Advanced Reactor Design

Week 7
External Diffusion Effects

Saba A. Gheni, Ph.D.
Chemical Engineering Department
ghenis@tu.edu.iq

COLLEGE OF ENGINEERING - كلية الهندسة
Tikrit University - جامعة تكريت

Introduction

- This lecture covers external diffusion effects in heterogeneous catalytic reactions.
- We will examine the role of mass transfer limitations in reaction rates and understand how external diffusion impacts overall reactor performance.
- The session will introduce diffusion models and their relevance in reactor design.

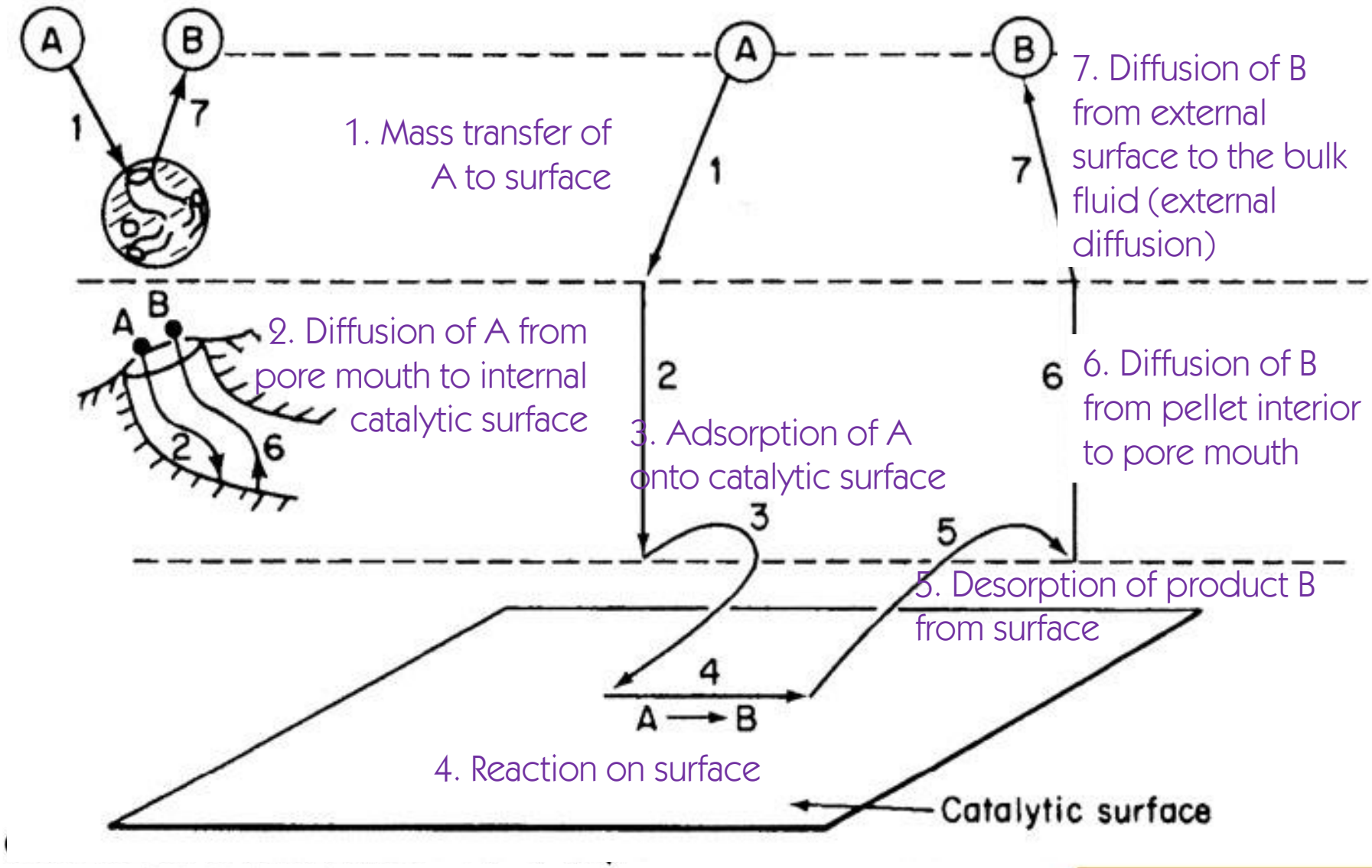
Topics to be Covered

- - Overview of Heterogeneous Catalytic Reactions
- - External Diffusion vs. Internal Diffusion
- - Molar Flux and Diffusion Models
- - Mass Transfer Coefficients and Correlations
- - Boundary Conditions and Transport Equations
- - Reaction-Limited vs. Transport-Limited Regimes
- - Practical Examples in Reactor Design

Objectives

- By the end of this lecture, students should be able to:
- - Understand the role of external diffusion in reaction kinetics.
- - Differentiate between transport-limited and reaction-limited scenarios.
- - Apply Fick's Law and mass transfer principles to catalytic systems.
- - Analyze reactor design considerations to mitigate diffusion limitations.
- - Use mass transfer coefficients and correlations in practical calculations.

Review: Steps in a Heterogeneous Catalytic Reaction



Review: Guidelines for Deducing Mechanisms

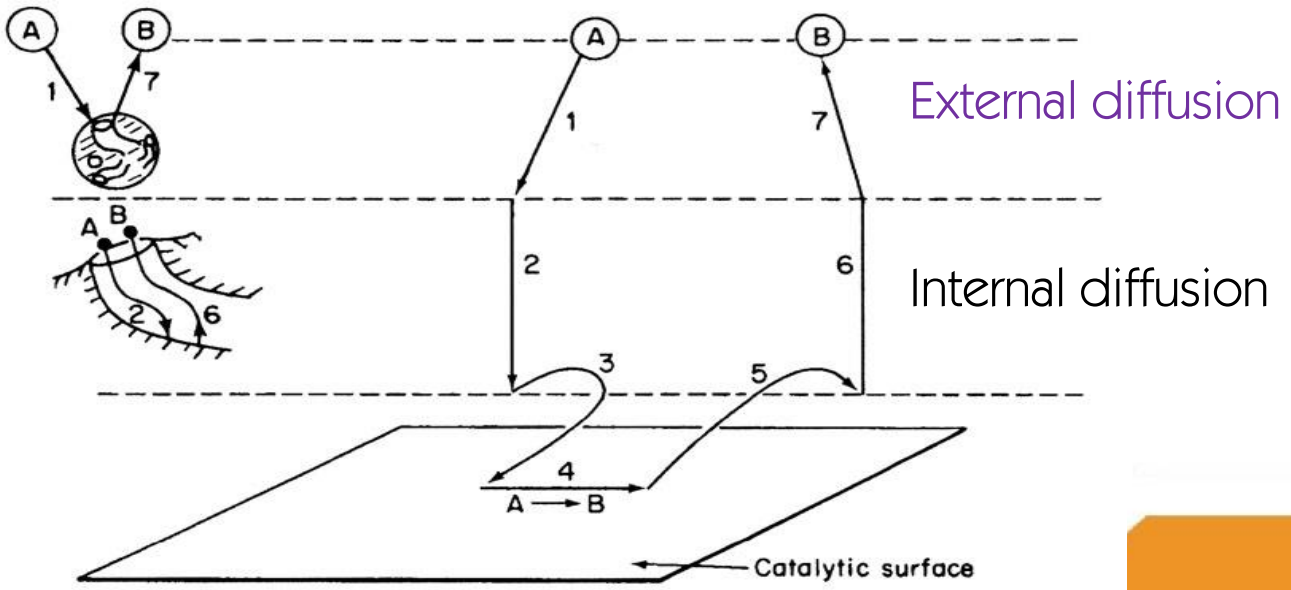
- **More than 70% of heterogeneous reaction mechanisms are surface reaction limited**
  - When you need to propose a rate limiting step, start with a surface reaction limited mechanism unless you are told otherwise
- If a species appears in the numerator of the rate law, it is probably a reactant
- If a species appears in the denominator of the rate law, it is probably adsorbed in the surface

$$i + j \rightarrow k$$

Generic equation: $$-r'_A = \frac{kP_iP_j}{1 + K_iP_i + K_jP_j + K_kP_k}$$

External Diffusion Effects

- Up until now we have assumed adsorption, surface reaction, or desorption was rate limiting, which means there are no diffusion limitations
- In actuality, for many industrial reactions, the overall reaction rate is limited by the rate of mass transfer of products and reactants between the bulk fluid and the catalyst surface
  - External diffusion (today)
  - Internal diffusion (L20, L21 & L21b)
- Goal: Overall rate law for heterogeneous catalyst with external diffusion limitations. This new overall reaction rate would be inserted into the design equation to get W, X_A, C_A, etc



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Mass Transfer

- Diffusion: spontaneous intermingling or mixing of atoms or molecules by random thermal motion
- External diffusion: diffusion of the reactants or products between bulk fluid and external surface of the catalyst
- Molar flux **(W)**
  - Molecules of a given species within a single phase will always diffuse from regions of higher concentrations to regions of lower concentrations
  - This gradient results in a molar flux of the species, (e.g., A), $\mathbf{W}_A$ (moles/area•time), in the direction of the concentration gradient
  - A vector:

$$\mathbf{W}_A = \mathbf{i}W_{Ax} + \mathbf{j}W_{Ay} + \mathbf{k}W_{Az}$$

Molar Flux $\mathbf{W}$ & Bulk Motion $\mathbf{B}_A$

Molar flux consists of two parts

- Bulk motion of the fluid, $\mathbf{B}_A$
- Molecular diffusion flux relative to the bulk motion of the fluid produced by a concentration gradient, $\mathbf{J}_A$
- $\mathbf{W}_A = \mathbf{B}_A + \mathbf{J}_A$ (total flux = bulk motion + diffusion)

Bulk flow term for species A, $\mathbf{B}_A$: total flux of all molecules relative to fixed coordinates ($\Sigma \mathbf{W}_i$) times the mole fraction of A (y_A):

$$\mathbf{B}_A = y_A \Sigma \mathbf{W}_i$$

Or, expressed in terms of concentration of A & the molar average velocity $\mathbf{V}$:

$$\mathbf{B}_A = C_A \mathbf{V} \rightarrow \mathbf{B}_A = C_A \Sigma y_i \mathbf{V}_i \qquad \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} = \frac{\text{mol}}{\text{m}^3} \cdot \frac{\text{m}}{\text{s}}$$

The total molar flux of A in a binary system composed of A & B is then:

$$\mathbf{W}_A = \mathbf{J}_A + C_A \mathbf{V} \quad \leftarrow \text{In terms of concentration of A}$$

$$\mathbf{W}_A = \mathbf{J}_A + C_A \Sigma y_i \mathbf{V}_i$$

$$\mathbf{W}_A = \mathbf{J}_A + y_A (\mathbf{W}_A + \mathbf{W}_B) \quad \leftarrow \text{In terms of mol fraction A}$$

Diffusional Flux of A, J_A & Molar Flux W

$$\mathbf{W}_A = \mathbf{J}_A + \mathbf{B}_A \quad \text{(total flux = diffusion + bulk motion)}$$

$$\mathbf{W}_A = \mathbf{J}_A + C_A \mathbf{V}$$

$$\mathbf{W}_A = \mathbf{J}_A + C_A \sum y_i \mathbf{V}_i$$

$$\mathbf{W}_A = \mathbf{J}_A + y_A (\mathbf{W}_A + \mathbf{W}_B)$$

Diffusional flux of A resulting from a concentration difference, $\mathbf{J}_A$, is related to the concentration gradient by Fick's first law:

$$\mathbf{J}_A = -cD_{AB}\nabla y_A \qquad \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$$

c: total concentration D_{AB}: diffusivity of A in B y_A: mole fraction of A

$$\nabla = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}$$ gradient in rectangular coordinates

Putting it all together:

$$\mathbf{W}_A = -cD_{AB}\nabla y_A + y_A \sum_i \mathbf{W}_i$$ General equation

$$\mathbf{W}_A = -cD_{AB}\nabla y_A + y_A (\mathbf{W}_A + \mathbf{W}_B)$$ molar flux of A in binary system of A & B

Effective diffusivity, D_{Ae}: diffusivity of A though multiple species

Simplifications for Molar Flux

$$\mathbf{W}_A = \mathbf{J}_A + \mathbf{B}_A \quad \text{(total flux = diffusion + bulk motion)}$$

General equation: $$\mathbf{W}_A = -cD_{AB}\nabla y_A + y_A \sum_i \mathbf{W}_i$$

$$\mathbf{W}_A = -cD_{AB}\nabla y_A + y_A (\mathbf{W}_A + \mathbf{W}_B)$$

Molar flux of A in binary system of A & B

- For constant total concentration: $cD_{AB}\nabla y_A = D_{AB}\nabla C_A$
- When there is no bulk flow: $\sum_i W_i = 0$
- For dilute concentrations, y_A is so small that: $y_A \sum_i W_i \approx 0$

For example, consider 1M of a solute diffusing in water, where the concentration of water is 55.6 mol water/dm^3

$$y_A = \frac{C_A}{C_A + C_W} = \frac{1}{1+55.6} \rightarrow y_A = 0.018 \approx 0$$

Evaluation of Molar Flux

Type 1: Equimolar counter diffusion (EMCD):

- For every mole of A that diffuses in a given direction, one mole of B diffuses in the opposite direction
- Fluxes of A and B are equal in magnitude & flow counter to each other: $\mathbf{W}_A = -\mathbf{W}_B$

$$W_A = -cD_{AB}\nabla y_A + y_A(W_A + W_B) \quad (y_A \approx 0 \text{ bulk motion})$$

$$\rightarrow W_A = -cD_{AB}\nabla y_A \quad \text{or for constant total concentration:} \quad W_A = -D_{AB}\nabla C_A$$

Type 2: Dilute concentration of A: $y_A \sum_i W_i \approx 0$

$$W_A = -cD_{AB}\nabla y_A + y_A(W_A + W_B) \rightarrow W_A = -cD_{AB}\nabla y_A$$

($y_A \approx 0$)

or constant C_{total} :

$$W_A = -D_{AB}\nabla C_A$$

Type 3: Diffusion of A though stagnant B: $\mathbf{W}_B = 0$

$$W_A = -cD_{AB}\nabla y_A + y_A(W_A + W_B) \rightarrow W_A = \frac{-1}{1-y_A} cD_{AB}\nabla y_A$$

($W_B \approx 0$)

Type 4: Forced convection drives the flux of A. Diffusion in the direction of flow (J_A) is tiny compared to the bulk flow of A in that direction (z):

$$W_A = -cD_{AB}\nabla y_A + C_A V_z \rightarrow W_A = C_A V_z$$

($-cD_{AB}\nabla y_A \approx 0$ diffusion)

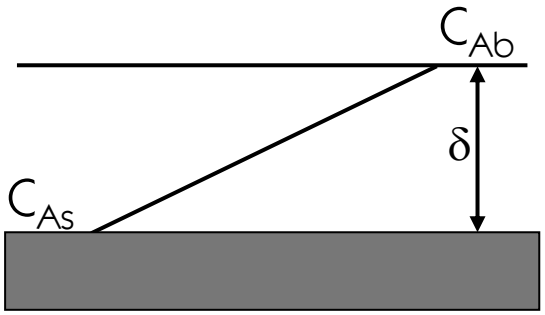
$$\rightarrow W_A = C_A \frac{\upsilon}{A_c}$$

υ ← volumetric flow rate

A_c ← cross-sectional area

Boundary Conditions

- Boundary layer
  - Hydrodynamics boundary layer thickness: distance from a solid object to where the fluid velocity is 99% of the bulk velocity U_0
  - Mass transfer layer thickness: distance δ from a solid object to where the concentration of the diffusing species is 99% of the bulk concentration
- Typically diffusive transport is modelled by treating the fluid layer next to a solid boundary as a stagnant film of thickness δ



C_{As}: Concentration of A at surface C_{Ab}: Concentration of A in bulk

In order to solve a design equation that accounts for external diffusion limitations we need to set the boundary conditions

Types of Boundary Conditions

1. Concentration at the boundary (i.e., catalyst particle surface) is specified:
   - If a specific reactant concentration is maintained or measured at the surface, use the specified concentration
   - When an instantaneous reaction occurs at the boundary, then $C_{As} \approx 0$
2. Flux at the boundary (i.e., catalyst particle surface) is specified:
   a) No mass transfer at surface (nonreacting surface)

$$W_A\big|_{surface} = 0$$

   b) Reaction that occurs at the surface is at steady state: set the molar flux on the surface equal to the rate of reaction at the surface

$$W_A\big|_{surface} = -r_A''$$

reaction rate per unit surface area (mol/m^2·sec)

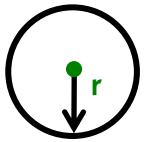
   c) Convective transport across the boundary layer occurs

$$W_A\big|_{boundary} = k_c\left(C_{Ab} - C_{As}\right)$$

3. Planes of symmetry: concentration profile is symmetric about a plane
   - Concentration gradient is zero at the plane of symmetry

Radial diffusion in a tube:

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



Radial diffusion in a sphere

Correlation for Convective Transport Across the Boundary Layer

For convective transport across the boundary layer, the boundary condition is:

$$W_A\big|_{boundary} = k_c\left(C_{Ab} - C_{As}\right)$$

The mass transfer coefficient for a single spherical particle is calculated from the Frössling correlation:

$$k_c = \frac{D_{AB}}{d_p}\,Sh$$

k_c: mass transfer coefficient D_{AB}: diffusivity (m^2/s)

d_p: diameter of pellet (m) Sh: Sherwood number (dimensionless)

$$Sh = 2 + 0.6\,Re^{1/2}\,Sc^{1/3}$$

Reynold's number $Re = \frac{U d_p}{\nu}$ Schmidt number: $Sc = \frac{\nu}{D_{AB}}$

ν: kinematic viscosity or momentum diffusivity (m^2/s); $\nu = \mu/\rho$

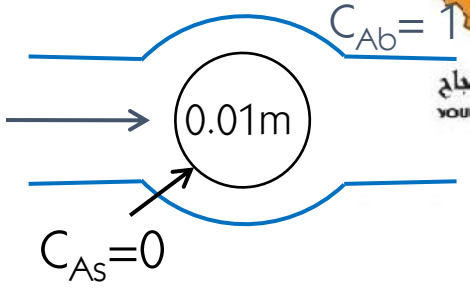
ρ: fluid density (kg/m^3) μ: viscosity ($kg/m \cdot s$)

U: free-stream velocity (m/s) d_p: diameter of pellet (m)

D_{AB}: diffusivity (m^2/s)

Rapid Rxn on Catalyst Surface

- Spherical catalyst particle in PBR
- Liquid velocity past particle U = 0.1 m/s
- Catalyst diameter d_p= 1 cm = 0.01 m
- Instantaneous rxn at catalyst surface $C_{As} \approx 0$
- Bulk concentration C_{Ab}= 1 mol/L
- $\nu \equiv$ kinematic viscosity = 0.5×10^{-6} m^2/s
- $D_{AB} = 1 \times 10^{-10}$ m^2/s



Determine the flux of A to the catalyst particle

The velocity is non-zero, so we primarily have convective mass transfer to the catalyst particle:

$$W_A\big|_{boundary} = k_c\left(C_{Ab} - C_{As}\right)$$

Compute k_c from Frössling correlation:

$$k_c = \frac{D_{AB}}{d_p} Sh \qquad Sh = 2 + 0.6\,Re^{1/2}\,Sc^{1/3} \qquad Re = \frac{U d_p}{\nu} \qquad Sc = \frac{\nu}{D_{AB}}$$

$$Re = \frac{0.1\,m/s\,(0.01m)}{0.5\times10^{-6}\,m^2/s} \rightarrow \boxed{Re = 2000} \qquad Sc = \frac{0.5\times10^{-6}\,m^2/s}{1\times10^{-10}\,m^2/s} \rightarrow \boxed{Sc = 5000}$$

$$Sh = 2 + 0.6(2000)^{1/2}(5000)^{1/3} \rightarrow \boxed{Sh = 461}$$

$$k_c = \frac{1\times10^{-10}\,m^2/s}{0.01m}\,461 \rightarrow k_c = 4.61\times10^{-6}\,\frac{m}{s}$$

Rapid Rxn on Catalyst Surface

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- Liquid velocity past particle U = 0.1 m/s
- Catalyst diameter d_p= 1cm = 0.01m
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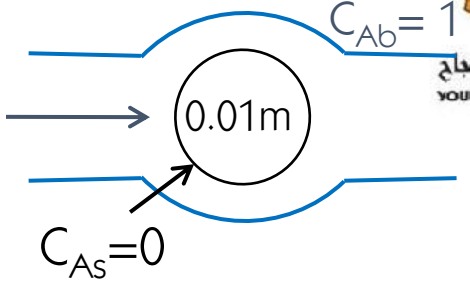

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The velocity is non-zero, so we primarily have convective mass transfer to the catalyst particle:

$$W_A|_{boundary} = k_c\left(C_{Ab} - C_{As}\right)$$

Computed k_c from Frössling correlation:

$$k_c = \frac{D_{AB}}{d_p}Sh \qquad k_c = 4.61\times10^{-6}\,\frac{m}{s}$$

$$W_A|_{boundary} = 4.61\times10^{-6}\,\frac{m}{s}\left(1\frac{mol}{L}\left(\frac{1000L}{m^3}\right) - 0\right) \rightarrow W_A|_{boundary} = 4.61\times10^{-3}\,\frac{mol}{m^2\cdot s}$$

Because the reactant is consumed as soon as it reaches the surface

$$W_A|_{boundary} = -r_{As}'' = 4.61\times10^{-3}\,\frac{mol}{m^2\cdot s}$$

For the previous example, derive an equation for the flux if the reaction were not instantaneous, and was instead at steady state ($W_{A|surface} = -r_A''$) and followed the kinetics: $-r_{AS}'' = k_r C_{As}$ (Observed rate is not diffusion limited)

$$k_c\left(C_{Ab} - C_{As}\right) = W_A\big|_{boundary} \qquad -r_{As}'' = k_r C_{As}$$

Because the reaction at the surface is at the steady state & not instantaneous:

$$C_{As} \neq 0 \qquad W_A\big|_{boundary} = -r_{As}'' = k_r C_{As}$$

So if C_{As} were in terms of measurable species, we would know $W_{A,boundary}$

Use the equality to put C_{As} in terms of measurable species (solve for C_{As})

$$k_c\left(C_{Ab} - C_{As}\right) = k_r C_{As} \rightarrow k_c C_{Ab} - k_c C_{As} = k_r C_{As} \rightarrow k_c C_{Ab} = k_r C_{As} + k_c C_{As}$$

$$\rightarrow k_c C_{Ab} = C_{As}\left(k_r + k_c\right) \rightarrow \frac{k_c C_{Ab}}{k_r + k_c} = C_{As}$$ Plug into $-r''_{As}$

$$W_A\big|_{boundary} = -r''_{As} = k_r C_{As} \rightarrow W_A\big|_{boundary} = -r''_{As} = \frac{k_r k_c C_{Ab}}{k_r + k_c}$$

Rapid rxn, $k_r >> k_c \rightarrow k_c$ in denominator is negligible

$$-r''_{As} = \frac{k_r k_c C_{Ab}}{k_r + k_c} \rightarrow -r''_{As} = \frac{k_r k_c C_{Ab}}{k_r} \rightarrow -r''_{As} = k_c C_{Ab}$$

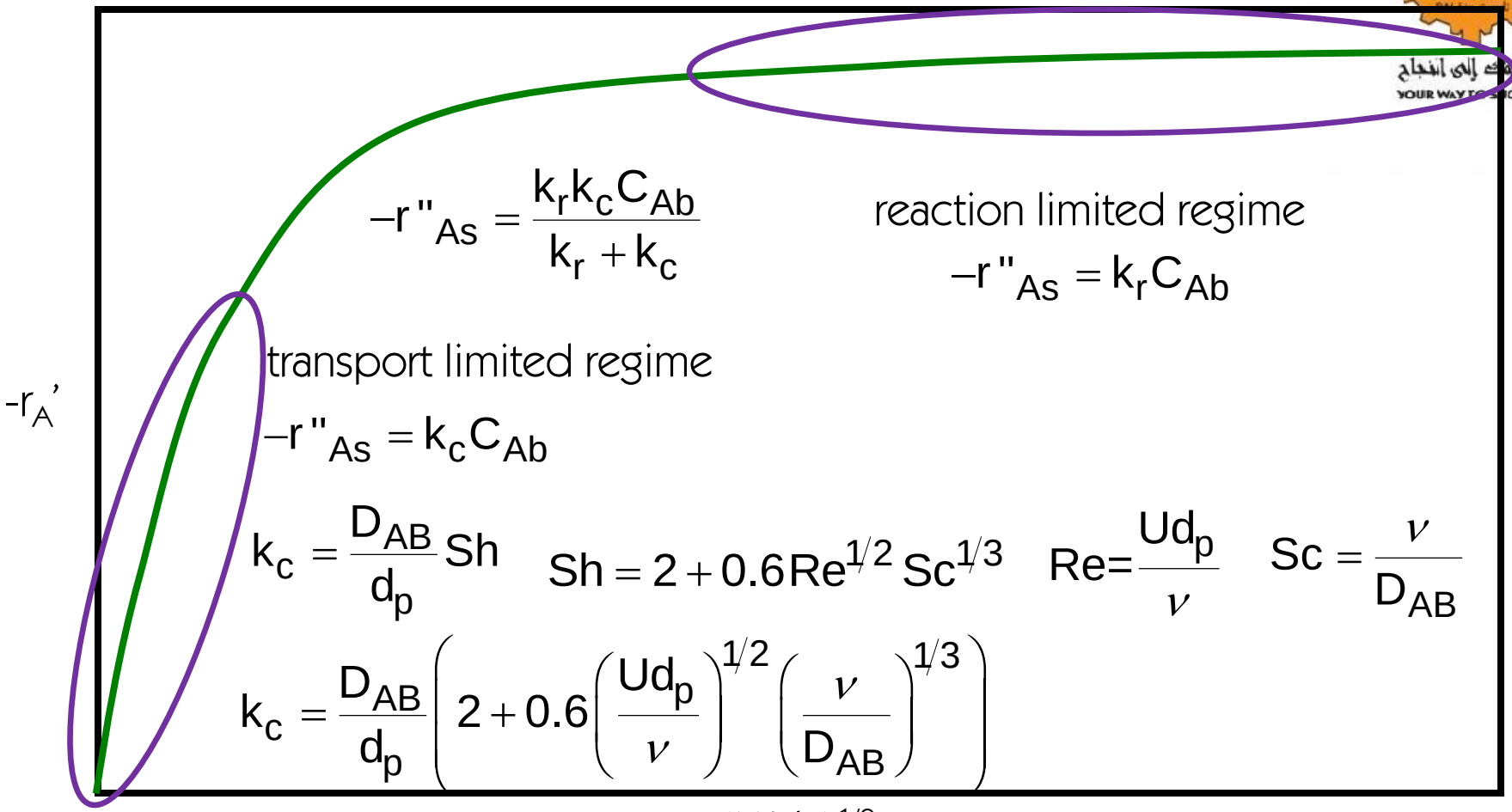
Diffusion limited

Slow rxn, $k_r << k_c \rightarrow k_r$ in denominator is negligible

$$-r''_{As} = \frac{k_r k_c C_{Ab}}{k_r + k_c} \rightarrow -r''_{As} = \frac{k_r k_c C_{Ab}}{k_c} \rightarrow -r''_{As} = k_r C_{Ab}$$

Reaction limited

Mass Transfer & Rxn Limited Reactions



When measuring rates in the lab, use high velocities or small particles to ensure the reaction is not mass transfer limited

Mass Transfer & Rxn Limited Reactions

$$-r''_{As} = \frac{k_r k_c C_{Ab}}{k_r + k_c}$$

reaction limited regime

$$-r''_{As} = k_r C_{Ab}$$

Proportionality is useful for assessing parameter sensitivity

transport limited regime

$-r_A'$

$$-r''_{As} = k_c C_{Ab}$$

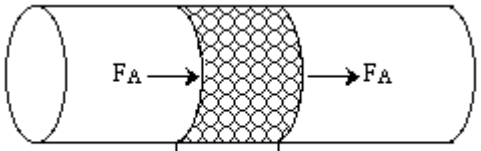
$$k_c = \frac{D_{AB}}{d_p} Sh \qquad Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \qquad Re = \frac{U d_p}{\nu} \qquad Sc = \frac{\nu}{D_{AB}}$$

$$k_c = \frac{D_{AB}}{d_p}\left(2 + 0.6\left(\frac{U d_p}{\nu}\right)^{1/2}\left(\frac{\nu}{D_{AB}}\right)^{1/3}\right)$$

$(U/d_p)^{1/2}$ = (fluid velocity/particle diameter)$^{1/2}$

$$k_c \propto \frac{D_{AB}^{2/3}}{\nu^{1/6}}\left(\frac{U^{1/2}}{d_p^{1/2}}\right) \rightarrow \frac{k_{c2}}{k_{c1}} = \left(\frac{U_2}{U_1}\right)^{1/2}\left(\frac{D_{AB2}}{D_{AB1}}\right)^{2/3}\left(\frac{\nu_1}{\nu_2}\right)^{1/6}\left(\frac{d_{p1}}{d_{p2}}\right)^{1/2}$$

Mass Transfer Limited Rxn in PBR



$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

A steady state mole balance on reactant A between z and z + Δz :

$$F_{Az}\big|_z - F_{Az}\big|_{z+\Delta z} + r''_A\, a_c (A_c \Delta z) = 0 \quad \text{where } a_c = \frac{6(1-\phi)}{d_p}$$

a_c: external surface area of catalyst per volume of catalytic bed (m^2/m^3)

ϕ: porosity of bed, void fraction d_p: particle diameter (m)

r''_A: rate of generation of A per unit catalytic surface area ($mol/s \cdot m^2$)

Divide out $A_c \Delta z$: $\dfrac{F_{Az}\big|_z - F_{Az}\big|_{z+\Delta z}}{A_c \Delta z} + r''_A\, a_c = 0$

Take limit as $\Delta z \rightarrow 0$: $-\dfrac{1}{A_c}\left(\dfrac{dF_{Az}}{dz}\right) + r''_A\, a_c = 0$

Put F_{az} and $-r_A''$ in terms of C_A: $F_{Az} = W_{Az} A_c = (J_{Az} + B_{Az}) A_c$

Axial diffusion is negligible compared to bulk flow (convection)

$$F_{Az} = B_{Az} A_c = U C_A A_c$$

$$-\frac{d(UC_A)}{dz} + r''_A\, a_c = 0$$

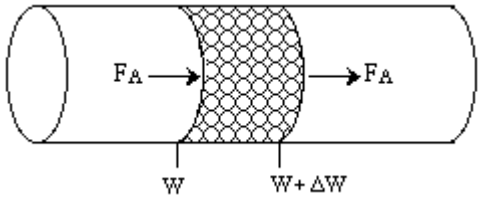
Substitute into the mass balance

$$\rightarrow -\left(U\frac{dC_A}{dz} + C_A\frac{dU}{dz}\right) + r''_A\, a_c = 0$$

($\frac{dU}{dz} = 0$)

$$\rightarrow -U\frac{dC_A}{dz} + r''_A\, a_c = 0$$

Mass Transfer Limited Rxn in PBR



$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D \qquad -U\frac{dC_A}{dz} + r''_A a_c = 0$$

At steady-state:

Molar flux of A to particle surface = rate of disappearance of A on the surface

$$-r''_A = W_{Ar} = k_c\left(C_A - C_{As}\right)$$ Substitute

mass transfer coefficient $k_c = D_{AB}/\delta$ (s^{-1}) δ: boundary layer thickness

C_{As}: concentration of A at surface C_A: concentration of A in bulk

$$-U\frac{dC_A}{dz} - k_c a_c\left(C_A - C_{As}\right) = 0$$ $C_{As} \approx 0$ in most mass transfer-limited rxns

$$\rightarrow -U\frac{dC_A}{dz} - k_c a_c C_A = 0$$ Rearrange & integrate to find how C_A and the r''_A varies with distance down reactor

$$\rightarrow -U\frac{dC_A}{dz} = k_c a_c C_A \rightarrow \int_{C_{A0}}^{C_A}\frac{dC_A}{C_A} = \int_0^z -\frac{k_c a_c}{U}dz \rightarrow \ln\frac{C_A}{C_{A0}} = -\frac{k_c a_c}{U}z$$

$$\rightarrow \frac{C_A}{C_{A0}} = \exp\left[-\frac{k_c a_c}{U}z\right] \rightarrow \boxed{C_A = C_{A0}\exp\left[-\frac{k_c a_c}{U}z\right]}$$

$$\boxed{-r''_A = k_c C_{A0}\exp\left[-\frac{k_c a_c}{U}z\right]}$$

Summary

- In this lecture, we explored the impact of external diffusion on catalytic reactions. We analyzed molar flux, diffusion mechanisms, and boundary conditions governing mass transfer. Key takeaways include differentiating between transport-limited and reaction-limited regimes, using mass transfer correlations, and applying diffusion principles in reactor design.