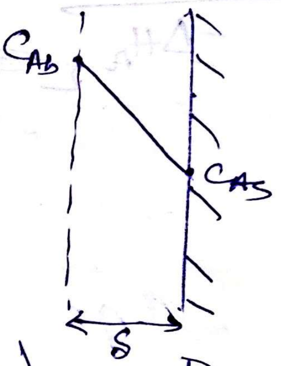
## Heterogeneous Reactor

In heterogeneous reaction more than one phase is present (fluid and solid). Since more one phase is present, movement of material from phase to phase is reqd. in rate eqn. Thus rate expression in general will incorporate mass transfer in addition to chemical kinetics term.

**Prob. 1** Dilute A diffuses through a stagnant liquid film onto a plain surface and reacts there to produce R, which diffuses back into the main stream. Develop the overall rate expression.

Given, $A(L) \xrightarrow{B(S)} R(L)$



$\delta$ = Film thickness

$C_{Ab}$ = Bulk conc. of A

$C_{AS}$ = Surface conc. of A.

$$-r'_A = -\frac{1}{S}\frac{dN_A}{dt}$$

$$= k' C_{AS} = K_m (C_{Ab} - C_{AS}) = \frac{D_{AB}}{\delta}(C_{Ab} - C_{AS})$$

Applying film theory for mass transfer,

$$K_m = \frac{D_{AB}}{\delta}$$

$$~~-r'_A~~ \quad k' C_{AS} = \frac{D_{AB}}{S}(C_{Ab} - C_{AS})$$

$$\left(k' + \frac{D_{AB}}{S}\right) C_{AS} = \frac{D_{AB} C_{Ab}}{S}$$

$$C_{AS} = \frac{D_{AB} \; C_{AB}}{S\left(k' + \frac{D_{AB}}{\delta}\right)}$$

$$-r'_A = \frac{k' \frac{D_{AB}}{S} C_{Ab}}{k' + \frac{D_{AB}}{\delta}} = \frac{C_{ABb}}{\left(\underbrace{\frac{1}{k'}}_{R_c \text{ (Resistance due to kinetics)}} + \underbrace{\frac{S}{D_{AB}}}_{R_m \text{ (Resistance due to mass transfer)}}\right)}$$

## Solid Catalyzed Reaction

It is an example of heterogeneous reaction. In most of the situation catalyst is solid and reacting medium is fluid. Catalyst generally of two types —

i) Biochemical Catalyst — Operates at room temp. and normal pressure. e.g. enzyme.

ii) Synthetic Catalyst - Operates at high temp. and pr.

Selection of catalyst for a particular reaction is based on extensive trial and error method because the exact mechanism for catalytic reaction in most of the cases are unknown. Catalyst can speed up or down speed of reaction but it never determine equilibrium or end point. Catalyst can reduce activation energy of reac$^n$ so that it perform at lower pr and temp. than reac$^n$ without catalyst.

## Factors that affect rate of catalytic Reaction

i) Surface Kinetics -

Adsorption of reactant on surface → Reaction on surface → Desorption of the product from surface.

ii) Pore Diffusion Resistance -

iii) Particle ΔT or Temp Gradient within Particle

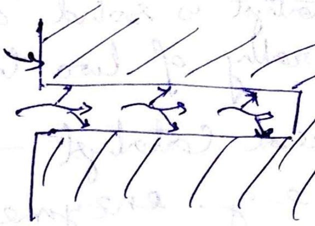
iv) Film ΔT — Temp. difference bet$^n$ catalyst surface and outside the film fluid. It also affect rate of reaction. To reduce film ΔT heat transfer coeff must be less or surface area must be large.

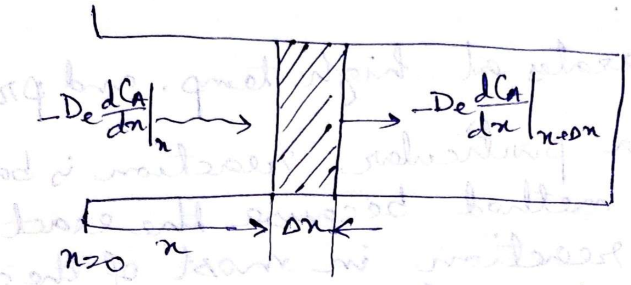
v) Film Diffusion Resistance -

# Pore Diffusion Resistance Combined with Surface Kinetics

Conside a sigle cylindrical pore of length L, with reactant A diffusing into the pore and reacting on the surface by a 1st order reaction.

$$-r'_A = -\frac{1}{S}\frac{dN_A}{dt} = k' C_A$$





Making a steady state material balance of reactant A –

i/p = o/p + disappearance

$$-D_e \frac{dC_A}{dx}\Big|_x \cdot \pi r^2 = -D_e \frac{dC_A}{dx}\Big|_{x+\Delta x} \cdot \pi r^2 + (-r'_A)(2\pi r \Delta x)$$

Or, $$\lim_{\Delta x \to 0} \frac{\left(\frac{dC_A}{dx}\Big|_{x+\Delta x} - \frac{dC_A}{dx}\Big|_x\right)}{\Delta x} = \frac{k' C_A \cdot 2\pi r}{\pi r^2 \cdot D_e}$$

$$\boxed{\frac{d^2 C_A}{dx^2} - \frac{2k'}{D_e r} C_A = 0}$$ → In terms of surface area

$$-r'''_A = -\frac{1}{V_c}\frac{dN_A}{dt} = k''' C_A$$

$$\frac{-r'''_A}{-r'_A} = \frac{S}{V_c} = \frac{k'''}{k'}$$

$$\frac{k'''}{k'} = \frac{2\pi r L}{\pi r^2 L} = \frac{2}{r}$$

$$\therefore k''' = \frac{2k'}{r}$$

$$\therefore \boxed{\frac{d^2 C_A}{dx^2} - \frac{k'''}{D_e} C_A = 0}$$ → In terms of volume.

B.C. 1: $x = 0$, $C_A = C_{As}$

B.C. 2: $x = L$, $\frac{dC_A}{dx} = 0$

∴ Solving we get —

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

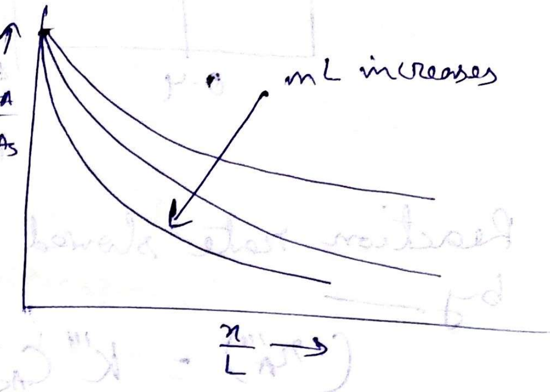
$$m = \sqrt{\frac{k'''}{D_e}}$$

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

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

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

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



Final expression

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

$$\boxed{\therefore \frac{C_A}{C_{A_S}} = \frac{\cosh(m(L-x))}{\cosh(mL)}} \rightarrow$$ Conc. profile within pore for 1st order reaction.

mL → Thiele Modulus $= \sqrt{\frac{k'''}{D_e}}\, L$

With increasing Theile modulus pore diffusion increases and actual reaction rate is slowed down.

Effectiveness Factor ε —

$$\varepsilon = \frac{\text{Actual mean reaction rate within the pore}}{\text{Reaction rate without pour diffusion resistance}}$$

$$= \frac{(-\bar{r}_A)_{mean}}{(-r_A)_{w.t.\ resistance}} = \frac{k''' \bar{C}_A}{k''' C_{A_S}} = \frac{\bar{C}_A}{C_{A_S}}$$

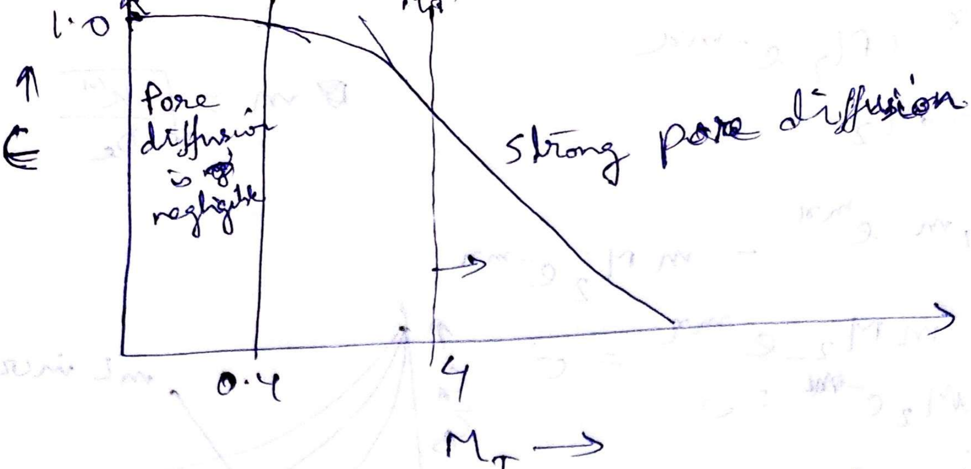
$$\bar{C}_A = \frac{1}{L}\int_0^L C_A \, dx$$

$$\bar{C}_A = \frac{1}{L}\int_0^L \frac{\cosh(m(L-x))}{\cosh(mL)} C_{A_S}\, dx$$

$$\frac{\bar{C}_A}{C_{A_S}} = \frac{1}{L\cosh(mL)} - \sinh(m(L-x)) \Big|_0^L$$

$$\varepsilon = \frac{1}{L\cosh(mL)} \left( \frac{\sinh mL - 0}{m} \right)$$

$$\varepsilon = \left(\frac{\tanh(mL)}{mL}\right) = \frac{\tanh M_T}{M_T} \quad [M_T = mL]$$



Reaction rate slowed down by pore diffusion is given by ——

$$(-r_A''') = k''' C_{As} \epsilon$$

The result for a single pore can approximate the behaviour of particle or various shape like sphere, cylinder or plate. Length of a catalyst particle is defined as ——

$$L_s = \frac{\text{Volume of particle}}{\text{Surface area available for reactant penetration}}$$

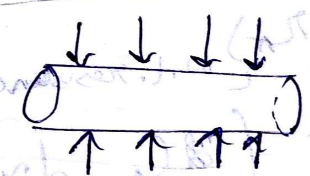
$$M_T = L\sqrt{\frac{k'''}{D_e}}$$

For spherical particle ——

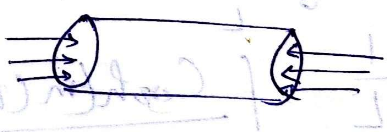
$$L_s = \frac{\frac{4}{3}\pi R^3}{4\pi R^2} = \frac{R}{3}$$

Cylindrical ~~particle~~ particle ——

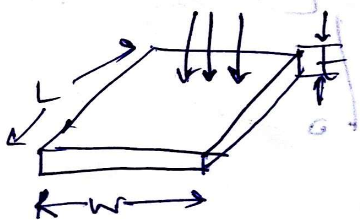
$$L_s = \frac{\pi R^2 L}{2\pi R L} = \frac{R}{2}$$



$$L_s = \frac{\pi R^2 L}{2\pi R^2} = \frac{L}{2}$$



## Plate



$$L_s = \frac{t}{2}$$

## Expression of $\epsilon$ for different particles

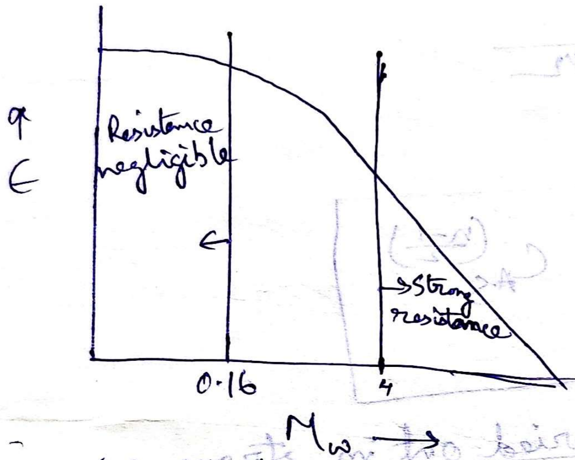
For plate shape particle, $\epsilon = \frac{\tanh M_T}{M_T}$

For spherical particle, $\epsilon = \frac{1}{M_T}\left[\frac{1}{\tanh(3M_T)} - \frac{1}{3M_T}\right]$

For cylindrical particle, $\epsilon = \frac{1}{M_T}\frac{I_1(2M_T)}{I_0(2M_T)}$ [$I_1, I_0$ = Bessell fn.]

Pore diffusion resistance can be determined ~~expression~~ experimentally by Wagner- ~~Waisz~~ Wasz modulus ($M_w$). ~~It only~~ ~~int~~

$$M_w = \frac{L_s^2\left(\frac{-r_A}{C_A}\right)_{obs}}{D_e} = M_T^2\epsilon$$



Comparing behaviour of particle size and rate, we can determine the diffusion regime.

$L_{s_1} \to (-r_A)_1$
$L_{s_2} \to (-r_A)_2$

$$\frac{(-r_A)_1}{(-r_A)_2} = \frac{k''' C_{As}\epsilon_1}{k''' C_{As}\epsilon_2}$$

For strong diffusion regime, $\frac{\epsilon_1}{\epsilon_2} = \frac{M_{T_2}}{M_{T_1}}$

$$\therefore \frac{(-r_A)_1}{(-r_A)_2} = \frac{M_{T_2}}{M_{T_1}} = \frac{L_{s_2}}{L_{s_1}}$$

If reac$^n$ rate is ~~increases~~ inverse of catalyst size, strong diffusion regime.

In diffusion free regime reac$^n$ rate is independent of catalyst size. $\frac{(-r_A)_1}{(-r_A)_2} = 1$

## Thiele Modulus for Arbitrary Reaction :-

$$M_T = \frac{(-r_{As}''')\,L}{\left[2D_e\int_{C_{Ae}}^{C_{As}}(-r_A''')\,dC_A\right]^{1/2}}$$ [For any order]

For n-th order irreversible reac$^n$ —

$$(-r_{As}''') = k''' C_{As}^{n}$$

$$\int_0^{C_{As}} k''' C_A^{n}\,dC_A = \frac{k''' C_{As}^{n+1}}{(n+1)}$$

$$M_T = \frac{k''' C_{As}^{n}\,L}{\left[\frac{k''' C_{As}^{n+1}}{(n+1)}\times 2D_e\right]^{1/2}}$$

$$\boxed{\therefore M_T = L\sqrt{\frac{(n+1)\,k'''}{2D_e}}\;C_{As}^{\left(\frac{n-1}{2}\right)}}$$

If n-th order reaction is carried out in strong pore diffusion regime, ~~what is r~~.

$$-r_A''' = k''' C_{As}^{n}\,\epsilon$$

$$\epsilon = \frac{1}{M_T},\quad \boxed{-r_A''' = \left(\frac{2}{n+1}\,\frac{k''' D_e}{L^2}\right)^{1/2} C_{As}^{\left(\frac{n+1}{2}\right)}}$$

$$-r_A''' = K_{obs}\,C_{As}^{\left(\frac{n+1}{2}\right)}$$

Due to pore diffusion n-th order reaction shows $\frac{n+1}{2}$ th ~~reac~~ order ~~read~~ reac$^n$

$$K_{obs} = \left(\frac{2}{(n+1)L^2}\right)^{1/2}\cdot\left(k''' D_e\right)^{1/2}$$

$$\log K_{obs} = \frac{1}{2}\log\left(k''' D_e\right) + \frac{1}{2}\log\left(\frac{2}{(n+1)\,L^2}\right)$$

$$k''' = k_0 \exp\left[-\frac{E_a}{RT}\right]$$

Mean free path of reactant molecule is very much greater than radius of pore. This is Knudsen diffusion —

$$\boxed{D_e = \cancel{D_0} \exp.\left[-\frac{E_d}{RT}\right]}$$

$$\therefore \ln k''' = \ln k_0 - \frac{E_a}{RT}$$

$$\ln D_e = \cancel{\Phi} \ln D_{e_0} - \frac{E_d}{RT}$$

$$\frac{d(\ln k''')}{dT} = \frac{E_a}{RT^2}$$

$$\frac{d(\ln K_{obs})}{dT} = \frac{1}{2RT^2}(E_a + E_d)$$

$$\frac{d(\ln D_e)}{dT} = \frac{E_d}{RT^2}$$

$$\ln(K_{obs}) = \ln K_{obs,0} - \frac{E_{obs}}{RT\cancel{^2}}$$

$$\boxed{\therefore E_{obs} = \frac{E_a + E_d}{2}}$$

In most of the cases, $E_d << E_a$

$$\boxed{\therefore E_{obs} \approx \frac{E_a}{2}} \rightarrow$$ This is catalytic effect observed activation energy is less than actual activation energy