

Grading Scheme :-

- ① Class Test - 10% (1)
- ② Mid Sem - 20%
- ③ Presentation + Report Submission (20%)
- ④ End-Sem - 50%

Homogeneous rxn :-

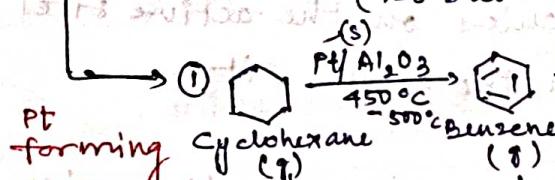
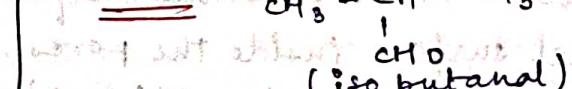
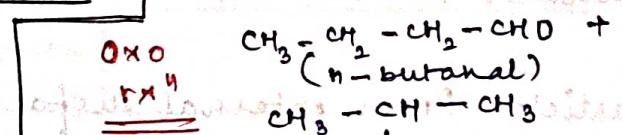
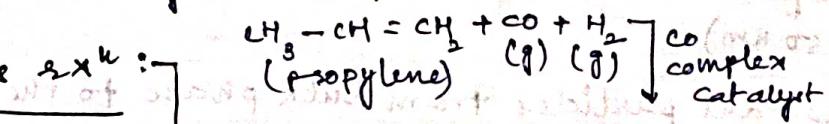
At least one of the reactant is in the liq. phase with the catalyst.

Catalytic

Non-catalytic

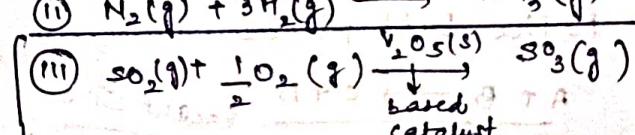
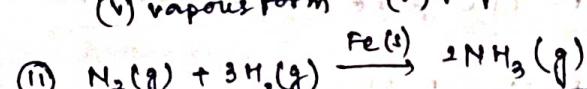
Burning of flame

Non-homogeneous rxn :-



forming Cyclohexane

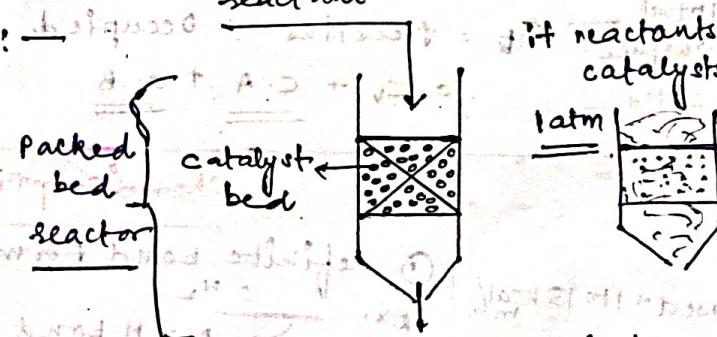
(v) vapour form → (v) vapour



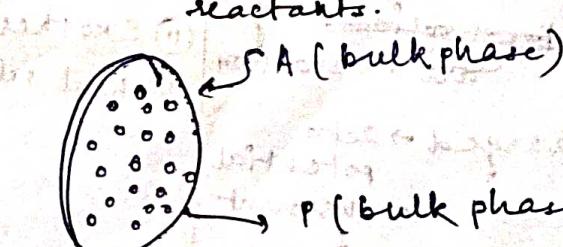
heat of contact process

reactant

Heterogeneous :-



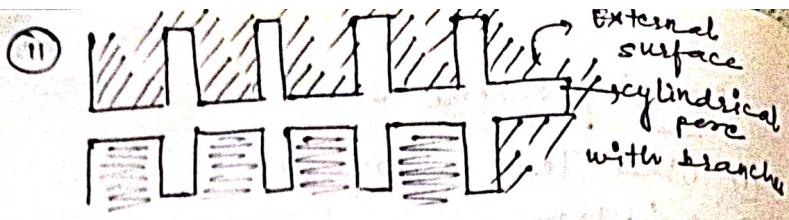
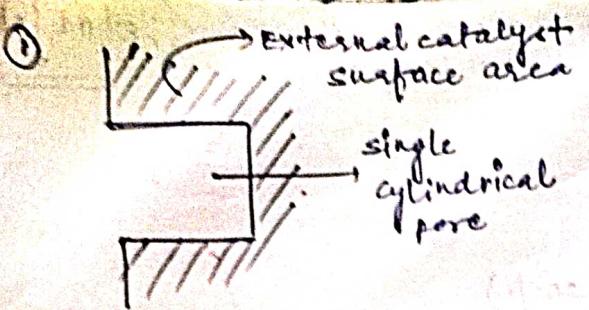
if reactants are in powder form and catalysts are also powdery → sticking of catalyst to reactor surface. Also, it will mix with reactant & become a part of the product which we don't want



R + unconverted
reactants

+ loosely bound particles

catalysts



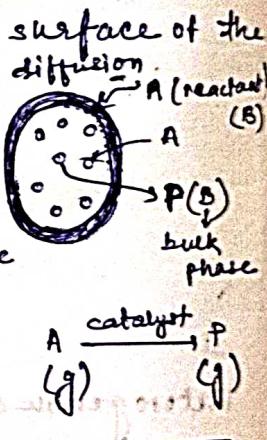
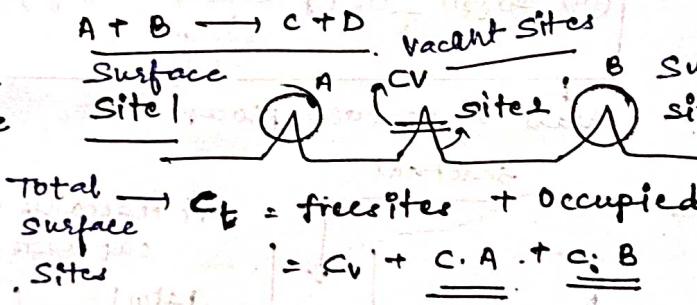
IUPAC Pores :-

- ① Micropores \rightarrow pore dia $\leq 2\text{ nm}$
- ② Meso pores \rightarrow ($2 - 50\text{ nm}$)
- ③ Macropores ($> 50\text{ nm}$)

7 steps :-

- ① Diffusion of reactant particles from bulk phase to the external surface of the catalyst.
- ② Transfer of reactant particles from external surface to pore mouth and from pore mouth to internal surface inside the pores.
- ③ Adsorption of reactant molecules on the active sites inside the pores.
- ④ Reactions will take place on the active sites.
- ⑤ Desorption of the products.
- ⑥ Diffusion of products to the pore mouth mouth - external surface of the catalyst particle.
- ⑦ Diffusion of product to the bulk phase.

Catalyst
active for catalytic rxn
inactive



Physisorption

- ① No bond formation
- ② Exothermic
- ③ $\text{heat released} \rightarrow 10 - 15 \text{ kcal/mol}$

$\text{O} \text{ O} \text{ O} \text{ O} \rightarrow$ Vanderwaal forces

~~bonds formation~~ ~~of interaction~~

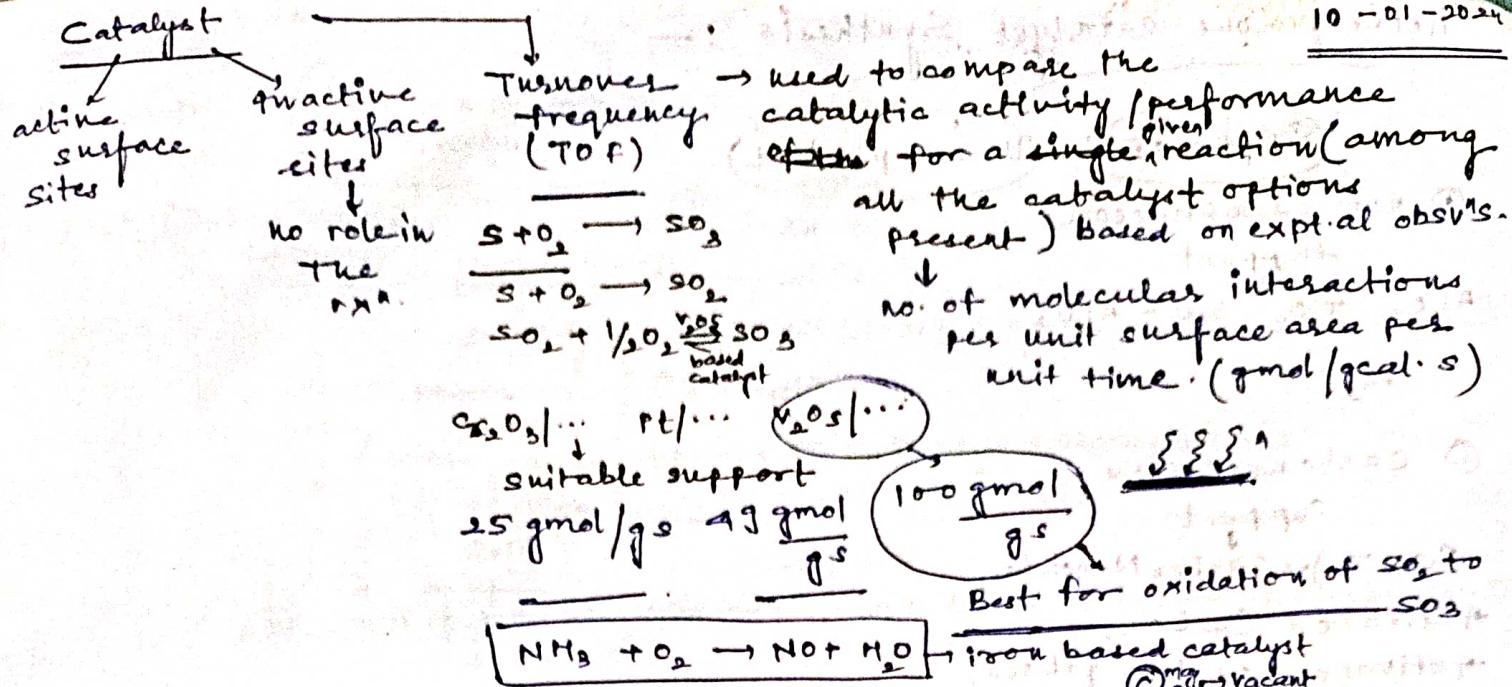
③ $\text{H}_2 \text{O} \text{ H}_2 \text{O} \rightarrow$ -vely charged \rightarrow zeta potential measurement

\downarrow methylene blue (cationic) \downarrow zeta sites \downarrow
 \downarrow electrostatic interaction \downarrow $(+ -)$
 δ/δ the adsorbate and the adsorbent

Chemisorption

- ① definite bond form will be there
- ② ex. $\text{M} - \text{H}$ bond - form?

- ② Exothermic
- ③ heat released $\rightarrow 10 - 100 \text{ kcal/mol}$



Isotherm (Adsorption) :-

\downarrow $A \rightarrow$ reactant molecule

\downarrow catalyst surface Let s be the active surface sites $A + S \rightleftharpoons A \cdot S$ (A gets adsorbed to the active site after some period of time)

$$\text{Total molar conc of active sites per unit g of catalyst} = \left(\frac{\# \text{ interac's} \rightarrow \text{active sites}}{\text{g of catalyst}} \right) \cdot \frac{\text{Avogadro's Number}}{\text{1 molecule}}$$

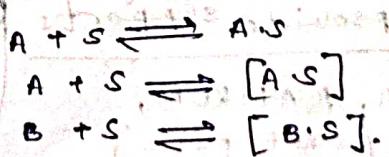
$$= C_f (\text{g mol/g catalyst})$$

$$\# \text{ Total molar conc of vacant sites } (C_v) = \left(\frac{\text{Total no. of interac's}}{\text{g of catalyst}} \right) \cdot \frac{\text{Avogadro's No.}}{(6.023 \times 10^{23})}$$

Total Site Balance

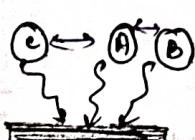
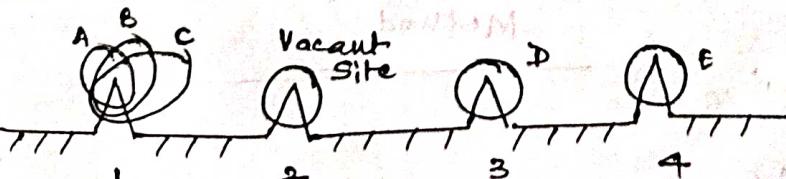
$$C_f = C_{As} + C_{Bs} + C_v$$

$$C_f = (C_{As} + C_{Bs} + C_v)$$



$$C_f = C_{As} + C_{Bs} + C_v$$

flow diagram :-



→ The survival of the fittest

In order for adsorpⁿ to take place A, B

and C will fight against each other since no.

of active sites remain the same

adsorption capacity/ quality

Heterogeneous Catalyst Synthesis :-

Supported Unsupported

① non carbonaceous support

Al_2O_3 , TiO_2 , SiO_2 , Al_2O_3 ,
 ZrO_2 , ...

② Carbonaceous support

(CNT) → Carbon Nanotubes,
Activated Carbon,
Activated carbon fibres,
graphene, graphene oxide,
Aerogels.

CNT → ① MWCNT

② SWCNT
→ Singlewalled

Properties of support materials:-

- ① high thermal stability ($> 1000^\circ\text{C}$)
- ② moderate to high surface area
- ③ relatively less reactive compared to the active metal/metal oxides

support + metal/
metal oxides

Supported catalyst

Companies that provide supports

MERCK, SIGMA, RAKEM,

LOBA CHEM etc (not pure enough)

Support (highly pure)

if not highly pure

Support + DI water (dropwise) $\xrightarrow[\text{stirring}]{\text{conc}}$ Paste → Transfer it to a muffle furnace operated at ($500 - 550^\circ\text{C}$)

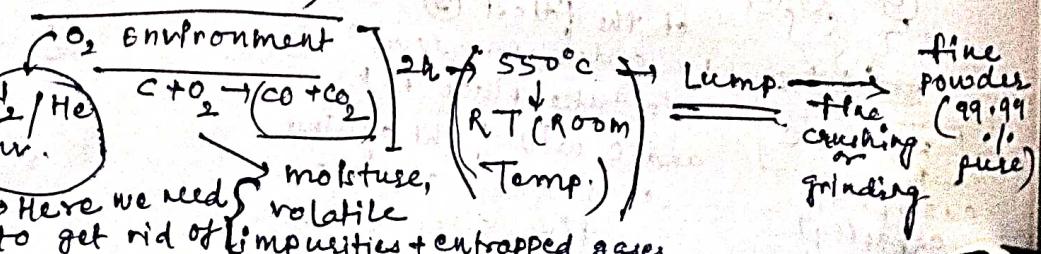
for Carbonaceous we need N_2/He Env.

to create inert

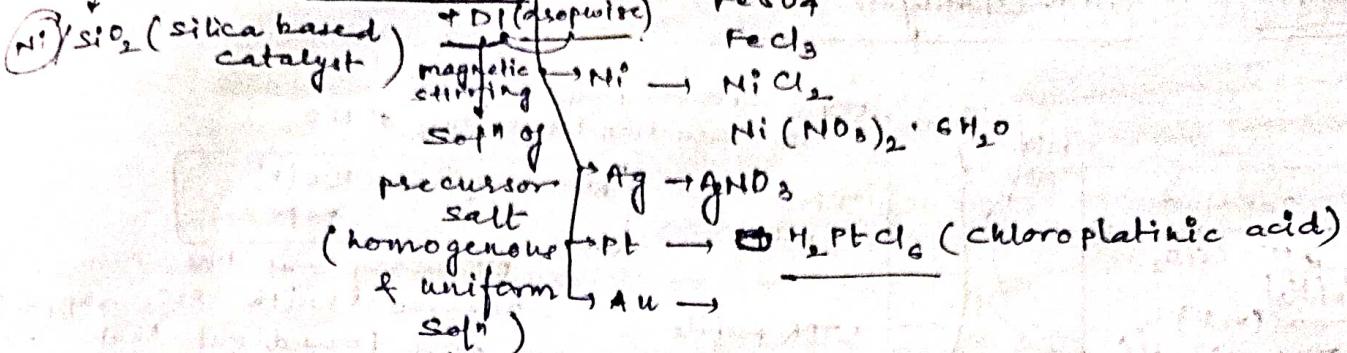
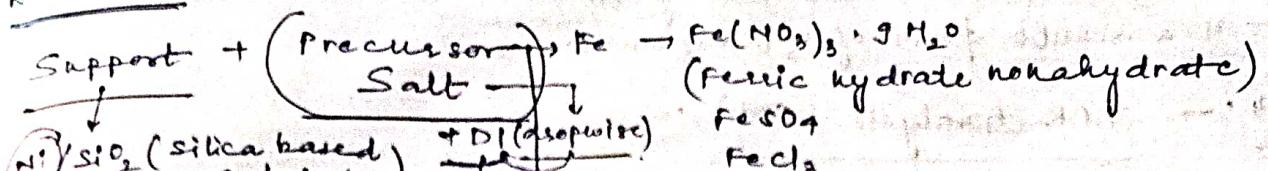
environment → Here we need moisture, (Temp.) volatile to get rid of impurities + entrapped gases

if support is not pure then catalyst deactivation (by poisoning → presence of sulphur) can take place

Wet Impregnation Method

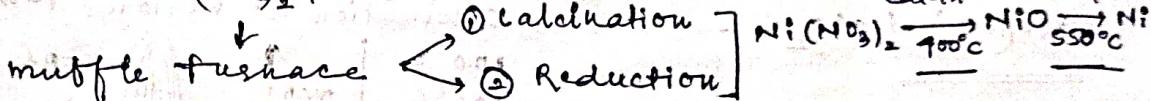
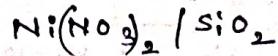


Next step → incorporate the active metal / metal oxide into the support

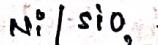
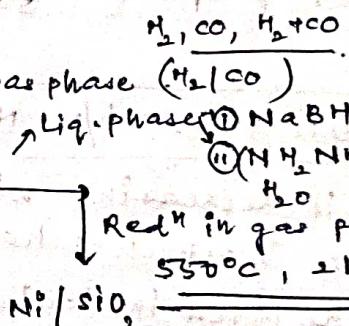
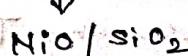
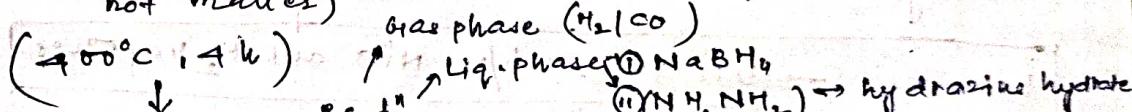
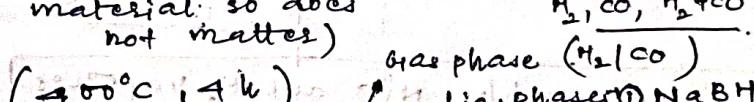


{ if not Uniform conc, randomness in distribution of precursor salt in the soln.

Support + Precursor salt ($\text{Ni}(\text{NO}_3)_2$, aq. soln.) Paste

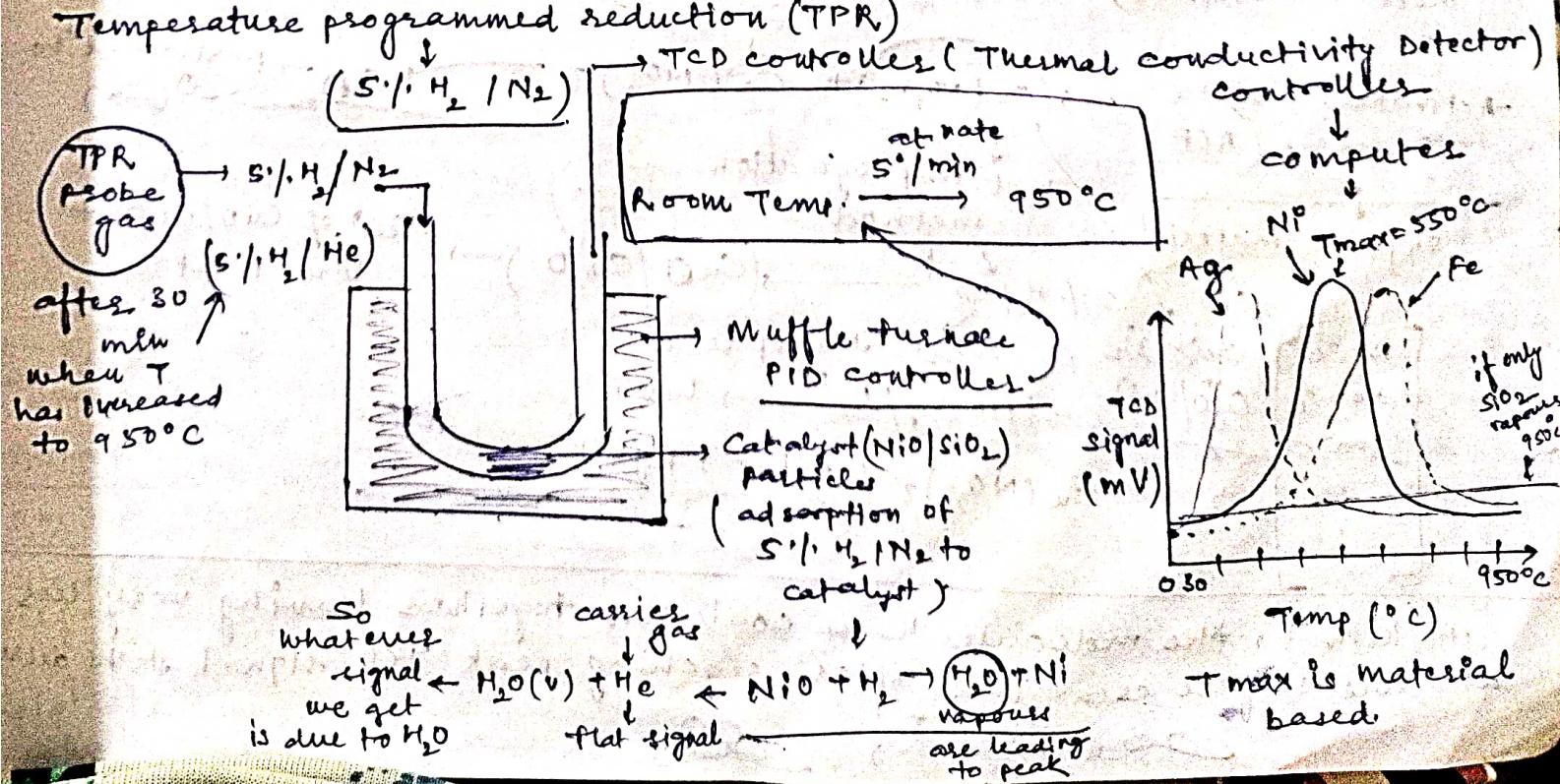


O_2 environment
 (non carbonaceous support material so does not matter)



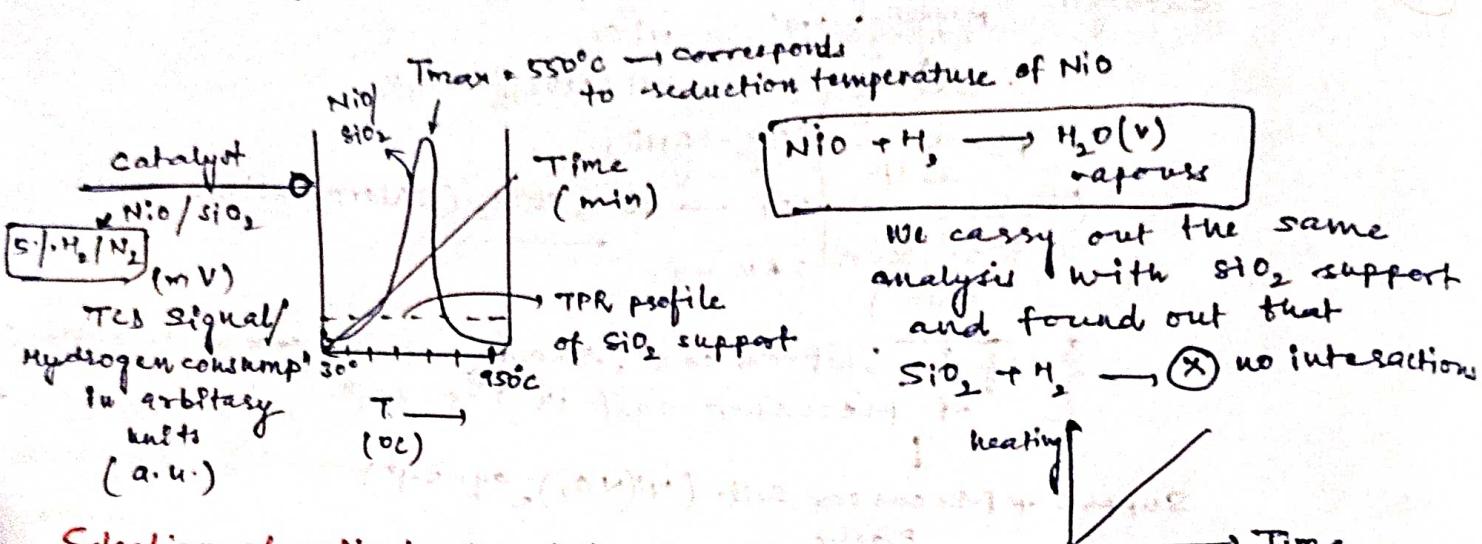
Optimisation of Calcination and reduction Temp. :-

Temperature programmed reduction (TPR)



at 550°C , we got the max. "red" of Ni. Peak corresponds to "red" of Ni_0 to $\text{Ni} \rightarrow$ as a result form" of H_2O vapours.

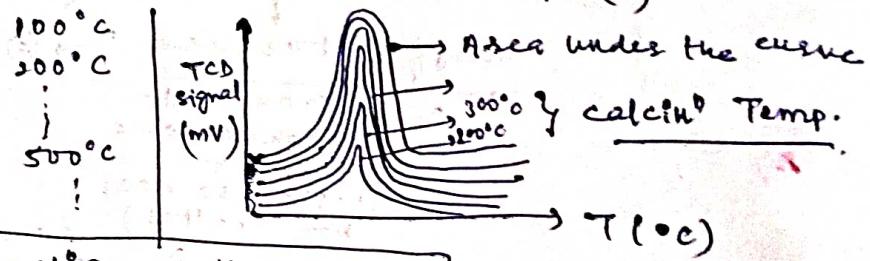
11/01/24 :- TPR Analysis (Ctd.) :-



Selection of optimised Calcination Temp. :-

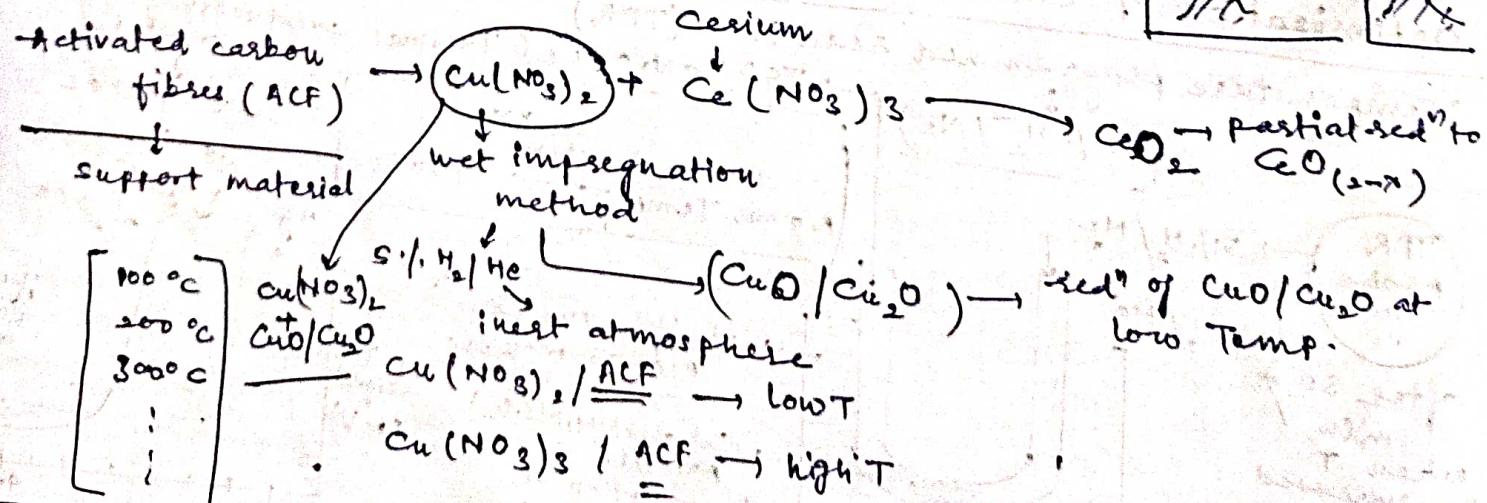
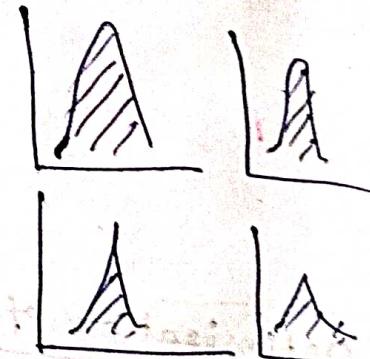
$\text{Ni}(\text{NO}_3)_2/\text{SiO}_2$, calcination at various Temps. (T) --

for every T we plot
TCD v/s T graph
signal



less area \rightarrow less interactions b/w NiO and H_2 vapours.

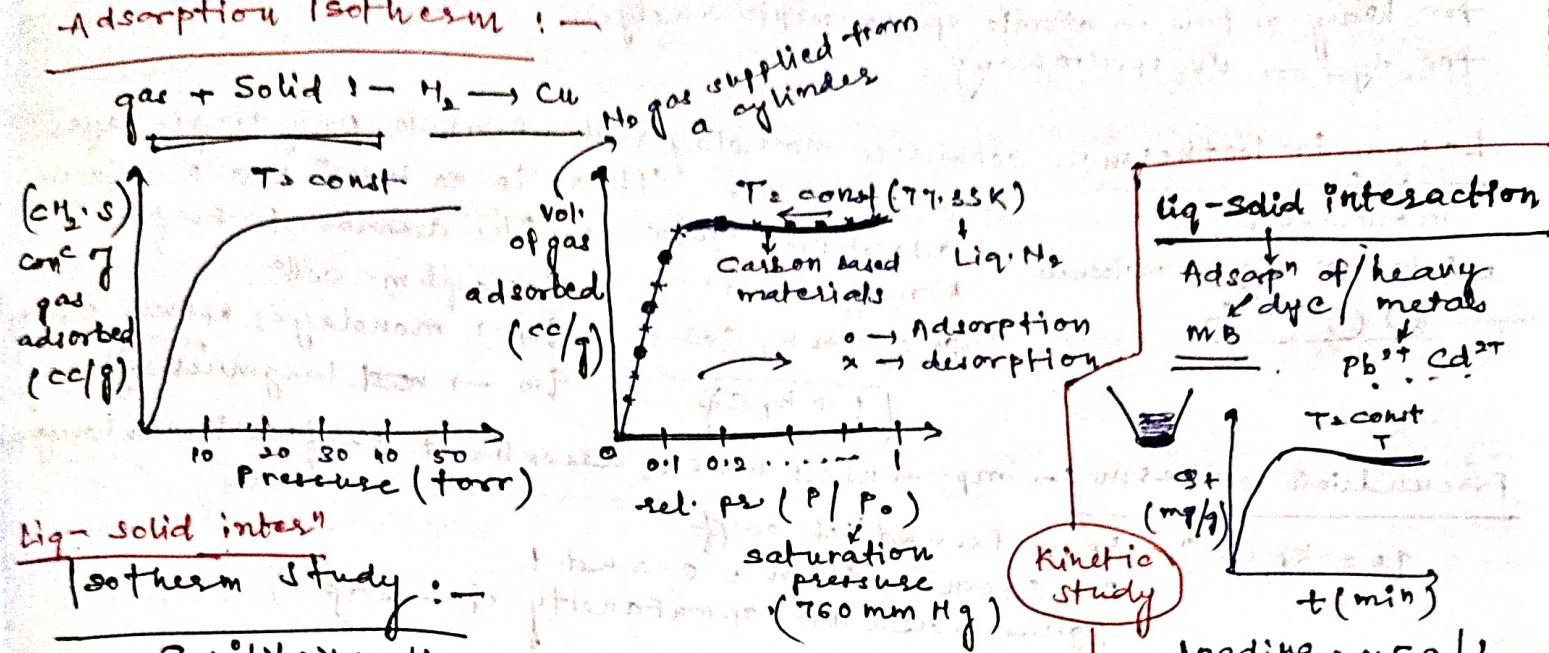
- density of peak is decreasing with increasing T .
- We choose the T which has more area under the graph. The area indicates interactions b/w the metal oxides and H_2 vapours. (more area means more interactions)



At high T , the molecules have coalesced together leaving very less available surface area. Thus, after reaching peak TCD signal starts decreasing.

Incorporation of ~~etc~~ salt mixtures to Al₂O₃ is done in the same way as the muffle furnace method.

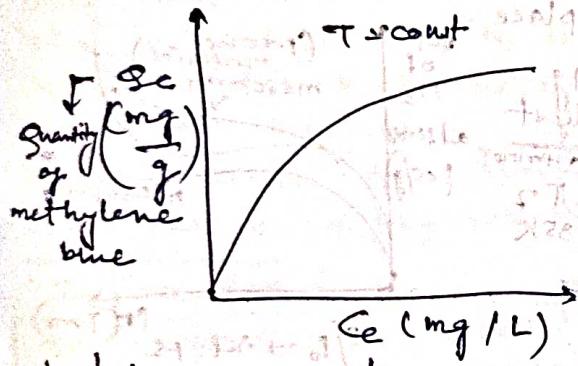
Adsorption Isotherm :-



Liq. solid inter"

Isotherm Study :-

Equilibrium time



We carry the expl'diff. conc. and agitate the mixture for the eqbm. time obtained.

$$\text{loading rate} = 0.5 \text{ g/L}$$

absorbent \rightarrow activated C molecules
adsorbate \rightarrow dye / heavy metals.

$$25 \text{ ppm MB in } 500 \text{ ml}$$

S_t = amt. of methylene blue adsorbed at a particular time (min)

Periodically we take out the soln and measure the amt. of adsorbate (S_t)

$$25 \text{ ppm.} = \text{mg/L}$$

$$\downarrow 18 \text{ ppm}$$

$$S_t = \frac{(C_i - C_t)V}{m}$$

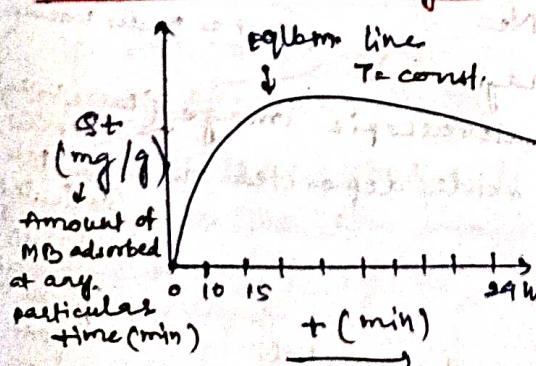
Vol. of adsorbate, in ml.

$$C_i = \text{mg/L} \quad C_f = \text{mg/L}$$

$$m = \text{mg}$$

based on kinetic study we obtain the eqbm time and based on the eqbm. time we carry on isotherm study

Batch Kinetic study :- Det. of adsorp' eqbm. time

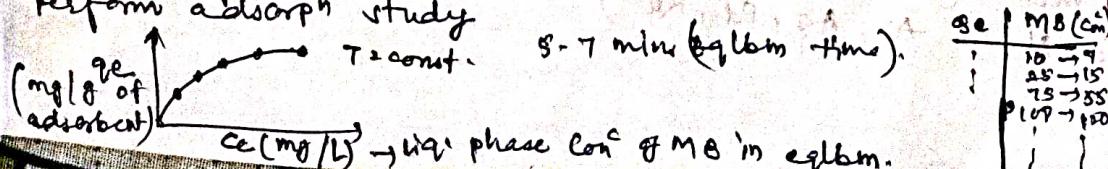


In the kinetic study, we select a conc. of adsorbate and perform the adsorp' study for 24 h. Periodically we collect the samples and measure the conc. of adsorbate in aq. phase.

Adsorp' Isotherm \rightarrow Here we select different conc. of MB.

Ex: 10 ppm, 25 ppm, 75 ppm, 100 ppm, 150 ppm . . .

We already know the eqbm. time \rightarrow based on that we perform adsorp' study



	S_t (mg/g)	M_0 (mg)
10 \rightarrow	7	70
25 \rightarrow	15	150
75 \rightarrow	35	350
100 \rightarrow	50	500
150 \rightarrow	70	700

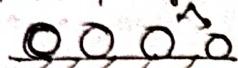
C_e (mg/L) \rightarrow liquid phase conc. of MB in eqbm.

15/01/24

Adsorpⁿ Isotherm :- By - Langmuir, Freundlich, Temkin, DR Models.
Based on the experimental data obtained, we fit the adsorption isotherm.

for heavy metals \rightarrow atomic spectroscopic analysis
for dyes \rightarrow UV spectroscopy.

Langmuir Isotherm :- considers monolayer of adsorbate. Only single layer adsorpⁿ occurs. There is no interⁿ b/w 2 adjacent adsorbate molecules. The adsorbent surface is homogeneous.



$$\text{q}_\text{e} = q_\text{m} K_\text{L} C_\text{e}$$

C_e eqbm. conc

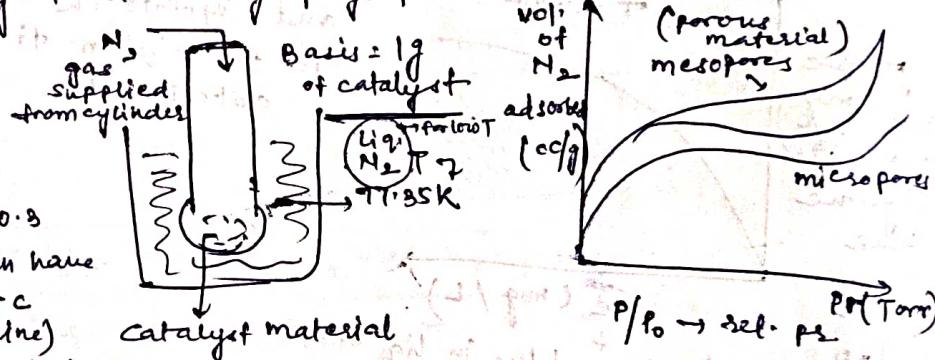
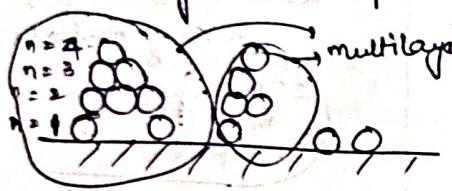
$q_\text{m} \rightarrow$ monolayer uptake capacity
 $q_\text{m} \rightarrow$ Langmuir affinity

Freundlich Isotherm :- imp. \rightarrow used when adsorbent surface is non-homogeneous.

$$\text{q}_\text{e} = k_\text{f} C_\text{e}^\gamma$$

γ = Exponent term ≈ 0 and 1
(gives idea abt. spontaneity of adsorpⁿ)

BET Isotherm :- in BET, before completion of a monolayer entirely, multilayer adsorpⁿ may start taking place.



$$\frac{P}{P_0} \text{ used till } 0.3$$

bcz we can have eqn $y = mx + c$
(straight-line)

$\frac{P}{P_0}$ - and we can calculate the surface area of the adsorbent

BET \rightarrow method used to get the surf. area of the adsorbent material.

$$S_{\text{BET}} = \frac{m^2}{g}$$

Can we use other gases (other than liq. N₂)
Yes CO₂ \rightarrow liq. krypton, liq. He

Simpler \rightarrow liq. N₂

Activated C is porous in nature.

Cathary condensⁿ \rightarrow when gaseous N₂ condenses inside pores and turns into liq. N₂.

SEM \rightarrow Scanning Electronic Microscopic Images

TEM imaging \rightarrow Transmission electron microscopic images (large voltages applied)

Dispersion \rightarrow Fraction of the active metal / metal oxides deposited on the active surface sites of the support.

Example of active metal parts :-

- 1.) They are transition metal oxides, transition metals, noble metals
- 2.) Example of transition metal oxides (Fe₂O₃, Cr₂O₃, V₂O₅, NiO, CuO)
- 3.) Ex. of transition metals (Ni, Cr, Cu, Fe, Co, Zn)
- 4.) Ex. of noble metals (Pt, Rh, Au, Ag, Pd, Ru...)

operates under vacuum
in suitable solvent if powdered form
generally 99.99% pure ethanol

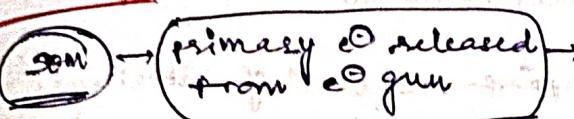
How to det. the size distribution? (catalytic support)

Σ NPs \rightarrow need to be prodn.

Q Why Σ NPs obtained by using support and not directly procured from the market? \rightarrow for a catalytic process the form in which we use the NPs plays an imp. part. When procured from the market, they can be in aggregate form (Lump) reducing the surf area available for adsorption. Thus we disperse Σ NPs on a support to get a uniform composition and increases surf. area available for adsorpⁿ.

What info can we obtain from BET?

BET	Surface area (m^2/g)	Total pore volume (cc/g)	Avg. pore diameter (μm)	PSD (Pore Size Distrib ⁿ)
				Σ M + Meso + Macro pores



Size of N_2 molecule = 3.54 \AA

We know the size of our pores. Now, we can find surf area using BET method. We know the size of N_2 molecules and if N_2 is passed, what will happen if size of adsorbate molecule is more than pore size?

Such particles can collide with the external pore surface \rightarrow physisorption \rightarrow leading to pore blockage \rightarrow effective surface area \downarrow .

How to find active sites? H_2 chemisorption

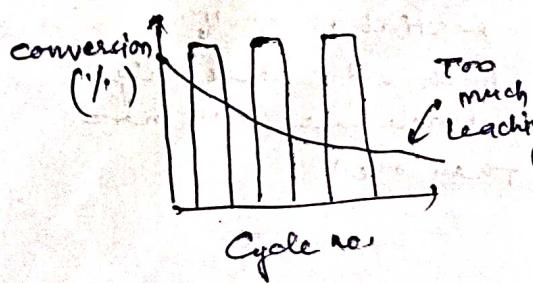
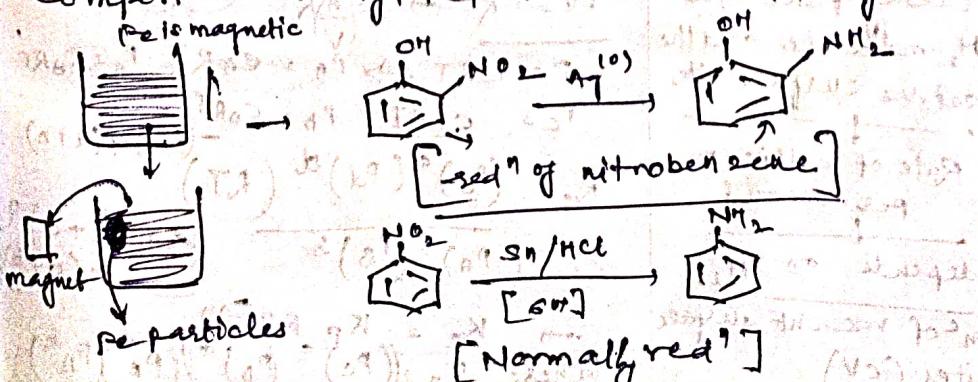
calcⁿ in N_2 env. $\rightarrow Cu_2O \rightarrow$ $\frac{Cu}{2} \downarrow$ (Cu NPs)
How to find if Cu or Cu_2O particle in vap. phase \rightarrow we don't have complete control over size. Thus if nm scale + mm scale presents, SEM may not give accurate pore size distribⁿ

EDS analysis \rightarrow Energy Dispersive X-Ray Spectroscopic analysis.

EDS analysis \rightarrow elemental composition of our catalyst \rightarrow C, N [Ag, C, N]

gives elemental composition of our catalyst \rightarrow C, N [Ag, C, N]. When Ag NPs are dispersed on γ -C₃N₄ support we get [Ag, C, N]. However, this method cannot determine the amount of H₂ (catalyst surface). To quantify how much H₂ is present in material \rightarrow C-H-N-S method is used. Using this, we get all the elemental composition. If moisture present we get only O₂ in sample and not H₂ as the method cannot determine H₂.

If bimetallic catalyst is used \rightarrow Ag-Fe₃O₄-SWCNT composite - certain techniques like EDS imaging mapping is to get the separate images of composition of Ag, Fe, etc. EDS mapping does not detect FeO phases.



No Carbonaceous support :-

Ex Pt NPs dispersed on SiO_2 or Al_2O_3 support.

Six shape of Pt and Si (magnific scale)

We can see img - check to det. the size of NPs dispersed on the support

Shape → spherical (of Pt NPs) macroporous

In Al_2O_3 support, there is low surf. area, so obtaining uniform distrib' is difficult, so we get clustered nanoparticles on the Al_2O_3 support (Pt NPs). In Al_2O_3 , the morphology can't be well defined.

In case of silica, we get a proper morphology.

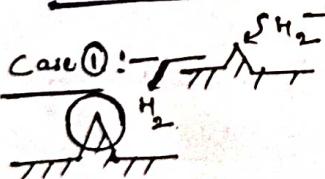
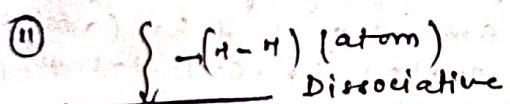
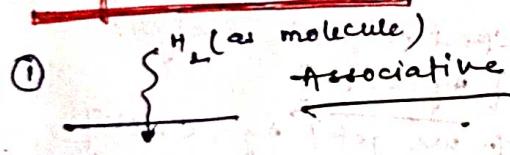
However, morphology cannot be used to compare the 2 types of support. We need to compare their activities in order to do so.

All nanoparticles (→ spherical) → on silica support → Calcul' of interlayer spacing, size distrib' of gold NPs etc. can be found through img. analysis

Graphitic C Nitride :- acts as a good support for biochemical ex's where bacteria (rod-shaped morphology) can be dispersed to degrade various dye molecules which are hazardous for humans. These dye molecules degrade to form N_2 , H_2O , CO_2 etc. (purific) w/ bacteria on a support that bacteria one copper acts as a catalyst to decompose toxic substances into environment friendly materials.

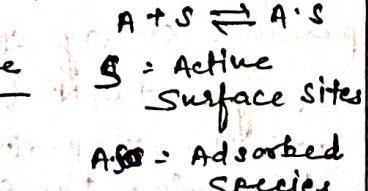
→ Sep. bacteria can also be used for degradation process (not on any support)

Langmuir Isotherm :-



$$\text{rate of attachment} = k_1(P_{\text{H}_2} C_V)$$

partial pr. of H_2 .
Each site holds only 1 molecule (not more than one)



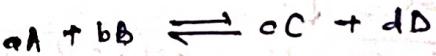
- (I) rate of attachment
- (II) rate of detachment
- (III) make use of eqbm. cond'
- (IV) Utiliz of total surface site Eq'

proportional to the rate of collision taking place b/w H_2 molecule and the active surface sites

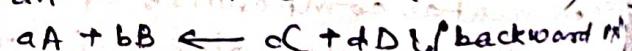
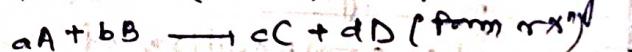
Rate of collision per second.

depends on P_{H_2}

Conc of vacant surface sites (C_V)



$a, b, c, d \rightarrow$ stoichiometric coeff' of reactants (A, B) and products (C, D) respectively



$$\text{forward rxn rate} = K_1 C_A^a C_B^b$$

$$\text{Backward rxn rate} = K_2 C_C^c C_D^d$$

at eqbm:— forward = backward

$$\Rightarrow \frac{k_1}{k_2} = \left(\frac{C_C^c C_D^d}{C_A^a C_B^b} \right)$$

$$\Rightarrow K_C = K_1 / K_2 = \left(\frac{C_C^c C_D^d}{C_A^a C_B^b} \right)$$

$$PV = nRT \rightarrow P = \frac{n}{V} RT$$

$$P = CRT \Rightarrow P_A = C_A RT \quad P_B = C_B RT$$

$$P_C = C_C RT \quad P_D = C_D RT$$

$$K_C = (P_C)^c (P_D)^d (RT)$$

$$\left(\frac{P_A}{P_B} \right)^a \left(\frac{P_B}{P_D} \right)^b \quad \left\{ \begin{array}{l} n = (c+d) \\ - (a+b) \end{array} \right.$$

$$\rightarrow K_C = \frac{K_P}{K_P} \frac{RT^{a+b}}{\left(\frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \right)} \quad \text{where } K_P = \left(\frac{P_C}{P_A} \right)^c \left(\frac{P_D}{P_B} \right)^d$$

$$\text{① rate of detachment} \propto \text{CH}_2\text{.S}$$

$$= k_{-1} \text{CH}_2\text{.S}$$

rate of adsorption at eqbm.

Total surface site Eqn: $C_t = C_v + \text{CH}_2\text{.S} \Rightarrow C_v = C_t - \text{CH}_2\text{.S}$

$$\text{② At eqbm: } -\text{attachment} = \text{detachment}$$

$$k_1 (\text{PH}_2) C_v = k_{-1} \text{CH}_2\text{.S}$$

$$k_1 (\text{PH}_2) C_v - k_{-1} \text{CH}_2\text{.S} = \text{redscrpt} = 0$$

k_1 and k_{-1} are constants of proportionality

k_1, k_{-1} and K are Temp. dependent

$$\frac{k_1}{k_{-1}} = K$$

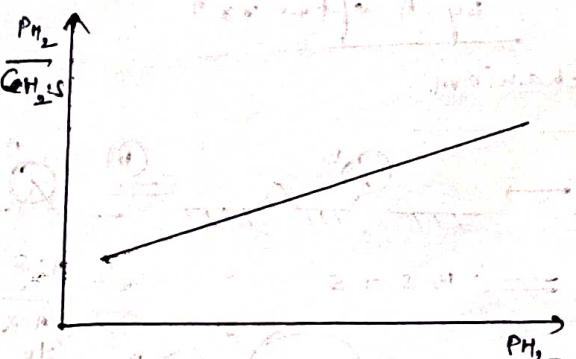
$$\text{CH}_2\text{.S} = \frac{k_1 \text{PH}_2 C_t}{1 + \text{PH}_2 \cdot K}$$

$$\text{CH}_2\text{.S} = f(\text{PH}_2)$$

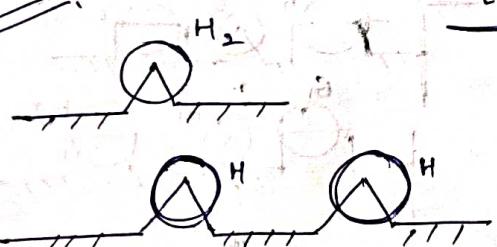
Langmuir Adsorpⁿ Isotherm 2 gas phases

for
Liq.
phase
Adsorpⁿ

$$q_e = q_m \cdot C_e K_L$$

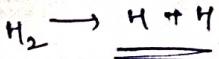


Dissociative adsorpⁿ isotherm model



active
adsorpⁿ surface sites needed
adjacent to each other

for dissociative adsorpⁿ of



① $\text{rattachment} \propto \text{PH}_2 \cdot C_v^2$ (\geq adj active surface sites lead to C_v^2)

$\text{rattachment} = k_1 \text{PH}_2 \cdot C_v^2$ k_1 = const. of proportionality for the attachment

② $\text{rdetachment} \propto (\text{CH}.S)^2$

$\text{rdetachment} = k_2 (\text{CH}.S)^2$

③ At eqbm: $\text{rattachment} = \text{rdetachment} \Rightarrow k_1 \text{PH}_2 \cdot C_v^2 = k_2 (\text{CH}.S)^2$

$$\frac{k_1}{k_2} = \frac{(\text{CH}.S)^2}{\text{PH}_2 \cdot C_v^2} \Rightarrow \sqrt{k_1 \text{PH}_2} \cdot C_v = \sqrt{k_2} (\text{CH}.S)$$

$$\Rightarrow \sqrt{k_1 \text{PH}_2} (\text{C}_t - \text{CH}.S) = \sqrt{k_2} (\text{CH}.S) \Rightarrow$$

$$\text{CH}.S = \frac{\sqrt{k_1 \text{PH}_2} \cdot \text{C}_t}{\sqrt{k_2} + \sqrt{k_1 \text{PH}_2}}$$

$$\frac{\sqrt{\text{PH}_2}}{\text{CH}.S} = \frac{\sqrt{k_2} + \sqrt{k_1 \text{PH}_2}}{\sqrt{k_1} \cdot \text{C}_t} = \sqrt{\frac{k_2}{k_1}} \left(1 + \sqrt{\frac{\text{PH}_2}{\text{C}_t}} \right)$$

$$\text{C}_t = \text{C}_v + \text{CH}.S$$

$$\rightarrow \text{C}_v = \text{C}_t - \text{CH}.S$$

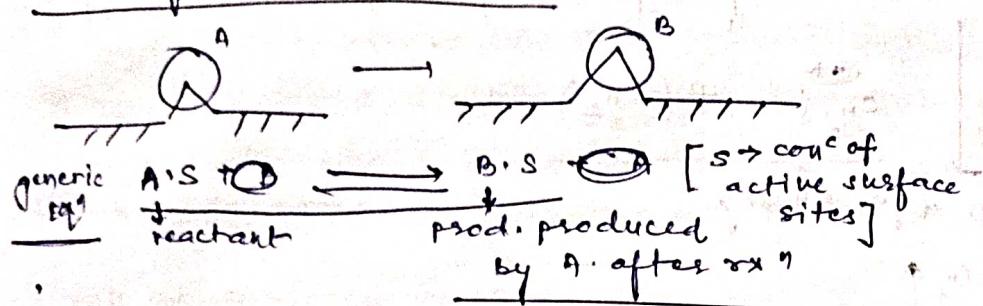
$$\frac{\sqrt{P_{H_2}}}{C_{H_2}} = \sqrt{\frac{k_3}{k_1 C_f}} \frac{P_f}{C_f} \frac{\sqrt{P_{H_2}}}{C_f}$$

$$\Rightarrow \frac{\sqrt{P_{H_2}}}{CH_3S} = \frac{1}{\bar{C}t} \sqrt{P_{H_2}} + \frac{1}{\sqrt{k_a} C t}$$

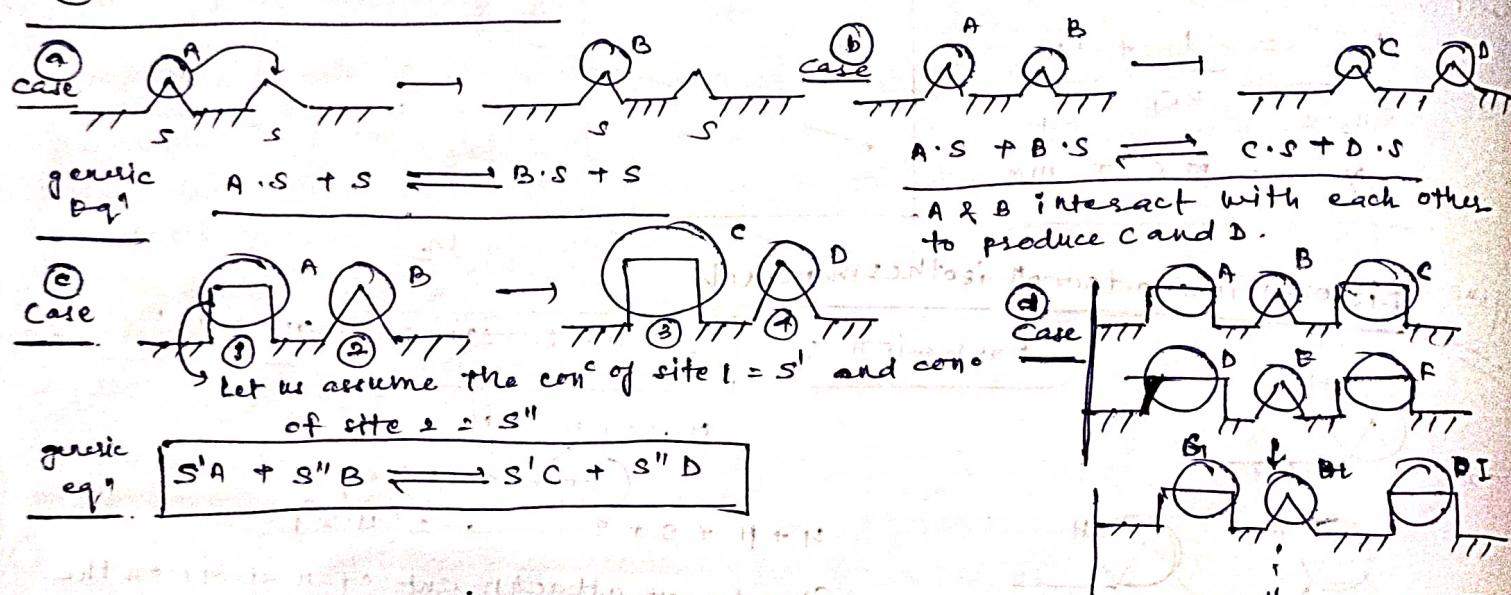
$$\left(k_A = k_1 \atop k_2 \right)$$

Langmuir - Hinshelwood Kinetics :-
 (Here we are only considering the surface rx's)

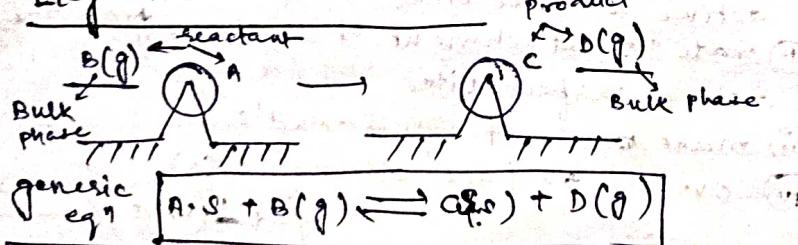
① Single site mechanism



⑪ Dual site mechanism



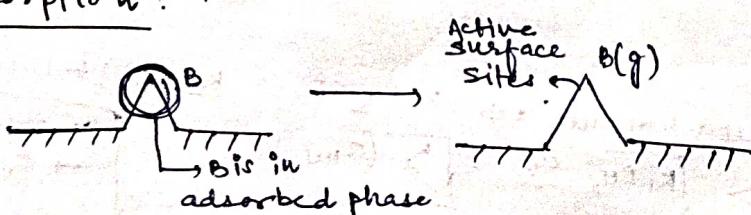
Eleg - Redefl Mechanism:



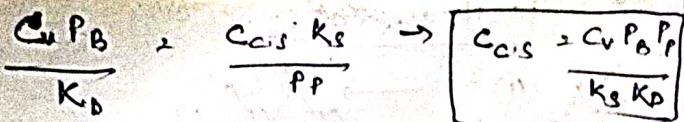
24/01/23 Catalytic process :-

~~① Adsorp^{"A}) ② Surface rx^{"B}) ③ Desorp["]~~

Description:-



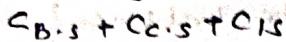
Generic eqⁿ: — $B \cdot S \rightleftharpoons B + S$ [S = active surface sites]
 Adsorbed phase



If one of the eq's is rate limiting then other 2 will be very fast.

$$C_{1,3} = C_{PB} K_1$$

$$C_t = C_V + C_V [\dots]$$



$$C_t = C_V + C_V \left[\frac{P_B P_p}{K_s K_D} + \frac{P_I K_I}{K_D} + \frac{P_B}{K_D} \right]$$

$$C_t = C_V \left[1 + \frac{P_I K_I}{K_D} + \frac{P_B}{K_D} + \frac{P_B P_p}{K_s K_D} \right]$$

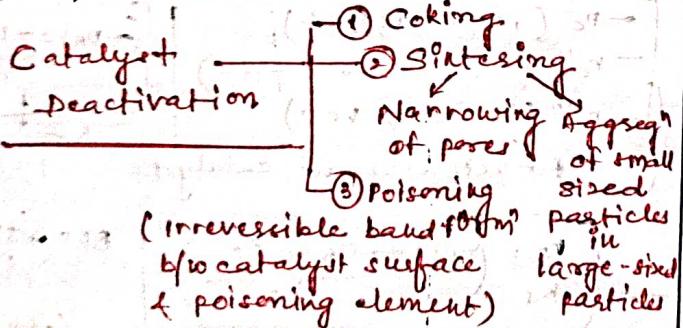
$$C_V = \frac{C_t}{\left\{ 1 + \frac{P_I K_I}{K_D} + \frac{P_B}{K_D} \left(1 + \frac{P_p}{K_s} \right) \right\}}$$

$$r_A = k_A \left[C_V P_c - \frac{C_{Cs}}{K_A} \right]$$

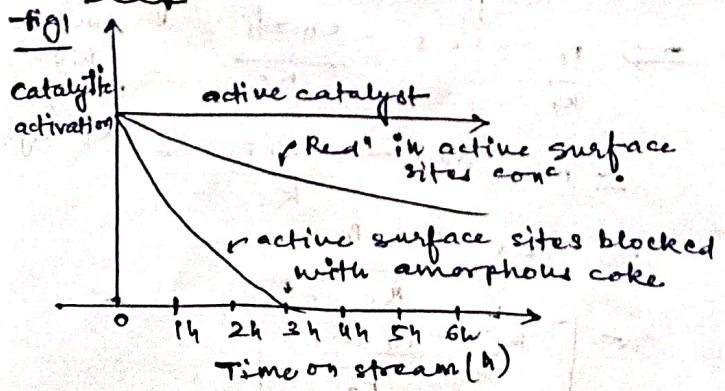
$$= K_A \left[\frac{C_t P_c}{1 + \frac{P_I K_I}{K_D} + \frac{P_B}{K_D} \left(1 + \frac{P_p}{K_s} \right)} - \frac{C_V P_B P_p}{K_s K_D K_A} \right]$$

$$= K_A C_V \left[P_c - \frac{P_B P_p}{K_s K_D K_A} \right]$$

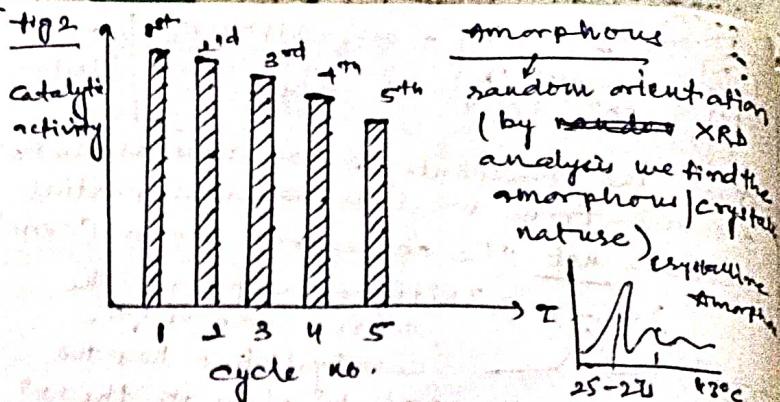
Coking on catalyst surface sites



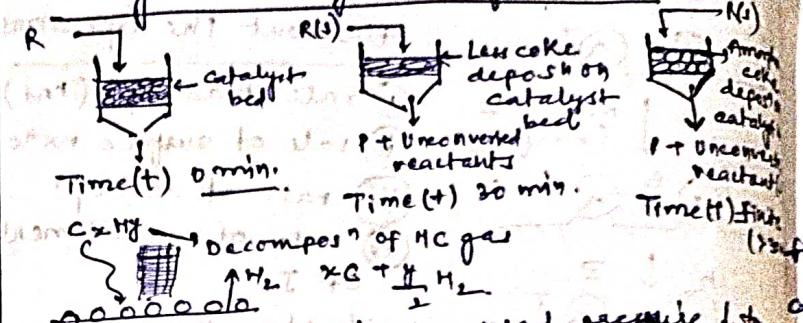
① Coking :-



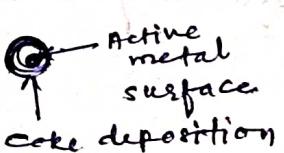
Interact b/w metal and support \rightarrow



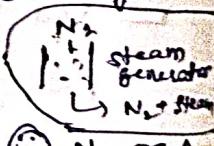
Coking on catalyst surface sites



promotes needs to be used, precise to reduce the coke depos'



When the active metal gets completely covered with coke, in the prod. we only get the HC, not H₂ gas is produced. In each step we keep losing active ss. Even after regen, 100%. recovery is not possible.

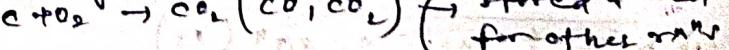


Regeneration of catalyst :-

done in the presence of ① O₂ ② N₂ or ③ N₂ + H₂O (steam) or N₂ + carbon steam

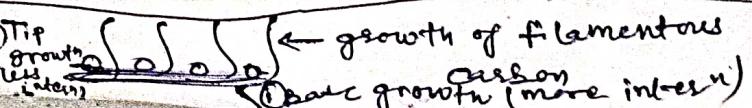
regen done after taking out the catalyst from the reactor and cooling it down to room temp.

passing of gases to remove the coke.



List of rxns relevant to coking :-

- 1.) Catalytic cracking of HC gas/vapor (HC's: Methane, Ethane, propane, propylene, acetylene, toluene, Benzene, ethanol)
- 2.) Steam reforming
- 3.) CO₂ reforming of molten methane HC gas
- 4.) oxidative hydrogenation of HC gas



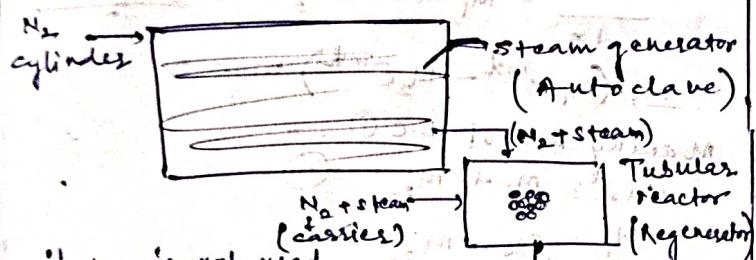
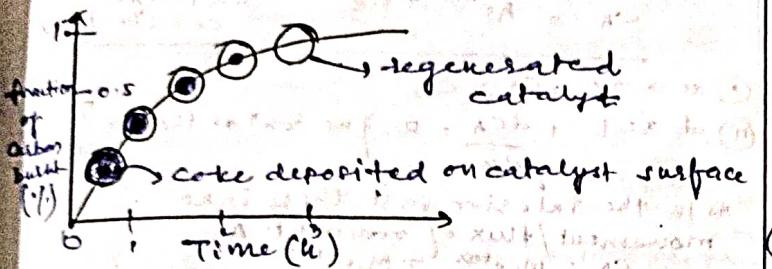
Catalyst regeneration :- coke particles to be eliminated

a) heating the catalyst (spent) in the air / oxygen ($\rightarrow \text{CO}_2 + \text{CO}$) would be evolved out of environment ($T = 250^\circ\text{C} - 300^\circ\text{C}$, 3 h operations).

b) heating the catalyst (spent) in the N_2 / or any other inert ($\text{He}, \text{Ar}, \text{Kr}$) medium ($T = 500^\circ\text{C} - 550^\circ\text{C}$, 2 h opns)

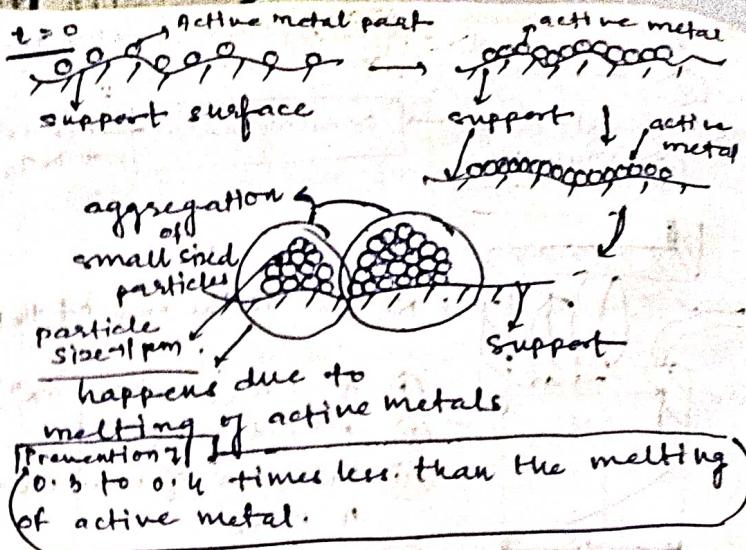
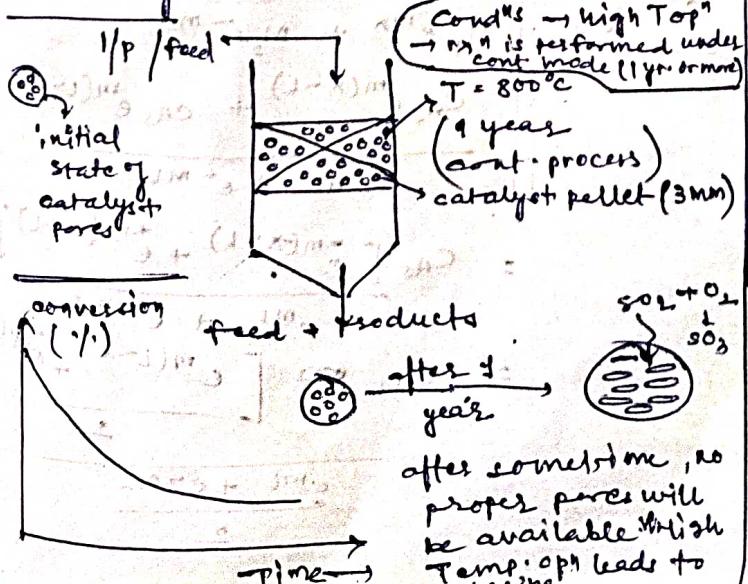
c) by passing a mixture of (steam + inert gas) at around 600°C .

Shrinking core Model :-

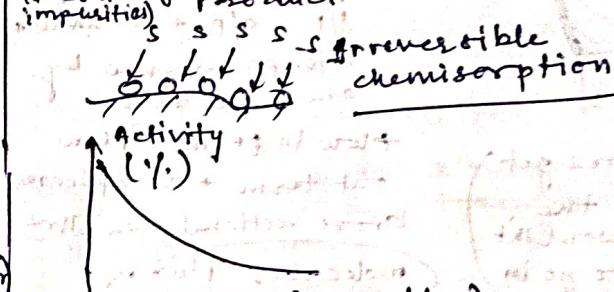
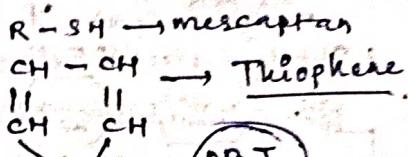
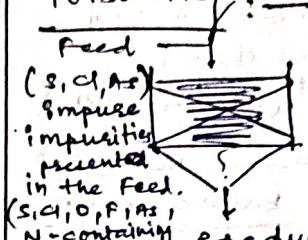


If N_2 is not used, steam will start to condense and the pipe connecting the autoclave and regenerator would get choked with H_2O . Hence more steam won't come in contact with coke, time of operation \uparrow .

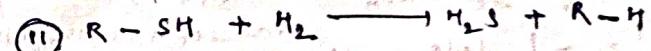
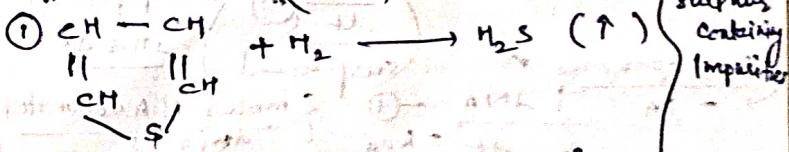
Sintering :- Narrowing of pores



Poisoning :-

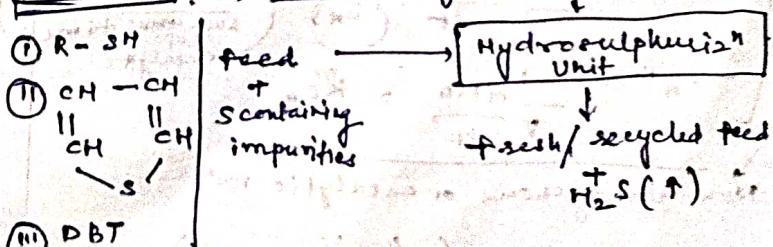


industry
 Feed \rightarrow pretreated (pure)
 (impure) Unit \rightarrow Treated fresh feed to be fed to the reactor
 (collected from nature Hydro sulphydril 2 h
 different sources) $(+ \text{H}_2)$, 300°C

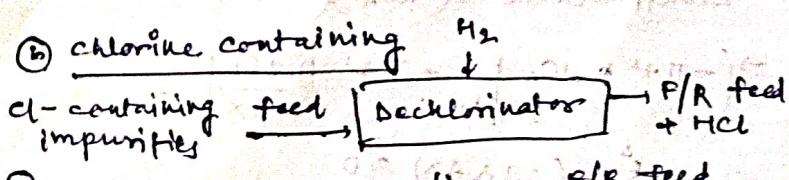


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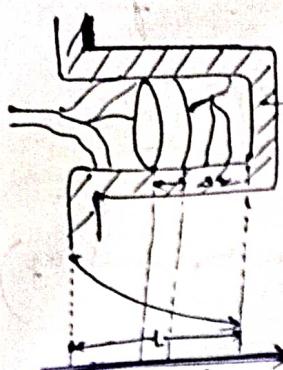
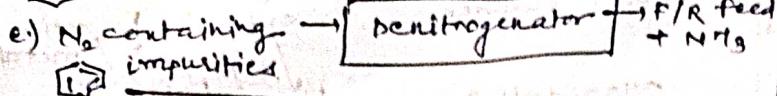
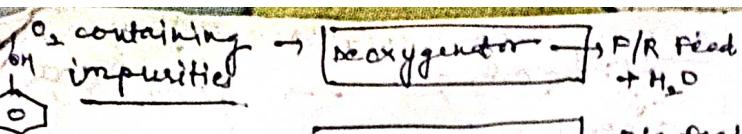
a) S containing



iii) DBT



c) As or any other heavy metals \rightarrow Adsorption \rightarrow F/R feed



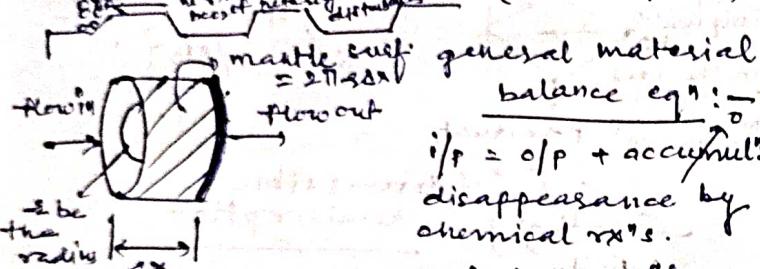
No rxn at the end of the pore

- ① $A \rightarrow R$ (gas phase rxn)
1st order rxn
- ② bulk conc^c of reactant
 $A \approx C_A$

④ surface concentration

$2\pi x_{out}$
(length of the pore)
of reactant A = C_{AS}

slit type pore (cylindrical shape)
pore structure (interior part)



$\frac{dC_A}{dx} = 0$ \Rightarrow o/p + accumul^t disappearance by chemical rxns.

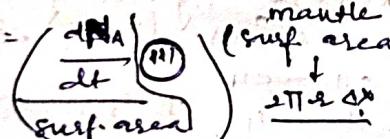
flow in term = flow out term + disappearance
cross sectional area = πr^2

molecular flux.

(if the pores get narrower the particles wouldn't be able to go in)

$$\left(-\frac{dC_A}{dx} \right) \pi r^2 = \left(-\frac{D dC_A}{dx} \right) \pi r^2 + \text{disappearance}$$

disappearance = $\frac{dNA}{dt}$ (surf area)
homogeneous rxn
- $r_A = \frac{1}{V} \frac{dNA}{dt} = k_A$ (moles of A converted)



$$-r_A' = \frac{1}{W} \frac{dNA}{dt} = k'_A \quad (\text{moles of A converted})$$

$$-r_A'' = \frac{1}{S} \frac{dNA}{dt} = k''_A \quad (\text{moles of A ...})$$

$$-r_A''' = \frac{1}{V} \frac{dNA}{dt} = k'''_A \quad (\text{catalyst})$$

Now homogeneous or catalytic rxns

disappearance = $(k''_A \cdot (2\pi r^2 A x))$

$$\rightarrow \left(-\frac{\pi r^2 D dC_A}{dx} \Big|_{in} + \pi r^2 D dC_A \Big|_{out} \right)$$

$$-k''_A (2\pi r^2 A x) \approx 0$$

$$\rightarrow \pi r^2 D \left[\frac{dC_A}{dx} \Big|_{out} - \frac{dC_A}{dx} \Big|_{in} \right] = 2\pi r^2 k''_A A x \approx 0$$

$$\rightarrow \frac{dC_A}{dx} \Big|_{out} - \frac{dC_A}{dx} \Big|_{in} = \frac{2k''_A C_A}{D} \approx 0$$

$$\rightarrow \left[\frac{dC_A}{dx} \Big|_{out} - \frac{dC_A}{dx} \Big|_{in} \right] = \frac{2k''_A C_A}{D} \approx 0$$

$$\Rightarrow \frac{d^2 C_A}{dx^2} - \frac{2k''_A C_A}{D} \approx 0$$

$$k''_A S = K V \Rightarrow K = k''_A S \approx \frac{V}{D}$$

$$\Rightarrow \frac{d^2 C_A}{dx^2} - \frac{K C_A}{D} \approx 0$$

$$C_A = Ae^{mx} + Be^{-mx} \quad A \& B \text{ are constants}$$

$$\textcircled{I} \text{ at } x=0, C_A = C_{AS}$$

$$\textcircled{II} \text{ at } x=L, \frac{dC_A}{dx} = 0 \quad \{ \text{no rxn at the end} \}$$

As in the interior part there is no movement/flux of reactant A.

$$C_A = M_1 e^{mx} + M_2 e^{-mx}$$

$$\frac{dC_A}{dx} = M_1 m e^{mx} - M_2 m e^{-mx} \approx 0$$

$$\Rightarrow (M_1 e^{mx} - M_2 e^{-mx}) m = 0$$

Making use of b.c. \textcircled{I} :-

$$C_{AS} = M_1 + M_2 \quad \textcircled{III}$$

$$M_1 = C_{AS} - M_2$$

$$(C_{AS} - M_2) e^{mx} = M_2 e^{-mx}$$

$$\Rightarrow C_{AS} e^{mx} = M_2 (e^{mx} + e^{-mx})$$

$$M_2 = \frac{C_{AS} e^{mx}}{e^{mx} + e^{-mx}}$$

$$M_1 = C_{AS} - M_2$$

$$= C_{AS} \frac{e^{-mx}}{e^{mx} + e^{-mx}}$$

$$\text{So, } C_A = M_1 e^{mx} + M_2 e^{-mx}$$

$$= C_{AS} e^{m(x-L)} + C_{AS} e^{m(L-x)}$$

$$= C_{AS} \left[\frac{e^{m(x-L)}}{e^{mx} + e^{-mx}} + \frac{e^{m(L-x)}}{e^{mx} + e^{-mx}} \right]$$

$$= C_{AS} \left[\frac{e^{m(L-x)}}{e^{mx} + e^{-mx}} + \frac{e^{m(x-L)}}{e^{mx} + e^{-mx}} \right]$$

$$= C_{AS} \left[\frac{e^{m(L-x)}}{e^{mx} + e^{-mx}} + \frac{e^{m(x-L)}}{e^{mx} + e^{-mx}} \right]$$

$$= C_{AS} \left[\frac{e^{m(L-x)}}{e^{mx} + e^{-mx}} + \frac{e^{m(x-L)}}{e^{mx} + e^{-mx}} \right]$$

$$\frac{c_A}{c_{A\text{as}}} = \frac{\cosh m(L-x)}{\cosh mL} \Rightarrow \frac{mL}{c_{A\text{as}}} = L \sqrt{\frac{k}{D}}$$

$mL \approx L \omega$ (< 0.4)
 $D = \text{Dominant}$

Low diffusional resistance (rx^n slow)

$k = \text{rate limiting}$

$L = \text{small (short type pore)}$

$mL > 4$

- (i) length of the pore is long
- (ii) rx^n rate is fast
- (iii) we have got more diffusional resistance [diffusion is rate limiting]

Effectiveness factor (γ) $\rightarrow \frac{D}{k}$

$\gamma = \frac{\text{actual mean rx}^n \text{ rate}}{\text{rx}^n \text{ rate when diffusion resistance are present in the system}}$

$\gamma = \left(\frac{r_A}{r_{A\text{as}}} \right)$ 1st order $\text{rx}^n \rightarrow r_A \propto \text{Conc}$

$$\gamma = \frac{c_A}{c_{A\text{as}}} e^{(kx/mL)}$$

progressive concentrate (drop in) \propto the f^n of Thiele modulus

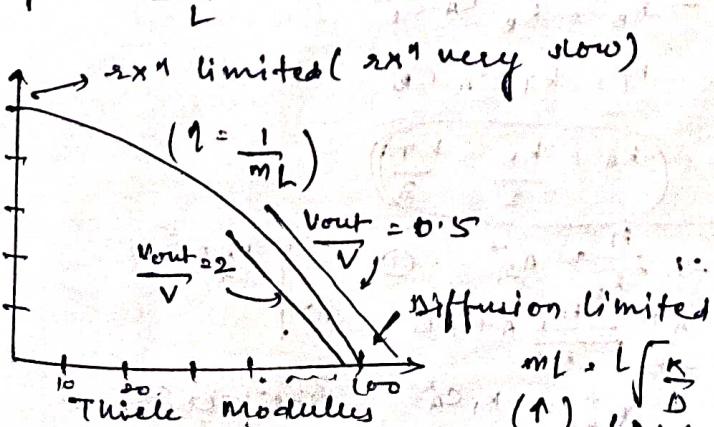
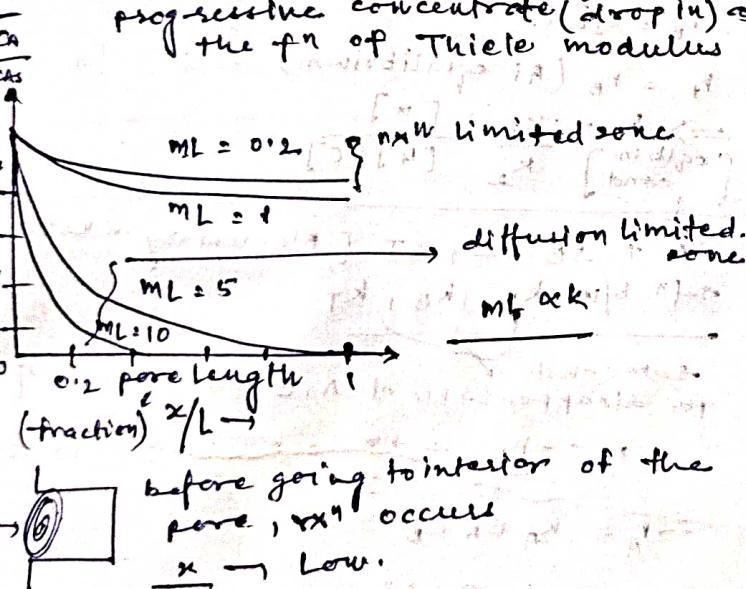
$$ML = 0.2 \quad \text{rx}^n \text{ limited zone}$$

$$ML = 1$$

diffusion limited zone

$$ML = 5$$

$$ML = 10$$

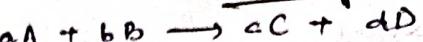


in some rx^n's, post rx^n vol. changes

$$V = V_0 (1 + \epsilon x)$$

vol. expansion factor. So the 2 parallel lines indicate change in volume conc \uparrow with vol. \downarrow .

Homogeneous rxns



a, b, c, d are stoichiometric coefficients of the reactants and products respectively

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = \frac{\text{moles of A converted}}{\text{per unit reactor vol. per unit time}}$$

$$= \frac{(\text{moles})}{(\text{dm}^3 \cdot \text{s})}$$

$$r_C = \frac{1}{V} \frac{dN_C}{dt} = \frac{\text{moles of C produced}}{\text{per unit reactor vol. per unit time}}$$

$$(-r_A) = (-r_B) = \frac{(n_a)}{a} = \frac{(n_d)}{d}$$

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = f \quad (\text{concentrate, Temp. dependent terms})$$

$$-r_A = (Kc_A^n) \quad n^{\text{th}} \text{ order rx}^n$$

in heterogeneous rx^n 2 more terms are considered \rightarrow mass transfer & heat-transfer terms

$K = \text{rx}^n \text{ rate const.}$

$$K = K_0 e^{-EA/RT}$$

$$K = K_0 T^m e^{-EA/RT}$$

$$E_A \rightarrow (\text{Toule / moles})$$

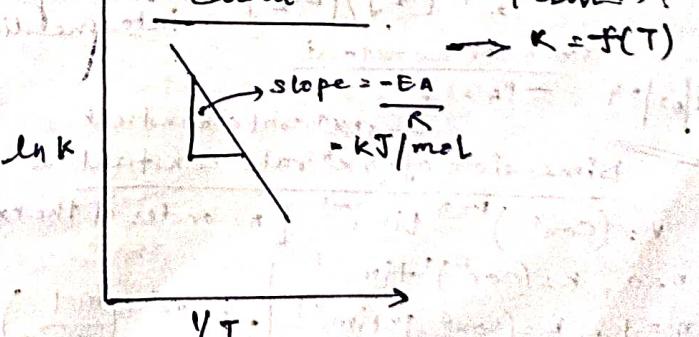
activation \rightarrow min. energy req. to start at rx^n

$$\begin{cases} m_c = 0 \\ m_2 = 1/2 \\ m_1 = 1 \end{cases}$$

Activ Energy

Calculation

$\rightarrow K = f(T)$

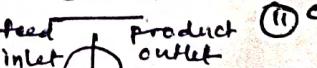


reactors
unsteady state \rightarrow steady (accumulⁿ) state

Batch

① PFR

② CSTR

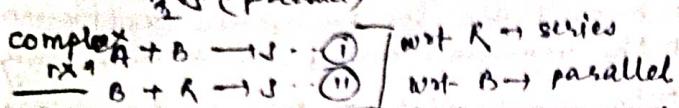
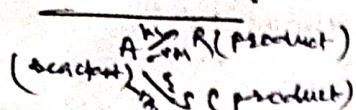
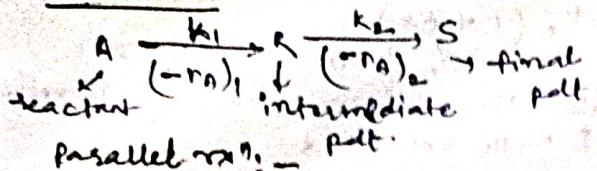


independent complex

rx^n's 1 - ① Single rx^n ($C \rightarrow P$)

② multiple rx^n's (series/parallel)

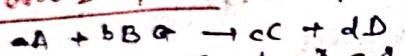
Series rxn:



molecularity: no. of molecules participating in a rxn.
 It can be 1, 2 and occasionally $\rightarrow 3$.

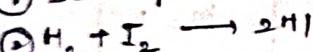
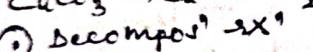
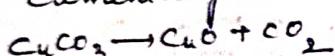
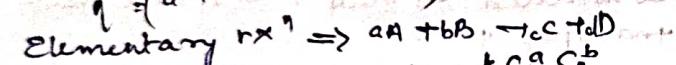
- 1 | (i) unimolecular $\xrightarrow{k_p} A \rightarrow R$
- 2 | (ii) bimolecular $\xrightarrow{k_p} A + A \rightarrow Pdt.$
 $A + B \rightarrow Pdt.$
- 3 | (iii) Termolecular $\xrightarrow{k_p} B + B \rightarrow Pdt.$
 $A + A + A \rightarrow Pdt.$
 $A + B + C \rightarrow Pdt.$
 $B + B + B \rightarrow Pdt.$

order of rxn:



$$-r_A = (k C_a^a C_b^b C_x^x C_y^y \dots)$$

$$q = (a + b + c + \dots)$$



Non Elementary rxn \Rightarrow det. the rate experimentally



$$-r_A = k_1 [HBr]/[Br_2]^{1/2}$$

$$\frac{k_1}{k_2} + \frac{[H_2]}{[Br_2]}$$
 unsteady intermediate

\Rightarrow rate constant

$$-r_A = k_1 C_A^n$$
 rxn rate constant

Dimension of rxn rate constant:

$$v = (conc)^{n-1} \text{ time}^{-1}$$
 [n = order of the rxn]

$$n=0, k_1 = (\text{conc})^0 \text{ time}^{-1}$$

$$n=1, k_1 = (\text{conc})^1 \text{ time}^{-1}$$

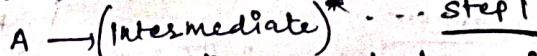
$$n=2, k_1 = (\text{conc})^{-1} \text{ time}^{-1}$$

rxn mechanism:

(i) non-chain

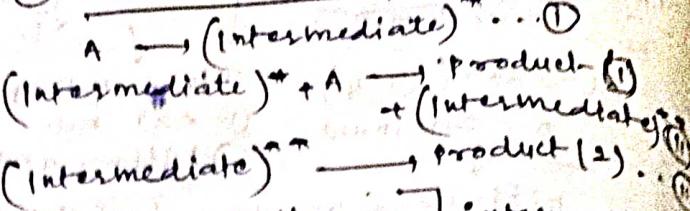


mechanistic steps



$(\text{intermediate})^* \rightarrow \text{Product}$... step 2

(i) chain mechanism

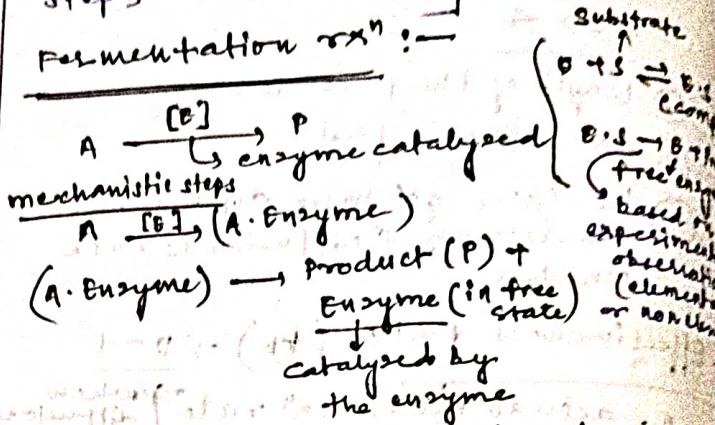


Step 1 \rightarrow Initiation

Step 2 \rightarrow propagation

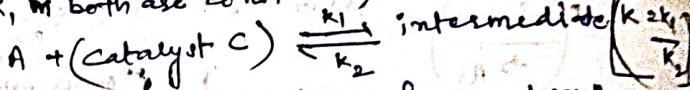
Step 3 \rightarrow Termination

Fermentation rxn:



$$-r_A = \frac{k [E_0] [A]}{M + [A]} \rightarrow \text{Michaelis-Menten Eqn}$$

(K, M both are constant)



$A + C \xrightleftharpoons{k_1} X$... (i) forward rxn

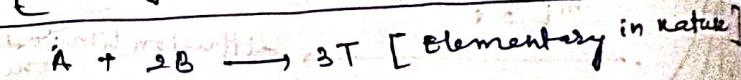
$X \xrightleftharpoons{k_2} A + C$... (ii) backward rxn

$$r_F = k_1 [A][C]$$

$$r_B = k_2 [X]$$

$$r_F = r_B \quad (\text{At equilibrium})$$

$$\Rightarrow \frac{k_2}{\text{equlbm. cond.}} \frac{k_1}{k_2} = \frac{[X]}{[A][C]}$$



$$-r_A = k_A [A] k_B [B]^2$$

rate const for disappearance of A, B and formation for disappearance of T

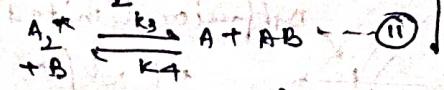
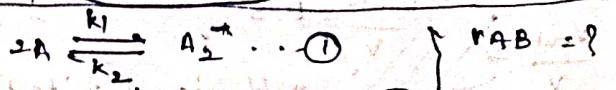
$$-r_A = -r_B = \frac{r_T}{2} = r$$

$$-r_A = k_A C_A C_B^2$$

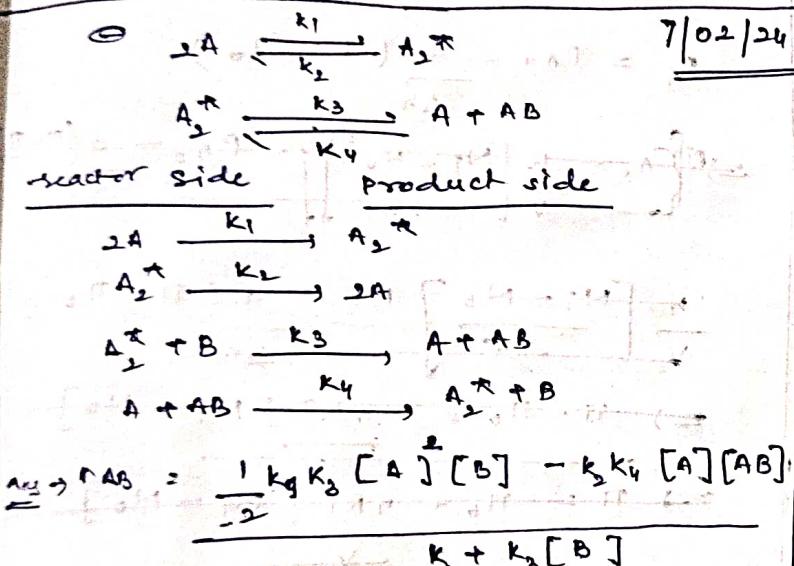
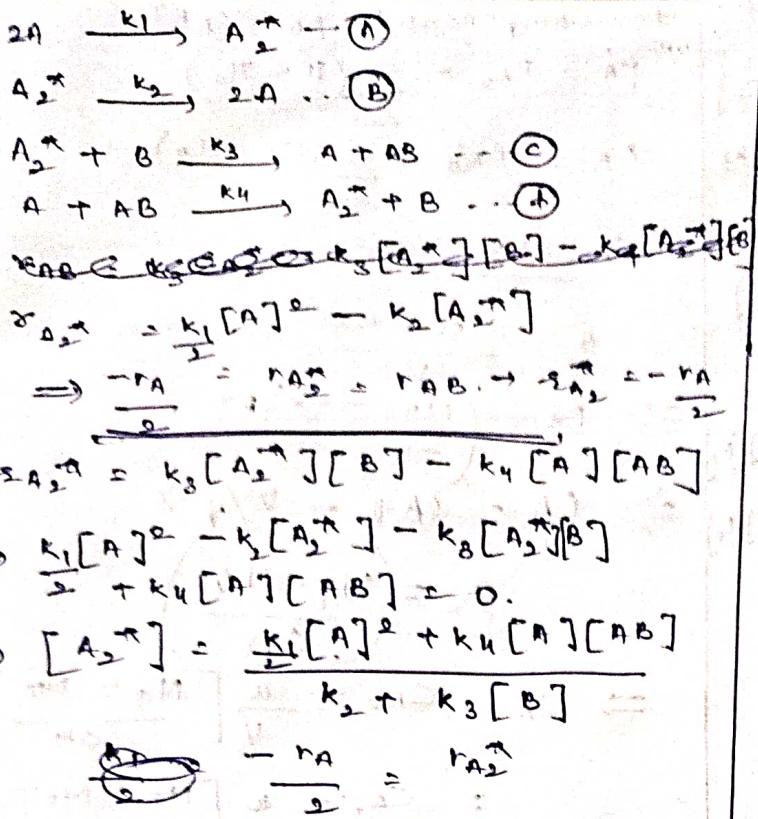
$$-r_B = k_B C_A C_B^2$$

$$-r_T = k_T C_A C_B^2$$

$$k_A = k_B = k_T \frac{2}{3}$$



$$2A \xrightleftharpoons[k_2]{k_1} k_1 C_A^2$$



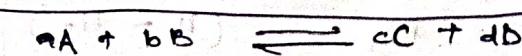
$$r_{A_2} = \frac{1}{2} K_1 C_A^2 - K_2 C_{A_2}^* - K_3 C_{A_2}^* C_B + K_4 C_A C_{AB} \quad \text{--- (1)}$$

$$r_{AB} = K_3 C_{A_2}^* C_B - K_1 C_A C_B \quad \text{--- (2)}$$

Since the concentration of A_2^* is very small, $r_{A_2}^* = 0$

$$\frac{1}{2} K_1 C_A^2 - K_2 C_{A_2}^* - K_3 C_{A_2}^* C_B + K_4 C_A C_{AB} = 0$$

$$\Rightarrow C_{A_2}^* = \frac{\frac{1}{2} K_1 C_A^2 + K_4 C_A C_{AB}}{K_2 + K_3 C_B}$$



$$\frac{-r_A}{\alpha} = \frac{-r_B}{\beta} = \frac{r_0}{C} = \frac{r_D}{\delta}$$

$$r_{AB} = K_3 \left[\frac{\frac{1}{2} K_1 C_A^2 + K_2 C_A C_B}{K_2 + K_3 C_B} \right] C_B - K_4 C_A C_B.$$

$$n_{AB} = \frac{\frac{1}{2} k_1 k_3 C_A^2 C_B + k_2 k_4 C_A C_B C_{AB}}{k_2 + k_3 C_B}$$

$$= \frac{\frac{1}{2} k_1 k_3 C_A^2 C_B - k_2 k_4 C_A C_B}{k_2 + k_3 C_B}$$

$k_2 + k_3 C_B$

$\Rightarrow n_{AB} = \frac{k_2 + k_3 C_B}{\frac{1}{2} k_1 k_3 C_A^2 C_B - k_2 k_4 C_A C_B}$

$k_2 + k_3 C_B$

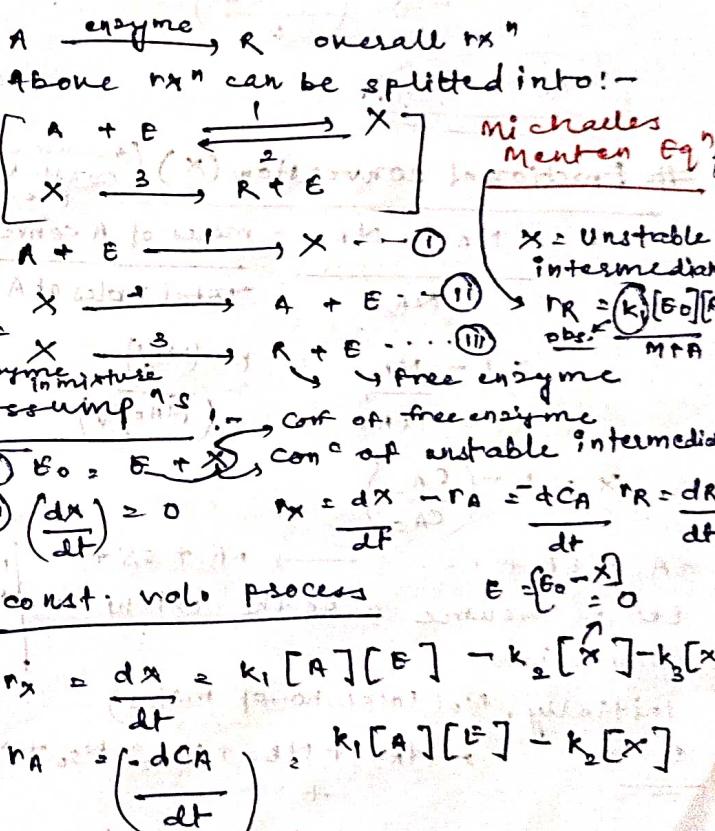
- ① k_2 value is very small.
- ② k_4 very small.

① $\Rightarrow n_{AB} = \frac{1/2 k_1 k_3 [A]^2 [B]}{k_3 C_B [A]}$

k_2 is low
 $k_3 [B] > k_2$
 $k_3 [A][AB] > k_2 k_1 [A]^2$
 k_2 is very small, thus neglected.

② $\Rightarrow n_{AB} = \frac{1/2 k_1 k_3 [A]^2 [B]}{k_3 C_B [A]}$ is neglected

$\Rightarrow n_{AB} = \frac{1/2 k_1 k_3 [A]^2 [B]}{k_2 + k_3 [B]}$



$$n_R = \frac{dR}{dt} = k_a [x]$$

$$\frac{dx}{dt} = k_1 [A][E_0 - x] - (k_2 + k_3)[x]$$

$$\Rightarrow [x] = k_1 [A] [\varepsilon_0] = k_1 [A] [\underline{\varepsilon_0}]$$

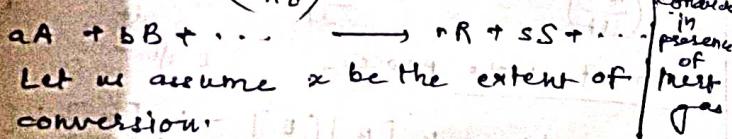
$$R = \frac{k_3 k_1 [A][B_0]}{k_1[A] + k_2 + k_3} - \frac{k_3 [A] + k_2 + k_3}{k_1}$$

$$\begin{aligned}
 r_A &= k_1[A][B_0] - k_2[x] \\
 &= k_1[A][B_0] - \frac{(k_1+k_2)k_1[A][B_0]}{k_1[A]+k_2+k_3} \\
 &= \frac{k_1[A][B_0](k_1[A]+k_2+k_3)}{k_1[A]+k_2+k_3} - \frac{(k_1[A]+k_2)k_1[A][B_0]}{k_1[A]+k_2+k_3} \\
 &= k_1^2[A]^2[B_0] + (k_2+k_3)k_1[A][B_0] \\
 &= k_1k_2[A][B_0] \\
 &= \frac{k_1k_2[A][B_0]}{k_1[A]+k_2+k_3} \\
 r_A &= k_2[A][B_0]
 \end{aligned}$$

$$r_R = -r_A$$

Fractional conversion (X) (assume const. vol.)

$$\begin{aligned}
 x_A &= \frac{N_{A_0} - N_A}{N_{A_0}} = \frac{\text{moles of A converted}}{\text{Total moles of A fed}} \\
 &= 1 - \frac{N_A}{N_{A_0}} = 1 - \frac{(N_A/V)}{(N_{A_0}/V)} \\
 X &= 1 - \left(\frac{C_A}{C_{A_0}} \right)
 \end{aligned}$$



Initially, N_0 (total no. of moles)

$$t=0 \quad N_0 = N_{A_0} + N_{B_0} + N_{R_0} + N_{S_0} + N_{\text{rest}}$$

$$\begin{aligned}
 t &= \frac{\text{no. of moles of comp. present at time } t}{\text{no. of moles of comp. present at } t=0} \\
 &\quad \times 100\%
 \end{aligned}$$

$$\begin{aligned}
 N_T &= (N_{A_0} - ax) + (N_{B_0} - bx) + \\
 &\quad (N_{C_0} + sx) + (N_{S_0} + sx) + N_{\text{rest}}
 \end{aligned}$$

$$\begin{aligned}
 N_T &= N_{A_0} + N_{B_0} + N_{C_0} + N_{S_0} - ax - bx + sx \\
 N_T &= \frac{N_{A_0} + \dots + N_{\text{rest}}}{N_0} + x[(a+s)-(a+b)] \\
 N_T &= N_0 + x \Delta n \quad [\text{where, } \Delta n = (a+s) - (a+b)] \\
 PV = nRT &\Rightarrow P = \frac{n}{V} RT \Rightarrow P = CRT
 \end{aligned}$$

for component A, $P_A = CRT$

$$P_A = P_{A_0} - \frac{a}{\Delta n} (\pi - \pi_0)$$

$$P_A = P_{A_0} + \frac{a}{\Delta n} (\pi - \pi_0)$$

$$C_A = \frac{N_A}{V} = \frac{P}{RT}$$

$$C_A = \frac{N_{A_0} - ax}{V}$$

$$\Rightarrow P_A = \frac{(N_{A_0} - ax)RT}{V}$$

$$\Rightarrow C_A = C_{A_0} - \frac{ax}{V} \times X$$

$$X = \frac{(N_T - N_0)}{\Delta n}$$

$$\Rightarrow C_A = C_{A_0} - \frac{a}{V} \left[\frac{N_T - N_0}{\Delta n} \right]$$

$$= C_{A_0} - \frac{a}{V} \left[\frac{N_T - N_0}{\Delta n} \right]$$

$$P_A = P_{A_0} - \frac{a}{\Delta n} (\pi - \pi_0)$$

$$\Rightarrow \left(C_{A_0} - \frac{a}{V} \left[\frac{N_T - N_0}{\Delta n} \right] \right) = P_{A_0} - \frac{a}{\Delta n} (\pi - \pi_0)$$

$$\frac{N_T - N_0}{V} RT = \frac{a}{\Delta n} (\pi - \pi_0)$$

$$\Rightarrow \pi - \pi_0 = \frac{N T - N_0}{V} RT [N_T - N_0]$$

$$\Rightarrow \pi = \pi_0 + \frac{N T - N_0}{V} RT [N_T - N_0]$$

$$\Rightarrow C_A = C_{A_0} - \frac{a}{\Delta n} \left(\frac{N_T - N_0}{V} \right)$$

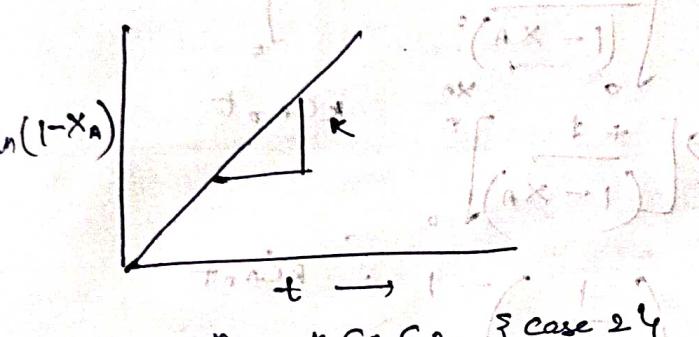
$$C_A = C_{A_0} - \frac{a}{\Delta n} (C_T - C_{T_0})$$

$$\Rightarrow P_A = CRT$$

$$\Rightarrow P_A = P_{A_0} - \frac{a}{\Delta n} (C_T RT - C_{T_0} RT)$$

$$\Rightarrow P_A = P_{A_0} - \frac{a}{\Delta n} (\pi - \pi_0)$$

$\xrightarrow{\text{case 1}}$ R (irrev. const. vol. process)
 $x_A \text{ & } t \quad \left\{ \begin{array}{l} \text{first order w.r.t A} \\ \text{1st order w.r.t B} \end{array} \right.$
 $-r_A = -\frac{1}{V} \frac{dN_A}{dt} = kC_A$
 $\Rightarrow -\frac{d}{dt} \left(\frac{N_A}{V} \right), \quad kC_A \Rightarrow -\frac{dC_A}{dt} = kC_A$
 $\Rightarrow \int \frac{dC_A}{C_A} = -\int dt \cdot k \Rightarrow \left(\ln C_A \right)_{C_{A_0}} = -kt$
 $\rightarrow \ln \left(\frac{C_A}{C_{A_0}} \right) = -kt$
 $\rightarrow \ln \left| \frac{C_A (1-x_A)}{C_{A_0}} \right| = -kt$
 $\Rightarrow -\ln |1-x_A| = kt$



$\xrightarrow{\text{case 2}}$ $-r_A = kC_A C_B$ $\left\{ \begin{array}{l} \text{case 2} \\ K = 1 \end{array} \right.$
 $A + B \xrightarrow{\text{R}}$
 $-r_A = -\frac{1}{V} \frac{dN_A}{dt} = kC_A$
 $\rightarrow -\frac{dC_A}{dt} = kC_A$
 $\Rightarrow -\left(\frac{dC_A}{dt} - \frac{C_A}{C_{A_0}} \right) = kt$
 $\Rightarrow \left[\frac{1}{C_{A_0}} - \frac{1}{C_A} \right] = kt$
 $\Rightarrow \frac{1}{C_A} - \frac{1}{C_{A_0}} = kt$
 $\rightarrow \frac{1 - (1-x_A)}{C_{A_0}(1-x_A)} = kt$
 $\rightarrow \frac{x_A}{C_{A_0}(1-x_A)} = kt$

$\frac{-dC_A}{dt} = kC_A C_B$
 $\Rightarrow \frac{dC_A}{C_A} = -kC_B dt$
 $\Rightarrow \int \frac{dC_A}{C_A} = -\int kC_B dt$
 $\Rightarrow \frac{C_A}{C_{A_0}} = e^{-kt}$
 $\Rightarrow C_A = C_{A_0} e^{-kt}$
 $C_B = C_{B_0} - C_{A_0} x_A$
 $N = C_{B_0} - C_{A_0}(1-x_A)$
 $\frac{dx_A}{dt} = \frac{C_{A_0} x_A}{(C_{B_0} - C_{A_0})(K-1)}$
 $A + B \rightarrow R$
 $C_A = C_{A_0} - C_{A_0} x_A \rightarrow t$
 $C_B = C_{B_0} - C_{A_0} x_A \rightarrow t$
 $\frac{dx_A}{dt} = -kC_A x_B$
 $= kC_{A_0}(1-x_A)$
 $- \frac{dC_A}{dt} = kC_{A_0} \left(\frac{C_{B_0} - x_A}{C_{A_0}} \right) (M - x_A)$
 $M = C_{B_0}/C_{A_0}$
 $\Rightarrow -\frac{d}{dt} C_{A_0} (1-x_A)$
 $= kC_{A_0} (1-x_A)(M-x_A)$
 $\Rightarrow \frac{dx_A}{dt} = k(1-x_A)(M-x_A)$
 $\Rightarrow \frac{dx_A}{(1-x_A)(M-x_A)} = \int k dt$
 $\Rightarrow \frac{1}{M} + \frac{x_A}{M-x_A} = \int k dt$
 $\Rightarrow \frac{\ln(1-x_A/M) - \ln(1-x_A/1')}{M-1} = kt$

$A + B \longrightarrow \text{Product}$ rxn is 1st order
w.r.t A
rxn is 2nd
order w.r.t B
and overall
 $\Rightarrow -r_A = -\frac{1}{V} \frac{dN_A}{dt} = k C_A C_B$
 $\Rightarrow -\frac{dC_A}{dt} = k(C_{A_0} - C_A x_A)(C_{B_0} - C_A x_A)$
 $\Rightarrow -\frac{d}{dt} [C_{A_0}(1-x_A)] = \frac{k C_{A_0}(1-x_A)}{C_{A_0}(\frac{C_{B_0}}{C_{A_0}} - x_A)}$
[Let $\frac{C_{B_0}}{C_{A_0}} = M$]
 $\Rightarrow \frac{dC_A}{dt} = k C_{A_0}^2 (1-x_A)(M-x_A)$
 $\Rightarrow \int_0^{x_A} \frac{dx_A}{(1-x_A)(M-x_A)} = k C_{A_0} \int_0^t dt$

$$\frac{dx_A}{(1-x_A)(M-x_A)} = \frac{1}{M-1} \left[\frac{(M-x_A) - (1-x_A)}{(M-x_A)(1-x_A)} \right] dx_A$$

$$= \frac{1}{M-1} \int \frac{dx_A}{1-x_A} - \frac{1}{M-1} \int \frac{dx_A}{M-x_A}$$

$$k C_{A_0} \cdot t = \frac{1}{M-1} \left[-\ln(1-x_A) \right]_0^{x_A}$$

$$- \frac{1}{M-1} \left[-\ln(M-x_A) \right]_0^{x_A}$$

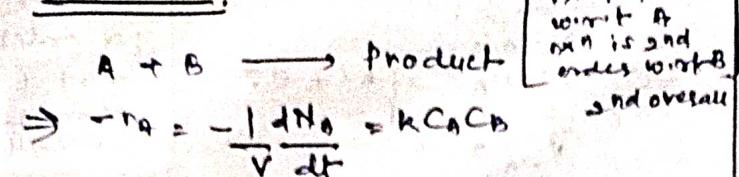
 $\Rightarrow k C_{A_0} (M-1) t = \ln \left| \frac{M-x_A}{M(1-x_A)} \right|$
Now, $M = \frac{C_{B_0}}{C_{A_0}}$
 $\Rightarrow \frac{k C_{A_0} (M-1) t}{C_{A_0}} = \ln \left| \frac{M-x_A}{M(1-x_A)} \right|$
 $\Rightarrow \ln \left| \frac{M-x_A}{M(1-x_A)} \right| = \frac{k(C_{B_0} - C_{A_0}) t}{C_{A_0}}$

$A + 2B \longrightarrow \text{Product}$ find out relationship b/w x_A & t
 $-r_A = k C_A C_B$
 $\Rightarrow -\frac{dC_A}{dt} = k(C_{A_0} - C_A x_A)(C_{B_0} - 2C_A x_A)$
 $\Rightarrow -\frac{d(C_{A_0} - C_A x_A)}{dt} = k C_{A_0}^2 (1-x_A)(M-2x_A)$
 $\Rightarrow \frac{dx_A}{(1-x_A)(M-2x_A)} = k C_{A_0}^2 (1-x_A)(M-2x_A)$
 $\Rightarrow \int_0^{x_A} \frac{dx_A}{(1-x_A)(M-2x_A)} = k C_{A_0} \int_0^t dt$

$$\left[\frac{1}{(1-x_A)} \right]_0^{x_A} = k C_{A_0} t$$

 $\Rightarrow \left(\frac{1}{1-x_A} \right) - 1 = k C_{A_0} t$
 $\Rightarrow \frac{x_A}{1-x_A} = k C_{A_0} t$

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$$\Rightarrow -\frac{dC_A}{dt} = k(C_{A_0} - C_A x_A)(C_{B_0} - C_A x_A)$$

$$\Rightarrow -\frac{d}{dt} [C_{A_0}(1 - x_A)] = \frac{k C_{A_0}(1 - x_A)}{C_{A_0}(C_{B_0} - x_A)}$$

$$\left[\text{Let } \frac{C_{B_0}}{C_{A_0}} = M \right]$$

$$\Rightarrow C_A + \frac{dx_A}{dt} = k C_{A_0} (1 - x_A) (M - x_A)$$

$$\Rightarrow \int_0^{x_A} \frac{dx_A}{(1 - x_A)(M - x_A)} = k C_{A_0} \int_0^t dt$$

$$\frac{dx_A}{(1 - x_A)(M - x_A)} = \frac{1}{M-1} \left[\frac{(M - x_A) - (1 - x_A)}{(M - x_A)(1 - x_A)} \right] dx_A$$

$$= \frac{1}{M-1} \int \frac{dx_A}{(1 - x_A)} - \frac{1}{M-1} \int \frac{dx_A}{M - x_A}$$

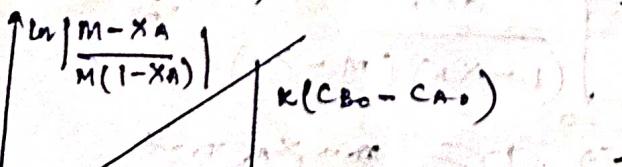
$$KC_{A_0} t = \frac{1}{M-1} \left[-\ln(1 - x_A) \right]_0^{x_A} - \frac{1}{M-1} \left[-\ln(M - x_A) \right]_0^{x_A}$$

$$\Rightarrow KC_{A_0} (M-1) t = \ln \left| \frac{M - x_A}{M(1 - x_A)} \right|$$

$$\text{Now, } M = \frac{C_{B_0}}{C_{A_0}}$$

$$\Rightarrow \frac{KC_{A_0} (C_{B_0} - C_{A_0}) t}{C_{A_0}} = \ln \left| \frac{M - x_A}{M(1 - x_A)} \right|$$

$$\Rightarrow \ln \left| \frac{M - x_A}{M(1 - x_A)} \right| = \frac{KC_{B_0} - KC_{A_0}}{C_{A_0}} t$$



Catalyst \longrightarrow product

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = KC_A^2$$

$$\Rightarrow -\frac{dC_A}{dt} = k (C_{A_0}(1 - x_A))^2$$

$$\Rightarrow -\frac{d[C_{A_0}(1 - x_A)]}{dt} = k C_{A_0}^2 (1 - x_A)^2$$

$$\Rightarrow -\frac{d[C_{A_0}(1 - x_A)]}{dt} = k C_{A_0}^2 (1 - x_A)^2$$

$$\Rightarrow \frac{dC_A}{dt} = k C_{A_0}^2 (1 - x_A)^2$$

$$\Rightarrow \int_0^{x_A} \frac{dx_A}{(1 - x_A)^2} = k C_{A_0} \int_0^t dt$$

$$\Rightarrow \left[\frac{-1}{1 - x_A} \right]_0^{x_A} = k C_{A_0} t$$

$$\Rightarrow \left(\frac{1}{1 - x_A} - 1 \right) = k C_{A_0} t$$

$$\Rightarrow \frac{x_A}{1 - x_A} = k C_{A_0} t$$

$A + 2B \longrightarrow \text{Product}$

$$-r_A = k C_A C_B \quad \text{find out rel' ship b/w } x_A \text{ & t}$$

$$\frac{dC_A}{dt} = k (C_{A_0} - C_{A_0} x_A)(C_{B_0} - 2C_{A_0} x_A)$$

$$\Rightarrow -\frac{d(C_{A_0} - C_{A_0} x_A)}{dt} = k C_{A_0}^2 (1 - x_A) (M - 2x_A)$$

$$\Rightarrow \frac{dx_A (C_{A_0})}{dt} = k C_{A_0}^2 (1 - x_A) (M - 2x_A)$$

$$\Rightarrow \int_0^{x_A} \frac{dx_A}{(1 - x_A)(M - 2x_A)} = \frac{k}{C_{A_0}} dt$$

$$\Rightarrow \frac{1}{M-2} \int_0^{x_A} \frac{M - 2x_A - 1 + 1 - 2x_A}{(1 - x_A)(M - 2x_A)} dx_A = k C_A t$$

$$\Rightarrow \frac{1}{M-2} \int \frac{1}{1-x_A} - \frac{2}{M-2x_A} dx_A = KC_{A_0} t$$

$$\Rightarrow \frac{1}{M-2} \left\{ -\ln(1-x_A) + \frac{2}{2} \ln(M-2x_A) \right\} = KC_{A_0} t$$

$$\Rightarrow \cancel{\frac{1}{M-2}} \frac{1}{M-2} \ln \left(\frac{M-2x_A}{M(1-x_A)} \right) = KC_{A_0} t$$

$$\Rightarrow \ln \left(\frac{M-2x_A}{M(1-x_A)} \right) = KC_{A_0} t - 2C_{A_0}$$

A + B + C → Product

$$-r_A = k C_A C_B C_C$$

$$- \frac{dC_A}{dt} = k (C_{A_0} - C_{A_0} x_A) (C_{B_0} - C_{A_0} x_A) (C_{C_0} - C_{A_0} x_A)$$

$$\Rightarrow - \frac{dC_A}{dt} = k C_{A_0}^3 (1-x_A) (M_B - x_A) (M_C - x_A)$$

$$\rightarrow + \frac{dx_A}{dt} = k C_{A_0}^2 (1-x_A) (M_B - x_A) (M_C - x_A)$$

$$\int_0^{x_A} -dx_A = \int_0^{x_A} \frac{k C_{A_0}^2 dt}{(1-x_A)(M_B-x_A)(M_C-x_A)} = k C_{A_0}^2 dt$$

$$\Rightarrow \int_0^{x_A} \frac{(M_B-x_A) - (M_C-x_A)}{(1-x_A)(M_B-x_A)(M_C-x_A)} dx_A = k C_{A_0}^2 t$$

$$\Rightarrow \frac{1}{(M-B)} \int \frac{1}{(1-x_A)(M_C-x_A)} - \frac{1}{(1-x_A)(M_B-x_A)} dx_A = k C_{A_0}^2 t$$

$$\Rightarrow \frac{1}{(M-B)} \left[\frac{1}{(M-C)} \frac{(M_C-x_A) - (1-x_A)}{(1-x_A)(M_C-x_A)} \right] - \frac{1}{(M-B)} \left[\frac{1}{(M-A)} \frac{(M_A-x_A) - (1-x_A)}{(1-x_A)(M_A-x_A)} \right] = k C_{A_0}^2 t$$

$$\Rightarrow \frac{1}{M-M'} \left[\frac{1}{(M'-C)} \frac{-\ln(1-x_A)}{(M'-C)} + \ln(M'-x_A) \right] - \frac{1}{(M-B)} \left[\frac{1}{(M-A)} \frac{-\ln(1-x_A)}{(M-A)} + \ln(M-A-x_A) \right] = KC_{A_0}^2 t$$

$$\Rightarrow \frac{1}{(M-M')} \left[\frac{1}{(M'-1)} \frac{\ln \left(\frac{M'-x_A}{M'(1-x_A)} \right)}{(M'-1)} \right] - \frac{1}{(M-B)} \left[\frac{1}{(M-A)} \frac{\ln \left(\frac{M-A-x_A}{M-A(1-x_A)} \right)}{(M-A)} \right] = KC_{A_0}^2 t$$