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)

Ch 10 assumes steps 1, 2, 6 & 7 are fast, so only steps 3, 4, and 5 need to be considered.

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
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: \[ -r'_A = \frac{kPP_j}{1 + K_iP_i + K_jP_j + K_kP_k} \]
L19: 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.

![Diagram of external and internal diffusion](image)
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), $W_A$ (moles/area•time), in the direction of the concentration gradient
  - A vector:
    
    $$W_A = iW_{Ax} + jW_{Ay} + kW_{Az}$$
Molar Flux $W$ & Bulk Motion $B_A$

Molar flux consists of two parts:

- Bulk motion of the fluid, $B_A$
- Molecular diffusion flux relative to the bulk motion of the fluid produced by a concentration gradient, $J_A$

$$W_A = B_A + J_A$$ (total flux = bulk motion + diffusion)

Bulk flow term for species A, $B_A$: total flux of all molecules relative to fixed coordinates ($\sum W_i$) times the mole fraction of A ($y_A$):

$$B_A = y_A \sum W_i$$

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

$$B_A = C_A V \rightarrow B_A = C_A \sum y_i V_i$$

$$\frac{\text{mol}}{m^2 \cdot s} = \frac{\text{mol}}{m^3} \cdot \frac{m}{s}$$

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

$$W_A = J_A + C_A V \leftarrow \text{In terms of concentration of A}$$

$$W_A = J_A + C_A \sum y_i V_i$$

$$W_A = J_A + y_A \left(W_A + W_B\right) \leftarrow \text{In terms of mol fraction A}$$
Diffusional Flux of A, $J_A$ & Molar Flux $W$

$$W_A = J_A + B_A$$ (total flux = diffusion + bulk motion)

$$W_A = J_A + C_A \mathbf{v}$$

$$W_A = J_A + C_A \sum_i y_i \mathbf{v}_i$$

$$W_A = J_A + y_A \left( W_A + W_B \right)$$

Diffusional flux of A resulting from a concentration difference, $J_A$, is related to
the concentration gradient by Fick's first law:

$$\frac{\text{mol}}{m^2 \cdot s} J_A = -c D_{AB} \nabla y_A$$

$c$: 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:

$$W_A = -c D_{AB} \nabla y_A + y_A \sum_i W_i$$  General equation

$$W_A = -c D_{AB} \nabla y_A + y_A \left( W_A + W_B \right)$$  molar flux of A in binary system of A & B

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

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Simplifications for Molar Flux

\[ W_A = J_A + B_A \quad \text{(total flux = diffusion + bulk motion)} \]

General equation:

\[ W_A = -cD_{AB} \nabla y_A + y_A \sum_i W_i \]

\[ W_A = -cD_{AB} \nabla y_A + y_A (W_A + W_B) \]

Molar flux of A in binary system of A & B

- For constant total concentration: \( cD_{AB} \sum_i y_A = D_{AB} \sum_i C_A \)
- 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:
  \[ W_A = -W_B \]
  \[ W_A = -cD_{AB} \nabla y_A + y_A (W_A + W_B) \]
  \[ \rightarrow W_A = -cD_{AB} \nabla y_A \]
  or for constant total concentration:  \( W_A = -D_{AB} \nabla C_A \)

**Type 2: Dilute concentration of A:** \( y_A \sum_i W_i ; 0 \)
\[ W_A = -cD_{AB} \nabla y_A + y_A (W_A + W_B) \rightarrow W_A = -cD_{AB} \nabla y_A \]
  or constant \( C_{total} \):
  \[ W_A = -D_{AB} \nabla C_A \]

**Type 3: Diffusion of A though stagnant B:** \( W_B=0 \)
\[ W_A = -cD_{AB} \nabla y_A + y_A (W_A + W_B) \rightarrow W_A = \frac{-1}{1-y_A} cD_{AB} \nabla y_A \]

**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 (\( z \)):
\[ W_A = -cD_{AB} \nabla y_A + C_A V_Z \rightarrow W_A = C_A V_Z \rightarrow W_A = C_A \frac{v}{A_c} \]

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
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 $\delta$ 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 $\delta$

\[ C_{Ab} \]

\[ C_{As} \]

$C_{As}$: 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)
      
      \[
      W_A\big|_{\text{surface}} = 0
      \]

   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
      
      \[
      W_A\big|_{\text{surface}} = -r_A''
      \]
      reaction rate per unit surface area (mol/m$^2$·sec)

   c) Convective transport across the boundary layer occurs
      
      \[
      W_A\big|_{\text{boundary}} = k_c \left( C_{Ab} - C_{As} \right)
      \]

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: \( \frac{dC_A}{dr} = 0 \) at \( r=0 \)
Radial diffusion in a sphere

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Correlation for Convective Transport Across the Boundary Layer

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

$$W_A \mid_{\text{boundary}} = k_c (C_{Ab} - C_{As})$$

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

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

- $k_c$: mass transfer coefficient
- $D_{AB}$: diffusivity ($m^2/s$)
- $d_p$: diameter of pellet (m)
- $\text{Sh}$: Sherwood number (dimensionless)

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

- $\text{Re}$: Reynold's number
- $\text{Sc}$: Schmidt number

- $\nu$: kinematic viscosity or momentum diffusivity ($m^2/s$); $\nu = \mu/\rho$
- $\rho$: fluid density ($kg/m^3$)
- $\mu$: viscosity ($kg/m \cdot s$)
- $U$: free-stream velocity (m/s)
- $D_{AB}$: diffusivity ($m^2/s$)
- $d_p$: diameter of pellet (m)
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 = $0.5 \times 10^{-6}$ m$^2$/s
• $D_{AB} = 1 \times 10^{-10}$ m$^2$/s

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

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

Compute $k_c$ from Frössling correlation:

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

$$\text{Re} = \frac{0.1 \text{ m/s} \times 0.01 \text{ m}}{0.5 \times 10^{-6} \text{ m}^2/\text{s}} \rightarrow \text{Re} = 2000$$

$$\text{Sc} = \frac{0.5 \times 10^{-6} \text{ m}^2/\text{s}}{1 \times 10^{-10} \text{ m}^2/\text{s}} \rightarrow \text{Sc} = 5000$$

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

$$k_c = \frac{1 \times 10^{-10} \text{ m}^2/\text{s}}{0.01 \text{ m}} \times 461 \rightarrow k_c = 4.61 \times 10^{-6} \text{ m/s}$$
Rapid Rxn on Catalyst Surface

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

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

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

Computed $k_c$ from Frössling correlation:

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

$$k_c = 4.61 \times 10^{-6} \ \text{m/s}$$

$$W_A\bigg|_{\text{boundary}} = 4.61 \times 10^{-6} \ \frac{\text{mol}}{\text{s}} \left( \frac{1}{\text{mol/L}} \left( \frac{1000\text{L}}{\text{m}^3} \right) - 0 \right) \rightarrow W_A\bigg|_{\text{boundary}} = 4.61 \times 10^{-3} \ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$$

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

$$W_A\bigg|_{\text{boundary}} = -r_{As}'' = 4.61 \times 10^{-3} \ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$$

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
For the previous example, derive an equation for the flux if the reaction were not instantaneous, and was instead at steady state \( (W_{A|\text{surface}} = -r_A") \) and followed the kinetics: \(-r_{AS}"=k_rC_{As}\) (Observed rate is not diffusion limited)

\[
k_c \left( C_{Ab} - C_{As} \right) = W_A \bigg|_{\text{boundary}} \quad \text{and} \quad -r_{As}" = k_rC_{As}
\]

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

\[
C_{As} \neq 0 \quad \text{and} \quad W_A \bigg|_{\text{boundary}} = -r_{As}" = k_rC_{As}
\]

So if \( C_{As} \) were in terms of measurable species, we would know \( W_{A,\text{boundary}} \)

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

\[
k_c \left( C_{Ab} - C_{As} \right) = k_rC_{As} \rightarrow k_cC_{Ab} - k_cC_{As} = k_rC_{As} \rightarrow k_cC_{Ab} = k_rC_{As} + k_cC_{As}
\]

\[
\rightarrow k_cC_{Ab} = C_{As} \left( k_r + k_c \right) \rightarrow \frac{k_cC_{Ab}}{k_r + k_c} = C_{As} \quad \text{Plug into } -r''_{As}
\]

\[
W_A \bigg|_{\text{boundary}} = -r''_{As} = k_rC_{As} \rightarrow W_A \bigg|_{\text{boundary}} = -r''_{As} = \frac{k_rk_cC_{Ab}}{k_r + k_c}
\]

Rapid rxn, \( k_r \gg k_c \rightarrow k_c \) in denominator is negligible

\[
-r''_{As} = \frac{k_rk_cC_{Ab}}{k_r + k_c} \rightarrow -r''_{As} = \frac{k_rk_cC_{Ab}}{k_r} \quad \text{Diffusion limited}
\]

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

\[
-r''_{As} = \frac{k_rk_cC_{Ab}}{k_r + k_c} \rightarrow -r''_{As} = \frac{k_rk_cC_{Ab}}{k_c} \quad \text{Reaction limited}
\]
Mass Transfer & Rxn Limited Reactions

- Transport limited regime
  \[-r''_{As} = k_c C_{Ab}\]
  \[k_c = \frac{D_{AB}}{d_p} Sh\]
  \[Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}\]

- Reaction limited regime
  \[-r''_{As} = k_r C_{Ab}\]

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

\[(U/d_p)^{1/2} \quad \text{(fluid velocity/particle diameter)}^{1/2}\]

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

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Mass Transfer & Rxn Limited Reactions

transport limited regime

\[-r''_{As} = k_c C_{Ab}\]

reaction limited regime

\[-r''_{As} = k_r C_{Ab}\]

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

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

Re = \frac{U d_p}{\nu}

Sc = \frac{\nu}{D_{AB}}

Proportionality is useful for assessing parameter sensitivity

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

\[k_{c2} = \left( \frac{U_2}{U_1} \right)^{1/2} \left( \frac{D_{AB2}}{D_{AB1}} \right)^{2/3} \left( \frac{\nu_1}{\nu_2} \right)^{1/6} \left( \frac{d_{p1}}{d_{p2}} \right)^{1/2}\]
Mass Transfer Limited Rxn in PBR

A steady state mole balance on reactant A between \( z \) and \( z + \Delta z \):

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

\( a_c \): external surface area of catalyst per volume of catalytic bed (m\(^2\)/m\(^3\))
\( \phi \): porosity of bed, void fraction
\( d_p \): particle diameter (m)

Divide out \( F_{A_z} \big|_z - F_{A_z} \big|_{z + \Delta z} \):

\[
\frac{A_c \Delta z}{A_c \Delta z} + r''_A a_c = 0
\]

Take limit as \( \Delta z \to 0 \):

\[
-1 \left( \frac{dF_{A_z}}{dz} \right) + r''_A a_c = 0
\]

Put \( F_{az} \) and \( -r''_A \) in terms of \( C_A \):

\[
F_{A_z} = W_{A_z} A_c = (J_{A_z} + B_{A_z}) A_c
\]

Axial diffusion is negligible compared to bulk flow (convection)

\[
\frac{d(UC_A)}{dz} + r''_A a_c = 0 \quad \Rightarrow \quad -U \frac{dC_A}{dz} \left( \frac{dU}{dz} + C_A \frac{dC_A}{dz} \right) + r''_A a_c = 0
\]

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Mass Transfer Limited Rxn in PBR

\[ \text{At steady-state:} \]
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 \( k_c = \frac{D_{AB}}{\delta} \) (s\(^{-1}\)) \( \delta \): 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

Rearrange & integrate to find how \( C_A \) and the \( r''_A \) varies with distance down reactor

\[ \rightarrow -U \frac{dC_A}{dz} = k_c a_c C_A \]

\[ \rightarrow -U \frac{dC_A}{dz} = k_c a_c C_A \]

\[ \rightarrow \int \frac{dC_A}{C_A} = \int^z -\frac{k_c a_c}{U} \, dz \]

\[ \rightarrow \ln \frac{C_A}{C_{A0}} = -\frac{k_c a_c}{U} z \]

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

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

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

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Review: Heterogeneous Catalyst

- We have looked at cases where
  1) Adsorption, surface reaction, or desorption is rate limiting
  2) External diffusion is rate limiting
  3) Internal diffusion is rate limiting - today

- Next time: Derive an overall rate law for heterogeneous catalyst where the rate limiting step is any of the 7 reaction steps. This new overall reaction rate would be inserted into the design equation to get $W$, $X_A$, $C_A$, etc.
Review: 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)
      \[ W_A \big|_{\text{surface}} = 0 \]
   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
      \[ W_A \big|_{\text{surface}} = -r_A'' \text{ reaction rate per unit surface area (mol/m}^2\text{·sec)} \]
   c) Convective transport across the boundary layer occurs
      \[ W_A \big|_{\text{boundary}} = k_c \left( C_{Ab} - C_{As} \right) \]

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

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Review: Transport & Rxn Limited Rates

Transport limited regime (Convective transport across boundary layer)

\[-r''_A = \frac{k_r k_c C_{Ab}}{k_r + k_c}\]

Used \(k_c(C_{Ab} - C_{As}) = k_r C_{As}\) to solve for \(C_{As}\) & plugged back into \(-r''_A = k_r C_{As}\)

Reaction limited regime:

\[-r''_A = k_c C_{Ab}\]

\[k_c = \frac{D_{AB}}{d_p} \text{Sh} \quad \text{Sh} = 2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3} \quad \text{Re} = \frac{U d_p}{\nu} \quad \text{Sc} = \frac{\nu}{D_{AB}}\]

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

\[\text{(fluid velocity/particle diameter)}^{1/2}\]

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

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Review: 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 \( z + \Delta z \):

\[
F_{Azu} - F_{Az(u+\Delta u)} + r''_A a_c (A_c \Delta z) = 0 \quad \text{where} \quad a_c = \frac{6(1-\phi)}{d_p}
\]

- \( a_c \): external surface area of catalyst per volume of catalytic bed (m²/m³)
- \( \phi \): porosity of bed, void fraction
- \( d_p \): particle diameter (m)
- \( r''_A \): rate of generation of A per unit catalytic surface area (mol/s·m²)
- \( A_c \): cross-sectional area of tube containing catalyst (m²)

1. Divide out \( A_c \Delta z \) and take limit as \( \Delta z \to 0 \)
2. Put \( F_{az} \) and \( -r''_A \) in terms of \( C_A \)
3. Assume that axial diffusion is negligible compared to bulk flow
4. Assume molar flux of A to surface = rate of consumption of A at surface
5. Rearrange, integrate, and solve for \( C_A \) and \( r''_A \)

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

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Shrinking Core Model

• Solid particles are being consumed either by dissolution or reaction
  • The amount of the material being consumed is shrinking
  • Drug delivery (pill in stomach)
  • Catalyst regeneration

• Regeneration of catalyst by burning off carbon coke in the presence of $\text{O}_2$
• Begins at the surface and proceeds to the core
• Because the amount of carbon that is consumed (burnt off) is proportional to the surface area, and the amount of carbon that is consumed decreases with time
Catalyst Regeneration

Coking-deactivated catalyst particles are reactivated by burning off the carbon

\[ C + O_2 \rightarrow CO_2 \]

- Oxygen (A) diffuses from particle surface \((r = R_0, C_A = C_{A0})\) through the porous pellet matrix to the unreacted core \((r = R, C_A = 0)\)
- Reaction of \(O_2\) with carbon at the surface of the unreacted core is very fast
- \(CO_2\) generated at surface of core diffuses out
- Rate of oxygen diffusion from the surface of the pellet to the core controls rate of carbon removal

Though the core of carbon (from \(r = 0\) to \(r = R_0\)) is shrinking with time (unsteady state), we will assume the concentration profile at any time is the steady state profile over distance \((R_0 - R)\): quasi-steady state assumption (QSSA)
Mole Balance on O₂ From r to r+Δr

Rate in - rate out + gen = accum

\[ W_{Ar} 4\pi r^2 \bigg|_r - W_{Ar} 4\pi (r+\Delta r)^2 \bigg|_{r+\Delta r} + 0 = 0 \]

Oxygen reacts at the surface, not in this region

\[ W_{Ar} r^2 \bigg|_{r+\Delta r} - W_{Ar} r^2 \bigg|_r = 0 \]

Divide by -4πΔr:

\[ \frac{d(W_{Ar}r^2)}{\Delta r} = 0 \]

Take limit as Δr→0:

\[ \frac{d(W_{Ar}r^2)}{dr} = 0 \]

Put \( W_{Ar} \) in terms of conc of oxygen (\( C_A \))

\[ W_A = -D_e \frac{dC_A}{dr} + y_A (W_A + W_B) \]

\( D_e \): effective diffusivity

For every mole of O₂ that enters, a mol of CO₂ leaves \( \rightarrow W_{O2} = -W_{CO2} \)

\[ W_A = -D_e \frac{dC_A}{dr} \]

Plug \( W_{Ar} \) into mole balance:

\[ \frac{d}{dr} \left( -D_e \frac{dC_A}{dr} r^2 \right) = 0 \]

Divide out \(-D_e\):

\[ \frac{d}{dr} \left( \frac{dC_A}{dr} r^2 \right) = 0 \]
Mole Balance on O\textsubscript{2} From r to r+\Delta r (2)

\[ \int \frac{d}{dr} \left( \frac{dC_A}{dr} r^2 \right) = 0 \quad \rightarrow \quad \frac{dC_A}{dr} r^2 = K_1 \]

\[ \int dC_A = \int \frac{K_1}{r^2} dr \quad \rightarrow \quad C_A = -\frac{K_1}{r} + K_2 \]

Use boundary conditions to determine the concentration profile \((C_A/C_{A0})\) in terms of the various radii \((R, R_0 \& r)\)

At \(r = R_0\), \(C_A = C_{A0}\) and at \(r = R\), \(C_A = 0\)

First use \(C_A = 0\) when \(r = R\) to determine \(K_2\)

\[ C_A = 0 = -\frac{K_1}{R} + K_2 \quad \rightarrow \quad \frac{K_1}{R} = K_2 \]

For any \(r\): \[ C_A = -\frac{K_1}{r} + \frac{K_1}{R} \quad \rightarrow \quad C_A = K_1 \left( \frac{1}{R} - \frac{1}{r} \right) \]

Next solve for when \(r = R_0 \& C_A = C_{A0}\)

\[ C_{A0} = -\frac{K_1}{R_0} + \frac{K_1}{R} \quad \rightarrow \quad C_{A0} = K_1 \left( \frac{1}{R} - \frac{1}{R_0} \right) \]

Take the ratio to determine \(C_A/C_{A0}\)

\[ \frac{C_A}{C_{A0}} = \frac{K_1 \left( \frac{1}{R} - \frac{1}{r} \right)}{K_1 \left( \frac{1}{R} - \frac{1}{R_0} \right)} \quad \rightarrow \quad \frac{C_A}{C_{A0}} = \frac{1/R - 1/r}{1/R - 1/R_0} \]

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Oxygen Concentration Profile & Flux

\[ C_A = \frac{C_{A0} \left(1/R - 1/r\right)}{1/R - 1/R_0} \]

\[ W_A = -D_e \frac{dC_A}{dr} \]

Finally determine the flux of oxygen to the surface of the core:

\[ W_A = -D_e \frac{d}{dr} \left[ \frac{C_{A0} \left(1/R - 1/r\right)}{1/R - 1/R_0} \right] \]

\[ W_A = \frac{-D_e C_{A0}}{(1/R - 1/R_0)r^2} \]

\[ \frac{C_A}{C_{A0}} = \frac{1/R - 1/r}{1/R - 1/R_0} \]

\[ C_{Ab} = C_{A0} \]

Oxygen concentration Profile at time t
Mass Balance on Carbon (C)

In – out + gen = accumulation

\[
0 - 0 + r''_c 4\pi R^2 = \frac{d\left(\frac{4}{3}\pi R^3 \rho_c \phi_C\right)}{dt}
\]

Elemental C does not enter or leave the surface

Change in the mass of the carbon core

\[
r''_c 4\pi R^2 = \frac{d\left(\frac{4}{3}\pi R^3 \rho_c \phi_C\right)}{dt} \rightarrow \frac{r''_c}{\rho_c \phi_C} = \frac{dR}{dt}
\]

Simplify mass balance:

The rate of carbon disappearance (-dR/dt) is equal to the rate of oxygen flux to the surface of the core, -W_{O2} = W_{CO2}, and this occurs at a radius of R so:

\[
r''_C = -W_A = W_B = \frac{D_e C_{A0}}{\left(1/R - 1/R_0\right)r^2} \rightarrow -r''_C = \frac{D_e C_{A0}}{R - R^2/R_0}
\]

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Time Required to Shrink Core to Radius R

\[ \frac{dR}{dt} = \frac{r''_c}{\rho C \phi C} \quad \Rightarrow \quad \frac{dR}{dR} = \frac{-D_e C_{A0}}{\rho C \phi C} \left( \frac{1}{R - R^2/R_0} \right) \]

Substitute \( r''_c \) into \(-dR/dt\), get like terms together, integrate, & solve for \( t \)

\[ \int \left( R - \frac{R^2}{R_0} \right) dR = \int_0^t \left( \frac{D_e C_{A0}}{\rho C \phi C} \right) dt \]

Integrate over 0 to \( t \) & \( R_0 \) to \( R \)

\[ \frac{R^2}{2} - \frac{R^3}{3R_0} \bigg|_R^{R_0} = \frac{D_e C_{A0}}{\rho C \phi C} t \]

Get common denominators

\[ \frac{3R_0 R^2}{6R_0} - \frac{2R^3}{6R_0} - \frac{3R_0^2}{6} - \frac{2R_0^2}{6} = \frac{D_e C_{A0}}{\rho C \phi C} t \]

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Time Required to Shrink Core to Radius R

\[ C + O_2 \rightarrow CO_2 \]

Solve for \( t \):

\[ \frac{3R_0^2}{6R_0} - \frac{2R^3}{6R_0} - \frac{R_0^2}{6} = \frac{-D_eC_{A0}}{\rho_C\phi_C} t \]

Factor out \( R_0^2/6 \)

\[ t = \frac{\rho_C\phi_C R_0^2}{6D_eC_{A0}} \]

At the core of the catalyst particle, \( R=0 \), then:

\[ t = \left( 1 - 3\left( \frac{R}{R_0} \right)^2 + 2\left( \frac{R}{R_0} \right)^3 \right) \frac{\rho_C\phi_C R_0^2}{6D_eC_{A0}} \]

Complete regeneration

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
L20: Internal Diffusion Effects in Spherical Catalyst Particles

Internal diffusion: diffusion of the reactants or products from the external pellet surface (pore mouth) to the interior of the pellet. (Chapter 12)

When the reactants diffuse into the pores within the catalyst pellet, the concentration at the pore mouth will be higher than that inside the pore and the entire catalytic surface is not accessible to the same concentration.

Though A is diffusing inwards, convention of shell balance is flux is in direction of increasing r. (flux is positive in direction of increasing r). In actuality, flux of A will have a negative sign since it moves inwards.
Basic Molar Balance for Differential Element

An irreversible rxn $A \rightarrow B$ occurs on the surface of pore walls within a spherical pellet of radius $R$:

Rate of $A$ in at $r = W_{Ar} \cdot \text{area} = W_{Ar} \times 4\pi r^2 \bigg|_r$

Rate of $A$ out at $r - \Delta r = W_{Ar} \cdot \text{area} = W_{Ar} \times 4\pi r^2 \bigg|_{r-\Delta r}$

The mole balance over the shell thickness $\Delta r$ is:

\[
\begin{align*}
\text{IN} & - \text{OUT} + \text{GEN} = \text{ACCUM} \\
W_{Ar} 4\pi r^2 \bigg|_r - W_{Ar} 4\pi r^2 \bigg|_{r-\Delta r} + r'_A \left(4\pi r_m^2 \Delta r\right) \rho_c = 0
\end{align*}
\]

Volume of shell

$r'_A$: rate of reaction per mass of catalyst (mol/g·s)

$\rho_c$: mass of catalyst per unit volume of catalyst (catalyst density)

$r_m$: mean radius between $r$ and $r - \Delta r$

Divide by $-4\pi \Delta r$ & take limit as $\Delta r \rightarrow 0$

\[
\frac{d\left(W_{Ar} r^2\right)}{dr} - r'_A r^2 \rho_c = 0
\]

Differential BMB in spherical catalyst particle
Diffusion Equation (Step 2)

\[ W_{Ar} 4\pi r^2 \bigg|_r - W_{Ar} 4\pi r^2 \bigg|_{r-\Delta r} + r'_A \left( 4\pi r_m^2 \Delta r \right) \rho_c = 0 \]

Steady state assumption implies equimolar counter diffusion, \( W_B = -W_A \) (otherwise A or B would accumulate)

\[ W_A = -cD_e \frac{dy_A}{dr} = -D_e \frac{dC_A}{dr} \]

Must use effective diffusivity, \( D_e \), instead of \( D_{AB} \) to account for:
1) Tortuosity of paths
2) Void spaces
3) Pores having varying cross-sectional areas

\[ D_e = D_{AB} \frac{\phi_p \sigma_c}{\phi_0} \]

- \( D_A \) bulk diffusivity
- \( \phi_p \) pellet porosity \((V_{\text{void space}}/V_{\text{void & solid}})\) (typical \( \sim 0.4 \))
- \( \sigma \) constriction factor (typical \( \sim 0.8 \))
- \( \tau \) tortuosity (distance molecule travels between 2 pts/actual distance between those 2 pts) (typical \( \sim 3.0 \))

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Diffusion & Rxn in a Spherical Catalyst

**BMB:** \( W_{Ar} 4\pi r^2 \bigg|_r - W_{Ar} 4\pi r^2 \bigg|_{r-\Delta r} + r'_A \left(4\pi r^2 \Delta r \right) \rho_c = 0 \)

\[
\rightarrow \frac{d \left(W_{Ar} r^2 \right)}{dr} - r'_A r^2 \rho_c = 0
\]

Diffusion: \( W_A = -cD_e \frac{d y_A}{d r} = -D_e \frac{d C_A}{d r} \)

Write the rate law based on surface area:

\[
-r''_A = k''_n C_A^n \quad \text{mol} \quad \text{m}^2 \cdot \text{s}
\]

Relate \( r'_A \) to \( r''_A \) by:

\[
\frac{\text{mol}}{\text{g cat} \cdot \text{s}} - r'_A = -r''_A S_a
\]

\[
S_a = \frac{\text{catalyst surface area}}{\text{mass of catalyst}}
\]

Insert the diffusion eq & the rate eq into the BMB:

\[
\frac{d}{dr} \left[ -D_e \frac{d C_A}{d r} r^2 \right] + r^2 \rho_C S_a k''_n C_A^n = 0
\]

Boundary Conditions:

\( C_A \) finite at \( r=0 \) \quad \( C_A = C_{As} \) at \( r=R \)

Solve to get \( C_A(r) \) and use the diffusion equation to get \( W_{Ar}(r) \)

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Dimensionless Variables

\[ \frac{d}{dr} \left[ -D_e \frac{dC_A}{dr} r^2 \right] + r^2 \rho_C S_A k''_n C_A^n = 0 \]

Put into dimensionless form

\[ \lambda = \frac{r}{R} \]

\[ (\Psi) \Psi = \frac{C_A}{C_{As}} \]

\[ \phi_n^2 = \frac{k''_n \rho_c R C_{As}^n}{D_e [(C_{As} - 0)/R]} \]

\[ \phi_n^2 = \frac{k''_n \rho_c R^2 C_{As}^{n-1}}{D_e} \]

Boundary Conditions:

\[ \Psi = 1 \text{ at } \lambda = 1 \]

\[ \Psi \text{ is finite at } \lambda = 0 \]

Thiele modulus for rxn of n\textsuperscript{th} order \( \equiv \phi_n \)

**Subscript** \( n = \text{reaction order} \)

\( \phi_n \) is small: surface reaction is rate limiting

\( \phi_n \) is large: internal diffusion is rate limiting

The solution for a 1\textsuperscript{st} order rxn:

\[ \Psi = \frac{C_A}{C_{As}} = \frac{1}{\lambda} \left( \frac{\sinh \phi_1 \lambda}{\sinh \phi_1} \right) \]

small \( \phi_1 \): surface rxn control, significant amount of reactant diffuses into pellet interior w/out reacting

large \( \phi_1 \): surface rxn is rapid, reactant is consumed very close to the external surface of pellet (A waste of precious metal inside of pellet)

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Internal Effectiveness Factor, $\eta$

Internal effectiveness factor:
1. the relative importance of diffusion and reaction limitations
2. a measurement of how far the reactant diffuses into the pellet before reacting

$$\eta = \frac{\text{actual (observed) overall rate of rxn}}{\text{rate of reaction if entire interior surface were exposed to } C_{As} \text{ & } T_s}$$

$$\eta = \frac{-r_A}{-r''_{As}} = \frac{-r''_{As}}{-r'_{As}} (\text{mass of catalyst})$$

For example, when $n=1$ (1$^{\text{st}}$ order kinetics, $-r''_{As}$)

$$\eta = \frac{4\pi R^2 \left(-W_{As} \bigg|_{r=R} \right)}{(-r_{As}) \frac{4}{3} \pi R^3} \rightarrow \eta = \left(\frac{4\pi R^2}{\rho_c S_a k_1 C_{As}}\right) \frac{\frac{dC_A}{dr}}{\frac{4}{3} \pi R^3} \rightarrow \eta = \frac{4\pi R^2 D_e C_{As} \left[\frac{d\phi}{d\lambda}\right]_{\lambda=1}}{\frac{4}{3} \pi R^3 \rho_c S_a k_1 C_{As}}$$

$$\rightarrow \eta = \left(\frac{3}{\phi_1^2}\right) (\phi_1 \coth \phi_1 - 1)$$

where $\coth x = \frac{\cosh x}{\sinh x} = \frac{(e^x + e^{-x})}{2}$, \(e^x + e^{-x}\) → $e^x - e^{-x}$
**Internal Diffusion & Overall Rxn Rate**

\[ -r''_A = \eta (-r''_{As}) \]

\( \eta \) quantifies how internal diffusion affects the overall reaction rate.

\[ -r''_A = \eta (-r''_{As}) \]

As particle diameter ↓, \( \phi_n \) ↓, \( \eta \to 1 \), rxn is surface rxn limited.

As particle diameter ↑, \( \phi_n \) ↑, \( \eta \to 0 \), rxn is diffusion limited.

This analysis was for spherical particles. A similar approach can be used to evaluate other geometries, non-isothermal rxn, & more complex rxn kinetics.

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Effectiveness Factor & Rxn Rate

\[ \eta = \frac{3}{\phi_1^2} \left( \phi_1 \coth \phi_1 - 1 \right) \quad \phi_1 = R \sqrt{\frac{\rho_c k_1 S_a}{D_e}} \quad -r'_A = \eta (-r'_{As}) = \eta (k_1 C_{As}) S_a \]

\[ R \downarrow \phi_1 \downarrow \eta \rightarrow 1 \quad \text{surface-reaction-limited} \]

when \( \phi_1 \gg, (\approx 30) \) \( \eta \) can be simplified to: \( \eta \approx \frac{3}{\phi_1} = \frac{3}{R} \sqrt{\frac{D_e}{k_1 \rho_c S_a}}, \ll 1 \)

\( \phi_1 \) is large, diffusion-limited reaction inside the pellet (external diffusion will have a negligible effect on the overall rxn rate because internal diffusion limits the rxn rate)

\[ \eta = \frac{-r'_A}{-r'_{As}} = \frac{3}{\phi_1^2} \left( \phi_1 \coth \phi_1 - 1 \right) \quad \text{internal-diffusion-limited:} \quad \eta ; \quad \frac{3}{R} \sqrt{\frac{D_e}{k_1 \rho_c S_a}} \]

\[ -r'_A = \eta (k_1 C_{As}) S_a \quad \rightarrow -r'_A = \frac{3}{R} \sqrt{\frac{D_e}{k_1 \rho_c S_a}} (k_1 C_{As}) S_a \quad \rightarrow -r'_A = \frac{3}{R} \sqrt{\frac{D_e S_a k_1}{\rho_c}} C_{As} \]

Overall rate for 1st-order rxn
Clicker Question

\[-r'_A = \eta \left(k_1 C_{As}\right) S_a\]

Overall rate for 1st-order rxn

\[\eta; \quad \frac{3}{R} \sqrt{\frac{D_e}{k_1 \rho_c S_a}} \quad \rightarrow \quad -r'_A = \frac{3}{R} \sqrt{\frac{D_e}{k_1 \rho_c S_a}} (k_1 C_{As}) S_a\]

When the overall rate of rxn when the reaction is limited by internal diffusion, which of the following would decrease the internal diffusion limitation?

(a) decreasing the radius R of the particle
(b) increasing the concentration of the reactant
(c) increasing the temperature
(d) increasing the internal surface area
(e) Both a and b
Total Rate of Consumption of $A$ in Pellet, $M_A$ (mol/s)

- At steady state, net flow of $A$ into pellet at the external surface completely reacts within the pellet
- Overall molar rxn rate = total molar flow of $A$ into catalyst pellet
- $M_A =$ (external surface area of pellet) x (molar flux of $A$ into pellet at external surface)
- $M_A =$ the net rate of reaction on and within the catalyst pellet

\[
M_A = -4\pi R^2 W_{Ar}\bigg|_{r=R} \rightarrow M_A = 4\pi R^2 \left( \frac{dC_A}{dr} \right)_{r=R} \right. \frac{dC_A}{dr} = \left( \frac{C_{As}}{R} \right) \frac{d}{d\left( \frac{r}{R} \right)} \bigg|_{r=R} \\
\rightarrow M_A = 4\pi R^2 D_e C_{As} \left( \frac{C_A}{C_{As}} \right) \left( \frac{r}{R} \right) \bigg|_{r=R} \rightarrow M_A = 4\pi R D_e C_{As} \frac{d\Psi}{d\lambda} \bigg|_{\lambda=1}
\]