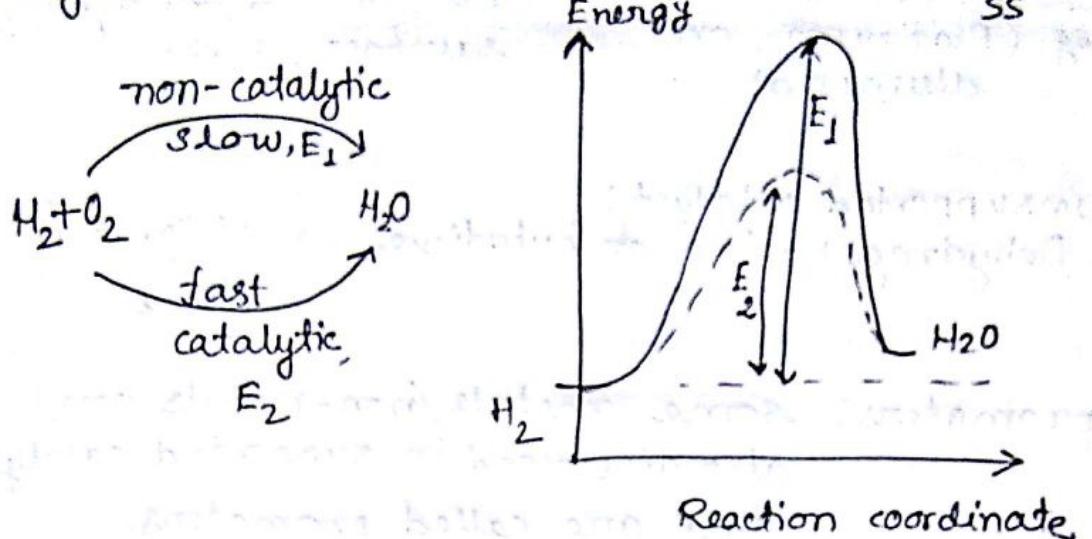


catalysts do not affect equilibrium

20/07/17

SS



Homogeneous catalyst \rightarrow soluble in reaction medium

e.g. Fridecraft alkylation R^nAlBr_3
(catalyst is HCl or H_2SO_4)

Heterogeneous catalysis \rightarrow surface phenomena
(porous catalysts are important as solid catalyst)
is important. Large surface area is preferable for this

e.g. $(\text{Alumina})(\text{s})$ used in cracking
 $(\text{silica})^+$

$300 \text{ m}^2 \text{ area/gram}$, pore radius -4 nm

Solid catalyst \rightarrow can be recovered after one cycle
 \rightarrow can be used after reviving (simply washing)

Molecular sieves \rightarrow catalysts which permit the entry of reactants in to the pores, according to the size.
(aluminosilicate catalyst, geopolymers)

Natural (amorphous)

Synthetic (crystalline) \rightarrow more active

supported catalyst \rightarrow some metals are put on the catalyst surface. ~~some~~
eg (Platinum on alumina)

unsupported catalyst:
Dehydrogenation of butadiene \rightarrow alumina + silica

promoters: some metals/non-metals are also dispersed in supported catalysts. These are called promoters, e.g. Potassium.

Supported Promoted Catalyst

Catalyst life

Deactivation of catalyst

Deposition of unwanted molecule on the catalyst surface. This leads to deactivation.

Catalyst cycle differs from catalyst to catalyst as well as reaction to reaction.

Solid catalyst \rightarrow surface phenomena

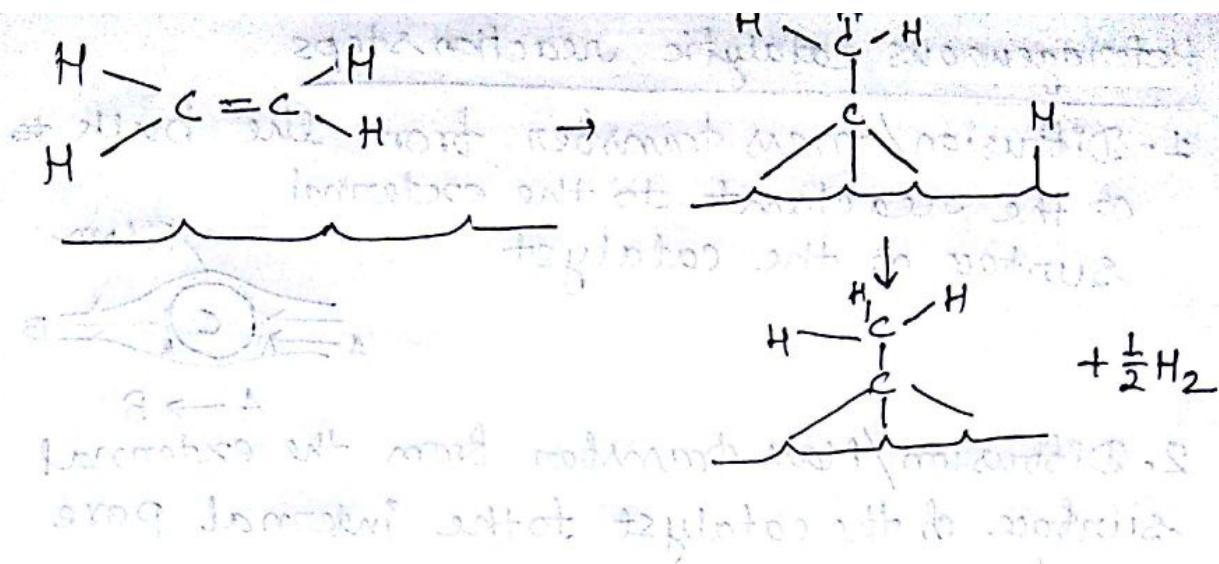
1) Adsorption of the reactant molecules on catalyst surface.

Physical
(1-15 kcal/gmole)

Not considered as first step in $r k^n$

\rightarrow Chemical (10-100 kcal/gmole)

Bonds are like bonds in initial molecule. Reaction occurs with chemical adsorption. Electronic structure of reactants change



For desired product, reaction parameters (temp., pressure) are required for chemisorption

Entire surface is not activated as catalyst.

There are active centres, which are surface irregularities in general.

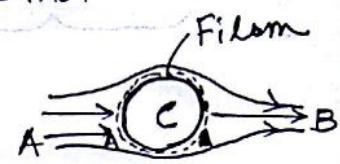
Active sites are those ~~ear~~ which can

$N \rightarrow$ no of molecules ^{re-}acting per active centre per second is called turn over frequency

$D \rightarrow$ fraction of metal ^{atom} dispersed on catalyst surface is called dispersion.

Heterogeneous catalytic reaction steps

1. Diffusion/mass transfer from the bulk to the reactant to the external surface of the catalyst



2. Diffusion/Mass transfer from the external surface of the catalyst to the internal pore surface

3. Adsorption of the reactants

4. Chemical reaction to form product

5. Desorption of product from pore surface

6. Diffusion/Mass transfer of the product from the internal surface to the external catalyst surface

7. Diffusion/mass transfer of the product from the external catalyst surface to the bulk

Slowest step out of these 7 steps, is the rate determination step.

Steps 1,2,6,7 are very fast

3,4,5 are slow

usually these three steps are considered for rate determination.

$$\frac{1}{C_A} - \frac{1}{C_{A_0}} = kt$$

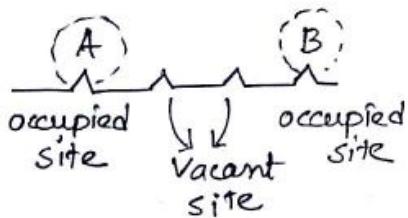
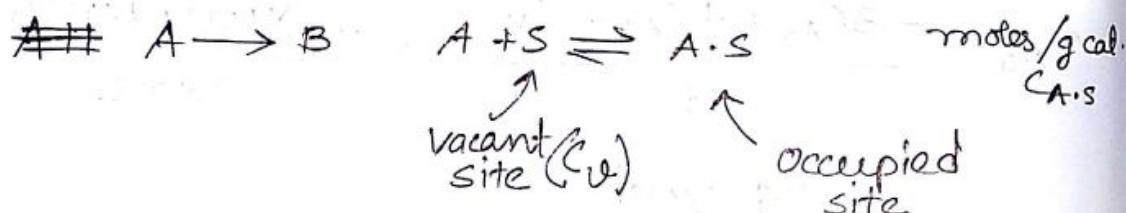
In integral approach, order is to be assumed beforehand then needed to be verified.

25/07/17

Adsorption Isotherm

'S' → active site on the catalyst surface

$$\frac{\text{no. of active sites}}{\text{unit mass of catalyst}} \times \frac{1}{N_0} = \frac{\text{moles}}{\text{g catalyst}}$$



total site concentration (C_t)

$$c_f = c_v + c_{A,S} \quad \text{site balance}$$

Amount of non reacting gas absorbed at same temperature but @ different pressure

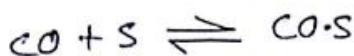
constructs adsorption isotherm

y. Non dissociative / Molecular adsorption

z. Dissociative adsorption

CO non reacting gas, considering only adsorption

y. Non dissociative



$$r_a \propto P_{CO} \cdot C_V$$

$$r_a = k_A P_{CO} C_V$$

z. Dissociative adsorption



$$r_d \propto P_C \cdot CO \cdot S$$

$$r_d = k_{dA} C_{CO \cdot S}$$

$$r_{ad} = k_A (P_{CO} C_V -$$

$$\frac{C_{CO \cdot S}}{K_A})$$

$$K_A = \frac{k_A}{k_{-A}} = \text{adsorption eqbm. const}$$

at eqbm, net rate of adsorption

$$r_{ad} = 0$$

$$P_{CO} C_V = \frac{C_{CO \cdot S}}{K_A}$$

$$C_{CO \cdot S} = K_A P_{CO} \cdot C_V \quad \dots \quad (1)$$



site balance

$$P_{CO} C_V - C_{CO \cdot S}$$

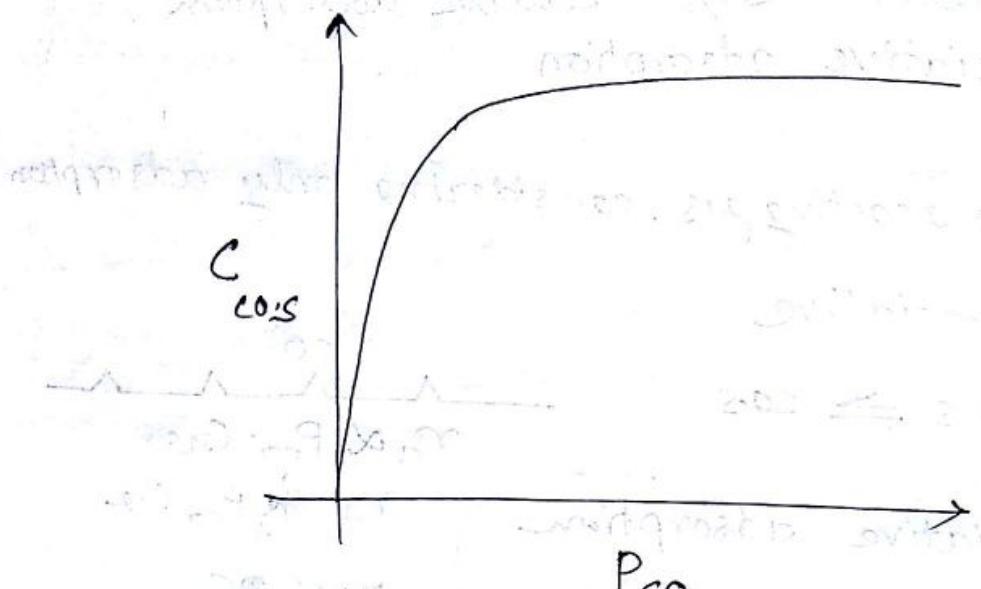
$$C_t = C_{CO \cdot S} + C_V$$

$$C_V = (C_t - C_{CO \cdot S}) \dots (2)$$

$$C_{CO \cdot S} = K_A P_{CO} (C_t - C_{CO \cdot S})$$

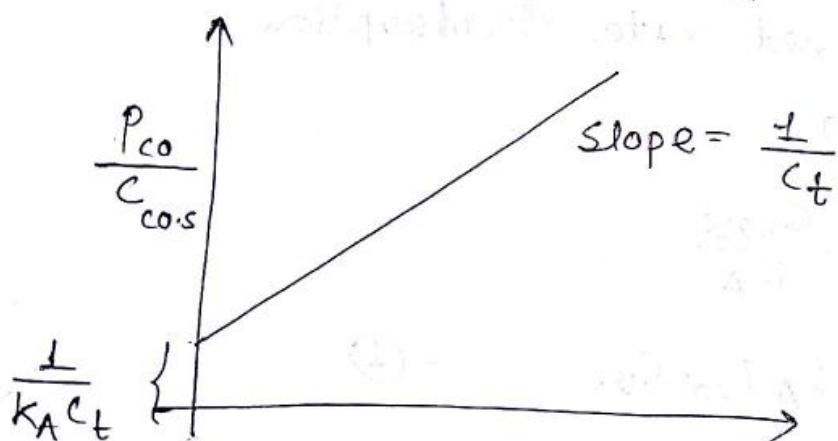
$$C_{CO \cdot S} (1 + K_A P_{CO}) = K_A P_{CO} \cdot C_t$$

$$C_{CO \cdot S} = \frac{K_A P_{CO} C_t}{1 + K_A P_{CO}} \quad | \text{ Langmuir Isotherm}$$



$$\frac{1}{C_{CO.S}} = \frac{P_1}{K_A P_{CO} C_t} + \frac{1}{C_t}$$

$$\boxed{\frac{P_{CO}}{C_{CO.S}} = \frac{1}{K_A C_t} + \frac{P_{CO}}{C_t}}$$



ii) Dissociative Adsorption



$$r_a = k_A P_{CO} \cdot C_p^2$$

$$r_{-a} = k_A C_{CS} C_{OS}$$

$$r_{ad} = k_A P_{CO} \cdot C_V^2 - k_A \cdot C_{OS} \cdot C_{CS}$$

$$= k_A \left(P_{CO} \cdot C_V^2 - \frac{C_{OS} \cdot C_{CS}}{k_A} \right)$$

at eqbm. $r_{ad} = 0$

$$P_{CO} \cdot C_V^2 = \frac{C_{OS} \cdot C_{CS}}{k_A}$$

Considering $C_{CS} = C_{OS}$

$$P_{CO} \cdot C_V^2 = \frac{C_{CS}^2}{k_A}$$

$$C_{CS}^2 = P_{CO} C_V^2 k_A$$

$$C_{CS} = (P_{CO} k_A)^{1/2} C_V \quad \text{--- (1)}$$

$$C_t = C_{CS} + C_{OS} + C_V$$

$$= C_V + 2C_{CS}$$

$$C_V = (C_t - 2C_{CS}) \quad \text{--- (2)}$$

$$C_{CS} = (C_t - 2C_{CS}) (P_{CO} k_A)^{1/2}$$

$$C_{CS} [1 + 2(P_{CO} k_A)^{1/2}] = C_t (P_{CO} k_A)^{1/2}$$

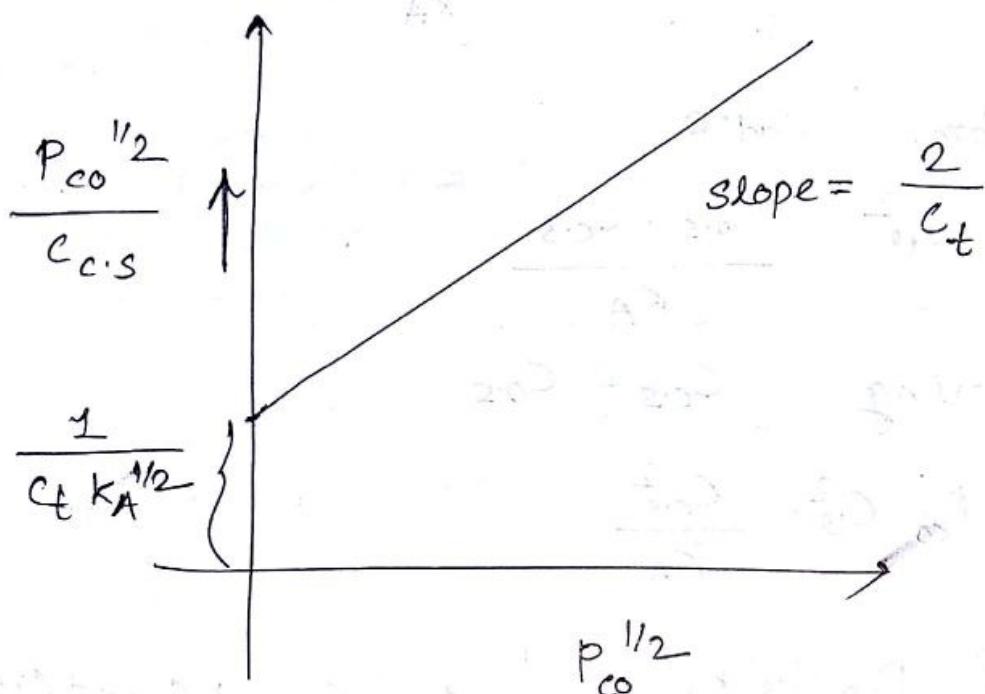
$$C_{CS} = \frac{C_t (P_{CO} k_A)^{1/2}}{1 + 2 (P_{CO} k_A)^{1/2}}$$

$$\text{total occupied site} = 2C_{CS} = \frac{2C_t (P_{CO} k_A)^{1/2}}{1 + 2 (P_{CO} k_A)^{1/2}}$$

$$C_{CS} (1 + 2 (P_{CO} k_A)^{1/2}) = C_t (P_{CO} k_A)^{1/2}$$

$$\frac{1}{C_{CS}} = \frac{1}{C_t (P_{CO} k_A)^{1/2}} + \frac{2}{C_t}$$

$$\frac{P_{CO}^{1/2}}{C_{c.s.}} = \frac{1}{C_t K_A^{1/2}} + \frac{2 P_{CO}^{1/2}}{C_t}$$



When both A & B are absorbed

$$C_{A.s.} = \frac{k_A P_A C_t}{1 + k_A P_A + k_B P_B}$$

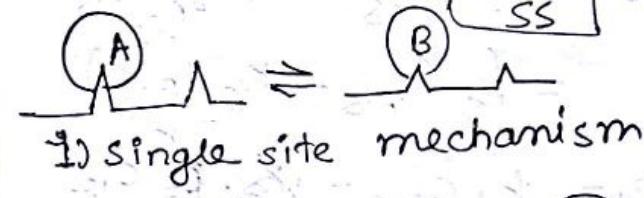
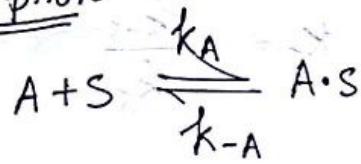
k_A = adsorption eqbm. const of A

k_B = n n n n B

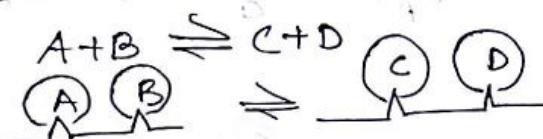
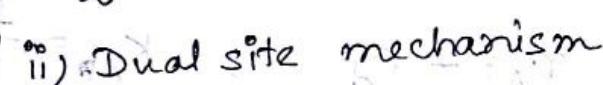
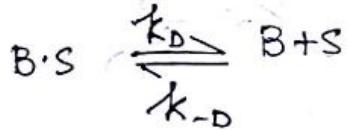
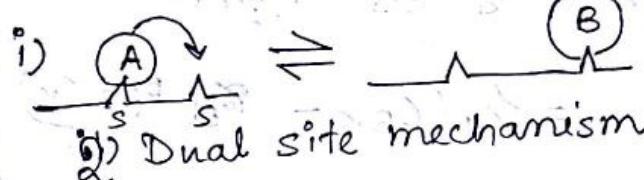
C_t = total concentration, moles/g.cat

27/07/17

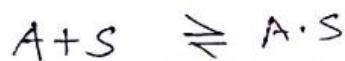
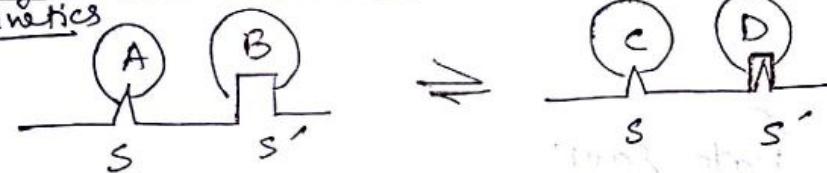
Adsorption



Reaction

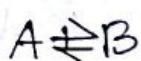
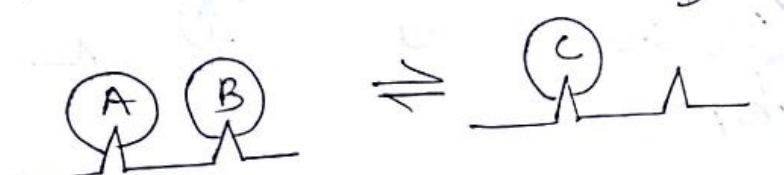


Langmuir - Hinshelwood kinetics



Eley - Riedel Kinetics

(At least one species will not be absorbed in the surface)



Rate eqns

$$r_A = k_A [A] [S]_v - k_{-A} [A \cdot S] = k_A P_A c_v - k_{-A} c_{A \cdot S}$$

$$\frac{dc_A}{dt} = k_A (c_A c_v - K_A c_{A \cdot S}) = k_A (P_A c_v - \frac{k_{-A}}{k_A} c_{A \cdot S})$$

$$r_s = k_s C_{A,S} - k_{s,k} \frac{C_{B,S}}{k_s} \quad r_s = k_s \left(C_{A,S} - \frac{k_s}{k_s} C_{B,S} \right)$$

$$= k_s \left(C_{A,S} - k_s \frac{C_{B,S}}{k_s} \right) \quad K_s = \frac{k_s}{k_s}$$

$$r_d = k_d C_{B,S} - k_{d,k} P_B C_v$$

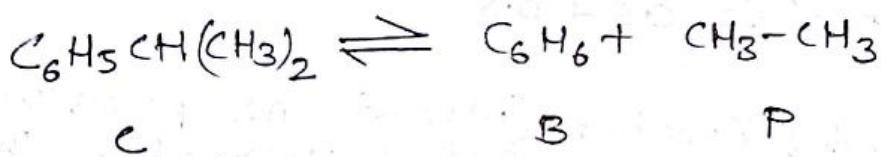
$$= k_d \left(C_{B,S} - \frac{P_B C_v}{k_d} \right)$$

$$r_A = -r_d \quad , \quad K_{AD} = \frac{1}{K_D} \quad K_D = \frac{k_D}{k_d}$$

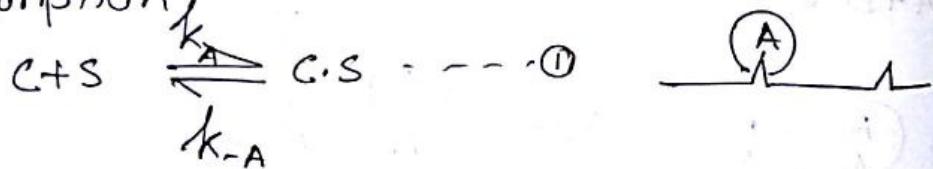
~~$$r_d = k_d (C_{B,S} - P_B)$$~~

Synthesising Rate law:

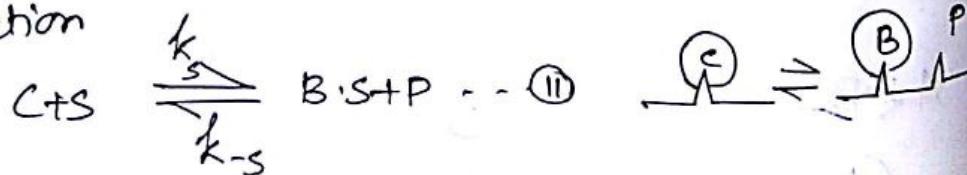
Cumene disproportionation reaction



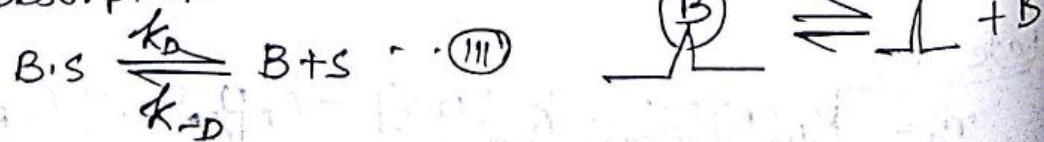
i) Adsorption



ii) Reaction



iii) Desorption



$$i) r_A = k_A P_C \cdot C_V - k_{-A} C_{C,S}$$

$$= k_A (P_C \cdot C_V - k_A \frac{C_{C,S}}{K_A}) \xrightarrow{\text{W}} \text{slower}$$

$$ii) r_S = k_S (C_{C,S} - \frac{P_B \cdot (v)}{K_D})$$

$$iii) r_S = k_S (C_{C,S} - \frac{C_{B,S} \cdot P_P}{K_S})$$

$$iv) r_D = k_D (C_{B,S} - \frac{P_B \cdot (v)}{K_D}) \\ = k_D (C_{B,S} - P_B \cdot (v \cdot K_{AB}))$$

At eqbm. and considering no accumulation of any species on the surface

$$-r_C = r_A = r_S = r_D$$

$$k_A \ll k_S, k_D$$

$$\frac{r_A}{k_A} \gg \frac{r_S}{k_S}, \frac{r_D}{k_D}$$

$$\frac{r_S}{k_S}, \frac{r_D}{k_D} \rightarrow 0$$

$$C_{C,S} = \frac{C_{B,S} P_P}{K_S} ; \quad C_{B,S} = \frac{P_B C_V K_{AB}}{-v} \quad \text{--- (IV)}$$

$$C_t = C_{V_e} + C_{C,S} + C_{B,S}$$

$$C_{V_e} = C_t - C_{B,S} - C_{C,S}$$

i) $C+S \rightleftharpoons C.S$

$$r_a = k_A (P_c \cdot C_{V_e} - \frac{C_{C,S}}{K_A})$$

$$= k_A (P_c \cdot C_{V_e} - \frac{P_B P_p K_{D,B}}{K_S} \cdot C_{V_e})$$

$$= k_A (P_c - \frac{P_B P_p K_{D,B}}{K_S}) C_{V_e}$$

$$r_a = k_A (P_c - \frac{P_B P_p K_{D,B}}{K_S}) \times \frac{C_t}{1 + \frac{P_B P_p K_D}{K_S} + P_B K_A}$$

ii) $C+S \rightleftharpoons B.S + P$

$$r_s = k_s (C_{C,S} - \frac{C_{B,S} P_p}{K_S})$$

$$C_{C,S} = \frac{P_B C_{V_e} K_{D,B} P_p}{K_S}$$

$$III) r_D = k_D (c_{B,S} - P_B \cdot c_D \cdot K_{AB})$$

$$\hookrightarrow \frac{k_1}{k_2} B + P$$

$$\hookrightarrow r_c = k_1 (P_C - \frac{P_B \cdot P_P}{K_P})$$

$$\hookrightarrow r_{AD} = k_{AD} (P_C - \left(\frac{\cancel{K_B P_B P_P}}{\cancel{K_S} \cancel{K_{ADC}}} \right) c_v)$$

$$= k_{AD} \left(P_C - \frac{P_B P_P}{K_P} \right) c_v$$

$$r_a = k_A (P_C - \frac{P_B P_P K_{DB}}{K_S}) x \quad \frac{c_t}{1 + \frac{P_B P_P K_D}{K_S} + P_B K_{ADC}}$$

$$-r_c = r_{AD} = k_{AD} \left(P_C - \frac{P_B P_P}{K_P} \right) x$$

$$\left(\frac{c_t}{1 + K_B P_B + \frac{K_B P_P P_B}{K_S}} \right)$$

for 1st order

$$C_A = C_{A_0} e^{-k_1 t}$$

& 0 order

$$C_{A_0} - C_A = \frac{k_1}{k_2} t$$

transition of order takes place at

$$k_1 C_A = \frac{k_1}{k_2} \quad \text{or} \quad C_A \approx \frac{1}{k_2}$$

01/08/17

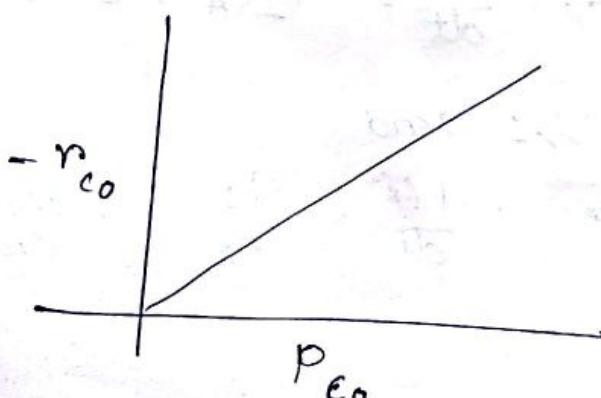
$$-r_c = r_{AD} = k_{AD} \left(P_c - \frac{P_B P_c}{K_p} \right) \left(\frac{C_t}{1 + K_B P_B + \frac{K_B P_B P_p}{K_s}} \right)$$

$$= \frac{C_t k_{AD} \left(P_c - \frac{P_B P_p}{K_p} \right)}{\left(1 + K_B P_B + \frac{K_B P_B P_p}{K_s} \right)}$$

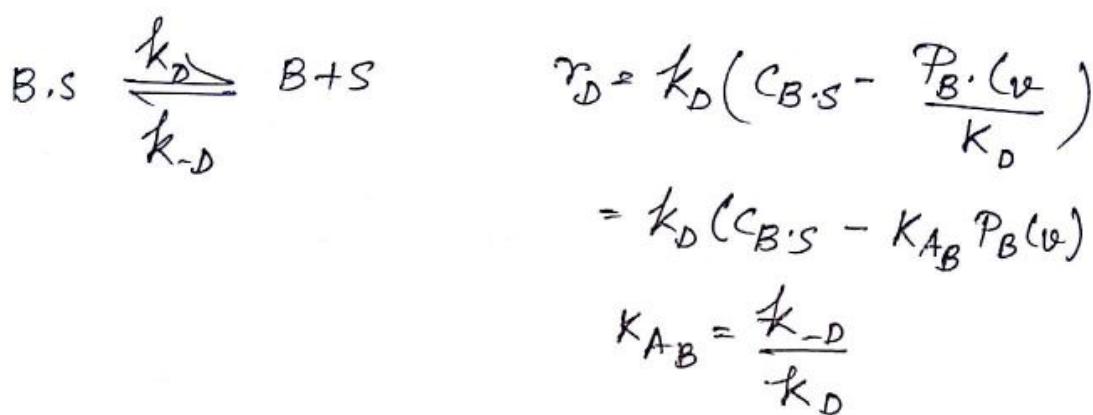
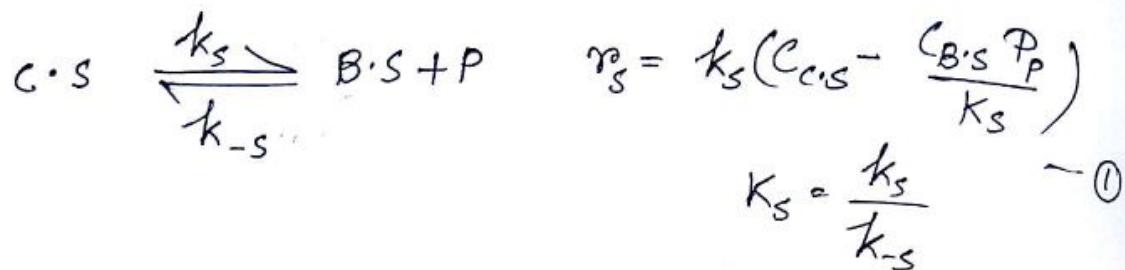
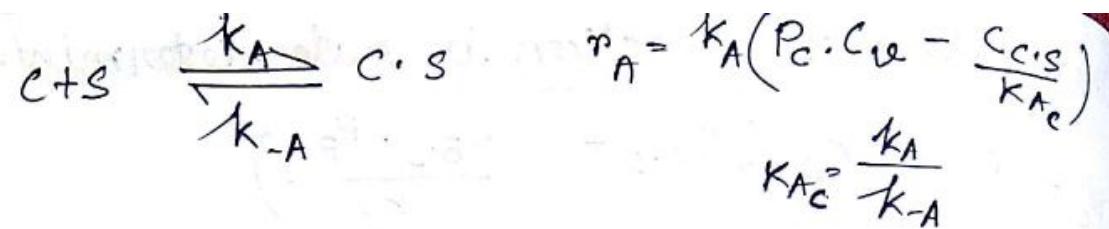
$$\Rightarrow \frac{K \left(P_c - \frac{P_B P_p}{K_p} \right)}{\left(1 + K_B P_B + \frac{K_B P_B P_p}{K_s} \right)}$$

at $t \approx 0$, $r_{c_0} = r_c$

$$r_{c_0} = K P_c \quad P_B = P_p = 0$$



⇒ This plot implies that adsorption is rate controlling step.



As surface reaction is rate determining

$$k_S \ll k_A, k_D$$

Hence

$$\frac{r_S}{k_S} \gg \frac{r_A}{k_A}, \frac{r_D}{k_D}$$

\therefore we can assume that,

$$P_C \cdot C_v = \frac{C_{C \cdot S}}{K_{AC}}$$

$$C_{C \cdot S} = K_{AC} P_C \cdot C_v$$

and $C_{B \cdot S} = K_{AB} P_B \cdot C_v$

from ①

$$n_s = k_s (K_{AC} P_c C_V - \frac{K_{AB} P_B C_V}{K_s})$$

$$= k_s (K_{AC} P_c C_V - \frac{P_p K_{AB} P_B C_V}{K_s}) \quad \dots \text{--- } ②$$

Now, from site balance,

$$C_t = C_A + C_{B,S} + C_{C,S}$$

$$= C_V + K_{AB} P_B C_V + K_{AC} P_c C_V$$

$$= C_V (1 + K_{AB} P_B + K_{AC} P_c)$$

$$C_V = \frac{C_t}{1 + K_{AB} P_B + K_{AC} P_c}$$

from ②

$$n_s = k_s (K_{AC} P_c - \frac{K_{AB} P_B P_p}{K_s}) \left[\frac{C_t}{(1 + K_{AB} P_B + K_{AC} P_c)} \right]$$

$$= k_s K_{AC} C_t \left(P_c - \frac{K_{AB} P_B P_p}{K_{AC} K_s} \right) \\ \frac{(1 + K_{AB} P_B + K_{AC} P_c)}$$

Now, $C \rightleftharpoons B + P$ for gas phase non-catalytic reaction

$$n_{S1} = k_{S1} (P_c - \frac{P_B P_p}{K_p})$$

partial pressure eqbm. const

$$K_p = \frac{K_{AC} K_s}{K_{AB}}$$

$$\gamma_D = k_D c_{c,s} \left(\frac{k_s}{P_p} - \frac{K_{AB} P_B}{P_c K_{AC}} \right)$$

$$= \frac{k_D \left(\frac{k_s}{P_p} - \frac{K_{AB} P_B}{P_c K_{AC}} \right) c_t}{\left(\frac{1}{P_c K_{AC}} + \frac{k_s}{P_p} + 1 \right)}$$

$$\gamma_D = \frac{k_D c_t (k_s P_c K_{AC} - K_{AB} P_B P_p)}{(P_p + k_s K_{AC} P_c + K_{AC} P_c P_p)}$$

$$= \frac{k_D K_{AB} \left(k_s \frac{K_{AC}}{K_{AB}} P_c - P_B P_p \right) c_t}{(P_p + k_s K_{AC} P_c + K_{AC} P_c P_p)}$$

at $t \approx 0$

$$P_p = P_B = 0 \quad P_c = P_{c_0}$$

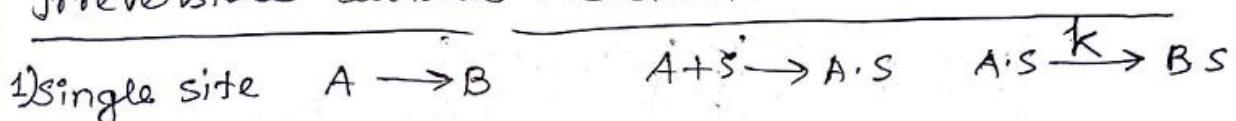
$$\gamma_{D_0} = \frac{\cancel{k_D} \cancel{K_{AB}} \cancel{k_s} \frac{K_{AC}}{\cancel{K_{AB}}} \cancel{P_{c_0}} c_t}{\cancel{k_s} \cancel{K_{AC}} \cancel{P_{c_0}}} = k_D c_t$$

03/08/17

Algorithm for determining reaction mechanism and limiting step

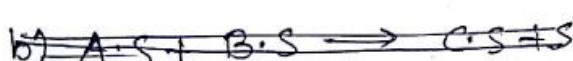
- 1) Select a mechanism
- 2) Assume a rate limiting step
- 3) Derive the rate law by following different steps associated with the mechanism and site balance.
- 4) Fit the experimental data in that predicted equation.

Irreversible surface-reaction controlled reaction:



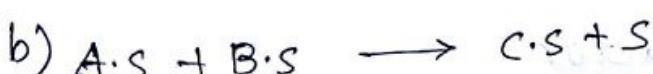
$$-\dot{r}_A = \frac{k P_A}{1 + K_A P_A + K_B P_B}$$

2) Dual site



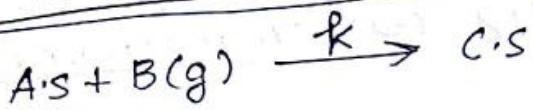
Langmuir
Hinshelwood
kinetics

$$-\dot{r}_A = \frac{k P_A}{(1 + K_A P_A + K_B P_B)^2}$$



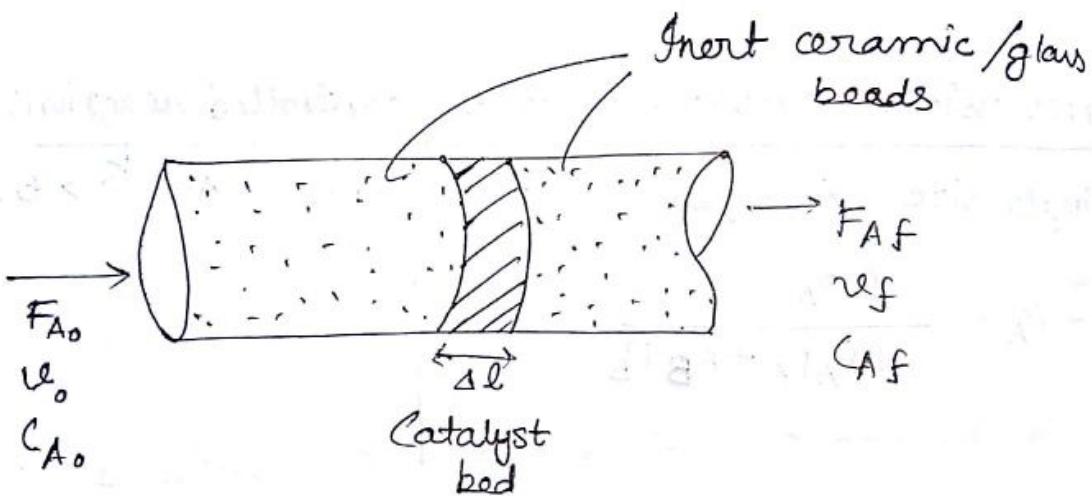
$$-\dot{r}_A = \frac{k P_A P_B}{(1 + K_A P_A + K_B P_B + K_C P_C)^2}$$

Eley - Riedel mechanism



$$-r_A = \frac{k P_A P_B}{(1 + K_A P_A + K_C P_C)}$$

Differential Reactor



- conversion in the reactant should be very low
- Heat associated with reaction is very less
- gradient less reactor; conc. gradient is very small
- isothermal reactor
- Reactant should pass through the catalyst bed
- Catalyst life should be long.

Mole balance of a differential reactor
weight of the catalyst = w

F_{A_0} = Initial molar flow rate, moles/s

F_{A_f} = Final " " " ", moles/s

r_A = rate of reaction, moles/g.cat.s

v_0, v_f = volumetric flow rate, initial, final respectively

C_{A_0} = initial conc. of reactant

C_{A_f} = final " " "

C_p = product concentration

flow in - flow out + rate of formation
= rate of generation

$$F_{A_0} - F_{A_f} + \frac{\text{rate of formation}}{w} \times w = 0$$

$$F_{A_0} - F_{A_f} + r_A \cdot w = 0$$

$$-r_A = \frac{F_{A_0} - F_{A_f}}{w} = \frac{v_0 C_{A_0} - v_f C_{A_f}}{w}$$

In terms of product conc.

$$-r_A = \frac{F_{A_0} X_A}{w} = \frac{F_p}{w} \quad X_A = \text{conversion of reactant}$$

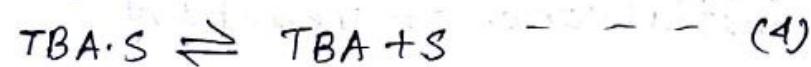
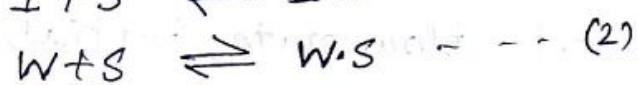
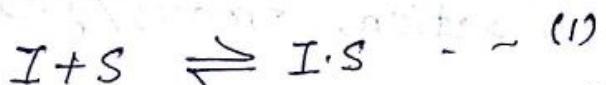
F_p = molar flow rate of product

$$-r_A = \frac{v_0 (C_{A_0} - C_{A_f})}{w} = \frac{v_0 C_p}{w}$$

$$-r_A = -r_A (C_{A_b}) = -r (C_{A_0}) \quad C_{A_b} = \frac{C_{A_0} + C_{A_f}}{2} \rightarrow C_{A_0}$$

Q11)

Tertiary butyl alcohol (TBA) was prepared produced by liquid phase hydration (w) of isobutene (I) over a solid catalyst. The reaction mechanism is believed to be



Derive a rate law assuming ~~surface step~~ adsorption
rate limiting

i) The reaction follows Eley-Rideal mechanism and rate limiting step is surface reaction

ii) Isobutene (I) and water (w) are adsorbed at different sites and TBA is not on the surface and surface reaction is order 0.

Determine the rate law.

Differential Reactor

06/08

Run No.	P _C	P _B	P _P	-r _A
Productivity In P _{in}	1	2	0.5	.
	1	1	1	1
	0.5	2	1	
Purified feed data	1	0	0	
	2	0	0	

$$-r_A = \frac{1}{V} \frac{dN_A}{dt} \rightarrow \text{homogeneous reaction}$$

$$-r_A = \frac{1}{W} \frac{dN_A}{dt} \rightarrow \text{heterogeneous reaction}$$

V = reactor volume
[in case of liquid reactant]

$$= \frac{1}{W} \frac{d(N_{A_0} X_A)}{dt}$$

W = weight of catalyst
[in case of solid]

Packed bed reactor for heterogeneous reaction

$$F_{A_0} \frac{dX_A}{dw} = -r'_A$$

Catalyst recovery is difficult in case of stirred tank reactor. For such cases specialised reactors are used.

e.g Spinning basket reactor : used for heterogeneous reaction

Berty reactor → Internal recycle
Agitator blades are coated with catalyst.
stream is used

Temperature dependence of rate law :



$$-r_A = \frac{k P_A}{1 + K_A P_A + K_B P_B}$$

Irreversible surface reaction controlled

At high temperature

$$-r_A = k P_A \quad (\text{neglecting adsorption})$$

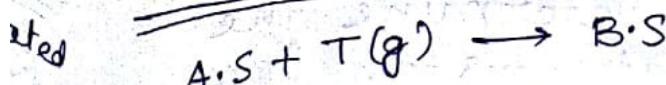
Reversible reaction surface reaction controlled

$$-r_A = \frac{k (P_A - \frac{P_B}{K_P})}{1 + K_A P_A + K_B P_B}$$

at high temp

$$-r_A = k (P_A - \frac{P_B}{K_P})$$

Evaluation of Rate law parameters



$$-r_A = \frac{k P_A P_T}{1 + K_A P_A + K_B P_B}$$

k, K_A, K_B
parameters

$$\frac{1}{-r_A} = \frac{1}{k P_A P_T} + \frac{K_A P_A}{k P_A P_T} + \frac{K_B P_B}{k P_A P_T}$$

Linearisation

$$\frac{P_A P_T}{-r_A} = \frac{1}{k} + \frac{K_A P_A}{k} + \frac{K_B P_B}{k}$$

$$-\frac{dC_A}{dt} = -r_A = k C_A^\alpha C_B^\beta$$

$$\ln \left(-\frac{dC_A}{dt} \right) = \ln k + \alpha \ln C_A + \beta \ln C_B$$

$\downarrow a_0 \quad \downarrow a_1 \quad \downarrow x_1 \quad \downarrow a_2 \quad \downarrow x_2$

$$y = a_0 + a_1 x_1 + a_2 x_2$$

$$y_j^o = a_0 + a_1 x_{1j} + a_2 x_{2j}$$

$$\sum_{j=1}^N y_j^o = a_0 + a_1 \sum_{j=1}^N x_{1j} + a_2 \sum_{j=1}^N x_{2j} \quad \dots \quad (1)$$

$$\sum_{j=1}^N x_{1j} y_j^o = a_0 \sum_{j=1}^N x_{1j} + a_1 \sum_{j=1}^N x_{1j}^2 + a_2 \sum_{j=1}^N x_{2j} x_{1j} \quad \dots \quad (2)$$

$$\sum_{j=1}^N x_{2j} y_j^o = a_0 \sum_{j=1}^N x_{2j} + a_1 \sum_{j=1}^N x_{1j} x_{2j} + a_2 \sum_{j=1}^N x_{2j}^2$$

Using least square analysis to determine the rate parameters. Determine the order, and specific rate constant from the data below for dissolution of MnO_2 in HBr. If the rate equation

$$-r_{\text{HBr}} = k C_{\text{HBr}}^\alpha$$

C_{A_0} (mol/dm ³)	0.1	0.5	1.0	2.0	4.0
$-r_{\text{A}}$ (mol HBr) $\times 10^2$	0.073	0.7	1.84	4.86	12.84

$$\ln(-r_A) = \ln k + \alpha \ln(C_{\text{HBr}})$$

$$Y_1 = a_0 + a_1 x_1$$

$$Y_1 x_1 = a_0 x_1 + a_1 x_1^2$$

N=5

Y_1	x_1	x_1^2	$Y_1 x_1$
0.073	0.1		
0.7	0.5		
1.84	1.0		
4.86	2.0		
12.84	4.0		

Deactivation of catalyst

08/08/17

1) Sintering / Aging

2) Fouling / coking

3) Poisoning

Keeping the catalyst for a long time, the active sites agglomerates and size no. of active sites decreases.

catalyst may be covered with metal from the container wall leading to decrease in active site

Change in crystal structure

Narrowing of pore at higher temperature

Sintering / Ageing

coke (carbon) may be deposited on the catalyst surface. This is called coking. catalyst is regenerated by burning the deactivated catalyst in stream of air although activity is much less compared to new one

Coking / Fouling

Some molecules / ions / species may stick to catalyst irreversibly resulting in poisoning

External diffusional mass transfer

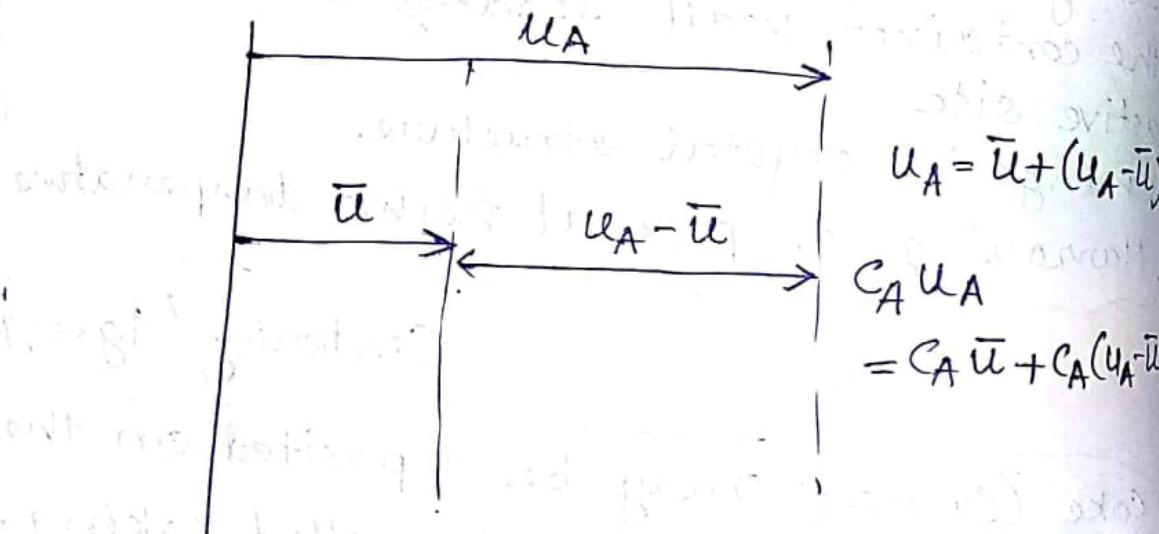
$$W_A = \vec{w}_{A_x} + \vec{w}_{A_y} + \vec{k} w_{A_z}$$

$$W_A = \frac{\text{moles}}{\text{area} \cdot \text{time}} = \text{diffusional flux}$$

$$W_A = J_A + B_A$$

Diffusional
flux

Flux due
to bulk
motion



u_A = total molar velocity of A in B

\bar{u} = average molar velocity due to bulk motion

$u_A - \bar{u}$ = Diffusional velocity of A in B

$$W_A = C_A \left(\frac{u_A C_A + u_B C_B}{C} \right) + \underbrace{c_A (u_A - \bar{u})}_{\text{Diffusional flux}}$$

$$W_A = \frac{C_A}{C} (u_A C_A + u_B C_B) + J_A$$

$$W_A = y_A (W_A + W_B) + J_A$$

Fick's 1st law of diffusion

$$J_A = - D_{AB} C \nabla y_A$$

$$\nabla = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z}$$

D_{AB} = Diffusivity of A in B, $\frac{cm^2}{s}$

$$C_A = \frac{\text{moles}}{\text{cm}^3} \text{ or } \frac{\text{moles}}{\text{dm}^3}$$

$$W_A = J_A + J_B$$

$$= - D_{AB} C \nabla y_A + C_A (u_A - u)$$

$$= - D_{AB} C \nabla y_A + \underbrace{y_A (W_A + W_B)}_{\text{bulk flux}}$$

1) Equimolar counter diffusion (EMCD)

$$W_A = - D_A C \nabla y_A$$

$$W_A = - W_B$$

$$= J_A$$

2) Dilute solution:

Bulk motion is negligible

$$W_A = J_A$$

Knudsen diffusion: When pore radii are very small and gaseous reactants are in dilute concentration.

$$W_A = J_A - D_K \nabla C_A$$

3) Diffusion through a stagnant gas

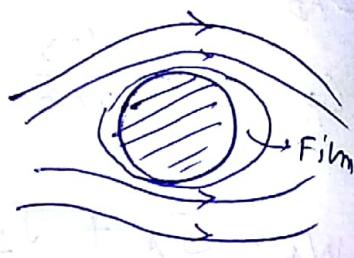
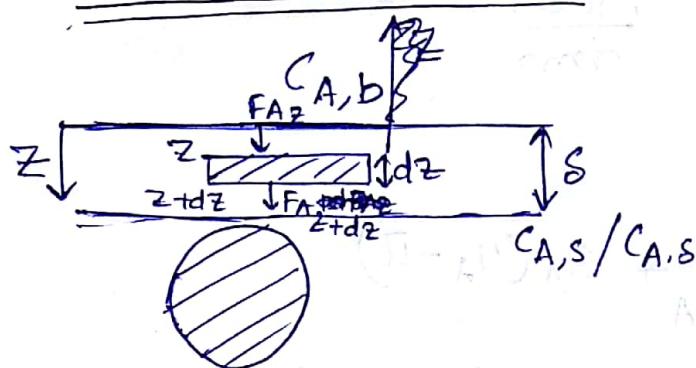
$$w_A = J_A + y_A w_A, \quad w_B = 0$$

3) Diffusion through a stagnant gas

$$W_A = J_A + \gamma_A W_A, \quad W_B = 0$$

17/08/17

Diffusion through film to the solid catalyst surface



$$C_{A,b} > C_{A,S} \text{ or } C_{A,S}$$

Boundary conditions

$$\text{When } z=0, \quad C_A = C_{AB}$$

$$z=S, \quad C_A = C_{AS}$$

Mole balance:

$$\begin{aligned} \text{rate in} - \text{rate out} + \cancel{\text{rate of formation}} &\rightarrow 0 \\ &= \cancel{\text{rate of accumulation}} \end{aligned}$$

$$F_{A,z} - F_{A,z+dz} + 0 = 0$$

$$\lim_{dz \rightarrow 0} \frac{F_{A,z} - F_{A,z+dz}}{dz} = 0$$

$$\frac{dF_{A,z}}{dz} = 0$$

If A_c is the surface area of the section dz

$$W_{A,z} = \frac{F_{A,z}}{A_c}$$

$$W_{A,z} = - D_{AB} \frac{dC_A}{dz}; \quad \text{Neglecting bulk flow}$$

$$\frac{dW_{A,z}}{dz} = - D_{AB} \frac{d^2 C_A}{dz^2}$$

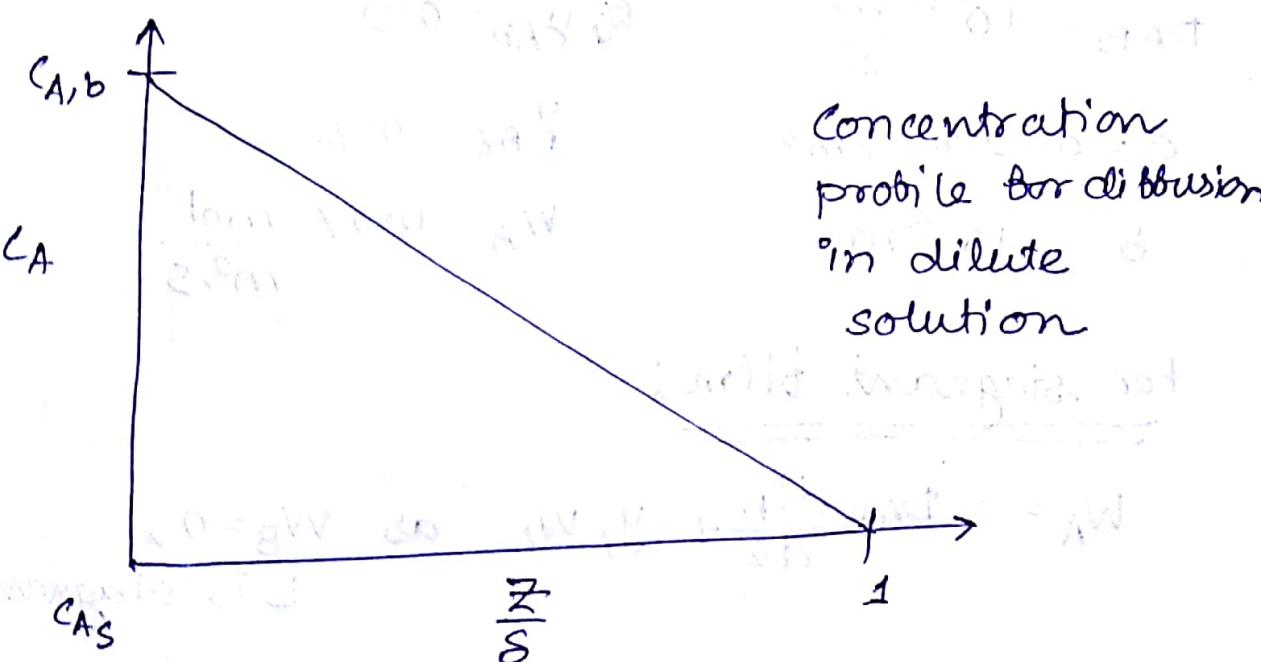
$$\frac{dC_A}{dz} = k_1 \quad C_A = k_1 z + k_2$$

$$C_{A,b} = k_2 \quad C_{A,S} = k_1 S + C_{A,b}$$

$$k_1 = \frac{C_{A,S} - C_{A,b}}{S}$$

$$C_A = \left(\frac{C_{A,S} - C_{A,b}}{S} \right) z + C_{A,b}$$

$$C_A = (C_{A,S} - C_{A,b}) \frac{z}{S} + C_{A,b}$$



Motor

EMCD \Rightarrow Equimolar counter diffusion

$$C_A = (C_{A,S} - C_{A,B}) \frac{z}{S} + C_{A,B}$$

For dilute solution and EMCD because for both the cases the expression of w_A

$$w_A = -D_{AB} \frac{dC_A}{dz}$$

$$w_A = -D_{AB} \frac{d}{dz} \left[(C_{A,S} - C_{A,B}) \frac{z}{S} + C_{A,B} \right]$$

$$w_A = -D_{AB} \frac{(C_{A,S} - C_{A,B})}{S}$$

$$w_A = D_{AB} \frac{(C_{A,B} - C_{A,S})}{S}$$

$$= D_{AB} \frac{\gamma_{A,B} - \gamma_{A,S}}{S}$$

$$D_{AB} = 10^{-6} \frac{m^2}{s} \quad \text{if } \gamma_{A,B} = 0.9$$

$$c = 0.1 \text{ mol/m}^3 \quad \gamma_{A,S} = 0.2$$

$$S = 10^{-6} \text{ m}$$

$$w_A = 0.07 \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$$

For stagnant film:

$$w_A = -D_{AB} \frac{dC_A}{dz} + \gamma_A w_A \quad \text{as } w_B = 0, \\ B \text{ is stagnant}$$

$$w_A(y_A - 1) = D_{AB} \frac{dy_A}{dz}$$

$$w_A \int_0^s = D_{AB} \cdot C \frac{dy_A}{dz}$$

$$w_A s = C D_{AB} \ln \left(\frac{y_{AS}}{y_{Ab}} \right)$$

$$w_A s = C D_{AB} \ln \left(\frac{y_{AS}-1}{y_{Ab}-1} \right)$$

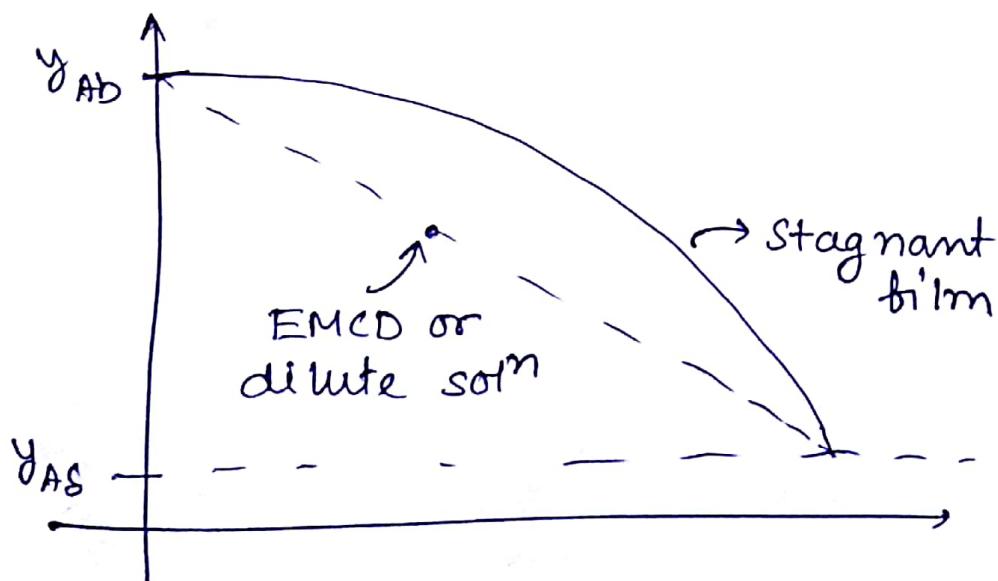
$$w_A = \frac{C D_{AB} \ln \left(\frac{y_{AS}-1}{y_{Ab}-1} \right)}{s}$$

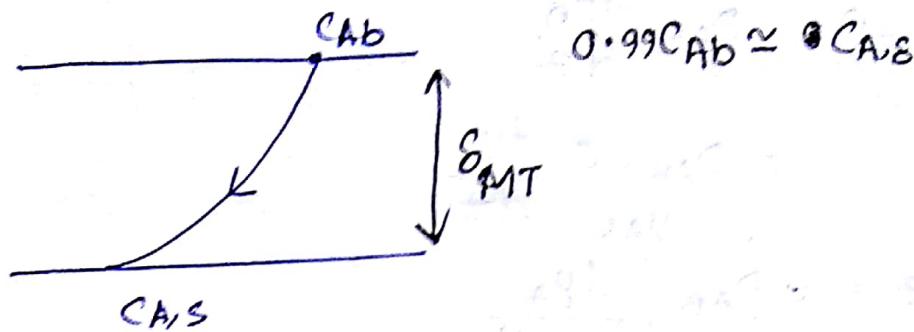
$$w_A = \frac{C D_{AB}}{s} \ln \left(\frac{1-y_{AS}}{1-y_{Ab}} \right)$$

$$w_A = \frac{0.1 \times 10^{-6}}{10^{-6}} \ln \left(\frac{0.8}{0.1} \right) = 0.208 \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$$

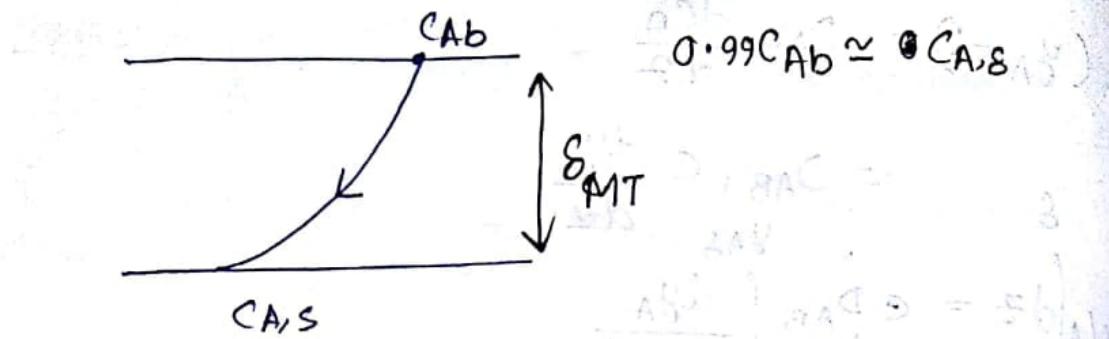
For stagnant film

$$y_A = 1 - (1-y_{Ab}) \left(\frac{1-y_{AS}}{1-y_{Ab}} \right)^{z/s}$$





$$0.99C_{AB} \approx C_{AS}$$



Mass transfer coefficient

21/08/17

For EMCP & dilute solution

$$W_A = \frac{D_{AB}}{S} (C_{Ab} - C_{A,S})$$

$$W_{A(P)} = \left(\frac{D_{AB}}{S} \right) (C_{Ab} - C_{A,S})$$

mass transfer coefficient at particular point

$$= \hat{k}_c (C_{Ab} - C_{A,S})$$

$$k_c = \frac{\int_A \hat{k}_c dA}{A}$$

$$W_A = k_c (C_{Ab} - C_{A,S})$$

For heat transfer

$$q_n = h (T_o - T_s) \quad Nu = \frac{h d}{k_t} \quad Pr = \frac{C_p \mu}{k_t} = \frac{\alpha_t}{k_t}$$

$$Pr = \frac{\gamma_t}{\alpha_t}$$

momentum diffusivity

Thermal diffusivity

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$$Nu = 2 + 0.6 Re^{1/2} Pr^{1/3}$$

For stagnant film, $Re = 0 \Rightarrow Nu = 2$

For laminar flow, $Nu = 0.6 Re^{1/2} Pr^{1/3}$

$Nu \rightarrow$ Sherwood no. (Sh)

$Pr \rightarrow$ Schmidt

$Pr \rightarrow$ ~~Prandtl~~ no. (Sc.)

$$Sh = \frac{R_c d_p}{D_{AB}}$$

$$h \rightarrow R_c$$

$$D_{AB} \rightarrow k_t$$

$$q''_z = h(T - T_s)$$

$$W_{A2} = R_c (C_{Ab} - C_{As})$$

$$Sc = \frac{\gamma}{D_{AB}} \quad D_{AB} \rightarrow \alpha_t$$

Similarly,

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \Rightarrow Frossling correlation$$

Calculate the mole flux of reactant A, through a single catalyst pellet 1cm in diameter, suspended in a large body of liquid. The reactant is present in dilute liquid. The reaction is considered to take place instantaneously at the external pellet surface. The bulk conc. of the reactant is 1M and the free system liquid velocity is 0.1 m/sec. The kinematic viscosity is 0.5 centistokes ($10^{-6} \text{ m}^2/\text{s}$) and the liquid

diffusivity of A is $10^{-10} \frac{m^2}{s}$

Soln

$$C_{AS} = 0$$

$$C_{A,b} = 1 \text{ M}$$

$$\gamma = 5 \times 10^{-7} \frac{m^2}{s}$$

$$d_p = 10^{-2} \text{ m}$$

$$V_\infty = 0.1 \text{ m/sec}$$

$$D_{AB} = 10^{-10} \frac{m^2}{s}$$

$$Sh = \frac{k_c d_p}{D_{AB}} = 2 + 0.6 Re^{1/2} Sc^{1/3}$$

$$Re = \frac{\rho V_\infty d_p}{\mu}$$

$$Sc = \frac{\gamma}{D_{AB}}$$

$$= \frac{V_\infty d_p}{\gamma}$$

$$= \frac{5 \times 10^{-7}}{10^{-10}}$$

$$= \frac{0.1 \times 10^{-2}}{5 \times 10^{-7}}$$

$$= 5000$$

$$= 2000$$

$$Sh = 2 + 0.6(2000)^{1/2}(5000)^{1/3}$$

$$\frac{k_c d_p}{D_{AB}} = 460$$

$$k_c = \frac{460 \times 10^{-10}}{10^{-2}} = 4.61 \times 10^{-6} \frac{m^3}{m^2 \cdot sec}$$

$$W_A = 4.61 \times 10^{-6} \frac{m^3}{m^2 \cdot sec} (1 - 0) \frac{\text{moles}}{L}$$

$$= 4.61 \times 10^{-6} \frac{m^3}{m^2 \cdot sec} \times 10^3 \frac{\text{moles}}{m^3}$$

$$= 4.61 \times 10^{-6} \times 10^3$$

$$= 4.61 \times 10^{-3} \frac{\text{moles}}{\text{m}^2 \cdot \text{sec.}}$$



$$-r_{AS} = \frac{k_r C_{AS}}{1 + K_A C_A + K_B C_B}$$

High temperature reaction, $T \gg k_B T$

$$K_A C_A + K_B C_B \ll 1$$

$$\Rightarrow -r_{AS} = k_r C_{AS}$$

At surface

$$w_A = r_{AS}$$



at the boundary layer,

$$w_A = k_c (C_{AB} - C_{AS})$$

$$w_A = k_c (C_{AB} - C_{AS}) = -r'_A = k_r C_{AS}$$

$$C_{AS} (k_r + k_c) = k_c C_{AB}$$

$$C_{AS} = \frac{k_c C_{AB}}{k_r + k_c}$$

$$-r'_A = \left(\frac{k_r k_c}{k_r + k_c} \right) C_{AB} = k_{eff} \cdot C_{AB}$$

\uparrow
Effective transport coefficient

Rapid reaction

$$k_r \gg k_c$$

$$\frac{k_c}{k_r} \ll 1$$

$$-r_A' = \frac{k_r k_c C_A}{k_r + k_c} = \frac{k_c C_A}{1 + \frac{k_c}{k_r}}$$

$$= k_{c,i} C_A$$

To increase rate, k_c should be increased

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}$$

For much larger value of Sc

$$Sh = 0.6 Re^{1/2} Sc^{1/3}$$

$$= 0.6 \left(\frac{dp u}{\nu} \right) \left(\frac{\nu}{D_{AB}} \right)^{1/3}$$

$$k_c = 0.6 \frac{D_{AB}}{dp} \left(\frac{dp u}{\nu} \right)^{1/2} \left(\frac{\nu}{D_{AB}} \right)^{1/3}$$

$$= 0.6 \underbrace{\left(\frac{D_{AB}^{2/3}}{\nu^{1/6}} \right)} \left(\frac{u}{dp} \right)^{1/2}$$

temperature
dependent

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Rapid reaction (Mass Transfer limited reaction)

31/08/17

$$k_r > k_c$$

$$-r_A' \approx k_c C_A$$

$k_c \rightarrow$ controlled by flow rate (u) of the reactant
 \rightarrow particle diameter

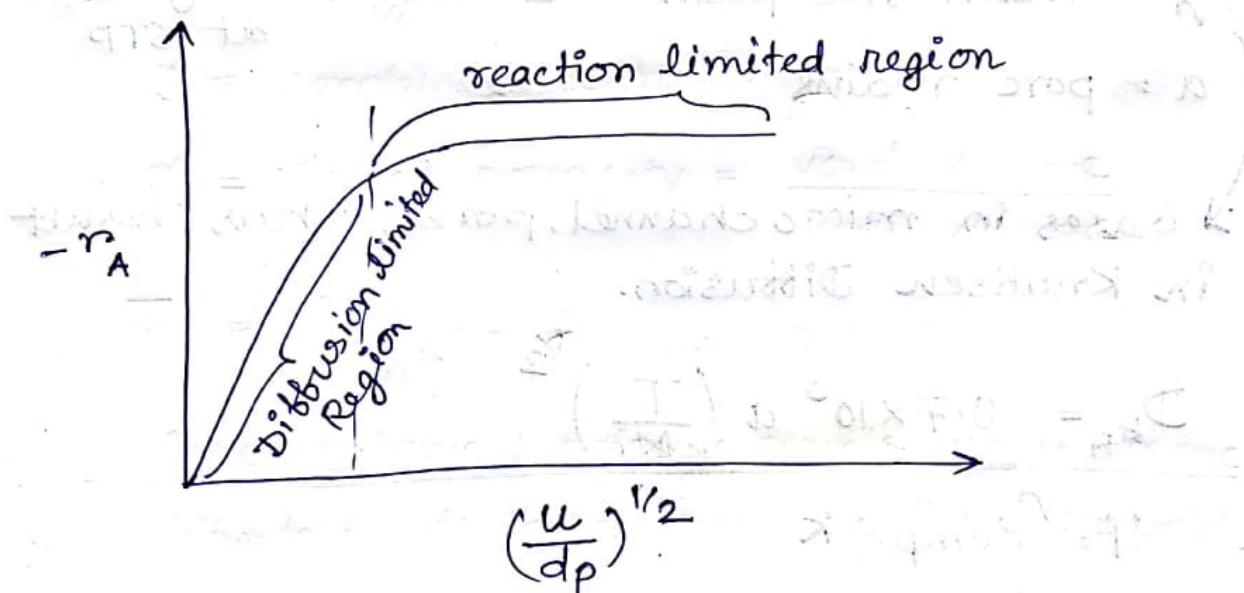
Slow reaction

$$k_r \ll k_c$$

$$-r_A' = \frac{k_r k_c C_A}{k_p + k_c} = \frac{k_r C_A}{1 + \frac{k_r}{k_c}}$$

$$\frac{k_r}{k_c} \ll 1 \Rightarrow -r_A' = k_r C_A$$

$-r_A' \rightarrow$ dependent on rate constant & concentration only



At low speed boundary layer thickness (δ_M) is significantly larger leading to diffusion limited reaction rate. On the contrary smaller δ_m results in due to high flow velocity.

→ Smaller d_p gives higher rate of r_{k^n} due to enhanced surface area.

Mass Transfer with reaction in a porous catalyst
(Internal resistance to mass transfer / pore diffusion) - al resistance

Bigger pore - bulk ~~interior~~ diffusion

Smaller pore - molecular + knudsen diffusion

bulk diffusion

- Molecular velocity (\bar{v})
- Mean free path (λ)
- D_{AB}

$$D_{AB} = \frac{1}{3} \bar{v} \lambda$$

Knudsen

- Molecular velocity (\bar{v})
- pore diameter a
- D_{KA}

$$D_{KA} = \frac{2}{3} a \bar{v}$$

\bar{v} = molecular velocity of reactant

λ = mean free path $\approx 1000 \text{ \AA}^\circ$ for gases at STP

a = pore radius

→ Gases in microchannel, pores; thus result in Knudsen Diffusion.

$$D_{KA} = 9.7 \times 10^3 a \left(\frac{T}{M_A} \right)^{1/2}$$

T = temp. K

M_A = molecular wt. of A

a = pore ~~real~~ diameter, cm

Combined diffusivity: D

$$\frac{1}{D} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}} \Rightarrow D = \frac{1}{\frac{1}{D_{AB}} + \frac{1}{D_{KA}}}$$

Effective diffusivity: D_e

Average diffusivity taking place at any position r of a spherical pellet and only radial variation in concentration is considered.

Radial flux (W_{AR}) normal to the diffusion.

Effective diffusivity considers the following:

- 1) Not all the area perpendicular in the direction of diffusion is not considered
- 2) Paths are tortuous
- 3) Varying cross sectional area of the pores

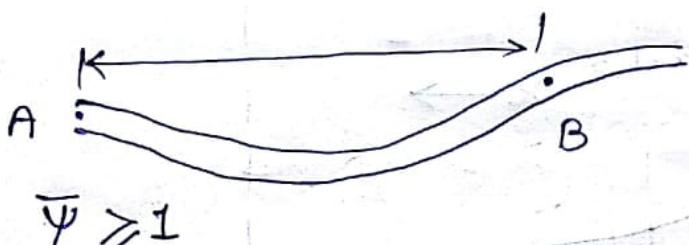
$$D_e = \frac{D \phi_p \sigma}{\bar{\psi}}$$

D = combined diffusivity

$$\phi_p = \text{Pellet porosity} = \frac{\text{void volume}}{\text{Total volume}}$$

$\bar{\psi}$ = Tortuosity

$\bar{\psi} = \frac{\text{Actual distance a molecule travels within the pore}}{\text{Shortest distance between those two points}}$



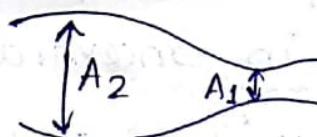
Ω = Constriction factor

≡ takes care of variation in pore area normal to the diffusion

- $\Omega = f^n$ (maximum to minimum pore area)

$$= f(\beta)$$

$$\beta = \frac{\text{Area } A_2}{\text{Area } A_1}$$



D = combined diffusivity

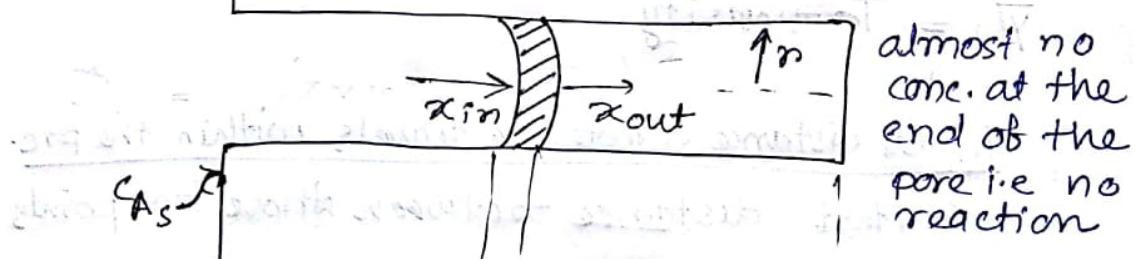
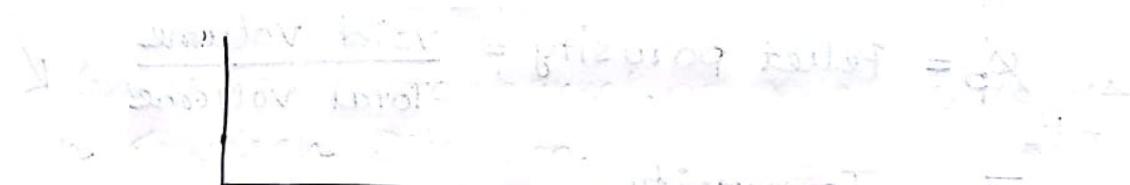
Mass Transfer with rK^n

Single cylindrical pore: 1st order reaction

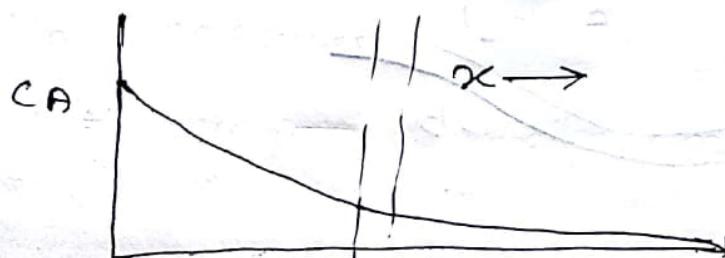


k_s = rate constant

$$N_A = \text{mole flux} = -D_{AB} \frac{dc_A}{dx}$$



almost no conc. at the end of the pore i.e. no reaction



Mole balance:

$$\text{Output} - \text{input} + \text{disappearance} = \text{accumulation}$$

$$-\pi r^2 D \left(\frac{dc_A}{dx} \right)_{\text{out}} + \pi r^2 D \left(\frac{dc_A}{dx} \right)_{\text{in}} + k_s c_A (2\pi r \Delta x) = 0$$

D = combined diffusivity

r = radius of the pore

c_A = concentration of reactant

$$D \frac{dc_A}{dx} = \text{mole flux}$$

k_s = first order rate const. based on unit surface area