Advanced Reactor Design

Week 8

External Diffusion Effects-continued

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Introduction

- This lecture continues the discussion on external diffusion effects in heterogeneous catalytic reactions.
- We will further analyze the impact of diffusion limitations, mass transfer coefficients, and effective transport parameters on overall reactor performance.
- The goal is to develop a comprehensive understanding of how external diffusion influences reaction kinetics and reactor design strategies.

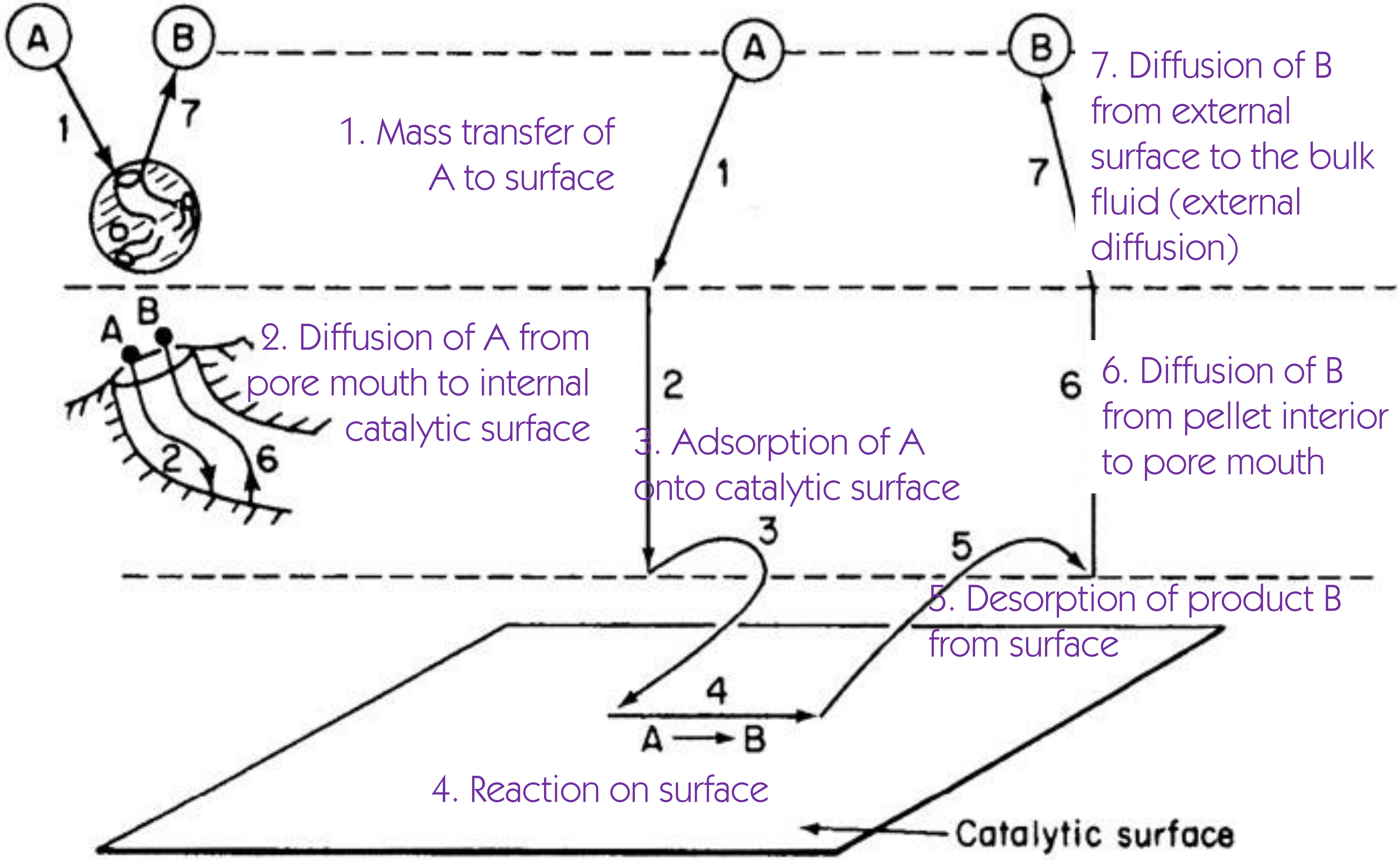
Topics to be Covered

- - Review of External Diffusion in Catalysis
- - Molar Flux and Diffusion Mechanisms
- - Transport Coefficients and Effective Diffusivity
- - Boundary Conditions for Mass Transfer
- - Correlation for Convective Transport
- - Reaction-Limited vs. Diffusion-Limited Regimes
- - Practical Applications in Reactor Design

Objectives

- By the end of this lecture, students should be able to:
- - Explain the principles of external diffusion and its impact on reaction kinetics.
- - Apply mass transfer equations to heterogeneous catalytic reactions.
- - Utilize boundary conditions in solving mass transfer problems.
- - Differentiate between reaction-limited and diffusion-limited systems.
- - Implement transport correlations in practical engineering calculations.

Review: Steps in a Heterogeneous Catalytic Reaction



1. Mass transfer of A to surface

2. Diffusion of A from pore mouth to internal catalytic surface

3. Adsorption of A onto catalytic surface

4. Reaction on surface

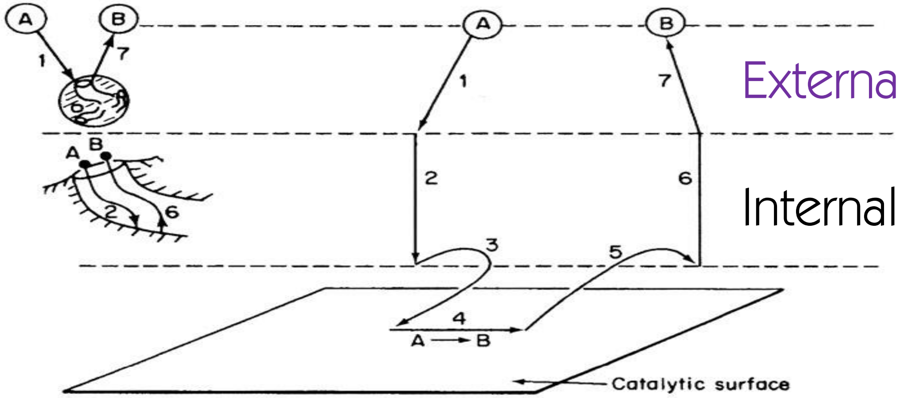
5. Desorption of product B from surface

6. Diffusion of B from pellet interior to pore mouth

7. Diffusion of B from external surface to the bulk fluid (external diffusion)

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
  - Internal diffusion
- 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



External diffusion

Internal diffusion

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 **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):

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

Or, expressed in terms of concentration of A & the <u>molar average velocity</u> **V**:

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

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

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

←In terms of concentration of A

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

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

←In terms of mol fraction A

Diffusional Flux of A, J_A & Molar Flux W

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

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

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

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

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

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

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

$$\nabla = i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z}$$ 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

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

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

Simplifications for Molar Flux

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

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

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

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: $\mathbf{W}_A = -\mathbf{W}_B$

$$W_A = -cD_{AB}\nabla y_A + \cancelto{0}{y_A(W_A + W_B)}$$ bulk motion ≈ 0

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

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

$$W_A = -cD_{AB}\nabla y_A + \cancelto{0}{y_A}(W_A + W_B) \rightarrow W_A = -cD_{AB}\nabla y_A$$

or constant C_{total}:

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

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

$$W_A = -cD_{AB}\nabla y_A + y_A(W_A + \cancelto{0}{W_B}) \rightarrow W_A = \frac{-1}{1-y_A}cD_{AB}\nabla y_A$$

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):

$$W_A = \cancelto{0}{-cD_{AB}\nabla y_A} + C_A V_z \rightarrow W_A = C_A V_z \rightarrow W_A = C_A \frac{\upsilon}{A_c}$$

diffusion ≈ 0

υ ← volumetric flow rate

A_c ← cross-sectional area

P14-2_B

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

$$\mathbf{U} = \sum y_i\mathbf{U}_i$$

Binary System

$$\mathbf{W}_A = C_A\mathbf{U}_A \text{ and } \mathbf{W}_B = C_B\mathbf{U}_B$$

$$\mathbf{U} = y_A\mathbf{U}_A + y_B\mathbf{U}_B$$

Multiply and divide by

$$\mathbf{U} = \left[\frac{C_A\mathbf{U}_A + C_B\mathbf{U}_B}{C}\right] = \frac{\mathbf{W}_A + \mathbf{W}_B}{C}$$

$$C_A\mathbf{U} = C_A\frac{\mathbf{W}_A + \mathbf{W}_B}{C} = y_A\left[\mathbf{W}_A + \mathbf{W}_B\right]$$

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

1. For equal molar counter diffusion

$$\mathbf{W}_{\mathrm{A}} = \mathbf{J}_{\mathrm{A}} + y_{\mathrm{A}}\left(\mathbf{W}_{\mathrm{A}} + \mathbf{W}_{\mathrm{B}}\right)$$

$$\mathbf{J}_{\mathrm{A}} = -D_{\mathrm{AB}}\nabla C_{\mathrm{A}}$$

$$\left(\mathbf{W}_{\mathrm{A}} = -\mathbf{W}_{\mathrm{A}}\right)$$

$$\mathbf{W}_{\mathrm{A}} = -D_{\mathrm{AB}}\nabla C_{\mathrm{A}}$$

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

2. Diffusion through a stagnant film,

3. For dilute concentration

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

2. Diffusion through a stagnant film, $W_B = 0$

$$\mathbf{J}_A = -D_{AB}\nabla C_A$$

$$\mathbf{W}_A = -D_{AB}\nabla C_A + y_A\mathbf{W}_A$$

$$\mathbf{W}_A = -\frac{D_{AB}}{1-y_A}\nabla C_A$$

3. For dilute concentration

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

2. Diffusion through a stagnant film, $W_B = 0$

$$\mathbf{W}_A = -D_{AB}\nabla C_A + y_A \mathbf{W}_A$$

$$\mathbf{W}_A = -\frac{D_{AB}}{1 - y_A}\nabla C_A$$

3. For dilute concentration

$$y_A << 1$$

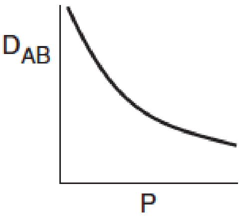
$$\mathbf{W}_A = -D_{AB}\nabla C_A$$

TABLE 14-2. DIFFUSIVITY RELATIONSHIPS FOR GASES, LIQUIDS, AND SOLIDS

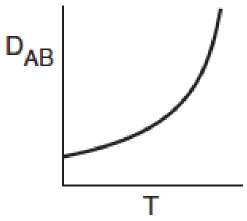
	Order of Magnitude		
Phase	cm^2/s	m^2/s	*Temperature and Pressure Dependences*[a]
Gas			
Bulk	10^{-1}	10^{-5}	$D_{AB}(T_2, P_2) = D_{AB}(T_1, P_1)\frac{P_1}{P_2}\left(\frac{T_2}{T_1}\right)^{1.75}$
Knudsen	10^{-2}	10^{-6}	$D_A(T_2) = D_A(T_1)\left(\frac{T_2}{T_1}\right)^{1/2}$
Liquid	10^{-5}	10^{-9}	$D_{AB}(T_2) = D_{AB}(T_1)\frac{\mu_1}{\mu_2}\left(\frac{T_2}{T_1}\right)$
Solid	10^{-9}	10^{-13}	$D_{AB}(T_2) = D_{AB}(T_1)\exp\left[\frac{E_D}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)\right]$

[a] μ_1, μ_2, liquid viscosities at temperatures T_1 and T_2, respectively; E_D, diffusion activation energy.

Gas:



Liquid:



Mass Transfer Coefficient

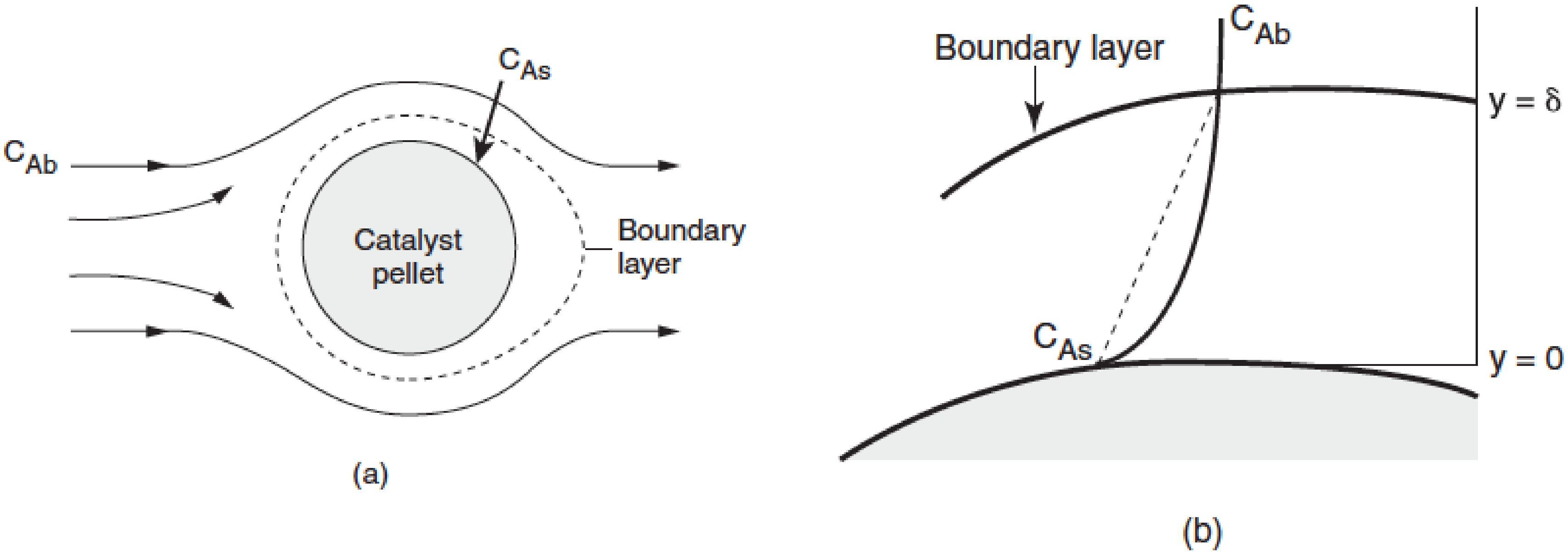
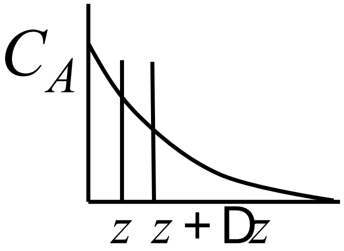


Figure 14-1 Boundary layer around the surface of a catalyst pellet.

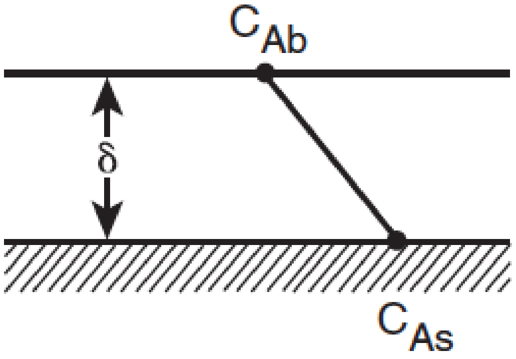


$$W_{Az}A_c\big|_z - W_{Az}A_c\big|_{z+\Delta z} + 0 = 0$$

Divid by $A_c\Delta z$

$$-\left[\frac{W_{Az}\big|_{z+\Delta z} - W_{Az}}{\Delta z}\right] = 0$$

$$\frac{dW_{Az}}{dz} = 0$$

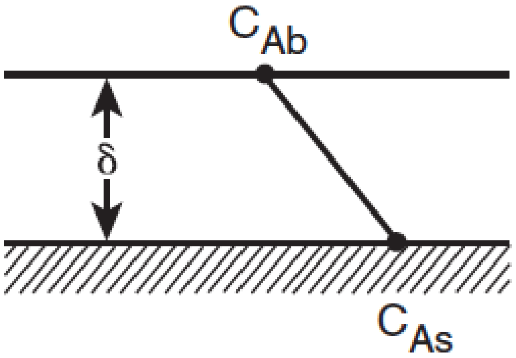


Concentration profile $C_A = C_{As} + (C_{Ab} - C_{As})\frac{z}{\delta}$ (14-25)

Figure 14-2 Concentration profile for EMCD in stagnant film model.

$$W_{Az} = -D_{AB}\frac{dC_A}{dz} = \frac{D_{AB}}{\delta}(C_{A0} - C_{As})$$

$$\boxed{k_c = \frac{D_{AB}}{\delta}} \qquad (14\text{-}27)$$



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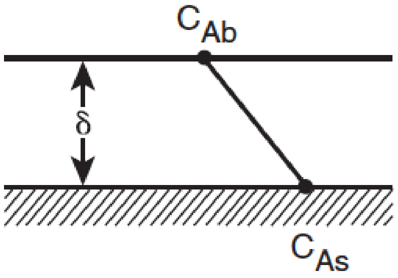
$$\boxed{k_c = \frac{D_{AB}}{\delta}} \quad (14\text{-}27)$$

$$\boxed{W_{Az} = k_c(C_{Ab} - C_{As})} \quad (14\text{-}28)$$



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$$\boxed{k_c = \frac{D_{AB}}{\delta}} \quad (14\text{-}27)$$

$$\boxed{W_{Az} = k_c(C_{Ab} - C_{As})} \quad (14\text{-}28)$$

$$\boxed{W_{Az} = \text{Flux} = \frac{\text{Driving force}}{\text{Resistance}} = \frac{C_{Ab} - C_{As}}{(1/k_c)}}$$

$$\mathrm{Sh} = \frac{k_c d_p}{D_{\mathrm{AB}}} = \frac{(\mathrm{m/s})(\mathrm{m})}{\mathrm{m^2/s}} \text{ dimensionless}$$

$$\mathrm{Sc} = \frac{\nu}{D_{\mathrm{AB}}} = \frac{\mathrm{m^2/s}}{\mathrm{m^2/s}} \text{ dimensionless}$$

$$\mathrm{Re} = \frac{r\,DU}{m} = \frac{\left(g/m^3\right)(m)(m/s)}{(gm/s)} \text{ dimensionless}$$

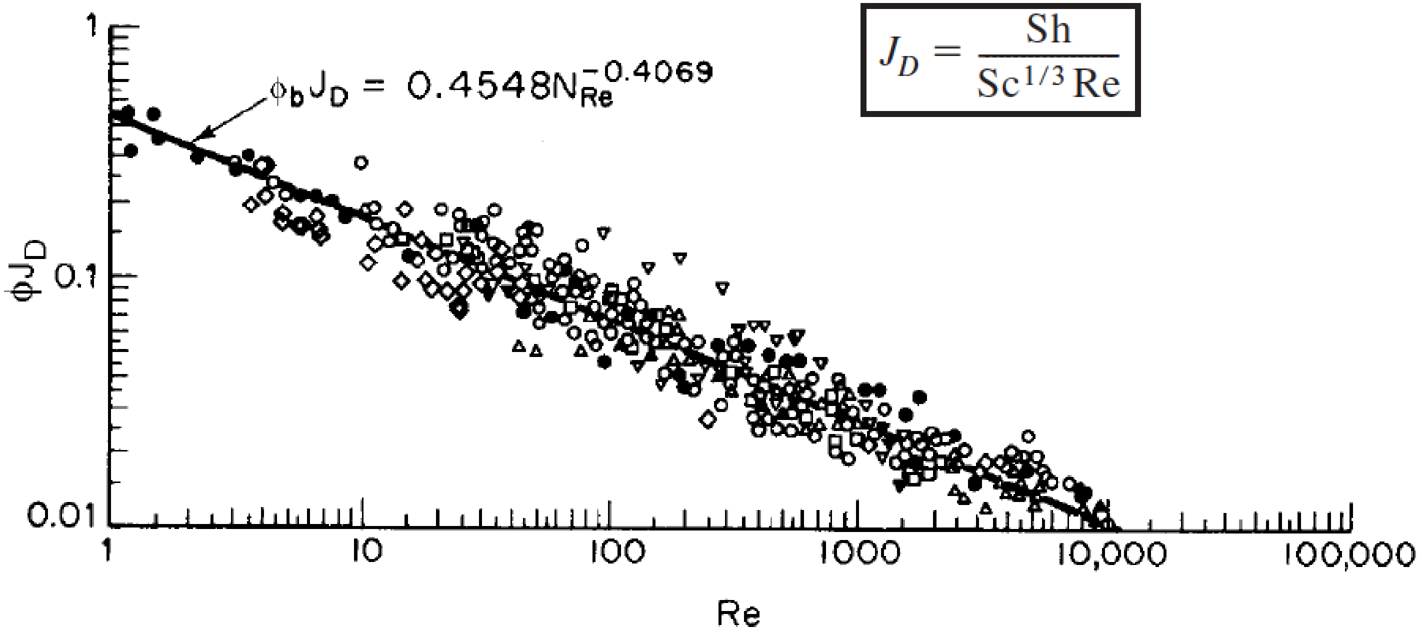
TABLE 14-4. MASS TRANSFER CORRELATIONS

Turbulent flow, mass transfer to pipe wall	$\mathrm{Sh} = .332\,(\mathrm{Re})^{1/2}\,(\mathrm{Sc})^{1/3}$
Mass transfer to a single sphere	$\mathrm{Sh} = 2 + 0.6\,\mathrm{Re}^{1/2}\,\mathrm{Sc}^{1/3}$
Mass transfer in fluidized beds	$\mathrm{Sh} = J_D\,\mathrm{Re}\,\mathrm{Sc}^{1/2}$
	$\phi J_D = \dfrac{0.765}{\mathrm{Re}^{.82}} + \dfrac{0.365}{\mathrm{Re}^{0.386}}$
Mass transfer to packed beds	$\mathrm{Sh} = J_D\,\mathrm{Re}\,\mathrm{Sc}^{1/2}$
	$\phi J_D = \underline{0.453}\quad \mathrm{Re}^{0.453}$

$$\mathrm{Sh}' = 1.0(\mathrm{Re}')^{1/2}\mathrm{Sc}^{1/3}$$

$$\left[\frac{k_c d_p}{D_{AB}}\left(\frac{\phi}{1-\phi}\right)\frac{1}{\gamma}\right] = \left[\frac{U d_p \rho}{\mu(1-\phi)\gamma}\right]^{1/2}\left(\frac{\mu}{\rho D_{AB}}\right)^{1/3}$$

$$J_D = \frac{\mathrm{Sh}}{\mathrm{Sc}^{1/3}\mathrm{Re}}$$



$$\phi J_D = \frac{0.765}{\mathrm{Re}^{0.82}} + \frac{0.365}{\mathrm{Re}^{0.386}}$$

$$k_c \propto \left(\frac{D_{AB}^{2/3}}{\nu^{1/6}}\right)\left(\frac{U^{1/2}}{d_p^{1/2}}\right)$$

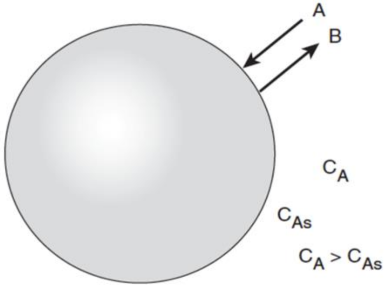


Figure 14-3 Diffusion to, and reaction on, external surface of pellet.

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

$$W_{ASurface} = -r''_{As}$$

$$W_A = k_C (C_A - C_{As}) = k_r C_{As}$$

We need to eliminate C_{As}.

$$C_{As} = \frac{k_c C_A}{k_r + k_c}$$

and the rate of reaction on the surface becomes

$$\boxed{W_A = -r''_{As} = \frac{k_c k_r C_A}{k_r + k_c}}$$

One will often find the flux to or from the surface as written in terms of an *effective* transport coefficient k_{eff}:

$$W_A = -r''_{As} = k_{\text{eff}} C_A$$

Case 1

$$k_{\text{eff}} = \frac{k_c k_r}{k_c + k_r}$$

$$k_r > k_c$$

$$k_{\text{eff}} = k_c$$

One will often find the flux to or from the surface as written in terms of an *effective* transport coefficient k_{eff}:

where

$$W_A = -r''_{As} = k_{\text{eff}}\, C_A$$

Case 1

$$k_c = 0.6\left(\frac{D_{AB}}{d_p}\right)\left(\frac{Ud_p}{v}\right)^{1/2}\left(\frac{v}{D_{AB}}\right)^{1/2}$$

$$k_c \sim (U/d_p)^{1/2}$$

$$-r''_{As} = k_c C_A$$

Case 2

One will often find the flux to or from the surface as written in terms of an *effective* transport coefficient k_{eff}:

$$W_A = -r''_{As} = k_{\text{eff}}\, C_A$$

where

$$k_{\text{eff}} = \frac{k_c k_r}{k_c + k_r}$$

Case 1

$$k_r > k_c$$

$$k_{\text{eff}} = k_c$$

$$k_c = 0.6\left(\frac{D_{AB}}{d_p}\right)\left(\frac{Ud_p}{v}\right)^{1/2}\left(\frac{v}{D_{AB}}\right)^{1/2}$$

$$k_c \sim (U/d_p)^{1/2}$$

$$-r''_{As} = k_c C_A$$

Case 2

$$k_r < k_c$$

$$W_A = -r''_{As} = \frac{k_r C_A}{1 + k_r/k_c} \approx k_r C_A$$

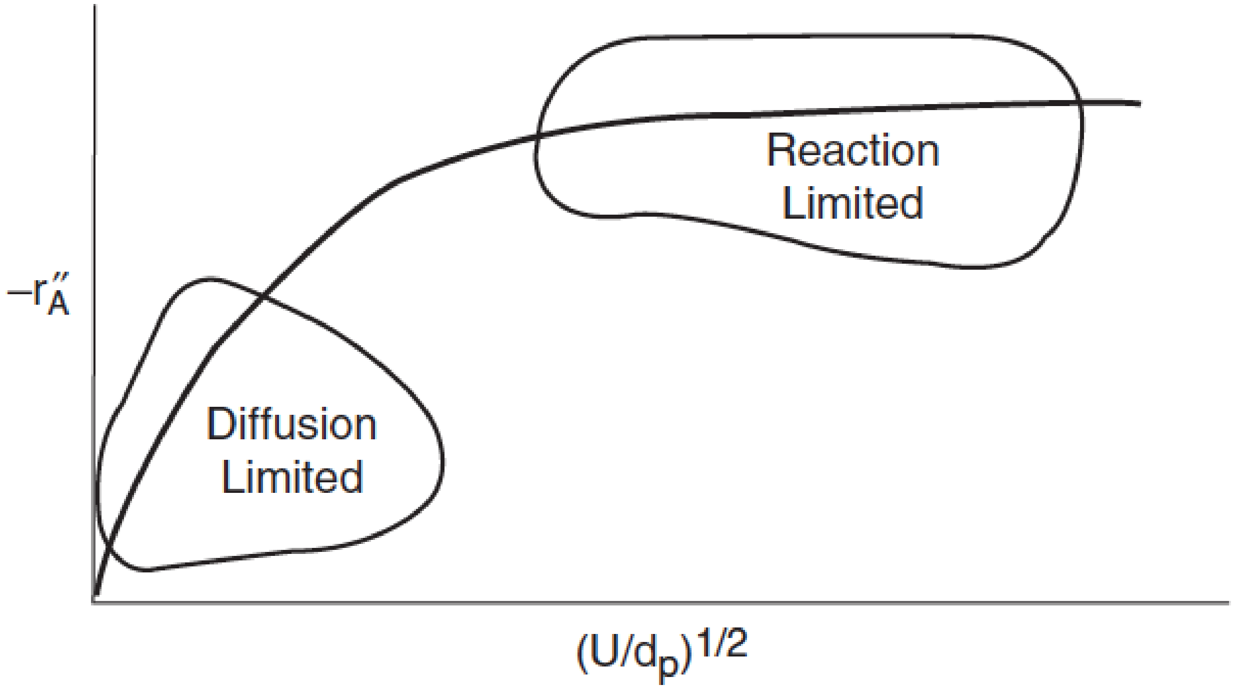
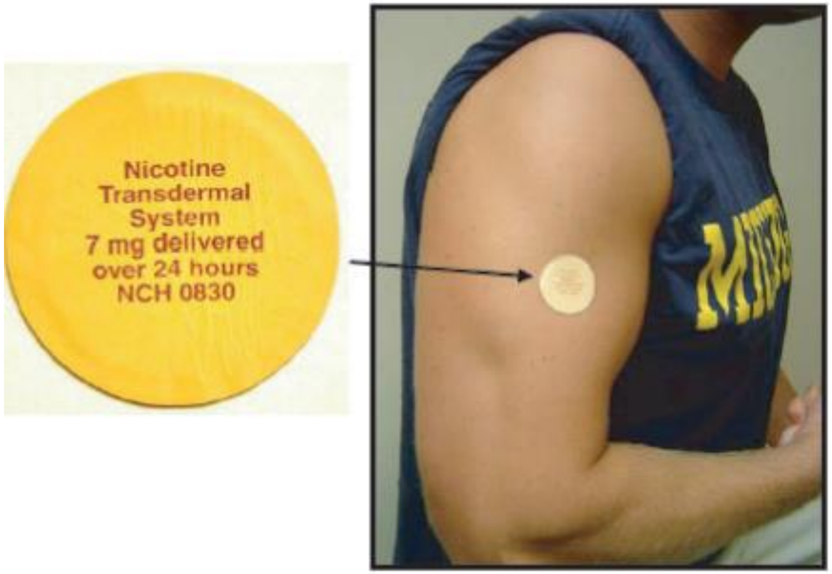
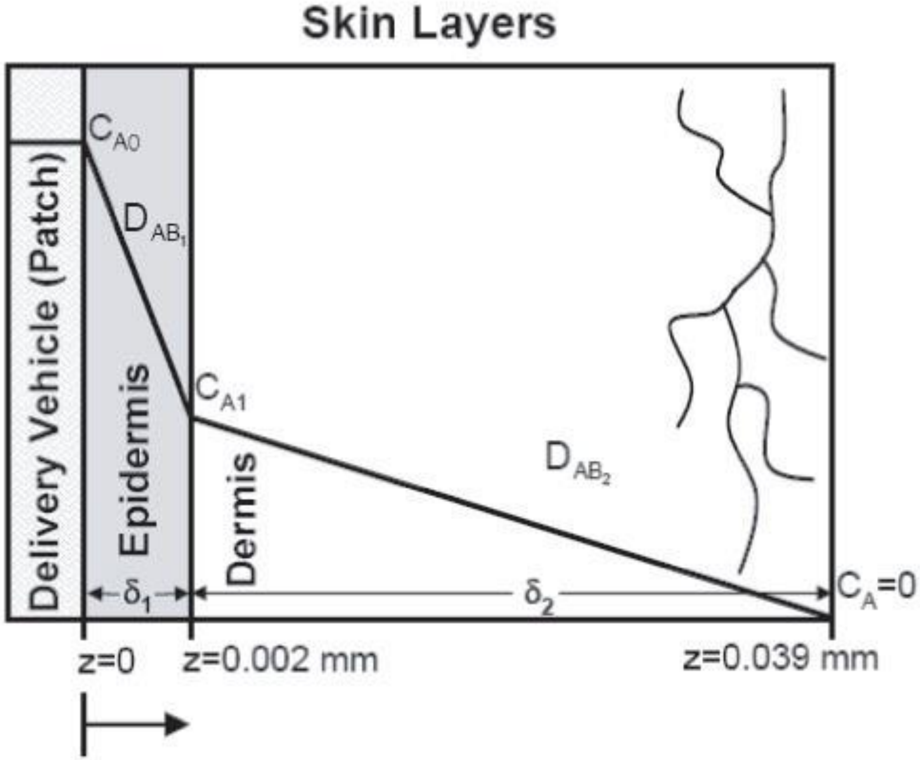


Figure 14-4 Regions of mass transfer–limited and reaction–limited reactions.

Transdermal drug delivery schematic





$$F_{A(z)} - F_{A(z+\Delta z)} + 0 = 0$$

$$-\frac{AW_{(z+\Delta z)} - AW_{A(z)}}{\Delta z} = 0$$

Step 1. Diffusion of A through the Epidermis film, which is stagnant reduces to

$$\frac{dW_{Az}}{dz} = 0$$

Step 2. Use Fick’s law to relate the flux W_{Az} and the concentration gradient

$$W_{A1} = - D_{A1} \frac{dC_A}{dz}$$

Step 3. State the boundary conditions

$$z = 0 \quad C_A = C_{A0}$$

$$z = d_1 \quad C_A = C_{A d 1}$$

Step 4. Next substitute for W_{Az} and divide by D_{A1} to obtain

$$\frac{d^2 C_A}{dz^2} = 0$$

Integrating twice

$$C_A = K_1 z + K_2$$

Step 4.

Using the boundary conditions we can eliminate the constants K_1 and K_2 to obtain the concentration profile

$$C_A = K_1 z + K_2$$

$$\frac{C_{A0} - C_A}{C_{A0} - C_A} = \frac{z}{\delta_1}$$

Step 5. Substituting *CA* we obtain the flux in the Epidermis layer

$$W_{A1} = -D_{A1}\frac{dC_A}{dz} = \frac{D_{A1}}{\delta}\left[C_{A0} - C_{A1}\right]$$

Step 6. Carry out a similar analysis for the Dermis layer starting with

$$\frac{d^2C_A}{dz^2} = 0$$

We find $z = \delta_1 \quad C_A = C_{A1}$

Substituting $z = \delta_2 \quad C_A = 0$

Step 7. At the interface between the Epedermis and Dermis layer, i.e., at *z* = δ_1

$$\frac{C_{A1} - 0}{C_{A1} - 0} = \frac{z}{\delta_2}$$

$$W_{A2} = \frac{D_{A2}}{\delta_2} C_{A1}$$

Substituting

$$W_{A2} = \frac{D_{A2}}{\delta_2} C_{A1}$$

Step 7. At the interface between the Epedermis and Dermis layer, i.e., at $z = \delta_1$

$$W_{A1} = W_{A2} = W_A$$

Equating Equations (E14-1.5) and (E14-1.6)

$$\frac{D_{A1}\left[C_{A0} - C_{A1}\right]}{\delta_1} = \frac{D_{A2}}{\delta_2} C_{A1}$$

Step 7. At the interface between the Epedermis and Dermis layer, i.e., at $z = \delta_1$

$$W_{A1} = W_{A2} = W_A$$

Equating Equations (E14-1.5) and (E14-1.6)

$$\frac{D_{A1}\left[C_{A0} - C_{A1}\right]}{\delta_1} = \frac{D_{A2}}{\delta_2} C_{A1}$$

Solving for C_{A1}

$$C_{A1} = \frac{\dfrac{D_{A1}}{} \dfrac{C_{A0}}{}}{\dfrac{\delta_1}{}} \Bigg/ 1 \;=\; \frac{\frac{D_{A1} C_{A0}}{\delta_1}}{\frac{D_{A1}}{\delta_1} + \frac{D_{A2}}{\delta_2}}$$

Step 7. At the interface between the Epedermis and Dermis layer, i.e., at $z = \delta_1$

$$W_{A1} = W_{A2} = W_A$$

$$W_A = \frac{D_{A2}\,\mathrm{C}_{\mathrm{A1}}}{\delta_2}$$

Substituting for C_{A1} in Equation (E14-1.10)

$$W_A = \frac{C_{A0}}{\dfrac{d_2}{D_{A2}} + \dfrac{d_1}{D_{A1}}} = \frac{C_{A0}}{R_1 + R_2}$$

$$F_A = A_p W_A = A_p \frac{C_{A0}}{R_1 + R_2} = A_p \frac{C_{A0}}{R}$$

If we consider there is a resistance to the drug release in the patch, R_P, then the total resistance is

$$R_T = R_p + R_1 + R_2$$

$$F_A = A_p W_A = \frac{A_p C_{A0}}{R_T}$$

If the resistance in the dermis layer is neglected

$$\boxed{F_A = A_p \left[\frac{D_{AB_1}}{\delta_1}\right] C_{Ap}}$$

$$\begin{bmatrix}\text{Molar}\\\text{rate in}\end{bmatrix} - \begin{bmatrix}\text{Molar}\\\text{rate out}\end{bmatrix} + \begin{bmatrix}\text{Molar rate of}\\\text{generation}\end{bmatrix} = \begin{bmatrix}\text{Molar rate of}\\\text{accumulation}\end{bmatrix}$$

$$F_{\mathrm{Az}}|_z \quad - \quad F_{\mathrm{Az}}|_{z+\Delta z} \quad + \quad r''_{\mathrm{A}} a_c (A_c \Delta z) \quad = \quad 0 \tag{14-51}$$

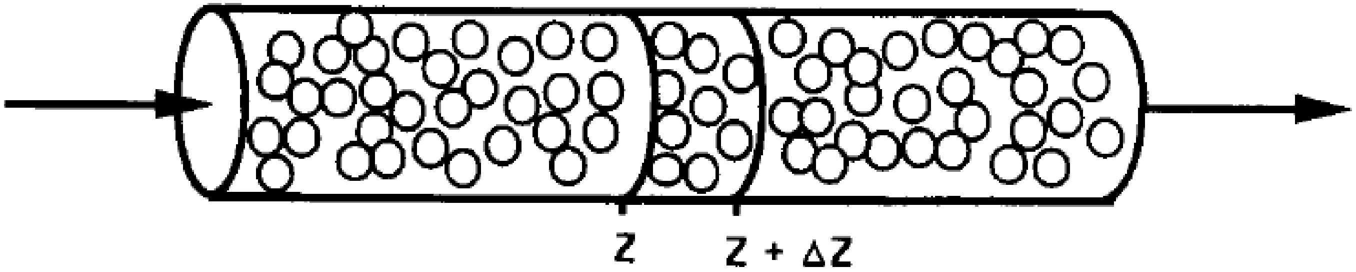


Figure 14-5 Packed-bed reactor.

$$-\frac{1}{A_c}\left(\frac{dF_{Az}}{dz}\right) + r''_A a_c = 0$$

$$-\frac{1}{A_c}\left(\frac{dF_{Az}}{dz}\right)+r'_A a_c=0$$

$$F_{Az}=A_c W_{Az}=\left(\overset{\text{Neglect}}{\cancel{J_{Az}}}+B_{Az}\right)A_c$$

$$=B_{Az}A_c=UC_A A_c$$

$$-\frac{UdC_A}{dz}+r'_A a_c=0_c$$

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

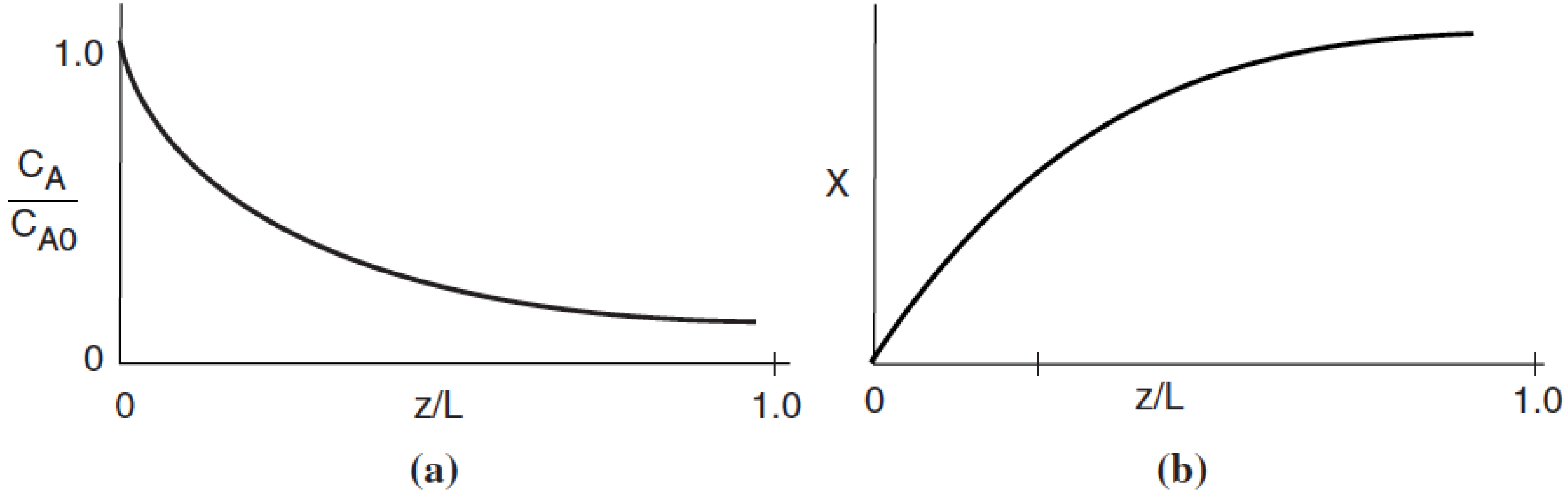
$$-r'_A = W_{Ar}$$

$$-U\frac{dC_A}{dz} - k_c a_c \left(C_A - C_{As}\right) = 0$$

$$-U\frac{dC_A}{dz} - k_c a_c C_A = 0$$

$$\frac{C_A}{C_{A0}} = \exp\left(-\frac{k_c a_c}{U} z\right)$$

$$-r'_A = k_c C_A = k_c C_{A0} \exp\left(-\frac{k_c a_c}{U} z\right)$$



(a) (b)

Figure 14-7 Axial concentration (a) and conversion (b) profiles in a packed bed.

$$X = \frac{C_{A0} - C_{AL}}{C_{A0}} = \frac{Moles\ \text{A Reacted}}{\text{Mole A Fed}}$$

$$\boxed{\ln\frac{1}{1-X} = \frac{k_c a_c}{U} L}$$

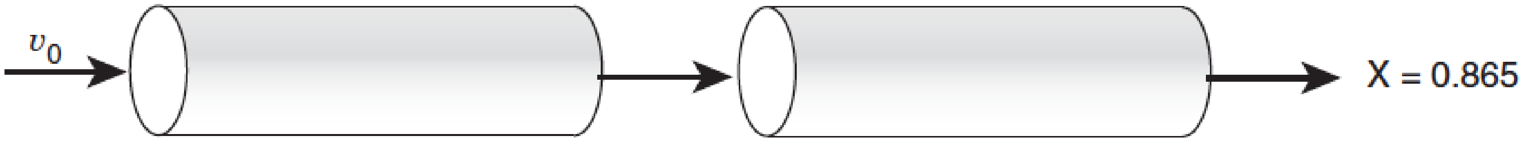


Figure E14-4.1 Series arrangement

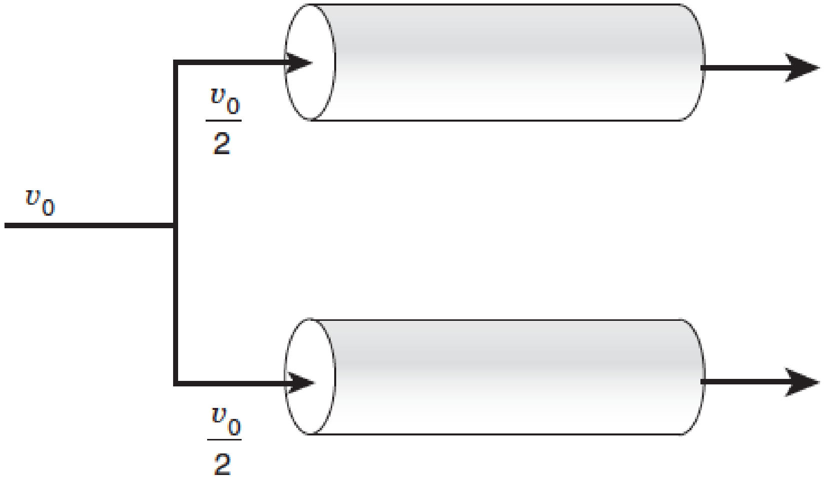


Figure E14-4.2 Parallel arrangement.

$$\ln\frac{1}{1-X}=\frac{k_c a_c}{U}L$$

$$\frac{\ln\dfrac{1}{1-X_2}}{\ln\dfrac{1}{1-X_1}}=\frac{k_{c2}}{k_{c1}}\left(\frac{L_2}{L_1}\right)\frac{U_1}{U_2}$$

$$X_1=0.865$$

$$X_2=?$$

$$\frac{\ln\dfrac{1}{1-X_2}}{\ln\dfrac{1}{1-X_1}} = \frac{k_{c2}}{k_{c1}}\left(\frac{L_2}{L_1}\right)\frac{U_1}{U_2}$$

$$X_1 = 0.865$$

$$L_2 = \frac{1}{2}L_1$$

$$U_2 = \frac{1}{2}U_1$$

$$X_1 = 0.865$$

$$X_2 = ?$$

$$k_c \,\alpha\, U^{1/2}$$

$$\frac{k_{c2}}{k_{c1}} = \left(\frac{U_2}{U_1}\right)^{1/2}$$

$$\frac{U_1}{U_2}\left(\frac{k_{c2}}{k_{c1}}\right) = \left(\frac{U_1}{U_2}\right)^{1/2}$$

$$\ln\frac{1}{1-X_2} = \left(\ln\frac{1}{1-X_1}\right)\frac{L_2}{L_1}\left(\frac{U_1}{U_2}\right)^{1/2}$$

$$=$$

$$\ln\frac{1}{1-X_2}=\left(\ln\frac{1}{1-X_1}\right)\frac{L_2}{L_1}\left(\frac{U_1}{U_2}\right)^{1/2}$$

$$=\left(\ln\frac{1}{1-0.865}\right)\left[\frac{\frac{1}{2}L_1}{L_1}\left(\frac{U_1}{\frac{1}{2}U_1}\right)^{1/2}\right]$$

$$=2.00\left(\frac{1}{2}\right)\sqrt{2}=1.414$$

$$X_2=0.76$$

One will often find the flux to or from the surface as written in terms of an *effective* transport coefficient k_{eff}:

$$W_{\text{A}} = -r''_{\text{A}s} = k_{\text{eff}}\,C_{\text{A}}$$

where

$$k_{\text{eff}} = \frac{k_c k_r}{k_c + k_r}$$

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

$$k_c = 0.6\left(\frac{D_{\text{AB}}}{d_p}\right)\text{Re}^{1/2}\,\text{Sc}^{1/3}$$

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

$$k_c = 0.6 \times \frac{D_{\text{AB}}^{2/3}}{\nu^{1/6}} \times \frac{U^{1/2}}{d_p^{1/2}}$$

$$k_c = 0.6 \times (\text{Term 1}) \times (\text{Term 2})$$

$$(U_2/U_1)^{0.5} = 2^{0.5} = 1.41 \text{ or } 41\%$$

$$k_r \ll k_c$$

$$W_{\text{A}} = -r''_{\text{A}s} = \frac{k_r C_{\text{A}}}{1 + k_r/k_c} \approx k_r C_{\text{A}}$$

$$F_A\big|_z = F_A\big|_{z+\Delta z} + r_A A_c \Delta z = 0$$

$$\frac{dF_A}{dz} + r_A A_c = 0$$

$$F_{Az} = A_c W_{Az}$$

$$W_{Az} = -D_{AB}\frac{dC_A}{dz} + C_A U_z$$

$$F_{Az} = W_{Az} A_c = \left[-D_{AB}\frac{dC_A}{dz} + C_A U_z\right] A_c$$

$$\boxed{D_{AB}\frac{d^2 C_A}{dz^2} - U_z\frac{dC_A}{dz} + r_A = 0}$$

Step 4. Next substitute for W_{Az} and divide by D_{A1} to obtain

$$\frac{d^2C_A}{dz^2}=0$$

Integrating twice

$$C_A=K_1z+K_2$$

using the boundary conditions we can eliminate the constants K_1 and K_2 to obtain the concentration profile

$$\frac{C_{A0}-C_A}{C_{A0}-C_A}=\frac{z}{d_1}$$

Step 5. Substituting CA we obtain the flux in the Epidermis layer

$$W_{A1}=-D_{A1}\frac{dC_A}{dz}=\frac{D_{A1}}{d}\left[C_{A0}-C_{A1}\right]$$

Table 14-1. Types of Boundary Conditions

---

1. Specify a concentration at a boundary (e.g., $\mathbf{z} = 0$, $C_A = C_{A0}$). For an instantaneous reaction at a boundary, the concentration of the reactants at the boundary is taken to be zero (e.g., $C_{As} = 0$). See Chapter 18 for the more exact and complicated Danckwerts' boundary conditions at $\mathbf{z} = 0$ and $\mathbf{z} = L$.
2. Specify a flux at a boundary.
   a. No mass transfer to a boundary,

$$W_A = 0 \tag{14-18}$$

   For example, at the wall of a nonreacting pipe. Species A cannot diffuse into the pipe so $W_A = 0$ and then

$$\frac{dC_A}{dr} = 0 \qquad \text{at } r = R \tag{14-19}$$

   That is, because the diffusivity is finite, the only way the flux can be zero is if the concentration gradient is zero.

   b. Set the molar flux to the surface equal to the rate of reaction on the surface,

$$W_A(\text{surface}) = -r''_A(\text{surface}) \tag{14-20}$$

   c. Set the molar flux to the boundary equal to convective transport across a boundary layer,

$$W_A(\text{boundary}) = k_c(C_{Ab} - C_{As}) \tag{14-21}$$

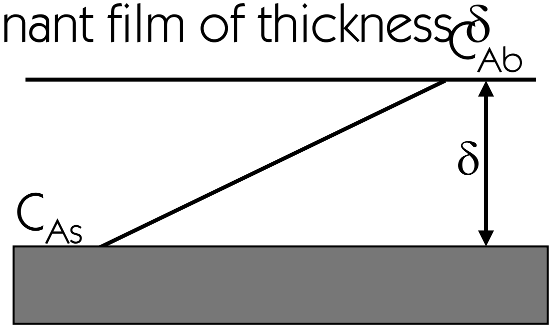
   where k_c is the mass transfer coefficient and C_{As} and C_{Ab} are the surface and bulk concentrations, respectively.

3. Planes of symmetry. When the concentration profile is symmetrical about a plane, the concentration gradient is zero in that plane of symmetry. For example, in the case of radial diffusion in a pipe, at the center of the pipe

$$\frac{dC_A}{dr} = 0 \qquad \text{at } r = 0 \tag{14-22}$$

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**

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

reaction rate per unit surface area (mol/m²·sec)

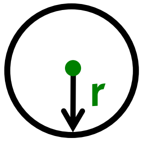
   c) **Convective transport across the boundary layer occurs**

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

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:

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

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)

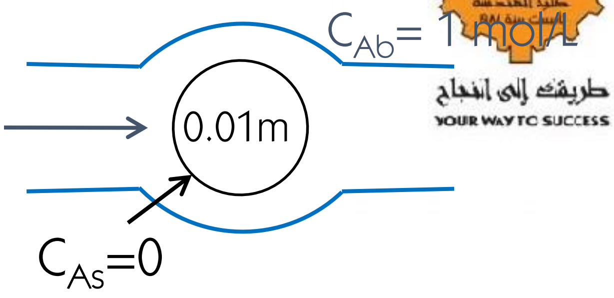
$$Sh = 2 + 0.6Re^{1/2}Sc^{1/3}$$

Reynold's number $Re = \frac{Ud_p}{\nu}$ 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 $= 0.5 \times 10^{-6}$ m²/s
- $D_{AB} = 1\times10^{-10}$ m²/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:

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

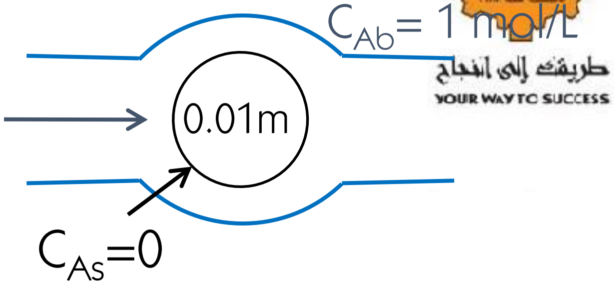
$$Re = \frac{0.1\,m/s\,(0.01m)}{0.5\times10^{-6}\,m^2/s} \rightarrow \boxed{Re = 2000} \qquad Sc = \frac{0.5\times10^{-6}\,m^2/s}{1\times10^{-10}\,m^2/s} \rightarrow \boxed{Sc = 5000}$$

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

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

Rapid Rxn on Catalyst Surface

- Spherical catalyst particle in PBR
- Liquid velocity past particle U = 0.1 m/s
- Catalyst diameter d_p= 1cm = 0.01m
- Instantaneous rxn at catalyst surface C_{As}**≈0**
- **Bulk concentration** C_{Ab}= 1 mol/L
- $\nu \equiv$ kinematic viscosity = 0.5×10^{-6} m²/s
- D_{AB} = 1×10^{-10} m²/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:

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

Computed k_C from Frössling correlation:

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

$$k_c = 4.61\times10^{-6}\,\frac{m}{s}$$

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

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

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

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})

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

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

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, $k_r \gg k_c \rightarrow k_c$ in denominator is negligible

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

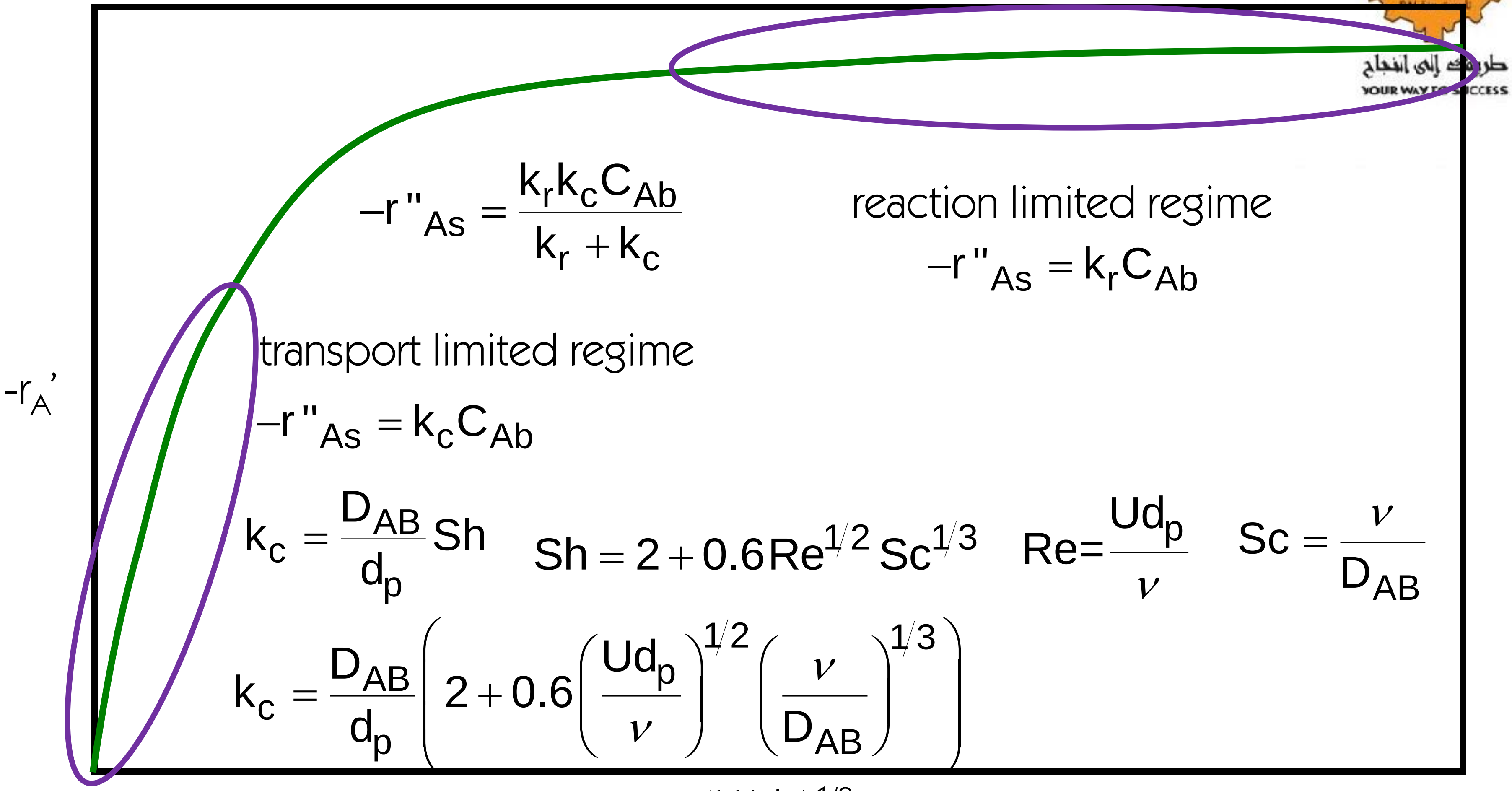
Diffusion limited

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

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

Reaction limited

Mass Transfer & Rxn Limited Reactions



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

reaction limited regime

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

transport limited regime

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

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

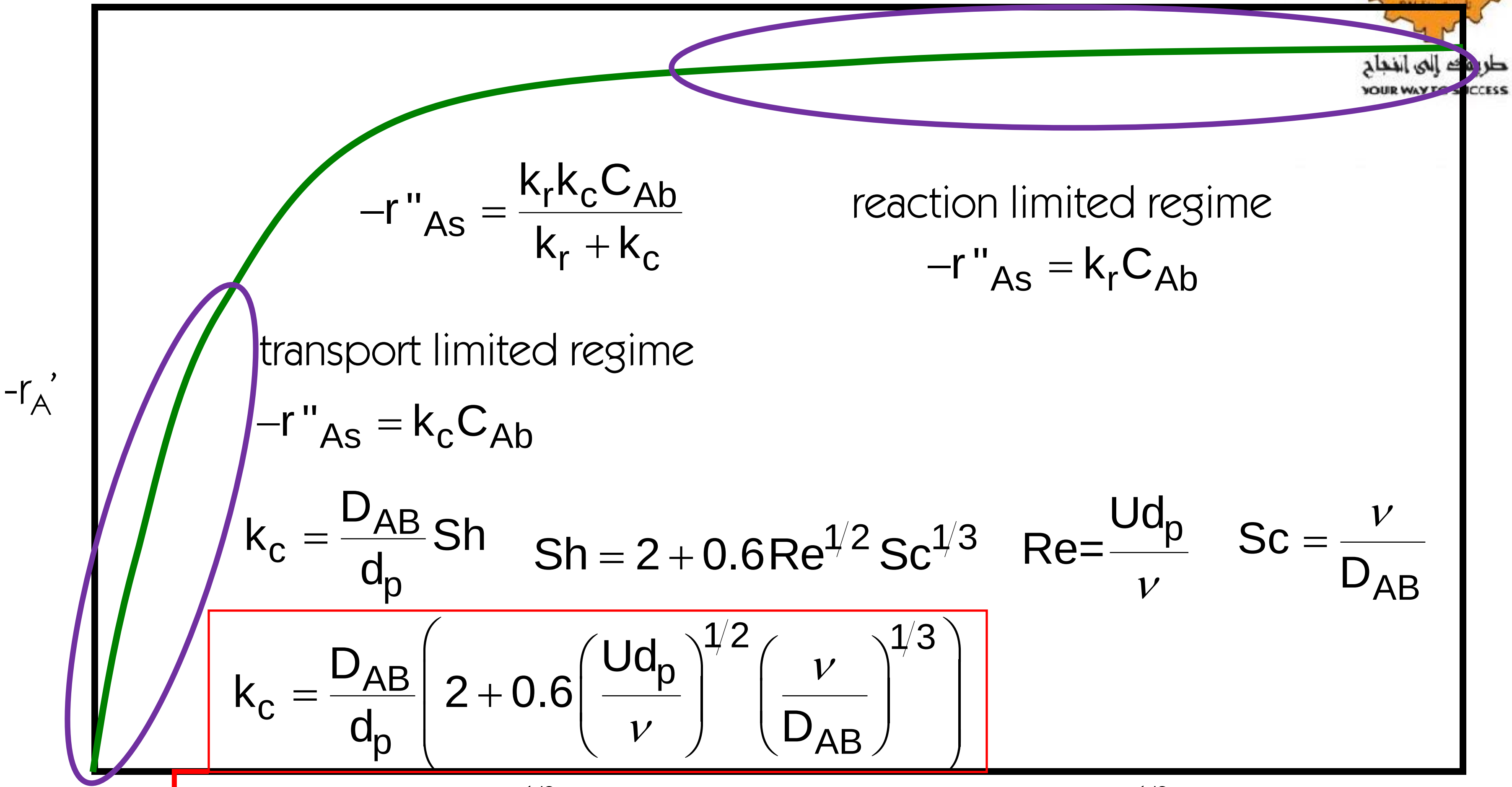
$$k_c = \frac{D_{AB}}{d_p}\left(2 + 0.6\left(\frac{U d_p}{\nu}\right)^{1/2}\left(\frac{\nu}{D_{AB}}\right)^{1/3}\right)$$

$(U/d_p)^{1/2}$

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

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

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

transport limited regime

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

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

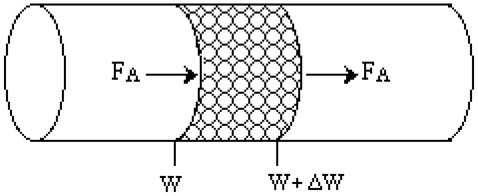
$$\boxed{k_c = \frac{D_{AB}}{d_p}\left(2 + 0.6\left(\frac{Ud_p}{\nu}\right)^{1/2}\left(\frac{\nu}{D_{AB}}\right)^{1/3}\right)}$$

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

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

Proportionality is useful for assessing parameter sensitivity

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 $\quad$ d_p: particle diameter (m)
r''_A: rate of generation of A per unit catalytic surface area (mol/s·m^2)

Divide out $A_c\Delta z$: $\quad \dfrac{F_{Az}\big|_{z} - F_{Az}\big|_{z+\Delta z}}{A_c \Delta z} + r''_A a_c = 0$ $\quad$ Take limit as $\Delta z \rightarrow 0$: $\quad -\dfrac{1}{A_c}\left(\dfrac{dF_{Az}}{dz}\right) + r''_A a_c = 0$

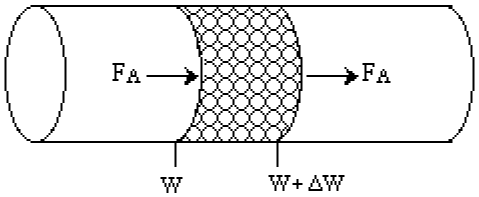
Put F_{az} and $-r_A''$ in terms of C_A: $\quad F_{Az} = W_{Az} A_c = (\cancel{J_{Az}} + B_{Az}) A_c$

Axial diffusion is negligible compared to bulk flow (convection)

$F_{Az} = B_{Az} A_c = U C_A A_c$ $\quad$ Substitute into the mass balance

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

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

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

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

Summary

- This lecture expanded on the topic of external diffusion limitations in catalysis.
- We reviewed molar flux concepts, transport coefficients, and diffusion boundary conditions.
- We also examined how reaction rates are influenced by mass transfer and how transport models help in designing efficient reactors.
- Understanding these principles is essential for optimizing reactor performance and addressing diffusion constraints.