

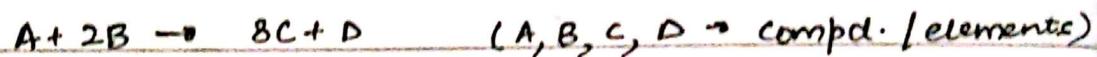
Enthalpy Balance with Chemical Balance

Exothermic rxn: heat is released

Endothermic rxn: heat is taken.

→ Energy is associated with every chemical rxn:

$\Delta H_R^\circ \rightarrow$ Standard Heat of Rxn:

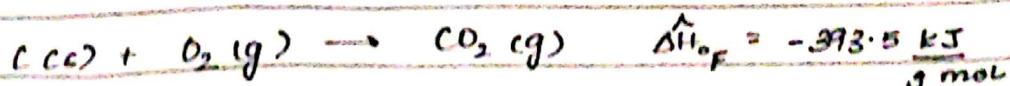
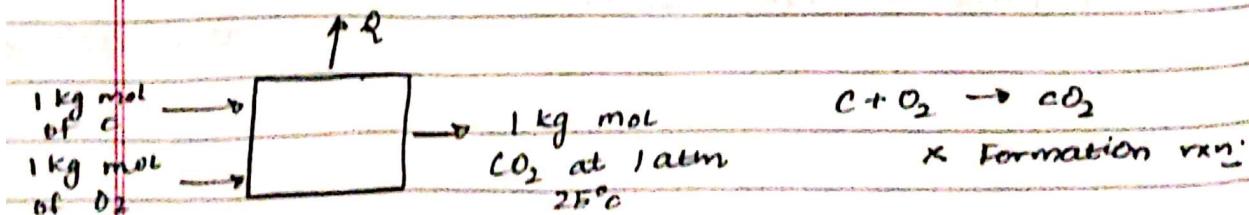


$$\hat{\Delta H}_R^\circ = 3 \times \text{Enthalpy of } C + \text{Enthalpy of } D \\ - 2 \times \text{Enthalpy of } B + \text{Enthalpy of } A$$

$$\therefore \hat{\Delta H}_R^\circ = \sum \text{Total Enthalpy of Pdts} \\ \uparrow - \sum \text{Total Enthalpy of Reactants}$$

At Std.
conditions

$\hat{\Delta H}_f^\circ \rightarrow$ It is enthalpy change associated
with formation of 1 mole of a
compound from its constituents in
their standard state, at 25°C and
1 atm pressure.



exothermic rxn: Constituents are
having more energy

$\Delta \hat{H}_F^\circ =$ All stable elements in std. form = 0

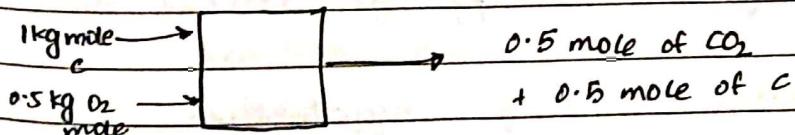
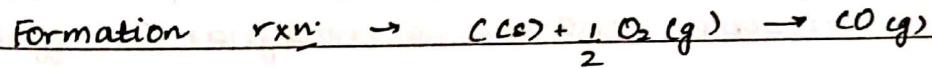
For thermal effects of chemical rxn, quantified by $\Delta \hat{H}_{op}$

For quantification of $\Delta \hat{H}_{op}$, we need to define std. heat of formation.

$$\Delta \hat{H}_{F, Br(g)}^\circ = 111.888 \frac{\text{kJ}}{\text{mol}} \rightarrow \text{Can be correct}$$

$$\Delta \hat{H}_{F, O_2(g)}^\circ = 62.3 \frac{\text{kJ}}{\text{mol}} \leftarrow \begin{matrix} \times 0 \\ \uparrow \end{matrix} \rightarrow \begin{matrix} \text{stable element} \\ \text{diatomic molecule} \end{matrix}$$

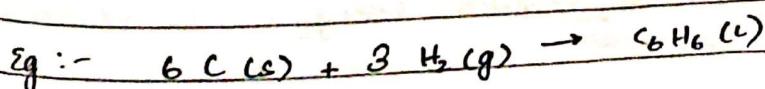
Finding $\Delta \hat{H}_{F, CO}^\circ$



Thus the above rxn. ① doesn't happen,

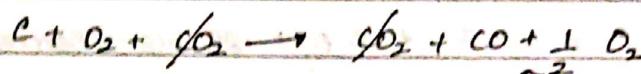
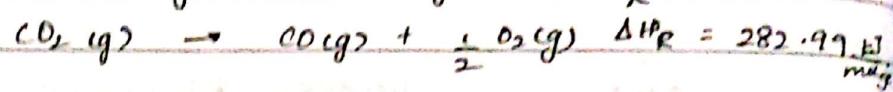
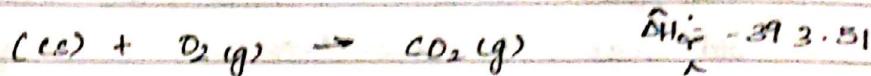
So how to calculate $\Delta \hat{H}_{F, CO(g)}$

\therefore Formation reaction can be real or fake (hypothetical)



Property used for writing Hess law i.e. reversibility of a chemical rxn:

$\hat{\Delta}H_{\text{of}}$ = sum of intermediate heat of formations



$$\hat{\Delta}H_R = \hat{\Delta}H_{\text{of}, \text{rxn}}$$

$$= -393.51 + 282.99$$

Any reaction we consider is perfectly reversible and the thermodynamic effects are also reversible.

Reversing the enthalpy sign reverses the rxn.

- Formation rxn. may be hypothetical
- When we use Hess law → we assume complete thermodynamic reversibility of a chemical rxn, which may or may not be possible.
- calculation of heat of rxn' based on heat of formation data of prod. and reactant doesn't consider activation energy.

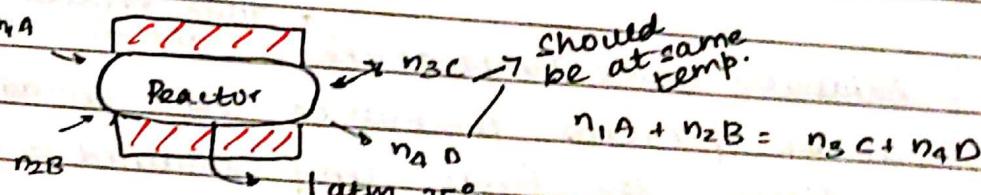
$$\hat{\Delta}H_F^o \text{CO(g)} = -110.52 \frac{\text{kJ}}{\text{g mole of CO}}$$

If we try to perform rxn of CO with stoichiometric amount of C and O₂, CO doesn't form

Formation rxn is fake, but it participates in other rxn's

Compounds with

Real formation rxn's $\hat{\Delta}H_F^o$ can be measured



1 atm, 25°C

All species in std. state

$$\hat{\Delta}H_{F,0}^o = n_3 \hat{\Delta}H_{F,C}^o + n_4 \hat{\Delta}H_{F,D}^o - n_1 \hat{\Delta}H_{F,A}^o - n_2 \hat{\Delta}H_{F,B}^o$$

Reaction only at
std. cond. in the
sense, the data can
be used only at std. cond.

Two diff stream in above diagram tells
that the ppts are in diff states

Utility of $\hat{\Delta}H_F^o$

for endothermic rxn:

↗ Saturated steam

we would like to maintain const. pressure
and temp, thus we have to ~~remove cont. remove~~ cont. supply
heat (exothermic rxn.) or cont. supply heat
(endothermic rxn.)

Standard Heat of combustion ($-\Delta\hat{H}_{\text{O}_2}$)

It is heat of rxn of combustion of a substance in its normal state at 25°C and 1 atm pressure.

(Isothermal cond.)

Keep in the rxn chamber under isothermal condition.

- Rise in temp. isn't allowed, starts at 25°C and ends at 25°C .

Adiabatic Flame Temperature ^{thus related to calorific value}

If we perform combustion rxn in adiabatic conditions, the final temp. obtained is (AFT)

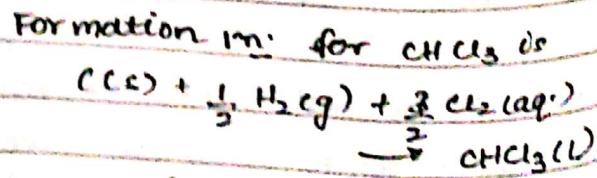
Higher AFT, higher the heat extracted from fuel.

If we are burning a fuel in atmosphere it's a midway between above two.

$\Delta\hat{H}_{\text{O}_2}$ → The state of final prod. must be specified

Calculation of $\hat{\Delta}H_{\text{p}}$ from $\Delta\hat{H}_{\text{O}_2}$:-

$\text{CHCl}_3 \text{ (g)}$



↑ Pseudo rxn:

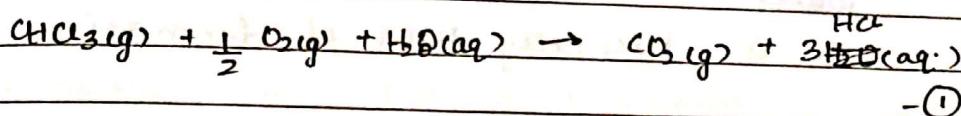
$$\hat{\Delta H}_{f,C, \text{CHCl}_3} = -121800 \text{ cal/mole}$$

$$\hat{\Delta H}_{f,O, \text{H}_2\text{O}} = -68.317 \text{ cal/mole g}$$

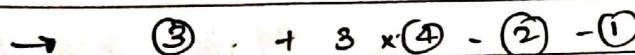
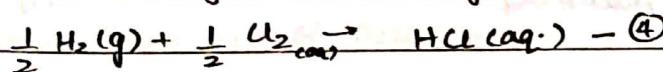
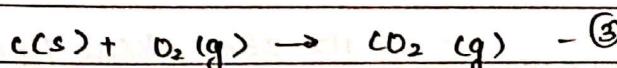
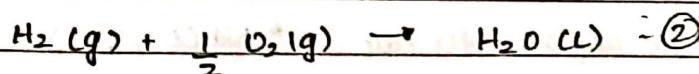
$$\hat{\Delta H}_{f,O, \text{CO}_2} = -94.051 \text{ cal/mole g}$$

$$\hat{\Delta H}_{f,O, \text{HCl}} = -40.023 \text{ cal/g mole}$$

Combustion rxn of CH_3Cl



Formal rxn :-



$$\therefore \hat{\Delta H}_{f,C, \text{CHCl}_3} = \hat{\Delta H}_{f,O, \text{CO}_2} + 3 \hat{\Delta H}_{f,O, \text{HCl}} - \hat{\Delta H}_{f,O, \text{H}_2\text{O}} - \hat{\Delta H}_{f,C, \text{CHCl}_3}$$

$$= -24.003 \text{ kcal/g mol}$$

\therefore One can find heat of formation from heat of combustion data.

Similarly, std. heat of rxn can be found out from heat of combustion.

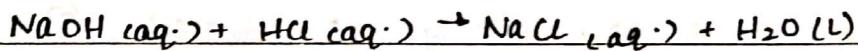
∴ Using Hess law → we can calculate
heat of combustion dat to
calculate (i) heat of formation
(ii) heat of rxn.

Heat of neutralization of acids and bases :-

Heat produced when 1 eq. of acid and 1 eq. of base react to produce salt and water.

It is basically heat of formation

Neutralization between dilute aq. soln. of NaOH and a dilute soln. of HCl.



$$\Delta \hat{H}_{\text{f}, \text{NaOH(aq.)}} = -112.236 \text{ kcal/g mol}$$

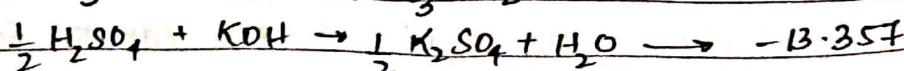
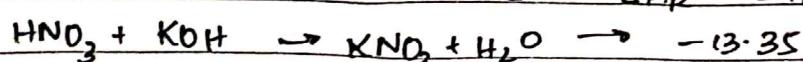
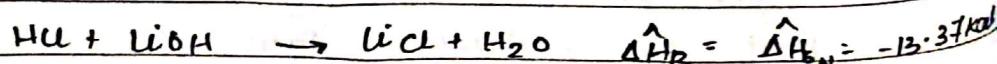
$$\Delta \hat{H}_{\text{f}, \text{HCl(aq.)}} = -40.023 \text{ kcal/g mol}$$

$$\Delta \hat{H}_{\text{f}, \text{NaCl(aq.)}} = -97.302 \text{ kcal/g mol}$$

$$\Delta \hat{H}_{\text{f}, \text{H}_2\text{O(l)}} = -68.317 \text{ kcal/g mol}$$

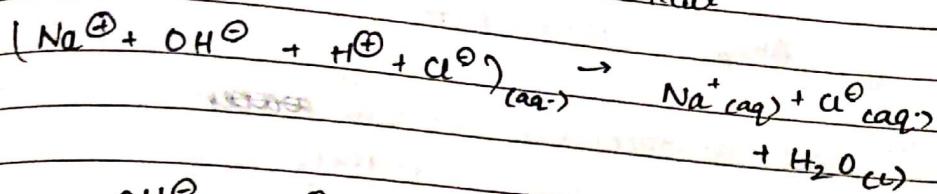
$$\therefore \Delta \hat{H}_{\text{rxn}} = -13.360 \text{ kcal}$$

For several other neutralization rxn's



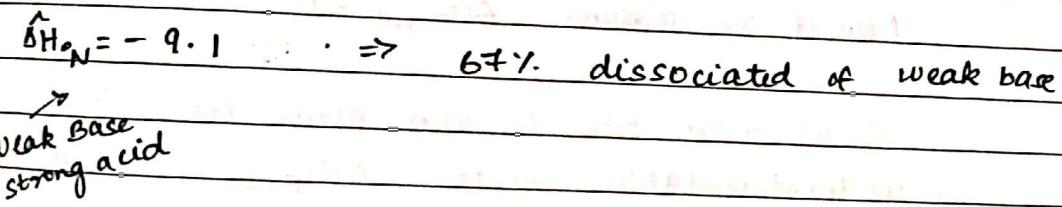
\uparrow heat of neutralisation

It remains same for strong base and strong acid
in their aq. soln. is -13.37 kcal



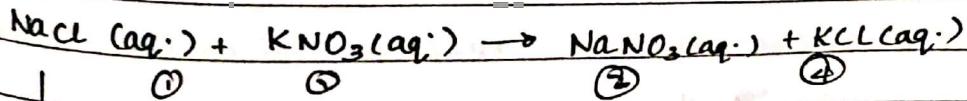
\uparrow For all strong acid + strong base
For strong acid and strong base, there is complete dissociation.

For dilute acids, there is incomplete dissociation, thus heat of neutralisation (mag.) is lesser.



Thermoneutrality of salt soln.:

We mix dilute aq. solution of two neutral salts ~~→~~ → there is no thermal effect, provided there is no precipitation or gas formation.



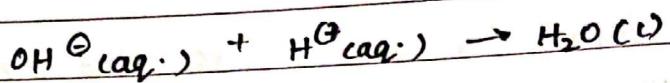
① ②

③

④

Dilute soln. of these two salts is mixed and water is allow to evaporate, then we will have all four salts (①, ②, ③, ④)

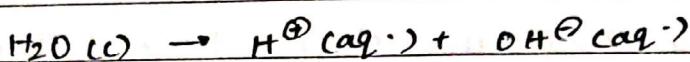
→ Double decomposition (final ppt. will partly form 2 diff. and partly not change)



$$\Delta H_{\text{f},\text{R}} = -13.36 \text{ kcal}$$

Heat of formation of ions.

$$\hat{\Delta H}_{\text{f,p}} = -68.317 \text{ kcal}$$



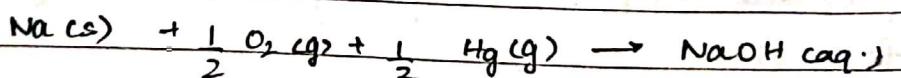
$$\Delta H_{\text{f}, \text{H}^\oplus \text{ and } \text{OH}^\ominus}$$

combined heat formation
rxn for H^\oplus and OH^\ominus
ions

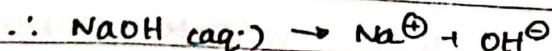
$$\text{Now if we assume } \Delta H_{\text{f}, \text{H}^\oplus} = 0$$

If we find ΔH_{f} of any other ion, it's
understandable that $\Delta H_{\text{f,ion}}$ is w.r.t
 $\Delta H_{\text{f}, \text{H}^\oplus}$

$$\text{we have } \hat{\Delta H}_{\text{f,NaOH(aq.)}} = -112.236 \frac{\text{kcal}}{\text{g mol}}$$



In aq. medium, NaOH will dissociate fully
to Na^\oplus and OH^\ominus



$$\Delta H_{\text{f}, \text{Na}^\oplus} = -112.236 - (-54.957)$$

$$= -57.729 \frac{\text{kcal}}{\text{g mol}}$$

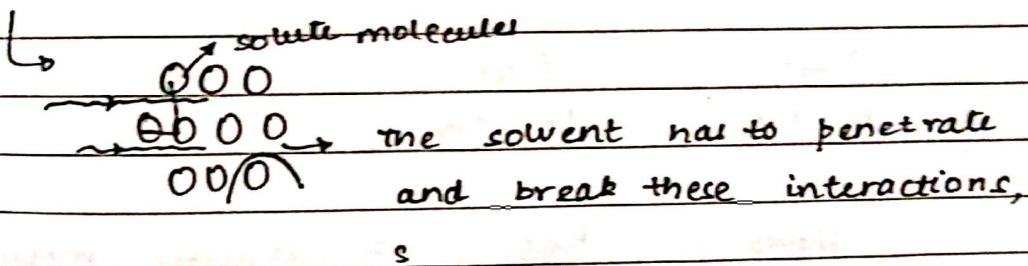
Heat of formation of ion.

Ideal soln :-

- No thermal effect

Real soln :-

- There is change of enthalpy during preparation of solution
- Enthalpy change associated with dissolution of a substance is termed as heat of soln or heat of dissolution
- For a neutral, non-dissociating salt is normally positive, and heat is absorbed from surrounding in an isothermal cond. for formation of solution, and the system cools.



Organic solvents which are apolar, are better suited to dissolve apolar materials.

Aq. solvents can dissolve more types of solutes.

→ The enthalpy change of a system, when one molecule of solute dissolves in n molecules of the solvent, while temp. is $25^\circ\text{C} \rightarrow$ std. integral heat of soln:

The value depends on n .

→ The asymptotic value of heat of soln for large $n, \rightarrow \infty$ is known as 'heat of soln at inf. dilution'

$$\text{Differential heat of condn} = \hat{\Delta H}_{\text{po}}|_{n_1, n_2} - \hat{\Delta H}_f|_{n_1, n_2}$$

↳ Dependent on both n_1, n_2

Humidity.

↳ Depends on temp, but doesn't have any direct explicit/implicit func. with temp.

- (i) Specific humidity (h) → Defined as mass of water vapour per mass of bone dry air
 ↳ Air having no moisture content
- Also called moisture content.

$$h = \frac{m_{H_2O}}{m_{\text{dry air}}} = \frac{18 n_{H_2O}}{29(n_T - n_{H_2O})}$$

$$\frac{n_{H_2O}}{n_T - n_{H_2O}} = \frac{P_{H_2O}}{P_T - P_{H_2O}}$$

$$H_{\text{msp}} = \frac{P_{H_2O}}{P_T - P_{H_2O}} = \frac{\text{Specific molal}}{\text{Humidity}}$$

- Tells how close we are to saturation
- (ii) Relative Humidity (R.H) → It is the ratio of partial pressure of water vapor (e_w) in a mixture to the saturated vapor pressure of water (e_{w^*}) at that temp.

$e_w, P_{H_2O}, P_v \rightarrow$ Partial pr. of water

$e_{w^*}, P_{H_2O,s}, P_s \rightarrow$ vapor pr. of water.

$$R.H = \phi = \frac{e_w}{e_{w^*}} \times 100$$

$$= \frac{P_{H_2O}}{P_{H_2O,s}} \times 100$$

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

Relative humidity is analogous to relative saturation γ_s , which is

$$R.H = \gamma_R = \left(\frac{P_v}{P_s} \times 100 \right) \quad \rightarrow \text{Partial p. of a vapor}$$

\hookrightarrow vapor pr. of pure liq.
 $= P \cdot P_{\text{at saturation}}$

γ_s saturation $y_p = \frac{n_v \times 100}{n_s}$

$n_s \rightarrow$ moles of vapor per mole of vapor free
 \rightarrow moles of vapor per mole of vapor gas at saturation
 free gas

$$n_v = \frac{P_v}{P_t - P_v} \quad \text{and} \quad n_s = \frac{P_s}{P_t - P_s}$$

$$\therefore y_p = \frac{n_v}{n_s} = \frac{P_v (P_t - P_s)}{P_s (P_t - P_v)}$$

$$y_p = y_R \times \left(\frac{P_t - P_s}{P_t - P_v} \right)$$

At 8 A.M. $\rightarrow 20^\circ C$

Moisture
in Air

At 12 P.M. $\rightarrow 30^\circ C$

\hookrightarrow Relative humidity will change

If we have a system where, no moisture can join, then relative specific humidity doesn't changes, at $30^\circ C$ $v.p > 20^\circ C v.p$, divisor goes up thus R.H. Also H doesn't change.



(3) Absolute humidity - Total amount of water vapor present in a given vol. of Air

$$A_H = \frac{m_w}{V_{net}} \quad m_w = \text{mass of water vp.}$$

V_{net} = Total Vol.

- combined vol. of mass

and water vapor mixture

$$C_p, \text{air} = 1.00 \text{ kJ/kg K}$$

$$C_p, \text{water vapour} = 1.88 \text{ kJ/kg K}$$

$$C_s = \text{Humid heat} = C_p + H C_p, \text{water vapour}$$

↑ specific
humidity

Humid Volume

Vol. of unit mass of dry air plus the water vapour present in it.

In S.I. unit

$$v' = \frac{22.415 \text{ m}^3}{1 \text{ kg mole of Air}} \times \frac{1 \text{ kg mole} \times T}{29 \text{ kg} \times \frac{273}{18}}$$

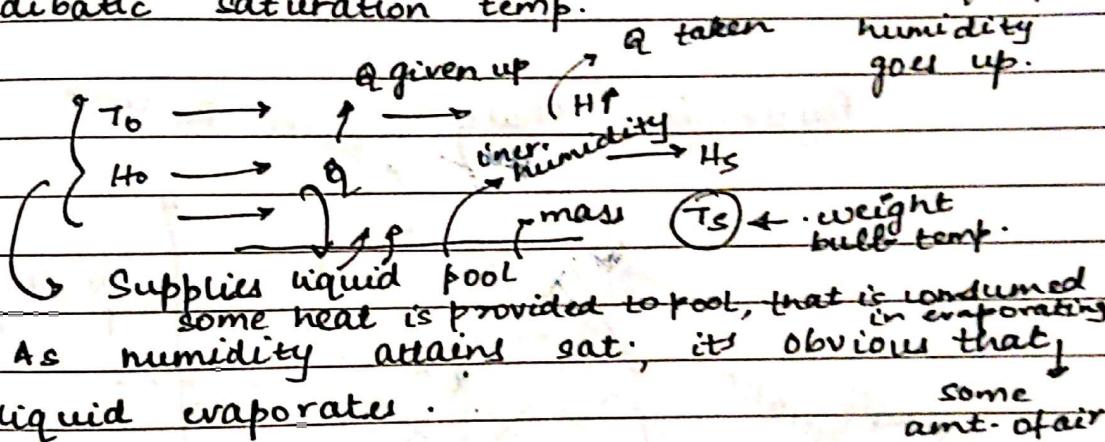
$$+ 22.415 \times \frac{1}{18} \times \frac{T}{273} \times 14$$

$$= \left(2.80 \times 10^{-3} + 4.56 \times 10^{-5} \frac{H}{\text{kg dry air}} \right) \text{ m}^3$$

Temperature

The thermometer we used till date is dry bulb thermometer.

Wet bulb temperature - It is the temp. a vol. of air would have, had it been cooled adiabatically to saturation by evaporation of water into it, while all the latent heat being supplied by \uparrow the vol. of air. It is very similar to the adiabatic saturation temp.



Temp. changes to T_s

The entire latent heat is supplied by air. The Q is providing latent heat to some water molecules, the consequence being there is a drop in temp., the water molecules the change phase to ^{being} vapour

$$(H_s - H_0) \Delta = (T_0 - T_s) C_s + Q$$

\uparrow humid heat

If we saturated the air under such adiabatic process

$T_{DB} - T_{WB}$: wet bulb depression

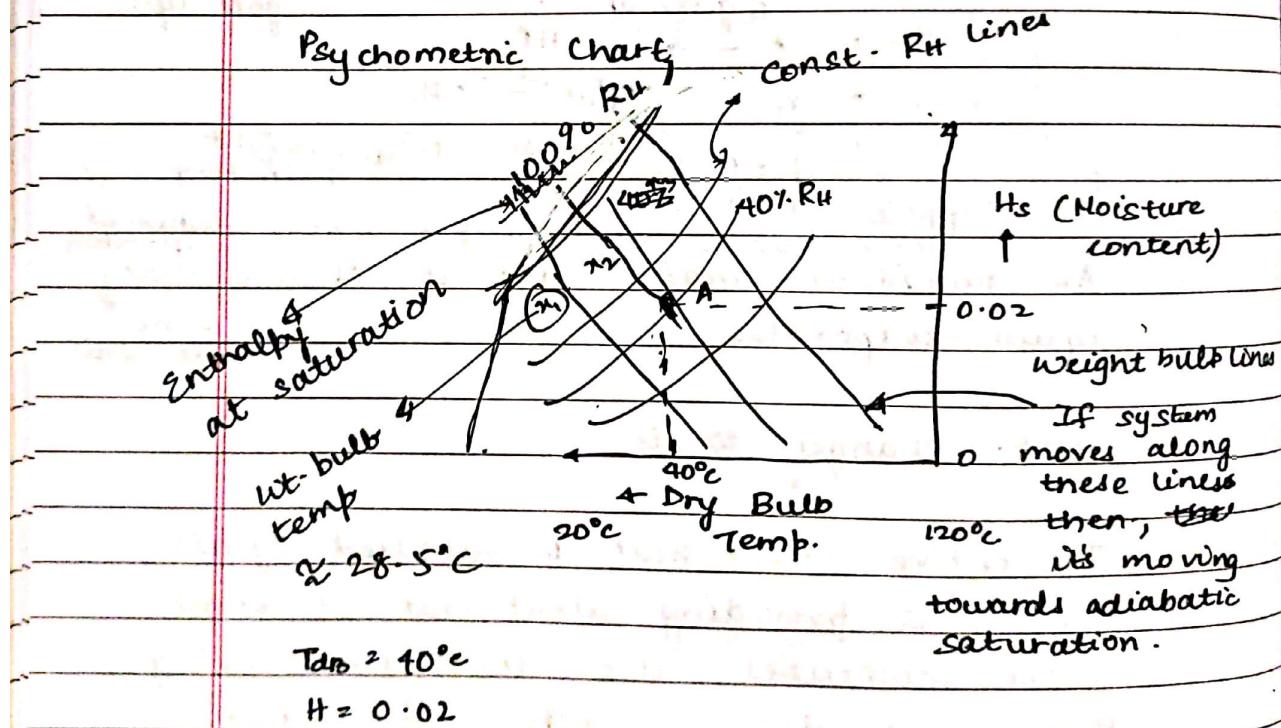
$T_s \rightarrow T_{WB}$

Temperature of waterbody hasn't changed.

In real life, process doesn't remain adiabatic, thus $T_s \neq T_{wb}$

The lower temp. that can be achieved is by adiabatic

T_s in that case will be higher than adiabatic saturation temp.



$A \rightarrow$ very close to 40%. RH and b/w 40-50
and by interpolation, 43% RH

$$R_H = 40\%$$

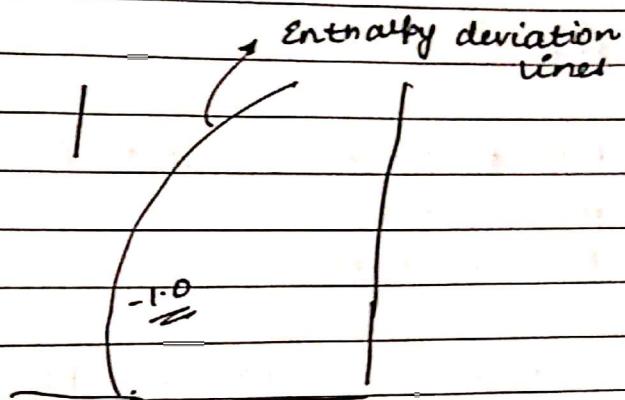
$$H = 0.02$$

$$41.5^\circ C \rightarrow T_{db}$$

$$T_w \rightarrow 25^\circ C$$

Two more sets

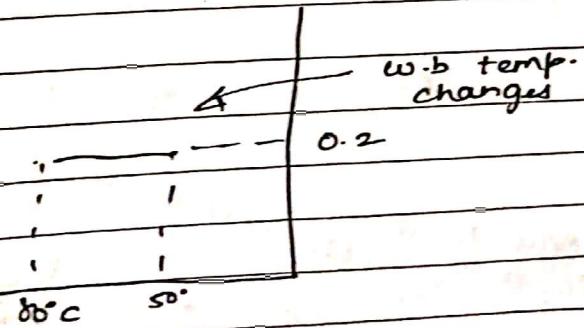
- ① Humid vol. line
- ② Enthalpy deviation line.



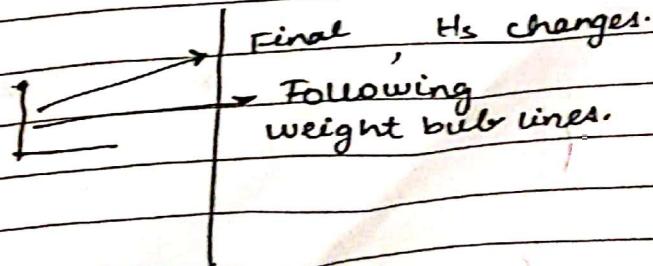
System

$$H_s = 0.02$$

$$T_{db} = 80^\circ C \rightarrow T = 50^\circ C \quad \text{Normally}$$



If it's cooled adiabatically



$T_{DB} = 80^\circ\text{C}$, $h_s = 0.03$ \rightarrow cools down to 22°C

Once touching
it follows the curve till 22°C

$T_{wb} = 34^\circ\text{C}$

$T_{wb} = 22^\circ\text{C}$

80 22