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

• Next goal: 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: Internal Diffusion Effects in Spherical Catalyst Particles

- Internal diffusion: diffusion of reactants or products from particle surface (pore mouth) to pellet interior
- Concentration at the pore mouth will be higher than that inside the pore

Step 1) Mole balance over the shell thickness $\Delta r$ is:

\[
\text{IN} - \text{OUT} + \text{GEN} = \text{ACCUM}
\]

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

$\rho_c$: catalyst density
$r_m$: mean radius between $r$ and $r - \Delta r$

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

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

Differential BMB in spherical catalyst particle

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

\[
\frac{d(W_A r^2)}{dr} - r_A r^2 \rho_c = 0 \quad \text{(step 1, BMB)}
\]

System at steady state, so EMCD: \( W_B = -W_A \)
(otherwise A or B would accumulate)

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

Rate law:

\[
-r''_A \left( \frac{\text{mol}}{m^2 \cdot s} \right) = k_n C_A^n \rightarrow -r'_A \left( \frac{\text{mol}}{g \text{ cat} \cdot s} \right) = -r''_A S_A
\]

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

Insert diffusion eq & rate eq into BMB:

\[
\frac{d}{dr} \left[ -D_e \frac{dC_A}{dr} r^2 \right] + r^2 \rho_c S_A k_n C_A^n = 0
\]

Solve for \( C_A(r) \) & get \( W_A(r) \) from diffusion eq

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

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

Boundary Conditions:

\[ \psi = 1 \text{ at } \lambda = 1 \quad \psi = \text{finite at } \lambda = 0 \]

Thiele modulus for rxn of nth order \( \equiv \phi_n \)

Subscript \( n \) = reaction order

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

\( \phi_n \) 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 \( \phi_1 \): 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 closed 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.
Review: Internal Effectiveness Factor, $\eta$

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

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

\[ \eta = \frac{-r_A}{-r_A} = \frac{-r''_A}{-r''_A} = \frac{-r'_A}{-r''_A} (\text{mass of catalyst}) \]

**Effectiveness factor vs $\phi_n$**

Reaction limited

Internal diffusion limited

$$\phi_n^2 = \frac{k_n R^2 S_a \rho_c C_{As} n^{-1}}{D_e}$$

- 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
Review: Effectiveness Factor & Rxn Rate

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

\( R \downarrow \phi_1 \downarrow \eta \rightarrow 1 \) surface-reaction-limited

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

\( \phi_1 \) 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)

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

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

Overall rate for 1st-order rxn

To increase the overall rate of a rxn limited by internal diffusion

1. decrease the radius \( R \)
2. increase the temperature
3. increase the concentration of \( A \)
4. increase the internal surface area

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
L21: Simultaneous Internal Diffusion & External Diffusion

Goal: Derive a new rate eq that accounts for internal & external diffusion
- $-r'_A$ is a function of reactant concentration
- Reactant conc is affected by internal & external diffusion
- Express reactant conc in terms of diffusion-related constants & variables
  → Use mole balance

At steady-state: transport of reactants from bulk fluid to external catalyst surface is equal to net rate of reactant consumption in/on the pellet

Molar rate of mass transfer from bulk fluid to external surface:

$$M_A = W_{Ar} (a_c) \Delta V$$

molar flux

external surface area per unit reactor volume

reactor volume

This molar rate of mass transfer to surface is equal to net rxn rate on & in pellet!

$$M_A = -r''_A \text{(external area + internal area)}$$
Basic Molar Balance at Pellet Surface

\[
\begin{align*}
\left( W_{Ar} \right)_{r=R} \times \left( a_c \Delta V \right) &= -r''_A \times \left( a_c \Delta V + S_a \rho_b \Delta V \right) \\
\end{align*}
\]

- \( a_c \): external surface area per reactor volume (m²/m³)
- \( \Delta V \): reactor volume (m³)
- \(-r''_A\): rate of reaction per unit surface area (mol/m²·s)
- \( S_a \): surface area of catalyst per unit mass of catalyst (m²/g cat)
- \( \rho_b \): bulk density, catalyst mass/ reactor volume \( \rho_b = \rho_c (1-\phi) \)
- \( \phi \): porosity of bed (void fraction)
- \( \rho_c \): catalyst density

\[
M_A = W_{Ar} \big|_{r=R} a_c \Delta V = -r''_A \left( a_c \Delta V + S_a \rho_b \Delta V \right)
\]

\[
M_A = W_{Ar} \big|_{r=R} a_c = -r''_A \left( a_c + S_a \rho_b \right)
\]

Typically external surface area \(<<<\) internal surface area

\[
M_A = W_{Ar} \big|_{r=R} a_c = -r'' S_a \rho_b
\]
Overall Molar Rate of Reaction

Overall rxn rate = flux to surface = rxn rate on & in pellet

\[ M_A = W_{Ar|_{r=R}} a_c = -r''_A S_a \rho_b \]

For external mass transport:

\[ W_{Ar|_{r=R}} = k_c (C_{Ab} - C_{As}) \]

Since internal diffusion resistance is also significant, the reactant conc at the internal surface is lower than the reactant conc at the external surface:

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

For a 1st order rxn: \(-r''_A = -\eta k_1 C_{As}\)

where the internal effectiveness factor:

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

Plug flux & 1st order rxn rate back into the mass balance:

\[ M_A = k_c (C_{Ab} - C_{As}) a_c = \eta k_1 C_{As} S_a \rho_b \]

Solve mass balance for \(C_{As}\)

\[ k_c C_{Ab} a_c - k_c C_{As} a_c = \eta k_1 C_{As} S_a \rho_b \]

\[ k_c C_{Ab} a_c = \eta k_1 C_{As} S_a \rho_b + k_c C_{As} a_c \]

\[ k_c C_{Ab} a_c = C_{As} (\eta k_1 S_a \rho_b + k_c a_c) \]

\[ \eta k_1 S_a \rho_b + k_c a_c = C_{As} \]
Overall Effectiveness Factors

\[ C_{As} = \frac{k_c a_c C_{Ab}}{k_c a_c + \eta k_1 S_a \rho_b} \]

Finally insert \( C_{As} \) into \(-r''_A\)

\[ -r''_A = \eta k_1 C_{As} \quad \rightarrow \quad -r''_A = \frac{\eta k_1 k_c a_c C_{Ab}}{k_c a_c + \eta k_1 S_a \rho_b} \]

Overall rxn rate with internal & external diffusion

Is this the overall rxn rate that we ALWAYS use for a surface reaction that has internal & external?

(a) Yes, we should always use this rate equation for a surface reaction
(b) No, we should only use this rate eq for processes that use spherical catalyst pellets
(c) No, we should only use this rate eq for processes that involve catalyst particles that have a constant density & even catalyst loading on the surface
(d) No, we should only use this rate eq for 1st order irreversible reactions
(e) b, c, & d
Overall Effectiveness Factors

\[ C_{As} = \frac{k_c a_c C_{Ab}}{k_c a_c + \eta k_1 S_a \rho_b} \]

Finally insert \( C_{As} \) into \(-r''_A\)

\[-r''_A = \eta k_1 C_{As} \rightarrow -r''_A = \frac{\eta k_1 k_c a_c C_{Ab}}{k_c a_c + \eta k_1 S_a \rho_b} \]

Overall rxn rate with internal & external diffusion

Remember, the internal effectiveness factor (based on \( C_{As} \)) is:

\[ \eta = \frac{\text{actual overall rate of reaction}}{\text{rate of rxn if entire interior surface were exposed to the external surface conditions}} \]

The overall effectiveness factor (based on \( C_{Ab} \)) is defined as:

\[ \Omega = \frac{\text{actual overall rate of reaction}}{\text{rate of reaction if entire interior surface were exposed to the bulk conditions}} \]

\[ \Omega = \frac{-r''_A}{-r''_{Ab}} \rightarrow \Omega = \frac{\eta k_1 C_{Ab}}{1 + \eta k_1 S_a \rho_b / k_c a_c} \]

\[ \rightarrow \Omega \left( -r''_{Ab} \right) = -r''_A \quad \text{Put into design eq to account for internal & external diffusion} \]
Rxn Rate Variation vs Reactor Conditions

External diffusion
\[-r'_A \propto k_c = \frac{D_{AB}}{d_p} Sh \rightarrow k_c = \frac{D_{AB}}{d_p} \left(2 + 0.6 \left(\frac{U d_p}{\mu/\rho}\right)^{1/2} \left(\frac{\mu/\rho}{D_{AB}}\right)^{1/3}\right)\]

Internal diffusion
\[-r'_A = \eta k_r C_A s_s \rightarrow \eta = \frac{3}{R^2 \rho_c k_{1S_s}} \left(\frac{\sqrt{\rho_c k_{1S_s}}}{D_e} \coth \left(R \frac{\sqrt{\rho_c k_{1S_s}}}{D_e}\right) - 1\right)\]

Surface reaction
\[-r'_A = k C_A\]

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Consider an isothermal catalytic reaction in a PBR where there is no pressure drop and the catalyst pellets are uniformly packed & spherical. The kinetics are 1st order, and k, all physical parameters, and the inlet conditions (pure A in feed, A→products) are given. Derive an equation for $X_A$, taking into account the diffusion to and within each catalyst particle, but ignore diffusion down the length of the reactor.

PBR design eq: \[ \frac{dX_A}{dW} = -r'_A \] Rate must account for diffusion & be in terms of catalyst surface area

1. Put rate in terms of the unit surface area: \[ -r'_A = -r''_A S_a \]

2. Account for diffusion limitations in rate eq: \[ -r''_A = \Omega (-r''_{Ab}) \rightarrow -r'_A = -r''_{Ab} \Omega S_a \]

3. Rate is 1st order: \[ -r''_{Ab} = kC_{Ab} \rightarrow -r'_A = kC_{Ab} \Omega S_a \]

4. Put into design eq: \[ F_{A0} \frac{dX_A}{dW} = kC_{Ab} \Omega S_a \]

5. Put $C_{ab}$ in terms of $X_A$: \[ C_{Ab} = C_{Ab0} (1 - X_A) \rightarrow \frac{dX_A}{dW} = k \Omega S_a C_{Ab0} (1 - X_A) \]

6. Integrate: \[ \frac{dX_A}{dW} = \frac{k \Omega S_a C_{Ab0} (1 - X_A)}{F_{A0}} \rightarrow \int_0^{X_A} \frac{dX_A}{(1 - X_A)} = \int_0^W \frac{W k \Omega S_a C_{Ab0}}{F_{A0}} dW \]
Consider an isothermal catalytic reaction in a PBR where there is no pressure drop and the catalyst pellets are uniformly packed & spherical. The kinetics are 1\textsuperscript{st} order, and \( k \), all physical parameters, and the inlet conditions (pure \( A \) in feed, \( A \rightarrow \text{products} \)) are given. Derive an equation for \( X_A \), taking into account the diffusion to and within each catalyst particle, but ignore diffusion down the length of the reactor.

6. Integrate:
\[
\int_0^{X_A} \frac{dX_A}{(1 - X_A)} = \int_0^W \frac{k \Omega S_a C_{A_0}}{F_{A_0}} dW \rightarrow -\ln(1 - X_A) = \frac{k \Omega S_a C_{A_0} W}{F_{A_0}}
\]

7. Solve for \( X_A \):
\[
\ln(1 - X_A) = \frac{-k \Omega S_a C_{A_0} W}{F_{A_0}} \rightarrow 1 - X_A = e \frac{-k \Omega S_a C_{A_0} W}{F_{A_0}}
\]
\[
\rightarrow X_A = 1 - e \frac{-k \Omega S_a C_{A_0} W}{F_{A_0}}
\]
\[
\rightarrow X_A = 1 - e \frac{-k \Omega S_a W}{v_0}
\]
$X_A$ for 1st order rxn executed in an isothermal PBR packed with spherical catalyst particles with internal & external diffusion limitations

$$X_A = 1 - e^{\frac{-k\omega S_a W}{\nu_0}}$$

For same conditions, eq derived in Fogler (12-71) for $X_A$ at end of reactor of length $L$ is:

$$X_A = 1 - e^{\frac{-k\omega S_a \rho_b L}{U}}$$

where: $\rho_b = \frac{\text{catalyst mass}}{\text{reactor volume}} = \frac{\text{kg}}{\text{m}^3}$

$L = z$, $U = \text{superficial velocity} = \frac{\nu_0}{A_c}$

Are these equations the same?

They differ in the exponent:

$$\frac{-k\omega S_a W}{\nu_0} \neq \frac{-k\omega S_a \rho_b L}{U}$$

$$\frac{W}{\nu_0} - \rho_b L \neq \frac{W}{\nu_0} \rho_b \left( \frac{L}{A_c} \right) A_c = V$$

$$\frac{W}{\nu_0} - \rho_b \frac{V}{\nu_0} \neq \frac{W}{\nu_0} \left( \frac{W}{V} \right) V \neq \frac{W}{\nu_0} = \frac{W}{\nu_0}$$

$$X_A = 1 - e^{\frac{-k\omega S_a W}{\nu_0}} = 1 - e^{\frac{-k\omega S_a \rho_b L}{U}} = X_A$$
Review: Simultaneous Internal Diffusion & External Diffusion

Goal: Derive a new rate eq that accounts for internal & external diffusion

- \(-r'_A\) is a function of reactant concentration
- Reactant conc is affected by internal & external diffusion
- Express reactant conc in terms of diffusion-related constants & variables

→ Use mole balance

At steady-state: transport of reactants from bulk fluid to external catalyst surface is equal to net rate of reactant consumption in/on the pellet

Molar rate of mass transfer from bulk fluid to external surface:

\[ M_A = \frac{W_{Ar}}{a_c} \Delta V \]

This molar rate of mass transfer to surface is equal to net rxn rate on & in pellet!

\[ M_A = -r''_A \text{ (external area + internal area)} \]

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Review: Basic Molar Balance at Spherical Pellet Surface

\[
M_A = W_{Ar |_{r=R}} a_c \Delta V = -r''_A (a_c \Delta V + S_a \rho_b \Delta V)
\]

- \(a_c\): external surface area per reactor volume (m²/m³)
- \(\Delta V\): reactor volume (m³)
- \(\phi\): porosity of bed (void fraction)
- \(-r''_A\): rate of reaction per unit surface area (mol/m²·s)
- \(-r'_A\): mol/g cat·s
- \(S_a\): surface area of catalyst per unit mass of catalyst (m²/g cat)
- \(\rho_b\): bulk density, catalyst mass/ reactor volume \(\rho_b = \rho_c (1-\phi)\)

\[
\begin{align*}
-r'_A &= -r''_A S_a \\
-r_A &= -r'_A \rho_c \\
-r_A &= -r''_A S_a \rho_c
\end{align*}
\]

Per mass cat → \(k'_n = k''_n S_a\) Per surface area → \(k_n = -k'_n \rho_c\) Per volume → \(k_n = k''_n S_a \rho_c\)

Cancel out \(\Delta V\) & \(a_c \approx 0\) since external surface area usually \(<<\) internal surface area (surface area of internal pores)

\[
\rightarrow M_A = W_{Ar |_{r=R}} a_c = -r''_A S_a \rho_b
\]
Review: Overall Molar Rate of Reaction

\[ M_A = \left. W_{Ar} \right|_{r=R} a_c = -r''_A S_a \rho_b \]

For external mass transport:\n\[ W_{Ar} \left|_{r=R} = k_c (C_{Ab} - C_{As}) \right. \]

Internal diffusion resistance is significant, so the reactant conc at the internal surface is lower than the reactant conc at the external surface:

\( \eta \): internal effectiveness factor

\[ \eta = \frac{-r''_A}{-r''_{As}} = \frac{\text{observed rxn rate}}{\text{rxn rate if no internal diff limit}} \rightarrow \eta(-r''_{As}) = -r''_A \]
For a 1\text{st} order rxn:

\[ -r''_A = -\eta k_1 C_{As} \]

Plug flux & 1\text{st} order rxn rate back into the mass balance, solve for \( C_{As} \):

\[ M_A = k_c (C_{Ab} - C_{As}) a_c = \eta k_1 C_{As} S_a \rho_b \rightarrow\rightarrow C_{As} = \frac{k_c C_{Ab} a_c}{\eta k''_1 S_a \rho_b + k_c a_c} \]

Insert \( C_{As} \) into \(-r''_A = \eta k_1 C_{As}\):

\[ -r''_A = \frac{\eta k_1 k_c a_c C_{Ab}}{k_c a_c + \eta k_1 S_a \rho_b} \]

Overall 1\text{st} order rxn rate with internal & external diffusion

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

Remember, the internal effectiveness factor is based on $C_{As}$:

$$\eta = \frac{\text{actual overall rate of reaction}}{\text{rate of rxn if entire interior surface were exposed to the external surface conditions}}$$

The overall effectiveness factor is based on $C_{Ab}$:

$$\Omega = \frac{\text{actual overall rate of reaction}}{\text{rate of reaction if entire interior surface were exposed to the bulk conditions}}$$

$$\Omega = \frac{-r''_A}{-r''_{Ab}} \quad \rightarrow \quad \Omega = \frac{\eta k_1 C_{Ab}}{1 + \eta k_1 S_a \rho_b / k_c a_c}$$

$$\rightarrow \Omega \left( -r''_{Ab} \right) = -r''_A \quad \text{Put into design eq to account for internal & external diffusion}$$
Review: Observed Rxn Rate Variation vs $F_{T0}$, $d_p$ & $T$

**External diffusion limited:**

$$-r'_A = k_c (C_{Ab} - C_{As})$$

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

**Internal diffusion limited:**

$$-r'_A = \eta k_r C_{As} S_a$$

$$\eta = \frac{3}{R^2 \frac{\rho_c k_1 S_a}{D_e}} \left( R \sqrt{\frac{\rho_c k_1 S_a}{D_e}} \coth \left( R \sqrt{\frac{\rho_c k_1 S_a}{D_e}} \right) - 1 \right)$$

**Surface reaction**

$$-r'_A = k C_A$$

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Whether the rate varies when $F_{T0}$ or particle size changes indicates tells us whether external diffusion, internal diffusion, or the surface rxn is limiting (slowing down) the observed rate.
Review: Rxn Rate Variation vs Reactor Conditions

When the observed rate of a reaction is limited by external diffusion, internal diffusion, or the surface rxn, the observed reaction kinetics are:

**Rate for external diff limited rxn:**

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

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

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

**Rate for internal diff limited rxn:**

\[-r'_A = \eta k_r C_{As} S_a \]

\[\eta = \frac{3}{R^2 \rho_c k_1 S_a} \left( R \sqrt{\frac{\rho_c k_1 S_a}{D_e}} \coth \left( R \sqrt{\frac{\rho_c k_1 S_a}{D_e}} \right) - 1 \right)\]

- \(R\): radius at particle surface
- \(D_e\): effective diffusivity

**Rate for surface reaction limited rxn:**

\[-r'_A = k C_A\]

Whether the rate varies when \(F_{T0}\) (at constant \(C_{T0}\)) or particle size changes indicates tells us whether external diffusion, internal diffusion, or the surface rxn is limiting (slowing down) the observed rate.
Observed Rxn Rate vs $F_{T0}$, $d_p$ & T

Rate for external diff limited rxn: 
$$-r'_A = k_c (C_{Ab} - C_{As}) \quad k_c = \frac{D_{AB}}{d_p} \left(2 + 0.6 \left(\frac{U d_p}{\mu / \rho}\right)^{1/2} \left(\frac{\mu / \rho}{D_{AB}}\right)^{1/3}\right)$$

$\eta$: diameter 
$U$: free-stream velocity (m/s), $\propto$ to flow rate ($F_T$, $F_{T0}$) for constant $C_{A0}$

Rate for internal diff limited rxn: 
$$-r'_A = \eta k_r C_{As} S_a \quad \eta = \frac{3}{R^2 \frac{\rho_c k_{1s} S_a}{D_a}} \left(R \sqrt{\frac{\rho_c k_{1s} S_a}{D_a}} \coth \left(R \sqrt{\frac{\rho_c k_{1s} S_a}{D_a}}\right) - 1\right)$$

$R$: radius at particle surface

Rate for surface reaction limited rxn: 
$$-r'_A = k C_A$$

According to these equations, if we increase the flow rate ($F_{T0}$) without increasing the concentration of reactants in the feed, the observed rxn rate will increase if the rxn is limited (slowed down) by:

a. **External diffusion**

b. Internal diffusion

c. The surface reaction

d. Either external & internal diffusion

e. Any of these (external diffusion, internal diffusion, or surface reaction)

Free-stream velocity ($U$), which is $\propto$ to flow rate for constant $C_{A0}$, is only in rate eq for a **external diffusion limited reaction**
The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction $A \rightarrow B$ was carried out in a PBR using the indicated catalyst $d_p$, $T$, and $F_{T0}$. $C_{A0}$ was the same in each trial.

Which, if any, of the conditions shown (flow rates, $T$, and $d_p$) is the reaction limited by external diffusion?

External diffusion limits the observed rate when increasing $F_{T0}$ increases $-r'_A$

- Need to find the points that have the same $T$ and $d_p$. If the rate increases when $F_{T0}$ increases, the trial at the lower flow rate is limited by external diffusion

Trial with $T = 400K$, $d_p = 0.8$ cm & $F_{T0} = 1000$ mol/h has a lower rate than the trial with $T = 400K$, $d_p = 0.8$ cm & $F_{T0} = 1500$ mol/h

Thus, rate is limited by external diffusion when $T = 400K$, $d_p = 0.8$ cm & $F_{T0} = 1000$ mol/h

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction $A \rightarrow B$ was carried out in a PBR using the indicated catalyst $d_p$, $T$, and $F_{T0}$. $C_{A0}$ was the same in each trial.

Which, if any, of the conditions shown (flow rates, $T$, and $d_p$) is the reaction limited by external diffusion?

External diffusion limits the observed rate when increasing $F_{T0}$ increases $-r'_A$.

- Need to find the points that have the same $T$ and $d_p$. If the rate increases when $F_{T0}$ increases, the trial at the lower flow rate is limited by external diffusion.

Trial with $T = 400K$, $d_p = 0.8$ cm & $F_{T0} = 1500$ mol/h has a lower rate than the trial with $T = 400K$, $d_p = 0.8$ cm & $F_{T0} = 2000$ mol/h.

Thus, rate is limited by external diffusion when $T = 400K$, $d_p = 0.8$ cm & $F_{T0} = 1500$ mol/h.

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction \( \text{A} \rightarrow \text{B} \) was carried out in a PBR using the indicated catalyst \( d_p \), \( T \), and \( F_{T0} \). \( C_{A0} \) was the same in each trial.

Which, if any, of the conditions shown (flow rates, \( T \), and \( d_p \)) is the reaction limited by external diffusion?

External diffusion limits the observed rate when increasing \( F_{T0} \) increases \( -r'_A \)
• Need to find the points that have the same \( T \) and \( d_p \). If the rate increases when \( F_{T0} \) increases, the trial at the \textit{LOWER} flow rate is limited by external diffusion

Trial with \( T = 400\text{K}, d_p = 0.8 \text{ cm} \) & \( F_{T0} = 2000 \text{ mol/h} \) has a lower rate than the trial with \( T = 400\text{K}, d_p = 0.8 \text{ cm} \) & \( F_{T0} = 3500 \text{ mol/h} \)

Thus, rate is limited by external diffusion when \( T = 400\text{K}, d_p = 0.8 \text{ cm} \) & \( F_{T0} = 2000 \text{ mol/h} \)

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction $A \rightarrow B$ was carried out in a PBR using the indicated catalyst $d_p$, $T$, and $F_{T0}$. $C_{A0}$ was the same in each trial.

Which, if any, of the conditions shown (flow rates, $T$, and $d_p$) is the reaction limited by external diffusion?

External diffusion limits the observed rate when increasing $F_{T0}$ increases $-r'_A$

- Need to find the points that have the same $T$ and $d_p$. If the rate increases when $F_{T0}$ increases, the trial at the **LOWER** flow rate is limited by external diffusion.

Trial with $T = 400K$, $d_p = 0.8$ cm & $F_{T0} = 3500$ mol/h has the same rate as the trial with $T = 400K$, $d_p = 0.8$ cm & $F_{T0} = 4000$ mol/h.

Rate is **NOT** limited by external diffusion when $T = 400K$, $d_p = 0.8$ cm & $F_{T0} = 3500$ mol/h or $T = 400K$, $d_p = 0.8$ cm & $F_{T0} = 4000$ mol/h.
The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction $A \rightarrow B$ was carried out in a PBR using the indicated catalyst $d_p$, $T$, and $F_{T0}$. $C_{A0}$ was the same in each trial.

Which, if any, of the conditions shown (flow rates, $T$, and $d_p$) is the reaction limited by external diffusion?

External diffusion limits the observed rate when increasing $F_{T0}$ increases $-r'_A$.

- Need to find the points that have the same $T$ and $d_p$. If the rate increases when $F_{T0}$ increases, the trial at the LOWER flow rate is limited by external diffusion.

For all remaining trials, increasing $F_{T0}$ does not increase the reaction rate, so no other trial conditions are external diffusion limited.

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction $A \rightarrow B$ was carried out in a PBR using the indicated catalyst $d_p$, $T$, and $F_{T0}$. $C_{A0}$ was the same in each trial.

Which, if any, of the conditions shown (flow rates, $T$, and $d_p$) is the reaction limited by internal diffusion?

Internal diffusion limits the observed rate when decreasing $d_p$ increases $-r'_A$.

- Need to find the points that have the same $T$. If the rate increases when $d_p$ decreases but does not change with $F_{T0}$, the trial at the larger $d_p$ is limited by internal diffusion.

Trial with $T = 400K$, $d_p = 0.8$ cm & $F_{T0} = 3500$ mol/h has a lower rate than the trial with $T = 400K$, $d_p = 0.6$ cm & $F_{T0} = 3500$ mol/h.

Thus, rate is limited by internal diffusion when $T = 400K$, $d_p = 0.8$ cm & $F_{T0} = 3500$ mol/h.
The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction $A \rightarrow B$ was carried out in a PBR using the indicated catalyst $d_p$, $T$, and $F_{T0}$. $C_{A0}$ was the same in each trial.

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Internal diffusion limits the observed rate when decreasing $d_p$ increases $-r'_A$.

• Need to find the points that have the same $T$. If the rate increases when $d_p$ decreases but does not change with $F_{T0}$, the trial at the larger $d_p$ is limited by internal diffusion.

Trial with $T = 400K$, $d_p = 0.8 \text{ cm}$ & $F_{T0} = 4000 \text{ mol/h}$ has a lower rate than the trial with $T = 400K$, $d_p = 0.6 \text{ cm}$ & $F_{T0} = 4000 \text{ mol/h}$.

Thus, rate is limited by internal diffusion when $T = 400K$, $d_p = 0.8 \text{ cm}$ & $F_{T0} = 4000 \text{ mol/h}$.

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Which, if any, of the conditions shown (flow rates, $T$, and $d_p$) is the reaction limited by **internal diffusion**?

Internal diffusion limits the observed rate when decreasing $d_p$ increases $-r'_A$.

- Need to find the points that have the same $T$. If the rate increases when $d_p$ decreases but does not change with $F_{T0}$, the trial at the larger $d_p$ is limited by internal diffusion.

Trial with $T = 400K$, $d_p = 0.6 \text{ cm}$ & $F_{T0} = 3500 \text{ mol/h}$ has a lower rate than the trial with $T = 400K$, $d_p = 0.2 \text{ cm}$ & $F_{T0} = 3500 \text{ mol/h}$.

Thus, rate is limited by internal diffusion when $T = 400K$, $d_p = 0.6 \text{ cm}$ & $F_{T0} = 3500 \text{ mol/h}$. 

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Internal diffusion limits the observed rate when decreasing $d_p$ increases $-r'_A$

- Need to find the points that have the same $T$. If the rate increases when $d_p$ decreases but does not change with $F_{T0}$, the trial at the larger $d_p$ is limited by internal diffusion.

Trial with $T = 400K$, $d_p = 0.6$ cm & $F_{T0} = 4000$ mol/h has a lower rate than the trial with $T = 400K$, $d_p = 0.2$ cm & $F_{T0} = 4000$ mol/h

Thus, rate is limited by internal diffusion when $T = 400K$, $d_p = 0.6$ cm & $F_{T0} = 4000$ mol/h
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Which, if any, of the conditions shown (flow rates, $T$, and $d_p$) is the reaction limited by internal diffusion?

Internal diffusion limits the observed rate when decreasing $d_p$ increases $-r'_A$.

- Need to find the points that have the same $T$. If the rate increases when $d_p$ decreases but does not change with $F_{T0}$, the trial at the larger $d_p$ is limited by internal diffusion.

Trial with $T = 400K$, $d_p = 0.2$ cm & $F_{T0} = 3500$ mol/h has a lower rate than the trial with $T = 400K$, $d_p = 0.1$ cm & $F_{T0} = 3500$ mol/h.

Thus, rate is limited by internal diffusion when $T = 400K$, $d_p = 0.2$ cm & $F_{T0} = 3500$ mol/h.

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Internal diffusion limits the observed rate when decreasing $d_p$ increases $-r'_A$
- Need to find the points that have the same $T$. If the rate increases when $d_p$ decreases but does not change with $F_{T0}$, the trial at the larger $d_p$ is limited by internal diffusion

Trial with $T = 400K$, $d_p = 0.2$ cm & $F_{T0} = 4000$ mol/h has a lower rate than the trial with $T = 400K$, $d_p = 0.1$ cm & $F_{T0} = 4000$ mol/h

Thus, rate is limited by internal diffusion when $T = 400K$, $d_p = 0.2$ cm & $F_{T0} = 4000$ mol/h

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Which, if any, of the conditions shown (flow rates, \( T \), and \( d_p \)) is the reaction limited by internal diffusion?

Internal diffusion limits the observed rate when decreasing \( d_p \) increases \( -r'_A \).

- Need to find the points that have the same \( T \). If the rate increases when \( d_p \) decreases but does not change with \( F_{T0} \), the trial at the larger \( d_p \) is limited by internal diffusion.

Trial with \( T = 400K \), \( d_p = 0.1 \text{ cm} \) & \( F_{T0} = 3500 \text{ mol/h} \) has the SAME rate as the trial with \( T = 400K \), \( d_p = 0.05 \text{ cm} \) & \( F_{T0} = 3500 \text{ mol/h} \)

Rate is NOT limited by internal diffusion when \( T = 400K \), \( d_p = 0.1 \text{ cm} \) & \( F_{T0} = 3500 \text{ mol/h} \) or \( T = 400K \), \( d_p = 0.05 \text{ cm} \) & \( F_{T0} = 3500 \text{ mol/h} \)
The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction $A \rightarrow B$ was carried out in a PBR using the indicated catalyst $d_p$, $T$, and $F_{T0}$. $C_{A0}$ was the same in each trial.

Which, if any, of the conditions shown (flow rates, $T$, and $d_p$) is the reaction limited by **internal diffusion**?

Internal diffusion limits the observed rate when decreasing $d_p$ increases $-r'_A$.

- Need to find the points that have the same $T$. If the rate increases when $d_p$ decreases but does not change with $F_{T0}$, the trial at the **larger** $d_p$ is limited by internal diffusion.

For all remaining trials, decreasing $d_p$ does not increase the reaction rate, so no other trial conditions are internal diffusion limited.

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction \( A \rightarrow B \) was carried out in a PBR using the indicated catalyst \( d_p \), \( T \), and \( F_{T0} \). \( C_{A0} \) was the same in each trial.

![Graph showing reaction rates](image)

Which, if any, of the conditions shown (flow rates, \( T \), and \( d_p \)) is the reaction limited by the surface reaction?

The surface reaction limits the reaction rate when the observed rxn rate increases when we increase \( T \), but it does not increase when we decrease \( d_p \) or increase \( F_{T0} \) without increasing \( C_{T0} \).

For all remaining trials, neither decreasing \( d_p \) nor increasing \( F_{T0} \) increases the reaction rate. Therefore, the surface reaction limits (slows down) the rates of the remaining trial conditions.

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction $A \rightarrow B$ was carried out in a PBR using the indicated catalyst $d_p$, $T$, and $F_{T0}$. $C_{A0}$ was the same in each trial.

For all remaining trials, neither decreasing $d_p$ nor increasing $F_{T0}$ increases the reaction rate. Therefore, the surface reaction limits (slows down) the rates of the remaining trial conditions. **Surface reaction limited (SRL):**

- $T = 400K$, $d_p = 0.1$ cm & $F_{T0} = 3500$ mol/h,
- $T = 400K$, $d_p = 0.05$ cm & $F_{T0} = 3500$ mol/h,
- $T = 400K$, $d_p = 0.1$ cm & $F_{T0} = 4000$ mol/h,
- $T = 400K$, $d_p = 0.05$ cm & $F_{T0} = 4000$ mol/h,
- $T = 300K$, all $d_p$ tested, & $F_{T0} = 4000$ mol/h & $T = 300K$, all $d_p$ tested, & $F_{T0} = 3500$ mol/h

Which, if any, of the conditions shown (flow rates, $T$, and $d_p$) is the reaction limited by the surface reaction?
The catalytic reaction $A \rightarrow B$ takes place in a fixed bed reactor containing spherical porous catalyst X22. The overall rxn rates at a point in the reactor are shown in the graph below. For which, if any, of the conditions shown (flow rates and temps) is the reaction limited by external diffusion?

External diffusion limited where $-r'_{A}$ ↑ linearly when $T$ ↑

<table>
<thead>
<tr>
<th>Type of Limitation</th>
<th>Variation of Reaction Rate with:</th>
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<tbody>
<tr>
<td></td>
<td>Superficial velocity</td>
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<tr>
<td>External</td>
<td>$U^{1/2}$</td>
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For $F_{T0} = 10$ mol/h, the rate of rxn increases approximately linearly with $T$ over the entire temperature range- external diffusion limited at $F_{T0} = 10$ and all $T$

For $F_{T0} = 100$ mol/h, the rate of rxn increases ~linearly with $T$ when $T > 360K$. The reaction is external diffusion limited when $F_{T0} = 100$ & $T > 360K$

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
The catalytic reaction \( A \rightarrow B \) takes place in a fixed bed reactor containing spherical porous catalyst X22. The overall reaction rates at a point in the reactor are shown in the graph below. For which, if any, of the conditions shown (flow rates and temps) is the reaction limited by surface reaction rate?

Surface reaction limited when \(-r'_A\) increases exponentially with \( T \uparrow \) but independent of superficial velocity (flow!)

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For conditions \( F_{T0} = 100, 1000 \& 5000 \text{ mol/h at } T< 360K \), rxn rate is independent of \( F_{T0} \) but exponentially dependent on \( T \rightarrow \) surface reaction limited.
The catalytic reaction $A \rightarrow B$ takes place in a fixed bed reactor containing spherical porous catalyst X22. The overall reaction rates at a point in the reactor are shown in the graph below. For which, if any, of the conditions shown (flow rates and temps) is the reaction limited by surface reaction rate?

**Surface rxn limited when** $-r'_A$ increases exponentially with $T \uparrow$ *but independent of velocity*

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For $F_{T0} = 100$, 1000 & 5000 mol/h at $T < 360K \rightarrow$ surface reaction limited

For conditions $F_{T0} = 1000$ & 5000 mol/h at $T < 366K$, rxn rate is independent of $F_{T0}$ but exponentially dependent on $T \rightarrow$ surface reaction limited

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Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
The catalytic reaction $A \rightarrow B$ takes place in a fixed bed reactor containing spherical porous catalyst X22. The overall rxn rates at a point in the reactor are shown in the graph below. For which, if any, of the conditions shown (flow rates and temps) is the reaction limited by internal diffusion?

Internal diffusion limited when $-r'_A$ increases exponentially with $T \uparrow$ & is independent of velocity

<table>
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<th>Type of Limitation</th>
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<th>Temperature</th>
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<tr>
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<tr>
<td>Internal</td>
<td>Independent</td>
<td>$d_p^{-1}$</td>
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For $F_{T0} = 1000 & 5000$ mol/h at $T > 367$K, rxn rate is roughly independent of $F_{T0}$ but exponentially dependent on $T$. The reaction rate is internal diffusion limited at $T > 370$K for $F_{T0} = 1000 & 5000$ mol/h

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
The catalytic reaction A → B takes place in a fixed bed reactor containing spherical porous catalyst X22. The overall rxn rates at a point in the reactor are shown in the graph below. For which, if any, of the conditions shown (flow rates and temps) is the reaction limited by internal diffusion?

Internal diffusion limited when $-r'_A$ increases exponentially with $T \uparrow$ & is independent of velocity.

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How do we know it’s not surface rxn limited at $F_{TO}=1000$ & $5000$ mol/h & $T>367K$?

As $T \uparrow$, the specific rate constant $k \uparrow$, the rate of the surface rxn & consumption of reactant $\uparrow$. Thus the reactant is more likely to be consumed before it reaches the core.
The catalytic reaction $A \rightarrow B$ takes place in a fixed bed reactor containing spherical porous catalyst $X_{22}$. The overall reaction rates at a point in the reactor are shown in the graph below. For a flow rate of 10 g mol/h, determine the overall effectiveness factor $\Omega$ at 360K.

For the reaction without diffusion limitations, we have:

$$\Omega = \frac{-r''_{A}}{-r''_{Ab}} \rightarrow \Omega = \frac{0.26}{0.70} \rightarrow \Omega = 0.37$$

What do we use for the rate of reaction if the interior was exposed to bulk conditions?

Use the reaction rate obtained under surface reaction limited conditions.
The catalytic reaction \( \text{A} \rightarrow \text{B} \) takes place in a fixed bed reactor containing spherical porous catalyst X22. The overall reaction rates at a point in the reactor are shown in the graph below. For \( F_{\text{T0}} = 5000 \text{ g mol/h} \), estimate the internal effectiveness factor \( \eta \) at 367K.

The internal effectiveness factor \( \eta \) is defined as:

\[
\eta = \frac{\text{actual overall rate of reaction}}{\text{rate of reaction if entire interior surface were exposed to the external surface conditions}}
\]

For the surface reaction limited regime, we have \( \eta \rightarrow 1.2 \). For the external diffusion limited regime, we have \( \eta \rightarrow 0.86 \).

What do we use for the rate of reaction if the interior was exposed to the conditions at the surface of the pellet?

Extrapolate the line for the surface reaction limited regime of the \( F_{\text{T0}} = 5000 \text{ mol/h} \) plot to estimate the reaction rate that would be obtained without internal diffusion.
Cl₂ is removed from a waste stream by passing the effluent gas over a solid granular absorbent in a tubular PBR. Presently 63.2% is removed and the reaction is external diffusion limited. If the flow rate were increased by a factor of 4, the particle diameter were decreased by a factor of 3, and the tube length (z) were increased by 1.5x, what percentage of Cl₂ would be removed (assume still external diffusion limited)? What guidelines (T, Cₐ, v) do you propose for efficient operation of this bed?

\[ X_{A1} = 0.632 \text{ for } d_p, z, \text{ and } v_0 \]

\[ X_{A2} = \? \text{ for } d_p/3, 1.5z_1, \text{ and } 4v_{0,1} \]

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\[ X_{A1} = 0.632 \text{ for } d_p, z, \text{ & } \nu_0 \]

\[ X_{A2} = ? \text{ for } d_{p1}/3, 1.5z_1, \text{ and } 4\nu_{0,1} \]

Need to relate \(X_A\) to reactor length in the presence of an external diffusion limit
A steady state mole balance on reactant A between $z$ and $z + \Delta z$:

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

$a_c$: external surface area of catalyst per volume of catalytic bed ($\text{m}^2/\text{m}^3$)

$\phi$: porosity of bed, void fraction

$d_p$: particle diameter ($\text{m}$)

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

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

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

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

Put $F_{az}$ and $-r'_A$ in terms of $C_A$:

$$F_{Az} = W_{Az} A_c = (J_{Az} + B_{Az}) A_c$$

Axial diffusion is negligible compared to bulk flow (convection)

$$\frac{d(U C_A)}{dz} + r''_A a_c = 0 \quad \text{Substitute into the mass balance}$$

$$-U \frac{dC_A}{dz} + C_A \frac{dU}{dz} + r''_A a_c = 0 \quad \rightarrow -U \frac{dC_A}{dz} + r''_A a_c = 0$$
Review: Mass Transfer Limited Rxn in PBR (continued)

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

At steady-state:

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

\[ -r''_A = W_{Ar} = k_c (C_A - C_{As}) \] 

Substitute mass transfer coefficient \( k_c = \frac{D_{AB}}{\delta} \text{ (s}^{-1}) \) \( \delta \): boundary layer thickness

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

\[ -U \frac{dC_A}{dz} - k_c a_c (C_A - C_{As}) = 0 \]

\( C_{As} \approx 0 \) in most mass transfer-limited rxns

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

\[ \int \frac{dC_A}{C_{A0}} = -k_c a_c \frac{C_A}{U} \]

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

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

\[ -r''_A = k_c C_{A0} \exp \left[ -\frac{k_c a_c}{U} z \right] \]
Cl\(_2\) is removed from a waste stream by passing the effluent gas over a solid granular absorbent in a tubular PBR. Presently 63.2\% is removed and the reaction is external diffusion limited. If the flow rate were increases by a factor of 4, the particle diameter were decreased by a factor of 3, and the tube length (z) were increased by 1.5x, what percentage of Cl\(_2\) would be removed (assume still external diffusion limited)? What guidelines (T, C\(_A\), \(\nu\)) do you propose for efficient operation of this bed?

\[ X_{A1} = 0.632 \text{ for } d_p, z, \& \nu_0 \]

\[ X_{A2} = ? \text{ for } d_{p1}/3, 1.5z_1, \text{ and } 4\nu_{0,1} \]

For an external diffusion limited rxn in a PBR, we found (L19):

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

\[ a_c : \text{external surface area of catalyst per catalyst bed volume} \]

\[ \phi : \text{porosity of bed} \]

\[ a_c = \frac{6(1-\phi)}{d_p} \]

In terms of \(X_A\):

\[
\frac{C_{A0}(1-X_A)}{C_{A0}} = \exp \left[ -\frac{k_c a_c}{U} \frac{z}{U} \right] \rightarrow \ln(1-X_A) = -\frac{k_c a_c}{U} \frac{z}{U} 
\]

Express \(X_A\) at 2 reaction conditions as a ratio:

\[
\frac{\ln(1-X_{A1})}{\ln(1-X_{A2})} = \frac{k_c a_{c1} z U_2}{k_c a_{c2} (1.5z) U_1} \]

Relate \(U\) to \(\nu_0\) & \(a_c\) to \(d_p\)

\[ U = \nu_0 / A_c \text{ where } A_c = \text{cross-sectional area of PBR} \]

\[ U_1 = \nu_{0,1} / A_c \Rightarrow U_1 = \frac{\nu_{0,1}}{U_2} \]

\[ U_2 = \nu_{0,2} / A_c \rightarrow U_2 = \frac{\nu_{0,2}}{U_1} \]
Cl\textsubscript{2} is removed from a waste stream by passing the effluent gas over a solid granular absorbent in a tubular PBR. Presently 63.2\% is removed and the reaction is external diffusion limited. If the flow rate were increased by a factor of 4, the particle diameter were decreased by a factor of 3, and the tube length (z) were increased by 1.5\times, what percentage of Cl\textsubscript{2} would be removed (assume still external diffusion limited)? What guidelines (T, C\textsubscript{A}, \nu) do you propose for efficient operation of this bed?

\[ X_{A1} = 0.632 \text{ for } d_p, z, \& \nu_0 \]

\[ \frac{\ln(1 - X_{A1})}{\ln(1 - X_{A2})} = \frac{k_{c1}a_{c1}zU_2}{k_{c2}a_{c2}(1.5z)U_1} \]

\[ a_{c1} = \frac{d_{p2}}{d_{p1}} \quad U_1 = \frac{\nu_{0,1}}{\nu_{0,2}} \quad \text{Typically the 2 is negligible so} \]

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

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

\[ k_{c1} = 0.6 \frac{D_{AB}^{2/3}}{\nu^{1/6}} \frac{U_1^{1/2}}{d_p^{1/2}} \]

\[ \frac{k_{c1}}{k_{c2}} = 0.6 \frac{D_{AB}^{2/3}}{\nu^{1/6}} \frac{U_2^{1/2}}{d_p^{1/2}} \]

How are \( k_{c1} \) and \( k_{c2} \) related?

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Cl₂ is removed from a waste stream by passing the effluent gas over a solid granular absorbent in a tubular PBR. Presently 63.2% is removed and the reaction is external diffusion limited. If the flow rate were increases by a factor of 4, the particle diameter were decreased by a factor of 3, and the tube length (z) were increased by 1.5x, what percentage of Cl₂ would be removed (assume still external diffusion limited)? What guidelines (T, Cₐ, υ) do you propose for efficient operation of this bed?

\[ X_{A1} = 0.632 \] for \( d_p, z, \& \upsilon_0 \)

\[ \ln \left( 1 - X_{A1} \right) = \frac{k_{c1}a_{c1}zU_2}{k_{c2}a_{c2}(1.5z)U_1} \]

\[ a_{c1} = \frac{d_{p2}}{d_{p1}} \]

\[ a_{c2} \]

\[ \frac{U_1}{U_2} = \frac{\upsilon_{0,1}}{\upsilon_{0,2}} \]

\[ k_{c1} = \frac{k_{c2}}{d_{p1}^{1/2}} \left( \frac{d_{p,2}^{1/2}}{U_2^{1/2}} \right) \]

\[ k_{c1} = \frac{U_1^{1/2}}{(d_{p,2}^{1/2})(U_2^{1/2})} \]

\[ X_{A2} = ? \] for \( d_{p,1/3}, 1.5z_1, \& 4\upsilon_{0,1} \)

\[ \ln \left( 1 - X_{A1} \right) = \frac{k_{c1}a_{c1}zU_2}{k_{c2}a_{c2}(1.5z)U_1} \]

\[ \frac{ \ln \left( 1 - X_{A1} \right) }{ \ln \left( 1 - X_{A2} \right) } = \left( \frac{U_1^{1/2}}{(d_{p,1}^{1/2})} \right) \left( \frac{d_{p,2}^{1/2}}{U_2^{1/2}} \right) \left( \frac{d_{p,2}}{d_{p,1}} \right) \left( \frac{z}{1.5z} \right) \frac{\upsilon_{0,2}}{\upsilon_{0,1}} \]

\[ \ln \left( 1 - X_{A1} \right) = \left( \frac{U_1^{1/2}}{U_2^{1/2}} \right) \left( \frac{d_{p,2}^{3/2}}{d_{p,1}^{3/2}} \right) \left( \frac{1}{1.5} \right) \frac{\upsilon_{0,2}}{\upsilon_{0,1}} \]

\[ \ln \left( 1 - X_{A1} \right) = \left( \frac{\upsilon_{0,2}^{1/2}}{\upsilon_{0,1}^{1/2}} \right) \left( \frac{d_{p,2}^{3/2}}{d_{p,1}^{3/2}} \right) \left( \frac{1}{1.5} \right) \frac{\upsilon_{0,2}}{\upsilon_{0,1}} \]

\[ \ln \left( 1 - X_{A1} \right) = \left( \frac{4\upsilon_{0,1}^{1/2} \left( d_{p,1}/3 \right)^{3/2}}{\upsilon_{0,1}^{1/2}d_{p,1}^{3/2}} \right) \left( \frac{1}{1.5} \right) \]

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.
Cl$_2$ is removed from a waste stream by passing the effluent gas over a solid granular absorbent in a tubular PBR. Presently 63.2% is removed and the reaction is external diffusion limited. If the flow rate were increased by a factor of 4, the particle diameter were decreased by a factor of 3, and the tube length ($z$) were increased by 1.5x, what percentage of Cl$_2$ would be removed (assume still external diffusion limited)? What guidelines ($T$, $C_A$, $v$) do you propose for efficient operation of this bed?

$$X_{A1}=0.632 \text{ for } d_p, z, & v_0$$

$$X_{A2}=? \text{ for } d_{p_1/3}, 1.5z_1, \text{ and } 4v_{0_1}$$

$$\frac{\ln(1 - 0.632)}{\ln(1 - X_{A2})} = \left(\frac{4v_{0_1}^{1/2} \left(d_{p_1/3}\right)^{3/2}}{v_{0_1}^{1/2}d_{p_1}^{3/2}}\right) \left(\frac{1}{1.5}\right) \rightarrow \frac{\ln(1 - 0.632)}{\ln(1 - X_{A2})} = 2(1/3)^{3/2} \times 0.667$$

$$\frac{\ln(0.368)}{\ln(1 - X_{A2})} = 0.257 \rightarrow \frac{-0.99967}{\ln(1 - X_{A2})} = 0.257$$

$$\rightarrow -3.8898 = \ln(1 - X_{A2}) \rightarrow e^{-3.8898} = 1 - X_{A2} \rightarrow 0.0204 = 1 - X_{A2}$$

$$\rightarrow X_{A2} = 0.98$$
Cl\(_2\) is removed from a waste stream by passing the effluent gas over a solid granular absorbent in a tubular PBR. Presently 63.2\% is removed and the reaction is external diffusion limited. If the flow rate were increased by a factor of 4, the particle diameter were decreased by a factor of 3, and the tube length (z) were increased by 1.5x, what percentage of Cl\(_2\) would be removed (assume still external diffusion limited)? What guidelines (T, C\(_A\), \(\nu\)) do you propose for efficient operation of this bed?

\[ X_{A1} = 0.632 \text{ for } d_p, z, \& \nu_0 \]
\[ X_{A2} = 0.98 \text{ for } d_p/3, 1.5z_1, \text{ and } 4\nu_{0,1} \]

Hint for T: The conversion of 0.98 is dependent on the reaction still being external diffusion-limited. How can we adjust the T, C\(_A\), and \(\nu\) to make sure that the process is not instead slowed down by the surface reaction, but without slowing down external diffusion?

<table>
<thead>
<tr>
<th>Type of Limitation</th>
<th>Variation of Reaction Rate with:</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Superficial velocity</td>
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<tr>
<td>External</td>
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<tr>
<td>Internal</td>
<td>Independent</td>
</tr>
<tr>
<td>Surface reaction</td>
<td>Independent</td>
</tr>
</tbody>
</table>

- To keep the rate of Cl\(_2\) consumption (surface reaction) faster than external diffusion (still in external diffusion limited regime), use high T

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$$X_{A1} = 0.632 \text{ for } d_p, z, \& \nu_0$$

$$X_{A2} = 0.98 \text{ for } d_{p1/3}, 1.5z_1, \text{ and } 4\nu_{0,1}$$

Hint: How does changing C$_A$ and $\nu$ influence the rate of external diffusion and the surface reaction?

• The mass transfer rate can be increased by increasing the concentration gradient, which is achieved by increasing the bulk concentration of A

$$k_c = 0.6 \frac{D_{AB}^{2/3} (\nu_{0,1}/A_c)^{1/2}}{\nu^{1/6} d_p^{1/2}}$$

• Increasing the volumetric flow rate $\nu_0$ increases the mass transfer coefficient but reduces the spacetime, and therefore $X_A$. The process also becomes reaction limited instead of external diffusion limited. $X_{A,\text{mass x-fer}} \propto k_c \propto \nu_0^{1/2}$ but $X_{A,\text{reaction}} \propto \tau \propto \nu_0^{-1}$ so the increase in $\nu_0$ may be offset by a reaction-limited decrease in conversion, assuming constant packed-bed properties. We would need the parameters for the reaction to evaluate whether increasing $\nu_0$ is a good idea.

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