

# MASS TRANSFER WITH REACTION IN A POROUS CATALYST (INTERNAL DIFFUSIONAL RESISTANCE TO MASS TRANSFER)

## Calculation of diffusivities:

In analysing Knudsen and bulk diffusivity, the important parameter is the size of the pore w.r.t the mean free path of the molecule.

Bulk diffusivity is a function of molecular velocity ( $\bar{v}$ ) and the mean free path ( $\lambda$ ) of the molecule, i.e., it is a function of temperature and pressure.

Knudsen diffusivity is a function of molecular velocity and pore radius  $a$ .

So, the expression of bulk diffusivity  $D_{AB}$  and Knudsen diffusivity  $D_K$  are

$$D_{AB} = \frac{1}{3} \bar{v} \cdot \lambda \left( \lambda \sim \frac{1}{P} \right) \quad \text{and} \quad D_K = \frac{2}{3} a \bar{v} \text{ cm}^2/\text{s}$$

For gases, at atmospheric pressure,  $\lambda \approx 1000\text{\AA}$  order of magnitude. So, diffusion in micropore ( $< 2\text{nm}$ ) is mainly Knudsen diffusion.

The working expression to evaluate  $D_K$  is,

$$D_K = 9.7 \times 10^3 a \left( \frac{T}{M} \right)^{1/2},$$

$T$  = Temperature, K,     $M$  = Molecular weight of A,

$a$  = pore radius of particle

Pore diffusion:

*Combined diffusivity*

$$D = \frac{1}{\frac{1}{D_{AB}} + \frac{1}{D_K}}$$

When pore radius is large, then the equation reduces to  $D = D_{AB}$

### *Effective diffusivity*

Pores of catalyst pellet are not straight and cylindrical, rather they are tortuous and having interconnecting pathways.

So, it is not possible to determine the diffusion at each and every point of this tortuous path.

Hence, Effective Diffusivity is defined as the average diffusivity taking place at any position  $r$  of a spherical pellet.

In this situation, only radial variation in concentration is considered. The radial flux  $W_{Ar}$  is based on the total area (solid + void) normal to the diffusion.

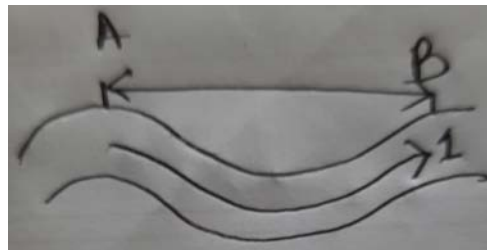
Effective diffusivity considers:

1. Not all the area normal to the direction of the flux are available (i.e., void) for the molecule to diffuse.
2. The paths are tortuous
3. Varying cross-sectional area of the pores.

Hence, effective diffusivity is expressed as,

$$D_e = \frac{D \phi_p \sigma}{\tau}$$

Where,  $\tau = \frac{\text{actual distance a molecule travels between two points}}{\text{Shortest distance between those two points}} = \text{Tortuosity}$



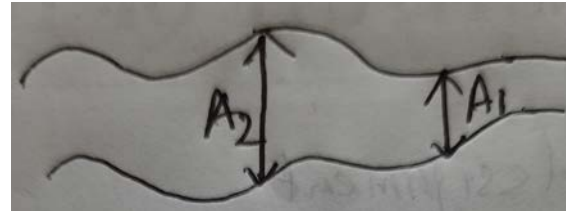
$$\varphi_p = \text{pellet porosity} = \frac{\text{volume of void space}}{\text{total volume (void + solid)}}$$

$\sigma$  = constriction factor

$\sigma$  accounts for the variation in the cross-sectional area that is normal to diffusion.

$$\sigma = f(\text{maximum to minimum pore area}) = f(\beta)$$

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



$D$  = combined diffusivity

# SINGLE CYLINDRICAL PORE: 1<sup>ST</sup> ORDER REACTION

## Flat Plate Geometry

Considering a single cylindrical pore with reactant A diffusing into the pore, a first order reaction  $A \rightarrow \text{product}$

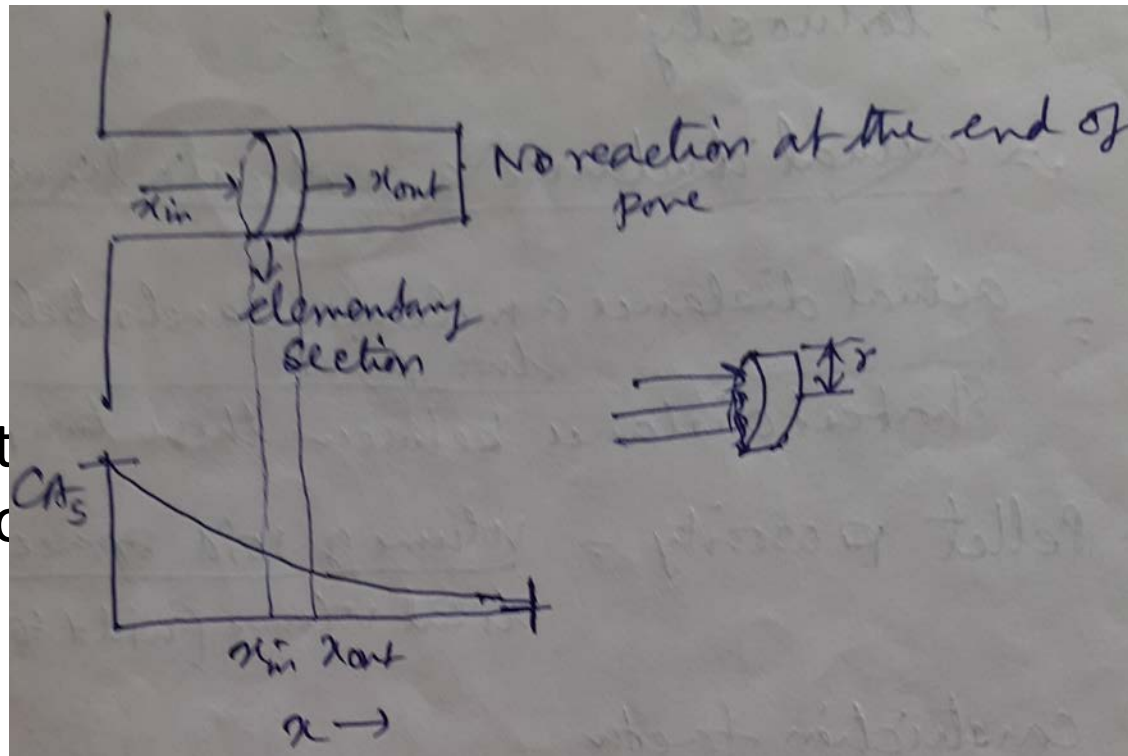
$$-\frac{1}{S} \frac{dN_A}{dt} = k_s C_A$$

$$N_A(\text{or } W_A) = \text{mole flux} = -D_{AB} \frac{dC_A}{dx}$$

The negative sign implies that  $C_A$  decreases with  $x$ .

A single cylindrical pore is considered and the picture shows the change in the concentration of the reactant from the pore mouth to the end of the pore.

An elementary section within the pore is considered, based on which the mole balance equation is presented.



Pore radius is  $r$ ,  $x$  axis is taken to denote the length of the pore.

$C_{As}$  is the concentration of A at the pore mouth and it is assumed there is almost no concentration is experienced at the end of the pore.

Mole balance:

Output – input + disappearance by reaction = accumulation

0



$$-\pi r^2 D \left( \frac{dC_A}{dx} \right)_{out} + \pi r^2 D \left( \frac{dC_A}{dx} \right)_{in} + k_s C_A (2\pi r \Delta x) = 0 \text{-----(1)}$$

$\pi r^2 N_A$  = Total flux throughout the cross-sectional area

$N_A = -D \left( \frac{dC_A}{dx} \right)$  (from Fick's 1<sup>st</sup> law)

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

$k_s C_A$  = rate of disappearance per unit surface area

$2\pi r \Delta x$  = Surface area of the element  $\Delta x$

$k_s$  = Rate constant based on surface



Dividing both sides by  $-\pi r^2 D \Delta x$ ,

$$\frac{\frac{dC_A}{dx_{out}} - \frac{dC_A}{dx_{in}}}{\Delta x} - \frac{2k_s}{rD} \cdot C_A = 0$$

Taking  $\Delta x \rightarrow 0$ ,

$$\frac{d^2 C_A}{dx^2} - \frac{2k_s}{rD} \cdot C_A = 0 \text{-----(2)}$$

the rate constant  $k_s$  is based on unit surface area.

Rate constant based on unit volume,  $k$  can be written as,

$$k_s \cdot S = k \cdot V$$

$$\therefore k = \frac{S}{V} k_s = \frac{\text{Surface}}{\text{Volume}} k_s = \frac{2\pi r l}{\pi r^2 l} \cdot k_s = \frac{2k_s}{r}$$

∴ The equation becomes,

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

This differential equation can be solved by taking auxiliary equations, the general solution is,

$$C_A = M_1 e^{mx} + M_2 e^{-mx} \text{ -----(3)}$$

Where,  $m = \sqrt{\frac{k}{D}} = \sqrt{\frac{2k_s}{rD}}$ ,  $M_1$  and  $M_2$  are constants

The boundary conditions are,

$C_A = C_{As}$  at  $x = 0$  and  $\frac{dC_A}{dx} = 0$  at  $x = L$ , at  $L$  there is no flux

Boundary conditions are put in eq (3) to get the values of  $M_1$  and  $M_2$

Differentiating eq (3),

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

at  $x = L$ ,  $\frac{dC_A}{dx} = 0$ ,

$$\therefore m(M_1 e^{mL} - M_2 \cdot e^{-mL}) = 0$$

$$\text{Or, } M_1 e^{mL} - M_2 \cdot e^{-mL} = 0, \quad m \neq 0$$

at  $x = 0$ ,  $C_A = C_{As}$

$$\therefore C_{As} = M_1 + M_2, \quad M_1 = C_{As} - M_2$$

$$\therefore (C_{As} - M_2)e^{mL} - M_2 \cdot e^{-mL} = 0$$

$$M_2 = \frac{C_{As} e^{mL}}{e^{mL} + e^{-mL}}$$

And

$$M_1 = \frac{C_{As} e^{-mL}}{e^{mL} + e^{-mL}}$$

Therefore, 
$$\frac{C_A}{C_{As}} = \frac{e^{m(L-x)} + e^{-m(L-x)}}{e^{mL} + e^{-mL}} = \frac{\cosh m(L-x)}{\cosh mL}$$

The continuous drop in concentration of reactant on moving into the pores is dependent on the dimensionless quantity  $mL$ , called Thiele Modulus.

To account for the variation in concentration, and also the rate of the reaction from the surface to the interior of the pores, a factor, called Effectiveness Factor ( $\eta$ ) is introduced.

$$\begin{aligned}
\eta &= \frac{r_p}{r_s} = \frac{\text{global rate with diffusion}}{\text{rate without diffusion}} \\
&= \frac{\text{observed rate (overall rate)}}{\text{rate at the surface (where pore diffusion is not considered)}} \\
&= \frac{\text{actual rate}}{\text{rate, if not slowed by diffusion}} = \frac{r_A \text{ with diffusion}}{r_A \text{ without diffusion}} \\
&= \frac{C_A}{C_{As}} \quad \text{for 1}^{\text{st}} \text{ order reaction}
\end{aligned}$$

$$\text{And, } \eta_{\text{1st order}} = \frac{\tanh mL}{mL}$$

It is observed that,  
for **small  $mL$** ,  $mL < 0.5$ , and  $\eta \approx 1$ .

This means that, the pore diffusion resistance is negligible or drop in concentration of the reactant within the pore is very small.

Moreover, for small values of  $mL$ , ( $mL = L \sqrt{\frac{k}{D}}$ ) where  $L$  is the effective length of pore,  $\eta \approx 1$ , i.e., either short pore length or slow reaction or rapid diffusion. ( $k$  and  $D$  are the rate constant and diffusivity respectively)

For **large  $mL$** ,

$$mL > 5 \text{ and } \eta \approx \frac{1}{mL},$$

This means that the reactant concentration drops rapidly within the pore and diffusion strongly influences the rate of the reaction, this is termed as strong pore resistance.

Hence, for a 1<sup>st</sup> order reaction, we can write,

$$-r_A = kC_A = kC_{As}\eta \quad (\text{as, } \frac{C_A}{C_{As}} = \eta)$$

$$\text{Again, } mL = L \sqrt{\frac{k}{D}}$$

So, for **no resistance to pore**,  $\eta \approx 1$  and

$$-r_A = kC_{As}$$

For **strong pore resistance**,  $\eta \approx \frac{1}{mL}$

$$-r_A = kC_{As}\eta = \frac{kC_{As}}{mL} = \frac{\sqrt{kD}}{L} C_{As}$$

