6}$$

$$= 10.08 \times 10^{-6} - 1.2672 \times 10^{-6}$$

$$= 90.91 \times 10^{-6}$$

Q) The molar enthalpy of binary soln  $H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)$   
find the  $\bar{H}_i$  at  $x_2 = 0.7$ .

$$\text{Ans} = 415.6$$

$$\bar{H}_i = H - x_2 \frac{\partial H}{\partial x_2}$$

$$\begin{cases} 400x_1 \\ 400x_2 \end{cases}$$

$$= 400x_1(1-x_2)$$

$$= 400 \times 0.3 + 600 \times 0.7 + (0.7 \times 0.3)(40 \times 0.3 + 20 \times 0.7)$$

$$= 0.7(600 + 40 \times 0.3)^2 + 2 \times 20(0.3 \times 0.7)$$

$$= 120 + 420 + 0.7(5.46) - 0.7(4.28) \quad \text{Ans} = 428.4$$

$$= 117.06$$

$$H = U + PV$$

$$H = \bar{U} + \bar{P}V$$

$$\rightarrow \bar{P}V \text{ dyami}$$

\* Chemical Potential ( $\mu_i$ ):—

$$\mu_i = \left( \frac{\partial U^t}{\partial n_i} \right)_{T, P, n_i \neq i}$$

$$dG = VdP - SdT + \sum \mu_i dn_i$$

$$dG^t = V^t dP - S^t dT + \sum \mu_i dn_i$$

At const T & P,

~~$$dG = \sum_{i=1}^N \mu_i dn_i$$~~

$$dG = \sum \left( \frac{\partial G^t}{\partial n_i} \right)_{T, P, n_i \neq i} dn_i$$

$$\mu_i = \left( \frac{\partial G^t}{\partial n_i} \right)_{T, P, n_i \neq i}$$

Effect of Temp on  $\mu_i$ :—

$$\frac{\partial \mu_i}{\partial T} = \left( \frac{\partial^2 G^t}{\partial T \partial n_i} \right)_{P, n_i \neq i}$$

$$dG^t = V^t dP - S^t dT$$

$$\left( \frac{\partial G^t}{\partial T} \right)_{P, n} = -S^t$$

$$\left( \frac{\partial G^t}{\partial P} \right)_{T, n} = V^t$$

$$\frac{\partial G^t}{\partial T} = -S^t$$

$$\frac{\partial^2 G}{\partial n_i \partial T} = -\frac{\partial S^t}{\partial n_i} = -\bar{s}_i$$

$$\boxed{\frac{\partial \mu_i}{\partial T} = -\left(\frac{\partial S^t}{\partial n_i}\right)_p = -\bar{s}_i}$$

### Effect of pressure on chemical potential

$$\frac{\partial \mu_i}{\partial P} = \left(\frac{\partial^2 G^t}{\partial P \partial n_i}\right)_{T, n_i \neq i}$$

$$dG^t = V^t dP - S^t dT$$

$$\left(\frac{\partial G^t}{\partial P}\right)_{T, n} = V^t$$

$$\frac{\partial^2 G^t}{\partial n_i \partial P} = \frac{\partial V^t}{\partial n_i} = +\bar{v}_i$$

$$\boxed{\left(\frac{\partial \mu_i}{\partial P}\right)_{T, n} = \bar{v}_i}$$

Sep 02, 14

Ideal gas :-

There is no interaction btw molecules.

Real gas :-

Molecular interaction is there but behaves as ideal at low & high T

\* Fugacity ( $f$ ) :-

comes from latin word 'fleethess'  $\rightarrow$  'escaping tendency'

$$dG = VdP - SdT$$

at isothermal condition

$$dG = VdP$$

$$dG = \frac{RT}{P} \cdot dP$$

$$V = \frac{RT}{P} \quad \begin{matrix} \text{for ideal gas} \\ \text{for 1 mol} \end{matrix}$$

Ideal gas

$$dG = RT d(\ln P)$$

$$d(\ln x) = \frac{1}{x} dx$$

Real gas

$$dG = RT d(\ln f)$$

$f = P$  for ideal gas  
 $f = \text{ext pressure exerted in case of real gas}$

Ideal gas

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} RT d(\ln P)$$

$$\Delta G = G_2 - G_1 = RT \ln \left( \frac{P_2}{P_1} \right)$$

Real gas

$$\Delta G = G_2 - G_1 = RT \ln \left( \frac{f_2}{f_1} \right)$$

by equating above eqns

$$\frac{f_2}{f_1} = \frac{P_2}{P_1}$$

$$f \propto p$$

for ideal gases  $c_i = 1$   
 $\rightarrow f = c p$

$$f = p$$

$$\boxed{\frac{f}{p} = 1}$$

$$\Delta G_f = RT \ln(f_2/f_1)$$

Standard state, for fugacity

low pressure  $p^0$

$$f^0 = p^0$$

$$\boxed{G - G^0 = RT \ln(f/f_0)}$$

at this  
time ideal gas

$$p^0 \rightarrow 0$$

$$\frac{f}{p} = 1$$

$p \uparrow$  from 0

$$f \uparrow$$

$$\boxed{f \neq p}$$

Real condition  
exist

Fugacity Coefficient ( $\phi$ ) :-

$\phi = \frac{\text{fugacity of the gas}}{\text{p}^0 \text{ of the ideal gas}}$  at same T

$$\boxed{\phi = \frac{f}{p}}$$

$$\boxed{f = \phi \cdot p}$$

$p \rightarrow 0$	$p^* \uparrow$	
$f \rightarrow p$	$f \uparrow$	$f < p$
$\phi \rightarrow 1$	$\phi \rightarrow 0$	$f/p$
real gas is approaching towards ideality.		gas is far away from ideality.

$$\Delta G = RT \ln (f/f^*)$$

1 if  $p^* \rightarrow 0$

$$f^* = p^*$$

$$\Delta G = RT \ln (f/p^*)$$

$$\left. \begin{array}{l} \ln (1/p^*) \\ \ln (f^*) \\ \ln \infty \end{array} \right\}$$

$$\boxed{\Delta G = -\infty}$$

\* Calculations for fugacity :- (using compressibility factor)<sup>(2)</sup>

$$dG = Vdp$$

$$dG = RT d(\ln f)$$

$$RT d(\ln f) = Vdp$$

$$d(\ln f) = \frac{V}{RT} dp$$

### Real gases

$$Z = \frac{\text{Vol. of real gas}}{\text{Vol. of ideal gas}}$$

$$Z = \frac{V}{RT/p}$$

$$\begin{array}{l} PV = R \\ V = RT/p \end{array}$$

$$PV = ZRT$$

$$\frac{V}{RT} = \frac{Z}{P}$$

$$d(\ln f) = \frac{2}{P} dP$$

Subtracting

$$\frac{dP}{P} \text{ on both sides.}$$

$$d(\ln f) - \frac{dP}{P} = \frac{2}{P} dP - \frac{dP}{P}$$

$$d(\ln f) - d(\ln P) = \left(\frac{2-1}{P}\right) dP$$

$$d(\ln f/P) = \frac{2-1}{P} dP$$

$$\int d(\ln f/P) = \int_0^P \frac{(2-1)}{P} dP$$

$$\ln(f/P) = \int_0^P \frac{(2-1)}{P} dP$$

$$\ln \phi = \int_0^P \frac{(2-1)}{P} dP$$

Molar

\* Calculating fugacity using Residual Volume ( $\alpha$ ) :-

$\alpha = \text{Vol. of gas} - \text{Vol. occupied by ideal gas.}$

$$\alpha = V - \frac{RT}{P}$$

$$V = \alpha + \frac{RT}{P}$$

$$dG = V dP$$

$$dG = RT d(\ln f)$$

$$d(\ln f) = \frac{V}{RT} dP$$

$$d(\ln f) = \frac{1}{RT} \left[ \alpha + \frac{RT}{P} \right] dP$$

$$d \ln f = \frac{\alpha}{RT} dp + \frac{1}{p} dp$$

$$d \ln f = \frac{\alpha}{RT} dp + d \ln p$$

$$\int d \ln (f/p) = \int_0^p \frac{\alpha}{RT} dp$$

$$\ln (f/p) = \int_0^p \frac{\alpha}{RT} dp$$

$$\boxed{\int_0^p \alpha \cdot dp = RT \ln (f/p)}$$

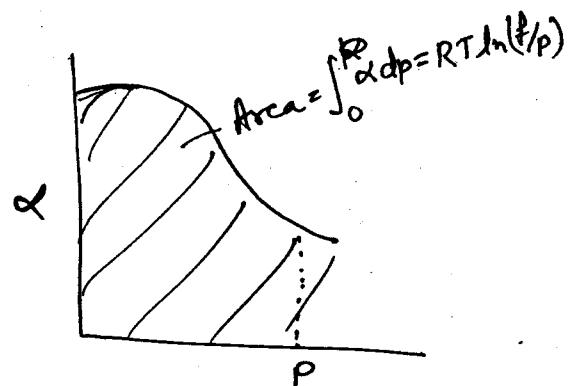
$$\alpha = V - \frac{RT}{p}$$

$$= \frac{ZRT}{p} - \frac{RT}{p}$$

$$\alpha = (Z-1) \frac{RT}{p}$$

as  $p \uparrow$ ,  $Z \rightarrow \text{low}$

$p \downarrow$ ,  $Z \rightarrow \text{high}$



Q) From the PVT data for a gas it is found that

$\int_0^{50} \alpha dp = -556.61 \text{ J/mol}$  • Find the fugacity at 50 bar and 300 K

$$RT \ln (f/p) = -556.61$$

$$\frac{8.314 \times 300}{\text{check!}} (\ln f - \ln 50) = -556.61$$

$$f = 40.62 \text{ bar}$$

\* Calculation using enthalpy and entropy of the system:-

$$\int_{G_0}^G dG = \int_{T_0}^T RT d(\ln f)$$

$$G_f - G_0 = RT \ln(f/f_0)$$

$$G_f = H - TS$$

$$G_0 = H^0 - TS^0$$

$$(H - TS) - (H^0 - TS^0) = RT \ln(f/f_0)$$

$$\ln(f/f_0) = \frac{(H - H^0)}{RT} - \frac{(S^0 - S)}{R}$$

$$\begin{cases} f^0 = p^0 \\ f = p \cdot p \end{cases}$$

Q) Determine the fugacity & fugacity coeff. of steam at 623K & 1000 kPa pressure using enthalpy and entropy data from steam tables. Assume steam behaves ideally at 101.3 kPa

Data:

$$\text{at } 1000 \text{ kPa, } 623 \text{ K, } H = 3159 \text{ kJ/kg}$$

$$S = 7.3 \text{ kJ/kg K}$$

$$\text{at } 101.3 \text{ kPa, } 623 \text{ K, } H = 3176 \text{ kJ/kg}$$

$$S = 8.38 \text{ kJ/kg K}$$

$$p^0 = 101.3 \text{ kPa} = f^0$$

$$H^0 = 3176 \text{ kJ/kg}$$

$$S^0 = 8.38 \text{ kJ/kg}$$

$$H = 3159 \text{ kJ/kg}$$

$$S = 7.3 \text{ kJ/kg K}$$

$$R = 8.314 \frac{\text{kJ}}{\text{kmol K}} = 8.314 \times \frac{1}{18 \text{ kg}} = 0.4618 \frac{\text{kJ}}{\text{kg K}}$$

$$\ln\left(\frac{f}{f^0}\right) = 0.8753$$

$$\frac{\phi p^0}{p}$$

$$1 - 8.663$$

$$(H - H^\circ) - T(S - S^\circ) = RT \ln(\frac{f}{f^\circ})$$

$$(3159 - 3176) - 623 \times (7.3 - 8.38) = 0.4618 \times 623 \times \ln(\frac{f}{f^\circ})$$

$$\ln(\frac{f}{f^\circ}) = 2.279$$

$$\frac{f}{f^\circ} = 9.76$$

$$f = 989.58 \text{ kPa}$$

$$\phi = \frac{f}{P} = \frac{989.58}{1000} \text{ kPa}$$

$$\phi = 0.98958$$

$\text{Ans}$

\*  $G - G^\circ = RT \ln(\frac{f}{f^\circ})$

$$G = G^\circ + RT \ln(\frac{f}{f^\circ})$$

$$f = \phi P$$

$$f^\circ = P^\circ$$

$$G = G^\circ + RT \ln\left(\frac{\phi P}{P^\circ}\right)$$

$$G = G^\circ + RT \ln\left(\frac{P}{P^\circ}\right) + RT \ln \phi$$

$$G - G^\circ = RT \ln\left(\frac{P}{P^\circ}\right) + RT \ln \phi$$

Change in  
Gibbs free  
Energy for  
real gas

= Change in Gibbs  
free energy for  
ideal gas +  $RT \ln \phi$

↓  
Due to Intermolecular forces.

$$RT \ln \phi \approx 0$$

$$\phi = 1, f = P$$

$\Rightarrow * \phi < 1$

$$\boxed{\Delta G^{\text{real}} < \Delta G^{\text{ideal}}}$$

$p \rightarrow 0, \phi \rightarrow 1, \text{ real gas} \rightarrow \text{ideality.}$

$p \rightarrow \infty, \phi \rightarrow 0, \text{ real gas far away from ideality.}$

Sep 03, 14

Effect of temp and pressure on fugacity:-

Temp

$$\ln \left( \frac{f}{f^{\circ}} \right) = \frac{G}{RT} - \frac{G^{\circ}}{RT}$$

$$\frac{\partial}{\partial T} \left( \ln \left( \frac{f}{f^{\circ}} \right) \right) = \left[ \frac{\partial}{\partial T} \left( \frac{G}{RT} \right) - \frac{\partial}{\partial T} \left( \frac{G^{\circ}}{RT} \right) \right]$$

$$= \frac{1}{R} \left[ \frac{\partial}{\partial T} \left( \frac{G}{T} \right) - \frac{\partial}{\partial T} \left( \frac{G^{\circ}}{T} \right) \right]$$

$$\begin{aligned} & \frac{\partial G}{\partial T} \left( \frac{1}{T} \right) \\ &= T \left( \frac{\partial G}{\partial T} \right)_{P, n} - G \cdot 1 \\ &= \frac{T \left( \frac{\partial G}{\partial T} \right)_{P, n} - G}{T^2} \end{aligned}$$

$$\frac{\partial}{\partial T} \left( \ln f - \ln f^{\circ} \right) = \frac{1}{R} \left[ -\frac{H}{T^2} + \frac{H^{\circ}}{T^2} \right]$$

$$= \frac{T(-S) - G}{T^2}$$

$$= -\frac{G - TS}{T^2}$$

$$= -\frac{(G + TS)}{T^2}$$

$$= -\frac{H}{T^2}$$

$$\frac{\partial}{\partial T} (\ln f) - \frac{\partial}{\partial T} (\ln f^{\circ}) = "$$

$$\boxed{\frac{\partial}{\partial T} (\ln f) = \frac{H^{\circ} - H}{RT^2}}$$

$T \uparrow, H \uparrow$

$(H^{\circ} - H) \downarrow \Rightarrow f \downarrow$

$f^{\circ} = \text{fugacity at std}$   
 $\text{std} \rightarrow \text{Const} \rightarrow 0.$

Press.

at const  $T, n$

$$dG = Vdp$$

$$dG = RTd(\ln f)$$

$$RTd(\ln f) = Vdp$$

$$\boxed{\frac{d(\ln f)}{dp} = \frac{V}{RT}}$$

## Fugacity in Solids & Liquids:-

$$\Delta G_f = 0$$

$$G_f^s - G_f^v = 0$$

$$G_f^s = G_f^v$$

$$\Delta G_f = G_f^s - G_f^v = RT \ln \left( \frac{f^s}{f^v} \right) = 0$$

At equilibrium,

$$G_f^s - G_f^v = RT \ln \left( \frac{f^s}{f^v} \right) = 0$$

$$\frac{f^s}{f^v} = 1$$

$$f^s = f^v$$

for liquids

$$f^L = f^v$$

## Calculation of fugacity in Solids & Liquids:-

$$f^v = \text{At low V.P}$$

at equilibrium,  $p = p^v$

$p \rightarrow \text{low press}$

System behave ideally.

$$p = p^v$$

$$p^v = \text{low}$$

at equilibrium

$$f^v = p^v = f^L$$

\* If V.P is high

$$RT d \ln f = V dP$$

$$\int_{f^s}^f d(\ln f) = \int_{P^s}^P \frac{V}{RT} dP$$

$$\ln\left(\frac{f}{f^s}\right) = \frac{V}{RT} (P - P^s)$$

} for ideal soln

Q) Calculate the fugacity of liquid water at 303K and 10 bar, If the saturation press at 303K is 4.241 kPa, and sp. vol<sup>m</sup> of liquid water at 303K is  $1.004 \times 10^{-3} \text{ m}^3/\text{kg}$ .

$$\ln\left(\frac{f}{4.241}\right) = \frac{1.004 \times 10^{-3}}{0.4618 \times 303} (1000 - 4.241)$$

$$\begin{aligned} 1 \text{ bar} &= 10^5 \text{ Pa} \\ &\approx 100 \text{ kPa} \end{aligned}$$

$$f =$$

\* Activity (a)  
(Relative fugacity)

ratio of fugacity to the fugacity in std. state for pure sub.

$$\alpha_{ij} = \frac{f_i}{f_{i^s}}$$

$$\Delta G = RT \ln(f/f^s)$$

$$\Delta G = RT \ln \alpha$$

Effect of temp :-

$$\Delta G = G - G^{\circ} = RT \ln(f/f^{\circ})$$

$$G - G^{\circ} = RT \ln \alpha$$

$$\frac{\partial \ln \alpha}{\partial T} = \frac{H^{\circ} - H}{RT^2}$$

### Effect of pressure :-

$$\frac{\partial \ln a}{\partial T} =$$

$$\Delta G = RT \ln a \approx V \Delta P$$

$$RT \frac{\partial(\ln a)}{\partial P} = V \Delta P$$

$$\boxed{\frac{\partial(\ln a)}{\partial P} = \frac{V}{RT}}$$

$$dG = \int_{P_0}^P RT d\ln a = \int_{P_0}^P V dP$$

$$RT \ln \frac{P}{P_0} \approx V(P - P_0) \quad \text{for ideal soln, } V \text{ constant}$$

$$\boxed{\ln a = \frac{V}{RT} (P - P_0)}$$

Q.) Determine the activity of solid ~~maximum~~ solid magnesium at 300K & 10 bar. If the ref. state is 300K & 1 bar. The density of Mg at 300K is  $1.745 \times 10^3 \text{ kg/m}^3$  and is assumed to be independent of ext. press. (M.W Mg = 24.22)

$$\ln a = \frac{24.22}{1.745 \times 10^3 \times 8.314 \times 300} (1000 - 100)$$

$$a = 1.00502 \approx$$

### \* fugacity in Solutions :-

$$dG = RT d\ln f$$

for pure soln

for real

$$d\bar{G} = RT d\ln \hat{f}$$

$$\hat{f}_i \neq \left( \frac{\partial \ln f}{\partial n_i} \right)$$

for any compn, in the soln

$$\hat{f} = \text{fugacity in soln}$$

$$d\bar{G}_i = RT d\ln \hat{f}_i$$

$$d\mu_i = RT d(\ln \bar{f}_i)$$

for real soln

723

$\bar{f}_i$  = fugacity of (i) in pure soln

$\bar{f}_i$  = " " " " real mixtures.

$$da = Vdp$$

for const T.

$$d\bar{f}_i = Vd\bar{P}_i$$

$$d\mu_i = Vd\bar{P}_i$$

for only ideal soln)

$$d\mu_i = RT d\ln \hat{f}_i$$

for both ideal & real soln

$$RT d\ln \hat{f}_i = Vd\bar{P}_i$$

$$d\ln \hat{f}_i = \frac{V}{RT} d\bar{P}_i$$

$$\int d\ln \hat{f}_i = \int_0^P \frac{V}{RT} d\bar{P}_i$$

$$\ln \hat{f}_i = \frac{1}{RT} \int_0^P Vd\bar{P}_i$$

$$\bar{P}_i = y_i P$$

$$d\bar{P}_i = P dy_i$$

$$\ln \hat{f}_i = \frac{1}{RT} \int_0^1 V \cdot P dy_i$$

$$\ln \hat{f}_i = \frac{P}{RT} \int_0^1 V dy_i$$

$$d\mu_i = RT d(\ln \hat{f}_i)$$

$$d\mu_i = Vd\bar{P}_i$$

$$RT d(\ln \hat{f}_i) = Vd\bar{P}_i$$

$$d\ln \hat{f}_i = \frac{V}{RT} d\bar{P}_i$$

Subtracting  $d(\ln P)$  BS

$$d\ln \left( \frac{\hat{f}_i}{P} \right) = \frac{V}{RT} d\bar{P}_i - d\ln P$$

$$\begin{aligned}
 d \ln \left( \frac{\hat{f}_i}{p} \right) &= \frac{V}{RT} [pd y_i + y_i dp] - d \ln p \\
 &= \frac{Vb}{RT} dy_i + \frac{V \cdot y_i}{RT} dp - \frac{dp}{p}
 \end{aligned}$$

$$\begin{cases} \hat{b}_i = y_i \cdot p \\ d \hat{p}_i = pd y_i + y_i dp \end{cases}$$

$$d \ln p = \frac{dp}{p}$$

$$d \ln \left( \frac{\hat{f}_i}{p} \right) = \frac{PV}{RT} dy_i + \left( \frac{V y_i}{RT} - \frac{1}{p} \right) dp$$

for constant composition  $dy_i = 0$

$$d \ln \left( \frac{\hat{f}_i}{p} \right) = \left( \frac{V \cdot y_i}{RT} - \frac{1}{p} \right) dp$$

$$\ln \left( \frac{\hat{f}_i}{p} \right) = \int_0^p \left( \frac{V \cdot y_i}{RT} - \frac{1}{p} \right) dp$$

Sep 04, 14

$$\int d \ln \left( \frac{\hat{f}_i}{p} \right) = \int_0^p \left( \frac{V \cdot y_i}{RT} - \frac{1}{p} \right) dp$$

$$\int d \ln \left( \frac{\hat{f}_i}{p} \right) = \frac{1}{RT} \int_0^p \left( V_i - \frac{RT}{p} \right) dp$$

$$\bar{p}_i = y_i \cdot p$$

$$p \Rightarrow \bar{p}_i / y_i$$

$$\int d \ln \left[ \frac{y_i \hat{f}_i}{\bar{p}_i} \right] = \frac{1}{RT} \int_0^p \left( V_i - \frac{RT}{p} \right) dp$$

$$d \ln y + d \ln \left( \frac{\hat{f}_i}{\bar{p}_i} \right) =$$

$$\int d \ln \left( \frac{\hat{f}_i}{\bar{p}_i} \right) = \frac{1}{RT} \int_0^p \left( V_i - \frac{RT}{p} \right) dp$$

$$\ln \left( \frac{\hat{f}_i}{\bar{p}_i} \right) = \frac{1}{RT} \int_0^p \left( V_i - \frac{RT}{p} \right) dp$$

for ideal mixture

$$PV^t = n^t RT$$

$$\therefore n^t = \sum n_i$$

$$\frac{\partial V^t}{\partial n_i} = \left( \frac{RT}{P} \right)_{n_i \neq 1}$$

$$\therefore PV^t = (n_1 + n_2) RT$$

$$\frac{\partial V^t}{\partial n_i} = \frac{RT}{P}$$

$$V_t = \frac{RT}{P}$$

for pure mixture,  $V_t = V_i$

for ideal pure mixture,

$$V_t = \frac{RT}{P}$$

$$\ln(f_i/p_i) = 0$$

$$f_i = p_i$$

fugacity of 'i' in mixture = partial p. of 'i' for ideal mixture.

\* Lewis Randall Model :-

It state that fugacity of a component in an ideal solution is directly proportional to molar fraction of the component in the solution.

$$\hat{f}_i \propto x_i$$

for liq.

$$\hat{f}_i = x_i f_i$$

$\hat{f}_i$  = fugacity of 'i' in ideal solution.

$x_i$  = mol fract<sup>n</sup> of 'i' in the sol<sup>n</sup>

$f_i$  = fugacity of 'i' in pure state.

### Validity :-

- ⇒ At low pressures,
- ⇒ Component concentration is present in excess.
- ⇒ When phys. prop. of all components are nearly same.

### Limitation :-

- ⇒ At high pressure, it is not valid.
- ⇒ <sup>Valid</sup> Only for the gaseous mixtures at low pressures
- ⇒ Not valid for all the liquid mixt.

### For liquids

#### Raoult's law :-

##### \* Ideal soln

- ⇒ PMP, of the soln is equal to Molar prop. of the soln.
- ⇒ When there is no intermolecular interaction b/w the molecules.
- ⇒ When there is no volume change, when components mixed together

$$\bar{V}_i = V_i$$

$$\bar{f}_i = x_i f_i$$

for ideal soln,  $\bar{f}_i = \bar{p}_i$

$$f_i = p_i^s$$

$$\bar{p}_i = x_i p_i^s$$

Raoult's law

#### Valid

- ⇒ Ideal soln
- ⇒ Variation from ideality

The partial pr. of the Component in the ideal sol<sup>n</sup> is directly proportional to mole fraction in the liquid sol<sup>n</sup>.

$$\bar{p}_i = y_i p$$

$$\bar{p}_i = y_i p = \kappa_i p_i$$

Valid for concentrated solutions.

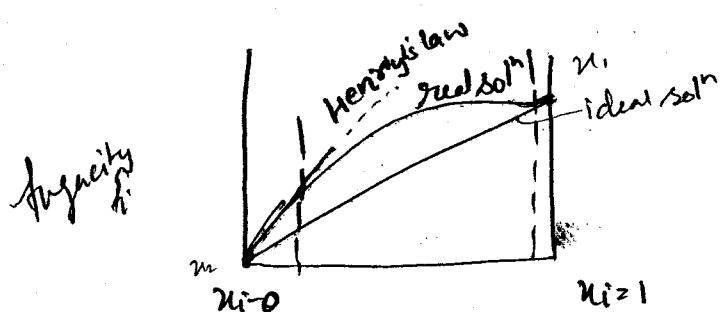
Henry's Law:-

$$\bar{p}_i \propto x_i$$

for dilute ideal sol<sup>n</sup> the fugacity of component is directly proportional to the mole fraction of the component in the sol<sup>n</sup>.

$$\bar{f}_i \propto x_i$$

$$\bar{f}_i = \kappa_i f_i$$



for the case  
it becomes  
ideal.

$$\text{if } x_1 \rightarrow 1, \quad \bar{f}_1 = 1 \quad \text{& in ideal soln, } \bar{f}_1 = 1$$

$$\text{if } x_1 \rightarrow 0, \quad \bar{f}_1 = 1 \quad \bar{f}_1 = 1$$

for dilute sol<sup>n</sup>

$$\bar{f}_i = \kappa_i f_i \text{ for } x_i \rightarrow 0$$

$$\text{for } x_i \rightarrow 1$$

$$\bar{f}_i = x_i f_i$$

at  $\bar{x}_i = 1$

→ Lewis - Randall Rule  
(Raoult's law)

$$\bar{f}_i = f_i$$

4R

$$\hat{f}_i = \bar{n}_i f_i$$

Raoult's Law

$$\hat{P}_i = \bar{n}_i P_i^s$$

Henry's Law

$$\hat{f}_i = \bar{n}_i H_i$$

### \* Activity in Solutions:-

Ratio of comp fugacity of the component in solution to the fugacity of component in the std. state.

$$a_i = \frac{\hat{f}_i}{f_i^0}$$

$$\int_{M_i^0}^{M_i} dM_i = \int_{f_i^0}^{\hat{f}_i} R + d(\ln \hat{f}_i)$$

$$\Rightarrow M_i = M_i^0 + RT \ln \left( \frac{\hat{f}_i}{f_i^0} \right)$$

$$M_i = M_i^0 + RT \ln a_i$$

$$a_i = \frac{\hat{f}_i}{f_i^0}$$

for ideal soln

$$\hat{f}_i = \bar{n}_i f_i$$

$$f_i = f_i^0$$

$$a_i = \bar{n}_i$$

for real sol<sup>n</sup>

$$\hat{f}_i \neq f_i^0$$

$$a_i \propto x_i$$

$$a_i = \gamma_i x_i$$

$\gamma_i$  = Activity coefficient.

$1 +$  indicates the extent to which sol<sup>n</sup> is non-ideal.

for real sol<sup>n</sup>

$$\hat{f}_i = \gamma_i x_i f_i$$

\* for ideal sol<sup>n</sup>

$$\gamma_i = 1$$

i.e.

$$If \quad x_i \rightarrow 1, \quad \gamma_i \rightarrow 1$$

$$x_i \rightarrow 0, \quad x_j \rightarrow 1, \quad \gamma_j \rightarrow 1$$

\* Effect of <sup>Temp.</sup> Pressure of  $\gamma_i$

$$\frac{\partial \ln \hat{f}_i}{\partial T} = \frac{H_i^0 - \bar{H}_i}{RT^2} \quad (1)$$

$$\frac{\partial \ln \hat{f}_i}{\partial T} = \frac{\bar{H}_i^0 - \bar{H}_i}{RT^2} \quad (2)$$

$$\hat{f}_i = \gamma_i \cdot x_i \cdot f_i$$

$$eq^n (2) - (1)$$

$$\frac{\partial}{\partial T} \ln \left( \frac{\hat{f}_i}{f_i} \right) = \frac{\bar{H}_i^0 - \bar{H}_i}{RT^2} - \frac{H_i^0 - \bar{H}_i}{RT^2}$$

$$\frac{\partial}{\partial T} \ln (Y_i \cdot x_i) = \frac{(\bar{H}_i^0 - \bar{H}_i)}{RT^2} - \frac{(H_i^0 - \bar{H}_i)}{RT^2}$$

$$\frac{\partial}{\partial T} \ln (Y_i x_i) = \frac{\bar{H}_i - H_i}{RT^2}$$

## \* Gibbs Duhem Equation

$$\sum_{i=1}^N n_i \cdot \bar{M}_i = 0$$

$$M^t = \sum n_i \bar{M}_i \quad (1)$$

$$M^t = M(T, P, n_1, n_2, \dots, n_i)$$

$$dM^t = \left(\frac{\partial M^t}{\partial T}\right)_{P,n} dT + \left(\frac{\partial M^t}{\partial P}\right)_{T,n} dP + \sum_{i=1}^N \left(\frac{\partial M^t}{\partial n_i}\right)_{T,P,n_i \neq i} dn_i$$

at constant T & P,

$$dM^t = \sum \bar{M}_i dn_i \quad (2) \quad \because \bar{M}_i = \frac{\partial M^t}{\partial n_i}$$

$$\text{from } dM^t = \sum \bar{M}_i \cdot dn_i + \sum n_i d\bar{M}_i \quad (3)$$

from eq (2) & (3),

$$\sum \bar{M}_i dn_i = \sum n_i d\bar{M}_i + \sum \bar{M}_i \cdot dn_i$$

$$\Rightarrow \sum n_i d\bar{M}_i = 0$$

General form of Gibbs Duhem eqn

$$\sum n_i d\bar{G}_i = 0$$

$$\sum n_i d\bar{M}_i = 0$$

for Binary Mixture

$$n_1 d\bar{M}_1 + n_2 d\bar{M}_2 = 0$$

$$n_1 d\bar{M}_1 = -n_2 d\bar{M}_2$$

$$n_1 d\bar{M}_1 = -n_2 d\bar{M}_2$$

$$n_1 \frac{d\bar{M}_1}{dn_1} = -n_2 \frac{d\bar{M}_2}{dn_2}$$

$$n_1 + n_2 = 1$$

$$dn_1 = -dn_2$$

$$x_1 \frac{d\mu_1}{dx_1} = x_2 \frac{d\mu_2}{dx_2}$$

$$x_1 \frac{d\mu_1}{dx_1} - x_2 \frac{d\mu_2}{dx_2} = 0$$

$$x_1 \frac{\partial \bar{V}_1}{\partial x_1} - x_2 \frac{\partial \bar{V}_2}{\partial x_2} = 0$$

$$x_1 \frac{d \ln \bar{f}_1}{dx_1} - x_2 \frac{d \ln \bar{f}_2}{dx_2} = 0$$

$$\checkmark x_1 \frac{d \ln \gamma_1}{dx_1} - x_2 \frac{d \ln \gamma_2}{dx_2} = 0$$

2009. 29

Q. > ~~P~~

$$\ln \gamma_2 = (1-x_2)^2$$

$$\ln \gamma_1 = ?$$

$$x_1 \frac{d \ln \gamma_1}{dx_1} - x_2 \frac{(2(1-x_2) \times (-1))}{(1-x_2)^2} = 0$$

$$\frac{d \ln \gamma_1}{dx_1} = \frac{2x_2 - 2x_2^2}{x_1}$$

$$\begin{aligned} d \ln \gamma_1 &= 2x_2(1-x_2) dx_1 \\ &= \frac{2(1-x_1)(x_1)}{x_1} dx_1 \\ &= \frac{2(x_1 - x_1^2)}{x_1} dx_1 \end{aligned}$$

= -

$$= -x_1(2-x_1)$$

Sep 08, 14

Q) For a binary mixture at constant temp & press. Which 1 of the following reln b/w activity coeff  $\gamma_i$  and mole fraction  $x_i$  is thermodynamically consistent.

a)  $\ln \gamma_1 = -1 + 2x_1 - x_1^2$ ,  $\ln \gamma_2 = \frac{1}{2}x_1^2$

~~b)~~ " ,  $\ln \gamma_2 = -x_1^2$

c) " ,  $\ln \gamma_2 = -\frac{1}{2}x_1^2$

d) " ,  $\ln \gamma_2 = x_1^2$

$$x_1 \frac{\partial \ln \gamma_1}{\partial x_1} = x_2 \frac{\partial \ln \gamma_2}{\partial x_2}$$

$$\Rightarrow \frac{\partial}{\partial x_1} (-1 + 2x_1 - x_1^2)$$

$$\Rightarrow x_1(2 - 2x_1) \Rightarrow 2(1 - x_1)$$

$$\cancel{\Rightarrow 2x_1 - 2x_1^2}$$

$$= -2x_1(x_1 - 1) \cancel{\frac{2x_1(1 - x_1)}{(1 - x_1)}}$$

$$\cancel{2(x_1 - x_2)}$$

$$x_1 \frac{\partial \ln \gamma_2}{\partial x_1} = 2x_2 x_1 = x_2 \frac{\partial \ln \gamma_2}{\partial x_2}$$

$$\ln \gamma_2 = 2 \left[ x_2 - \frac{x_2^2}{2} \right] = 2 \left[ 1 - x_1 - \frac{1 - x_1^2 + 2x_1}{2} \right]$$

$$\cancel{\geq 2x_2 + -\frac{x_2^2}{2}}$$

$$\cancel{= 2 \left[ 2 - \frac{2x_1 - 1 - x_1^2 + 2x_1}{2} \right]} = (1 - x_1^2)$$

$$2x_1 = \frac{\partial \ln \gamma_2}{\partial x_1}$$

$$-2x_1 \partial x_1 = \partial \ln \gamma_2$$

$$\boxed{\ln \gamma_2 = -x_1^2 + C}$$

$$x_2 \rightarrow 1$$

$$\gamma_2 \rightarrow 1$$

$$\ln \gamma_2 = -x_1^2$$

$$\ln \gamma_2 = 0 \Rightarrow C = 0$$

Q) In a binary mix,  $\gamma_1$  for the entire range of composition is given by  $R \ln \gamma_1 = Ax_1^2 + Bx_2^2$  where  $A$  &  $B$  are arbitrary const. Define exp. for  $\ln \gamma_2$  =

$$\frac{1}{R}(A+B)(1-x_1)^2$$

$$x_1 \frac{\partial \ln \gamma_1}{\partial x_1} = x_2 \frac{\partial \ln \gamma_2}{\partial x_2}$$

$$\frac{\partial \ln \gamma_1}{\partial x_1} = \frac{1}{R}(A+B) \cdot 2x_1(1-x_1)(-1)$$

$$x_1 \frac{\partial \ln \gamma_1}{\partial x_1} = \frac{1}{R}(A+B)(-2x_1 x_2)$$

$$x_2 \frac{\partial \ln \gamma_2}{\partial x_2} = -\frac{2x_2 x_1}{R}(A+B)$$

$$\ln \gamma_2 = \left(\frac{A+B}{R}\right) x_1^2 + C$$

$$R \ln \gamma_2 = Ax_1^2 + Bx_2^2$$

### \* Property Change of Mixing

for ideal sol<sup>n</sup>  $M = \sum x_i M_i$

for real sol<sup>n</sup>  $M = \sum x_i M_i + \Delta M$

$$\Delta M = M - \sum x_i M_i$$

Prop. of change of  
mixt.

$$\Delta M = \sum x_i \bar{M}_i - \sum x_i M_i$$

for real soln

$$M = \sum x_i \bar{M}_i$$

$$\Delta M = \sum x_i (\bar{M}_i - M_i)$$

### \* Free Energy change of Mixing :-

$$\int_{\bar{G}_i}^{\bar{G}_i} \frac{d\bar{G}_i}{\bar{G}_i} = \int_{\bar{f}_i}^{\bar{f}_i} RT d\ln \bar{f}_i$$

$$\bar{G}_i - G_i^\circ = RT \ln \left( \bar{f}_i / f_i^\circ \right)$$

$$\bar{G}_i - G_i^\circ = RT \ln \bar{a}_i$$

$$\Delta G = \sum x_i (\bar{G}_i - G_i^\circ)$$

$$\Delta G = RT \sum x_i \ln \bar{a}_i$$

for ideal soln  $a_i = \bar{a}_i$

$$\Delta G = RT \sum x_i \ln x_i$$

for pure soln  $x_i \rightarrow 1$

$$\Delta G = 0$$

### \* Volume Change of Mixing :-

$$\left( \frac{\partial \bar{G}_i}{\partial P} \right)_{T, \bar{a}_i} = V_i$$

$$\left( \frac{\partial \bar{G}_i}{\partial P} \right)_{T, a_i} = \bar{V}_i$$

$$\bar{V}_i - V_i = \left( \frac{\partial \bar{G}_i}{\partial P} \right)_{T, \bar{a}_i} - \left( \frac{\partial \bar{G}_i}{\partial P} \right)_{T, a_i}$$

$$= \frac{\partial}{\partial P} (\bar{G}_i - G_i^\circ)$$

$$\therefore \bar{G}_i - G_i^\circ = RT \ln a_i$$

$$(\bar{V}_i - v_i) = RT \frac{\partial}{\partial P} (\ln a_i)$$

$$\Delta V = \sum x_i (\bar{V}_i - v_i)$$

$$= \sum x_i (RT \frac{\partial}{\partial P} \ln a_i)$$

$$\boxed{\Delta V = RT \sum x_i \frac{\partial \ln a_i}{\partial P}}$$

for ideal soln

$$a_i = x_i$$

$$\boxed{\Delta V = RT \sum x_i \frac{\partial}{\partial P} \ln x_i}$$

for pure system

$$\boxed{\Delta V = 0}$$

homogeneous mixture  
or pure mixture or not!

\* Enthalpy change of Mixing :-

$$\frac{\partial}{\partial T} \left( \frac{G_i}{T} \right)_{P, n} = -\frac{H_i}{T^2}$$

$$\frac{\partial}{\partial T} \left( \frac{\bar{G}_i}{T} \right)_{P, n} = -\frac{\bar{H}_i}{T^2}$$

$$\Delta H = \sum x_i (\bar{H}_i - H_i)$$

$$\bar{H}_i - H_i = T \left[ -\frac{\partial}{\partial T} \left( \frac{\bar{G}_i}{T} \right) \right]_{P, n} - T^2 \left[ -\frac{\partial}{\partial T} \left( \frac{G_i}{T} \right) \right]_{P, n}$$

$$\Delta H = \sum x_i \left[ T^2 \left[ -\frac{\partial}{\partial T} \left( \frac{\bar{G}_i - G_i}{T} \right) \right] \right]_{P, n}$$

$$\Delta H = T^2 \sum x_i \left[ -\frac{\partial}{\partial T} \left\{ \frac{RT \ln a_i}{T} \right\} \right]_{P, n}$$

$$\boxed{\Delta H = -RT^2 \sum x_i \left[ \frac{\partial}{\partial T} \ln a_i \right]_{P, n}}$$

for ideal soln

$$\boxed{\Delta H = -RT^2 \sum x_i \frac{\partial}{\partial T} \ln x_i}$$

for pure soln

$$\boxed{\Delta H = 0}$$

\* Entropy change of Mixing :-

$$\Delta S = \sum n_i (\bar{s}_i - s_i)$$

$$\left( \frac{\partial G_i}{\partial T} \right)_{P,n} = -s_i$$

$$\left( \frac{\partial \bar{G}_i}{\partial T} \right)_{P,n} = -\bar{s}_i$$

$$dG = VdP - SdT$$

$$G = f(P, T)$$

$$dG = \left( \frac{\partial G}{\partial P} \right)_T dP$$

$$+ \left( \frac{\partial G}{\partial T} \right)_P dT$$

$$\left( \frac{\partial G}{\partial P} \right)_{T,n} = V$$

$$\left( \frac{\partial G}{\partial T} \right)_{P,n} = -S$$

$$\Delta S = \sum n_i \left( -\frac{\partial \bar{G}_i}{\partial T} + \frac{\partial G_i}{\partial T} \right)_{P,n}$$

$$= \sum n_i - \frac{\partial}{\partial T} (\bar{G}_i - G_i)$$

$$= \sum n_i \left[ - \frac{\partial}{\partial T} RT \ln a_i \right]$$

$$\Delta S = -RT \sum n_i \ln a_i$$

for ideal soln

$$\Delta S = RT \sum n_i$$

$$= - \sum n_i \left[ RT \frac{\partial}{\partial T} \ln a_i + R \ln a_i \right]$$

$$= -R \sum n_i \left[ \frac{\partial \ln a_i}{\partial \ln T} + \ln a_i \right]$$

$$T \frac{\partial}{\partial T} = \frac{1}{\partial \ln T}$$

$$\Delta S = -R \sum n_i \frac{\partial \ln a_i}{\partial \ln T} - R \sum n_i \ln a_i$$

for ideal & pure soln

$$\Delta S = 0$$

$$a_i = n_i$$

$$n_i \rightarrow 1$$

for ideal soln

$$\Delta S = -R \sum n_i \frac{\partial \ln n_i}{\partial \ln T} - R \sum n_i \ln n_i$$

$$\Delta S = -R \sum n_i \ln n_i$$

$$n_i = \text{const.}$$

$$\frac{\partial \ln n_i}{\partial \ln T} > 0$$

Q) The  $\Delta H$  of mixing for a binary mix. at 298 K and 1 bar is given by the eqn  $\Delta H = \kappa_1 \kappa_2 (40x_1 + 20x_2)$  where  $\Delta H$  is in J/mol &  $x_1$  &  $x_2$  are composition of L & 2. The enthalpies of the pure liquids at same temp & pres are 400 J/mol & 600 J/mol. Determine the numerical values of partial molar enthalpy at infinite dilution at 298 K and 1 bar.

Sep 09, 14

$$\bar{H}_1^\infty = 420 \text{ J/mol}$$

$$\bar{H}_2^\infty = 640 \text{ J/mol}$$

$$\bar{H}_1 = H - \kappa_2 \frac{\partial H}{\partial x_2}$$

$$\Delta \bar{H}_1 = 20(1-x_1)^2(2x_1 + 1)$$

$$\bar{H}_2 = H - \kappa_1 \frac{\partial H}{\partial x_1}$$

$$\Delta \bar{H}_2 = 40x_2^3$$

$$\Delta \bar{H}_1 = \Delta H - \kappa_2 \frac{\partial \Delta H}{\partial x_2}$$

$$\Delta \bar{H}_2 = \Delta H - \kappa_1 \frac{\partial \Delta H}{\partial x_1}$$

$$= 40x_1^2x_2 + 20x_1x_2^2 - x_2 \left\{ \frac{\partial}{\partial x_2} \{ 40x_2 + 20x_2^3 - 60x_2^2 \} \right\}$$

$$= 40x_1^2x_2 + 20x_1x_2^2 - x_2 \{ 40 + 60x_2^2 - 120x_2^3 \}$$

$$= 40x_1^2x_2 + 20x_1x_2^2 - 40x_2 - 60x_2^3 + 120x_2^4$$

$$= 20x_2^3 + 120x_2^4$$

at  $x_1 \rightarrow 0$

$$\Delta \bar{H}_1^\infty = 20 \text{ J/mol}$$

at  $x_2 \rightarrow 0$

$$\Delta \bar{H}_2^\infty = 40 \text{ J/mol}$$

$$\left. \begin{array}{l} \bar{H}_1^\infty = H_1 + \Delta \bar{H}_1^\infty \\ = 400 + 20 = 420 \text{ J/mol} \end{array} \right\}$$

$$\left. \begin{array}{l} \bar{H}_2^\infty = H_2 + \Delta \bar{H}_2^\infty \\ = 600 + 40 = 640 \text{ J/mol} \end{array} \right\}$$

Q) At 300 K and 1 bar, the volumetric data for a liquid mixture of benzene and cyclohexane are given by  $109.4 \times 10^{-6} - 16.8 \times 10^{-6}x - 2.64 \times 10^{-6}x^2 \text{ m}^3$ , where  $x$  is the mole fraction of benzene. Determine the expression for volume change of mixing for the standard state based on Lewis Randell Rule.

$$V = 109.4 \times 10^{-6} - 16.8 \times 10^{-6}x - 2.64 \times 10^{-6}x^2$$

$$\bar{V}_1 = V - x_2 \frac{\partial V}{\partial x_2}$$

$$\bar{V}_2 = V - x_1 \frac{\partial V}{\partial x_1}$$

$$\Delta V = \sum x_i (\bar{V}_i - V_i)$$

$$\Delta V = x_1 (\bar{V}_1 - V_1) + x_2 (\bar{V}_2 - V_2)$$

$$= 109.4 \times 10^{-6} - 16.8 \times 10^{-6} (1-x_2) - 2.64 \times 10^{-6} (1-x_2)^2 \\ - x_2 \left( -16.8 \times 10^{-6} (-1) - 2.64 \times 10^{-6} (1-x_2)(2)(-1) \right)$$

$$= 109.4 \times 10^{-6} - 16.8 \times 10^{-6} + 16.8 \times 10^{-6} x_2 - 2.64 \times 10^{-6} \\ - 2.64 \times 10^{-6} x_2^2 + 5.28 \times 10^{-6} x_2 - 16.8 \times 10^{-6} x_2 \\ - 5.28 \times 10^{-6} x_2 + 5.28 \times 10^{-6} x_2^2$$

$$\bar{V}_1 = 89.96 \times 10^{-6} + 2.64 \times 10^{-6} x_2^2$$

$$\bar{V}_2 = 109.4 \times 10^{-6} + 2.64 \times 10^{-6} x_1^2$$

$$V_1 = \bar{V}_1 |_{x_2=0}$$

$$V_2 = \bar{V}_2 |_{x_1=0}$$

Acc to ques  
based on Lewis Randell Rule  
ideal soln

$$V_1 = 89.96 \times 10^{-6} \text{ m}^3/\text{mol}$$

$$V_2 = 109.4 \times 10^{-6} \text{ m}^3/\text{mol}$$

$$\Delta V = \bar{x}_1 (V_1 - V_1) + \bar{x}_2 (V_2 - V_2)$$

$$= (1-\bar{x}_2) (89.96 \times 10^{-6} + 2.64 \times 10^{-6} \bar{x}_2^2 - 89.96 \times 10^{-6})$$

$$+ (1-\bar{x}_1) (109.4 \times 10^{-6} + 2.64 \times 10^{-6} \bar{x}_1^2 - 109.4 \times 10^{-6})$$

$$= 2.64 \times 10^{-6} \bar{x}_2^2 - 2.64 \times 10^{-6} \bar{x}_2^3$$

$$+ 2.64 \times 10^{-6} \bar{x}_1^2 - 2.64 \times 10^{-6} \bar{x}_1^3$$

$$= 2.64 \times 10^{-6} \left[ \{ \bar{x}_2^2 (1-\bar{x}_2) \} + \{ \bar{x}_1^2 (1-\bar{x}_1) \} \right]$$

$$= 2.64 \times 10^{-6} [\bar{x}_1 \bar{x}_2^2 + \bar{x}_1^2 \bar{x}_2]$$

$$= 2.64 \times 10^{-6} \bar{x}_1 \bar{x}_2 [\bar{x}_2 + \bar{x}_1]$$

Check ans yourself

### Excess property :-

$$M^E = M^{\text{real}} - M^{\text{id}}$$

$M^E > 0$  +ve deviation from ideality (How much the real mix is deviating from ideality.)

$M^E < 0$  -ve deviation from ideality.

### Excess change of Mixing

$$\Delta M^E = \Delta M^{\text{real}} - \Delta M^{\text{id}}$$

$$\Delta M^{\text{real}} = M^{\text{real}} - \sum x_i M_i$$

$$\Delta M^{\text{id}} = M^{\text{id}} - \sum x_i M_i$$

$$\Delta M^E = \{M^{\text{real}} - z x_i M_i\} - \{M^{\text{id}} - z x_i M_i\}$$

$$\Delta M^E = M^{\text{real}} - M^{\text{id}} = M^E \quad / \quad \bar{M}_T^E = \partial \ln M^E$$

⇒ Excess Gibbs free Energy :-

$$G^E = \Delta G_i^E = \Delta G_i - \Delta G_i^{\text{id}}$$

$$\Delta G_i^E = \Delta G_i - \Delta G_i^{\text{id}}$$

$$\Delta G_i = RT \ln \frac{f_i}{f_i^{\circ}}$$

$$\Delta G_i^{\text{id}} = RT \ln \frac{f_i^{\text{id}}}{f_i^{\circ}}$$

for real soln

$$f_i = \gamma_i x_i f_i^{\circ}$$

for ideal soln

$$f_i^{\text{id}} = x_i f_i^{\circ}$$

$$\Delta G_i = RT \ln \gamma_i x_i$$

$$\Delta G_i^{\text{id}} = RT \ln x_i$$

$$\Delta G_i^E = RT \ln \gamma_i x_i - RT \ln x_i$$

$$\Delta G_i^E = RT \ln \gamma_i$$

⇒ Calculations for Activity coefficient :-

\* Wohl's Equation :-

$$\ln \gamma_1 = z_1^2 \left[ A + 2 \left( B \frac{q_1}{q_2} - A \right) z_1 \right]$$

$$\ln \gamma_2 = z_2^2 \left[ B + 2 \left( A \frac{q_2}{q_1} - B \right) z_2 \right]$$

$$z_1 = \frac{x_1}{x_1 + x_2 (q_2/q_1)} \quad , \quad z_2 = \frac{x_2}{x_2 + x_1 (q_1/q_2)}$$

$q_1$  &  $q_2$  = molar volume fraction of 1 & 2

$z_1$  &  $z_2$  = Effective molar fraction of 1 & 2

Arithm. constants.

→ Margules Equation :-

3 Suffix Equation :-

$$-q_1 = q_2$$

$$\ln Y_1 = Z_1^2 [A + 2(B-A)Z_1]$$

$$\ln Y_2 = Z_2^2 [B + 2(A-B)Z_2]$$

$$Z_1 = \frac{x_1}{x_1+x_2}, \quad Z_2 = \frac{x_2}{x_1+x_2}$$

2 Suffix Equation :-

$$A=B, \quad q_1 = q_2$$

$$\ln Y_1 = Z_1^2 A$$

$$\ln Y_2 = Z_2^2 B$$

$$Z_1 = \frac{x_1}{x_1+x_2}, \quad Z_2 = \frac{x_2}{x_1+x_2}$$

→ Van Laar Equation :-

$$\ln Y_1 = Z_1^2 [A + 2(B \frac{q_1}{q_2} - A)Z_1]$$

$$\ln Y_2 = Z_2^2 [B + 2(A \frac{q_2}{q_1} - B)Z_2]$$

$$\text{tr} \quad \frac{q_1}{q_2} = \frac{A}{B}$$

$$\ln Y_1 = Z_1^2 \cdot A$$

$$\ln Y_2 = Z_2^2 \cdot B$$

$$Z_1 = \frac{x_1}{x_1+x_2(B/A)}, \quad Z_2 = \frac{x_2}{x_2+x_1(A/B)}$$

2008

Q1) A binary mix. containing comp 1 & 2, forms an azeotrope at 105.4°C & 1.013 bar. The liq phase mole fraction of comp 1 of this azeotrope is 0.62 at 105.4°C. The pure component vapour press. 1 & 2 is 0.878 bar & 0.665 bar resp. Assume that vapour phase is ideal gas mixt.

$$A = \left[ 1 + \frac{x_2 \ln y_2}{x_1 \ln y_1} \right]^2 \ln y_1, \quad B = \left[ 1 + \frac{x_1 \ln y_1}{x_2 \ln y_2} \right]^2 \ln y_2$$

26)

The activity coeff ( $y_1, y_2$ )

A) 0.88, 0.66 ~~C~~ 1.15, 1.52

B) 1.52, 1.15 D) 1.52, 0.88

27.7 A &amp; B

A) 0.92, 0.87 C) 1.52, 1.15

~~B~~ 1.12, 1 D) 1, 1.21

Sol<sup>b</sup>

$$x_1 = 0.62$$

$$p_1^s = 0.878 \text{ bar}$$

$$p_2^s = 0.665 \text{ bar}$$

$$\hat{f}_i = x_i y_i f_i$$

$$\bar{f}_i = x_i y_i p_i^s$$

$$y_i p = x_i y_i p_i^s$$

$$y_i = \frac{p}{p_i^s}$$

$$y_1 = \frac{1.013}{0.878} = 1.1537$$

$$y_2 = \frac{1.013}{0.665} = 1.52$$

at azeotropic pt

$$x_i = y_i$$

$$A = \left[ 1 + \frac{0.38 \ln 1.52}{0.62 \ln 1.15} \right]^2 \ln 1.15$$

$$= 1.12$$

$$B = \left[ 1 + \frac{0.62 \ln 1.15}{0.38 \ln 1.52} \right]^2 \ln 1.52$$

$$= 0.998 \approx 1$$

2005

Q: The van

activity coeff model for a binary mix is given by

$$\ln Y_1 = \frac{A^*}{\left( 1 + \frac{A^*}{B^*} \cdot \frac{x_1}{x_2} \right)}$$

$$\underline{A^*} = 3 \quad 0.5$$

$$\ln Y_2 = \frac{B^*}{\left( 1 + \frac{B^*}{A^*} \cdot \frac{x_2}{x_1} \right)}$$

given,  $Y_1 = 1.40, x_1 = 0.25$   
 $Y_2 = 1.25, x_2 = 0.75$

$$A^*, B^*$$

$$A^* = \left( 1 + \frac{A^*}{B^*} \cdot \frac{x_1}{x_2} \right) \ln Y_1 \quad \left| \begin{array}{l} B^* = \left( 1 + \frac{B^*}{A^*} \cdot \frac{x_2}{x_1} \right) \ln Y_2 \\ = 0.2231 + 0.6693 \frac{B^*}{A^*} \end{array} \right.$$

$$= 0.3364 + 1.0092 \frac{A^*}{B^*}$$

$$A^* B^* = 0.3364 B^* + 1.0092 A^* \quad \left| \begin{array}{l} A^* B^* = 0.2231 A^* + 0.6693 B^* \end{array} \right.$$

$$B^* \neq 0.2231 + 0.6693 \frac{B^*}{A^*}$$

$$0.2231 A^* + 0.6693 B^* = 0.3364 B^* + 0.1121 A^*$$

$$0.3329 B^* = -0.111 A^*$$

$$B^* = -0.3334 A^*$$

$$A^* (-0.3334 A^*) = 0.3364 \times (-0.3334 A^*) + 0.1121 A^*$$

$$-0.3334 A^* = 0.1121$$

Sep 10/13

2011

Q1> The partial molar enthalpy of mixing in (J/mol) for benzene & cyclohexane at 300 K & 1 bar are given by:

$$\Delta h_1 = 3600 x_2^2$$

$$\Delta h_2 = 3600 x_1^2$$

1.) when one mole of benzene is added to 2 mole of cyclohexane the enthalpy change in kJ

a) 3600

b) 2020

c) 2800

d) 800

2010

Q2) An equimolar liq. mixture of species 1 & 2 is in equilibrium with its vapour at 400 K. At this temp. the VP of species are 180 kPa, 120 kPa. Assuming that Raoult's Law is valid.

$y_1 = ?$

$P_1^s = 180 \text{ kPa}$

$A = 0.6$

$P_2^s = 120 \text{ kPa}$

$$\bar{P}_i = x_i P_i^s$$

$$\bar{P}_1 = x_1 P_1^s, \bar{P}_2 = x_2 P_2^s$$

equimolar  $x_1 = x_2 = 0.5$

$$\bar{P}_1 = y_1 P$$

$$y_1 P = x_1 P_1^s$$

$$y_2 P = x_2 P_2^s$$

$$(1-y_1) P = x_2 P_2^s$$

$$\frac{x_2 P_2^s}{(1-y_1)} = \frac{x_1 P_1^s}{y_1}$$

$$(0.5 \times 120) y_1 = (0.5 \times 180) (1-y_1)$$

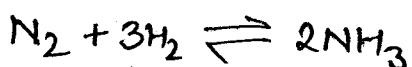
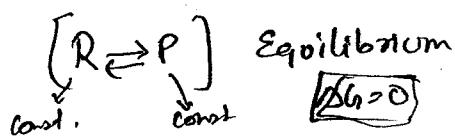
$$60y_1 = 90 - 90y_1$$

$$150y_1 = 90$$

$$y_1 = 0.6 =$$

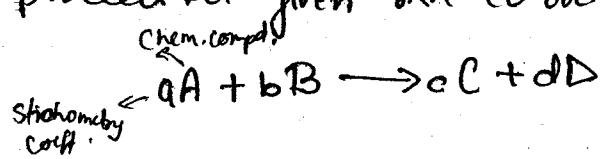
### \* Chemical Rxn Equilibria :-

A  $\xrightarrow[\text{chemical changes}]{\text{Chemical}}$  B



### \* Extent of rxn (Conversion) :- Rxn co-ordinate ( $\epsilon$ )

It is the parameter used to measure the extent upto which rxn will proceed at given rxn co-ordinate.



$$\sum \nu_i A_i = 0$$

$$\nu_A A + \nu_B B + \nu_C C + \nu_D D = 0$$

$$(-a)A + (-b)B + (c)C + (d)D \geq 0$$

$$aA + bB \rightarrow cC + dD$$

$$\Delta n_i \propto \nu_i$$

$$\frac{\Delta n_A}{\nu_A} = \frac{\Delta n_B}{\nu_B} = \frac{\Delta n_C}{\nu_C} = \frac{\Delta n_D}{\nu_D} = \epsilon$$

$$\frac{dn_A}{\nu_A} = \frac{dn_B}{\nu_B} = \frac{dn_C}{\nu_C} = \frac{dn_D}{\nu_D} = d\epsilon$$

extent is always same

$$\frac{dn_i}{\nu_i} = d\epsilon$$

$$\int_{n_{i0}}^{n_i} dn_i = \int_0^{\epsilon} \nu_i \cdot d\epsilon$$

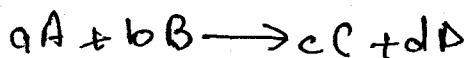
$$n_i - n_{i0} = \nu_i \cdot \epsilon$$

$$n_i = n_{i0} + \nu_i \epsilon$$

$$\sum n_i = \sum n_{i0} + \sum \nu_i \epsilon$$

$$n = n_0 + \epsilon \cdot \nu$$

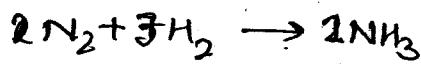
$$\nu = \sum \nu_{i, \text{part}} - \sum \nu_{i, \text{react.}}$$



$$\nu = d + c - (a + b)$$

$$y_i = \frac{n_i}{n} \approx \frac{n_{i0} + \nu_i \epsilon}{n_0 + \nu \epsilon}$$

Q) A gas mixture containing 2 mol of N<sub>2</sub>, 7 mol of H<sub>2</sub>, & 1 mol of NH<sub>3</sub>. Initially undergoes the following rxn. derive the expression for mole fraction N<sub>2</sub>, H<sub>2</sub> and NH<sub>3</sub>.



2 mol N<sub>2</sub>

7 mol H<sub>2</sub>

1 mol NH<sub>3</sub>

$$y_i = \frac{n_{i,0} + \nu_i \epsilon}{n_0 + \nu \epsilon}$$

$$\nu = 2-3-1 = (-2)$$

$$\nu = 1 - (-2) = 3$$

$$\epsilon = -8$$

$$y_{\text{N}_2} = \frac{2 + (-1)\epsilon}{10 + (-2)\epsilon} = \frac{2 - \epsilon}{10 - 2\epsilon} = \frac{1 - \epsilon}{5 - \epsilon}$$

$$y_{\text{H}_2} = \frac{7 - 3\epsilon}{10 - 2\epsilon}$$

$$y_{\text{NH}_3} = \frac{1 + 2\epsilon}{10 - 2\epsilon}$$

Q) For a rxn  $2A + 3B \rightarrow 6C$  what will be the mole fraction of A, B, & C. finally if there were 3 moles of A, 4 mole of B are present & the extent of rxn is  $\epsilon = 0.65$

$$\nu = 6 - 2 - 3 = 1$$

$$y_A = \frac{3 + (2)0.65}{7 + (1)0.65} = 0.222$$

$$\epsilon = 0.65$$

$$C = 0$$

$$y_B = \frac{4 + (-3)0.65}{7 + (1)0.65} = 0.2679$$

$$y_C = \frac{0 + (6)0.65}{7 + (1)0.65} = 0.5098$$

$$n_{AO} = 3$$

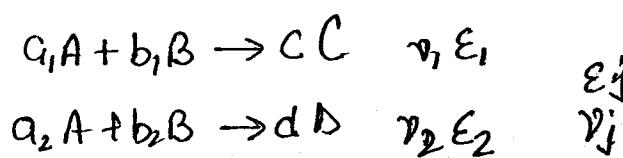
$$\begin{aligned} n_A &= n \cdot y_A \\ &= (1 + 0.65) \times 0.222 \\ &= 1.683 \text{ moles} \end{aligned}$$

$$x_A = \frac{n_{AO} - n_A}{n_{AO}}$$

$$x_A = 0.439$$

Conversion

If more than one rxn



1050 - 100  
300 - 100  
1300 - 200  
2000

900 + 400  
1300  
300

$$dn_{Ai} = n_i d\epsilon$$

i = no. of Components

j = no. of rxn

$$\int_{n_{i0}}^{n_i} dn_i = \int_0^{\epsilon_j} \nu_{i,j} d\epsilon_j$$

$$n_i = n_{i0} + \sum_j \nu_{i,j} \epsilon_j$$

$$n = \sum_{i=1}^N n_i$$

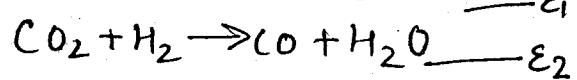
$$n = \sum_{i=1}^N n_i = \sum_{i=1}^N n_{i0} + \sum_{i=1}^N \sum_{j=1}^m \nu_{i,j} \epsilon_j$$

$$n = n_0 + \sum_{j=1}^m \left\{ \sum_{i=1}^N \nu_{i,j} \epsilon_j \right\}$$

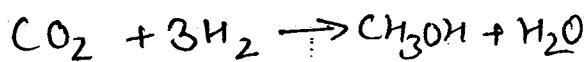
$$n = n_0 + \sum_j \nu_j \epsilon_j$$

$$y_i = \frac{n_i}{n_0} = \frac{n_{i0} + \sum_j \gamma_{ij} \epsilon_j}{n_0 + \sum_j \gamma_j \epsilon_j} \quad * \quad *$$

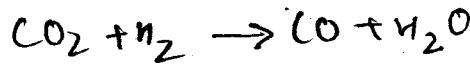
Q) A gas mixture containing 3 moles of  $\text{CO}_2$ , 5 moles of  $\text{H}_2$  & 1 mole of  $\text{H}_2\text{O}$  undergoing a following rxn.  $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$



Find the mole fraction of each component in term of extent of rxn.



$$\gamma_1 = -2, \epsilon_1$$



$$\gamma_2 = 0, \epsilon_2$$

$$y_{\text{CO}} = 3 + 1$$

$$n = n_0 + \sum_j \gamma_j \epsilon_j$$

$$= 9 + (-2)\epsilon_1 + 0\epsilon_2$$

$$= 9 - 2\epsilon_1$$

$$n_{\text{CO}_2} = 3 + \gamma_{(\text{CO})_1} \epsilon_1 + \gamma_{(\text{CO}_2)_2} \epsilon_2$$

$$n_i = n_{i0} + \sum_j \gamma_{ij} \epsilon_j$$

$$= 3 + (-1)\epsilon_1 + (-1)\epsilon_2$$

$$= 3 - \epsilon_1 - \epsilon_2$$

$$n_{\text{H}_2} = 5 + (-3)\epsilon_1 + (-1)\epsilon_2$$

$$= 5 - 3\epsilon_1 - \epsilon_2$$

$$n_{\text{H}_2\text{O}} = 1 + \epsilon_1 + \epsilon_2$$

$$n_{\text{CH}_3\text{OH}} = 0 + 1\epsilon_1$$

$$n_{\text{CO}} = 0 + \epsilon_2$$

$$y_{CO_2} = \frac{3-\varepsilon_1-\varepsilon_2}{9-2\varepsilon_1}$$

$$y_{H_2} = \frac{5-3\varepsilon_1-\varepsilon_2}{9-2\varepsilon_1}$$

$$y_{H_2O} = \frac{1+\varepsilon_1+\varepsilon_2}{9-2\varepsilon_1}$$

$$y_{CH_3OH} = \frac{\varepsilon_1}{9-2\varepsilon_1}$$

$$y_{CO} = \frac{\varepsilon_2}{9-2\varepsilon_1}$$

for Single rxn System :-

$$y_i = \frac{n_{i0} + \gamma_i \epsilon}{n_0 + \gamma \epsilon}$$

$$\text{Zos } x_i = \frac{n_{i0} - n_i}{n_{i0}}$$

$$n_i = n_{i0} + \gamma_i \epsilon$$

$$x_i = \frac{-\gamma_i \epsilon}{n_{i0}}$$

-ve sign indicates reactant or prod.

$$x_i = \frac{|\gamma_i| \epsilon}{n_{i0}}$$

Effect of Inert on Eqn Conversion :-

$$\pi y_i \cdot k = k_{\phi} \cdot k_p$$

$$k = k_p = k_y \cdot p^{\nu}$$

$$\frac{k}{p^{\nu}} = k_y$$

$$k_y = \pi y_i^{\gamma_i}$$

$$= \pi \left( \frac{n_i}{n} \right)^{\gamma_i}$$

$$\Rightarrow \pi \left( \frac{n_i}{n} \right)^{\gamma_i} = \frac{k}{p^{\nu}}$$

$$\frac{\pi n_i^{\gamma_i}}{n^{\nu}} = \frac{k}{p^{\nu}}$$

$$\pi n_i^{\gamma_i} = k \left( \frac{n}{p} \right)^{\nu}$$

total moles

$$n = \sum n_i + n_{\text{inert}}$$

$$\pi = pdt$$

$$P_1 P_2 P_3 = \sum_{i=1}^3 \pi_i^3$$

- for  $\gamma > 0$ ,as Inerts  $\uparrow$ 

$$n \uparrow$$

$$x_A \uparrow$$

if  $\gamma < 0$ Inerts  $\uparrow$ 

$$n \uparrow$$

$$x_A \downarrow$$

$$n_{\text{pdt}} \propto n^\gamma$$

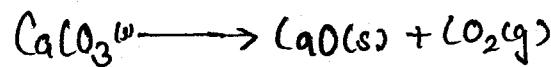
$$n_{\text{pdt}} \propto \frac{1}{n^{\gamma-1}}$$

!

!

!

\* Pressure of decomposition :-



$$K = \frac{a_{\text{CaO}} \cdot a_{\text{CO}_2}}{a_{\text{CaCO}_3}}$$

Activity of solids is almost 1.

$$K \approx a_{\text{CO}_2}$$

$$K = \frac{f_{\text{CO}_2}}{f^{\circ}_{\text{CO}_2}}$$

$$K \approx f_{\text{CO}_2}$$

$$K = \bar{P}_{\text{CO}_2}$$

If  $P_{\text{CO}_2} > \bar{P}_{\text{CO}_2}$

if  $P_{\text{CO}_2} < \bar{P}_{\text{CO}_2}$

Decomposition of  $\text{CaCO}_3$  will take place.  $\text{CaO}$  &  $\text{CO}_2$  will combine to form  $\text{CaCO}_3$ .

$$K_p = k_p \cdot p^2$$

$$\bar{p}_i = c_i RT$$

$$K_p = \prod c_i^{n_i} (RT)^{n_p}$$

$$K_p = K_c (RT)^{n_p}$$

$$K_c = \prod c_i^{n_i}$$

Q) For the rxn  $A \rightarrow B$ , it is found that the equilibrium is attained at following compositions.

T(K)	Composition of A	% mol
317	31	
391	43	

Assuming activity is equal to mole fraction. Calculate the standard free energy of the rxn at 317 K & at 391 K also find out the equilibrium constant standard heat of entrxn which is constant for all range of temp.

at 317

$$K = \frac{y_B^{n_B}}{y_A^{n_A}} = \frac{y_B}{y_A} = \frac{0.69}{0.31} = 2.258$$

at 391

$$K = \frac{y_B}{y_A} = \frac{0.57}{0.43} = 1.325$$

$$\Delta G^\circ \big|_{317} = -RT \ln K$$

$$= -8.314 \times 317 \times \ln 2.258$$

$$= -2.146 \text{ kJ/mol}$$

$$\Delta G^\circ \big|_{391} = -RT \ln K$$

$$= -8.314 \times 391 \times \ln 1.325$$

$$= -0.914 \text{ kJ/mol}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{\Delta H_R}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\Delta H_R^\circ = -7.218 \text{ kJ/mol}$$

- 1.  $\Delta H_R < 0$  Exothermic
- 2.  $\Delta H_R > 0$  Endothermic

### \* Phase Rule / Gibbs Phase Rule :-

Relation b/w

No. of phases, no. of species, no. of intensive variable.

$$F = C - \pi + 2$$

for non-reacting system.

$F$  = Degree of freedom

$C$  = no. of chemical species

$\pi$  = no. of phases present in the system.

$2$  = no. of intensive partial variable (temp, press).

Ice starts融ing at  $4^\circ\text{C}$  & completely freezes at  $0^\circ\text{C}$ .

$F < 0$

System is in disequilibrium,

$$F = C - \pi + 2 - \gamma$$

$\gamma$  = no. of independent chem. rxn.

$$G_i^E = RT \ln Y_i$$

$$\Delta G^E = RT \sum \ln Y_i$$