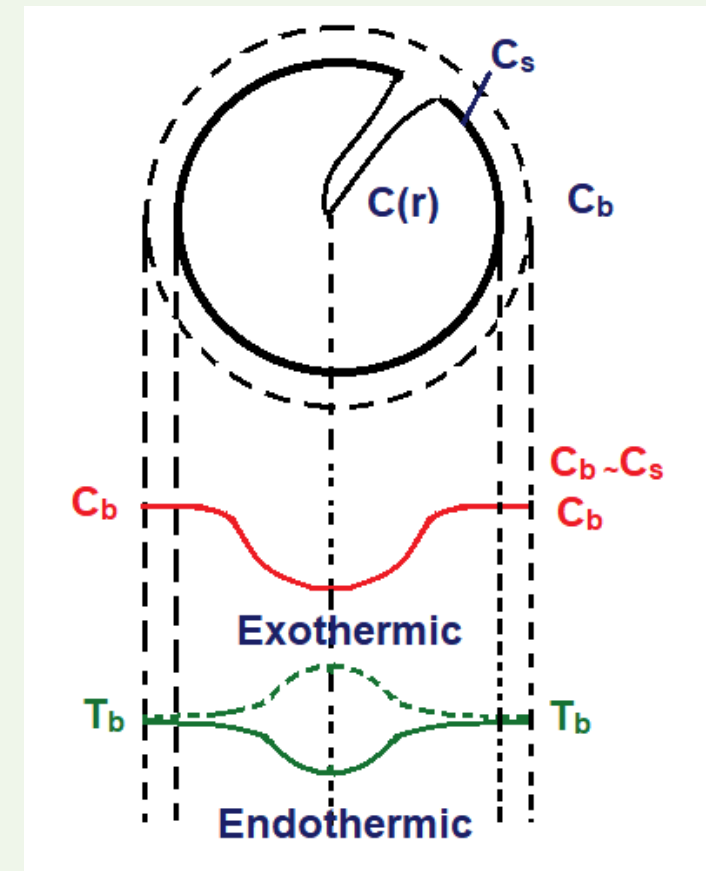


Internal Transport Processes – Reaction and Diffusion in Porous Catalysts

Book: *Chemical Engineering Kinetics*, J. M. Smith, 3rd Edition (Chapter 11), 2nd Edition (Chapter 11)
Elements of Chemical Reaction Engineering, H.S. Fogler, 4th Edition (Chapter 12)

- In case of porous catalyst pellets, it is seen that *all the active surface is internal*
- In the heterogenous reaction sequence, the mass transfer of the reactants take place first from the bulk fluid to the external surface of the catalyst pellet. The reactants then diffuse from the external surface into the pores within the pellet, with reaction taking place only on the catalytic active site in the pore
- The reaction that takes place within the pellet consumes reactant and releases (or absorbs) the heat of reaction
- This results in **'internal' concentration and temperature gradients** which can be large enough to cause significant variation in reaction rate with position inside the pellet
- The *effect of intra-pellet mass transfer* is to *reduce reactant concentration within the pellet*, thus reducing the average rate
- The *effect of temperature gradient* is to *increase the rate for an exothermic reaction* (as temperatures inside the pellet are greater than surface temperature) or *reduce the rate for an endothermic reaction*



- Diffusion through a **porous solid** matrix play an important role in gas-solid reactions
- When the reactant solid is porous, *diffusion through the pore space is necessary for the reactant gas to gain access to the solid surface*
- In a similar manner, the *removal of gaseous products* will also involve this process
- Pore diffusion also plays an important role in reaction of **non-porous solids** when the solid product layer formed is itself porous. *The supply of gaseous reactant and removal of gaseous product have to be accomplished by diffusion through the product layer*

- The diffusion rates in the porous catalysts *cannot simply be predicted by using the bulk diffusivity corrected for reduction in cross-sectional area*
- This is because:
 - the **pore structure in the catalyst is complex** - tortuous, random and interconnected arrangement of the porous region makes the length of the diffusion path unknown
 - **different molecular phenomena are responsible for diffusive transfer** such as bulk diffusion, Knudsen diffusion, surface diffusion
 - complexities associated with **multicomponent diffusion**

A diffusivity term called **effective diffusivity (D_e)** is used to describe the rate of mass transfer in such cases

$$N_i = -D_{e,i} \frac{dC_i}{dx}$$

where N_i = diffusive flux (moles of i diffusing per unit pellet surface area per unit time)

$D_{e,i}$ = effective diffusivity of component i

C_i = concentration of i

x = length co-ordinate

The effective diffusivity is predicted by

- combining the established equations for diffusion in a single cylindrical pore with
- a geometrical model of the pore structure of the catalyst pellet

Bulk diffusion (D_{AB})

- This is the predominant mode of diffusion when **mean free path is small compared to pore diameter**
- The probability of molecules colliding with each other is greater than the probability of it colliding with the wall
- Bulk diffusion is the main mode of diffusion for large pores (diameter > 1000 Å at 1 atm) and high pressures
- Bulk diffusion is *independent of pore diameter*

$$D_{AB} \propto \frac{T^{3/2}}{P}$$

- D_{AB} can be calculated by the **Chapman-Enskog formula**

$$D_{AB} = 0.0018583 \frac{T^{3/2} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}}{P \sigma_{AB}^2 \Omega_{AB}}$$

where D_{AB} = bulk diffusivity, cm²/s

T = temperature, K

P = total pressure of gas mixture, atm

M_A, M_B = molecular weights of gases A and B

σ_{AB} = Lennard-Jones potential energy function constant for molecular pair AB

Ω_{AB} = collision integral (= 1 for molecules that are rigid spheres)

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$$

σ_{AB} and Ω_{AB} obtained from tables

Knudsen diffusion (D_K)

- This is the main mode of mass transfer when **mean free path is larger than the pore diameter**
- The molecules collide more frequently with the wall than with each other
- This is the main mode of diffusion for pores of small diameter and low pressures
- Knudsen diffusivity *depends on average molecular velocity \bar{v} and pore radius r*

$$D_K = \frac{2}{3} r \bar{v} \quad \text{where} \quad \bar{v} = \left(\frac{8RT}{\pi M} \right)^{1/2}$$

$$D_K (\text{cm}^2/\text{s}) = 9.7 \times 10^3 r \sqrt{\frac{T}{M}}$$

where D_K = Knudsen diffusivity, cm^2/s

T = temperature, K

M = molecular weight of the gas

r = pore radius, cm

- Knudsen diffusion is not observed in liquids

Surface diffusion

- Surface diffusion is due to the migration of the material from one site on the surface to another
- This is usually small and is neglected in most cases

In many catalysts and reaction conditions, *both bulk and Knudsen diffusion contribute* to mass transfer in the pore volume

In a binary mixture of A and B gases

$$D = \frac{1}{\frac{(1 - \alpha y_A)}{D_{AB}} + \frac{1}{D_K}}$$

where y_A is the mole fraction of A, D is the combined diffusivity

$$\alpha = 1 + \frac{N_B}{N_A} \quad \text{where } N_A, N_B \text{ are the molal flux of A and B}$$

If the reaction is $A \rightarrow B$, $N_B = -N_A$ (equimolar counter diffusion)

and $\alpha = 0$

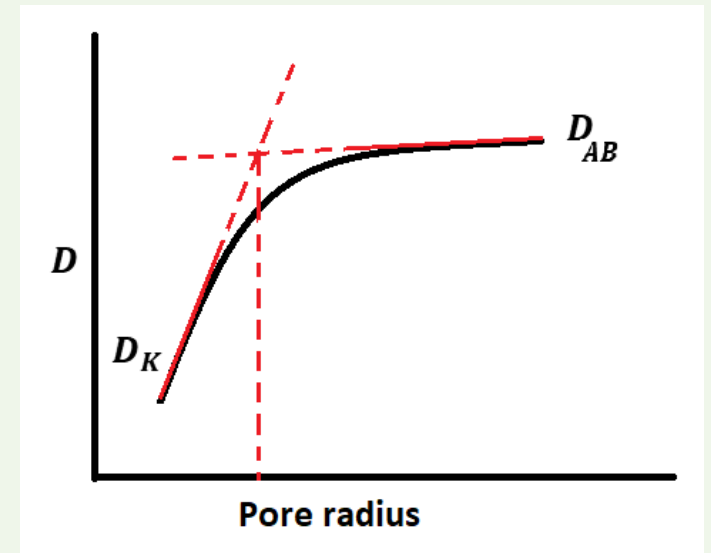
Therefore,

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

Bosanquet formula

When pore radius is large, $D_K \rightarrow \infty$ and $D = D_{AB}$

When pore radius is small, $D_K \rightarrow \text{low}$ and $D = D_K$



The combined diffusivity, D is then converted to effective diffusivity, D_e by means of models for pore structure

Parallel pore model

This model is used to represent the *monodisperse pore size distribution* in a catalyst

For any pore,

$$D_e = \frac{\varepsilon_p D}{\tau}$$

$$\text{where } \varepsilon_p = \text{pellet porosity} = \frac{\text{pore volume (void volume) of particle}}{\text{total volume of particle}} = \frac{v_g \rho_s}{v_g \rho_s + 1} = \rho_p v_g$$

values are usually between 0.3 ~ 0.6

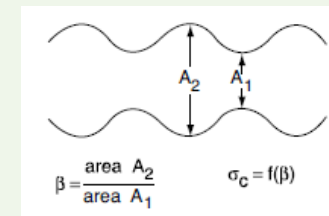
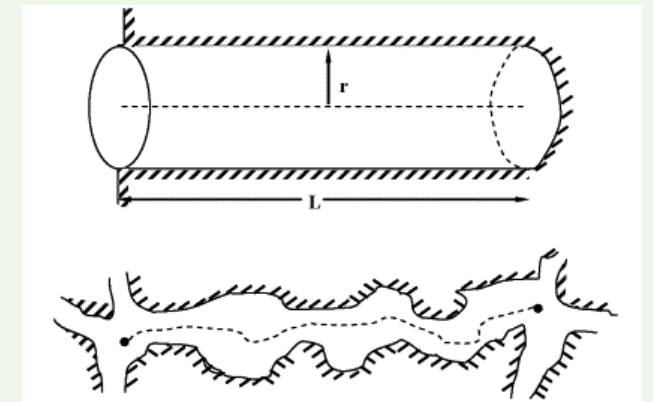
$$\tau = \text{tortuosity} = \frac{\text{actual distance travelled between two points}}{\text{shortest distance between two points}}$$

$\tau > 1$ (usually 2-7) (This factor has a lot of uncertainty associated with it)

In some cases, the effective diffusivity may have another term associated with it

$$D_e = \frac{\varepsilon_p D \sigma_c}{\tau}$$

$$\sigma_c = \text{constriction factor} \quad \sigma_c = f(\beta) \quad \beta = \frac{A_2}{A_1}$$



Random pore model

This model is developed for a **bidisperse system**, where there exists both macro and micro void volume distribution

$$D_e = D_M \varepsilon_M^2 + \varepsilon_\mu^2 \frac{(1+3\varepsilon_M)}{(1-\varepsilon_M)} D_\mu$$

where D_M and D_μ are found by estimating the combined diffusivity for both macro and micro region

$$\frac{1}{D_M} = \frac{1}{D_{AB}} + \frac{1}{(D_K)_M}$$

$$\frac{1}{D_\mu} = \frac{1}{D_{AB}} + \frac{1}{(D_K)_\mu}$$

ε_M and ε_μ are porosity in the macro and micro regions

Using this model for monodisperse systems,

For pellets with only macropores, $\varepsilon_\mu = 0$ and $D_e = D_M \varepsilon_M^2$

For pellets with only micropores, $\varepsilon_M = 0$ and $D_e = D_\mu \varepsilon_\mu^2$

Comparing, these equations with the random pore model,

$$\varepsilon = \frac{1}{\tau}$$

Typically effective diffusivities range from 10^{-2} to 10^{-3} cm²/s