~~Addn. of~~ Engineering Chemistry (Monday)

Fuels

→ Calorific Values -

High ⊕ HCV (Gross) - includes latent heat of vap

Low ⊖ LCV (net) = HCV -

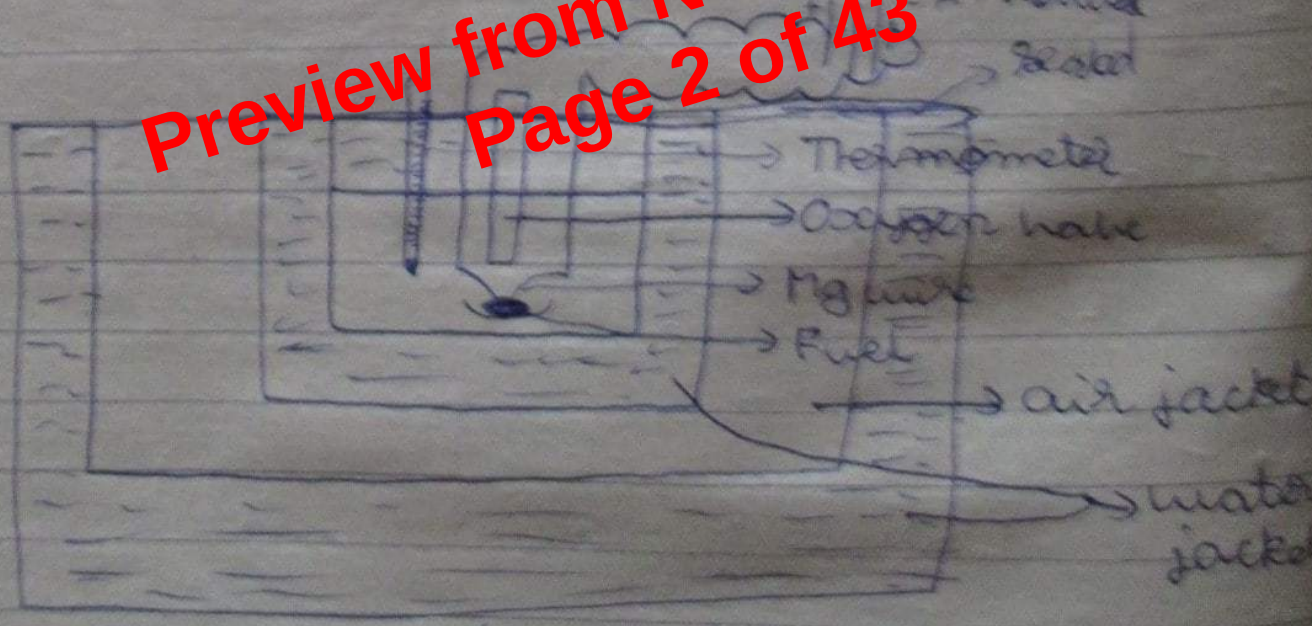
$$LCV = HCV - \frac{9}{100} \times H \times 587 \text{ cal/g}$$

(% age of H; latent heat of vap)

→ Prop of fuel - • moderate ignition temp • cheap • easily available • high CV • Lower

→ Determination of C.V. of a fuel -

* Bomb Calorimeter - for solid non volatile



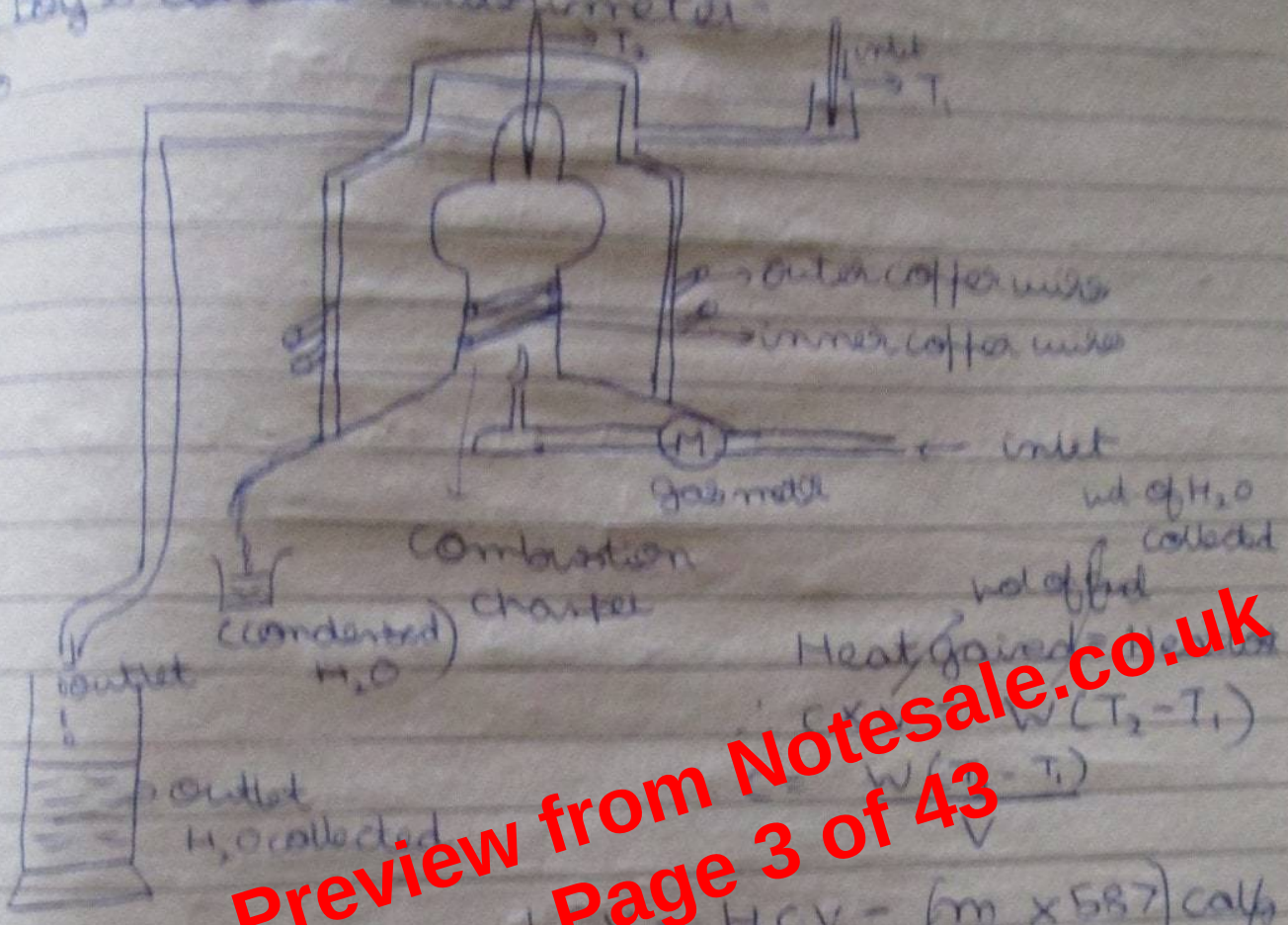
(Calorific value) Heat gained = Heat lost (wt of H_2O; water eq; diff in temp)

$C \times x = (W + w)(T_2 - T_1)$

• Corrections - ① Mg wire correct^n (heat given)
② Acid correct^n (due to acid made by H_2O)
③ Cooling effect (error in temp due to surroundings)

So, $Cx = (W+w)(T_2 - T_1 + \Theta) - (Q+D)$

* Boy's Coloum Calorimeter



wt of H_2O collected

Heat gained by H_2O

$Cx = W(T_2 - T_1)$

$\frac{W(T_2 - T_1)}{V}$

$HCV = \left(\frac{m}{V} \times 587\right)$ cal/l

mass of condensed H_2O.

* Dulong's Formula - to measure theoretical CV

$HCV = \frac{1}{100}\left[8080C + 34500\left(H - \frac{O}{8}\right) + 2240S\right]$ cal/g

$\left(H - \frac{O}{8}\right)$ Halve

contains 'H' of H_2O So, we sub it from

In H_2O → 16g of O → 2g H

1g of O → $\frac{1}{8}$g H

∴ Og of O → $\left(\frac{O}{8}\right)$ of H

Now if 3 phases in one comp (α, β, γ) and each one phase is std phase, so,

$$\mu_\alpha = \mu_\beta \rightarrow \text{chem. pot. of } \alpha = \beta$$
$$\mu_\alpha = \mu_\gamma$$

Now, no. of eq^ns or var possible at eq^n are

$$C(P-1)$$

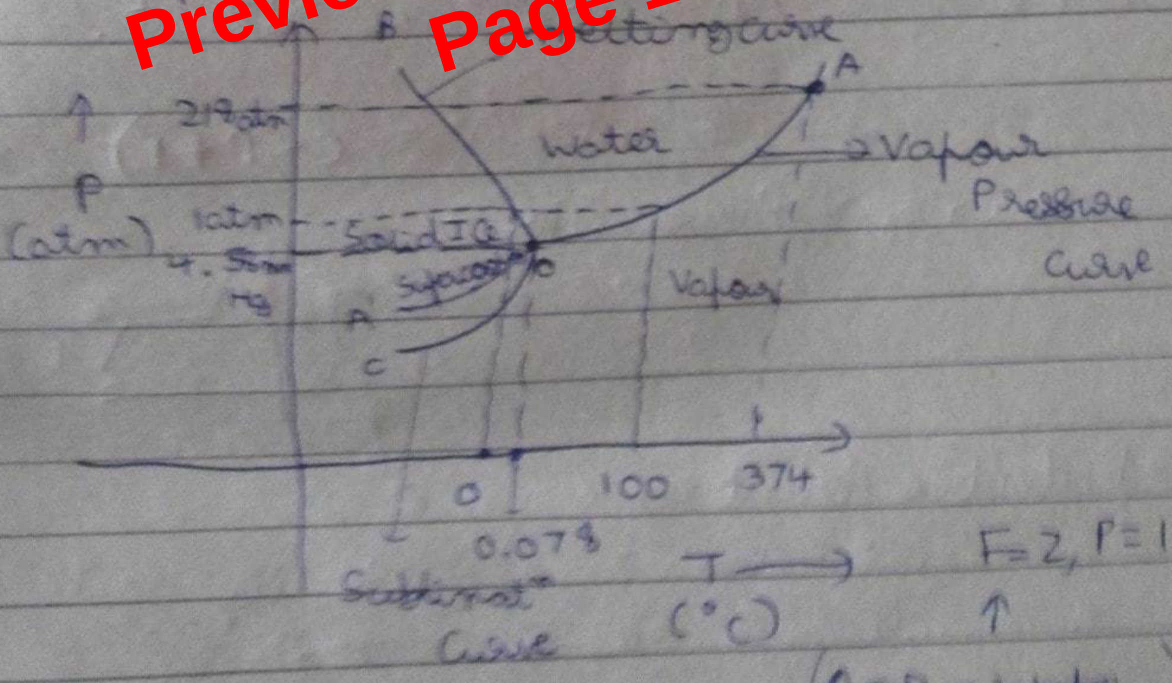
$$\therefore \quad F = (\text{Total no. of var} - \text{Total no. of relat}^n)$$

$$F = (P(C-1)+2) - (C(P-1))$$

$$F = C - P + 2$$

Adv. - • simple method to classify eq^n states
• explains behaviour of sys

⇒ One Component System - (Water System).



F=2, P=1.

AOB = Water
AOC = Vapour
BOC = Ice

O = Triple pt. (F=0, P=3)

AO = Vapour - Liq
OB = Ice - water → F=1, P=2

→ Poison - Negative catalyst

→ Characteristics of a good catalyst -

• retain back after rxn • at optimum temp

• specific in their act" • selective in nature

→ Homogeneous catalyst -

• Acid-Base • Enzymes • Wilkinson's

→ Acid - Base Catalyst -

They are of two types - Specific & General

• S. Acid - catalysed by H^+ ions only (Arrhenius acid only)

Eg - Inversion of cane sugar

• S. Base - catalysed by OH^- ions only (Arrhenius Base only)

Eg - Hydrolysis of ester

• G. Acid - catalysed by all types of acid (Lewis acid, Lowry-Bronsted acid)

Eg - $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + I_2 \xrightarrow[ClCH_2COO^-]{ClCH_2COOH} CH_3-\overset{O}{\overset{\|}{C}}-CH_2I$

(can lose a proton)

(iodination of acetone)

• G. Base - catalysed by all types of base

Eg - $NH_2NO_2 \xrightarrow{CH_3COO^-} N_2O + H_2O$

(decomp. of nitramide cat. by acetate ions)

$$\text{Rate} = -\frac{d[S]}{dt} = k_3[SH^+][A^-]$$

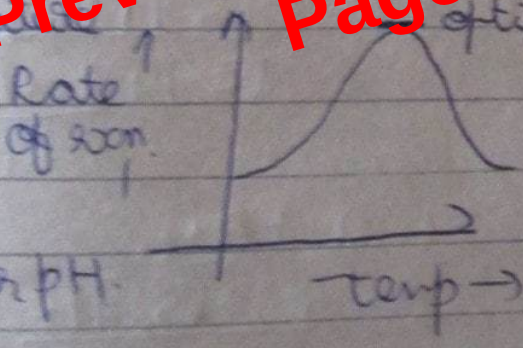
Applying SSA,

$$[SH^+][A^-] = \frac{k_1[S][AH^+]}{k_1 + k_3}$$

$$\text{Rate} = \frac{k_1 k_3 [S][AH^+]}{k_2 + k_3}$$ → general acid

⇒ Enzyme Catalysis -

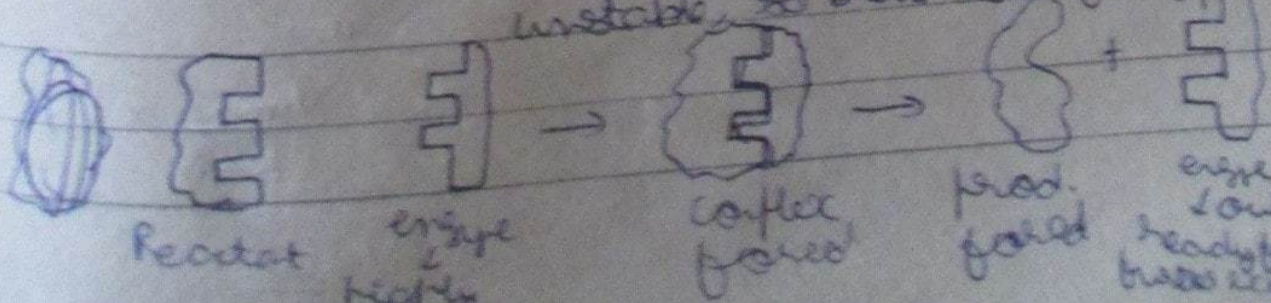
- Biological processes → highly
- specific in nature - work at optimum temp (37°C)
- work only at optimum pH (7.4)
- Inhibitors ↓
- Co-enzymes - metal ions like Na^+, Ca^{2+}, Cu^{2+}, Mg^{2+} etc
- Temperature



- if temp ↑, denaturation occurs, polymer destroys.

⇒ Mechanism of Enzyme action -

- Lock & Key Model
- intermediate formed - decrease energy of activation



→ Kinetics of Enzyme Catalysis (Michaelis Menten mech)

$$S + E \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [ES] \quad \text{(fast)}$$

$$[ES] \xrightarrow{k_3} P + E \quad \text{(slow)}$$

So, Rate $= k_3[ES]$

By SSA,

$$k_1[S][E] - k_2[ES] - k_3[ES] = 0$$

$$[ES] = \frac{k_1[S][E]}{k_3 + k_2}$$

$[E]$ → can't be det. So,

$$[E] = [E_0] - [ES]$$

$$[ES] = \frac{[S][E_0]}{[S] + \frac{k_2 + k_3}{k_1}} \quad \frac{k_2 + k_3}{k_1} = K_m \text{ (Michaelis Menten const)}$$

∴ For initial rate,

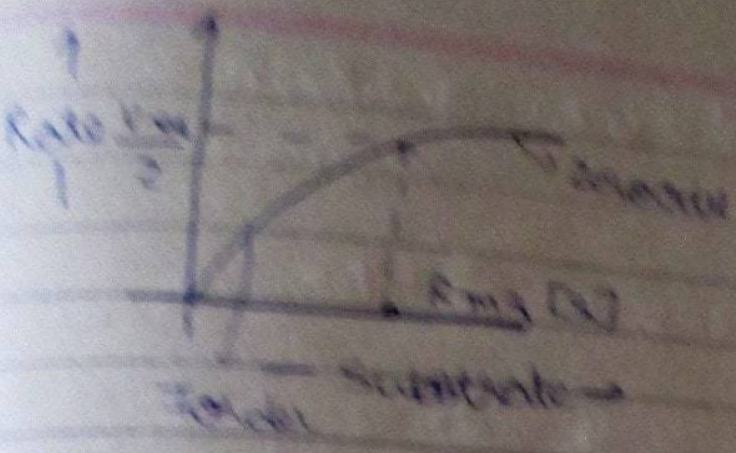
$$r_0 = \frac{k_3[S_0][E_0]}{[S_0] + K_m}$$

I. $[S_0] >> K_m$, $r_0 = k_3[E_0] = V_{max} = k_{max}$ (zero order)

II. $K_m >> [S_0]$, $r_0 = \frac{k_3[E_0][S_0]}{K_m}$ → 1st order

$$r = \frac{V_{max}}{K_m} \times [S]$$

If $K_m = S$, $r = \frac{V_{max}}{2}$



→ Catalysis by Metal Salts

Wilkinson's catalysis

Tris (triphenyl) phosphine Rhodium(I)

→ Mechanism