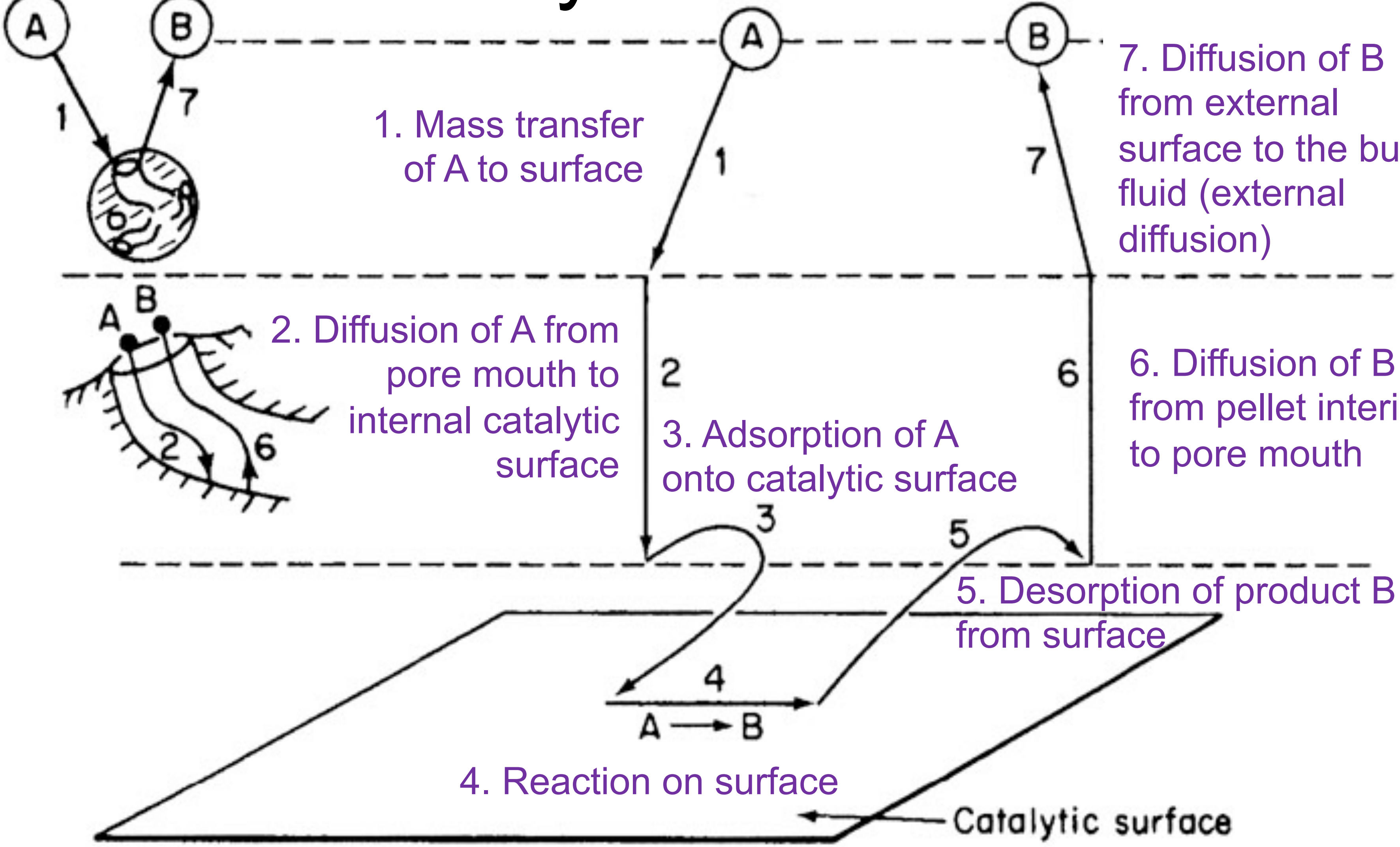
Review: Steps in a Heterogeneous Catalytic Reaction



1. Mass transfer of A to surface

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

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

3. Adsorption of A onto catalytic surface

6. Diffusion of B from pellet interior to pore mouth

5. Desorption of product B from surface

4. Reaction on surface

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

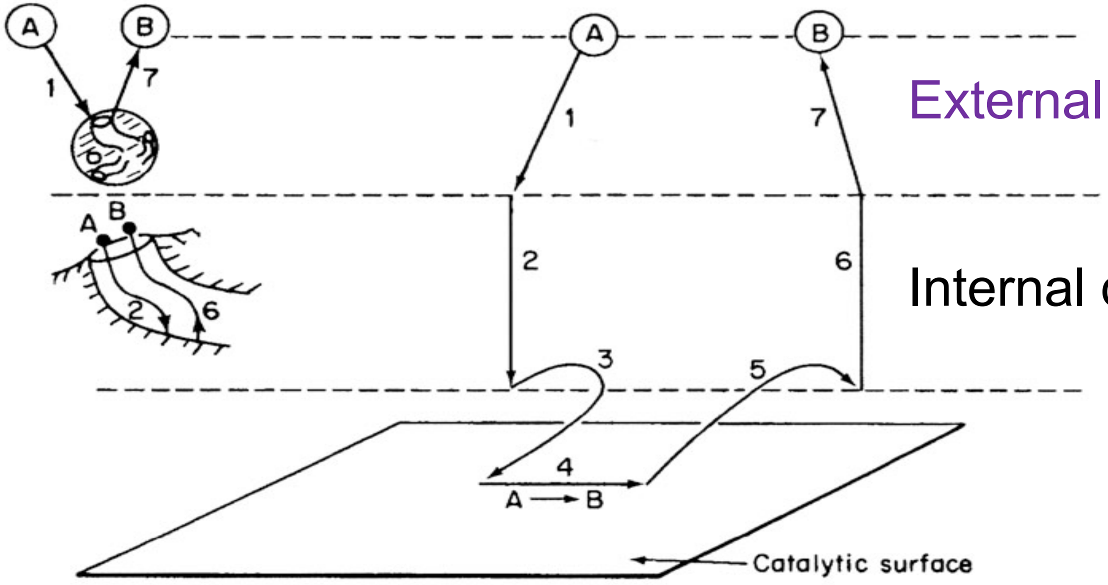
$$i + j \rightarrow k$$

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

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

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



External diffusion

Internal diffusion

Slides courtesy of Pı ... is at Urbana-Champaign.

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:

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

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

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:

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

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

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

Diffusional Flux of A, J_A & Molar Flux $\mathbf{W}$

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

$$\begin{aligned} \mathbf{W}_A &= \boxed{\mathbf{J}_A} + C_A \mathbf{V} \\ \mathbf{W}_A &= \boxed{\mathbf{J}_A} + C_A \sum y_i \mathbf{V}_i \\ \mathbf{W}_A &= \boxed{\mathbf{J}_A} + y_A \left(\mathbf{W}_A + \mathbf{W}_B \right) \end{aligned}$$

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

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

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: $y_A \sum_i W_i \ ; \ 0$

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

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

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

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:

$\mathbf{W}_A = - \mathbf{W}_B$ $\qquad W_A = -cD_{AB}\nabla y_A + \cancelto{0}{y_A\left(W_A + W_B\right)}$ 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: $y_A \sum_i W_i \; ; \; 0$

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

or constant C_{total} :

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

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

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

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):

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

diffusion ≈ 0

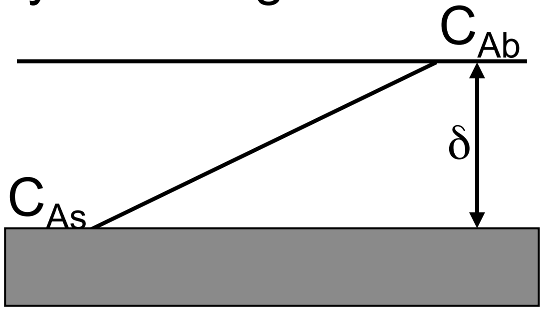
$\leftarrow$ volumetric flow rate

$\leftarrow$ cross-sectional area

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 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

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

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

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

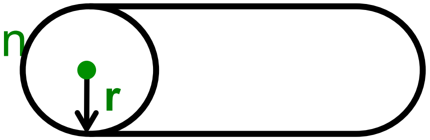
reaction rate per unit surface area (mol/m²·sec)

   c) Convective transport across the boundary layer occurs

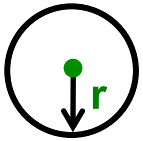
$$W_A\Big|_{boundary} = k_c\left(C_{Ab} - C_{As}\right)$$

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

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:

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

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_p: diameter of pellet (m)

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

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)

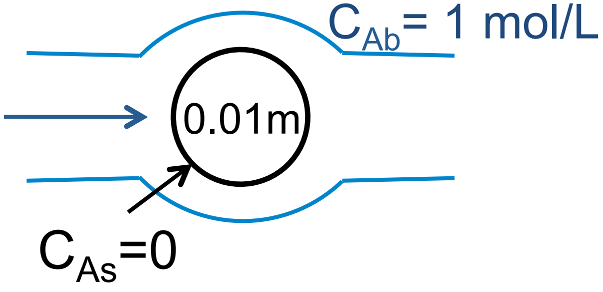
d_p: diameter of pellet (m)

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

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

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



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:

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

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

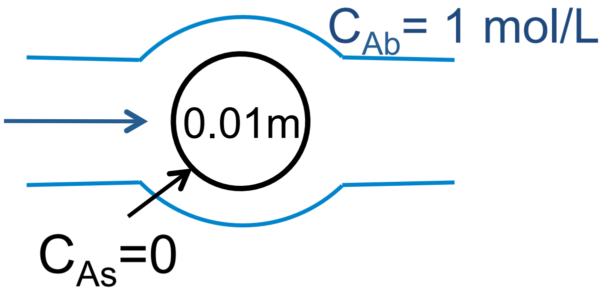
$$Sh = 2 + 0.6(2000)^{1/2}(5000)^{1/3} \rightarrow \boxed{Sh = 461}$$

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

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

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 $C_{As} \approx 0$
- Bulk concentration C_{Ab}= 1 mol/L
- $\nu \equiv$ kinematic viscosity = 0.5 x 10^{-6} m^2/s
- D_{AB} = 1×10^{-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:

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

Computed k_C from Frössling correlation:

$$k_c = \frac{D_{AB}}{d_p} Sh \qquad k_c = 4.61 \times 10^{-6} \frac{m}{s}$$

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

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

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

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 ($W_{A|surface} = -r_A''$) 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

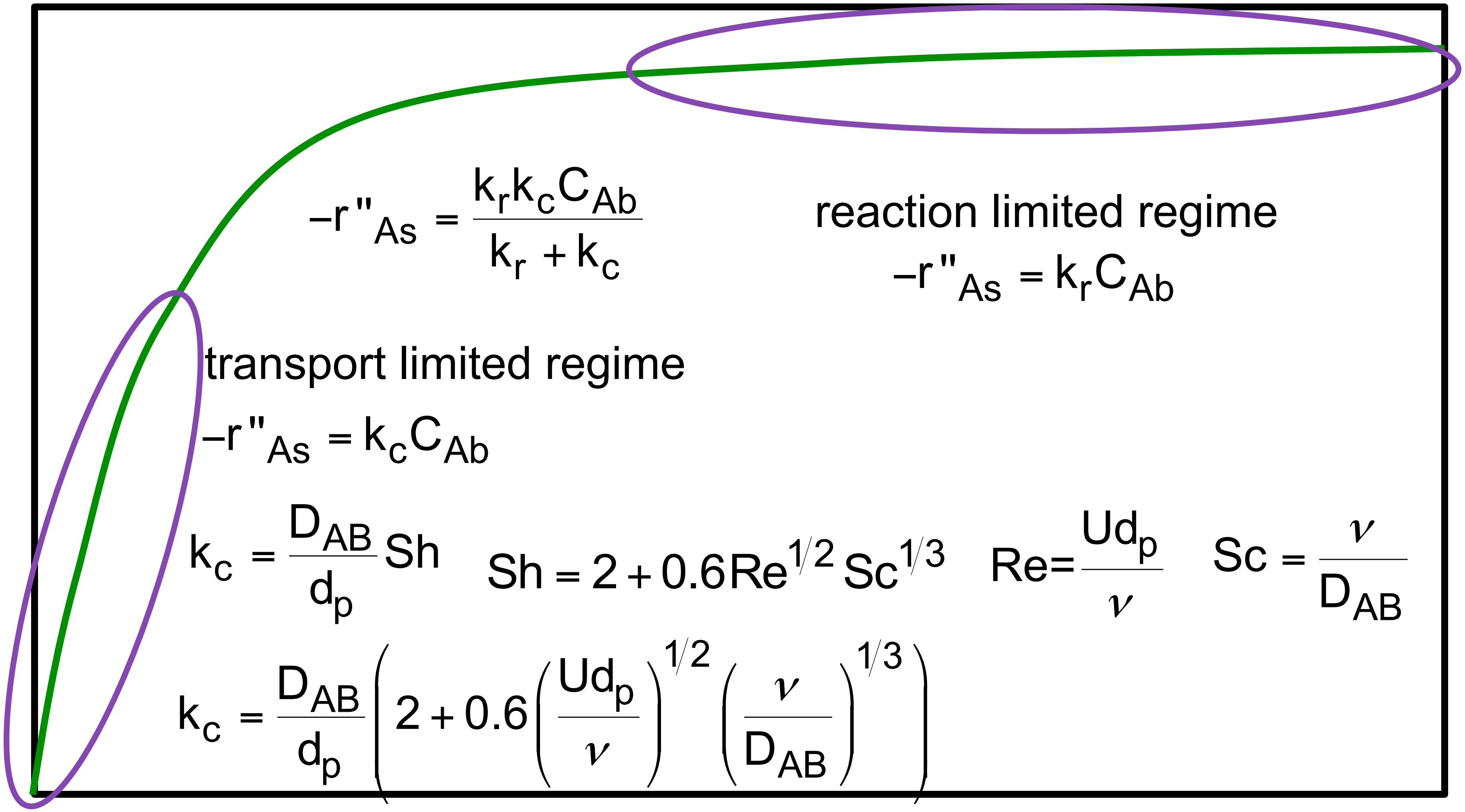
Slow rxn, $k_r \ll k_c \rightarrow k_r$ in denominator is negligible

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

Reaction limited

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

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

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

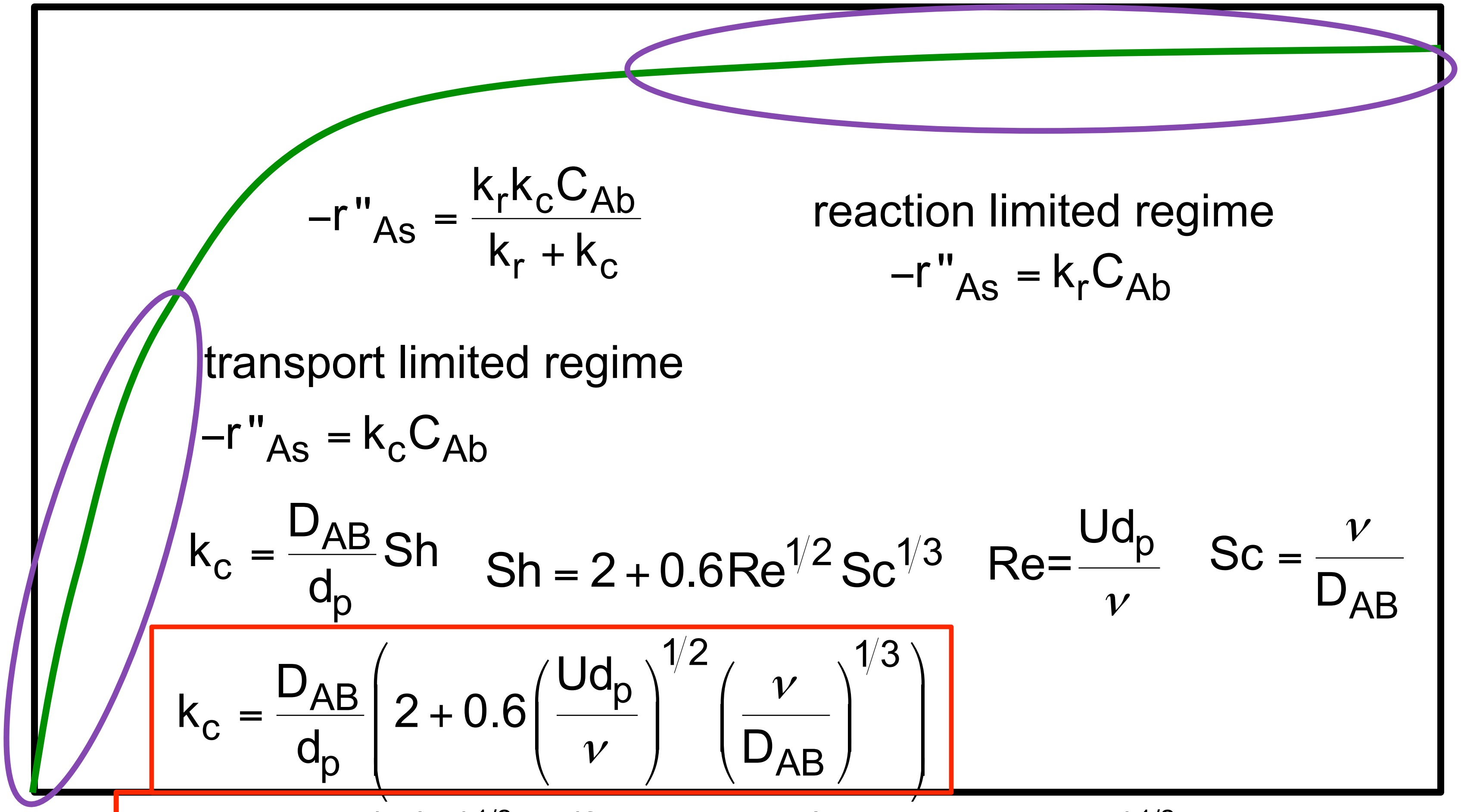
$$k_c=\frac{D_{AB}}{d_p}Sh \qquad Sh=2+0.6Re^{1/2}Sc^{1/3} \qquad Re=\frac{Ud_p}{\nu} \qquad Sc=\frac{\nu}{D_{AB}}$$

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

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



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

reaction limited regime

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

transport limited regime

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

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

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

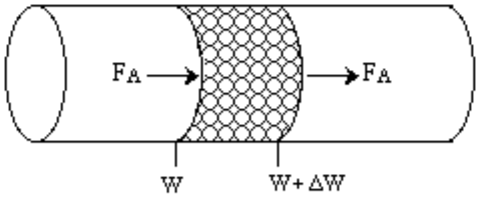
$(U/d_p)^{1/2}$ = (fluid velocity/particle diameter)$^{1/2}$

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

Proportionality is useful for assessing parameter sensitivity

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

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 $A_c \Delta z$:

$$\frac{F_{Az}\big|_{z} - F_{Az}\big|_{z+\Delta z}}{A_c \Delta z} + r''_A\, a_c = 0$$

Take limit as $\Delta z \rightarrow 0$:

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

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

Axial diffusion is negligible compared to bulk flow (convection)

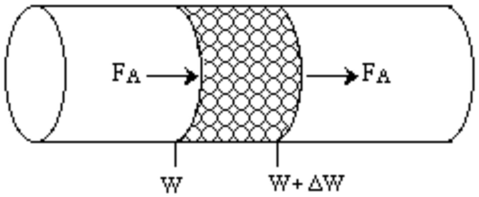
$$F_{Az} = B_{Az} A_c = U C_A A_c$$

Substitute into the mass balance

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

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

Mass Transfer Limited Rxn in PBR



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

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

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

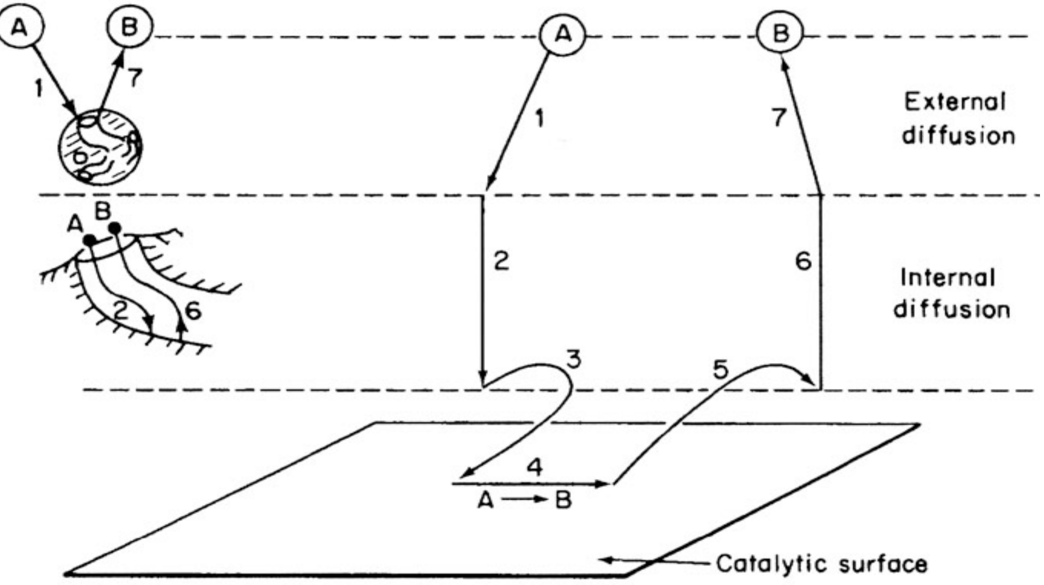
$$\rightarrow -U\frac{dC_A}{dz} = k_c a_c C_A \quad \rightarrow \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^z -\frac{k_c a_c}{U}dz \quad \rightarrow \ln\frac{C_A}{C_{A0}} = -\frac{k_c a_c}{U}z$$

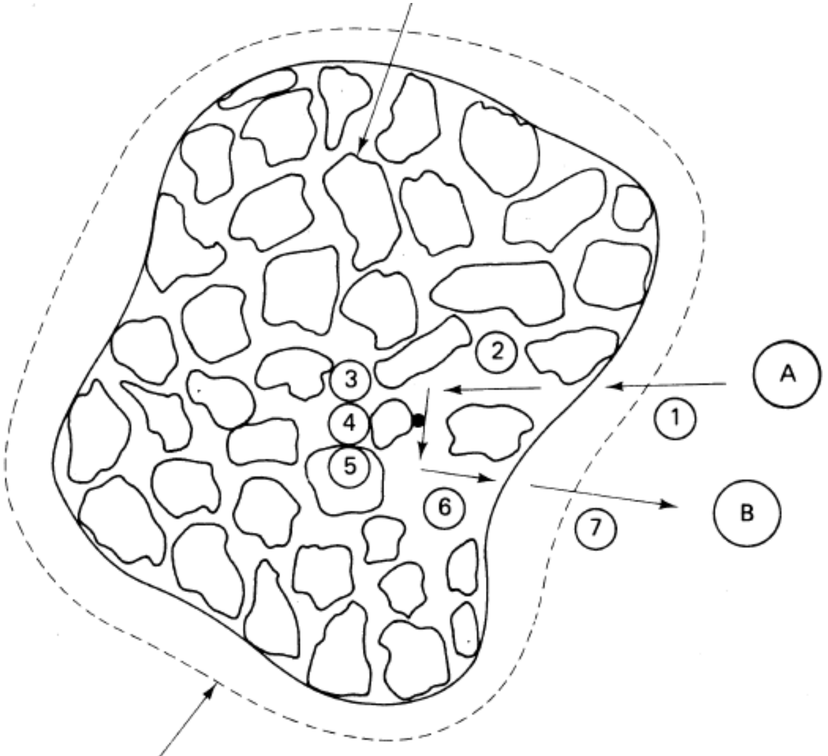
$$\rightarrow \frac{C_A}{C_{A0}} = \exp\left[-\frac{k_c a_c}{U}z\right] \rightarrow \boxed{C_A = C_{A0}\exp\left[-\frac{k_c a_c}{U}z\right]} \boxed{-r''_A = k_c C_{A0}\exp\left[-\frac{k_c a_c}{U}z\right]}$$

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

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 as 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

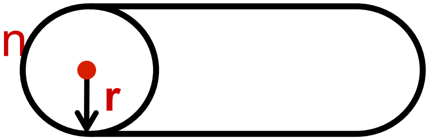
$$W_A\big|_{\text{surface}} = \boxed{-r_A''}$$ reaction rate per unit surface area (mol/m^2·sec)

   c) Convective transport across the boundary layer occurs

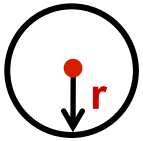
$$W_A\big|_{\text{boundary}} = k_c\left(C_{Ab} - C_{As}\right)$$

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:



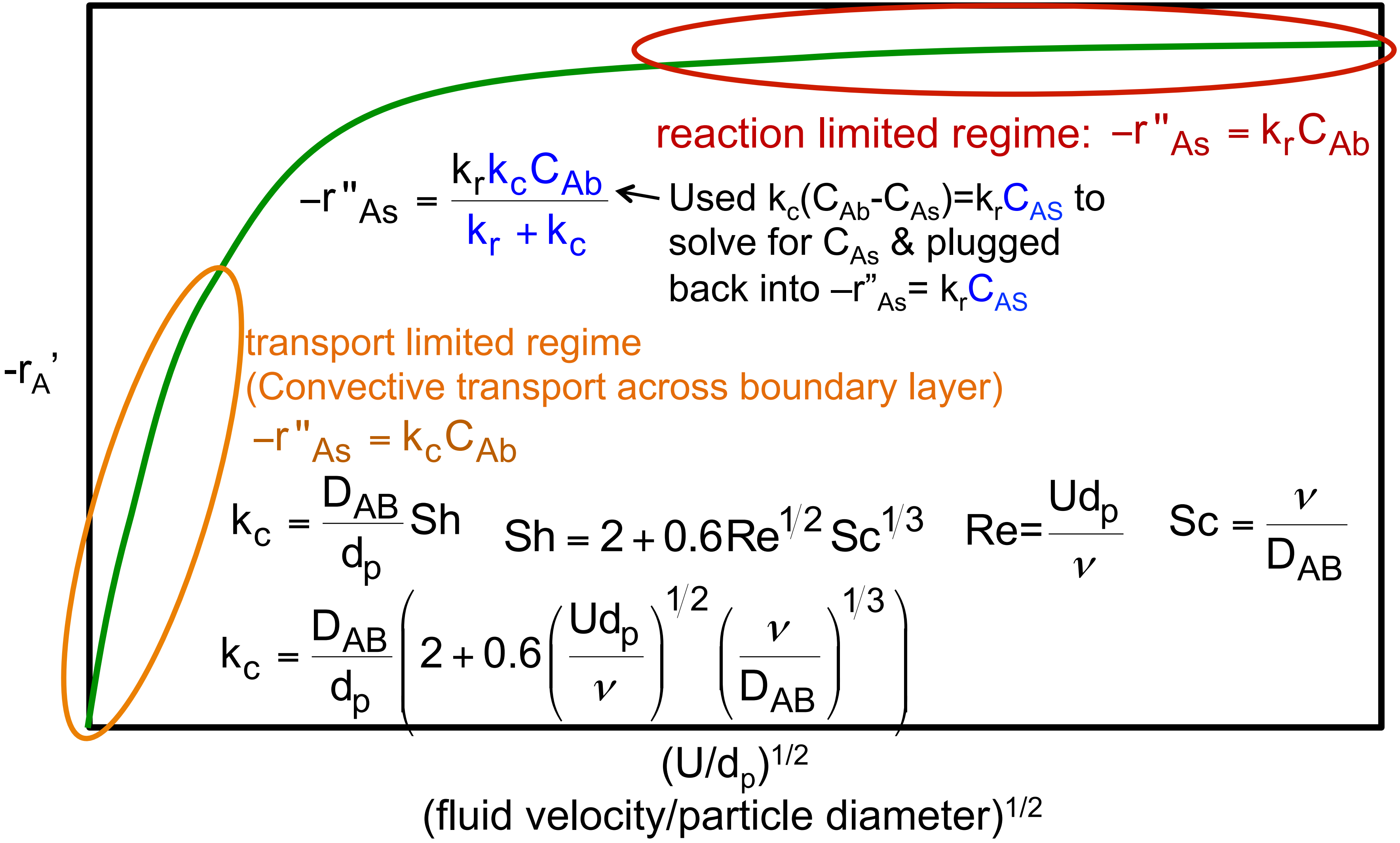
$$\frac{dC_A}{dr} = 0 \text{ at } r=0$$



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



reaction limited regime: $-r''_{As} = k_r C_{Ab}$

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

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

transport limited regime
(Convective transport across boundary layer)

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

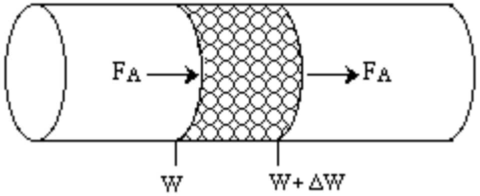
$$k_c = \frac{D_{AB}}{d_p} Sh \qquad Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \qquad Re = \frac{U d_p}{\nu} \qquad Sc = \frac{\nu}{D_{AB}}$$

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

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 + Δz :

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

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

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

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

A_c: cross-sectional area of tube containing catalyst (m^2)

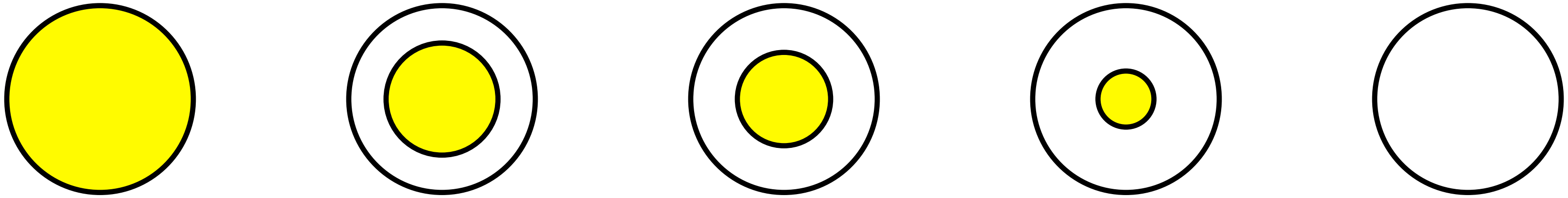
1. Divide out $A_c\Delta z$ and take limit as $\Delta z\rightarrow 0$
2. Put F_{az} and $-r_A''$ in terms of C_A
3. Assume that axial diffusion is negligible compared to bulk flow
4. Assume molar flux of A to surface = rate of consumption of A at surface
5. Rearrange, integrate, and solve for C_A and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

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

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



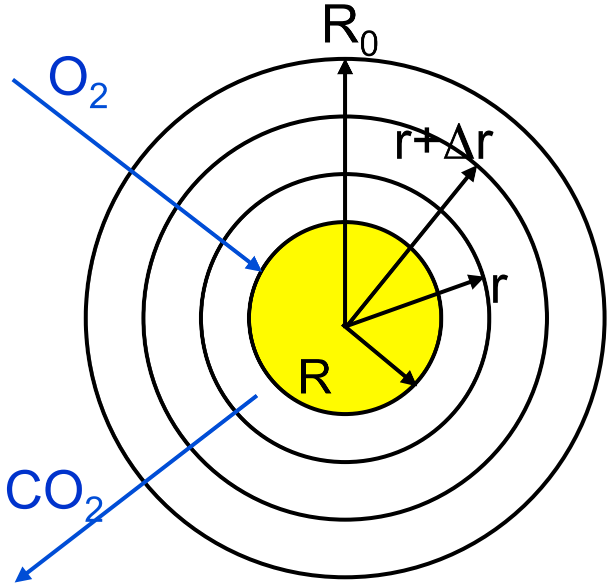
- Regeneration of catalyst by burning off carbon coke in the presence of O_2
- Begins at the surface and proceeds to the core
- Because the amount of carbon that is consumed (burnt off) is proportional to the surface area, and the amount of carbon that is consumed decreases with time

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

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

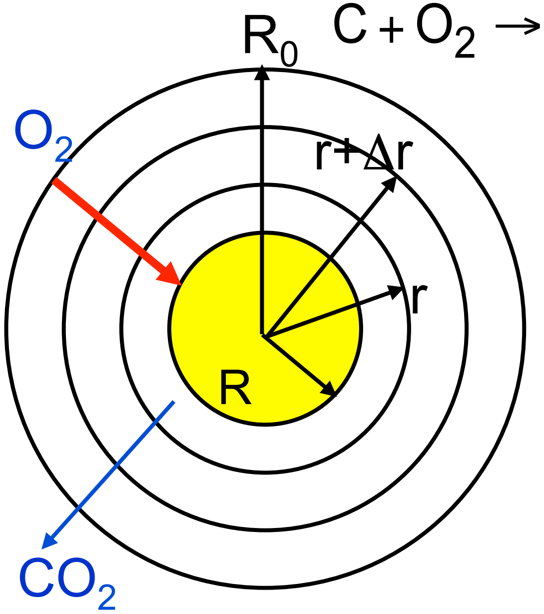
r : radius R_0:outer radius of particle   R: radius of unreacted core   r = 0 at core

What is the rate of time required for the core to shrink to a radius R?

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)

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

Mole Balance on O_2 From r to r+Δr



$C + O_2 \rightarrow CO_2$

Rate in - rate out + gen = accum

$$W_{Ar}4\pi r^2\Big|_r - W_{Ar}4\pi r^2\Big|_{r+\Delta r} + 0 = 0$$

Oxygen reacts at the surface, not in this region

Divide by -4πΔr: $\rightarrow \dfrac{W_{Ar}r^2\Big|_{r+\Delta r} - W_{Ar}r^2\Big|_r}{\Delta r} = 0$

Take limit as Δr→0: $\rightarrow \dfrac{d\left(W_{Ar}r^2\right)}{dr} = 0$

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

$$\mathbf{W}_A = -D_e\frac{dC_A}{dr} + y_A\left(\mathbf{W}_A + \mathbf{W}_B\right)$$

D_e: effective diffusivity

For every mole of O_2 that enters, a mol of CO_2 leaves → W_{O2}=-W_{CO2} $\rightarrow \mathbf{W}_A = -D_e\dfrac{dC_A}{dr}$

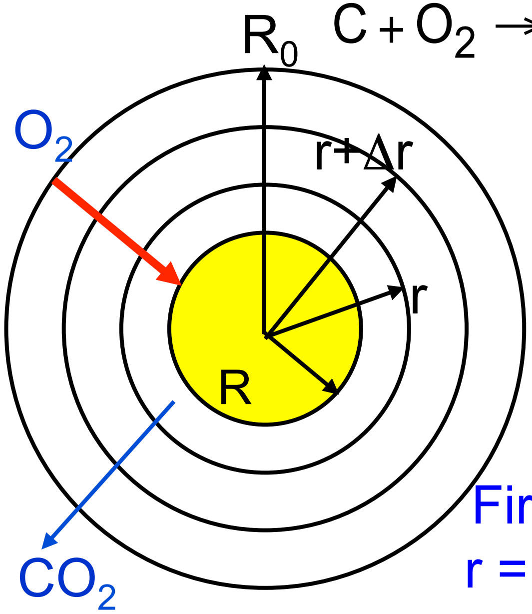
Plug W_{Ar} into mole balance: $\dfrac{d}{dr}\left(-D_e\dfrac{dC_A}{dr}r^2\right) = 0$

Divide out $-D_e$: $\rightarrow \dfrac{d}{dr}\left(\dfrac{dC_A}{dr}r^2\right) = 0$

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

Mole Balance on O_2 From r to r+Δr (2)

$C + O_2 \rightarrow CO_2$



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

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

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

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

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

Next solve for when $r = R_0$ & $C_A=C_{A0}$

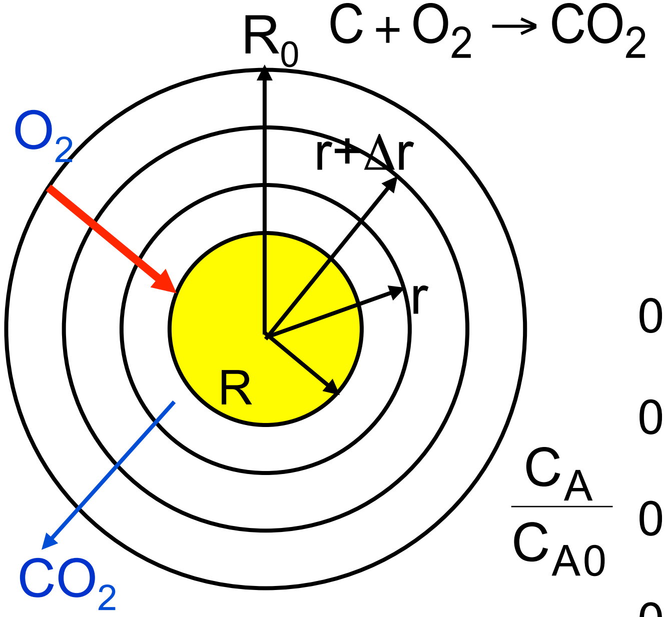
$$C_{A0} = -\frac{K_1}{R_0} + \frac{K_1}{R} \quad \rightarrow C_{A0} = K_1\left(\frac{1}{R} - \frac{1}{R_0}\right)$$

Take the ratio to determine C_A/C_{A0}

$$\rightarrow \frac{C_A}{C_{A0}} = \frac{\cancel{K_1}(1/R - 1/r)}{\cancel{K_1}(1/R - 1/R_0)} \quad \rightarrow \boxed{\frac{C_A}{C_{A0}} = \frac{1/R - 1/r}{1/R - 1/R_0}}$$

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

Oxygen Concentration Profile & Flux

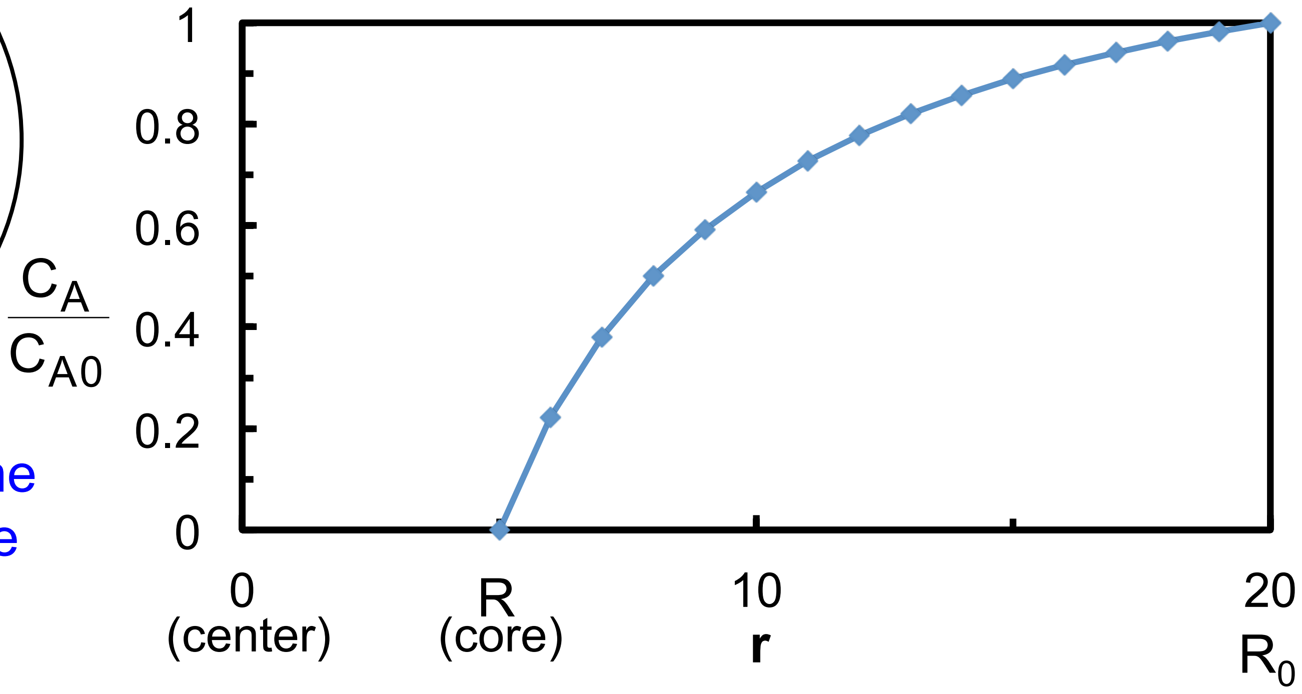


$$\boxed{\frac{C_A}{C_{A0}} = \frac{1/R - 1/r}{1/R - 1/R_0}}$$

C_A: oxygen concentration

$C_{Ab} = C_{A0}$

Oxygen concentration Profile at time t



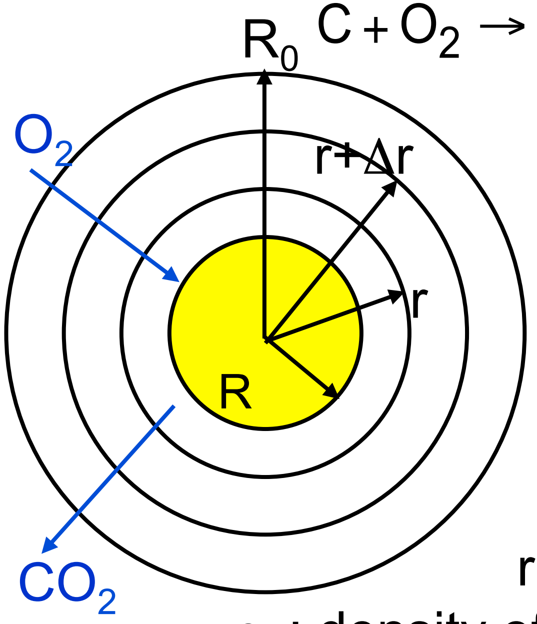
Finally determine the flux of oxygen to the surface of the core:

$$\mathbf{W}_A = -D_e \frac{dC_A}{dr}$$

$$C_A = \frac{C_{A0}\left(1/R - 1/r\right)}{1/R - 1/R_0} \rightarrow \mathbf{W}_A = -D_e \frac{d}{dr}\left[\frac{C_{A0}\left(1/R - 1/r\right)}{1/R - 1/R_0}\right] \rightarrow \mathbf{W}_A = \frac{-D_e C_{A0}}{\left(1/R - 1/R_0\right) r^2}$$

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

Mass Balance on Carbon (C)



$$C + O_2 \rightarrow CO_2$$

In – out + gen = accumulation

$$\underbrace{0 - 0}_{} + r''_c\, 4\pi R^2 = \frac{d\left(\frac{4}{3}\pi R^3 \rho_C \phi_C\right)}{dt}$$

Elemental C does not enter or leave the surface

Change in the mass of the carbon core

r''_C: rate of C gen. per unit surface area of core (mol/s·m^2)

ρ_C: density of solid C ϕ_C: fraction of the volume of the core that is C

Simplify mass balance:

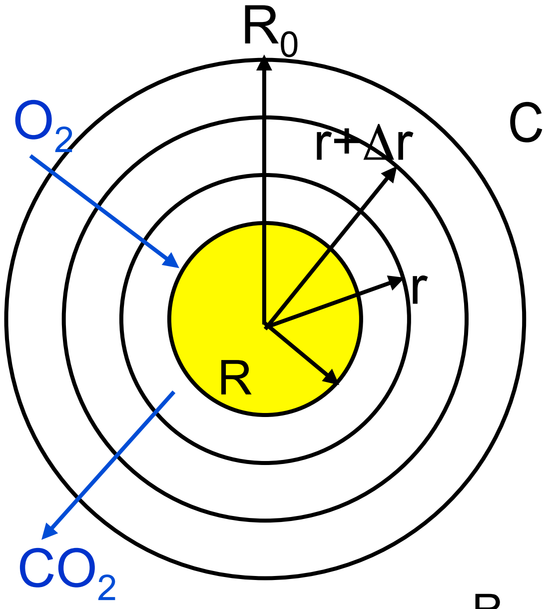
$$r''_c\, 4\pi R^2 = \frac{d\left(\frac{4}{3}\pi R^3 \rho_C \phi_C\right)}{dt} \rightarrow \frac{r''_c}{\rho_C \phi_C} = \frac{dR}{dt}$$

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:

$$r''_C = -\mathbf{W}_A = \mathbf{W}_B = \frac{D_e C_{A0}}{\left(1/R - 1/R_0\right) r^2} \rightarrow -r''_C = \frac{D_e C_{A0}}{R - R^2/R_0}$$

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



$C + O_2 \rightarrow CO_2$

$$\frac{dR}{dt} = \frac{r''_c}{\rho_C \phi_C} \qquad -r''_c = \frac{D_e C_{A0}}{R - R^2/R_0}$$

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

$$\rightarrow \frac{dR}{dt} = \frac{-D_e C_{A0}}{\rho_C \phi_C}\left(\frac{1}{R - R^2/R_0}\right)$$

$$\rightarrow \int_{R_0}^{R} \left(R - R^2/R_0\right) dR = \int_0^t \frac{-D_e C_{A0}}{\rho_C \phi_C} dt$$

Integrate over 0 to t & R_0 to R

$$\rightarrow \left.\frac{R^2}{2} - \frac{R^3}{3R_0}\right]_{R_0}^{R} = \frac{-D_e C_{A0}}{\rho_C \phi_C} t \quad \rightarrow \frac{R^2}{2} - \frac{R^3}{3R_0} - \frac{R_0{}^2}{2} + \frac{\cancel{R_0}{}^3}{3\cancel{R_0}} = \frac{-D_e C_{A0}}{\rho_C \phi_C} t$$

$$\rightarrow \frac{R^2}{2} - \frac{R^3}{3R_0} - \frac{R_0{}^2}{2} + \frac{R_0{}^2}{3} = \frac{-D_e C_{A0}}{\rho_C \phi_C} t$$

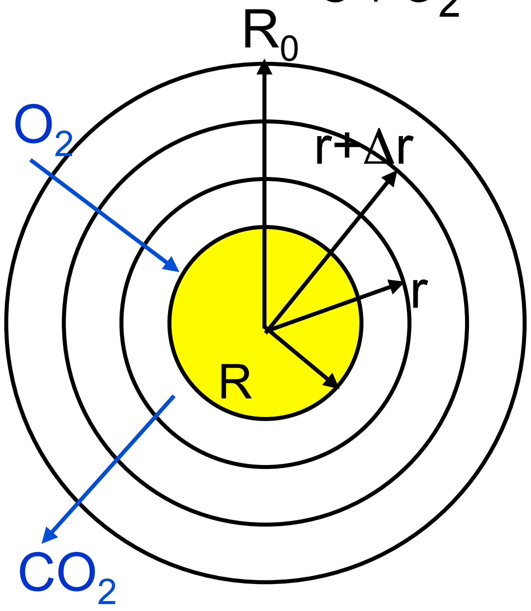
Get common denominators

$$\rightarrow \frac{3R_0R^2}{6R_0} - \frac{2R^3}{6R_0} - \frac{3R_0{}^2 - 2R_0{}^2}{6} = \frac{-D_e C_{A0}}{\rho_C \phi_C} t \quad \rightarrow \frac{3R_0R^2}{6R_0} - \frac{2R^3}{6R_0} - \frac{R_0{}^2}{6} = \frac{-D_e C_{A0}}{\rho_C \phi_C} t$$

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

$C + O_2 \rightarrow CO_2$



$$\rightarrow \frac{3R_0R^2}{6R_0} - \frac{2R^3}{6R_0} - \frac{R_0^{\ 2}}{6} = \frac{-D_eC_{A0}}{\rho_C\phi_C}t$$

Solve for t:

$$\rightarrow \left(\frac{3R_0R^2}{6R_0} - \frac{2R^3}{6R_0} - \frac{R_0^{\ 2}}{6}\right)\left(-\frac{\rho_C\phi_C}{D_eC_{A0}}\right) = t$$

Factor out $R_0^{\ 2}/6$

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

Factor out -1

$$\rightarrow \left(1 - \frac{3R^2}{R_0^{\ 2}} + \frac{2R^3}{R_0^{\ 3}}\right)\frac{\rho_C\phi_C R_0^{\ 2}}{6D_eC_{A0}} = t \quad \rightarrow \boxed{\left(1 - 3\left(\frac{R}{R_0}\right)^2 + 2\left(\frac{R}{R_0}\right)^3\right)\frac{\rho_C\phi_C R_0^{\ 2}}{6D_eC_{A0}} = t}$$

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

$$\rightarrow t = \left(1 - 3\left(\frac{0}{R_0}\right)^2 + 2\left(\frac{0}{R_0}\right)^3\right)\frac{\rho_C\phi_C R_0^{\ 2}}{6D_eC_{A0}} \quad \rightarrow \boxed{t = \frac{\rho_C\phi_C R_0^{\ 2}}{6D_eC_{A0}}}$$

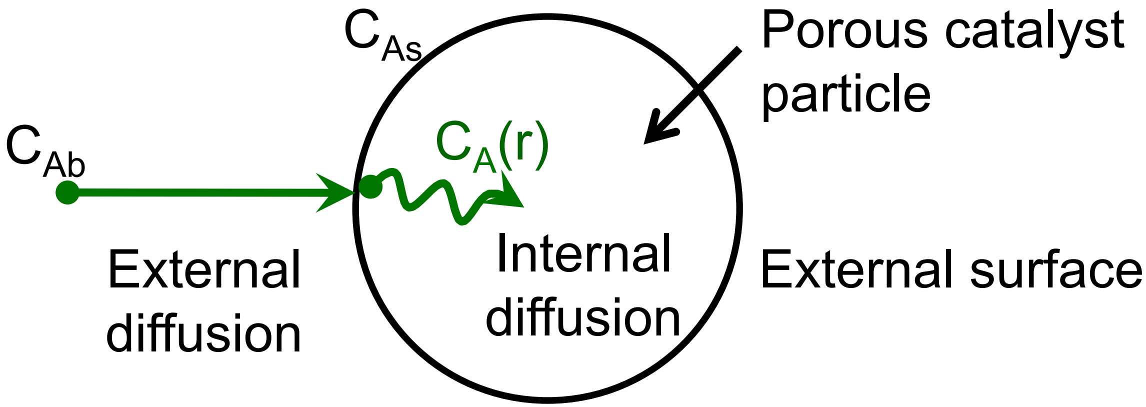
Complete regeneration

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.



C_{As}

C_{Ab}

$C_A(r)$

Porous catalyst particle

External diffusion

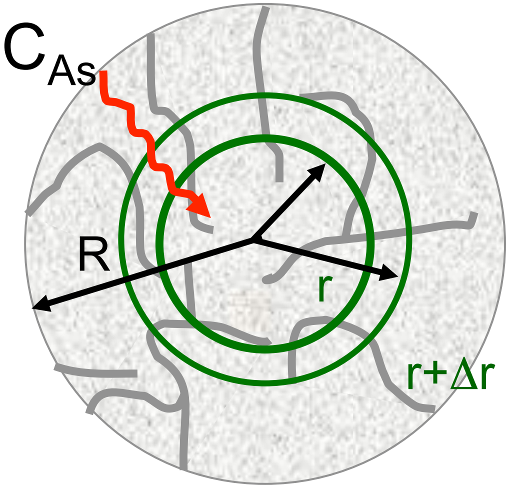
Internal diffusion

External surface

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.

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

Basic Molar Balance for Differential Element



Spherical shell of inner radius r & outer radius r+Δr

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

Rate of A **in** at *r* = W_{Ar} · area = $W_{Ar} \times 4\pi r^2\big|_r$

Rate of A **out** at *r* - Δ*r* = W_{Ar} · area = $W_{Ar} \times 4\pi r^2\big|_{r-\Delta r}$

The mole balance over the shell thickness Δ*r* is:

IN - OUT + GEN =ACCUM

$$W_{Ar}4\pi r^2\big|_r - W_{Ar}4\pi r^2\big|_{r-\Delta r} + r'_A\underbrace{\left(4\pi r_m{}^2\Delta r\right)}_{\text{Volume of shell}}\rho_c = 0$$

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

ρ_c: mass of catalyst per unit volume of catalyst (catalyst density)

r_m: mean radius between *r* and *r* - Δ*r*

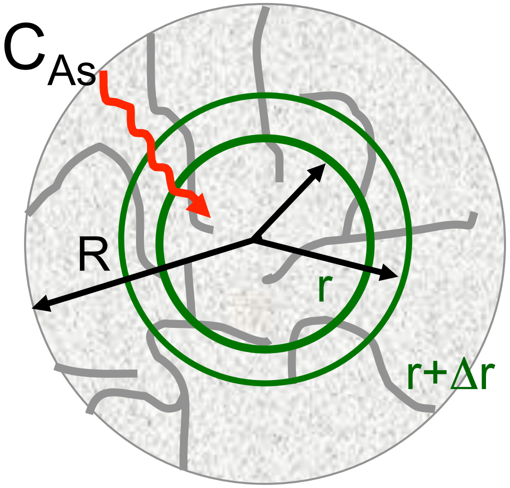
Divide by -4πΔr & take limit as Δr →0

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

Differential BMB in spherical catalyst particle

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

Diffusion Equation (Step 2)



IN - OUT + GEN =ACCUM

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

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

$$\mathbf{W}_A = -cD_e\frac{dy_A}{dr} = -D_e\frac{dC_A}{dr}$$

Must use effective diffusivity, D_e, instead of D_{AB} to account for:

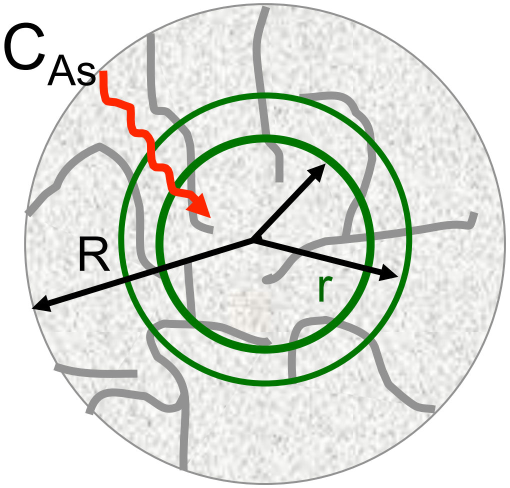
1) Tortuosity of paths
2) Void spaces
3) Pores having varying cross-sectional areas

$$D_e = D_{AB}\frac{\phi_p\sigma_c}{\tilde{\tau}}$$

D_A	bulk diffusivify
ϕ_p	pellet porosity ($V_{\text{void space}}/V_{\text{void \& solid}}$) (typical ~ 0.4)
σ	constriction factor (typical ~ 0.8)
$\tilde{\tau}$	tortuosity (distance molecule travels between 2 pts/actual distance between those 2 pts) (typical ~ 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



$$\text{BMB}: \; W_{Ar}4\pi r^2\big|_r - W_{Ar}4\pi r^2\big|_{r-\Delta r} + r'_A\left(4\pi r_m{}^2\Delta r\right)\rho_c = 0$$

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

Diffusion: $\mathbf{W_A} = -cD_e\frac{dy_A}{dr} = -D_e\frac{dC_A}{dr}$

Write the rate law based on surface area: $-r''_A = k''_n C_A{}^n \quad \frac{\text{mol}}{\text{m}^2\cdot\text{s}}$

Relate r'$_A$ to r''$_A$ by: $\frac{\text{mol}}{\text{g cat}\cdot\text{s}} \quad -r'_A = -r''_A S_a \qquad S_a = \frac{\text{catalyst surface area}}{\text{mass of catalyst}}$

$$\text{BMB}: \frac{d\left(W_{Ar}r^2\right)}{dr} - r'_A r^2\rho_c = 0$$

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

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

Boundary Conditions:
C_A finite at r=0 $\qquad C_A = C_{As}$ 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

$$\lambda=\frac{r}{R}\qquad \text{(Psi) }\Psi=\frac{C_A}{C_{As}}\qquad \phi_n{}^2=\frac{k''_n S_a\rho_c R C_{As}{}^n}{D_e\left[\left(C_{As}-0\right)/R\right]}\rightarrow\phi_n{}^2=\frac{k''_n S_a\rho_c R^2 C_{As}{}^{n-1}}{D_e}$$

$$\frac{d^2\Psi}{d\lambda^2}+\frac{2}{\lambda}\left(\frac{d\Psi}{d\lambda}\right)-\phi_n{}^2\Psi^n=0$$

Boundary Conditions:

$\Psi=1$ at $\lambda=1$ $\Psi=$finite at $\lambda=0$

Thiele modulus for rxn of nth order ≡ ϕ_n

Subscript n = reaction order

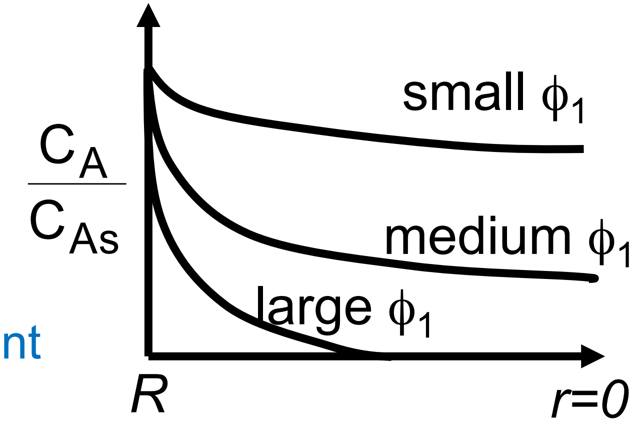
$$\phi_n{}^2=\frac{\text{"a" surface rxn rate}}{\text{"a" diffusion rate}}$$

ϕ_n is small: **surface reaction** is rate limiting

ϕ_n is large: **internal diffusion** is rate limiting

The solution for a 1st order rxn:

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



small ϕ_1: surface rxn control, significant amount of reactant diffuses into pellet interior w/out reacting

large ϕ_1: surface rxn is rapid, reactant is consumed very closed to the external surface of pellet (A waste of precious metal inside of pellet)

Internal Effectiveness Factor, η

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

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

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

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

$$\eta = \frac{4\pi R^2\left(-W_{As}\big|_{r=R}\right)}{\left(-r_{As}\right)\frac{4}{3}\pi R^3} \rightarrow \eta = \frac{\left(4\pi R^2\right)D_e\left[\frac{dC_A}{dr}\right]_{r=R}}{\rho_c S_a k''_1 C_{As}\frac{4}{3}\pi R^3} \rightarrow \eta = \frac{4\pi R^2 D_e C_{As}\left[\frac{d\phi}{d\lambda}\right]_{\lambda=1}}{\frac{4}{3}\pi R^3 \rho_c S_a k''_1 C_{As}}$$

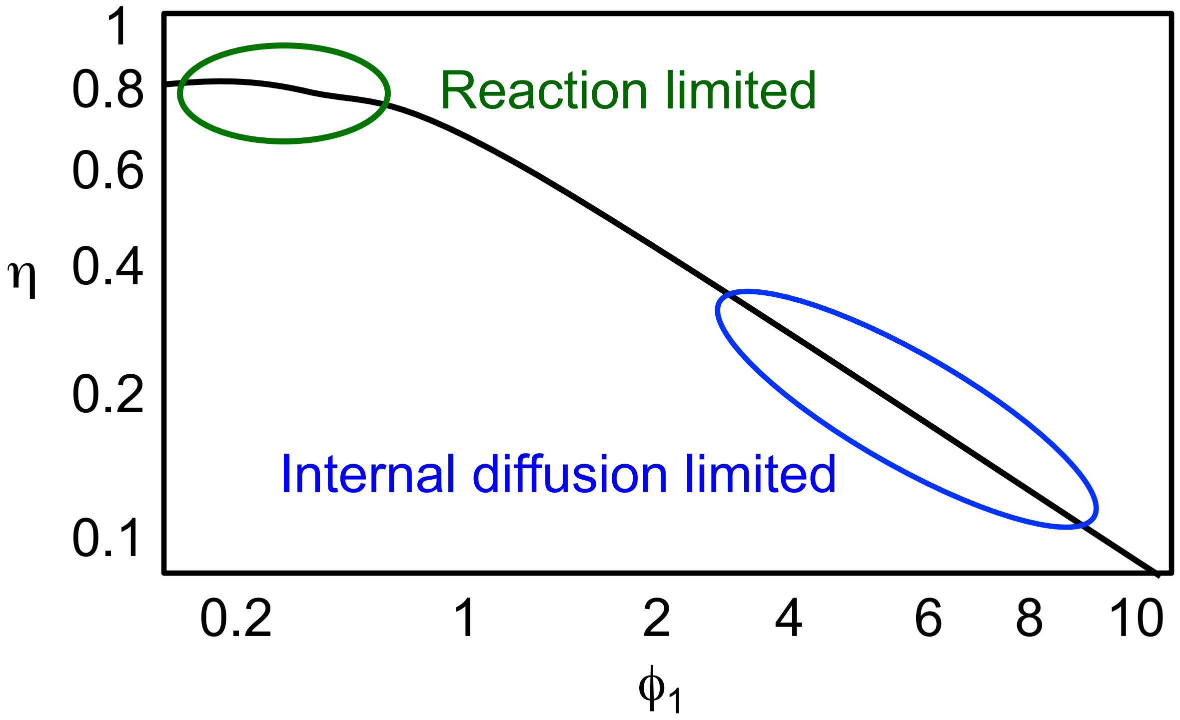
$$\rightarrow\rightarrow \eta = \left(\frac{3}{\phi_1^2}\right)\left(\phi_1 \coth\phi_1 - 1\right) \text{ where } \coth x = \frac{\cosh x}{\sinh x} = \frac{\left(e^x + e^{-x}\right)/2}{\left(e^x - e^{-x}\right)/2} \rightarrow \frac{e^x + e^{-x}}{e^x - e^{-x}}$$

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

Internal Diffusion & Overall Rxn Rate

$-r''_A = \eta(-r''_{As})$ η quantifies how internal diffusion affects the overall rxn rate

Effectiveness factor vs ϕ_n



As particle diameter ↓, ϕ_n ↓, $\eta \rightarrow 1$, rxn is surface rxn limited

As particle diameter ↑, ϕ_n ↑, $\eta \rightarrow 0$, 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

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

$R \downarrow \quad \phi_1 \downarrow \quad \eta \rightarrow 1$ surface-reaction-limited

when ϕ_1 >>,($\approx$ 30) η can be simplified to: $\eta \cong \frac{3}{\phi_1} = \frac{3}{R}\sqrt{\frac{D_e}{k_1 \rho_c S_a}}, << 1$

ϕ_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)

$$\eta = \frac{-r'_A}{-r'_{As}} = \frac{3}{\phi_1^2}\left(\phi_1 \coth\phi_1 - 1\right)$$

internal-diffusion-limited: $\eta \approx \frac{3}{R}\sqrt{\frac{D_e}{k_1 \rho_c S_a}}$

$$-r'_A = \eta\left(k_1 C_{As}\right)S_a \rightarrow -r'_A = \frac{3}{R}\sqrt{\frac{D_e}{k_1 \rho_c S_a}}\left(k_1 C_{As}\right)S_a \rightarrow -r'_A = \frac{3}{R}\sqrt{\frac{D_e S_a k_1}{\rho_c}}C_{As}$$

Overall rate for 1st-order rxn

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

Clicker Question

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

Overall rate for 1st-order rxn

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

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

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

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 <u>on</u> and <u>within</u> the catalyst pellet

$$M_A = -4\pi R^2 \left. W_{Ar} \right|_{r=R} \rightarrow M_A = 4\pi R^2 \left.\left(D_e \frac{dC_A}{dr} \right)\right|_{r=R} \qquad \frac{dC_A}{dr} = \left(\frac{C_{As}}{R} \right) \left. \frac{d\left(\frac{C_A}{C_{As}} \right)}{d\left(\frac{r}{R} \right)} \right|_{r=R}$$

$$\rightarrow M_A = 4\pi R^{\cancel{2}} \frac{D_e C_{As}}{\cancel{R}} \left. \frac{d\left(\frac{C_A}{C_{As}} \right)}{d\left(\frac{r}{R} \right)} \right|_{r=R} \qquad \rightarrow M_A = 4\pi R D_e C_{As} \left. \frac{d\Psi}{d\lambda} \right|_{\lambda=1}$$

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