

n, watson, katz

Mech eq but thermodynamically  
equilb  
eg.

to make

of medicine

Ayurveda is the ea

phase change of dig to gas  
as a gas cylinder

flash evaporation

gas cylinder

when regulator,  
it is open  
system having  
energy with  
these change

Found in the Himalayas

velvet

a win

in the world starts  
The sarus crane

The tiger is the

0/0

D1

## First law of Thermodynamics

$\Delta U = q + w$  → path function ( $\therefore$  no state func)

closed system

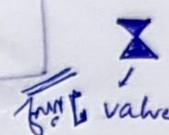
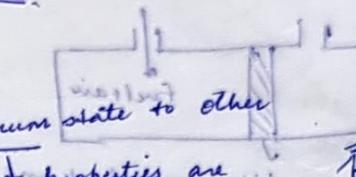
Open system

Closed

Isolated

$\Delta U = 0 \rightarrow$  isolated system

process → change from one equilibrium state to other



properties are in balance

$$\rightarrow \Delta U = dq + dw$$

→ open system & mass changes

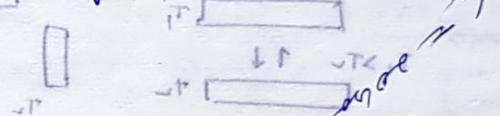
needle valve  
↓  
point for strain gas ←  
cylinder

→ Intensive property = size independent

→ Extensive = size dependent (energy, entropy, momentum)

size is very small

→ nano scale - intensive property becomes extensive bcoz of alteration  
in bond structure (band gap) (the size is very  
small)



→ Extensive = intensive.  
Extensive

Thermodynamic equilibrium

Mechanical equilibrium

state → unsteady state



steady state

static

steady state

dynamic

steady

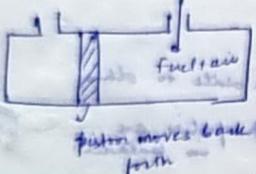
state

flow vol.?

flow rate

&lt;p

→ Thermodynamic cycle (constant engine) Mechanical cycle  $\rightarrow$  work done  
 → Two stroke engine.



$$\text{volume between } = 0 \rightarrow V_0$$

mixtures are most stable + cross

$$V_1 + V_2 = V_0$$

equilibrium mixtures are most stable

### Components of Energy

(conduction) convection / radiation  $\rightarrow$  perfect insulator

directional heat transfer  $\rightarrow$  insulator + hot to cold

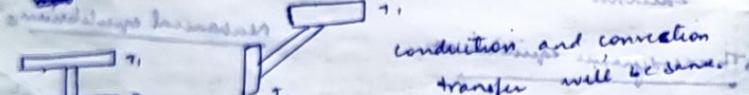
radiation  $\rightarrow$  insulator + cold to hot



(view factor)  $\rightarrow$  radiation will be different (Nero)

convection - insulated

insulated  $\rightarrow$  no heat transfer



conduction and convection transfer will be same as

if  $d \rightarrow \infty$  no work, as

as has to be more but that is not

possible we use a shaft

we rotate it faster to generate more work

Types of work

(mechanical work)

shaft work

electrical

shaft work

Radius  $= R$

Torque  $= T \cdot R \cdot I_{\text{ext}}$  to induce distance corresponding to a revolution with  $2\pi A$  to

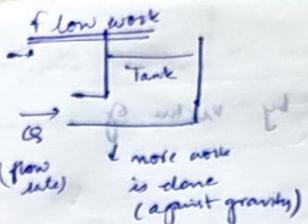
$P = \frac{T}{I}$

$S = 2\pi R \cdot A$

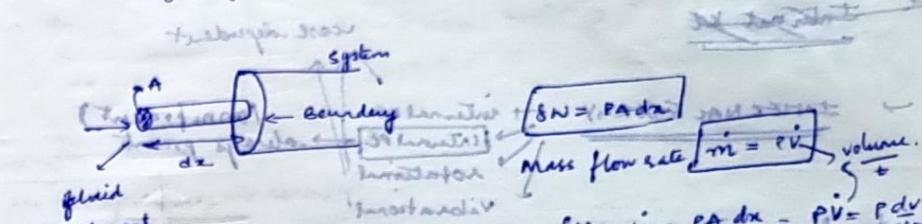
$W_s = 2\pi R \cdot I$

$W_s = 2\pi R \cdot T$

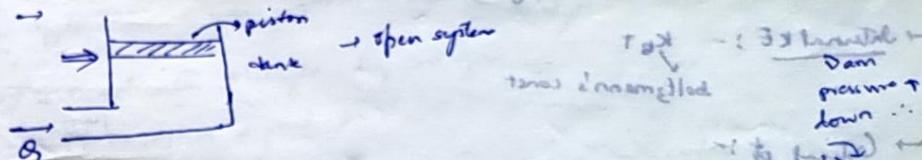
$W_s = 2\pi R \cdot T$



waterfalls effect water  $\rightarrow$   
 reservoir pressure : 39  
 water falls down in



$\frac{dN}{dt} = \dot{m} = \rho V$  volume  
 water  $\frac{dN}{dt} = \dot{m} = \rho A \frac{dx}{dt} = \rho V = \rho dV/dt$



$T_{\text{ext}} \rightarrow 33^{\circ}\text{C}$  dam pressure down

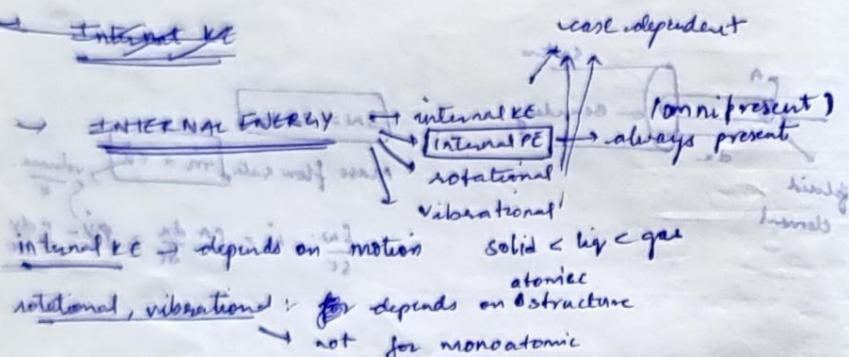
water is made to slide down

$dE = (dQ)(\frac{dV}{V} + dP)$

→ Viscous ~~eff~~ dissipation

→ PE :- energy possessed by a system by virtue of its body force.

→ Internal KE



→ Internal KE :-  $K_B T$  boltzmann's const

→ Critical pt :-

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

$$PV = RT$$

force excluded volume connected

Vanderwaals force dipole-dipole interaction

3 types permanent hydrogen bond induced - induced dipole-dipole bond

dispersive force or London forces

$$F = \frac{A}{R^6} \frac{1}{r^6}$$

$$\frac{B}{r^{12}} = \frac{A}{r^6} \Rightarrow \text{net force}$$

attractive force

repulsive force

critical separation distance (order of 10nm)

Hardsphere model

→ Internal PE does not depend on  $T$   $q_1 < q_2$   $q_2 > q_1$

→ Vanderwaals force is gravity independent

→ Brownian motion :- particles move randomly up, down -  
gravity  $\approx 0$

→ gas pressure  $\rightarrow$  collision

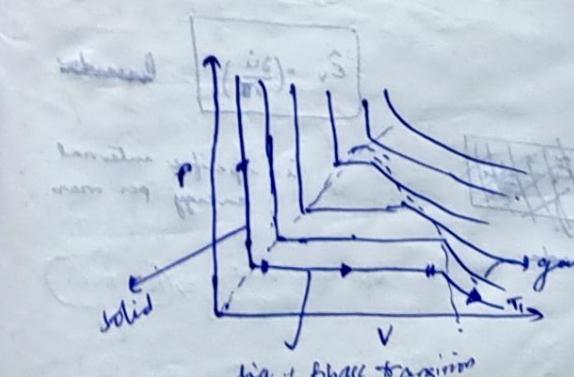
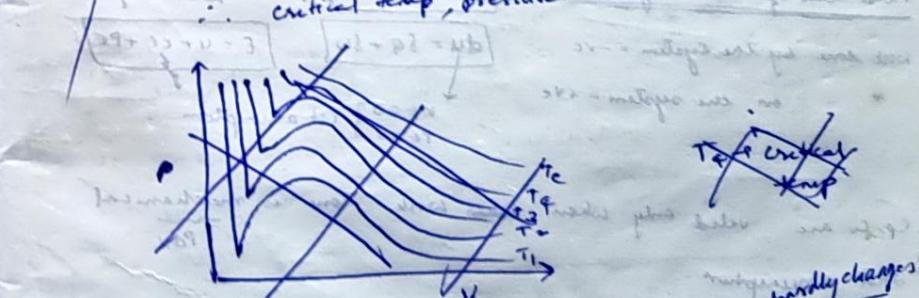
→ Critical pressure :-

→ critical temp :- temp above which whatever pressure is applied, a gas cannot be liquified

→ intermolecular strength liq  $>$  gas

→  $PE \rightarrow$  doesn't depend on  $T$

→ liquification  $\rightarrow$  Pressure will bring the molecules closer which might overcome the  $KE$   $\frac{1}{k_B T}$





$$P = \frac{2}{3} \left( \frac{v}{V} \right) \left( \frac{1}{2} m \bar{u}^2 \right)$$

$$PV = \frac{2}{3} n N_A \left( \frac{1}{2} m \bar{u}^2 \right)$$

$n$  = no. of moles

$$PV = \frac{2}{3} n v T$$

avg translational  
KE

molar

$$(KE \times N_A) \times 1 \text{ mole}$$

Now from ideal gas law:-

$$PV = nRT$$

$$\frac{2}{3} n v T = nRT$$

$$v_T = \frac{3}{2} R T$$

Now we have

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

$$i_C = \frac{3}{2} R$$

molar

$$i_{CP} = \frac{5}{2} R$$

(gas)

$$du = \delta Q + \delta W$$

$$H = U + PV$$

$$PV = nRT$$

$$PV = RT$$

$$\frac{\partial H}{\partial T} = \frac{\partial U}{\partial T} + P \frac{\partial V}{\partial T}$$

const p

→ stokes fluid :- internal energy = internal KE  
 different stokes fluid bcoz it has H-bonds  
 $H_2O$  is not a very good stokes fluid bcoz it has H-bonds

→ He, Ar → test examples of ideal gas  
 monatomic gases are examples of ideal gas  
 not always.

$$f = mc^2$$

mass defect

$$dH = dU + PV$$

$$\frac{dH}{dT} = \frac{du}{dT} + \frac{d(PV)}{dT}$$

$$C_P = C_V + R$$

$$N = n N_A$$

Heating / cooling of a substance (with / without phase change)

Cps → latent heat of fusion

CPL → latent heat of vaporisation

Cp  
vapour

### Vapour pressure

→ Pressure exerted on the liquid surface due to its own vapour at equilibrium.

→ closed system

→ higher vapour pressure → higher collisions → more no. of molecules.

→ van der waals law & potential energy is only due to induced polarity.

→ as heating & evaporation T → avg KE ↑ → no. of molecules capable of changing phase ↑

→ Boiling & all the molecules overcome potential energy

→ organic solvents <  $H_2O$  → BP

→  $C_p = a + bT + cT^2$  → check whether T is  $^{\circ}\text{C}$  or  $\text{K}$   
 $\int c_p dT = f(a)$

→  $C_m = \text{mean } C_p$

### Heat capacity of solid

→ Petit and Dulong law

$$\frac{C}{\text{mol weight}} = \frac{\text{cal}}{\text{g K}}$$

(heat capacity of solid  $\rightarrow$  liq, gas compare)

→ Heat capacity of all crystalline solid elements is nearly const and equal to  $6.2 \text{ cal/g atom K.} = C$

→ The rule applies for elements with atomic weight  $> 40$   
 When applied at const volume conditions

$$\boxed{C_{\text{solid}} > C_{\text{liq}} > C_{\text{gas}}} \rightarrow \text{check?}$$

g-atom → mass of 1 mole of an element equal in grams to the atomic wt

for compounds

Kopp Rule (can be used for  $\text{I}_{\text{eq}}$ )

The heat capacity of a solid compound is approximately equal to the sum of heat capacities of the constituent elements.

Solid ( $< 40$ ) (heat capacity)

$$C \rightarrow 1.8 \quad H \rightarrow 2.3 \quad O \rightarrow 4 \quad P \rightarrow 5.4$$

$$B \rightarrow 2.7 \quad S_i \rightarrow 3.8 \quad F \rightarrow 5.0 \quad \text{rest all} \rightarrow 6.2$$

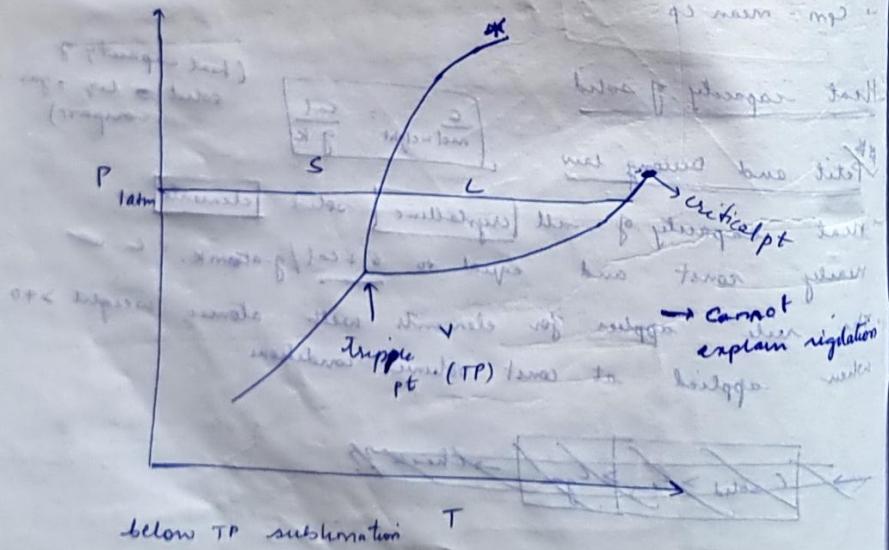
Kopp rule (eq)

$$C \rightarrow 2.8 \quad H \rightarrow 4.3 \quad Si \rightarrow 5.8 \quad P \rightarrow 7.4 \\ O \rightarrow 6 \quad B \rightarrow 4.7 \quad F \rightarrow 7.0 \quad \text{rest all} \rightarrow 8.0 \\ ( > 4.0 )$$

Cypas

$C_{\text{gas}} < C_{\text{solid}} < C_{\text{liq}}$

## PHASE DIAGRAM



→ camphor, naphthalene

sublens  
below room temp  
critical temp

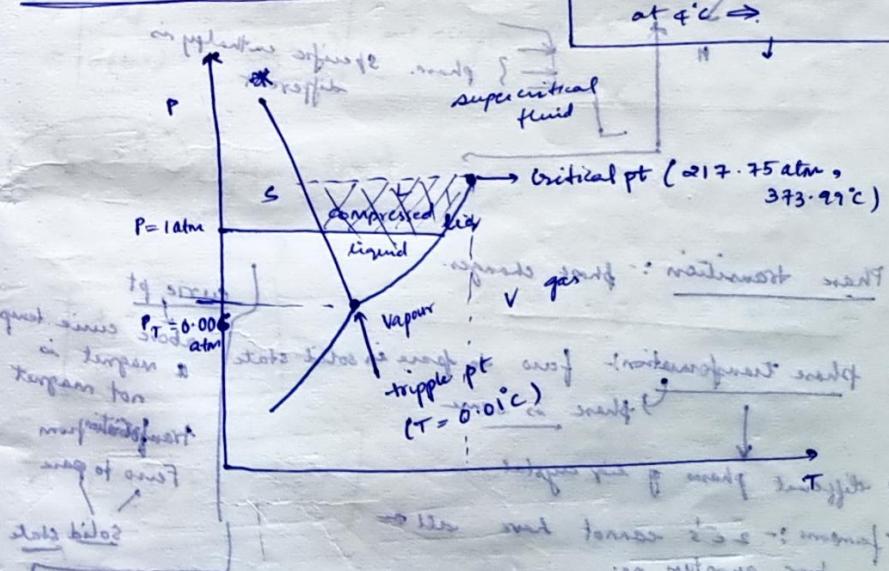
→ gas/vapour

$\rightarrow$  triple form  $> 100\text{ m}$  temp

multiple forms of protein  
which are identical in  
function

slope of S-L is +ve  $\rightarrow$  other? to water freshwater aquifer  
-ve slope for water

## PHASE DIAGRAM OF $H_2O$



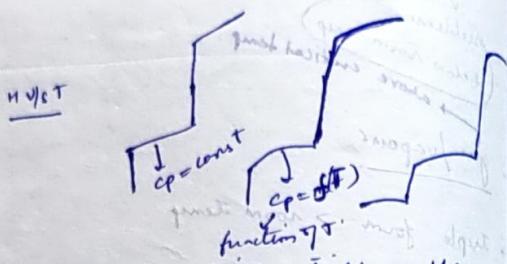
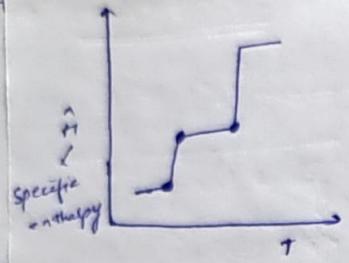
slope of the line at s-l boundary

+ve  $\rightarrow$  for others ~~for greater~~ aqueous intercalated materials - size  
-ve  $\rightarrow$  for H<sub>2</sub>O ~~water~~ related increase internal energy (S to L)

→ more energy is required to overcome intermolecular forces (F =  $\frac{1}{r^6}$ )

→ Squeezing: - When two cubes of ice are pressed, they melt.

join : (PT, Melting pt of ice +)  
 $\text{density of H}_2\text{O} > \text{ice}$



→ the pts where the function is not differentiable → phase boundary.

$\rightarrow$  super heated steam : steam at  $150^{\circ}\text{C}$  ~~saturated liquid~~ latent heat is different

$\rightarrow \text{N}_2\text{O}$  at  $100^\circ\text{C}$ , 1 atm  $\rightarrow$  saturated vapour  $\rightarrow$  latent heat is different for saturated liquid and saturated vapour

both. DINEGWY OF 1810

specific enthalpy is different

$\rightarrow$   $m^2 \cdot 2^k - 4 \cdot 15$  } by division  $\leftarrow$   2

→ Phase transition: phase changes | curie, pt

→ phase transformation's favo to form in solid state  
a magnet  $\Rightarrow$  not magnet

different phases of ice crystal

$\rightarrow$  famous :-  $2e^-$ 's cannot have all the same quantum no.

→ Base on → prepared → to → div. crystal

$\rightarrow$  Bose-Einstein condensation: super fluidity of helium at  $T = 0$

$(\int dt \delta)$  ~~is isolated left~~ ~~display~~ ~~is isolated left~~ ~~display~~

super fluid  $\rightarrow$  viscosity  $\propto 0$

Super conductor: Resistance = 0

(+ 31° F. + 9° Fahrenheit, T. 9) - west

with  $\epsilon$ -substitution.

Heat of vapourisation:-

$$\text{Heat of fusion} = \frac{223.1 + 28P \cdot S - \left( \frac{\partial T}{\partial P} \right)_{S=0} P \cdot S}{\left( \frac{\partial T}{\partial P} \right)_{T=0} - P \cdot I}$$

- Heat of vapourisation

Estimated from  $P^* \text{ vs } T$  relation ( $P^* \rightarrow \text{vapour pressure}$ )

$$\frac{dp^*}{dT} = \frac{\hat{M}}{T(V_g - V_L)} \rightarrow \begin{array}{l} \text{latent heat } q_v = 5 \\ \text{vapourisation} \\ \text{temp } \rightarrow \text{molar specific volume } = ? \end{array}$$

(3) also isothermal

$$\Rightarrow \frac{dp^*}{d(\ln r)} = \frac{\hat{\alpha} \hat{n}}{(\hat{v}_g - \hat{v}_L)} \rightarrow clayperon equation$$

$$\hat{v}_g > \hat{v}_L$$

density

$$\Rightarrow \frac{dp^*}{d(\ln r)} = \frac{\partial r}{\partial \ln C_A}$$

$$\Rightarrow \boxed{\frac{dp^*}{dT} = \frac{\hat{A}n_v}{T \partial_u}}$$

$$\Rightarrow \hat{V}_g = \frac{RT}{P^*}$$

$$\Rightarrow d(\ln P^*) = \frac{dN}{R^T} dT$$

$$\ln\left(\frac{P_1}{P_2}\right) = \Delta H_f \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

→ Chen's equation (x)

$$\Delta \hat{H}_v = RT_b \left[ \frac{3.978 / T_b}{1.07 - (T_b / T_c)} \right] + 3.938 + 1.555 \ln \frac{P_c}{P_v}$$

Slope =  $\frac{1}{T_b}$   
y-intercept =  $3.938 + 1.555 \ln \frac{P_c}{P_v}$

$T_b$  = normal boiling temp.  $\Rightarrow$  water  $T_2 / V_2$   $\Rightarrow$  wavy lines

$T_c$  = critical temperature

$P_c$  = critical pressure

$$\frac{\partial \hat{H}_v}{\partial T} = \frac{\partial \hat{V}}{\partial T} = \frac{\partial \hat{V}}{\partial P} \cdot \frac{\partial P}{\partial T} = \frac{\partial \hat{V}}{\partial P} \cdot \frac{\partial \hat{P}}{\partial T} = \frac{\partial \hat{V}}{\partial P} \cdot \frac{\partial \hat{P}}{\partial T} = \frac{\partial \hat{V}}{\partial P} \cdot \frac{\partial \hat{P}}{\partial T}$$

→ Favoutoni rule (x)

$$\frac{\Delta \hat{H}_v}{T_b} = 21 \quad \rightarrow \text{works well for apolar liq}$$

no cal per g  $T_b$   
and  $T \propto V$

means non-polar liq

$$\frac{\hat{V}_a}{(\hat{V} - \hat{V}_a)} = \frac{\hat{g}_b}{(T_b) b}$$

→ Kirkley-Kowalsky equation for non-polar liq (x)

$$\frac{\Delta \hat{H}_v}{T_b} = 8.75 + 4.571 \log \frac{T_b}{T_c}$$

not valid for polar liq.

→ Graham and Watson eq (x)

$$\log \frac{P^*}{T_b} = -\frac{A}{T_b} + B - C$$

$$-20(T_b - b)^2$$

we can find vapour pressure

$$\frac{\hat{V}_a}{N \hat{V}} = \frac{\hat{g}_b}{T_b}$$

$T_b$  = reduced pressure

$$T_b = \frac{P^*}{P_c} \quad \text{const}$$

specific volume =  $\frac{1}{\hat{V}}$

$$\frac{\hat{V}_a}{\hat{V}} = \frac{\hat{g}_b}{T_b}$$

Q)  $T_b = 100^\circ\text{C}$ ,  $P = 0.101 \text{ MPa}$

$$\Delta \hat{H}_v = 2300 \text{ kJ/kg}$$

find the condition of  $H_2O$   
(also a mixt)

it is not  
pure  
mixt

Q) Find the internal energy and specific enthalpy for

(a) Water at  $0.4 \text{ MPa}$ ,  $225^\circ\text{C}$   $\rightarrow T = 325^\circ\text{C}$   $e = 293 \text{ kJ/kg}$

quasi-reversible

(b) Water at  $3.0 \text{ MPa}$ ,  $0.01 \text{ m}^3 \text{ kg}$   $\rightarrow$   $T < T_c$   $\rightarrow$  liquid

(c) Water at  $1.0 \text{ MPa}$ ,  $100^\circ\text{C}$   $\rightarrow$   $T > T_c$   $\rightarrow$  between liquid and vapour

$$P = 101 \text{ kPa} \quad T = 100^\circ\text{C}$$

atmospheric pressure

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

$\Delta H_f = 0 \text{ kJ/mol}$

$\Delta U_f = 0 \text{ kJ/mol}$

$\Delta H_f = 0 \text{ kJ/mol}$

$\Delta U_f = 0 \text{ kJ/mol}$

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$\Delta U_f = 0 \text{ kJ/mol}$

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$\Delta H_f = 0 \text{ kJ/mol}$

$\Delta U_f = 0 \text{ kJ/mol}$

$\Delta H_f = 0 \text{ kJ/mol}$

100  $\rightarrow$   $325^\circ\text{C}$   $\rightarrow$   $\text{vapour}$   $\rightarrow$   $\text{gas}$

$$3.0 \text{ MPa} = \text{saturation pressure} \quad P = 101 \text{ kPa}$$

$$(0.021 - 0.01) \frac{20}{0.01} + 0.021 = 0.021(20.0) + \left( \frac{0.021 - 0.01}{0.01} \right) b$$

$$\rightarrow P, T \rightarrow \text{saturated liq} \rightarrow \text{vapour} \rightarrow \text{mixture} \rightarrow \text{superheated liq} \rightarrow \text{superheated vapour} \rightarrow T > \text{saturation temp}$$

$$P = 101 \text{ kPa} = \text{const}$$

sol) let the vapour fraction be  $x$

liq "  $1-x$

$$x(2676) + (1-x)(419) = 2300$$

$$2257x = 2300 - 419$$

$$x = 0.833$$

quality factor  $\eta$

used for  $H_2O$ , steam mix

min

Q) 0.4 NPa,  $725^{\circ}\text{C}$  at  
super heated  $\text{H}_2\text{O}$  vapour,  $\rightarrow$  steam table  
 Table B.1  $\rightarrow$   $T > T_b$   
 $\therefore$  saturated  
 $\therefore$  go to  
super heated  
stable

(i) Find the density of steam at  $525^{\circ}\text{C}$ , 1.4 MPa

$$\rightarrow T = 880^\circ C \quad \hat{V} = 0.25215 \frac{m^3}{kg} \quad \hat{u} = 3121.1 \text{ kJ/kg}$$

$$\rightarrow T = 600^\circ C \quad \hat{v} = 0.2857 \text{ c} \quad \hat{u} = 3294.4 \quad \hat{h} = 3294.8$$

$$\hat{h}_{520} = (0.25)(\hat{h}_{520}) + (0.25)\hat{h}_{600} = h_{520} + \frac{25}{100}(h_{600} - h_{520})$$

$$V_{9.15} = \frac{1}{\text{density}} \quad \boxed{\text{density} = 3.837 \text{ kg/m}^3}$$

Q) Find the density of steam at  $\frac{12 \text{ MPa}}{100^\circ\text{C}}$ . Ans. 1.194

has  $\hat{u} = 1760 \text{ kN/kg}$  → additional data

80) ~~saturated~~  
~~put  $\times h$   $\leftarrow$  pure vapour~~  
~~now~~  
~~we have two phases~~  
~~at below spec~~  
~~• highest latent~~  
~~vapour~~  
~~phase rule~~

$\therefore$  we have a min  
Water vapour, water min

$$1960 = x(798.4) + (1-x)(2784.8) \quad | \quad x = \text{fraction of big}$$

$$x = 0.4153 \quad 1-x = 0.5846$$

$$\hat{v} = (0.001131)(\pi) + (1-\pi)(0.1633)$$

$$V = 0.0950$$

$$d = 10.42 \text{ kg/m}^3$$

$$Q) \quad 9.22) \quad P = 350 \text{ kPa} \\ V = 0.02 \text{ m}^3 \\ W = \int -P \, dV$$

$$W = -P \Delta V \quad W = -P [V_2 - V_1]$$

$$W = -350 \times 10^3 [0.15 - 0.02]$$

$$1kPa = \frac{1kN}{m^2}$$

$\pi = A$

$$W = -45.5 \text{ kJ/m}^2$$

$$W = -45.5 \text{ kPa m}^3/\text{m}^2$$

$$\frac{P_{\text{atm}}}{P_{\text{gas}}} = \frac{K_P}{K_J}$$

$$\text{Q. 2.42) } P = 300 \text{ kN/m}^3$$

Find the internal energy

$$= 10^3 \text{ c} \quad h = 6.05 \times 10^5 \text{ s/gmol}$$

of the gas at 300 K

$$\text{Sol.) } h = \bar{u} + \bar{v} \bar{w} t$$

~~$R \neq \bar{u} + \bar{v} \bar{w}$~~        ~~$M = u$~~

$$-MN = 9 \quad 32.028 = T = \frac{6 \cdot 0.5 \times 10^5}{\underline{0.200}} = U + (8.314)(303)$$

$$a) 9 \cdot 214) \quad D = 5 \text{ cm} \quad l = 10 \text{ cm}$$

$$\Delta H = \Delta U + \Delta(PV) \quad (\text{enthalpy with respect to surroundings})$$

$$\Delta H = -2.26 \times 10^5 \text{ J/kg mol}$$



Specific volume = const

$V_s = 0.323 \text{ m}^3/\text{kg}$

$\text{V}_v = 0.323 \text{ kg/m}^3$

$t = 127^\circ\text{C}$

$\text{V}_c = 0.00125 \text{ m}^3/\text{kg}$

$\text{V}_f = 0.270 \text{ m}^3/\text{kg}$

from steam table

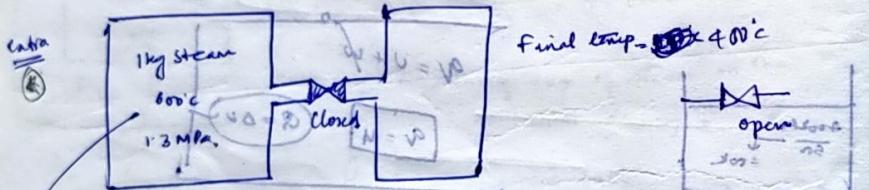
$$0.323 = x(v_0) + (1-x)(v_1)$$

converted to 100%

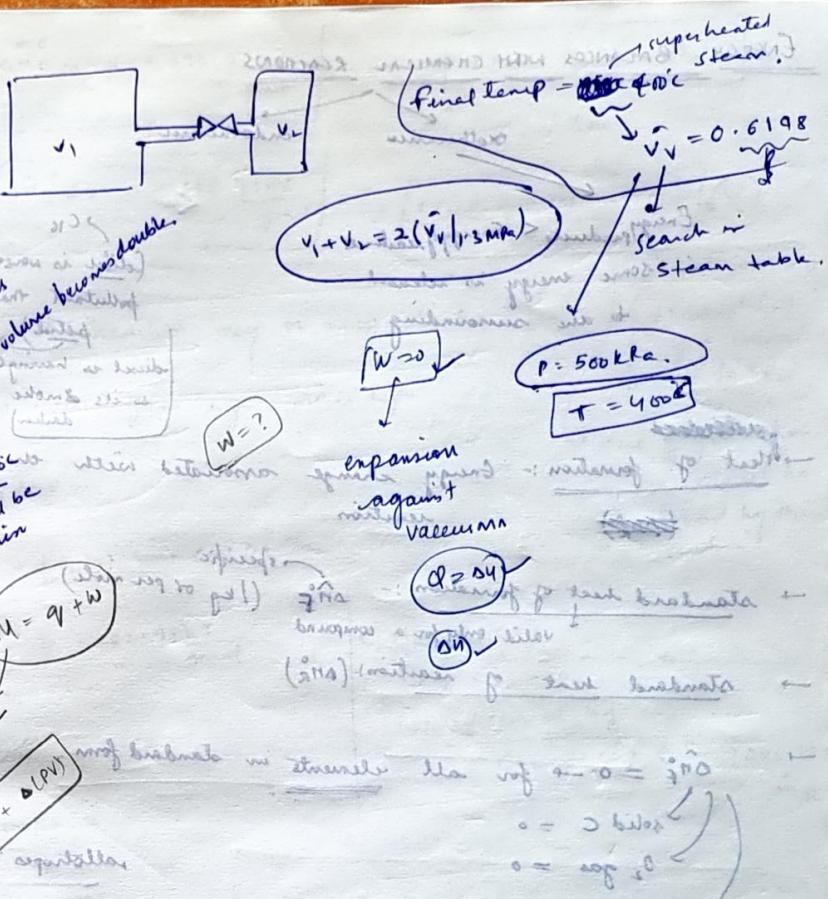
**Min of 2q**

With Parrot  
3' fcc = 7  
having an array of data

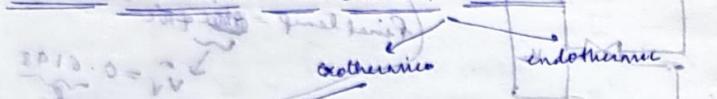
$$\text{Q 9.2-32) } \frac{V_1}{V_2} = 4 \quad P_1 = 1000 \times 6.894 \text{ kPa} \approx 6894 \text{ kPa}$$



$$\begin{aligned}
 & \text{upward shear} \quad \leftarrow 24000 \text{ N/m}^2 \\
 & \sigma = 1.2 \text{ MPa} \quad \tau = 1.4 \text{ MPa} \\
 & 0.33393 \text{ m} \quad + \quad 0.2857 \text{ m} \\
 & \Rightarrow V(1.2 \text{ m}) = N \quad \Rightarrow \tau = 0.309945 \\
 & \frac{V}{V_{\text{max}}} = \frac{N}{N_{\text{max}}} = 0.32 \quad \Rightarrow \tau = 0.309945 \\
 & \text{max shear force} = 0.309945 \cdot 24000 \text{ N/m}^2 \\
 & \text{max shear stress} = 0.309945 \cdot 1.2 \text{ MPa} = 0.371934 \text{ MPa}
 \end{aligned}$$



## ENERGY BALANCES WITH CHEMICAL REACTIONS



Energy products < Energy of reactants  $\rightarrow$  heat must be released to the surrounding.

→ Heat of formation :- Energy change associated with the reaction

→ standard heat of formation :-  $\Delta H_f^\circ$  (specific / kg or per mole) valid only for a compound

→ standard heat of reaction ( $\Delta H_r^\circ$ )

→  $\Delta H_f^\circ = 0 \rightarrow$  for all elements in standard form.

- solid C = 0
- O<sub>2</sub> gas = 0
- H<sub>2</sub>O liquid + 0  
it is compound

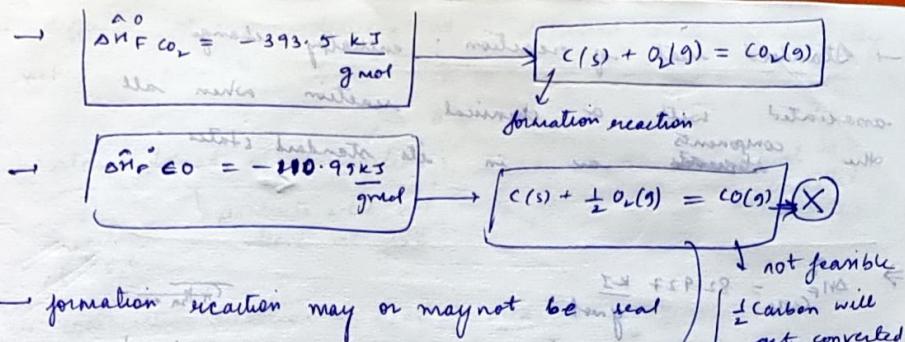
isotropes ??

→ heat of one mole of one compound from its constituent elements  
Formation

→ enthalpy change of formation of one mole of compound from its constituents elements in their standard state (25°C, 1 atm) → standard heat of formation

→  $\Delta H_r^\circ$ ,  $\Delta H_f^\circ$

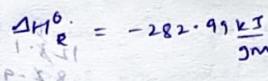
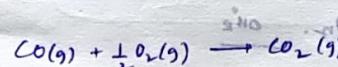
$> C_{10}$   
diesel is worse pollutant than petrol  
diesel is having carbon soot so its smoke is darker



→ formation reaction may or may not be useful

→ diesel → viscosity is high, MP is high

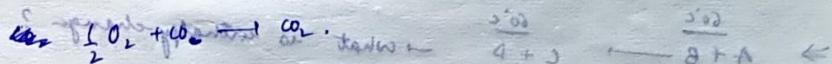
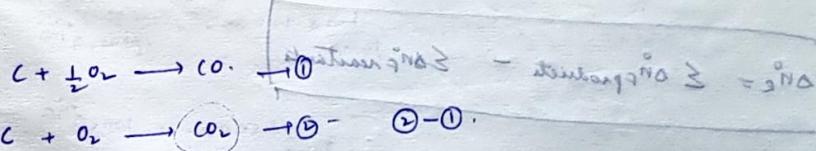
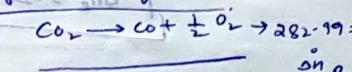
→ Hess Law



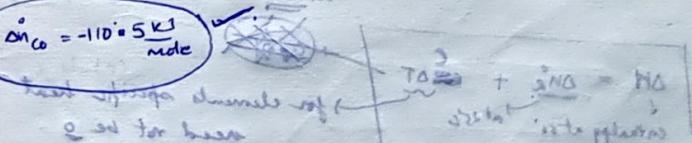
6 J 6

~~-282.99~~

followed by



$$\Delta H_r^\circ = \Delta H_f^\circ_{CO_2} - \Delta H_f^\circ_{CO}$$



$$\text{isotopes} = \frac{\Delta H^\circ}{\Delta H^\circ} \text{ test balance for } \frac{\Delta H^\circ}{\Delta H^\circ} =$$

→ Standard heat of reaction: enthalpy change associated with a chemical reaction when all the components standards are in its standard states

$\Delta H_F^\circ = (H_{\text{prod}}^\circ - H_{\text{react}}^\circ)$

$\Delta H_F^\circ = 82.927 \text{ kJ}$  (standard hydrogen reference point)

$\Delta H_F^\circ = -123.10 \text{ kJ}$  (first ionization potential of carbon)

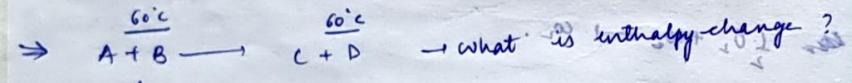
enthalpy of standard ad reference  $0^\circ \text{C}$  and  $1 \text{ atm}$



$$\Delta H_F^\circ = -123.10 - (82.927) \quad \Delta H_F^\circ = -206.027$$

$$\Delta H_F^\circ = \frac{123.1}{82.9} = 1.50$$

$$\Delta H_F^\circ = \sum \Delta H_F^\circ \text{products} - \sum \Delta H_F^\circ \text{reactants}$$



standard heat of reaction  $\Delta H_F^\circ$  is given at  $25^\circ \text{C}$   $= 0^\circ \text{K}$

$$\Delta H = \Delta H_F^\circ + C_p \Delta T$$

for elements specific heat need not be 0

at standard state  $\Delta H_F^\circ = \text{enthalpy at } 25^\circ \text{C}$

→ different streams leaving at different temp is logically not possible.

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

standard heat of combustion: highly exothermic / heat is generated

reactants products will not leave at  $25^\circ \text{C}$ .

combustion reaction → heat of reaction

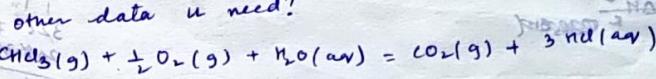
$\Delta H_F^\circ$

$$\Delta H_F^\circ / \Delta H_F^\circ / \Delta H_F^\circ$$

(write the phases)

a) Given  $\Delta H_F^\circ$  for  $\text{CH}_3\text{Cl}(g)$  is  $-121.800 \text{ kcal/g mol}$ . find  $\Delta H_F^\circ, \text{CH}_3\text{Cl}(l)$

what other data is needed?



sol)  $\Delta H_F^\circ, \text{H}_2\text{O}(l) = -62.317 \text{ kcal/g mol}$

$$\Delta H_F^\circ, \text{CO}_2(l) = -94.051.8 \text{ kcal/g mol} = (-11400 \text{ J}) + (-1) \cdot 10^3 \text{ J}$$

$$\Delta H_F^\circ, \text{H}_2\text{O}(l) = -40023 \text{ kcal/g mol} = \frac{\text{mass of } 1.00 \text{ g}}{\text{mass of } 1.00 \text{ g}} = \text{H}_2\text{O}(l), 25^\circ \text{C}$$

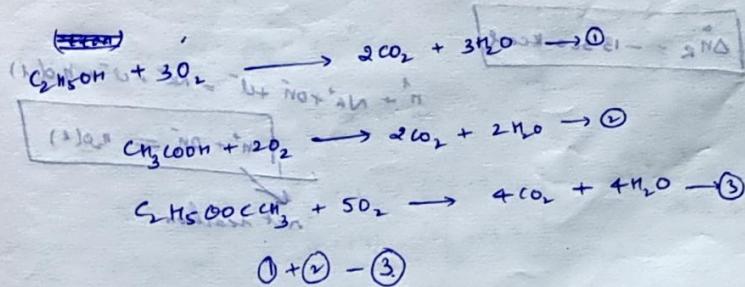
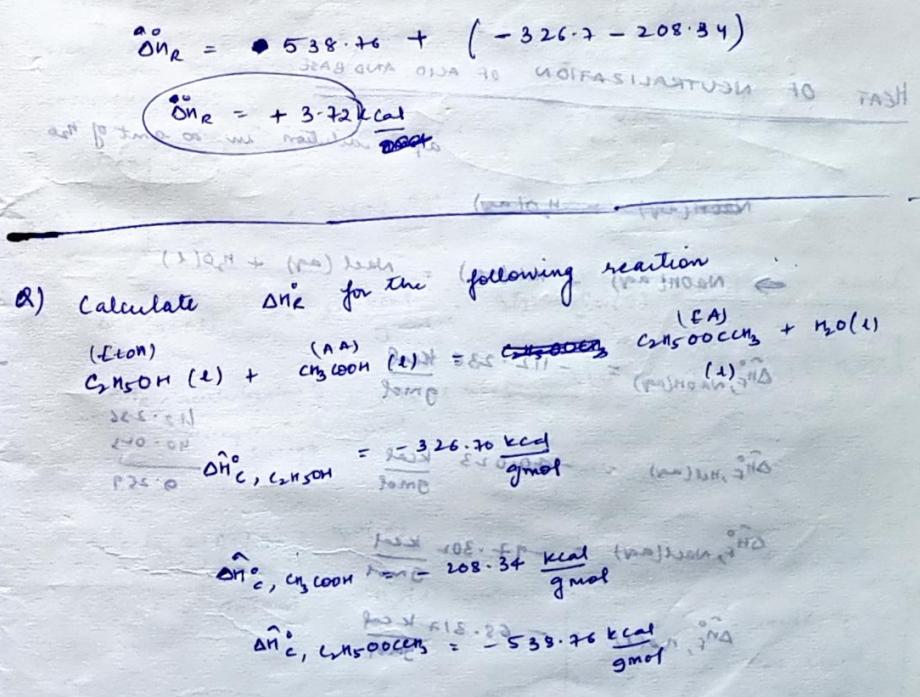
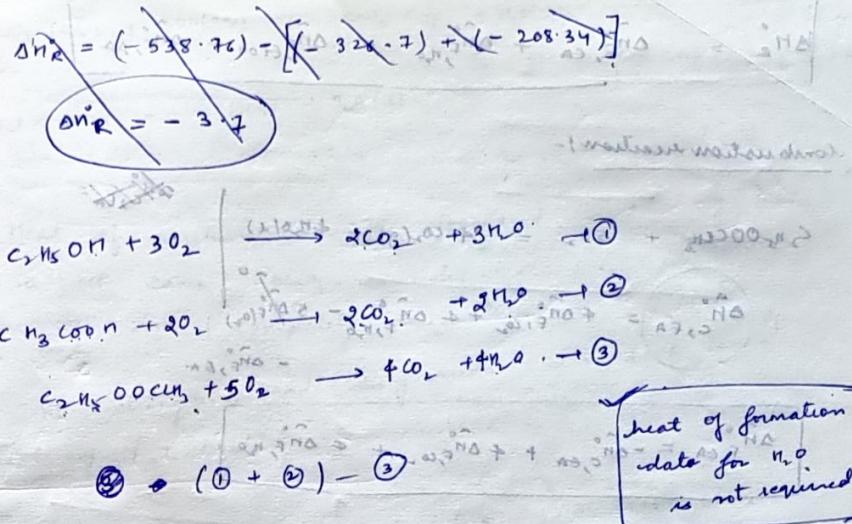
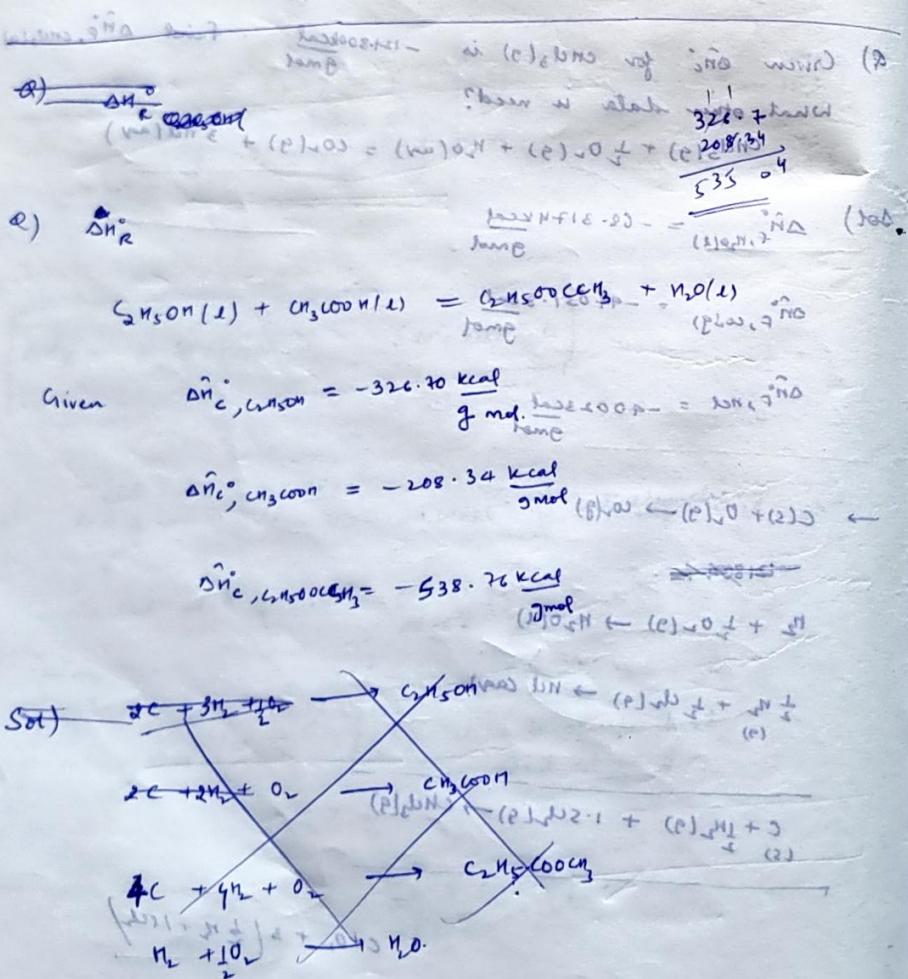
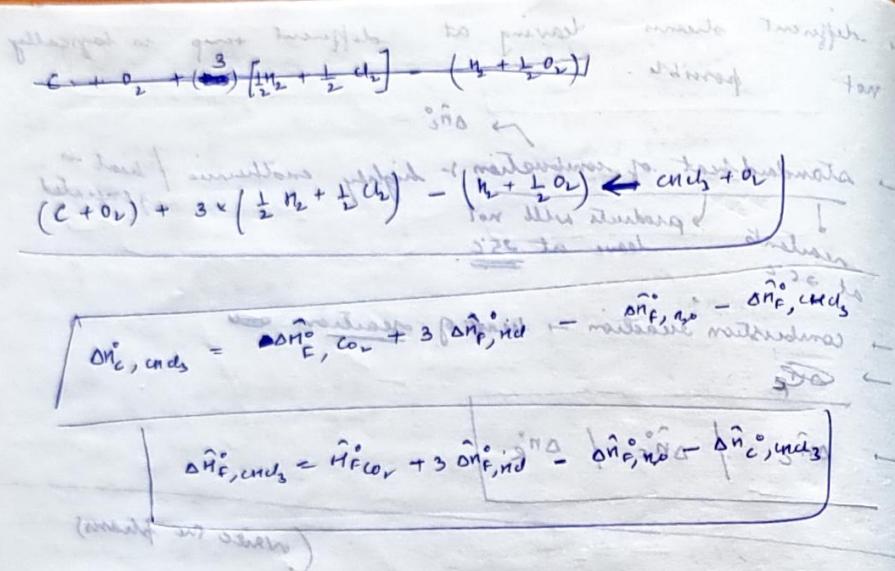
$$\text{C}(s) + \text{O}_2(g) \xrightarrow{25^\circ \text{C}} \text{CO}_2(g) \quad \frac{\text{mass of } 1.00 \text{ g}}{\text{mass of } 1.00 \text{ g}} = 1102.816 \cdot 25^\circ \text{C}$$

$$\text{H}_2 + \frac{1}{2}\text{O}_2(g) \xrightarrow{25^\circ \text{C}} \text{H}_2\text{O}(l) \quad \frac{\text{mass of } 1.00 \text{ g}}{\text{mass of } 1.00 \text{ g}} = 1102.816 \cdot 25^\circ \text{C}$$

$$\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2(l) \xrightarrow{25^\circ \text{C}} \text{HCl}(l) \quad \frac{\text{mass of } 1.00 \text{ g}}{\text{mass of } 1.00 \text{ g}} = 1102.816 \cdot 25^\circ \text{C}$$

$$\text{C} + \frac{1}{2}\text{H}_2(l) + 1.5\text{Cl}_2(l) \xrightarrow{25^\circ \text{C}} \text{CH}_3\text{Cl}(l) \quad \frac{\text{mass of } 1.00 \text{ g}}{\text{mass of } 1.00 \text{ g}} = 1102.816 \cdot 25^\circ \text{C}$$

$$0.11 \text{ C} + \text{O}_2 + 3(\frac{1}{2}\text{H}_2 + 1.5\text{Cl}_2)$$



$$\Delta H_r^\circ = \Delta H_{F, EA}^\circ + \Delta H_{F, H_2O}^\circ - \Delta H_{F, EtOH}^\circ - \Delta H_{F, AA}^\circ = \Delta H_A$$

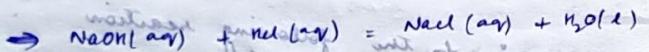
Combustion reaction:-



$$\begin{aligned} \Delta H_{c, FA}^\circ &= \Delta H_{F, CO_2}^\circ + 4\Delta H_{F, H_2O}^\circ - 5\Delta H_{F, O_2}^\circ \\ &\quad - \Delta H_{F, EA}^\circ - \Delta H_{F, CO}^\circ - \Delta H_{F, H_2O}^\circ \\ \Delta H_{c, FA}^\circ &= -(\Delta H_{F, EA}^\circ + \Delta H_{F, CO}^\circ + \Delta H_{F, H_2O}^\circ) \end{aligned}$$



HEAT OF NEUTRALIZATION OF ACID AND BASE



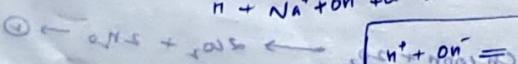
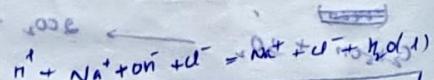
$$\Delta H_{F, NaOH(aq)} = -112.23 \frac{\text{kcal}}{\text{gmol}}$$

$$\Delta H_{F, H_2O(l)} = -140.023 \frac{\text{kcal}}{\text{gmol}}$$

$$\Delta H_{F, NaOH(aq)} = -97.302 \frac{\text{kcal}}{\text{gmol}}$$

$$\Delta H_{F, H_2O(l)} = -68.317 \frac{\text{kcal}}{\text{gmol}}$$

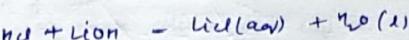
$$\Delta H_r^\circ = -13.360 \text{ kcal}$$



$$\textcircled{1} - \textcircled{2} + 0$$



heat of neutralization



Heat of neutralization for strong acid and strong base is almost same bcoz molecules exists in the form of ions (completely dissociate)

All strong bases and strong acids will have same heat of neutralization.

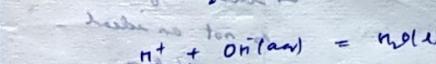
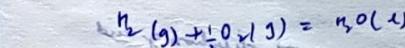
Weak acid + weak base =  $\Delta H_r^\circ < 13.36 \text{ kcal}$  bcoz weak acid and weak base will not dissociate completely

Strong acid + weak base =  $\Delta H_r^\circ > 13.36 \text{ kcal}$

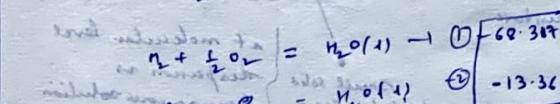
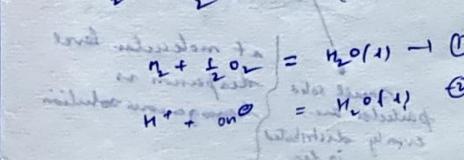
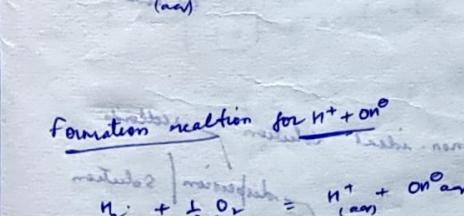
Strong base + weak acid =  $\Delta H_r^\circ < 13.36 \text{ kcal}$

$\Delta H_{F, H_2O(l)} = -68.317 \frac{\text{kcal}}{\text{gmol}} \rightarrow H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$

$\Delta H_r^\circ, \text{ neutralization } B = -13.36 \text{ kcal}$



Formation reaction for  $H^+ + OH^-$



Mess law:- reverse of the reaction has equal and opp heat of reaction

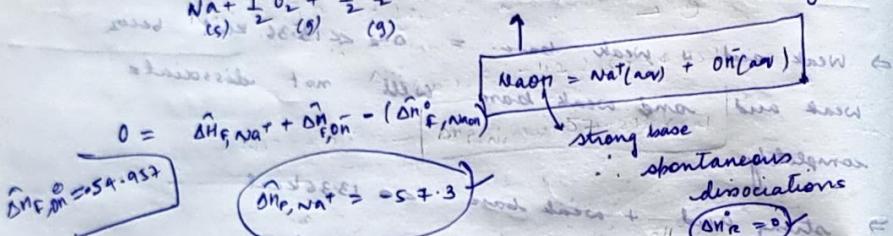
$$\textcircled{1} - \textcircled{2} \Rightarrow -68.317 + 13.36 \Rightarrow -54.957 \text{ kcal}$$

Combined heat of formation for  $H^+(aq)$  and  $OH^-(aq)$  is  
 $-54.957 \text{ kcal}$

+ we assign  
 $\Delta_{\text{f}}^{\circ} F, H^+ = 0 \rightarrow \text{assumption}$

$\Delta_{\text{f}}^{\circ} F, OH^- = -54.957 \text{ kcal}$  → enthalpy for heat of solution  
 and mass transfer in aqueous systems is very small due to strong interactions between solute and solvent.

$\Rightarrow \Delta_{\text{f}}^{\circ} F, NaOH = ? \quad \Delta_{\text{f}}^{\circ} F, NaOH = -112.236 \text{ kcal/mol}$  molal heat of solution



Ideal solution → heat of solution  
 Weighted avg of enthalpies of two solutions → any property is weighted avg (or sum) of individual properties

for example:  $NaCl + KCl$  → not an ideal solution

→ If heat of solution ≠ 0 → non-ideal solution

Two cases:  
 1)  $\Delta_{\text{f}}^{\circ} F, \text{ soln} = \Delta_{\text{f}}^{\circ} F, \text{ solute} + \Delta_{\text{f}}^{\circ} F, \text{ solvent}$  → dispersion solution  
 2)  $\Delta_{\text{f}}^{\circ} F, \text{ soln} < \Delta_{\text{f}}^{\circ} F, \text{ solute} + \Delta_{\text{f}}^{\circ} F, \text{ solvent}$  → colloid

→ foam → valence interaction  
 $\Delta_{\text{f}}^{\circ} F, \text{ soln} < \Delta_{\text{f}}^{\circ} F, \text{ solute} + \Delta_{\text{f}}^{\circ} F, \text{ solvent}$  → low temp high humid air  
 → smog → solid + air + liquid interaction with water (absorb prop. substances)  
 → smoke → air + solid

→ Ideal solution / Non-ideal solution  
 atleast one property is not weighted sum  
 generally enthalpy

Heat of solution: Enthalpy change of solution when one mole of solute dissolves in  $n_1$  moles of solvent at standard conditions. This is known as standard integral heat of solution. Its value depends on  $n_1$ .

- differential heat of solution:
- heat of solution at  $\infty$  dilution: Increase  $n_1$ . At a point upon increasing  $n_1$ , heat of solution will not change.

differential: Enthalpy change from  $n_1$  to  $n_1 + 1$  for  $(n_1 + 1)$  → not const

heat of solution:  $H_s = n_1 H_1 + n_2 H_2 + \Delta_{\text{f}}^{\circ} F_{\text{solute}}$  → solute  
 $\Delta_{\text{f}}^{\circ} F_{\text{solute}} = \Delta_{\text{f}}^{\circ} F_{\text{solute}} - \Delta_{\text{f}}^{\circ} F_{\text{solvent}}$  → solvent

$\Delta_{\text{f}}^{\circ} F_{\text{solute}} = 0 \rightarrow$  ideal solution  
 $\Delta_{\text{f}}^{\circ} F_{\text{solute}} \neq 0 \rightarrow$  real soln.

$\Delta_{\text{f}}^{\circ} F_{\text{solute}} = +ve \rightarrow$  supply energy from outside  
 $= -ve \rightarrow$  energy is released & soln will become hot

→ reaction proceeds in the direction where energy decreases

$\rightarrow \Delta H_{25, n_2} = +ve \rightarrow n_2 > n_1 N_1 + n_2 N_2$  → similar to evaporation  
 solution contains more energy → i.e. energy must be supplied from outside

$\rightarrow \Delta H_{25, n_2} = -ve \rightarrow n_2 < n_1 N_1 + n_2 N_2$  solution has less energy but excess energy is released on the surrounding

$$\hat{n}_s = \hat{n}_1 + n_2 \hat{n}_2 + \Delta n_{25, n_2}$$

area path  
relative

→ adiabatic flame temp :-

→ defining plot :-

reference substance plot

### PSYCHROMETRY

(humid air → mixture)

air flow

→ Science of humidity

amount of water vapour in air

→ Why is excess air used in combustion? → trying to cover equipment v efficiency.

→ recuperator

equipment for waste heat recovery.

e.g. car exhaust

(flue gas)

→ how to measure humidity? → indirectly done using thermometers

specific humidity

→ Humidity → relative humidity

absolute humidity

absolute humidity

$$H = \frac{m_{\text{water}}}{m_{\text{dry air}}}$$

$$\phi = \frac{P_w}{P_{w^*}} \times 100$$

$P_w$  = Partial pressure of water vapour

$P_{w^*}$  = saturated vapour pressure of water

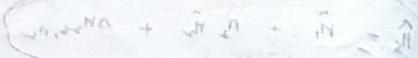
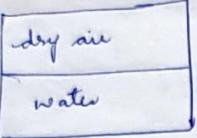
Dew formation

$$AH = \frac{m_{\text{water}}}{V_{\text{net}}} = \frac{m_{\text{water}}}{kg/m^3}$$

$V_{\text{net}} = \text{combined volume of water vapour + air mix}$

$$H_{MSP} = \frac{P_{w^*}}{P_{\text{total}} - P_{w^*}}$$

specific metal humidity



$P_w^*$  are functions of temp

Dew formation: at night  $P_w^*$  drops  
not an isothermal process

same relative humidity  $\leftarrow$  low temp  $\phi = \frac{5}{100}$   
high temp  $\rightarrow$  more no. of water molecules in air  $\phi = \frac{50}{100}$

$\epsilon_w$  depends on system & time

$\Rightarrow$  Relative saturation ( $\gamma_r$ ) =  $\frac{P_v}{P_s} \times 100 = \gamma_{r, \text{sat}}$

~~particular~~  $P_v$  = partial pressure of water vapour

$P_s$  = vapour pressure of pure water



$\Rightarrow$  Humid heat ( $C_s$ )  $\rightarrow$  Cp of humid air

Humid volume ( $\tilde{V}$ ): (specific volume of humid air per unit of dry air)

$$\tilde{V} = \left( 0.2415 \frac{m^3}{kg \text{ dry air}} \right) \left( \frac{1 \text{ kg dry air}}{2.9 \text{ kg air}} \right) \left( \frac{T}{273} \right)$$

$C_s = C_p, \text{air} + (H)(C_p, \text{water vapour})$

In SI unit

$C_s = 1.00 + 1.88 \times \left( \frac{kg}{kg \text{ dry air}} \right)$

$$\tilde{V} = \tilde{V}' + (H) \left( \frac{2.415 m^3}{1 \text{ kg dry air}} \right) \left( \frac{1 \text{ kg vapour}}{18 \text{ kg vapour}} \right) \left( \frac{T}{273} \right)$$

$$\tilde{V} = \left[ 0.8 \times 10^{-3} T + 4.58 \times 10^{-2} T ({}^\circ C) \right] \frac{m^3}{kg \text{ dry air}}$$

$$\text{and } \frac{m^3}{kg \text{ dry air}} = \frac{m^3}{(2.9 - 0.8) \text{ kg}}$$

### ① Specific humidity ( $\epsilon_w$ )

$$\epsilon_w = \frac{M_{H_2O}}{M_{\text{air}}}$$

Molar

### ② Relative humidity ( $\gamma_r$ )

$$\gamma_r = \frac{P_v}{P_s} \times 100$$

$P_v$  = partial pressure of vapour

$(P_s)$  = vapour pressure  $\leftarrow$  partial pressure of vapour at saturation  
at fixed temperature

### ③ Absolute humidity ( $\epsilon_p$ )

$$\epsilon_p = \frac{M_{H_2O}}{V_{\text{total}}} \text{ where } V_{\text{total}} = \text{total volume}$$

### γ saturation ( $\gamma_s$ )

$$\gamma_s = \frac{n_v}{n_s} \times 100$$

$n_v$  = moles of vapour per moles of vapour free air

$$\frac{n_v}{1} = \frac{P_v}{P - P_v}$$

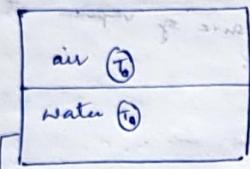
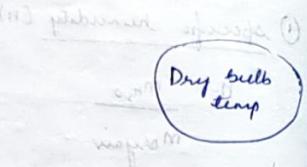
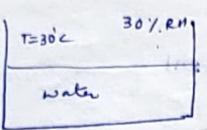
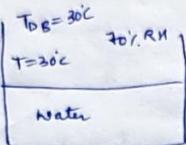
$P$  = total pressure

$$\frac{n_s}{1} = \frac{P_s}{P - P_s}$$

$$\gamma_p = \frac{n_v}{n_s} = \frac{P_v}{P_s} \times \frac{P - P_s}{P - P_v}$$

$$\gamma_p = \gamma_s \left( \frac{P - P_s}{P - P_v} \right)$$

## WET BULB TEMPERATURE



We want the air to get saturated. Air supplies latent heat to  $H_0$ . Air supplies latent heat to  $H_0$ . Temp of air +, water vapour, humidity  $T, RH$ .

→ until the air becomes saturated this process goes on

$$\text{Q}_0 \times \frac{V_m}{27} = H_0 \rightarrow \text{saturated air}$$

After saturation both evaporation and condensation take place (water cannot hold more water vapour)

### Wet bulb temp or adiabatic saturation temp

It is the temp that a volume of air would have had it been cooled adiabatically to saturation by evaporation of  $H_0$  into it while all latent heat being supplied by the volume of air itself -

$$\left( \frac{H_0}{V_m} \right) \times N = q_0$$

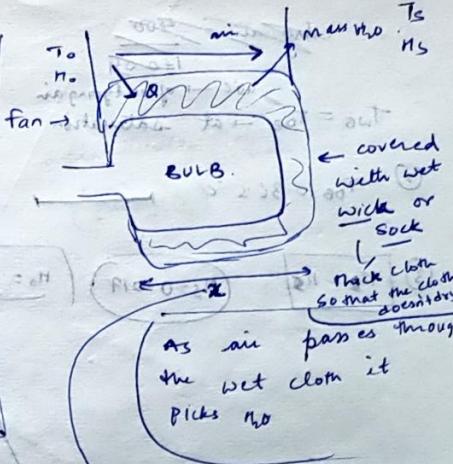
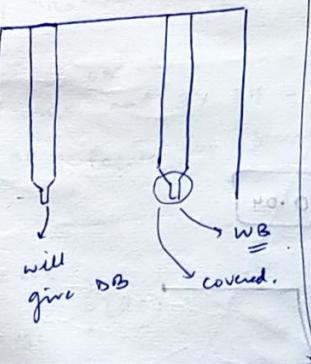
- mass transfer starts first  $\rightarrow H_0$  at room temp also evaporation takes place.
- temp wise there is no driving force
- Once saturation is achieved, rate of evaporation = rate of condensation → dynamic equilibrium.

→ Difference between dry bulb temp and wet bulb temp is dew wet bulb depression.

$$T_{DB} > T_{WB}$$

$$T_{DB} = T_{WB} \rightarrow 100\% \text{ saturation}$$

→ Sling psychrometer is used to measure wet bulb temp



Initial temp  $T_0$

Initial specific humidity  $H_0$

$$(H_s - H_0)\lambda = (T_0 - T_s) e_s \rightarrow k_s \text{ of air}$$

& humid heat

$\Rightarrow Q_{net} = 0 \rightarrow \therefore \text{the system is adiabatic}$

Within the length  $x$ , velocity of air should be such that it should get saturated

## PSYCHOMETRIC CHART

Q) Air at  $60^{\circ}\text{C}$  dry bulb temp and  $H = 0.04$ . Find the process numbers  
Air is adiabatically saturated. Find the process numbers

① Find the water taken by this air  $\rightarrow M_s - M_o$

② At what temp a dry bulb temp should fall in order to form dew

③ At night the temp drops to  $22^{\circ}\text{C}$ , find the amt of water condensed.

$$\text{Sol: } ① M_o = 0.04 \quad M_s = 0.049$$

$$\rightarrow M_s - M_o = 0.09 \Rightarrow \text{water taken by this air}$$

dry air  $\rightarrow 400$

$T_{DB} = 60^{\circ}\text{C}$

$$T_{WB} = T_{DB} \rightarrow \text{at saturation}$$

$$② T_{DB} = 36.5^{\circ}\text{C}$$

$$③ M_o = M_s$$

$$M_s = 0.019$$

$$M_o = 0.04$$

$$M_o = \frac{500}{1.04} \text{ kg/m}^3$$

$$M_o = 482.61 \text{ kg/m}^3$$

$$1.5 (zT - zT') = k (H - zH')$$

$$h_T = 0$$

$$0 = N$$

$$1.0 = g_m R$$

Q) 400 kg of air with specific humidity 0.04 and dry bulb temp with  $60^{\circ}\text{C}$  is adiabatically saturated. Find the water taken by the air.

$$\text{Sol: } H = \frac{M_{s,o}}{M_{air}}$$

(1) adiabatically

M<sub>air</sub> (—) (wet) psychrometric

$$M_{air} + M_{oair} = H$$

$$M_{oair} = \frac{M_{air}}{H+1}$$

$$\text{m<sub>air</sub> = } \frac{M_{air}}{H+1} = 384.2 \text{ kg}$$

$$M_{oair} = (H_s - M_o) M_{oair}$$

$$M_{oair} = 3.46 \text{ kg}$$

Q) Air at  $60^{\circ}\text{C}$  and  $3\%$ . RH is adiabatically humidified to  $80\%$ . Locate the process. (process ②)

$$② T_{DB} = 60^{\circ}\text{C}$$

$$T_{WB} = 25^{\circ}\text{C}$$

$$③ T_{DB} = ? \quad H = 0.04 \quad T_{WB} = 44^{\circ}\text{C}$$

$$\text{enthalpy at saturation} = 204 \text{ kJ/kg}$$

$$\text{enthalpy deviation} = -4 \text{ kJ}$$

$$③ \rightarrow W_B$$

$$0.045$$

$$\frac{M_{s,o}}{V_{net}}$$

$$M_{s,o}$$

- ⇒ wet bulb temp reflects a humidity on temp scale
- relative  
temperature difference is 3°  
saturation can be achieved in 3 ways  
isothermally (I)  
adiabatically (V)  
horizontally (dew) (-)

Q) 500kg/hr air enters a drier. The initial moisture content of the feed air is 0.015 and  $T_{DB} = 110^\circ\text{C}$ . The drier is operated adiabatically. The air leaves the drier at 90% RH. Find out all possible parameters of the outlet air. How much water can be removed by this drying process.

Sol)  $T_{WB} = 38.5^\circ\text{C}$  (read)  $\eta_s = 0.045$

$T_{DB} = 41^\circ\text{C}$   
Entropy of saturation =  $15.7 \text{ J/kg}\cdot\text{K}$

humidity = 0.95

deviation is between 0 and 0.5

$\rho_f / \rho_{s,0} = \text{moisture ratio}$

deviation?  
interpolation?

Moisture =  $492.61 \text{ kg/hr}$

$M_{H_2O} \text{ removed} = 14.77$

$M_{H_2O} \times (\eta_s - \eta_o)$

$14.77 \times 0.045 = 0.66$

$0.66 = 0.5$

$k_c = \frac{T_b}{T_s}$