

## Lecture # 34 CHE331A

# Diffusion and Reaction in Heterogeneous Catalysis

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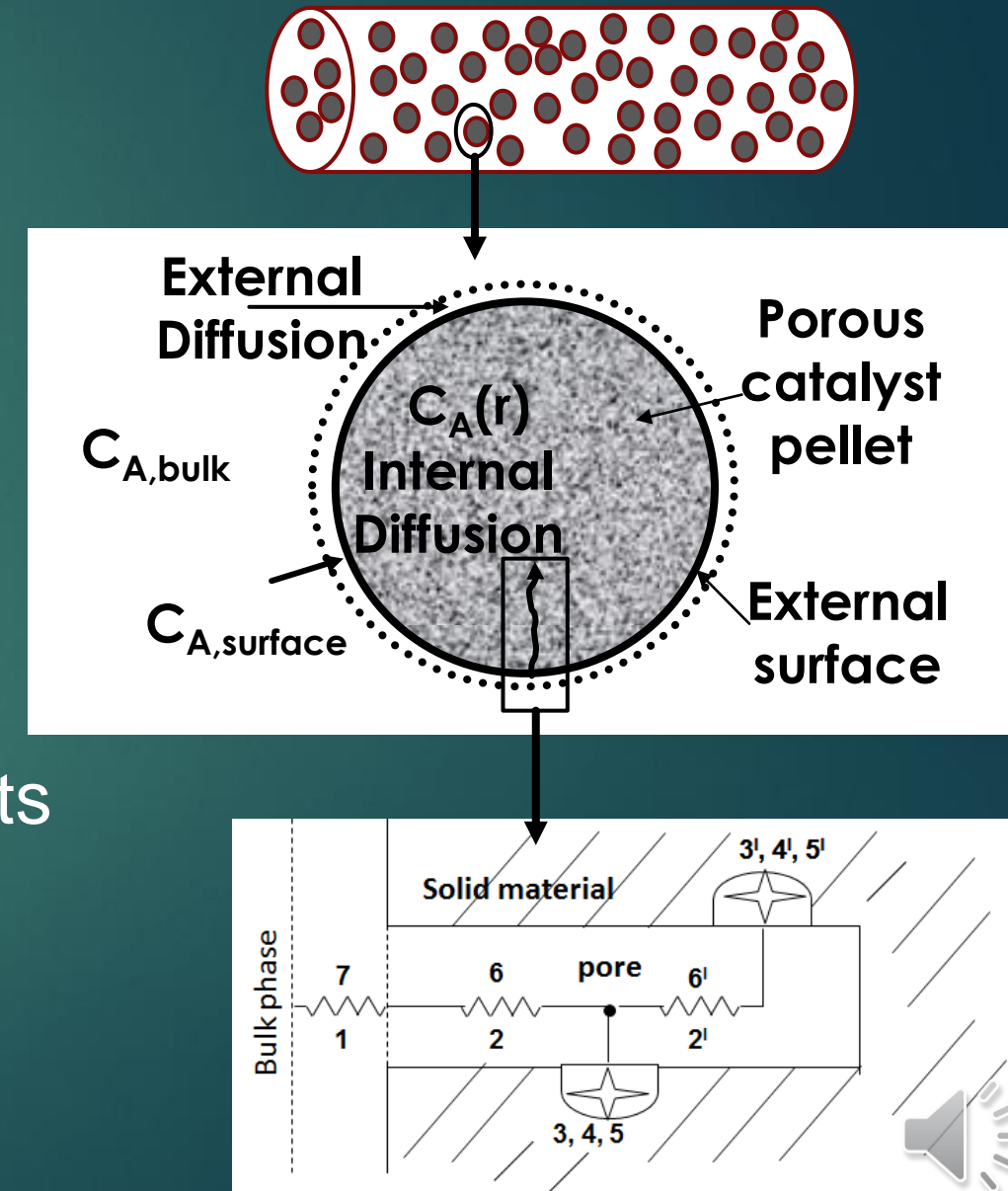
2020-2021 1<sup>st</sup> semester

- ❑ Catalysis
- ❑ Kinetics of Catalytic Reactions
  - ❑ Langmuir-Hinshelwood kinetics
  - ❑ Rate-limiting/controlling step
- ❑ Diffusion and Reaction in porous catalysts



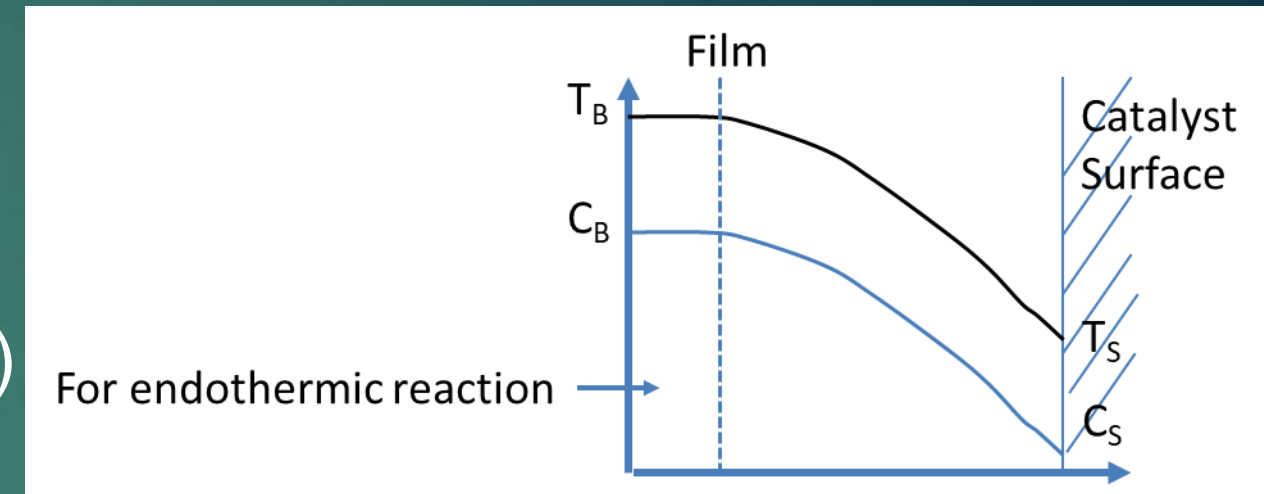
# Activity of the catalyst also depends on how effectively the material can be transported

- ▶ Steps 3, 4 and 5 were discussed
- ▶ Steps 1, 7 and 2, 6 are related to transport of material
- ▶  $C_{A,bulk}$  to  $C_{A,surface}$  is step 1 (or 7)
  - External diffusion
- ▶  $C_{A,surface}$  to  $C_A(r)$  is step 2 (or 6)
  - Internal diffusion – absent for porous catalysts
- ▶ For step 1 the difference between  $C_{A,b}$  and  $C_{A,s}$  depends on the rate of mass transfer and of surface reaction



# Heat and mass transfer coefficient depends on type of reactor

- ▶ Types of reactors containing heterogeneous catalysts (multi-phase systems):
  - fixed bed,
  - fluidized bed, and
  - 3 phase reactors (slurry & trickle bed)
- ▶  $C_{A,b}$  and  $T_b$  – bulk conc & temperature
- ▶  $C_{A,s}$  and  $T_s$  – surface concentration & temperature
- ▶ For fixed bed reactors is when in a two phase system, the reacting fluid flows through the fluid filled with stationary catalyst particles or pellets
  - Reaction and diffusion simultaneously occurring



# At steady state the rate of reaction is equal to the rate of diffusion

► Rate of diffusion:  $r = k_m \cdot a_m (C_{A,b} - C_{A,s})$

- $k_m$  mass transfer coefficient
- $a_m$  external surface area per unit mass

► Rate of reaction:  $r = k C_{A,s}^n$

- $n^{\text{th}}$  order reaction with rate constant  $k$

► At steady state:  $k_m \cdot a_m (C_{A,b} - C_{A,s}) = k C_{A,s}^n$

► For diffusional control  $k_m \cdot a_m \ll k$  the reaction is very fast and  $C_{A,s} \approx 0$

- And,  $r = k_m \cdot a_m (C_{A,b}) \rightarrow$  always 1st order

► For kinetic control  $k_m \cdot a_m \gg k$  and  $C_{A,s} \approx C_{A,b} \rightarrow r = k C_{A,b}^n$



# A more detailed analysis provides with better understanding

► For a first order reaction:  $r = kC_{A,s} = k_m \cdot a_m (C_{A,b} - C_{A,s})$

► Thus,  $C_{A,s} = \frac{k_m \cdot a_m}{k + k_m \cdot a_m} C_{A,b} = \frac{1/k}{1/k + 1/k_m \cdot a_m} C_{A,b}$

$\Rightarrow r = kC_{A,s} = k \frac{1/k}{1/k + 1/k_m \cdot a_m} C_{A,b} = k_{obs} C_{A,b}$  where,  $1/k_{obs} = 1/k + 1/k_m \cdot a_m$

► In design:  $k$  and  $k_m \cdot a_m$  are known and  $k_{obs}$  is calculated and rate is calculated in terms of  $C_{A,b}$

► In interpreting kinetic data:  $k_{obs}$  is measured,  $k_m a_m$  is known and  $k$  can be calculated

► For non first order reactions direct solution is not always possible

- Numerical calculations may be required





# Mass transfer coefficients can be determined from correlations

- ▶  $k_m a_m$  determined from dimensionless groups → characterize the flow conditions
  - Sherwood number,  $\frac{k_m \rho}{G}$ , is an empirical function of Reynolds number,  $\frac{d_p G}{\mu}$ , and Schmidt number,  $\frac{\mu}{\rho D}$
- ▶ Commonly  $j$  – *factors* are used that is defined as  $j_D = \frac{k_m \rho}{G} \left( \frac{a_m}{a_t} \right) \left( \frac{\mu}{\rho D} \right)^{2/3}$ 
  - where, ratio  $a_m/a_t$  – allows for difference in effective and total transfer area
- ▶ For Reynolds number  $> 10$   $j_D = \frac{0.458}{\varepsilon_B} \left( \frac{d_p G}{\mu} \right)^{-0.407}$ 
  - where,  $G$  is the superficial mass velocity;  $d_p$  is the cat. particle dia;  $\mu$  is the viscosity,  $\rho$  is the fluid density;  $D$  is the molecular diffusivity; and  $\varepsilon_B$  is the void fraction of bed



## Steps take to calculate $k_m a_m$

- ▶ Calculate Reynolds number and Schmidts number from the properties given
- ▶  $j_D$  is then calculated and then the value of  $k_m a_m$  is calculated by

$$k_m a_m = j_D \frac{G}{\rho} a_t \left( \frac{\mu}{\rho D} \right)^{-2/3}$$

- ▶ The above requires the calculation of the diffusivity D, which is achieved by the Chapman-Enskog equation from kinetic theory

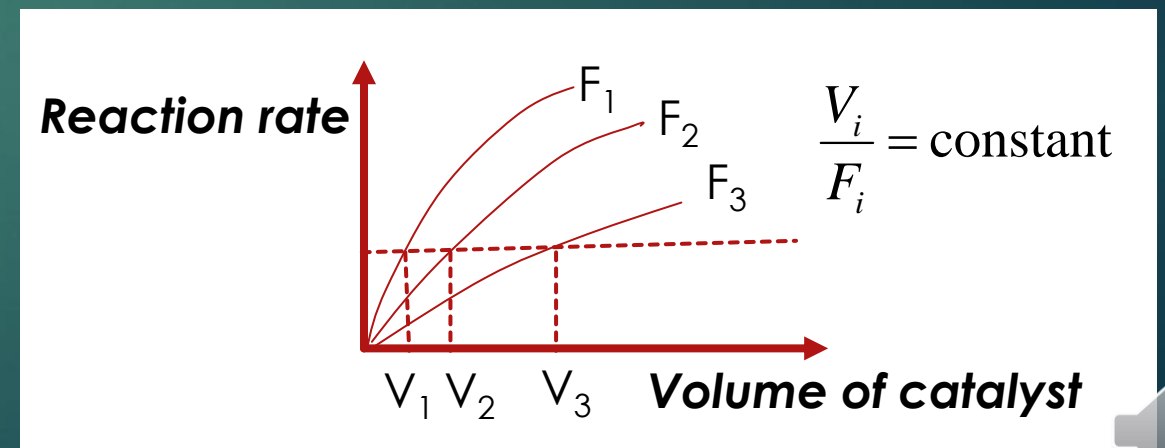
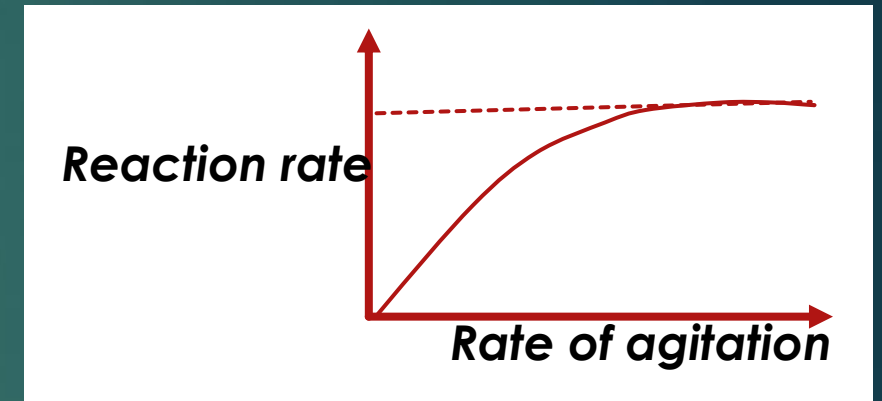
- ▶ For a binary gas A and B 
$$D_{AB} = 1.859 \times 10^{-3} \cdot T^{3/2} \left[ \frac{\left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}}{P_t \sigma_{AB}^2 \Sigma_{AB}} \right]$$

- ▶ Where,  $T$  is in K;  $M_A$  and  $M_B$  are molecular weights in g/mol;  
 $P_t$  is total pressure in atm;  $\sigma_{AB}$  is average collision diameter in Å;  
 $\Sigma_{AB}$  is temperature dependent collision integral



# Effects of external gradient can be seen

- ▶ Required to increase relative velocity of fluid and catalyst particle to decrease external gradient
- ▶ In a slurry reactor this means adequate agitation
  - Asymptotic value corresponds to external mass transfer effects that are small enough to be neglected
- ▶ For fixed bed, the rate should be the same at the same value of space time,
  - with different values of  $V$  and  $F$  so that  $V/F$  are the same





# Mears criterion used to determine presence of external mass transfer

- Based on the observed reaction rate,  $(-r_A)_{obs}$ , and other measured variables we can check if mass transfer from bulk gas phase to catalyst surface can be neglected

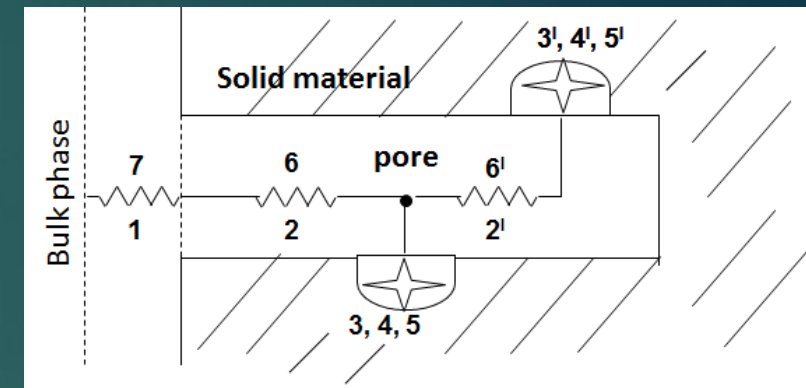
$$\frac{(-r_A)_{obs} \cdot \rho_b \cdot R \cdot n}{k_m C_{A,b}} < 0.15$$

- Where,  
 $n$  is the reaction order;  $R$  is the catalyst particle radius;  
 $\rho_b$  is the bulk density of the catalyst bed;  
 $C_{A,b}$  is the bulk concentration;  
 $k_m$  is the mass transfer coefficient



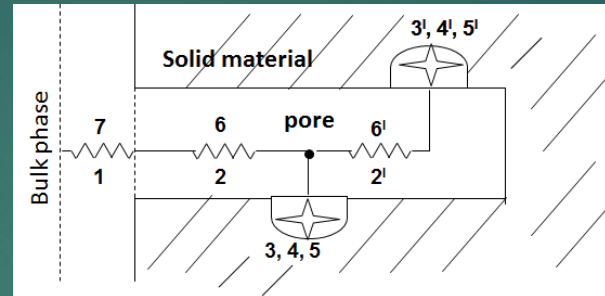
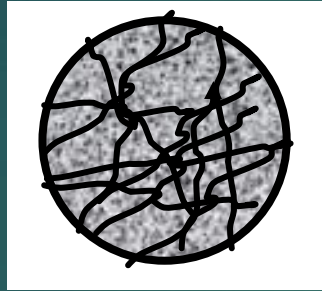
# Internal transport of reactants and products for porous catalysts is required to access all the active sites

- ▶ Involves steps 2 and 6 dealing with the physical transport of material
- ▶ Molecules need to be transported unhampered into and out of the pores by diffusion
  - Pore sizes in porous catalysts are small enough to neglect convective transport
- ▶ Diffusional resistance do exist and we need to estimate how large/small it is
- ▶ Pore structures are complicated so instead of diffusivity → effective diffusivity
- ▶ Effective diffusivity corrects for decrease in cross-sectional area due to solid phase, and also considers other factors responsible for resistance in flow



# Other factors involved in determining effective diffusivity

- ▶ Pores are tortuous, random and interconnected

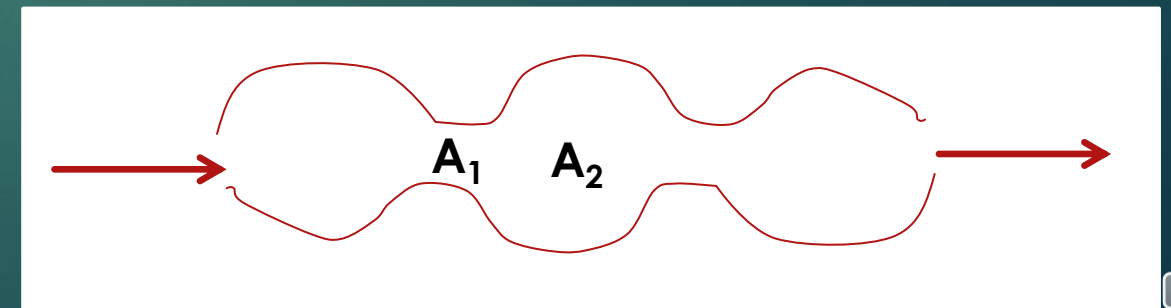
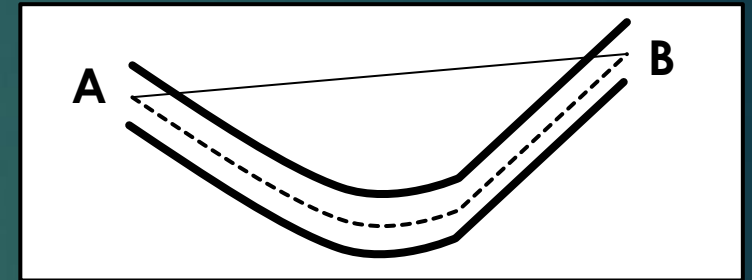


- ▶ Diffusion in the pores are influenced by the presence of the pore walls
  - Molecules may collide more frequently with the walls than another molecule.
  - Happens for gaseous systems and called **Knudsen diffusion**
- ▶ Contribution of surface diffusion
  - Though small in most cases, it must be considered in detailed analysis of diffusion
  - Difficult to access and not considered initially



# Three main pore characteristics are required

- ▶  $\varphi_p$  is the pellet porosity and is typically about 0.4
  - Ratio of [volume of void space] to the [total volume (voids + solids)]
- ▶  $\tau$  is the tortuosity and is typically about 3.0
  - Ratio of [actual distance travelled by a molecule] to the [shortest distance between the points] as shown
- ▶  $\sigma$  is the constriction factor and is typically about 0.8
  - Accounts for variation of cross-sectional area normal to diffusional flow
  - $A_1 = A_2$  implies  $\sigma = 1$  and
  - $10A_1 = A_2$  then  $\sigma = 10$



# Effective diffusivity for a pore system can be calculated based on the pellet properties

- ▶ Effective diffusivity,  $D_{eff}$ , is given (for parallel pore model) by:  $D_{eff} = \frac{D_A \varphi_P \sigma}{\tau}$ 
  - where,  $\varphi_P$  is the porosity;  $\sigma$  is the constriction factor;  $\tau$  is the tortuosity
- ▶  $D_A = \frac{1}{\frac{(1-\alpha y_A)}{D_{AB}} + \frac{1}{(D_k)_A}}$  where,  $\alpha = 1 + \frac{N_A}{N_B}$ ,
  - For A diffusing in a mixture of A & B, and for  $A \rightarrow B$ ,  $N_A = -N_B$  and  $\alpha = 0$
- ▶ Thus, for  $A \rightarrow B$   $D_A = \frac{1}{\frac{1}{D_{AB}} + \frac{1}{(D_k)_A}}$
- ▶  $D_{AB}$  is determined from the Chapman-Enskog formula (previously shown)
- ▶  $(D_k)_A$  formula also exist for its determination





# Summary

- ▶ For multiphase systems it is important to recognize that transport processes are integral to the catalytic phenomena
- ▶ For common heterogeneous catalysts two modes are important
  - External pore diffusion
  - Internal pore diffusion
- ▶ External pore diffusion is important for porous and non-porous catalysts
  - The effects of external pore diffusion can be estimated
- ▶ Internal pore diffusion is important in porous catalysts
  - Need to determine effective diffusivity to estimate its impact

