

$\alpha_p = \eta k_p C_s$, whereas, rate of the reaction when no pore diffusion is acting overall rate of $\eta_s k_p C_s$.
the reaction in the catalyst-particle, when internal diffusional resistance is acting

Two sizes of the catalyst-particle are taken r_1 & r_2 for a typical reaction $A \rightarrow B$. corresponding rates of the reaction are α_{p1} & α_{p2} .

Effectiveness-factors are η_1 & η_2 and Fude modulus ϕ_s , & ϕ_{s2} .

$$\alpha_{p1} = \eta_1 k_p C_s$$

$$\phi_{s1} = \frac{r_1}{3} \sqrt{\frac{k_p f_p}{D_s}}$$

$$\alpha_{p2} = \eta_2 k_p C_s$$

$$\phi_{s2} = \frac{r_2}{3} \sqrt{\frac{k_p f_p}{D_s}}$$

$$\therefore \frac{\alpha_{p1}}{\alpha_{p2}} = \frac{\eta_1}{\eta_2} - (1)$$

$$\frac{\phi_{s1}}{\phi_{s2}} = \frac{r_1}{r_2} - (2)$$

Assume η_1 and find out the values of η_2 from 2 diff formula and equate

\Rightarrow rate of the reaction within the pores
rate of the reaction on the surface
of the catalyst.

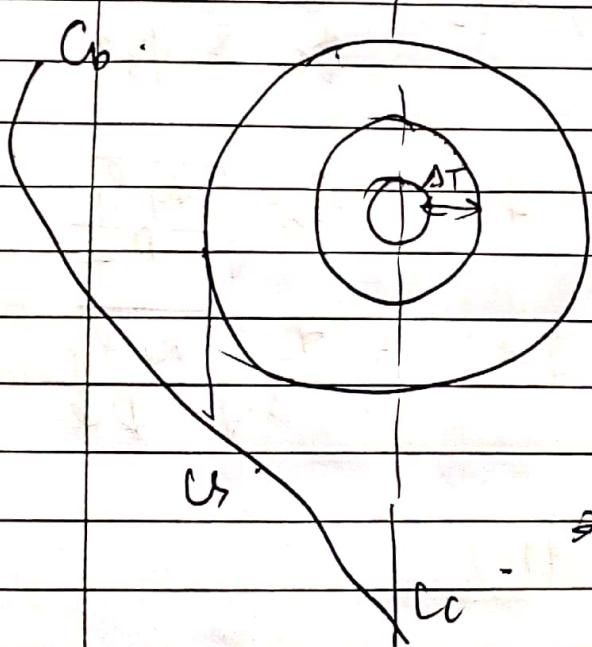
$$\Rightarrow \frac{r_p'}{r_s}$$

$$r_p' = \eta r_s' \Rightarrow \eta f(GT)$$

non-isothermal effectiveness factor

NON-ISOTHERMAL EFFECTIVENESS FACTOR

(per mass transfer).



$$\left(-4\pi r^2 D_e \frac{dc}{dr} \right)_r - \left(4\pi r^2 D_e \frac{dc}{dr} \right)_{r+\Delta r}$$

$$= 4\pi r^2 \Delta r \rho_p k_p C$$

$$\Rightarrow \frac{dc}{dr^2} + \frac{2}{r} \frac{dc}{dr} - \frac{k_p \rho C}{D_e} = 0$$

ρ_p = density of the catalyst particle

$\rho_p k_p C$ = rate per unit vol.

D_e = effective diffusivity

$4\pi r^2 \Delta r$ = volume of the differential element Δr .

For heat transfer, energy balance

$$\left(4\pi r^2 k_e \frac{dT}{dr} \right)_s - \left(-4\pi r^2 k_e \frac{dT}{dr} \right)_{r+Δr}$$

$$\rightarrow 4\pi r^2 \Delta r \rho c \Delta H$$

k_e = effective thermal diffusivity

ΔH = heat of int rxn.

taking limit $\Delta r \rightarrow 0$, k_e is not dependent on temp, and dividing both sides with $4\pi \Delta r k_e$,

$$\boxed{\frac{d^2T}{dr^2} + \frac{2}{r} \frac{dT}{dr} - \frac{k_e \rho c}{k_2} \Delta H = 0}$$

Boundary conditions

① $\frac{dc}{dr} = 0$ at $r=0$ &

$$c = g \text{ at } r = r_s$$

② $\frac{dT}{dr} = 0$ at $r=0$ &

$$T = T_s \text{ at } r = r_s$$

$$k_1 \ell_p c = D_e \left(\frac{d^2 c}{dr^2} + \frac{2}{r} \frac{dc}{dr} \right) - 1 \textcircled{a}$$

$$k_1 \ell_p c = \frac{k_e}{\Delta H} \left(\frac{d^2 T}{dr^2} + \frac{2}{r} \frac{dT}{dr} \right) - 2 \textcircled{a}$$

Comparing ① @ 2 ② @ 1

$$D_e \left(\frac{d^2 c}{dr^2} + \frac{2}{r} \frac{dc}{dr} \right) = \frac{k_e}{\Delta H} \left(\frac{d^2 T}{dr^2} + \frac{2}{r} \frac{dT}{dr} \right)$$

Integrating, putting boundary conditions,

$$(T - T_s) = \frac{\Delta H D_e}{K_e} (C - C_s)$$

Dankohlen eqⁿ

For max heat change, $C = 0$

reaction is very fast, so the reactants are depleted as soon as they reach the surface of the pellet

$$T_c - T_s = - \frac{\Delta H D_e}{K_e} \cdot C_s$$

$$3 (\phi)_s = n_s \sqrt{\frac{(k_1)_s \ell_p}{D_e}}$$

ϕ_s determined
at surface
temperature

$(k_1)_s$ = reaction rate constant at T_s

②

Arrhenius eqn

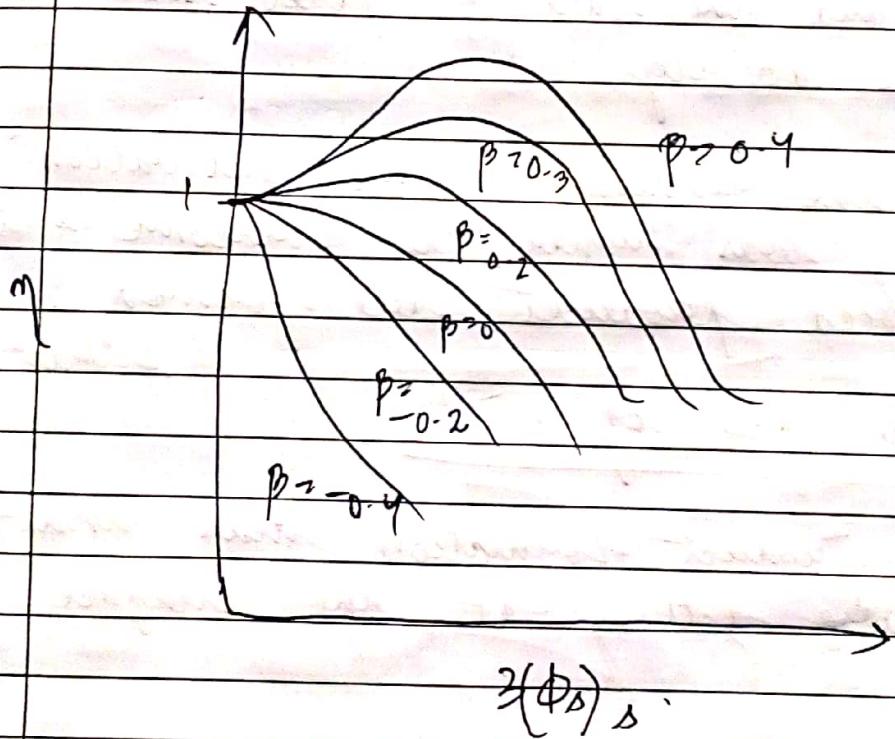
$$\gamma = \frac{E}{RgT}$$

$Rg \rightarrow$ gas constant
 $E \rightarrow$ activation energy

③

Heat of reaction parameter

$$\beta = \frac{(-\Delta H)D_L G}{K_C T_S}$$



$\beta > 0 \rightarrow$ Isothermal rxn

$\beta > 0 \rightarrow$ Exothermic "

$\beta < 0 \rightarrow$ Endothermic rxn

The heat buildup on the surface of the catalyst pellet is much less than the heat buildup inside the catalyst pellet

This is because the heat buildup on the surface is dissipated due to the flow of gas outside.

Different temperatures are diff. pts. used in catalyst; highest temp. at the core.

Disadvantages of $\eta > 1$

- ① Due to temp. buildup, the active sites melt and the catalyst pellet loses its sintered catalytic activity.
- ② Some side reaction, whose activation energy was higher, is overcome and undesired products are formed.

Advantages of $\eta > 1$ (selectivity)

- ① More product formation than what we are getting at the surface.

For endothermic rxn, kinetically controlled

11
Solid Catalyst : JM Smith

Assumptions of Langmuir Adsorption Isotherm

all the active sites exchange uniformly towards the adsorption of reactant molecules and the nature of the complex formed are same, no interaction b/w 2 adjacent adsorbed complexes, monomolecular layer mechanism of adsorption formation of complex is same for all

$$\begin{aligned}r_A &= k_1 P (1-\theta) \\r_D &= k_2 \theta\end{aligned}$$

At eq, $r_A = r_D$.

$$k_1 P (1-\theta) = k_2 \theta$$

$$k_1 P = \theta (k_2 + k_1 P)$$

$$K = \frac{k_1}{k_2} = \text{adsorp. const.}$$

$$\theta = \frac{k_1 P}{k_2 + k_1 P} = \frac{K P}{1 + K P} \rightarrow \frac{V}{V_m}$$

V = vol of adsorbed $\xrightarrow{\text{reactant}}$ at any time

V_m = monomolecular vol of the adsorbed gas.

d_p = diameter of catalyst particle,

External surface area / vol.

$$= \frac{\pi d_p^2}{\pi d_p^3/6} = 6/d_p$$

If particle density is ρ_p , the surface area per unit of particle

$$S_g = \frac{6}{\rho_p d_p}$$

8/10/19

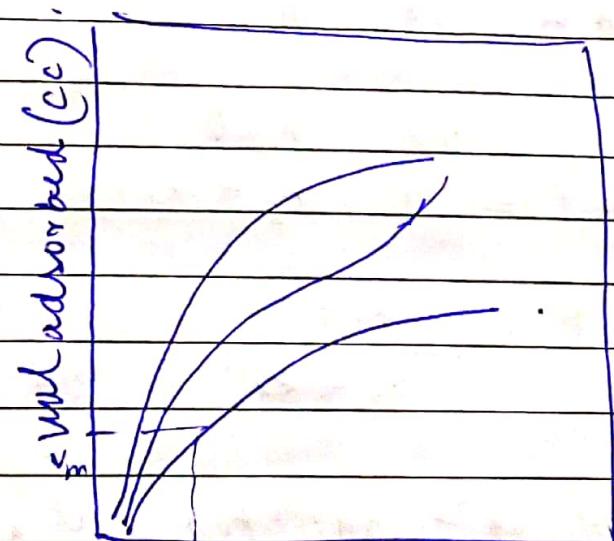
Physical adsorption means that the gas molecules are adsorbed all over the surface.

↓

This is the whole surface area.

This does not give an account of the number of active sites on the catalyst-surface.

He is used \rightarrow std non-adsorbable gas.



He - N₂
mixture



diff. partial
pressures of N₂.

pressure
partial pressure.

at lower pressure, we can catch the monomolecular volume.

Langmuir - Isotherm eqⁿ.

$$\frac{KP}{1+KP} = \frac{V}{V_m}$$

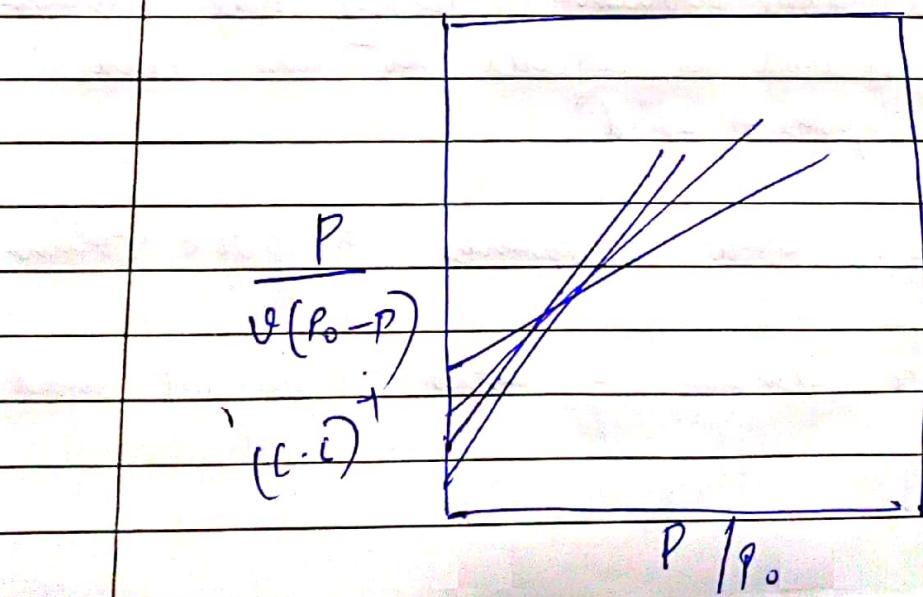
$$\frac{1}{KP} + 1 \rightarrow \frac{V_m}{V}$$

$$\Rightarrow \frac{P}{V} = \frac{1}{KV_m} + \frac{P}{V_m}$$

BET equation for multilayer adsorption

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{C V_m P_0}$$

P_0 = saturation vapour pressure of the gas
 C = constant at a particular temperature and gas - solid system



$$\text{Intercept - I} \rightarrow \frac{1}{V_m \cdot C}$$

$$\text{Slope S} \rightarrow \frac{C-1}{V_m C}$$

$$V_m \rightarrow \frac{1}{I+S}$$

a = area of a molecule

↓ projected area

$$S_g = \left(\frac{V_m N_A}{V} \right) a$$

N_A = Avogadro number

= No. of molecules / mole

V = volume per mole = 22400 cc/mol

V_m = volume per molecule

$$\alpha = 1.09 \left[\frac{M}{N_A P} \right]^{2/3}$$

ρ = density of the molecule

How to determine the pore volume?

a) Dip the catalyst-pellet inside the He container. He easily occupies the pore volume. The volume of He displaced is equal to the solid volume.

b) Dip the catalyst-pellet inside Hg container. Hg has high surface tension, and does not fill up the pore volume. Hence the volume of Hg displaced is equal to the total volume (pore + solid).

The difference b/w 2 volumes = pore volume

To calculate density of solid, neglect mass of air

Determination of pore volume and solid density by He-Hg method - 11

void fraction or porosity

$\epsilon_p = \frac{\text{void (pore) volume of particle}}{\text{total volume of the particle}}$

$$\rightarrow \frac{m_p V_g}{m_p V_g + \frac{m_p}{\rho_s}}$$

$$\rightarrow \frac{V_g}{V_g + \frac{1}{\rho_s}}$$

$$\rightarrow \frac{V_g}{V_g + \frac{1}{\rho_s}} = \frac{V_g \rho_s}{V_g \rho_s + 1}$$

$\rho_s = \text{solid density}$ -

11/10/19
6.4

Bidispersed pellet

micro pores ($< 200 \text{ \AA}$) \rightarrow pores inside the particles
macro pores ($> 100 \text{ \AA}$) \rightarrow pores between the particles
silica gel \rightarrow non-porous catalyst
(mono dispersed - pellet - system)

pellets of aluminum is bimodispersed
pore system

(Q) In our experiment - to determine the pore volume and catalyst particle porosity, following data are obtained:

mass of catalyst sample $\rightarrow 101.5 \text{ gm}$

vol. of He displaced $\rightarrow 45.1 \text{ cc}$

vol. of Hg displaced $\rightarrow 82.7 \text{ cc}$

Calculate required properties

$$\text{pore volume} \rightarrow \frac{82.7 - 45.1}{101.5 \text{ gm}} = 0.37 \text{ cc/gm}$$

$$E_p \rightarrow \frac{82.7 - 45.1}{82.7} \rightarrow 0.45$$

Problem: A catalyst - (cylindrical) has

mass $= 3.15 \text{ gm}$

dia $= 1''$

Thickness $= 0.25''$

vol $= 3.22 \text{ cm}^3$

The particles contained micropores and pelleting process introduced macropores. From experiment—
vol of pellet = $0.645 \text{ cc/gm of pellet}$
" " " = $0.4 \text{ cc/gm of pellet}$

^{micropore}
Calculate A. Density of pellet
B. Macropore void fraction of pellet

C. Micropore

D. Solid fraction

E. Density of particle

F. Density of solid phase

G. Void fraction of particle and pellet

$$A. \text{ Density of pellet} = \frac{3.15}{3.22} \rightarrow 0.978 \text{ gm/cc}$$

$$B. \text{ Macropore void fraction of pellet} \rightarrow 0.2$$

$$\frac{0.645}{3.22} \rightarrow 0.2$$

$$C. \text{ Micropore void fraction} \rightarrow \frac{0.4 \times 3.15}{3.22} \rightarrow 0.39$$

$$D. \text{ Solid fraction} \rightarrow 1 - 0.2 - 0.39 = 0.4087$$

$$E. \text{ Density of solid phase} \rightarrow \frac{3.15}{3.22 \times 0.4087}$$

$$\rightarrow 2.39 \text{ gm/cc}$$

$$\rightarrow 1.21 \text{ gm/cc}$$

$$F. \text{ Density of particle} \rightarrow \frac{3.15}{3.22 \times (1 - 0.2)} \rightarrow 0.4 \text{ gm/cc}$$

$$G. \text{ Void fraction of particle} \rightarrow \frac{0.4 \times 3.15}{3.22 - 0.645} \rightarrow 0.789$$

2/10/19

~~SSS~~ Vapor pressure of N_2 \propto pore radius

Volume of N_2 desorbed \propto v.p. of N_2

\therefore Vol. of N_2 desorbed \propto pore radius

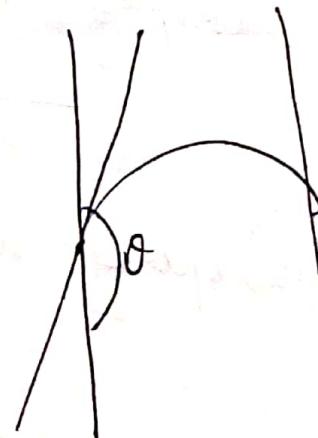
The volume of the larger pores is measured by the Hg method (because Hg is a heavy metal, and cannot enter inside the smaller pores). The volume of the smaller pores is done by

N_2 desorption method

For Hg penetration method,

Equating applied force and force due to surface tension

$$\pi a^2 p = 2 \pi a \sigma \cos \theta$$
$$\Rightarrow a = \frac{2 \sigma \cos \theta}{p}$$



σ \Rightarrow surface tension

a \Rightarrow radius of pore A

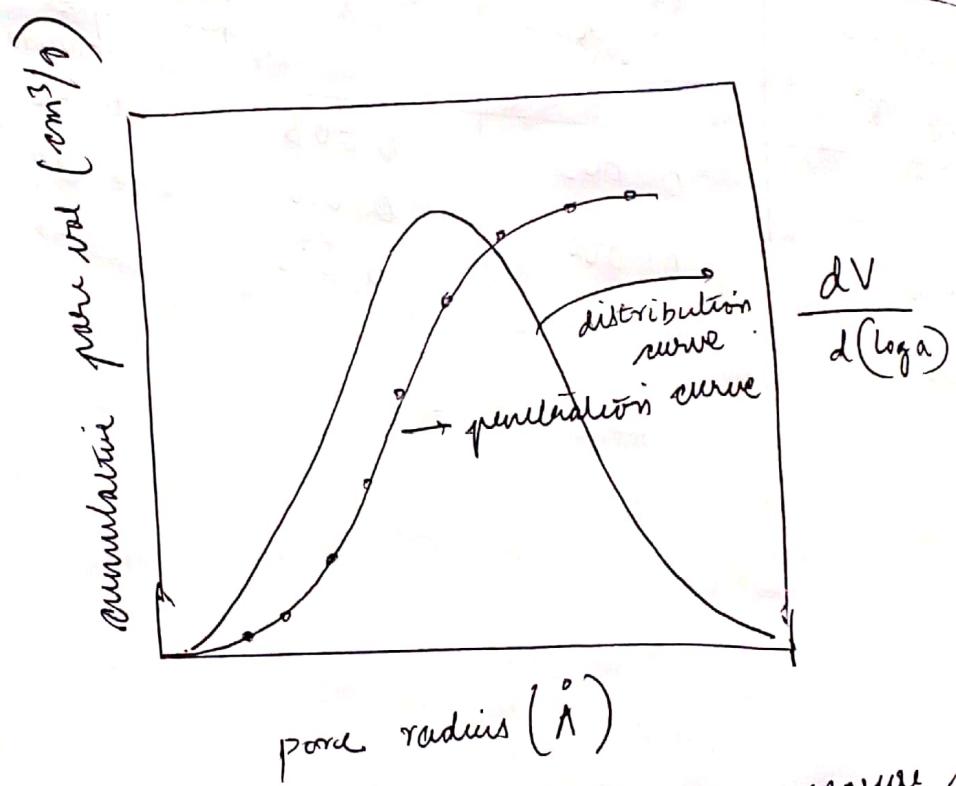
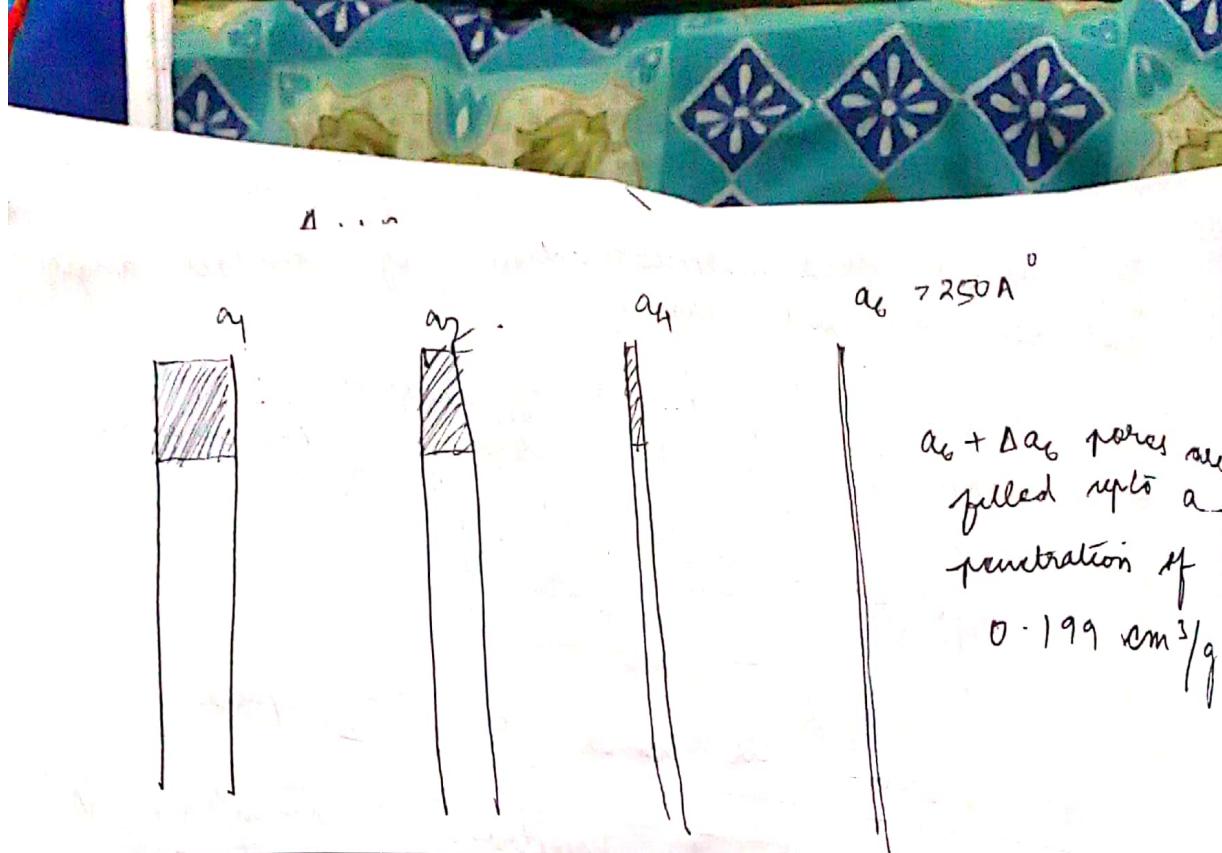
θ \Rightarrow contact angle between the Hg and the pore wall.

140° is a good approximation of contact angle between Hg and ceramic. ↓
 material of catalyst is known for Hg - ceramic combination.

$$a(A^\circ) \rightarrow \frac{8.75 \times 10^5}{P(\text{psi})}$$

Hg : proximate data of VO_2 pellet

Pressure lb/in ²	Hg conc m ³	Penetration (vol. of Hg going cm ³ /g inside pore)	$\Delta V(\text{cm}^3)$ Cumulative pore volume (w.r.t. lowest pore radius)	$a(1^\circ)$
116	0.002	0.003	0.196	7543.1
310	0.006	0.010	0.189	2822.58
344	0.010	0.016	0.183	2543.6
1				
1				
1				
1				
1				
1				
1				
1900	0.122	0.196	0.003 (0.199 - 0.196)	460.53
2320	0.124	0.198	0.001 (0.199 - 0.197)	377.
3500	0.125	0.199	0	250.



High pressure Hg porosimeter can measure pore vol of pore size $> 100 \text{ \AA}$. $P_0 = 1 \text{ atm} - \text{pa of Hg}$

Nitrogen desorption $< 100 \text{ \AA}$

higher pressure \rightarrow liq N_2 enters thin Hg film
 $\text{at } \frac{P}{P_0} \rightarrow 1$, all the small pores get filled up with liq N_2 .

22/11/11

C.S

$$\alpha - \gamma = - \frac{2 \sigma V_1 \cos \theta}{RT \ln(P/P_0)}$$

V_1 = molal volume of condensed liquid

σ = surface tension

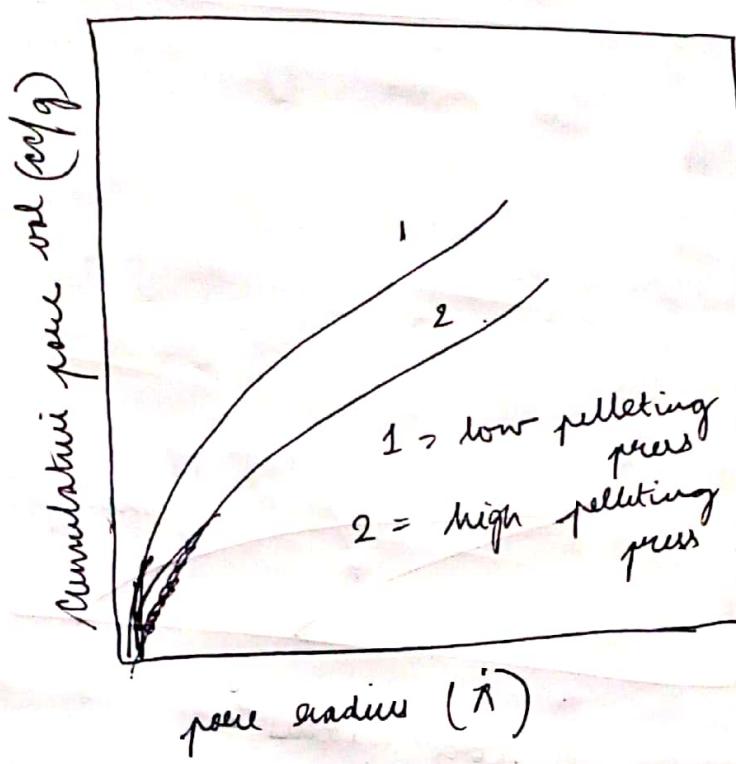
θ = contact angle between the solid and liquid.

S \rightarrow thickness of N_2 (liq) adsorbed on the ext. surface of catalyst.

$$S(\text{Å}) = 9.52 \left(\log \frac{P_0}{P} \right)^{-\frac{1}{n}}$$

$$\alpha - \gamma \rightarrow 9.52 \left(\log \frac{P_0}{P} \right)^{-1}$$

More the pelleting pressure less the macropore volume



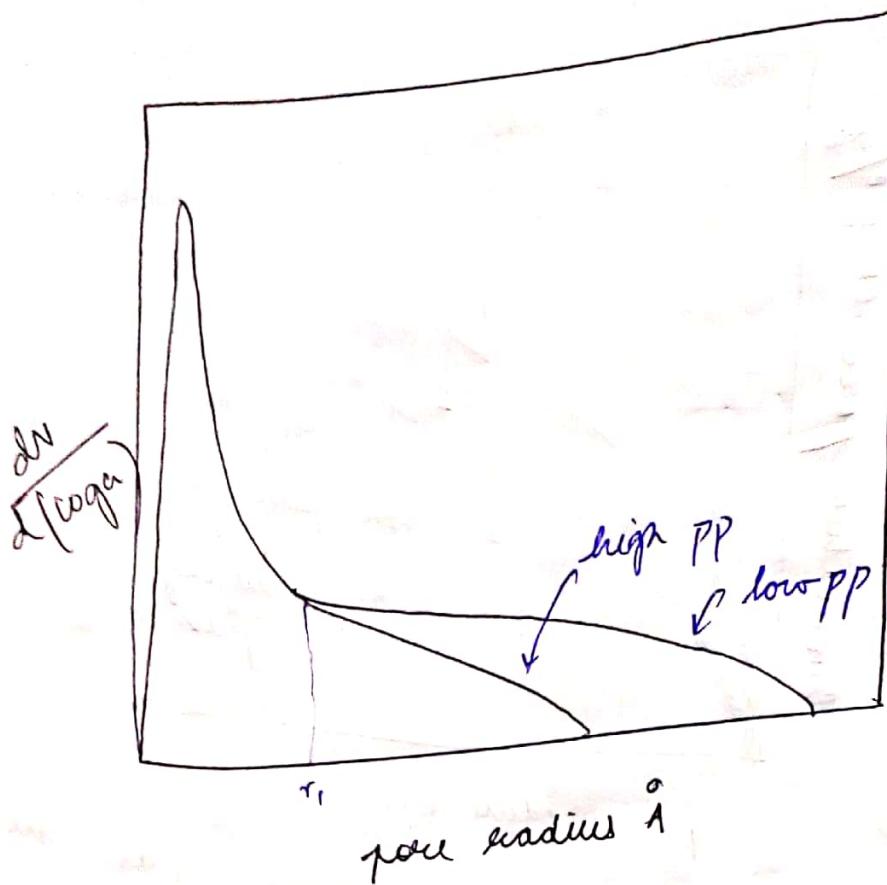
The change in pelleting pressure has no effect on micropore, but considerable effect on macropore.

larger cumulative vol

Micro pore is the inherent property of a catalyst pellet, hence pelleting pressure has no effect on the penetration of N_2 inside micropores. Hence, there is no difference in the penetration due to change in pelleting pressure.

$A + bB \rightarrow C$
 $PP \rightarrow$ filtering pressure

5. M'



Wheeler's Parallel Pore Model (the pores are assumed to be cylindrical)

$$m_p S_g = (2\pi \bar{a} \bar{L}) n \quad \text{--- (1)}$$

$$m_p V_g = (\pi \bar{a}^2 \bar{L}) n \quad \text{--- (2)}$$

m_p = mass of the particle.

S_g = $\frac{\text{pore}}{\text{surface area of particles}} / \text{unit mass}$

V_g = $\frac{\text{pore}}{\text{volume of the particle}} / \text{unit mass}$

\bar{a} = avg. pore radius

\bar{L} = avg. length of pores

n = no. of pores

$$\bar{a} = \frac{2V_g}{S_g}$$

2 samples of silica-alumina cracking catalyst have particle densities of 1.12 g/cc and 0.962 g/cc. The true density of the solid material in each case is 2.37 g/cc. The surface area of the 1st sample is 467 m²/g and 2nd sample is 372 m²/g. Which sample has the larger mean pore radius and determine the mean pore radius in each case.

Take basis = 1 g of sample

$$= \text{mp} \cdot (467) \rightarrow (2\pi \bar{a}_1 \bar{L}_1)^{-n_1}$$

$$= \text{mp} \cdot (372) \rightarrow (2\pi \bar{a}_2 \bar{L}_2)^{-n_2}$$

$$1 \cdot V_g = \pi \bar{a}^2 \bar{L} \cdot n$$

$$10^4 \times 467 \rightarrow \frac{2}{\bar{a}}$$

$$\frac{1}{\bar{L}_1} \rightarrow \frac{1}{1.126} \text{ cc/g}$$

$$\frac{1}{\bar{L}_2} \rightarrow \frac{1}{0.962} \text{ cc/g}$$

$$\rightarrow 1.04 \text{ cc/g.}$$

$$\bar{a}_1 = \frac{2V_g}{467} \rightarrow \frac{2 \times 0.888}{467 \times 10^4}$$

$$\rightarrow \frac{0.004}{800000} \text{ cm} \times 10^{-4} \rightarrow 0.04 \times 10^{-4}$$

$$\rightarrow \frac{0.04}{38030} \times 10^{-4} \rightarrow 10^{-4} \text{ cm} \rightarrow 38.03 \text{ Å}$$

$$\bar{a}_2 = \frac{2 \times 1.04}{372} \rightarrow 0.0056 \text{ cm}$$

$$\rightarrow 0.056 \text{ m} \rightarrow \underline{56} \text{ Å}$$

$$\text{Q. } \begin{array}{l} 0.888 \text{ cc/g} \\ 1.04 \text{ cc/g} \end{array}$$

$$\begin{array}{l} 0.422 \text{ cc/g} \\ 0.466 \end{array} \left. \begin{array}{l} 0.466 \\ 0.618 \end{array} \right\}$$

Assumption: The mass of air is neglected.

$$\bar{a}_1 = \frac{2 \times 0.466}{467 \times 10^4} \Rightarrow 20 \times 10^{-10} \text{ m} \\ \Rightarrow 20 \text{ \AA}$$

$$\bar{a}_2 = \frac{2 \times 0.618}{372 \times 10^4} \Rightarrow 33.23 \text{ \AA}$$

Q. True density of solid material in an saturated alumina particle is 3.67 gm/cc. The density of the particle determined by mercury displacement is 1.547 gm/cc. The surface area by adsorption measurement is 175 m²/gm. From this info, find the pore vol/gm, porosity of the particles and mean pore radius.

$$\rho_s = 3.67 \text{ gm/cc}$$

The bulk density of bed of alumina particles in a 250 cc graduate is 0.81 gm/cc. what fraction of the total volume of the bed is

void space for the particles and what fraction is void space within the particles?

$$S_g \Rightarrow 175 \text{ m}^2/\text{gm}$$

$$V_g \Rightarrow \frac{1}{1.547} = \frac{1}{3.67} = 0.374 \text{ cc/gm}$$

$$\frac{mp S_g}{mp V_g} = \frac{(2\pi \bar{a}^2 l)^n}{(\pi \bar{a}^2 l)^n}$$

$$\frac{S_g}{V_g} = \frac{(2\pi \bar{a}^2 l)^n}{(\pi \bar{a}^2 l)^n}$$

$$\frac{S_g}{V_g} = \frac{2}{\bar{a}}$$

$$\frac{175 \times 10^4}{0.374} = \frac{2}{\bar{a}}$$

$$\Rightarrow \bar{a} \Rightarrow \frac{2 \times 0.374}{175 \times 10^4} = 4.2743 \times 10^{-7} \text{ cm} \\ \Rightarrow 42.743 \text{ \AA}$$

$$\text{Porosity} = \frac{0.374}{\frac{1}{1.547}} = 0.578$$

$$\delta_{\text{bed}} = 0.81 \text{ gm/cc}$$

$$V_{\text{bed}} \Rightarrow 250 \text{ cc}$$

$$\text{mass}_{\text{bed}} = 250 \times 0.81 = 202.5 \text{ gm}$$

Q: An 8.01 gm ^{sample} of silica gel is studied with N_2 absorption at $-195.8^\circ C$. The following data are obtained.

Pressure (mm Hg)	6	25	140	230	285
Volume adsorbed (cm ³) (at 0°C and 1 atm)	61	127	170	197	215

Estimate the surface area of catalyst (cm²/gm)

$$P_0 = 1 \text{ atm} = 760 \text{ mm Hg}$$

$P_0 - P$	754	735	620	530	475
$\frac{P}{V(P_0 - P)}$	1.3×10^{-4}	2.67×10^{-4}	1.32×10^{-3}	2.2×10^{-3}	2.71×10^{-3}
$\frac{P}{P_0}$	7.89×10^{-3}	0.033	0.187	0.303	0.375

$$\frac{P}{V(P_0 - P)}^2 = \frac{1}{V_m C} + \frac{(C-1)P}{C V_m P_0}$$

$$\frac{C-1}{C V_m} \Rightarrow \frac{28-8}{350-100} \Rightarrow \frac{20}{250} \Rightarrow \frac{4}{50} \frac{28}{100}$$

$$0.7 \times 10^{-4} \Rightarrow \frac{1}{V_m C} \Rightarrow 0.08 \times 10^{-4} \Rightarrow 0.008$$

$$0.8 \times 10^{-2} \Rightarrow \frac{C-1}{C V_m} \Rightarrow C-1 = \frac{800}{7}$$

$$\Rightarrow C = \frac{800}{7} + 1 = \frac{87}{7}$$

$$V_m \rightarrow \frac{1}{0.7 \times 10^{-9} \times 115.28} \\ \rightarrow \frac{10^9}{0.7 \times 115.28} = 123.9$$

$$\alpha = 1.09 \left[\frac{28}{6.023 \times 10^{23} \times 0.808} \right]^{4/3}$$

$$\rightarrow 1.09 \times 3.211 \times 10^{-15.33} \times 10^{-0.39-15} \\ \rightarrow 1.637 \times 10^{-15}$$

$$sg \rightarrow \alpha \left[\frac{N_0 V_m}{V} \right] \rightarrow \frac{1.637 \times 10^{-15} \times 6.023 \times 10^{23} \times 123.9}{22400}$$

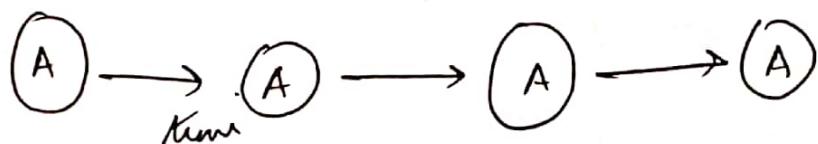
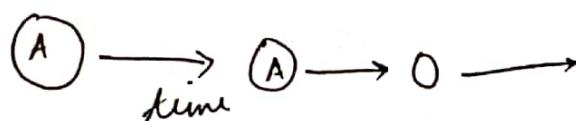
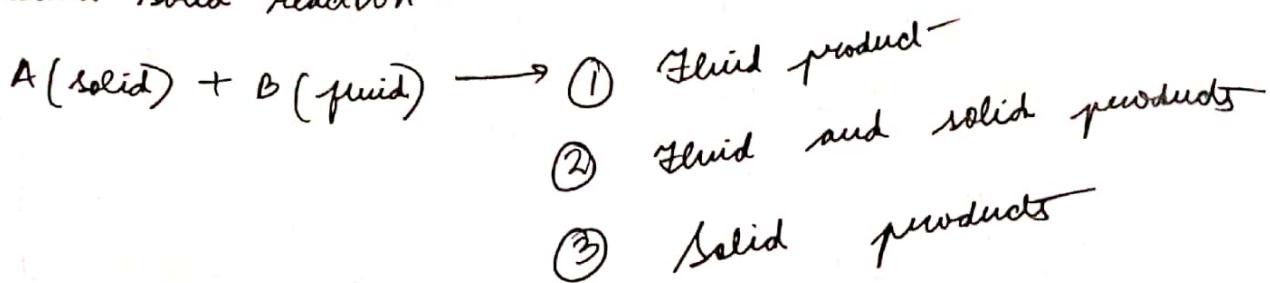
$$\rightarrow 0.05454 \times 10^8 \rightarrow 8.01 \text{ gm} \\ \rightarrow 5.454 \times 10^6 \text{ gm}^2 \rightarrow 8.01 \text{ gm} \\ \rightarrow 5.454 \times 10^2 \text{ m}^2 \rightarrow 8.01 \text{ gm}$$

~~$$sg \rightarrow \frac{68.08 \text{ m}^2 \text{ gm}}{22400}$$~~

$$sg \text{ gm} \rightarrow \frac{22400}{139} \rightarrow 161.15$$

Non catalytic heterogeneous reaction

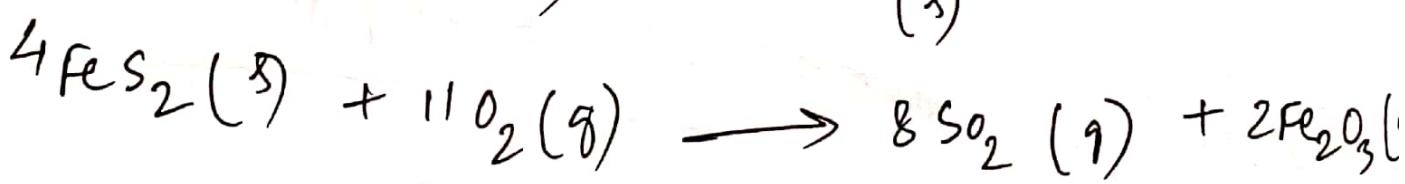
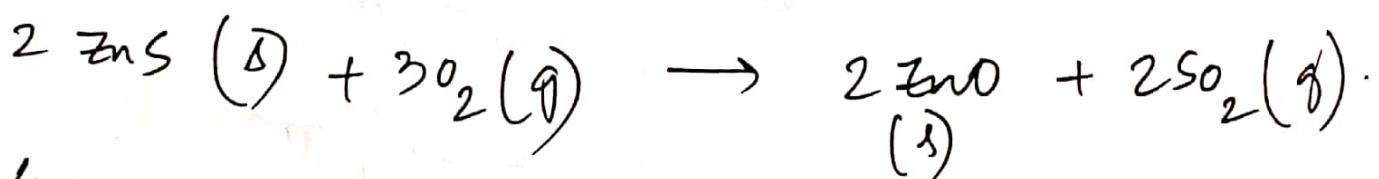
Fluid solid reaction



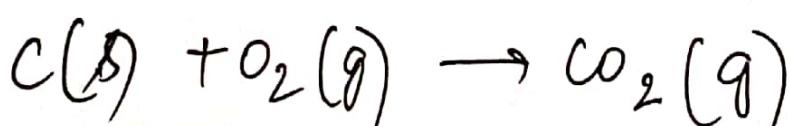
Formed (not plating) product which adheres to the surface of the reactant \rightarrow unchanged volume of the solid material

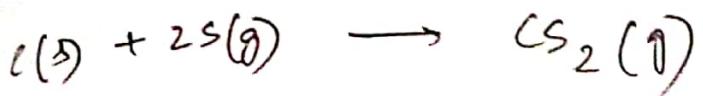
e.g. roasting of ZnS (e.g. FeS_2 , ZnS)

↓
conversion of sulphide to oxide



Changing vol of solid





Model Selection:

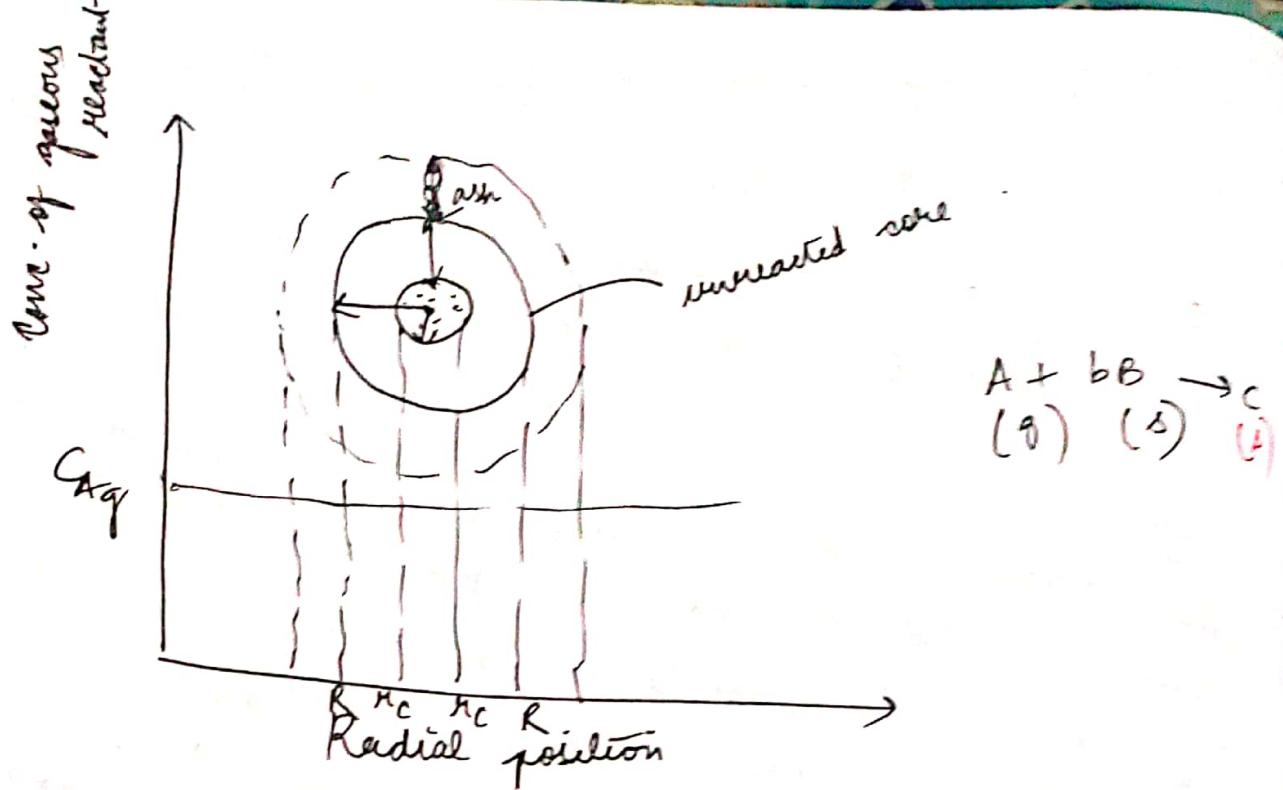
Progressive conversion model

- ① Unreacted core model

- Steps:
- The gaseous reactant B makes a film around the sphere, and B molecules have to overcome the diffusional resistance of their own film to reach the surface of the solid (A) ash layer.
- ② Penetration and diffusion of the gaseous reactant through the blanket of ash to the surface of the unreacted core.
- ③ Chemical reaction b/w A & B.
- ④ Diffusion of the gaseous product through the ash layer to the exterior surface of the solid.
- ⑤ Diffusion of the gaseous product through the gas film back to mean bulk fluid.

RATE CONTROLLING STEPS

- ① Gas - Film controlled



C_{Ag} (conc. of A on the surface of unreacted core) = 0.

No diffusional resistance in the ash layer

$$C_{Ag} = C_{AC} = 0 \quad S \rightarrow \text{surface of solid}$$

S_{ex} = External surface area of the unchanging particle



$$dN_B = b dN_A$$

$$\Rightarrow -\frac{1}{S_{ex}} \frac{dN_B}{dt} = -\frac{1}{4\pi R^2} \frac{dN_B}{dt}$$

$$\Rightarrow -\frac{b}{4\pi R^2} \frac{dN_A}{dt}$$

at equilibrium,
rate of $\text{exn} \Rightarrow$ rate of mass transfer

$$-\frac{b}{4\pi R^2} \frac{dN_A}{dt} \Rightarrow b \text{ kg} (\text{Cag} - \text{Cas})$$

$$\Rightarrow b \text{ kg Cag}$$

ρ_B = molar density of B in the solid B

V = volume of the solid B

Then, the moles of B present in solid B
= $N_B = \rho_B V$

$$\begin{aligned} -dN_B &= -b dN_A \\ &= \rho_B dV = -\rho_B d \left(\frac{4}{3} \pi r_c^3 \right) \\ &= -4\pi \rho_B r_c^2 dr_c. \end{aligned}$$

Now

$$-\frac{1}{\text{Sec}} \frac{dN_B}{dt}$$

$$\Rightarrow -\frac{1}{4\pi R^2} \rho_B r_c^2 \frac{dr_c}{dt}$$

$$\Rightarrow -\rho_B \frac{r_c^2}{R^2} \frac{dr_c}{dt} \Rightarrow b \text{ kg Cag}$$

$$\Rightarrow -\frac{\rho_B}{R^2} \left\{ \int_R^{r_c} r_c^2 dr_c \right\} \Rightarrow b \text{ kg Cag dt}$$

$$\Rightarrow -\frac{\rho_B}{R^2} \left(\frac{r_c^3}{3} - \frac{R^3}{3} \right) \Rightarrow b \text{ kg Cag dt}$$

$$t = \frac{l_B R}{3 b \text{ kg Cag}} \left[1 - \left(\frac{r_c}{R} \right)^3 \right]$$

for complete conversion, $r_c = 0$

Time required for complete conv -

$$\boxed{t = \frac{l_B R}{3 b \text{ kg Cag}}}$$

$$\frac{t}{\tau} = 1 - \left(\frac{r_c}{R} \right)^3$$

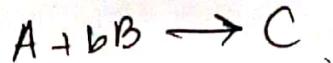
$1 - x_B = \frac{\text{volume of unreacted core}}{\text{total volume of the particle}}$

$$\Rightarrow \frac{\frac{4}{3} \pi r_c^3}{\frac{4}{3} \pi R^3} = \left(\frac{r_c}{R} \right)^3$$

$$x_B = 1 - \left(\frac{r_c}{R} \right)^3 = \frac{t}{\tau} \Rightarrow \boxed{x_B = \frac{t}{\tau}}$$

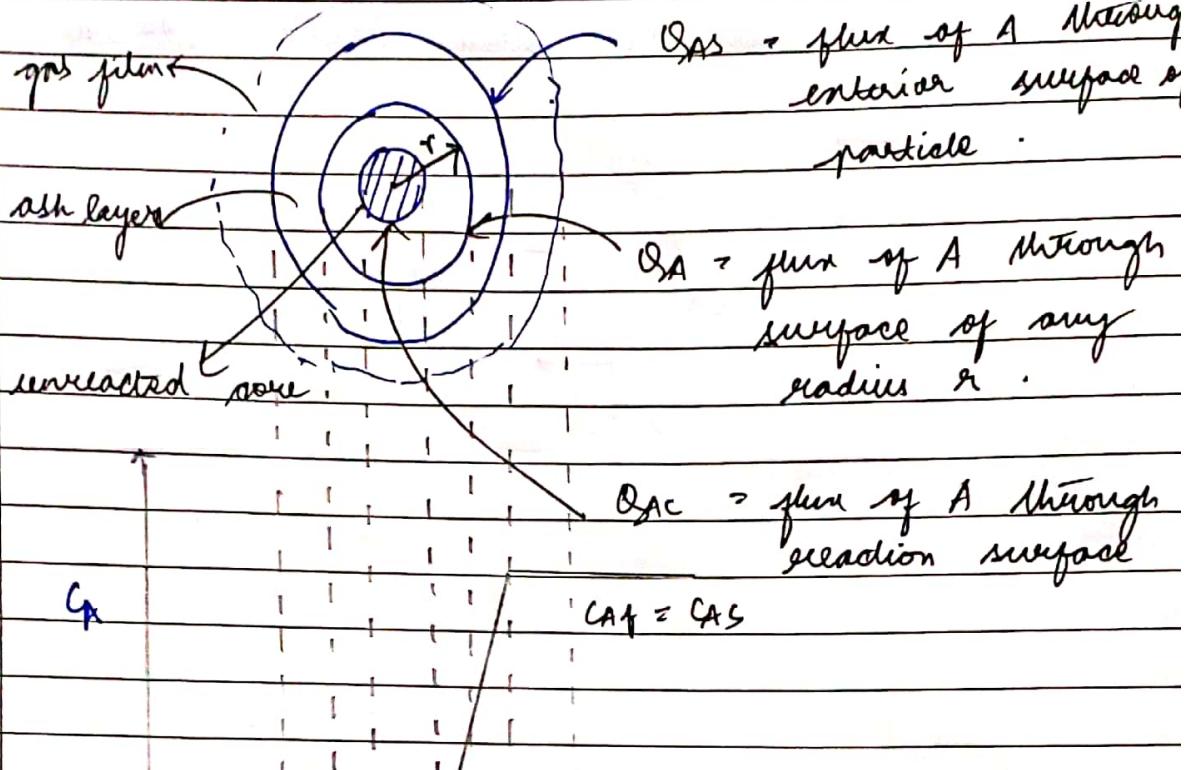
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Fractional conversion

04/11/19



UNREFACTED CORE MODEL

(ash layer controls)



At a particular instant, the volume of unreacted core is assumed to

$$R \approx r_c \approx R$$

Rate of reaction on the unreacted core = Rate of mass transfer through the ash layer

$$\text{Assuming } -\frac{dN_A}{dt} = 4\pi r^2 Q_A = 4\pi r^2 Q_{AS} = 4\pi r^2 C_A S$$

Consider Fick's law (equimolar counter diffusion)

A & C are in same stoichiometry

$$Q_A = D_c \frac{dC_A}{dr}$$

$$-\frac{dN_A}{dt} = 4\pi r^2 D_c \frac{dC_A}{dr}$$

Integrating R to r_c ,

$$-\frac{dN_A}{dt} \cdot \left(\frac{1}{R} - \frac{1}{r_c} \right) = 4\pi D_c \quad \left. \begin{array}{l} CAC = 0 \\ CAG \rightarrow CAS \end{array} \right\}$$

$$\Rightarrow -\frac{dN_A}{dt} \cdot \left(\frac{1}{r_c} - \frac{1}{R} \right) \rightarrow 4\pi D_c \ CAG$$

$$-b dN_A = -4\pi \rho_B r_c^2 dr_c$$

$$-\frac{dN_A}{r_c} = -\frac{4\pi \rho_B}{b} r_c^2 dr_c$$
$$-\rho_B \int_{r_c=R}^t \left(\frac{1}{r_c} - \frac{1}{R} \right) r_c^2 dr_c = b D_c CAG \int_0^t dt$$

$$t = \frac{\rho_B R^2}{6 b D_c CAG} \left[1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \right]$$

Time required for total conversion $r_c = 0$

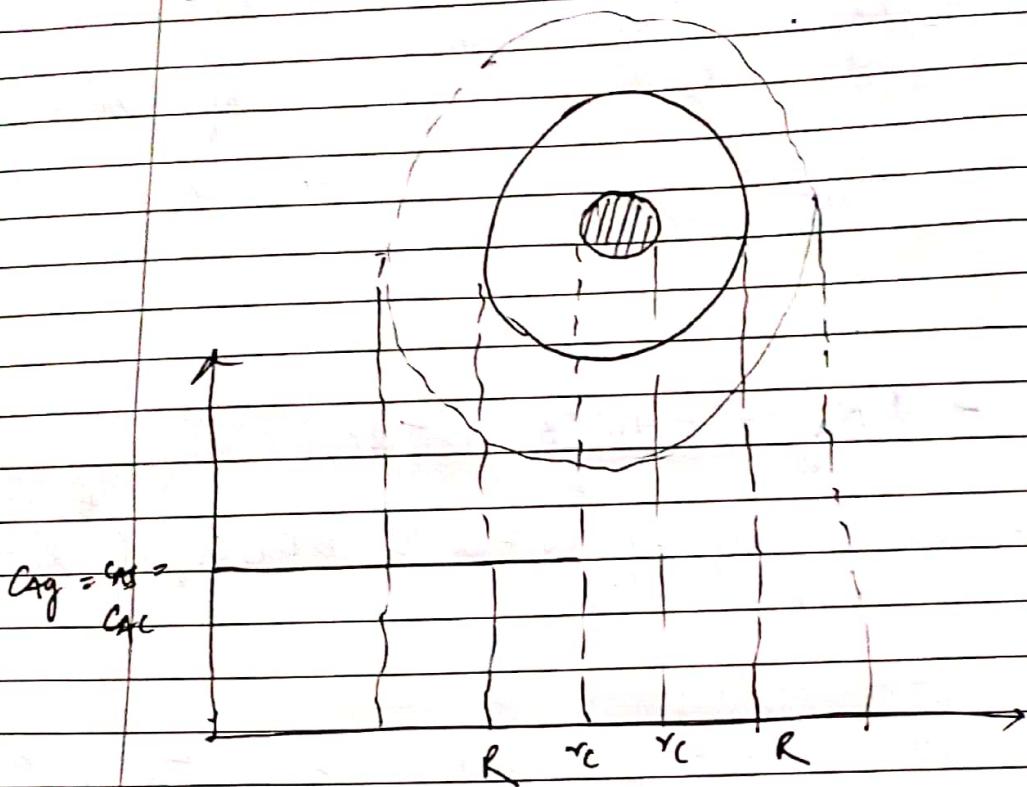
$$\gamma = \frac{\rho_B R^2}{6 b D_c CAG}$$

In terms of fractional conversion of B, x_B

$$\frac{t}{\gamma} = 1 - 3(1-x_B)^{2/3} + 2(1-x_B)$$

$$\frac{t}{\gamma} = 1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3$$

Chemical Reaction Controlled



$$\frac{C_{ag}}{C_{AC}} =$$

$$-\frac{1}{4\pi r_c^2} \frac{dN_B}{dt} \rightarrow -\frac{b}{4\pi r_c^2} \frac{dN_A}{dt} \rightarrow bK_s C_{ag}$$

K_s = 1st order rate controlled.

$$-\frac{1}{4\pi r_c^2} \ell_B 4\pi r_c^2 \frac{dr_c}{dt} = -\ell_B \frac{dr_c}{dt} = bK_s C_{ag}$$

$$\Rightarrow -\ell_B \left\{ dr_c \right\}_{R}^{r_c} = bK_s C_{ag} \left\{ dt \right\}_{0}^{t}$$

$$t = \frac{\ell_B}{bK_s C_{ag}} (R - r_c)$$

time required for complete conversion $x_c = 0$.

$$\tau = \frac{C_B R}{b k_F C_A}$$

Fraction conversion x_B

$$\frac{t}{\tau} \rightarrow 1 - \frac{r_c}{R} \rightarrow 1 - (1 - x_B)^{1/3}$$

SHRINKING CORE MODEL

$$\frac{dV}{dt}$$

$$Sh = 2 + 0.6 (R_e)^{1/2} (S_c)^{1/3}$$

and you know R_e ,

$$Sh = 2$$

y_f, y_f = mole fraction of A in the bulk.

$$\frac{k_F dP y_f}{D_0} = 2, \quad k_F = \frac{2 D e}{d P y_f} = \frac{D}{R y_f}$$

$$dN_B \rightarrow C_B dV = 4\pi C_B R^2 dR$$

$$\Rightarrow -\frac{1}{S_{ex}} \frac{dN_B}{dt} = -\frac{C_B 4\pi R^2}{4\pi R^2} \frac{dR}{dt} \Rightarrow -\frac{C_B dR}{dt} = -b k_F C_A$$

Stokes Regime: $Re < 1$ $A + bB \rightarrow C$

$$Ro \rightarrow R$$

$$dN_B = f_B dV = 4\pi f_B R^2 dR$$

$$- \frac{1}{S_{ex}} \frac{dN_B}{dt} = - f_B \frac{4\pi R^2}{4\pi R^2} \frac{dR}{dt}$$
$$= - f_B \frac{dR}{dt} = b kg \text{ Cag}$$

$$Sh = 2$$

$$\frac{kg dy}{D} = 2$$
$$kg = \frac{2De}{dy} = \frac{D}{Ry}$$

$$\int_{Ro}^R R dR = - \frac{b Cag D e}{f_B y} \int_{-}^{+} dt$$

$$\tau = \frac{t \cdot \gamma \cdot R_0}{2 \cdot \gamma \cdot \rho \cdot e}$$

time required for complete conversion

$$\frac{t}{\tau} \Rightarrow 1 - \left(\frac{R}{R_0} \right)^2 = 1 - (1 - x_0)^2$$

Limitations of Shrinking Core Model

Chp 25

Fluid-
particle
reaction
kinetics

Both the models (S.C model and P.R model) found to be operating simultaneously (experimental)

② Because of the presence of the nth layer

Q. A batch of solids of uniform size is treated by gas in a uniform environment. Solid is converted to give a non-flaking powder according to S.C model. Conversion = $7/8$ in reaction time = 1 hr. = 1 min. What mechanism is rate controlling?

CHEMICAL
RXN. CONTROLLED

$$\tau = 2$$

$$x_0 = 7/8$$

$$t = 1$$

$$\frac{t}{\tau} = 1 - (1 - x_0)$$

$$= 1 - \left(1 - \frac{7}{8}\right)$$

$$\Rightarrow 1 - \frac{1}{8} = \frac{7}{8}$$

Gas film controlled : $\frac{1}{t} = \frac{1}{k_f} (1 - \frac{x_0}{x})^{\frac{1}{2}}$

$$\Rightarrow 1 - \frac{x_0}{x} = \left(\frac{1}{k_f t}\right)^2$$

$$= 1 - \frac{1}{64} = \frac{63}{64} \neq \frac{1}{4}$$

Ash Layer controlled : $\frac{1}{t} = 1 - 3 \left(1 - \frac{x_0}{x}\right)^{1/3} + 2 \left(1 - \frac{x_0}{x}\right)$

$$= 1 - 3 \left(\frac{1}{4}\right)^{1/3} + 2 \cdot \frac{1}{4}$$

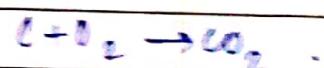
$$= 1 - \frac{3}{4} + \frac{1}{2}$$

$$= \frac{1}{2}$$

Both the ash layer and the chemical reaction are found to be rate controlling.

0-08 Rev
 Calculate the time needed to burn to completion particles of graphite ($l_0 = 5 \text{ mm}$, $\rho_B = 2.2 \text{ g/cc}$, $k' = 20 \text{ cm}^2/\text{s}$) in an 8% O_2 stream for the high gas velocity and, assume that film diffusion does not offer any resistance to transfer & $T_{burn} = 900^\circ\text{C}$.

$$l_0 = \frac{2.2}{12} = 0.1833 \text{ mmole/cc}$$



Chemical non-controlled :

$$PV = RT$$

$$\gamma = \frac{P_B R}{b k_B T_B} \Rightarrow \frac{0.1833 \times 5 \times 10^{-3}}{1.92 \frac{\text{N}}{\text{mole} \text{K}}} \text{ Pa} = \frac{P}{\rho} = \frac{RT}{M}$$

$$= 1000 \text{ Pa} \quad \frac{273}{273 + 900} \text{ K} = 0.29 \text{ Pa}$$

