

## 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

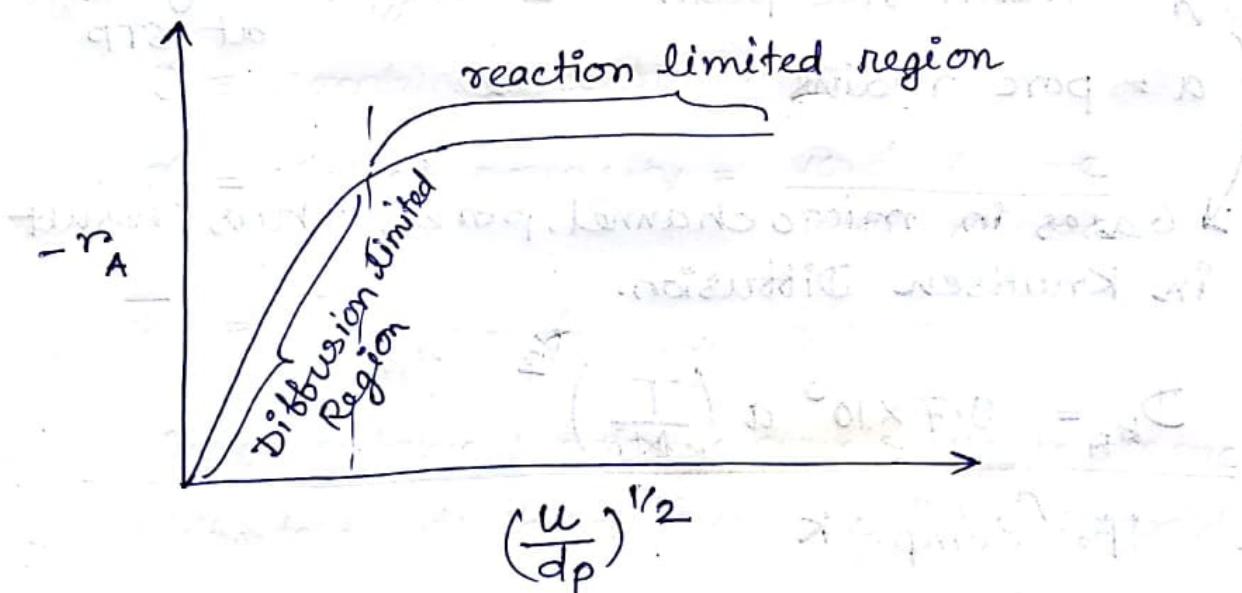
## Slow reaction

$$k_r \ll k_c$$

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

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

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



At low speed boundary layer thickness ( $\delta_M$ ) is significantly larger leading to diffusion limited reaction rate. On the contrary smaller  $\delta_M$  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 ( $\lambda$ )
- $D_{AB}$

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

Knudsen

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

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

$\bar{v}$  = molecular velocity of reactant

$\lambda$  = 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

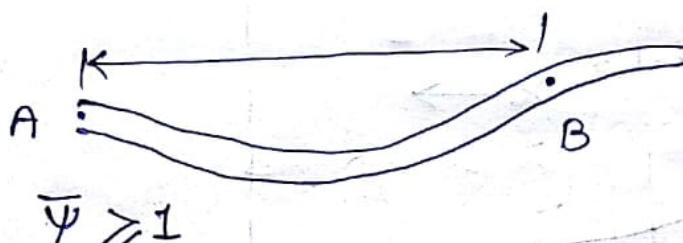
$$D_e = \frac{D \phi_p \sigma}{\bar{\psi}}$$

$D$  = combined diffusivity

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

$\bar{\psi}$  = Tortuosity

Actual distance a molecule travels within the pore  
Shortest distance between those two points



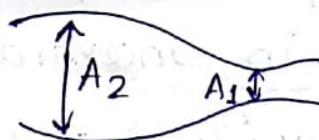
$\Omega$  = Constriction factor

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

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

$$\Omega = f(\beta)$$

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



$D$  = combined diffusivity

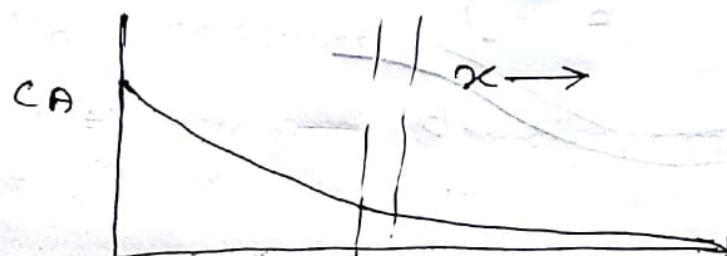
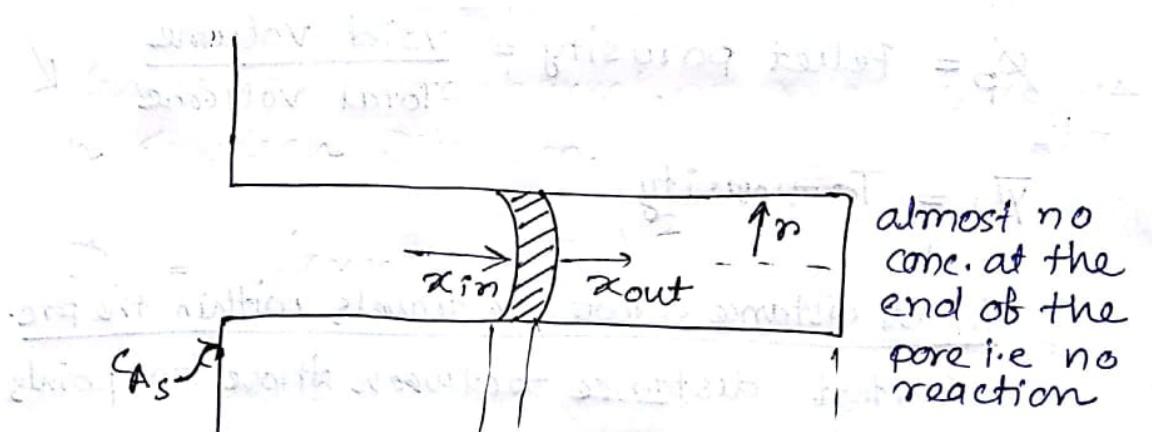
Mass Transfer with  $r k^n$

Single cylindrical pore: 1<sup>st</sup> order reaction



$k_s$  = rate constant

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



## Mole balance:

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

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

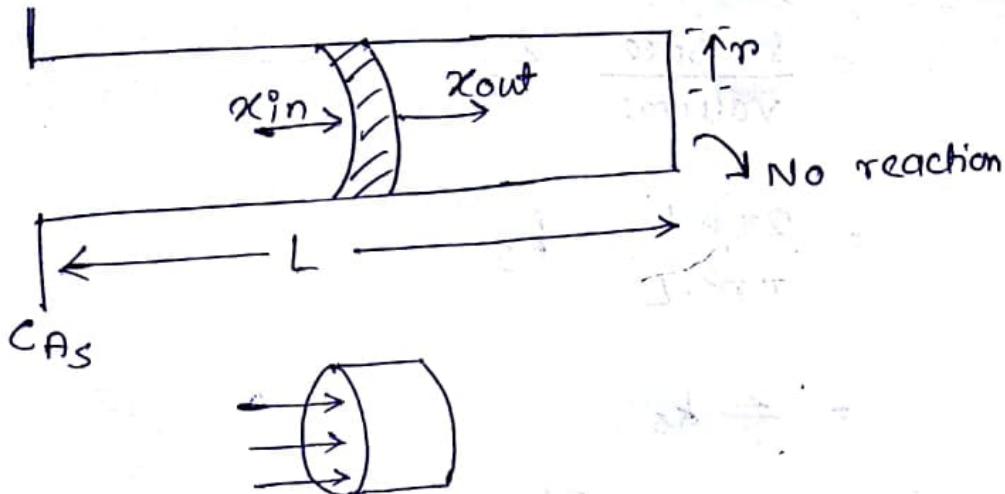
$D$  = combined diffusivity

$r$  = radius of the pore

$c_A$  = concentration of reactant

$D \frac{dc_A}{dx}$  = Mole flux

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



Pore diffusion: Flat plate geometry, single cylindrical pore, 1<sup>st</sup> order reaction

Mole balance,  
output - input + disappearance = - accumulation

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

Dividing both sides with  $\pi r^2 D \Delta x$

$$\frac{\left( \frac{dC_A}{dx} \right)_{\text{out}} - \left( \frac{dC_A}{dx} \right)_{\text{in}}}{\Delta x} = \frac{2 k_s}{D r} (A=0)$$

taking,  $\Delta x \rightarrow 0$

$$\frac{d^2 C_A}{dx^2} = \frac{2 k_s}{D r} (A=0)$$

$$k_s \cdot s = k \cdot v$$

$k$  = rate const. per unit vol.

$$k = \frac{s}{v} k_s$$

$$k = \frac{S}{V} k_s$$

$$= \frac{\text{surface}}{\text{volume}} k_s$$

$$= \frac{2\pi r \cdot L}{\pi r^2 \cdot L} k_s$$

$$= \frac{2}{r} k_s$$

Replacing  $\frac{2k_s}{r}$  by  $k$

$$\frac{d^2 C_A}{dx^2} - \frac{k C_A}{D} = 0$$

Solving the above equation by taking auxiliary equation, the solution is

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

Where  $M_1$  &  $M_2$  are the constant

Boundary conditions:

$$\text{when } x=0, \quad C_A = C_{AS}$$

$$\text{when } x=L, \quad \frac{dC_A}{dx} = 0$$

$$m = \sqrt{\frac{k}{D}} = \sqrt{\frac{2k_s}{r \cdot D}}$$

$$\left. \frac{dC_A}{dx} \right|_{x=L} = M_1 m e^{mL} - M_2 e^{-mL} = 0$$

$$M_1 m e^{mL} - M_2 e^{-mL} = 0$$

$$\frac{M_1}{M_2} \neq \quad M_1 e^{mL} - M_2 e^{-mL} = 0$$

$$\text{at } x=0; C_A = C_{AS}$$

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

$$\frac{M_2}{M_1} = e^{2mL} \quad | \quad C_{AS} = M_1 (1 + e^{2mL})$$

$$M_1 = \frac{C_{AS}}{(1 + e^{2mL})} \quad M_2 = \frac{C_{AS} e^{2mL}}{(1 + e^{2mL})}$$

$$C_A = M_1 \frac{C_{AS}}{(1 + e^{2mL})} e^{mx} + \frac{C_{AS} e^{2mL}}{(1 + e^{2mL})} e^{-mx}$$

$$\frac{C_A}{C_{AS}} = \left[ \frac{e^{mx} + e^{2mL-mx}}{1 + e^{2mL}} \right]$$

$$= e^{mx} \left[ \frac{1 + e^{2m(L-x)}}{1 + e^{2mL}} \right]$$

$$\frac{C_A}{C_{AS}} = \frac{e^{m(L-x)} + e^{-m(L-x)}}{e^{mL} + e^{-mL}}$$

$$= \frac{\cosh m(L-x)}{\cosh mL}$$

$$mL = \sqrt{\frac{k}{D}} \rightarrow \text{Effective length of pore} \\ = \text{Thiele Modulus} \leftarrow \text{dimension}$$

↓ How conc. is dropping within the pore.

- $\eta$  = effectiveness factor
- =  $\frac{\text{rate of reaction with diffusion}}{\text{rate of reaction without diffusion}}$
- =  $\frac{\text{rate of reaction within the pore}}{\text{rate of reaction on the surface}}$
- =  $\frac{\text{actual rate of reaction within pore}}{\text{rate if not slowed by pore diffusion}}$
- =  $\frac{r_p}{r_s}$

$$\cancel{r_s} < r_p \quad r_p < r_s$$

as  $c_A < c_{A,s}$

small  $ml$

$$ml(\phi) < 0.5 \rightarrow \eta \approx 1 \quad ml \equiv \phi$$

For 1<sup>st</sup> order reaction

$$\eta = \frac{\tanh ml}{ml}$$

$$ml = L \sqrt{\frac{k}{D}}$$

$ml$  small

- $L$  is very small, pore is short in length
  - Smaller rate of reaction,  $k$  is small
  - Rapid diffusion within the pore.
- $D \rightarrow$  larger

large  $mL$

$$mL > 5, \quad \eta = \frac{1}{mL}$$

- pore diffusional resistance is smaller  
→  $L$  is larger  
→  $D_p$  is smaller

For 1<sup>st</sup> order  $r_A \propto k^n$

$$-r_A = kC_A = \eta kC_{A,s} \quad \left[ \frac{C_A}{C_{A,s}} = \eta \text{ for 1<sup>st</sup> order} \right]$$

$$\eta = \frac{\int_0^L \frac{C_A}{C_{A,s}} dx}{\int_0^L dx} = \frac{\int_0^L \frac{\cosh m(L-x)}{\cosh mL} dx}{\int_0^L dx} = \frac{\int_0^L \cosh m(L-x) dx}{L \cosh mL}$$

$$\tanh mL$$

$$mL$$

For 1<sup>st</sup> order with

$$-r_A = k C_A = \eta k C_{AS}$$

for strong pore resistance

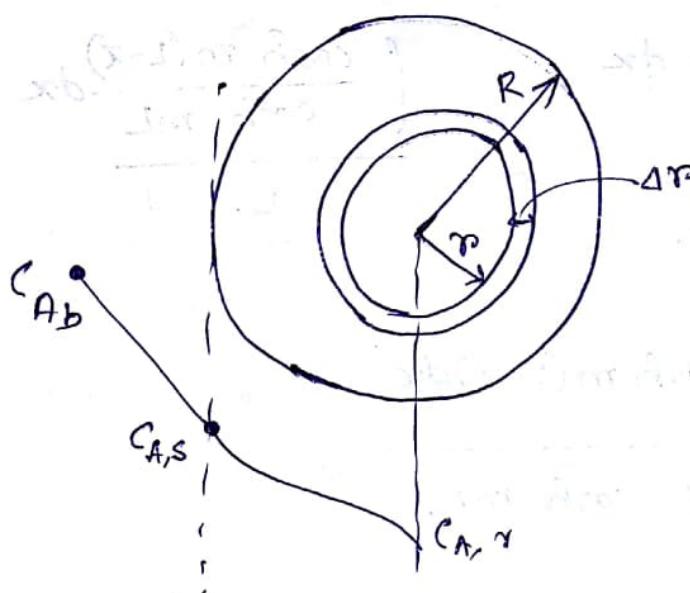
$$= \frac{k C_{AS}}{mL} = \frac{k C_A}{\sqrt{\frac{k}{D}} L} = \frac{(kD)^{1/2} C_A}{L}$$

For no pore resistance,

$$-r_A = k C_{AS} = k C_A, \eta \approx 1$$

07/09/17

Pore Diffusion in a Spherical pellet:



#### Assumptions

- \* Uniform porosity of entire sphere
- \* Isothermal
- \* Effective diffusivity is independent of conc. variation

$k_L$  = rate const. per unit mass of catalyst  
kmol/kg-at.hr.

Mole Balance,

$$\text{Output} - \text{Input} + \text{disappearance} = 0$$

$$-4\pi r^2 D_e \left( \frac{dc_A}{dr} \right)_R - \left( -4\pi r^2 D_e \left( \frac{dc_A}{dr} \right)_{r_1+2r_1} \right) = 4\pi r^2 \Delta r \rho_p k_L C_A$$

Dividing both side with  $4\pi \Delta r D_e$

$$\frac{\frac{1}{r^2} \left[ \left( -r^2 \frac{dc_A}{dr} \right)_R + \left( r^2 \frac{dc_A}{dr} \right)_{r+2r} \right]}{\Delta r} = \frac{\rho_p k_L C_A}{D_e}$$

Taking  
 $\Delta r \rightarrow 0$

limit

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \left( \frac{dCA}{dr} \right) \right) = \frac{p_p k_1(C_A)}{De}$$

## Differentiating

$$\frac{1}{r^2} \left\{ 2r \frac{dC_A}{dr} + r^2 \frac{d^2C_A}{dr^2} \right\} = \frac{P_p k_{1A}}{De}$$

$$\frac{d^2 C_A}{dt^2} + \frac{2}{\tau_1} \frac{d C_A}{dt} = \frac{P_p k_{11} C_A}{D_e} \quad \dots \dots \dots \quad (1)$$

boundary conditions

$$C_A = C_{AS} \quad @ \quad r = R$$

$$\frac{dC_A}{dr} = 0 \quad @ \quad r = 0$$

$$\frac{C_A}{C_{AS}} = \frac{f(\tau)}{\tau} = \frac{f}{\tau}$$

$$p \frac{C_A}{C_{AS}} = f$$

$$\frac{p}{C_{AS}} \frac{dC_A}{dY} + \frac{C_A}{C_{AS}} = \frac{df}{dY}$$

$$\frac{1}{C_{AS}} \frac{dC_A}{d\tau} + \frac{1}{C_{AS}} \frac{d(C_A)}{d\tau} + \frac{\tau}{C_{AS}} \frac{d^2C_A}{d\tau^2} = \frac{df}{d\tau^2}$$

$$\frac{m}{C_{AS}} \frac{d^2 C_A}{d\tau^2} + \frac{2}{C_{AS}} \frac{dC_A}{d\tau} = \frac{d^2 f}{d\tau^2}$$

$$\frac{d^2C_A}{dr_1^2} + \frac{2}{r} \frac{dC_A}{dr_1} = \frac{C_A s}{r^0} \frac{d^2f}{dr_1^2} \quad \dots \quad (2)$$

Comparing 1 & 2

$$\frac{P_p k_L C_A}{D_e} = \frac{C_{AS}}{r} \frac{d^2 f}{dr^2}$$

$$\frac{d^2 f}{dr^2} = \frac{P_p k_L C_A}{D_e C_{AS}} \cdot r = \frac{P_p k_L r}{D_e} \frac{C_A}{C_{AS}}$$

$$\frac{d^2 f}{dr^2} = \frac{P_p k_L}{D_e} \cdot f, \quad f \left[ f = r \frac{C_A}{C_{AS}} \right] \quad \text{③}$$

Boundary conditions

$$r=0, \quad f=0$$

$$r=R, \quad f=R$$

$$\frac{f}{r} = \frac{C_A}{C_{AS}} = \frac{C_1}{r} \cosh\left(\sqrt{\frac{P_p k_L \cdot r}{D_e}}\right) + \frac{C_2}{r} \left( \sinh\left(\sqrt{\frac{P_p k_L}{D_e}} \cdot r\right) \right)$$

at  $r=0$

$$0 = \frac{C_1}{r} \times 1$$

$$\sinh(0) = 0$$
$$\cosh(0) = 1$$

$$C_1 = 0$$

Now at  $r=R, \quad C_A = C_{AS}$

$$0 + \frac{C_2}{R} \sinh\left(\sqrt{\frac{P_p k_L}{D_e}} \cdot R\right) = 1$$

$$C_2 = \frac{R}{\sinh\left(\sqrt{\frac{P_p k_L}{D_e}} \cdot R\right)}$$



$$\frac{C_A}{C_{AS}} = \frac{R}{r} \frac{\sinh(\sqrt{\frac{P_p k_L}{De}} \cdot r)}{\sinh(\sqrt{\frac{P_p k_L}{De}} \cdot R)}$$

$$\frac{C_A}{C_{AS}} = \frac{R}{r} \frac{\sinh(3\phi_s \frac{r}{R})}{\sinh(3\phi_s)}$$

$$\text{where } \phi_s = \frac{R}{3} \sqrt{\frac{k_L P_p}{De}}$$

$\phi_s$  = Thiele Modulus of a spherical porous pellet

Determination of the rate for the whole pellet

rate of diffusion = rate of reaction

$$= \frac{4\pi R^2 De \left( \frac{dC_A}{dr} \right)}{w}, w = \text{mass of pellet}$$

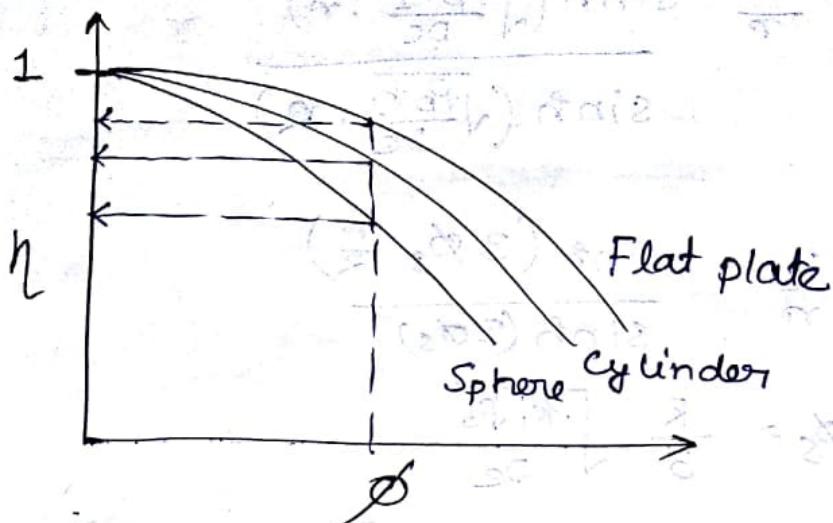
$$= \frac{4\pi R^2 De \frac{dC_A}{dr}}{\frac{4}{3}\pi R^3 P_p}$$

$$= \frac{3}{R P_p} De \left( \frac{dC_A}{dr} \right)$$

Effectiveness Factor

$$\eta = \frac{r_p}{r_s} = \frac{3 De}{R P_p k_L C_{AS}} \left( \frac{dC_A}{dr} \right), k_L C_{AS} = r_s$$

$$\eta_s = \frac{1}{\phi_s} \left[ \frac{1}{\tanh(3\phi_s)} - \frac{1}{3\phi_s} \right]$$



$$\phi = mL = L \sqrt{\frac{k_L}{De}}, \text{ for unit mass}$$

$$\phi_s = L \sqrt{\frac{k_L p_p}{De}}$$

For flat plate

$$\eta = \frac{\tan h \phi_s}{\phi_s} \text{ is } 1^{\text{st}} \text{ order reaction}$$

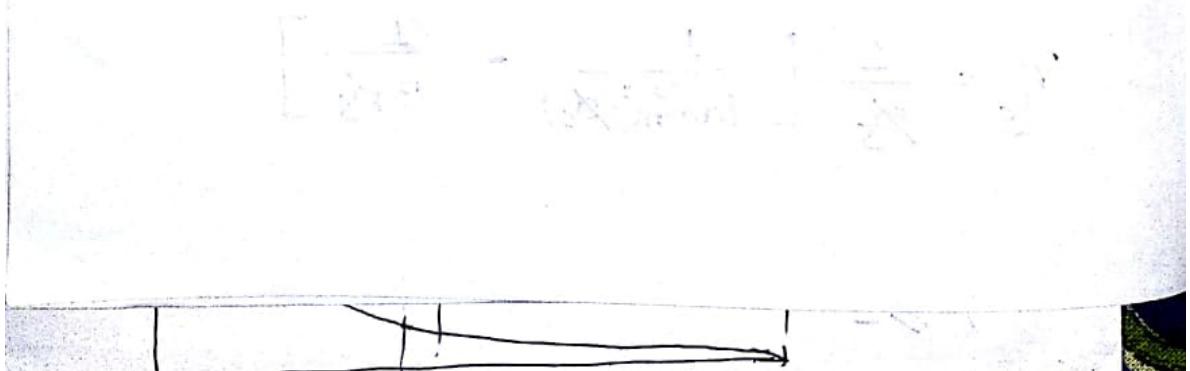
$$\phi_s \rightarrow 0, \eta \rightarrow 1$$

$$\phi \rightarrow 0.5, \eta \rightarrow \frac{1}{\phi_s}$$

For non spherical geometry

$$R_{\text{nonsp}} = 3 \left( \frac{V_p}{S_p} \right) = R$$

$$\text{For spherical pellet } \frac{V_p}{S_p} = \frac{\frac{4}{3} \pi R^3}{4 \pi R^2} = \frac{R}{3}$$

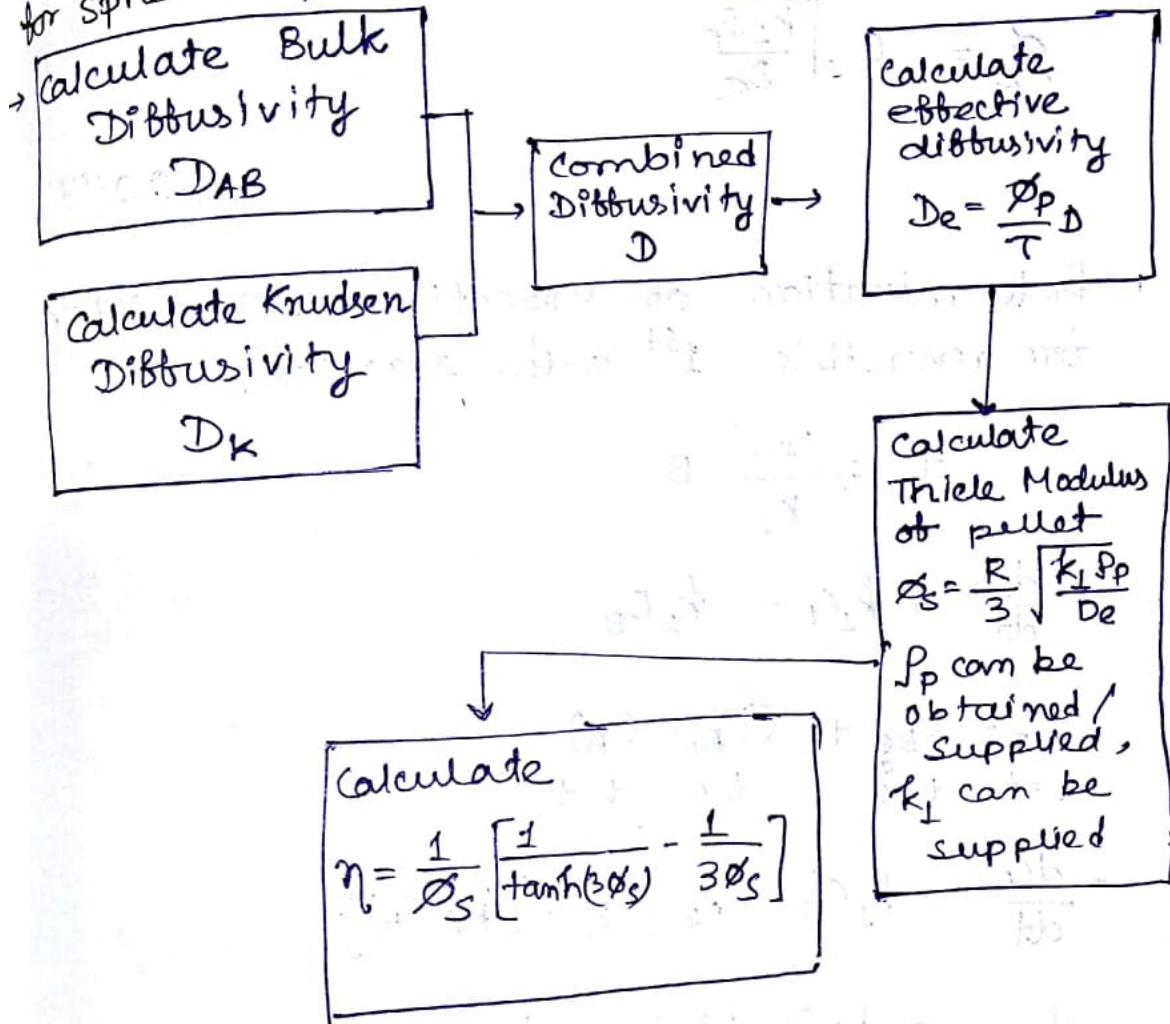


$$\eta_s = \frac{1}{\phi_s} \left[ \frac{1}{\tanh(3\phi_s)} - \frac{1}{3\phi_s} \right]$$

$$\phi_s = L \sqrt{\frac{k_1 P_p}{D_e}} = \frac{R}{3} \sqrt{\frac{k_1 P_p}{D_e}} \text{ for sphere}$$

$$L = \frac{R}{3}$$

steps for determination of effectiveness factor  
for spherical pellet



## Reversible Reaction

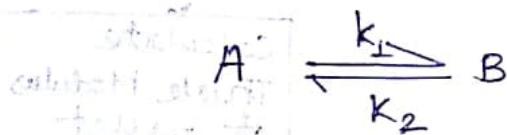


- Effectiveness factor for slow reaction is  
→ large  
→ characteristic length  $L \uparrow$ , effectiveness  $\downarrow$

$$\phi_s = L \sqrt{\frac{k_1 p_f}{D_e}}$$

12/09/17

Determination of effectiveness factor for reversible 1<sup>st</sup> order reaction.



$$-\frac{dC_A}{dt} = k_1 C_A - k_2 C_B$$

$$C_B = C_{B_0} + (C_{A_0} - C_A)$$

$t=t$     $t=0$     $t=0$     $t=t$

$$-\frac{dC_A}{dt} = k_1 C_A - k_2 \{ C_{B_0} + (C_{A_0} - C_A) \}$$

$$= k_1 C_A + k_2 C_A - k_2 (C_{B_0} + C_{A_0})$$

at eqbm, forward rate = reverse rate

$$k_1 C_A \text{ eqbm} = k_2 C_B \text{ eqbm},$$

$$\frac{C_{B \text{ eqbm}}}{C_{A \text{ eqbm}}} = \frac{k_1}{k_2} = K$$

$k_2 = \frac{k_1}{K}$   
Eqbm. const.

put the value of  $K_2$  in eq<sup>n</sup> ①

$$-\frac{dc_A}{dt} = k_1 c_A + \frac{k_1}{K} c_A - \frac{k_1}{K} (c_{A_0} + c_{B_0})$$

$$= k_1 \left\{ \frac{k+1}{K} c_A - \frac{1}{K} (c_{A_0} + c_{B_0}) \right\}$$

$$K = \frac{c_{B \text{ eqbm}}}{c_{A \text{ eqbm}}} = \frac{c_{B_0} + (c_{A_0} - c_{A \text{ eqbm}})}{c_{A \text{ eqbm}}}$$

$$= \left( \frac{c_{B_0} + c_{A_0}}{c_{A \text{ eqbm}}} \right) - 1$$

$$(c_{B_0} + c_{A_0}) = c_{A \text{ eqbm}} (K+1)$$

putting the value of  $(c_{A_0} + c_{B_0})$  in eq<sup>n</sup> ②

$$-\frac{dc_A}{dt} = k_1 \left\{ \frac{k+1}{K} c_A - \frac{k+1}{K} c_{A \text{ eq}} \right\}$$

$$= k_1 \left( \frac{k+1}{K} \right) (c_A - c_{A \text{ eqbm}})$$

$$k_R = k_1 \left( \frac{k+1}{K} \right) \quad \text{and} \quad c' = (c_A - c_{A \text{ eqbm}})$$

Mass balance eq<sup>n</sup> for reversible 1<sup>st</sup> order reaction for spherical pellet catalyst

$$\begin{aligned} & \left( -4\pi r^2 \Delta e \frac{dc'}{dr} \right)_{r_1} - \left( -4\pi r^2 \Delta e \frac{dc'}{dr} \right)_{r_1 + \Delta r} \\ & = 4\pi r^2 \Delta e \rho k_R c' \end{aligned}$$

Taking limit  $\Delta r \rightarrow 0$

$$\frac{d^2 c'}{dr^2} + \frac{2}{r} \frac{dc'}{dr} - \frac{k_r P_p c'}{De} = 0$$

Boundary condition

$$r=0, \frac{dc'}{dr} = 0$$

$$r=R, c' = c_s$$

$$\phi_s' = \frac{r_s}{3} \sqrt{\frac{k_t (k+1) P_p}{k De}}$$

Effectiveness of reversible  $\tau k^n$  is more compared to irreversible  $\tau k^n$  as  $\phi_s < \phi_s'$

$$\phi_s = \frac{r_s}{3} \sqrt{\frac{k_t P_p}{De}}$$

$$k > 0$$

$$\Rightarrow \frac{k+1}{k} > 1$$

$$\Rightarrow \boxed{\phi_s' > \phi_s}$$

Reversible  $\tau k^n$

Irreversible  $\tau k^n$

Significance of intraparticle diffusion:

For slow  $\tau k^n$

$\eta$  in  $(0.7 - \eta)$  for normal size pellet

For fast  $\tau k^n$

$\eta \approx 0.1$  for normal size pellet



$$\boxed{\phi_s \leq \frac{1}{3}, \quad \eta \approx 1}$$

↓  
Overcome intrapellet diffusion

$$\boxed{r_s \sqrt{\frac{k_1 P_p}{D_e}} \leq 1, \phi_s \leq \frac{1}{3}}$$

$$r_s^2 \frac{k_1 P_p}{D_e} \leq 1$$

Replacing  $k_1$  by  $r_p$

$$r_s^2 \frac{r_p P_p}{c_s D_e} \leq 1$$

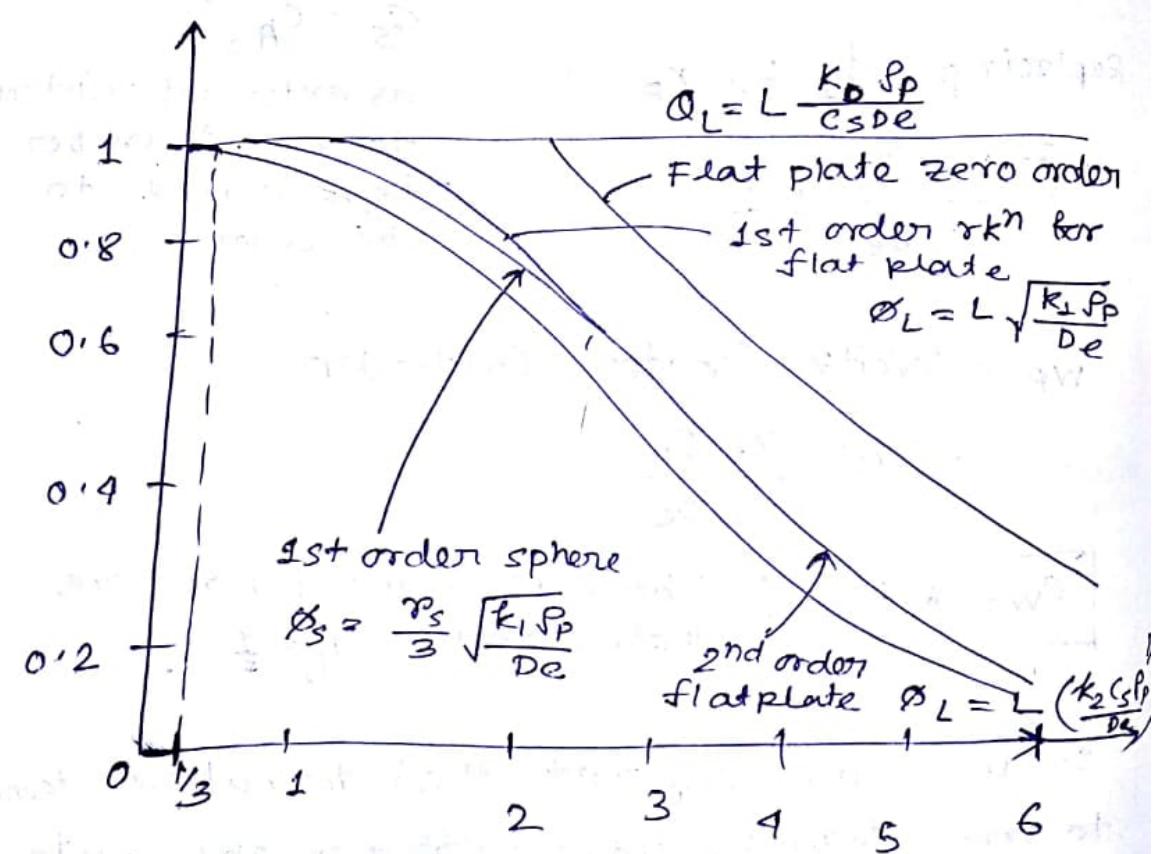
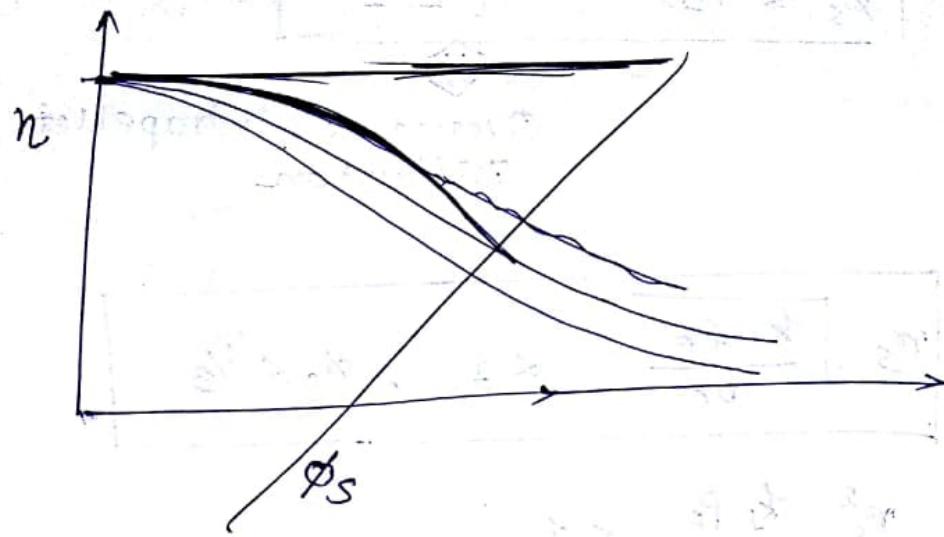
Assuming  
 $c_s = c_{A_b}$   
as external resistance  
to mass transfer  
is assumed to  
be zero.

$C_{wp}$  = Weitz Prater Criterion

$$= r_s^2 \frac{r_p P_p}{c_s D_e}$$

$$\boxed{C_{wp} \leq 1} \Rightarrow \text{There is almost no pore diffusion i.e. } \eta = 1$$

So we can say that, the internal resistance to mass transfer has no effect on the rate of reaction.



Q) Dehydrogenation of butane at atmospheric pressure using a Chromia-Alumina catalyst is done at  $530^\circ\text{C}$ . Spherical catalyst size of  $d_p = 0.32\text{ cm}$ , the experimental data suggest a 1<sup>st</sup> order  $nk^n$  with rate const. of  $0.94 \frac{\text{cm}^3}{\text{sec} \cdot \text{cat.}}$

Pore radius is given as  $110\text{ \AA}$ . Assuming Knudsen diffusivity at low pressure and estimating the pore volume  $0.35 \frac{\text{cm}^3}{\text{cm}^3}$ , predict an effectiveness factor  $\phi$  of the catalyst. Use the parallel pore model with a tortuosity factor of 3.

For parallel pore model, pores are parallel and of uniform  $a$ , with no inter-connection.

# Mass and Heat Transfer with reaction

10/10/19

$\eta$  = actual rate of the reaction in the pellet  
rate of the reaction on the catalyst surface

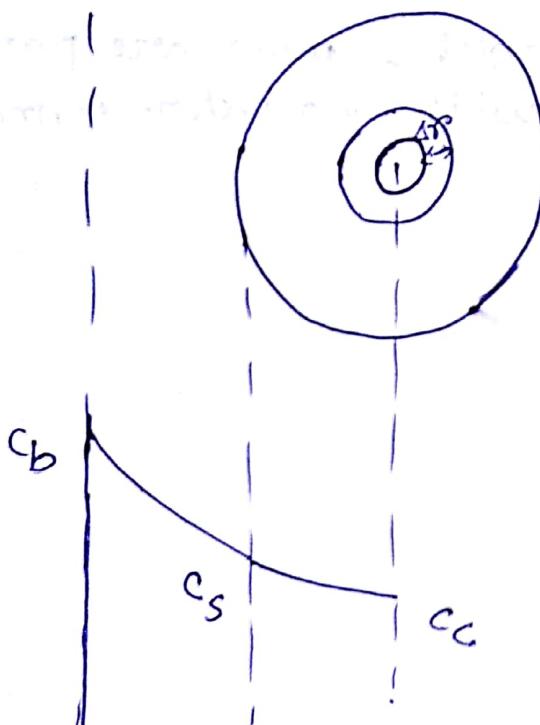
$$\eta = \frac{r_p}{r_s}$$

$$r_s = r_p$$

$$r_p = \eta r_s$$

$$r_p = \eta r_s = \eta f(T_s, c_s)$$

$\eta \equiv$  non-isothermal effectiveness factor  
 (considering both mass and heat transfer)



$c_b$  = conc. of reactant at bulk

$c_s$  = conc. of the reactant on the external surface of catalyst

$c_c$  = reactant conc. at core of the catalyst.

Mole balance for only mass transfer taken in account

$$\left( -4\pi r^2 D_e \frac{dc}{dr} \right)_{r_1} - \left( -4\pi r^2 D_e \frac{dc}{dr} \right)_{r_1 + \Delta r}$$

$$= 4\pi r^2 \Delta r \rho_p k_{\perp} c \quad \dots \textcircled{1}$$

$\rho_p k_{\perp} c$  = rate of the reaction / vol. of catalyst

$4\pi r^2 \Delta r^2$  vol. of the differential element  $\Delta r$

considering heat transfer (alone)

$$\left( -4\pi r^2 k_e \frac{dT}{dr} \right)_{r_1} - \left( -4\pi r^2 k_e \frac{dT}{dr} \right)_{r_1 + \Delta r}$$

$$= 4\pi r^2 \Delta r \rho_p k_{\perp} c \Delta H \quad \text{conductivity}$$

$k_e$  = effective thermal diffusivity

$\Delta H$  = heat of reaction

taking  $\Delta r \rightarrow 0$

$k_e$  is also considered as independent of temperature

dividing both sides of eqn<sup>②</sup> by  $4\pi r k_e$

$$\frac{d^2 T}{dr^2} + \frac{2}{r} \frac{dT}{dr} - \frac{k_{\perp} \rho_p c}{k_e} \Delta H = 0 \quad \dots \textcircled{3}$$

boundary condition

$$\frac{dc}{dr} = 0 \quad \text{when} \quad r = 0$$

$$c = c_s \quad \text{when} \quad r = r_s$$

$s_p k_1 c \Rightarrow$  rate of the reaction / vol of catalyst

$$\frac{dc}{dr^2} + \frac{2}{r} \frac{dc}{dr} - \frac{k_1 s_p c}{D_e} = 0 \quad \dots \textcircled{4}$$

boundary conditions

$$\frac{dT}{dr} = 0 \text{ at } r=0$$

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

comparing eqn (3 & 4)

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

integrating twice

$$T - T_s = \frac{\Delta H}{k_e} \frac{D_e}{K_e} (c - c_s)$$

$$-T_s = \frac{\Delta H \Delta e}{K_e} (c - c_s)$$

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in Kohler equation change  
maximum temperature rise, when  $c_s = 0$

$$T - T_s = \frac{-\Delta H \Delta e}{K_e} \cdot c_s$$

1. Thiele modulus

$$3(\phi_s)_s = r_s \sqrt{\frac{(K_1)_s P_p}{\Delta e}}$$

$\phi_s$  = Thiele modulus determined at the surface

$(K_1)_s$  = rate const. at surface at temp  $T_s$

2. Arrhenius number

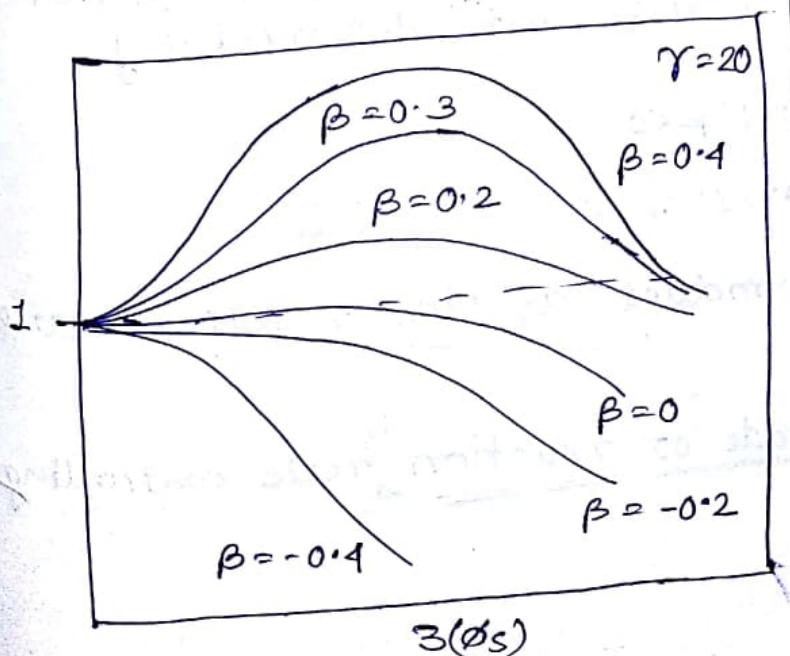
$$\gamma = \frac{E}{R_g T_s}$$

Gas phase resistance =  $R_g$   
 $R_g$  = universal gas const.

3. Heat of reaction parameter

$$\beta = \frac{(-\Delta H) \Delta e c_s}{K_e T_s}$$

$\beta < 0$ : endothermic  
 $\beta > 0$ : exothermic  
 $\beta = 0$ : isothermal



(n)  $\eta > 1 : \beta > 0$

nonisothermal

Advantages

$\beta > 0$ ; The temperature within the pore is higher than that on surface. Thus the rate const. within the pore will be higher compared to surface. Thus rate of reaction within pore will be higher than on surface

- At higher temp within the pore, the product formed may be disintegrated

- If activation energy of other undesired reaction is less than that of desired reaction, there will be side products (undesired)

Disadvantages

- Due to high temperature, there might be sintering of active site. At high temperature there might be agglomeration of catalyst active sites

- Mass transfer plays an important role in exothermic reaction i.e. mass transfer resistance will be rate determining

Endothermic:  $\beta < 0$

$\beta < 0$  Endothermic,  $\eta < 1$

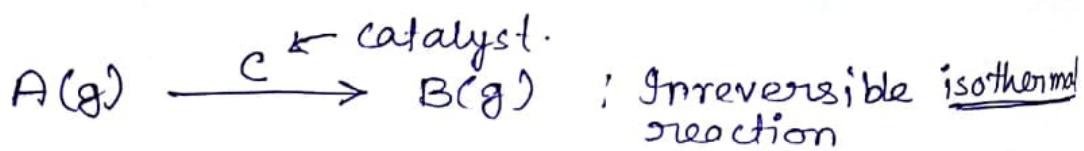
- Uniform product as side reactions are suppressed
- Intrinsic rate of reaction is rate controlling

## Solid catalyst: Heterogeneous Process

- Global rate of reaction
  - Intrinsic rate of  $r k^n$
  - Heat transfer
  - Mass transfer
- Local rate of reaction at a point

### Steps

1. Mass transfer of the reactants from the bulk to the surface of the catalyst
2. Mass transfer of the reactants from the ~~surface~~ to  $\uparrow$  within pore
3. Adsorption of reactants on surface
4. Surface reaction
5. Desorption of products
6. Reverse of step 2 for product
7. Reverse of step 1 for product



- Catalyst is non porous; steps 2 & 6 are not involved

$$r_p = \frac{\text{rate of the reaction}}{\text{mass of the catalyst}}$$

$$r_v = \frac{\text{rate of reaction}}{\text{volume of catalyst bed}}$$

steps 3, 4, 5 are clubbed together  
 so effectively there are 2 steps, excluding  
 the 7th step also

→ Mass transfer of the reactants from the  
 bulk to the surface of the catalyst.

$$r_p = k_m a_m (C_b - C_s)$$

$$r_p = \frac{(C_b - C_s)}{\frac{1}{k_m a_m}}$$

$k_m$  = mass transfer coefficient per unit area

$a_m$  = area per unit mass of catalyst

2 → chemical reaction

$$r_p = k C_s$$

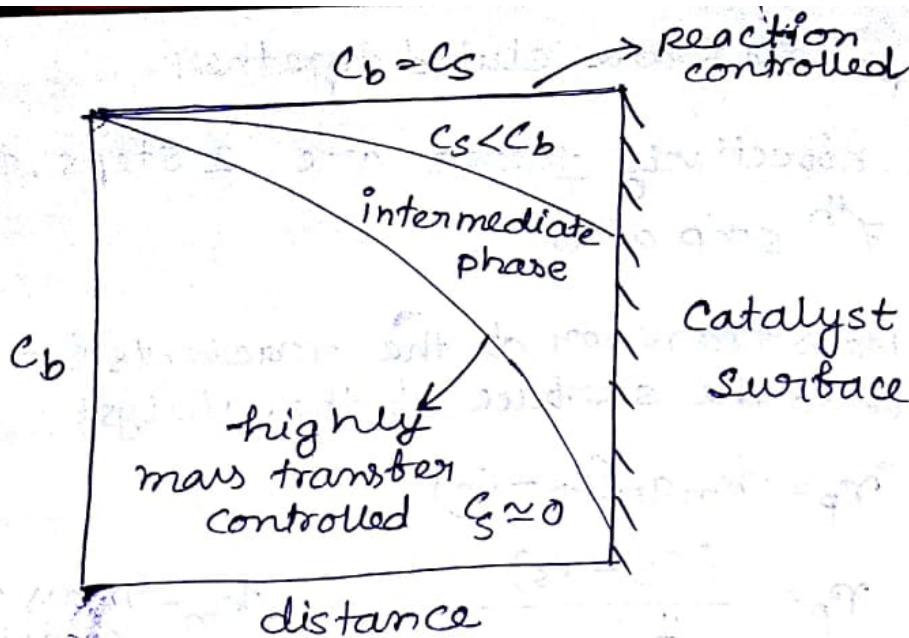
$$C_s = \frac{k_m a_m}{k_m a_m + K} C_b$$

$$r_p = \frac{k k_m a_m}{k_m a_m + K} C_b$$

$$= \frac{C_b}{\frac{1}{K} + \frac{1}{k_m a_m}}$$

~~$C_b = C_s$~~   $C_b - C_s \neq 0$  driving force for the reaction  
 as there will be no effective resistance

⇒  $C_b \neq C_s$



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- Isotherm is plotted by plotting rate of adsorption with pressure at constant pressure

### Langmuir isotherm

- Entire surface is energetically same
- All the active sites should be energetically same
- No two adsorbed component interact
- All components are adsorbed by same mechanism.
- Extent of adsorption is lesser than one mono molecular adsorption.

$$r_A = k P (1 - \theta)$$

↑ Accounts for  
Already occupied surface

$$r_d = k' \theta$$

$$k P (1 - \theta) = k' \theta$$

$$\theta = \frac{k P}{k' + k P} = \frac{k P}{1 + k P} = \frac{v}{v_m}$$

→ reaction controlled

Catalyst surface

$$K = \text{equilibrium const.} = \frac{k}{k'}$$

$v$  = volume of gas adsorbed

$v_m$  = monomolecular layer volume of gas

$$\frac{1}{Kp} + 1 = \frac{v_m}{v}$$

$$\frac{1}{Kv_m} + \frac{P}{v_m} = \frac{P}{v_m}$$

--- ①

High surface area is required for solid catalyst.

$d_p$  = diameter of solid catalyst particle  
area/volume of catalyst

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

If  $\rho_p$  = density of the particle

$$S_g = \frac{6}{\rho_p d_p} \rightarrow \text{surface area per gram catalyst}$$

Solid catalyst should be porous to have high surface area.

- pore structure (shape, size, interconnection)
- pore volume
- density
- pore volume distribution

Affecting factor

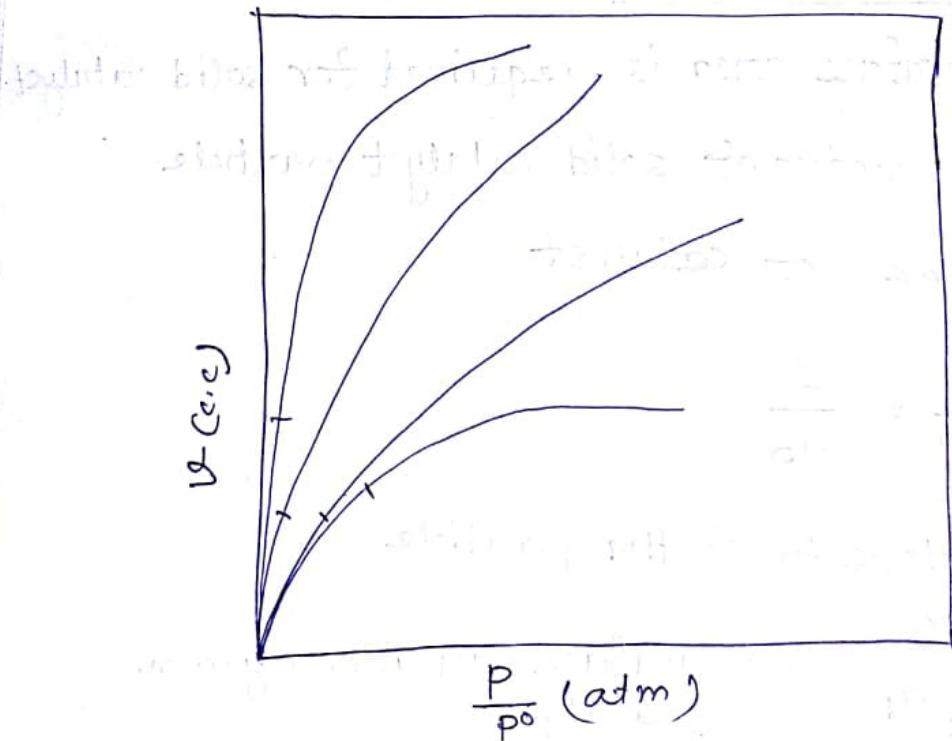
To determine area

A gas is allowed to adsorb at the solid surface at its normal boiling point. Usually the gas is  $N_2$  because it is inert.

We need to determine the volume of  $N_2$  to form a monomolecular layer. The process is called BET surface area determination.

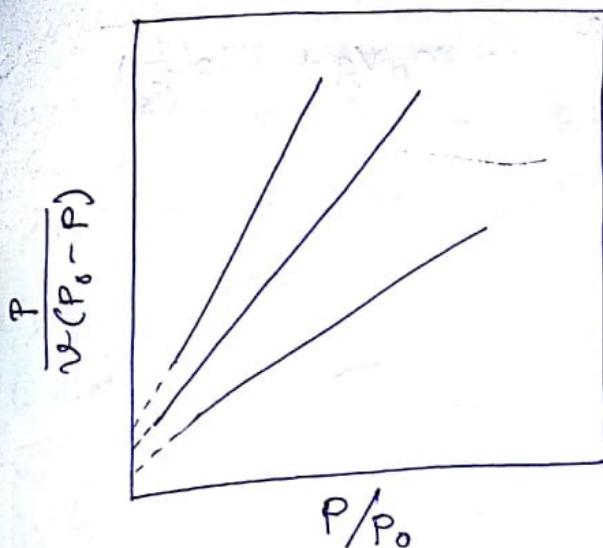
Drawbacks:

- chemisorption is used in chemical reaction
- Gas is adsorbed on entire surface. So result is much higher compared to the actual active surface.



$$\frac{1}{Kv_m} + \frac{P}{v_m} = \frac{P}{v} \rightarrow \text{monomolecular layer}$$

$$\frac{P}{v(P-P_0)} = \frac{1}{v_m c} + \frac{(c-1)P}{(v_m P_0)} \rightarrow \text{multilayer adsorption}$$



$$\text{Intercept} = \frac{1}{v_m c}$$

$$\text{Slope} = \frac{c-1}{c v_m}$$

$$S_g = \left( \frac{v_m N_a}{v} \right) \alpha$$

No. of molecules per mole

area occupied by one molecule

molecular mass

= projected area of molecule

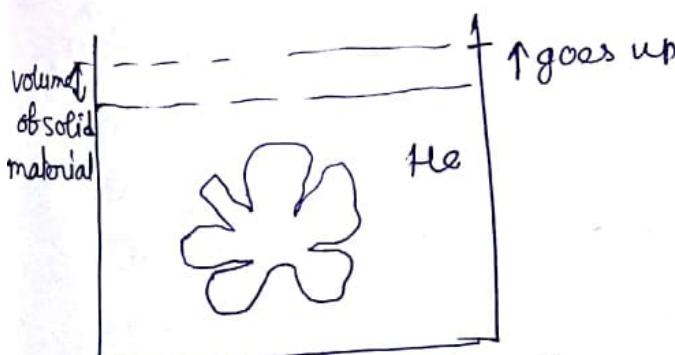
$$\alpha = 1.09 \left[ \frac{M}{N_a P} \right]^{2/3}$$

density

void volume and solid density

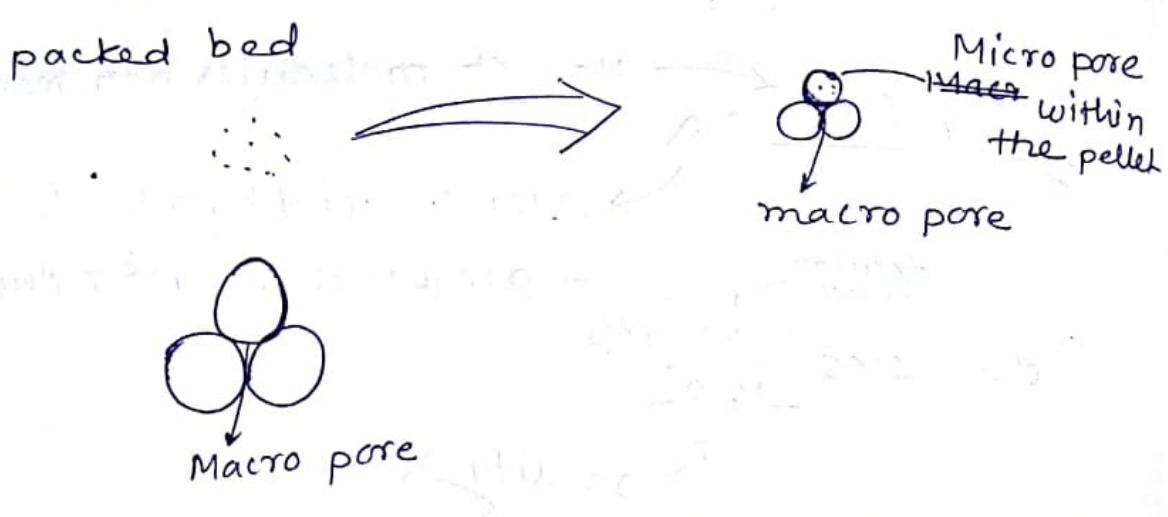
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Helium mercury method is used to find solid volume



$$\epsilon_p = \frac{\text{void volume}}{\text{Total volume}} = \frac{m_p v_g}{m_p v_g + m_p \left(\frac{1}{\rho_s}\right)}$$

$$= \frac{v_g \rho_s}{v_g \rho_s + 1}$$



Micro pore  $\Rightarrow$  can not be changed, property of catalyst

Macro pore  $\Rightarrow$  depends on pelletizing pressure.

In an experiment to determine the pore volume and catalyst particle porosity, the following data were obtained on a sample of activated silica (granular). Mass of the catalyst gram 101.5 g. Volume of He displaced by sample 45.1 cc. Volume of mercury displaced by sample ~~87.2~~ <sup>82.7</sup> cc.

$$\text{Ans} \quad V_g = \frac{82.7 - 45.1}{101.5} = \frac{37.6}{101.5} \frac{\text{cc}}{\text{g}}$$

$$= 0.37 \frac{\text{cc}}{\text{g}}$$

$$\rho_p = \frac{101.5}{45.1} = 2.2506 \text{ g/c.c.}$$

$$\epsilon_p = \frac{0.37 \times 2.2506}{0.37 \times 2.2506 + 1} = 0.4544$$

A  
Q1 Hydrogenation catalyst is prepared whose gross measurements are

$$\text{mass} = 3.15 \text{ g}$$

$$\text{diameter} = 1"$$

$$\text{Thickness} = \frac{1}{4} "$$

$$\text{Volume} = 3.22 \text{ c.c}$$

The catalyst particle contain micropores and the pelleting process introduces macro pores.

The macropore volume of the pellet is 0.645 cc and micropore volume is 0.4 cc/g particle

From this information calculate

- 1) Density of pellet  $\rho_p$
- 2) Macro pore void fraction in the pellet
- 3) Micro " " " " " "
- 4) Solid fraction
- 5) Density of the particles
- 6) Density of the solid phase
- 7) void fraction of the ~~catalyst~~ particle

Sol<sup>n</sup>

$$1) \rho_p = 0.9783 \text{ g/cm}^3$$

$$2) \text{Macro pore void fraction } \epsilon_{\text{macro}}$$

$$= \frac{0.645/3.15}{3.22/3.15}$$

$$= 0.2$$

$$3) \text{Micro pore void fraction } \epsilon_{\text{micro}}$$

$$= \frac{0.4 \times 3.15}{3.22}$$

$$= 0.3913$$

$$4) \text{solid fraction} = (1 - 0.2 - 0.3913)$$

$$= 0.4087$$

$$5) \text{actual } (\rho_p) = \frac{3.15}{0.4087 (1 - 0.2) 3.22}$$

$$= 1.223 \text{ g/cm}^3$$

$$6) \rho_s = \frac{3.15}{0.4087 \times 3.22} = 2.3936 \text{ g/c.c}$$

$$7) \epsilon_p = \frac{(0.3913 + 0.2)}{= 0.5913}$$

For a single particle, the void fraction is to be calculated from on the basis of micro porosity

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- Mercury can not enter smaller pores (less than  $200\text{ \AA}$  in size)
- For smaller pores (where mercury porosimeter can not be used), nitrogen desorption method is used at higher  $\frac{P}{P_0}$
- Nitrogen desorption provide both micro & macro pore volume.
- As pressure is increased on liquid nitrogen, layers start to grow and pores are filled up with liquid condensed nitrogen, when  $\frac{P}{P_0} \approx 1$
- When pressure is lowered, desorption takes place initially from the bigger pores followed by the smaller ones in later stages
- Kelvin eq<sup>n</sup> gives a relation pore radius =  $f\left(\frac{P}{P_0}\right)$ , where pore radius gives the radius of pores, beyond which all pores are empty at that particular  $\left(\frac{P}{P_0}\right)$  value.

### Kelvin eq<sup>n</sup>

$$a - \delta = \frac{-2\sigma V_1 \cos \theta}{RT \ln\left(\frac{P}{P_0}\right)}$$

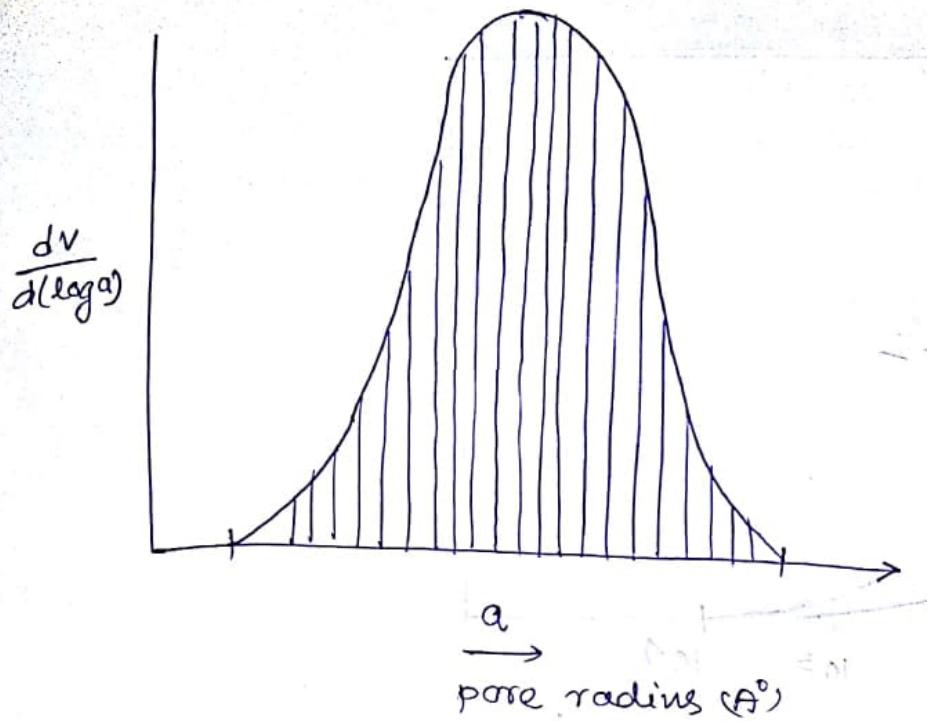
$a$  = pore radius  $\text{A}^\circ$

$\delta$  = thickness of  $\text{N}_2$  on the surface

$\sigma$  = surface tension of  $\text{N}_2$

$\theta$  = contact angle between  $\text{N}_2$  and pore wall.

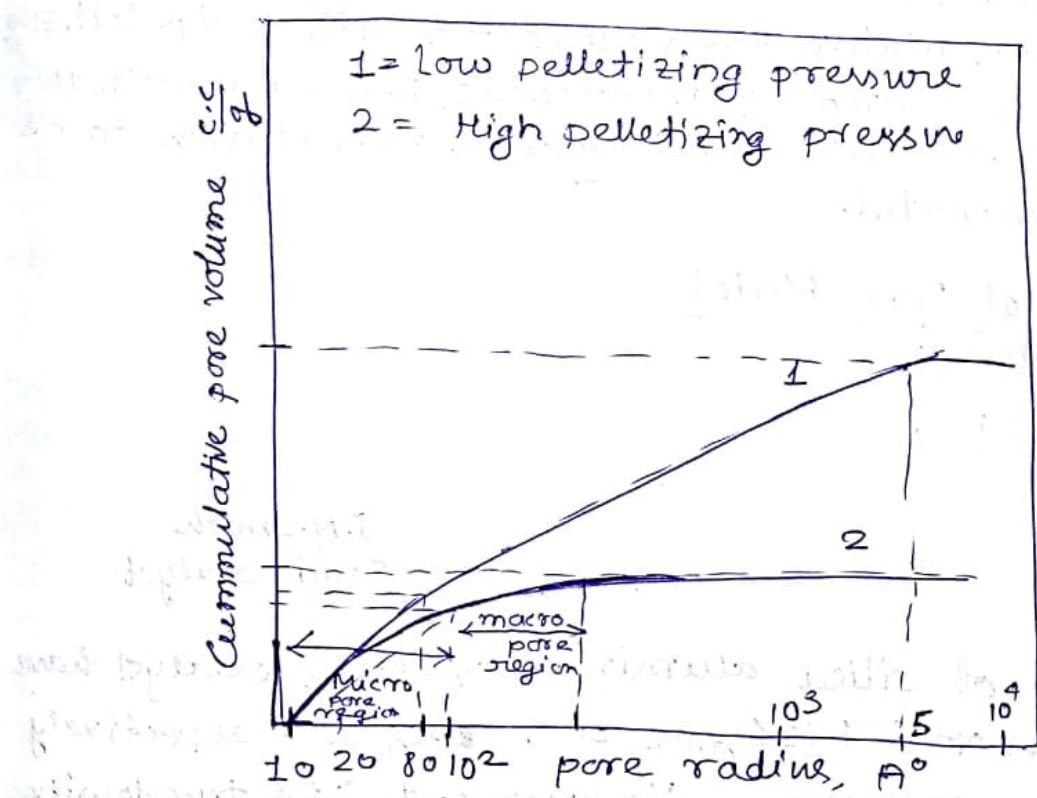
$$\delta(\text{A}^\circ) = 9.52 \left(\log \frac{P_0}{P}\right)^{-1/2}$$

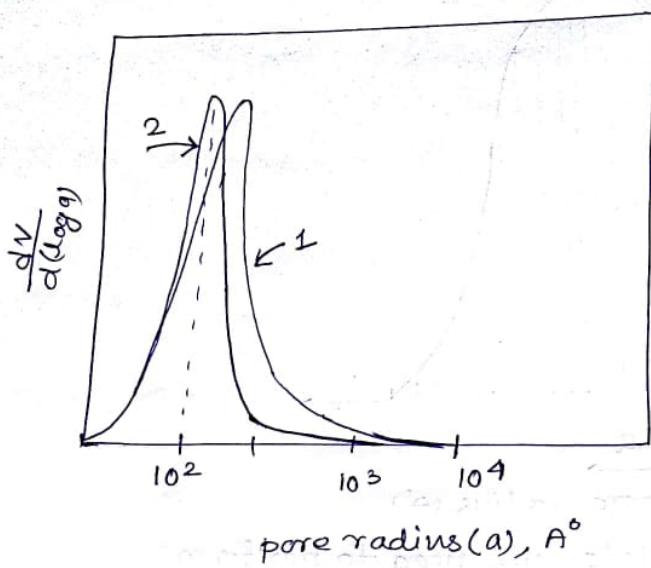


\* For bidispersed pellets, we need to perform

mercury penetration method - Macro pore  
nitrogen desorption " - Micro pore

• Effect of Pelletizing pressure on macro-pore volume





Sol<sup>m</sup>

Cat 1

$$(\bar{a})_1 = \left( \frac{2Vg}{Sg} \right)$$

basis: 1

$$m_p =$$

$$Sg_1 =$$

$$Sg_2 =$$

$$\bar{a}_1 =$$

$$\bar{a}_2 =$$

Q1

Ans 8.01  
adsorptive

Pressure, t

vol. adsor  
cm<sup>3</sup>, at 0°C  
1 atm

Vapor f  
the su

$$f_{N_2} \alpha$$

$$\alpha =$$

- With increasing pressure, macropore volume decreases but micro pore volume is invariant
- Desorbed volume gives cumulative pore volume
- \* As a result, until when there is no significant difference in between cumulative pore volume for different pelletizing pressure is dominated by micropores, beyond which there is significant variation leading to the conclusion to be macropore dominated.

\* Willer Parallel Pore Model

$$m_p Sg = (2\pi \bar{a} L) n$$

$$m_p Vg = (\pi \bar{a}^2 L) n$$

$$\bar{a} = \frac{2Vg}{Sg}$$

J.M. Smith  
Solid catalyst.

Q2 Two samples of silica alumina cracking catalyst have particle densities of 1.126 g/c.c & 0.9162 g/c.c respectively as determined by mercury displacement. The true density of solid catalyst in each case is 2.37 g/c.c. The surface area of 1<sup>st</sup> one is 467 m<sup>2</sup>/g and that of the 2<sup>nd</sup> is 372 m<sup>2</sup>/g. Which sample has the larger mean pore radius?

Soln  
Cat 1

$$(\bar{a})_1 = \left( \frac{2Vg}{Sg} \right)_1$$

basis: 1 g of catalyst

$$m_p = 1 \text{ g}$$

$$Sg_1 = 4.67 \times 10^6 \frac{\text{cm}^2}{\text{g}}$$

$$Sg_2 = 3.72 \times 10^6 \frac{\text{cm}^2}{\text{g}}$$

Cat 2

$$(\bar{a})_2 = \left( \frac{2Vg}{Sg} \right)_2$$

$$Vg_1 = 0.466 \text{ cc/g}$$

$$Vg_2 = 0.618 \text{ cc/g}$$

areas

$$\bar{a}_1 = \frac{2 \times 0.466}{4.67 \times 10^6} = 1.99 \times 10^{-7} \text{ cm}^2 = 19.9 \text{ \AA}^2$$

$$\bar{a}_2 = \frac{2 \times 0.618}{3.72 \times 10^6} = 3.32 \times 10^{-7} \text{ cm}^2 = 33.2 \text{ \AA}^2$$

reference  
estimating  
2, there  
to be

02/11/17

Q||

An 8.01 g sample of catalyst is studied with N<sub>2</sub> nitrogen adsorption at -195.8°C. The following data are given:

Pressure, Hg mm	6	25	140	230	285	320
vol. adsorbed cm <sup>3</sup> , at 0°C and 1 atm	61	127	170	197	215	230

Vapor pressure of nitrogen at -195.8°C is 1 atm. Estimate the surface area  $\text{m}^2/\text{g}$  of the catalyst.

$$P_{N_2 \text{ at } (-195.8^\circ\text{C})} = 0.808 \text{ g/l.c}$$

$$\alpha = 16.2 \times 10^{-16} \text{ cm}^2/\text{molecule}$$

{ To be remembered.

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usity

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s  
radius?