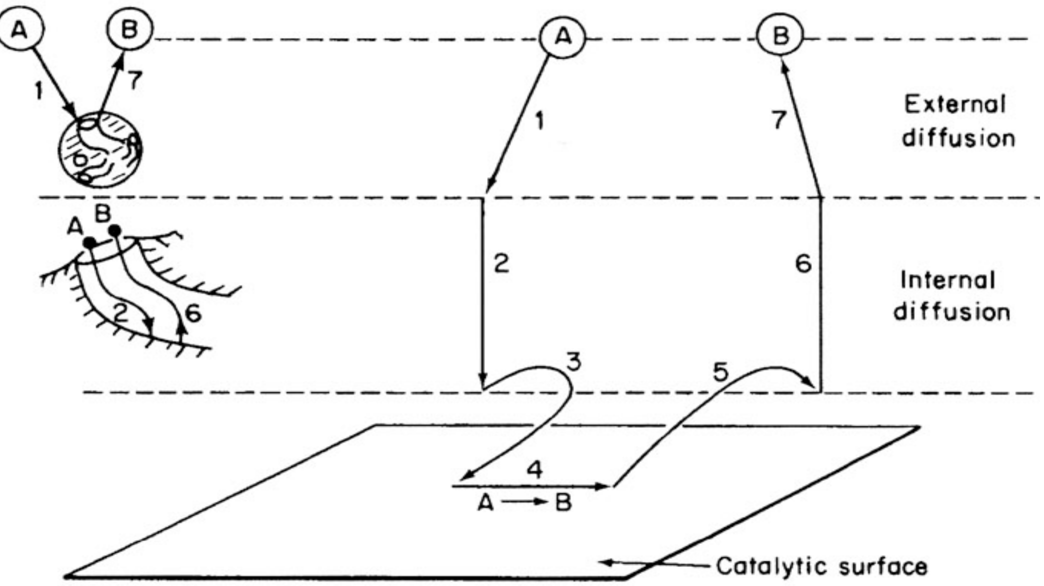
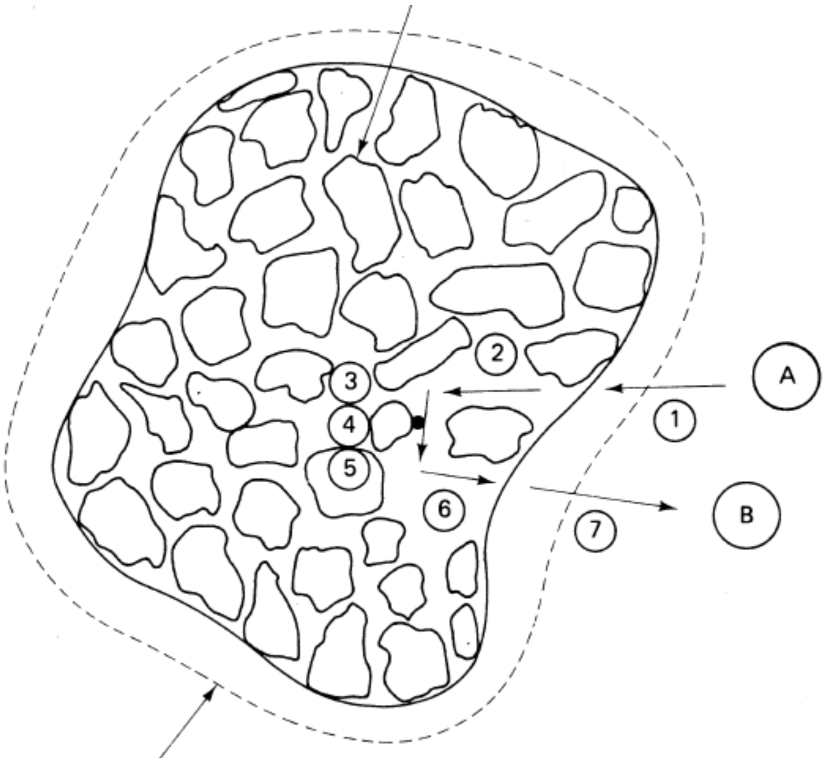
Review: Heterogeneous Catalyst

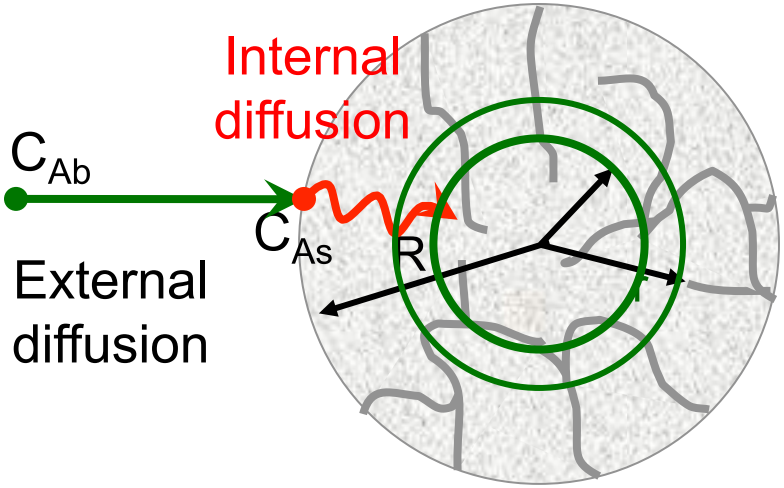
- We have looked at cases where
    1) Adsorption, surface reaction, or desorption is rate limiting
    2) External diffusion is rate limiting
    3) Internal diffusion is rate limiting
- Next goal: Derive an overall rate law for heterogeneous catalyst where the rate limiting step as any of the 7 reaction steps. This new overall reaction rate would be inserted into the design equation to get W, X_A, C_A, etc





Review: 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 Δ*r* is:

IN - OUT + GEN = ACCUM

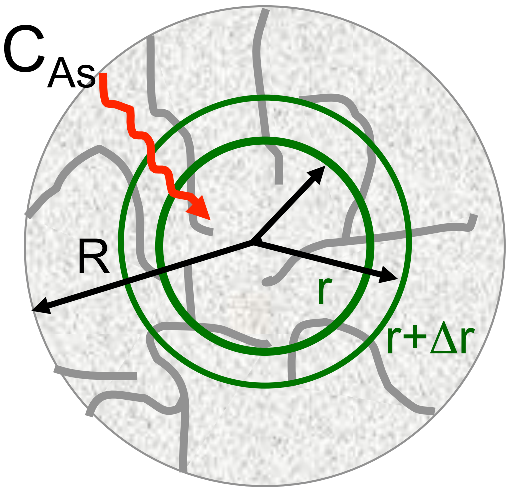
$$W_{Ar}4\pi r^2\big|_r - W_{Ar}4\pi r^2\big|_{r-\Delta r} + r'_A\underbrace{\left(4\pi r_m{}^2\Delta r\right)}_{\text{Volume of shell}}\rho_c = 0$$

r'_A: rxn rate per mass of catalyst
ρ_c: catalyst density
r_m: mean radius between *r* and *r* - Δ*r*

Divide by -4π/Δr & take limit as Δr →0 $\rightarrow \dfrac{d\left(W_{Ar}r^2\right)}{dr} - r'_A r^2\rho_c = 0$ Differential BMB in spherical catalyst particle

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

Review: Diffusion & Rxn in Spherical Catalyst



$$\frac{d\left(W_{Ar}r^2\right)}{dr}-r'_A r^2\rho_c=0 \quad \text{(step 1, BMB)}$$

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

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

Rate law:

$$-r''_A\left(\frac{\text{mol}}{m^2\cdot s}\right)=k_nC_A{}^n \rightarrow \quad -r'_A\left(\frac{\text{mol}}{\text{g cat}\cdot s}\right)=-r''_A S_A \qquad S_A=\frac{\text{catalyst surface area}}{\text{mass of catalyst}}$$

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 $W_{Ar}(r)$ 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

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

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

Boundary Conditions:

Ψ =1 at λ=1 $\qquad$ Ψ =finite at λ=0

Thiele modulus for rxn of nth order ≡ ϕ_n

Subscript n = reaction order

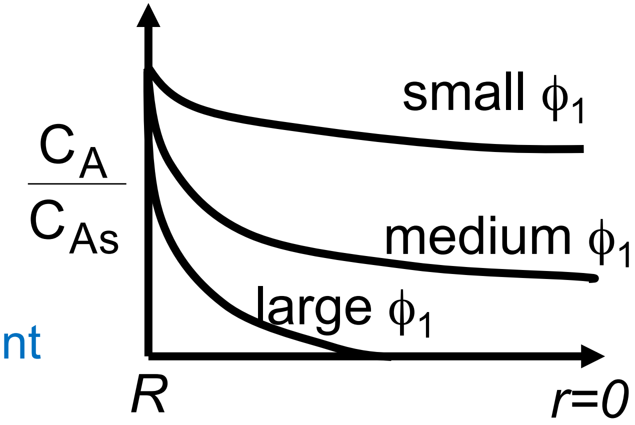
$$\phi_n{}^2 = \frac{\text{"a" surface rxn rate}}{\text{"a" diffusion rate}}$$

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

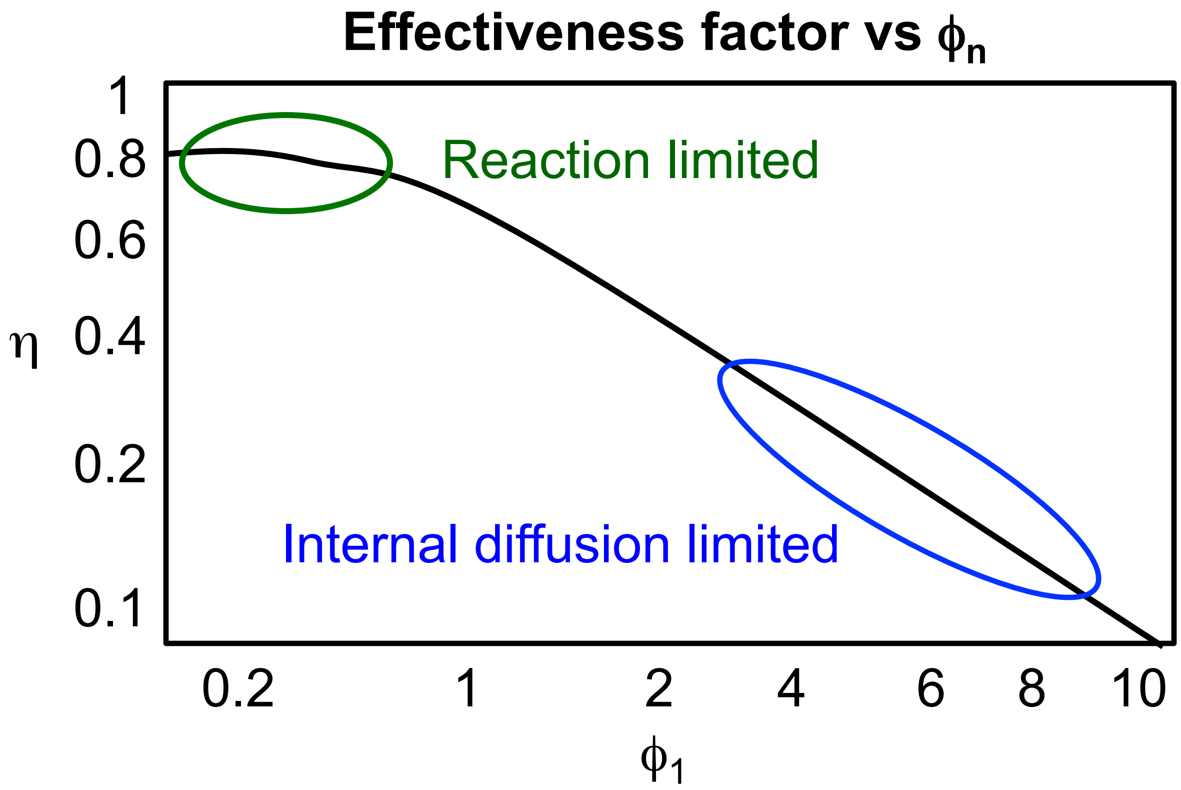
large ϕ_1: surface rxn is rapid, reactant is consumed very closed to the external surface of pellet (A waste of precious metal inside of pellet)

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

Review: Internal Effectiveness Factor, η

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

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



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

- 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

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

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

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)

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

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

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

Overall rate for 1st-order rxn

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

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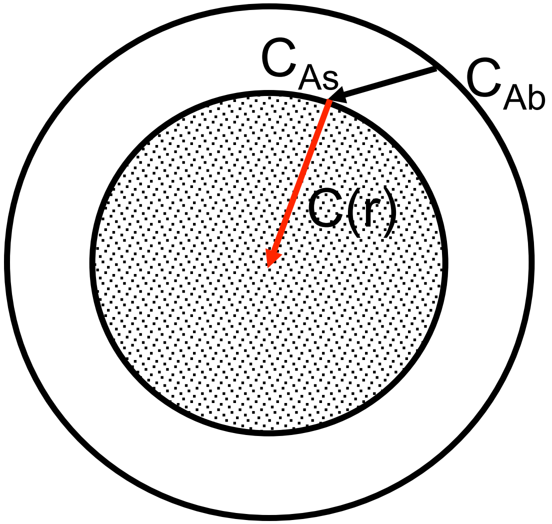
L21: Simultaneous Internal Diffusion & External Diffusion

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:

$$M_A = \underbrace{W_{Ar}}_{\text{molar flux}}\left(\underbrace{a_c}_{\text{external surface area per unit reactor volume}}\right)\underbrace{\Delta V}_{\text{reactor volume}}$$

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

$$M_A = -r''_A\left(\text{external area} + \text{ internal area}\right)$$

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

Basic Molar Balance at Pellet Surface

$$\left[\begin{array}{c}\text{Flux:}\\ \text{bulk to}\\ \text{external}\\ \text{surface}\end{array}\right] \times \left[\begin{array}{c}\text{External}\\ \text{S.A.}\end{array}\right] = \left[\begin{array}{l}\text{Actual rxn}\\ \text{rate per}\\ \text{unit total}\\ \text{S.A.}\end{array}\right] \times \left[\begin{array}{c}\text{external +}\\ \text{internal S.A.}\end{array}\right]$$

$$\left(W_{Ar}\right)_{r=R} \times \left(a_c \Delta V\right) = -r''_A \times \left(a_c \Delta V + S_a \rho_b \Delta V\right)$$

a_c: external surface area per reactor volume (m^2/m^3)

ΔV: reactor volume (m^3)

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

S_a: surface area of catalyst per unit mass of catalyst (m^2/g cat)

ρ_b: bulk density, catalyst mass/ reactor volume $\rho_b = \rho_c(1-\phi)$

ϕ: porosity of bed (void fraction) ρ_c: catalyst density

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

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

Typically external surface area <<< internal surface area

$$\rightarrow M_A = W_{Ar}\big|_{r=R} a_c = -r''_A S_a \rho_b$$

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

Overall Molar Rate of Reaction

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

$$M_A = W_{Ar}\big|_{r=R}\, a_c = -r''_A S_a \rho_b$$

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

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

$$\eta = \frac{-r''_A}{-r''_{As}} \rightarrow \eta\left(-r''_{As}\right) = -r''_A$$

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:

$$M_A = k_c\left(C_{Ab} - C_{As}\right)a_c = \eta k_1 C_{As} S_a \rho_b$$

Solve mass balance for C_{As}

$$\rightarrow k_c C_{Ab} a_c - k_c C_{As} a_c = \eta k_1 C_{As} S_a \rho_b \qquad \rightarrow k_c C_{Ab} a_c = \eta k_1 C_{As} S_a \rho_b + k_c C_{As} a_c$$

$$\rightarrow k_c C_{Ab} a_c = C_{As}\left(\eta k_1 S_a \rho_b + k_c a_c\right) \qquad \rightarrow \frac{k_c C_{Ab} a_c}{\eta k_1 S_a \rho_b + k_c a_c} = C_{As}$$

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 $-r''_A$

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

Overall rxn rate with internal & external diffusion

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 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
$\boxed{\text{(e) b, c, \& d}}$

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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

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

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

$$\rightarrow \Omega\left(-r''_{Ab}\right) = -r''_A$$

Put into design eq to account for internal & external diffusion

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

Rxn Rate Variation vs Reactor Conditions

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

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

Surface reaction $-r'_A = kC_A$

Type of Limitation	**Variation of Reaction Rate with:**		
	Superficial velocity	**Particle size**	**Temperature**
External	$U^{1/2}$	$d_p^{-3/2}$	Linear
Internal	Independent	d_p^{-1}	Exponential
Surface reaction	Independent	Independent	Exponential

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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: $F_{A0}\frac{dX_A}{dW} = -r'_A$

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: $-r''_A = \Omega\left(-r''_{Ab}\right) \rightarrow -r'_A = -r''_{Ab}\Omega S_a$
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: $C_{Ab} = C_{Ab0}\left(1-X_A\right) \rightarrow F_{A0}\frac{dX_A}{dW} = k\Omega S_a C_{Ab0}\left(1-X_A\right)$
6. Integrate: $\rightarrow \frac{dX_A}{dW} = \frac{k\Omega S_a C_{Ab0}\left(1-X_A\right)}{F_{A0}} \rightarrow \int_0^{X_A}\frac{dX_A}{\left(1-X_A\right)} = \int_0^{W}\frac{k\Omega S_a C_{Ab0}}{F_{A0}}dW$

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6. Integrate: $\int_0^{X_A} \frac{dX_A}{(1-X_A)} = \int_0^{W} \frac{k\Omega S_a C_{Ab0}}{F_{A0}} dW \rightarrow -\ln(1-X_A) = \frac{k\Omega S_a C_{Ab0} W}{F_{A0}}$

7. Solve for X_A: $\rightarrow \ln(1-X_A) = \frac{-k\Omega S_a C_{Ab0} W}{F_{A0}} \quad \rightarrow 1-X_A = e^{\frac{-k\Omega S_a C_{Ab0} W}{F_{A0}}}$

$$\rightarrow X_A = 1-e^{\frac{-k\Omega S_a C_{Ab0} W}{F_{A0}}} \qquad \rightarrow X_A = 1-e^{\frac{-k\Omega S_a W}{\upsilon_0}}$$

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X_A for 1st order rxn executed in an isothermal PBR packed with spherical catalyst particles with internal & external diffusion limitations

$$\boxed{X_A = 1 - e^{\frac{-k\Omega S_a W}{\upsilon_0}}}$$

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

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

where: $\rho_b = \frac{\text{catalyst mass}}{\text{reactor volume}} = \frac{\text{kg}}{\text{m}^3}$ L= z U=superficial velocity=$\frac{\upsilon_0}{A_c}$

Are these equations the same?

They differ in the exponent: $\frac{\cancel{-k\Omega S_a} W}{\upsilon_0} \overset{?}{=} \frac{\cancel{-k\Omega S_a}\rho_b L}{U}$

$$\rightarrow \frac{W}{\upsilon_0} \overset{?}{=} \frac{\rho_b L}{\frac{\upsilon_0}{A_c}} \rightarrow \frac{W}{\upsilon_0} \overset{?}{=} \frac{\rho_b (L) A_c}{\upsilon_0} \xrightarrow{(L)A_c = V} \frac{W}{\upsilon_0} \overset{?}{=} \frac{\rho_b V}{\upsilon_0} \rightarrow \frac{W}{\upsilon_0} \overset{?}{=} \frac{(W/\cancel{V})\cancel{V}}{\upsilon_0} \rightarrow \frac{W}{\upsilon_0} = \frac{W}{\upsilon_0}$$

$$X_A = 1 - e^{\frac{-k\Omega S_a W}{\upsilon_0}} = 1 - e^{\frac{-k\Omega S_a \rho_b L}{U}} = X_A$$

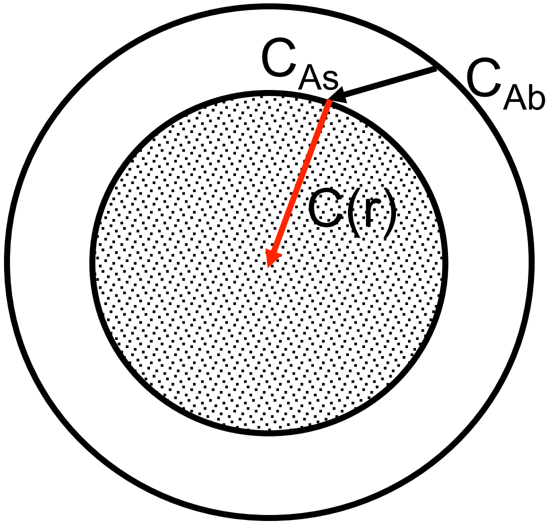
Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

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

W_{Ar}: molar flux

a_c: external surface area per unit reactor volume

ΔV: reactor volume

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

$$M_A = -r''_A\left(\text{external area} + \text{ internal area}\right)$$

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

$$\begin{bmatrix}\text{Flux:}\\ \text{bulk to}\\ \text{external}\\ \text{surface}\end{bmatrix} \text{x} \begin{bmatrix}\text{External}\\ \text{S.A.}\end{bmatrix} = \begin{bmatrix}\text{Actual rxn}\\ \text{rate per}\\ \text{unit total}\\ \text{S.A.}\end{bmatrix} \text{x} \begin{bmatrix}\text{external +}\\ \text{internal S.A.}\end{bmatrix}$$

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

a_c: external surface area per reactor volume (m^2/m^3)

ΔV: reactor volume (m^3) ϕ: porosity of bed (void fraction)

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

$-r'_A$: mol/g cat·s $-r_A$: mol/volume·s

S_a: surface area of catalyst per unit mass of catalyst (m^2/g cat)

ρ_b: bulk density, catalyst mass/ reactor volume $\rho_b = \rho_c(1-\phi)$

per volume

$$-r'_A = -r''_A S_a \qquad -r_A = -r'_A \rho_c \qquad -r_A = -r''_A S_a \rho_c$$

per surface area

per mass cat→ $k'_n = k''_n S_a$ $\qquad k_n = -k'_n \rho_c \qquad k_n = k''_n S_a \rho_c$

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

$$\rightarrow M_A = W_{Ar}\big|_{r=R} a_c = -r''_A S_a \rho_b$$

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Review: Overall Molar Rate of Reaction

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

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

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

η: internal effectiveness factor

$$\eta = \frac{-r''_A}{-r''_{As}} = \frac{\text{observed rxn rate}}{\text{rxn rate if no internal diff limit}} \rightarrow \eta\left(-r''_{As}\right) = -r''_A$$

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

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

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

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 1st 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 **<u>overall</u> effectiveness factor** is based on C_{Ab}:

Omega

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

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

$\rightarrow \Omega\left(-r''_{Ab}\right) = -r''_A$ Put into design eq to account for internal & external diffusion

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

Review: Observed Rxn Rate Variation vs F_{T0}, d_p & T

External diffusion limited: $-r'_A = k_c\left(C_{Ab} - C_{As}\right) \quad k_c = \frac{D_{AB}}{d_p}\left(2 + 0.6\left(\frac{Ud_p}{\mu/\rho}\right)^{1/2}\left(\frac{\mu/\rho}{D_{AB}}\right)^{1/3}\right)$

Internal diffusion limited: $-r'_A = \eta k_r C_{As} S_a \quad \eta = \frac{3}{R^2 \frac{\rho_c k_1 S_a}{D_e}}\left(R\sqrt{\frac{\rho_c k_1 S_a}{D_e}} \coth\left(R\sqrt{\frac{\rho_c k_1 S_a}{D_e}}\right) - 1\right)$

Surface reaction $-r'_A = kC_A$

Type of Limitation	Variation of Reaction Rate with:		
	Superficial velocity	**Particle size**	**Temperature**
External	$U^{1/2}$	$d_p^{-3/2}$	Linear
Internal	Independent	d_p^{-1}	Exponential
Surface reaction	Independent	Independent	Exponential

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:

$$-r'_A = k_c\left(C_{Ab} - C_{As}\right) \qquad k_c = \frac{D_{AB}}{d_p}\left(2 + 0.6\left(\frac{Ud_p}{\mu/\rho}\right)^{1/2}\left(\frac{\mu/\rho}{D_{AB}}\right)^{1/3}\right)$$

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

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

ν: kinematic viscosity (m^2/s); $\nu=\mu/\rho$ ρ: fluid density (kg/m^3) μ: viscosity

---

Rate for internal diff limited rxn:

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

R: radius at particle surface

D_e: effective diffusivity

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

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

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

d_p: diameter

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

Rate for internal diff limited rxn: $-r'_A = \eta k_r C_{As} S_a$ $\quad \eta = \frac{3}{R^2 \frac{\rho_c k_1 S_a}{D_e}}\left(R\sqrt{\frac{\rho_c k_1 S_a}{D_e}}\coth\left(R\sqrt{\frac{\rho_c k_1 S_a}{D_e}}\right) - 1\right)$

R: radius at particle surface

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

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

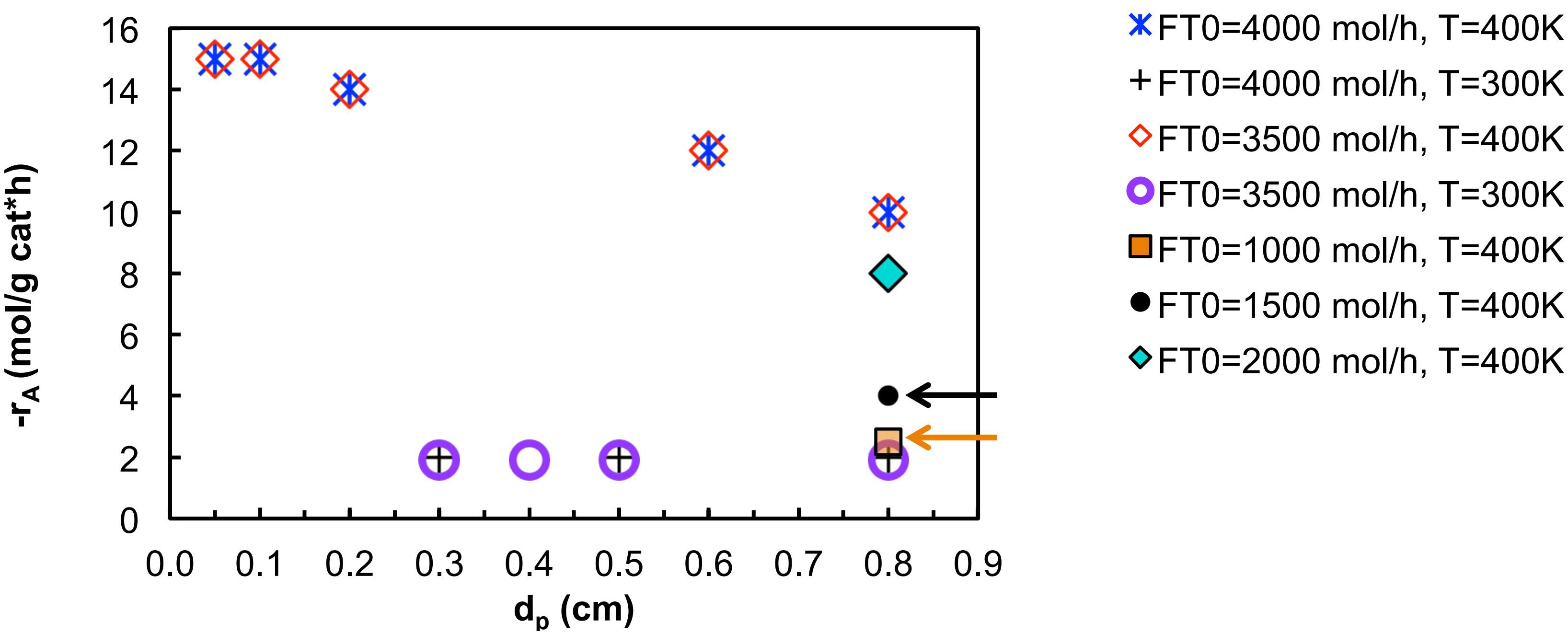
d. Either external & internal diffusion

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

Free-stream velocity (U), which is ∝ to flow rate for constant C_{A0}, is only in rate eq for a **external diffusion limited reaction**

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→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 $-r'_A$

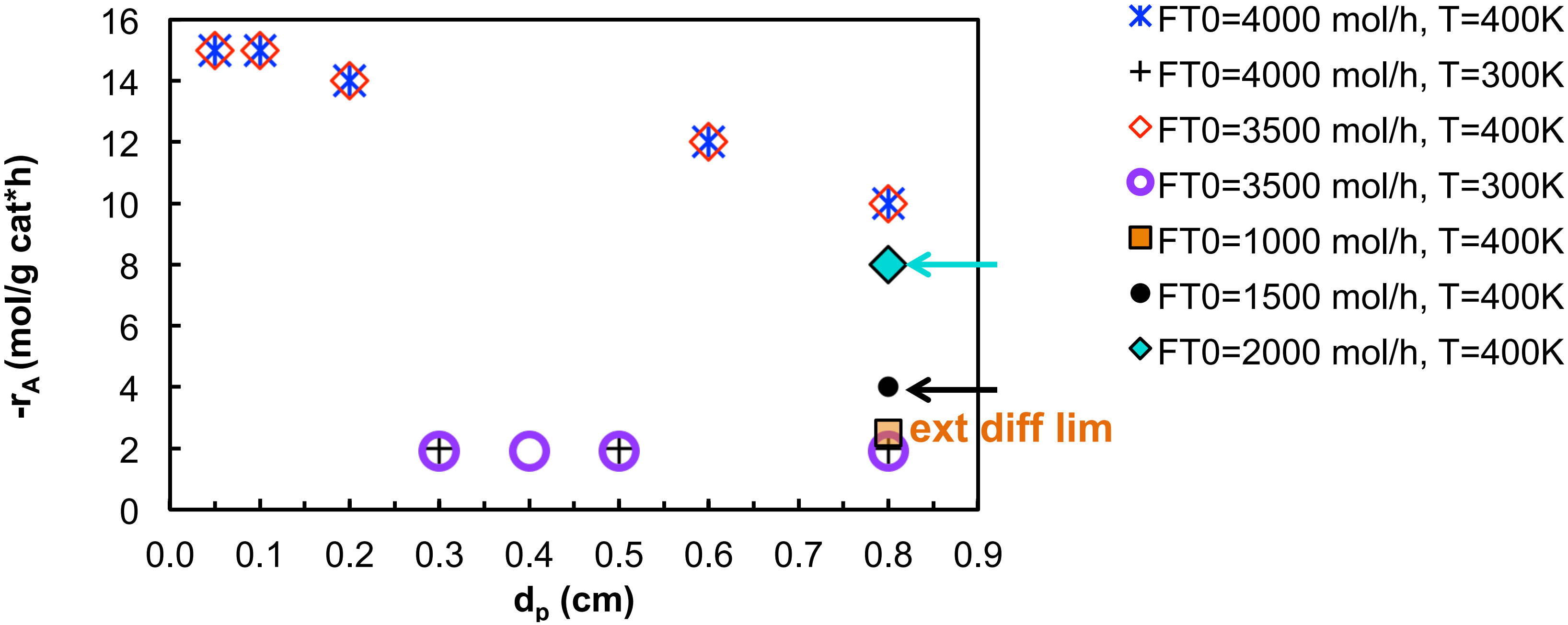
- Need to find the points that have the same T and d_p. If the rate increases when F_{to} increases, the trial at the ***LOWER*** flow rate is limited by external diffusion

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→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 $-r'_A$

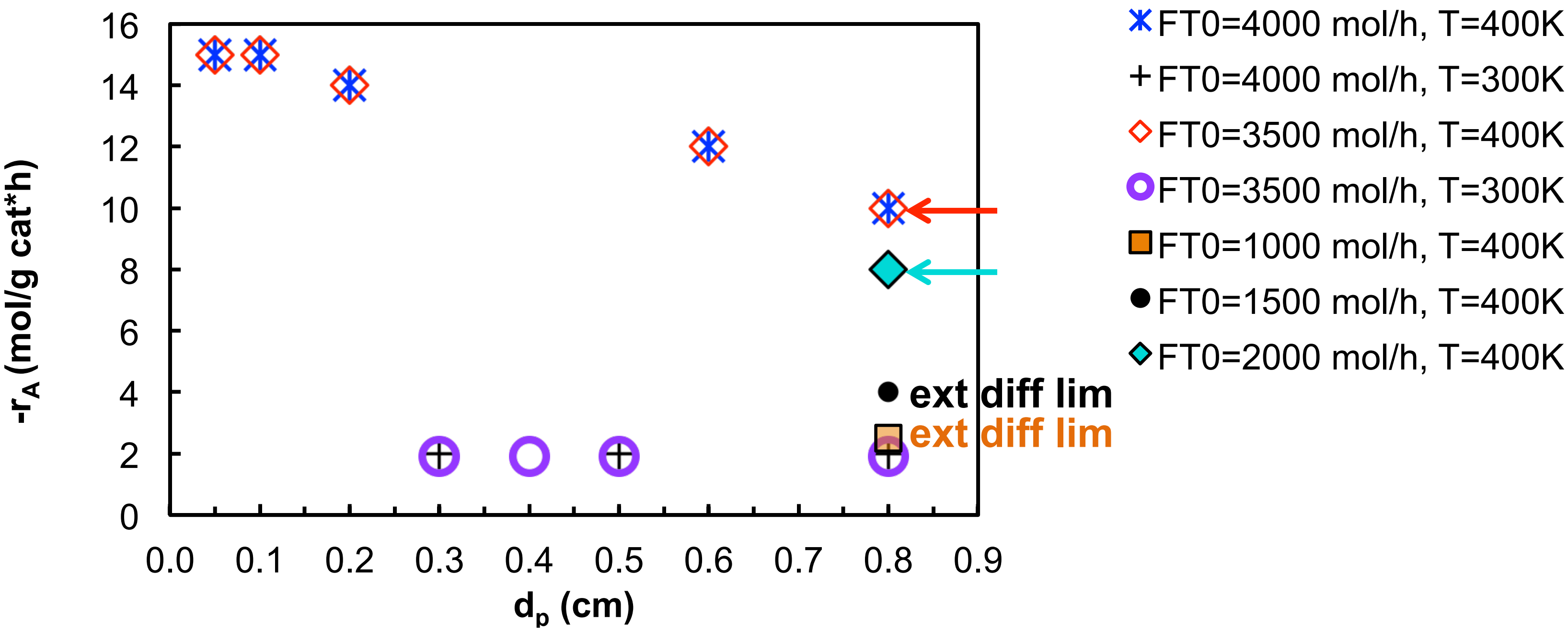
- Need to find the points that have the same T and d_p. If the rate increases when F_{to} increases, the trial at the ***LOWER*** flow rate is limited by external diffusion

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 A→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 $-r'_A$

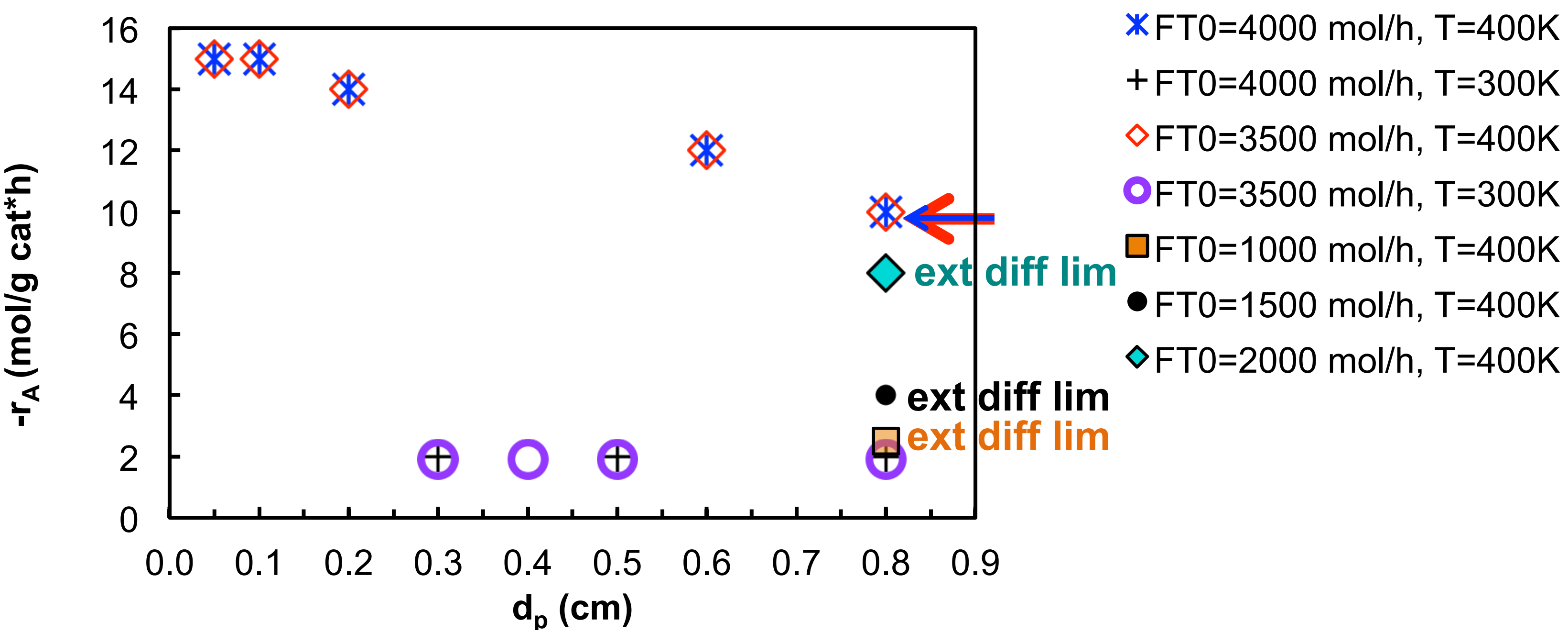
- Need to find the points that have the same T and d_p. If the rate increases when F_{to} increases, the trial at the ***LOWER*** flow rate is limited by external diffusion

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

Thus, rate is limited by external diffusion when T = 400K, d_p= 0.8 cm & F_{T0}= 2000 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→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?**

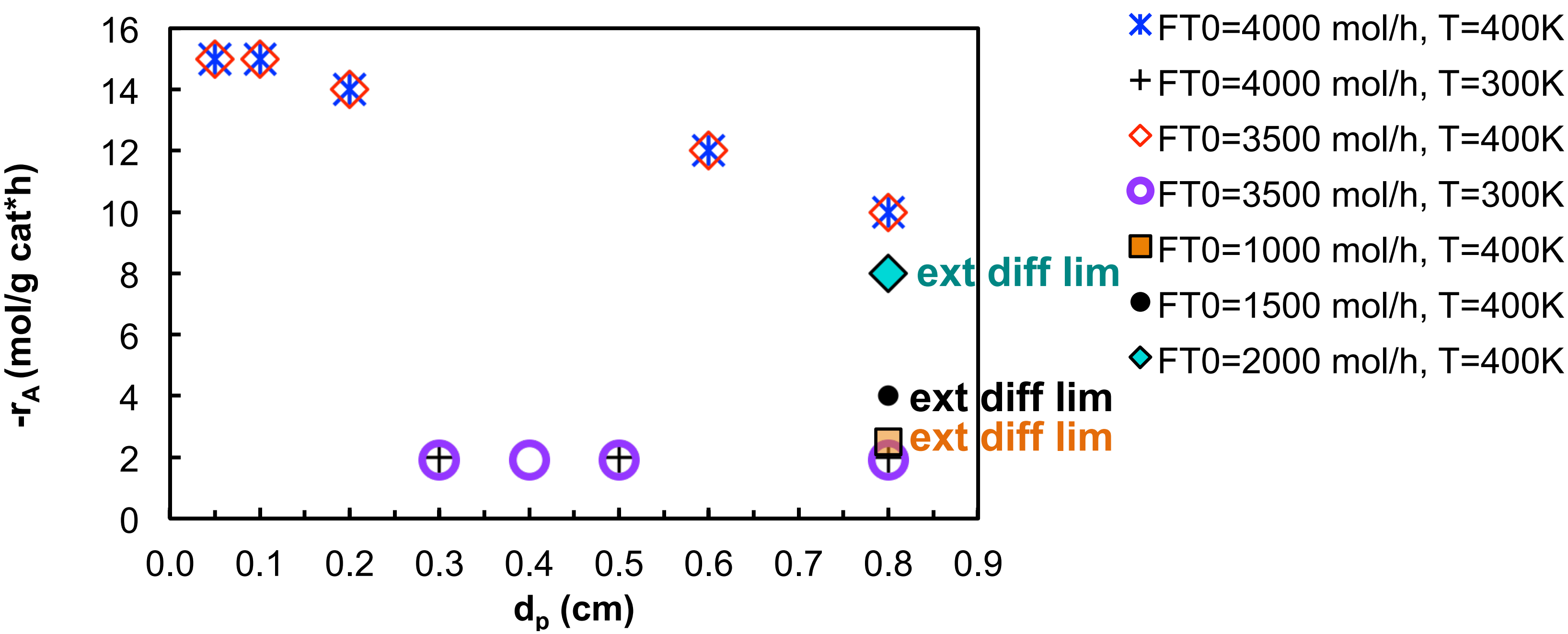
External diffusion limits the observed rate when increasing F_{T0} increases $-r'_A$

- Need to find the points that have the same T and d_p. If the rate increases when F_{to} 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→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?**

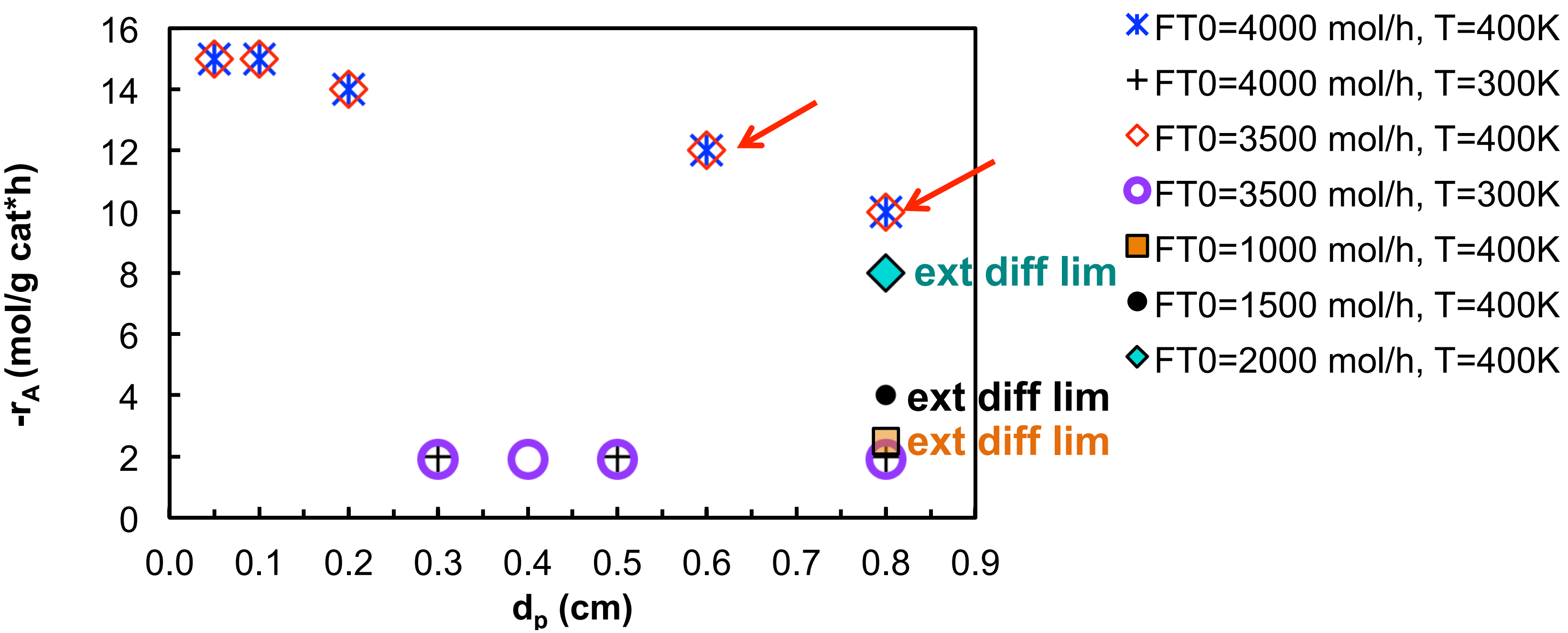
External diffusion limits the observed rate when increasing F_{T0} increases $-r'_A$

- Need to find the points that have the same T and d_p. If the rate increases when F_{to} 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→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 $-r'_A$

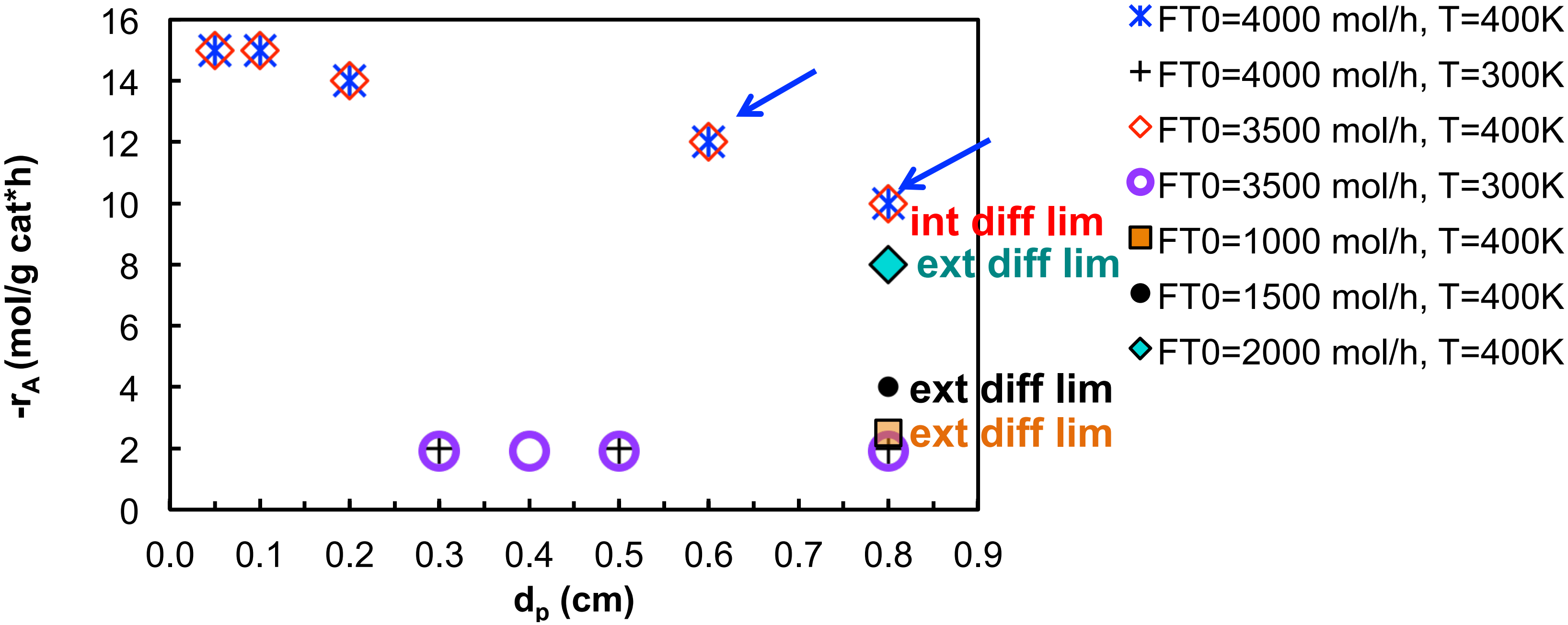
- Need to find the points that have the same T. If the rate increases when d_p decreases but does not change with F_{T0}, the trial at the ***larger*** **d_p** is limited by internal diffusion

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

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→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 $-r'_A$

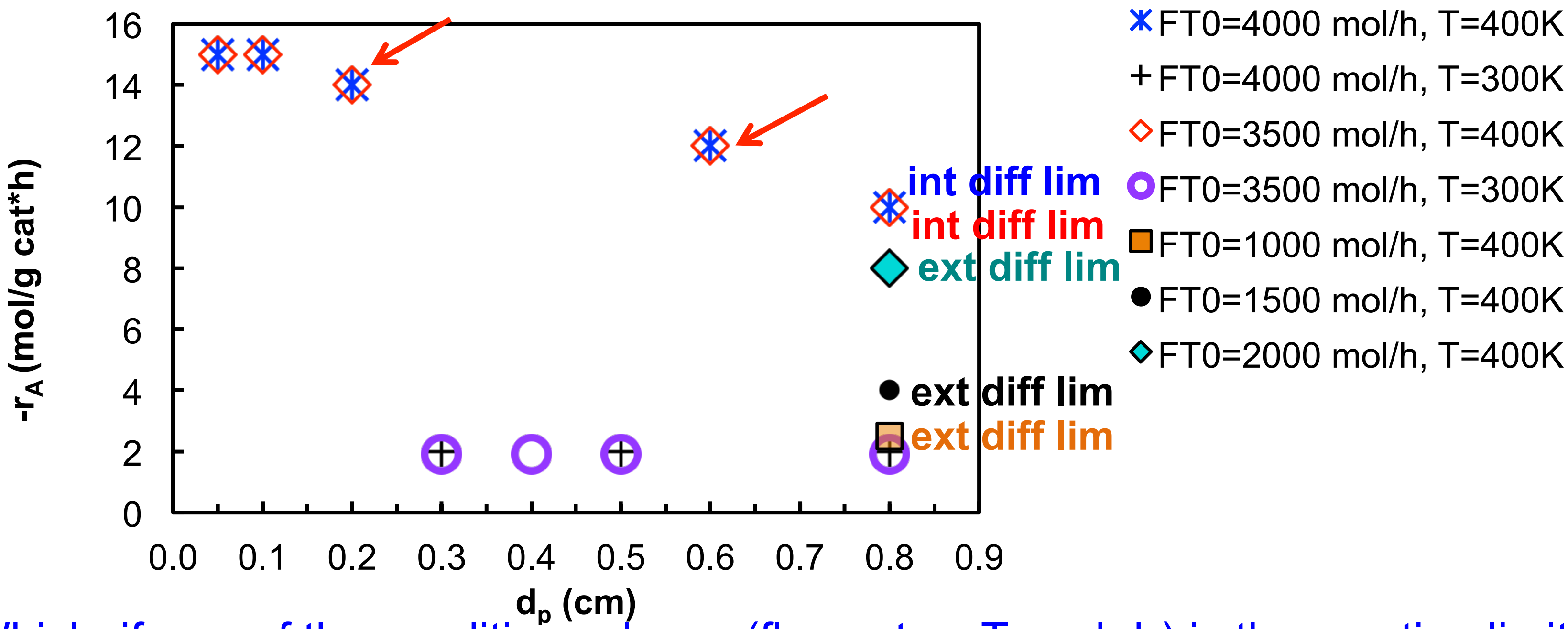
- Need to find the points that have the same T. If the rate increases when d_p decreases but does not change with F_{T0}, the trial at the ***larger* d_p** is limited by internal diffusion

Trial with T = 400K, <u>d_p= 0.8 cm</u> & F_{T0}= 4000 mol/h has a lower rate than the trial with T = 400K, <u>d_p= 0.6 cm</u> & F_{T0}= 4000 mol/h

Thus, rate is limited by internal diffusion when T = 400K, d_p= 0.8 cm & F_{T0}= 4000 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→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= 0.6 cm & F_{T0}= 3500 mol/h has a lower rate than the trial with T = 400K, d_p= 0.2 cm & F_{T0}= 3500 mol/h

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

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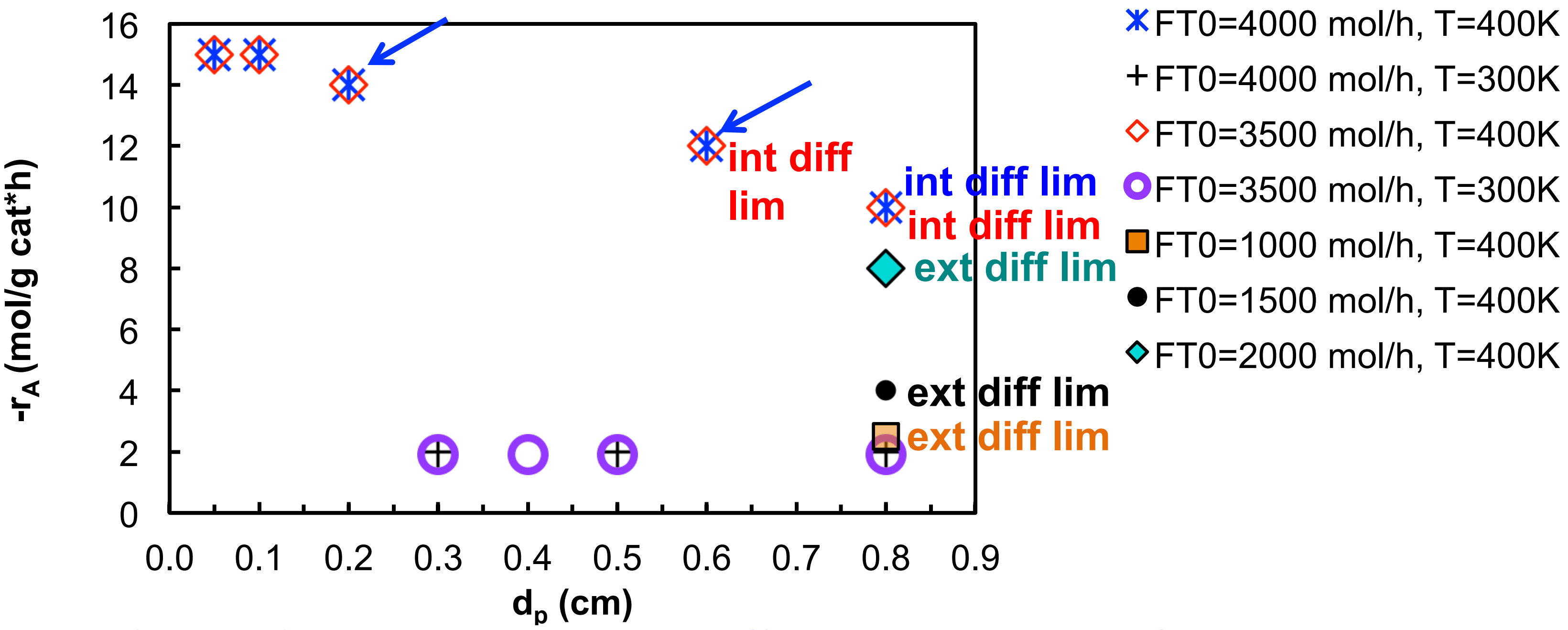
The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction A→B was carried out in a PBR using the indicated catalyst d_p, T, and F_{T0}. C_{A0} was the same in each trial.



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

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

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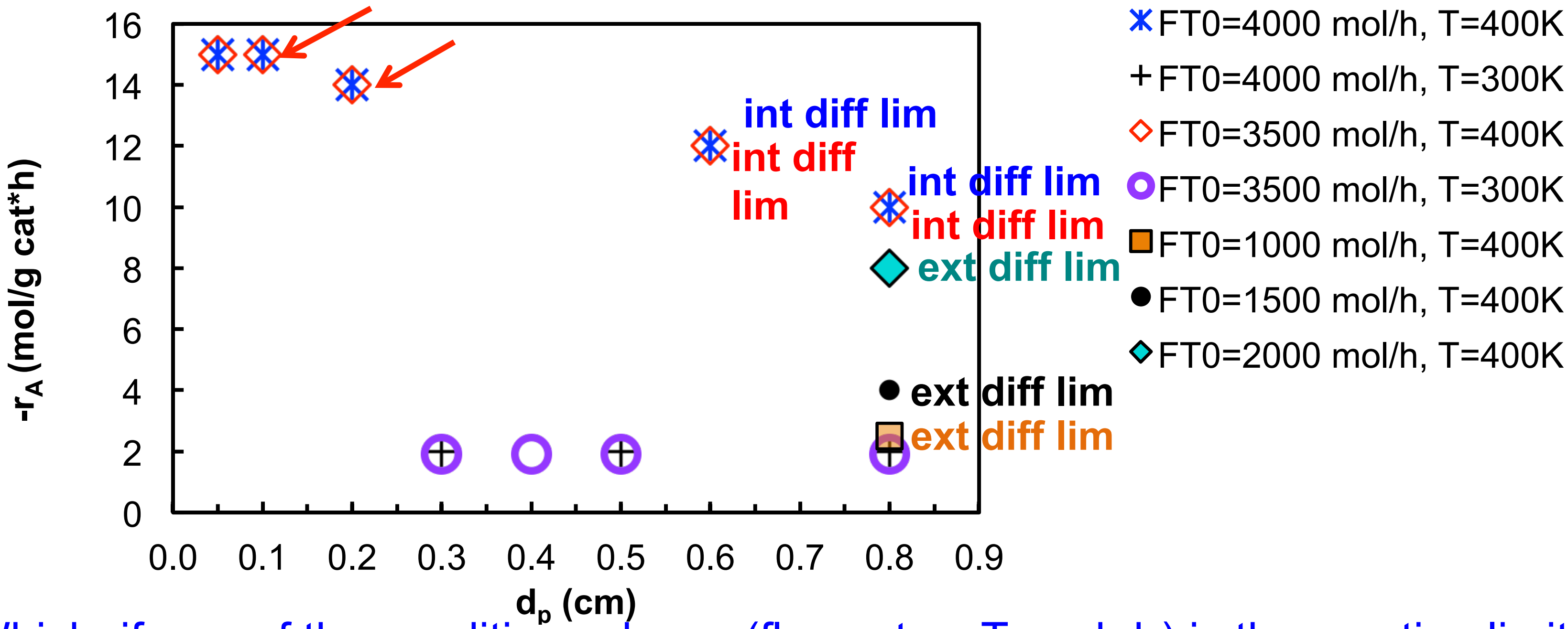


Which, if any, of the conditions shown (flow rates, T, and d_p) is the reaction limited by **internal diffusion?**

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

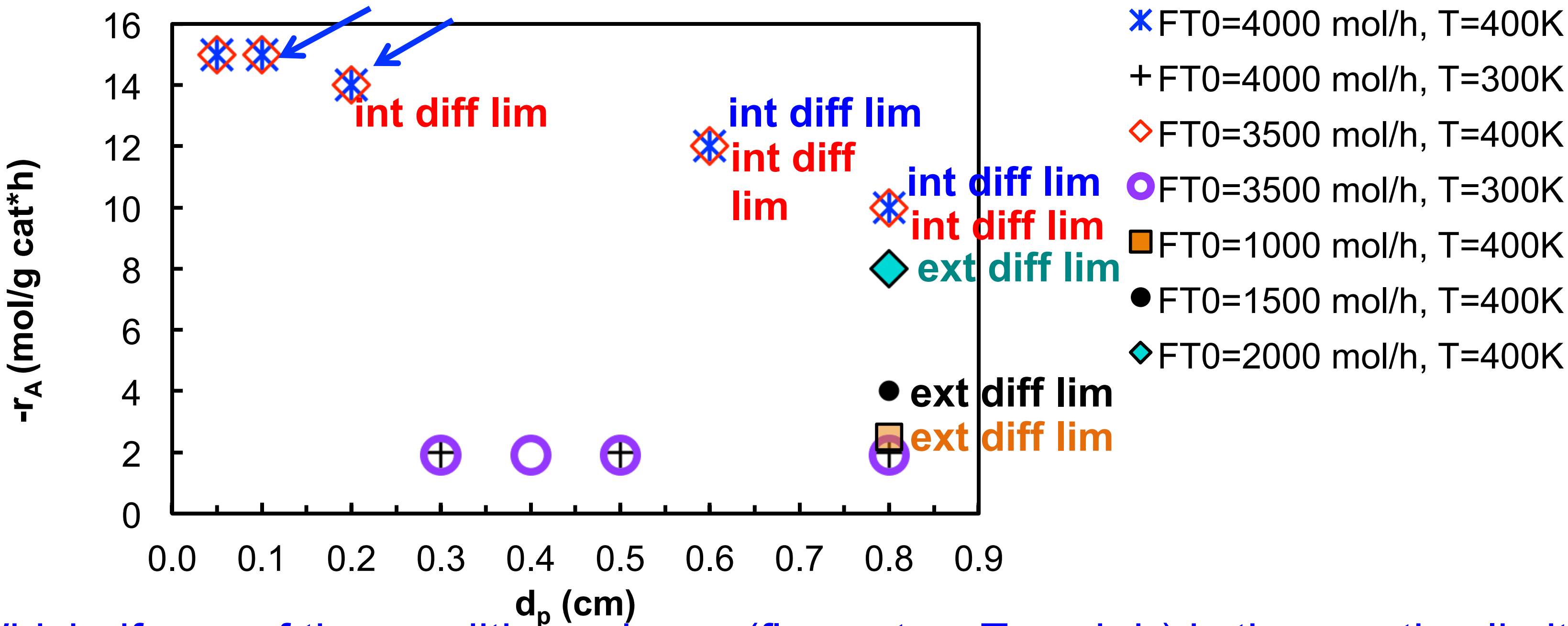
- Need to find the points that have the same T. If the rate increases when d_p decreases but does not change with F_{T0}, the trial at the ***larger*** **d_p** is limited by internal diffusion

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

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→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= 0.2 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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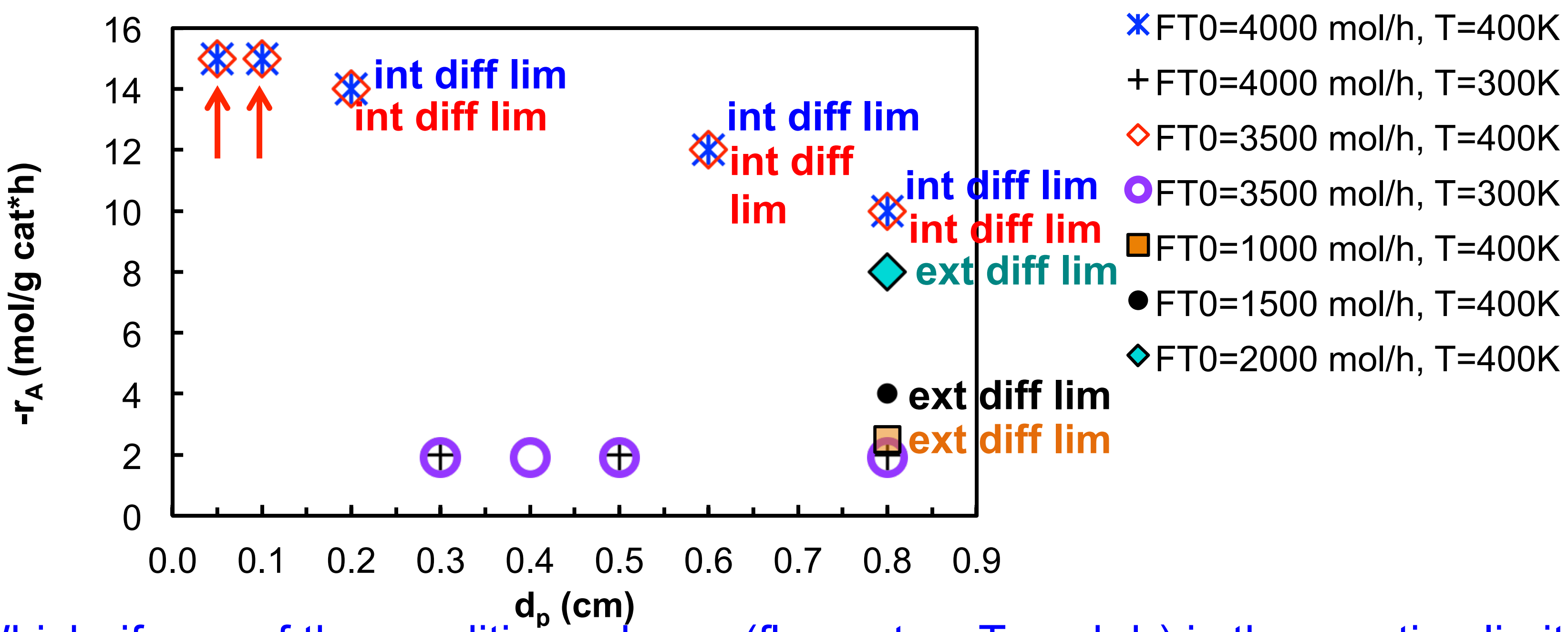
The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction A→B was carried out in a PBR using the indicated catalyst d_p, T, and F_{T0}. C_{A0} was the same in each trial.



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

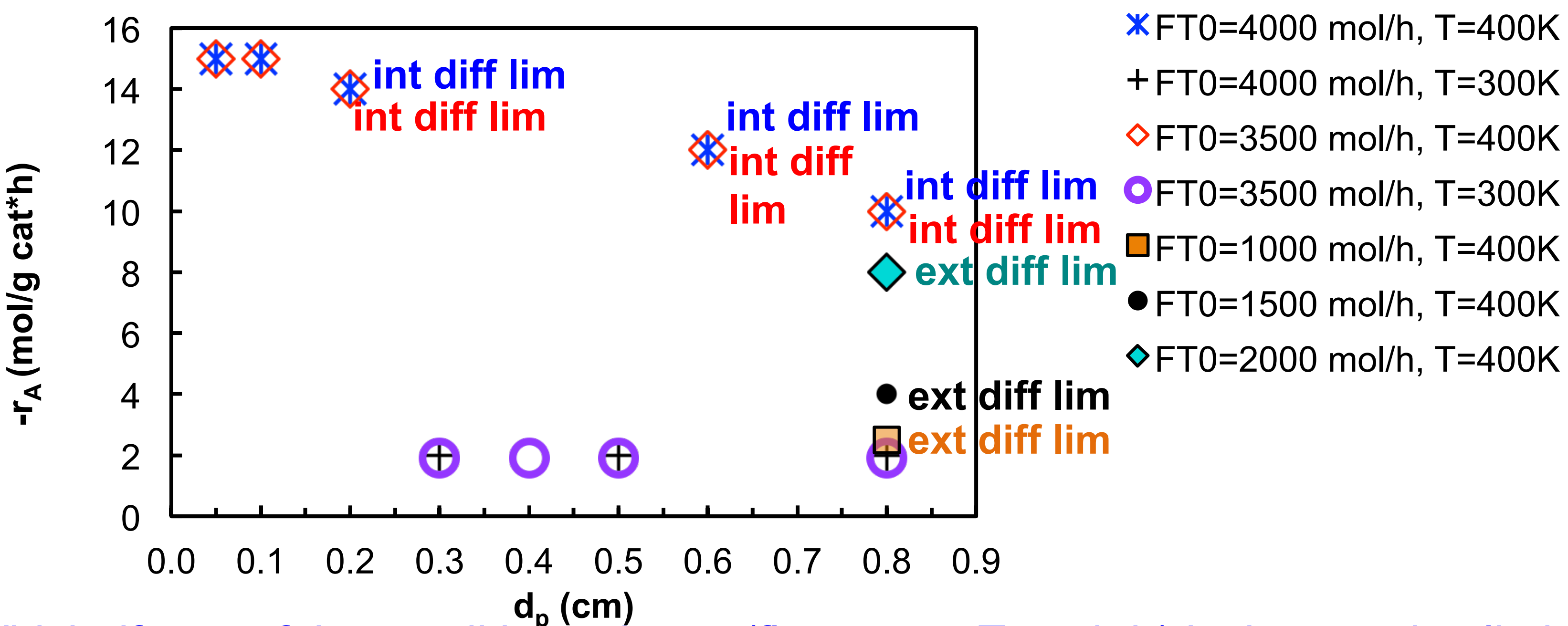
Internal diffusion limits the observed rate when decreasing d_p increases $-r'_A$

- 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, <u>d_p= 0.1 cm</u> & F_{T0}= 3500 mol/h has the SAME rate as the trial with T = 400K, <u>d_p= 0.05 cm</u> & F_{T0}= 3500 mol/h

Rate is **NOT** limited by internal diffusion when T = 400K, d_p= 0.1 cm & F_{T0}= 3500 mol/h or T = 400K, d_p= 0.05 cm & F_{T0}= 3500 mol/h

The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction A→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?**

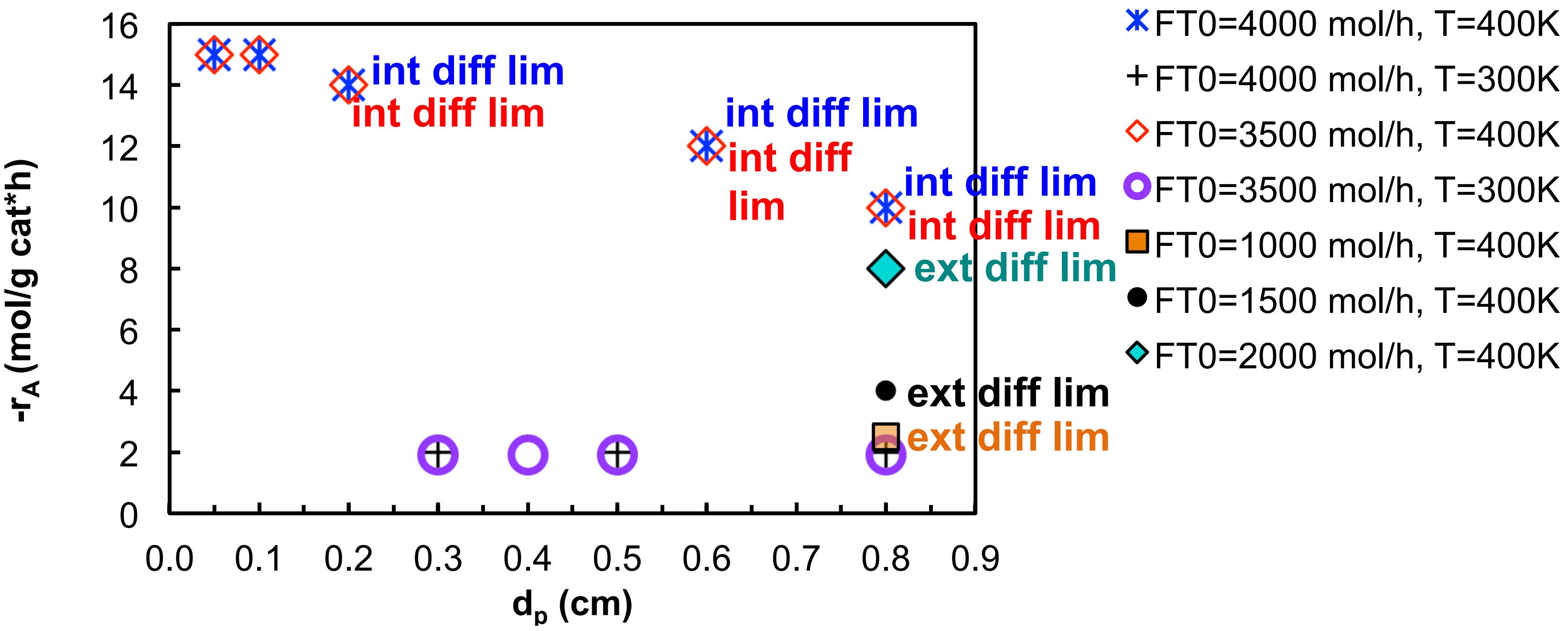
Internal diffusion limits the observed rate when decreasing d_p increases $-r'_A$

- 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→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.

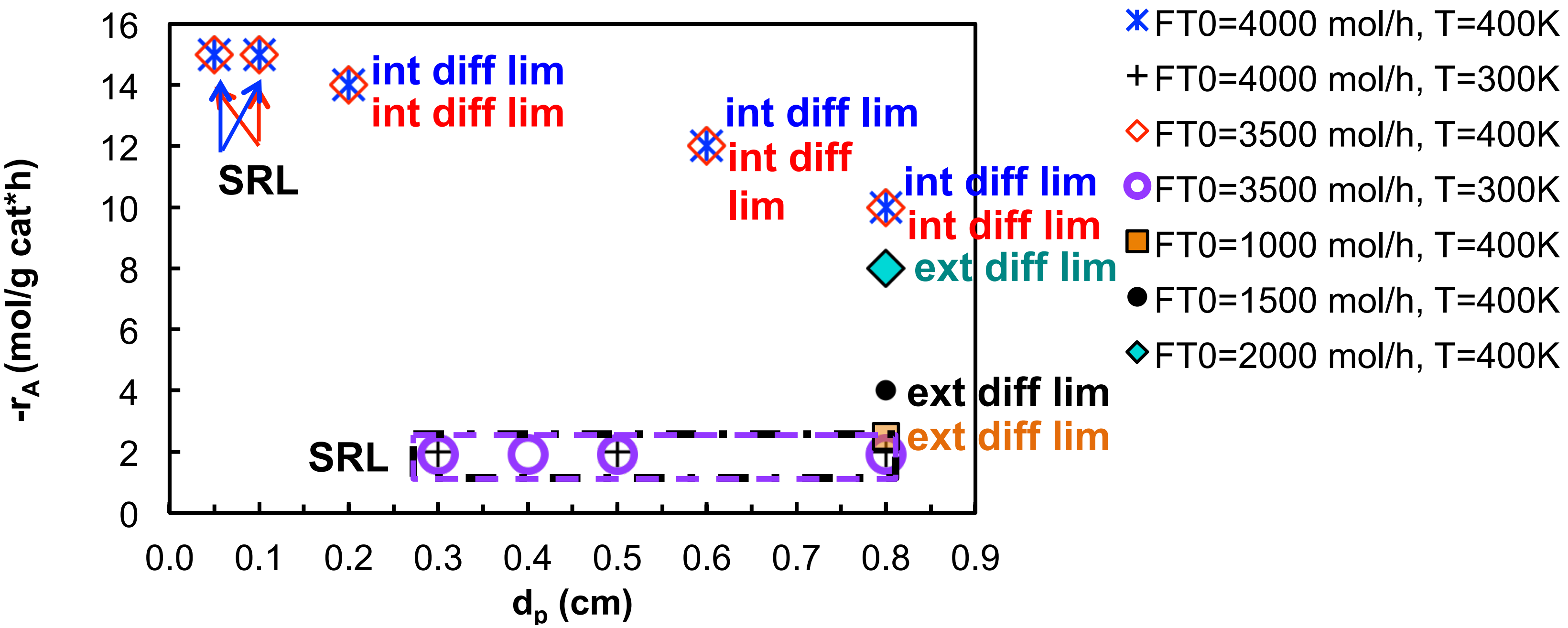


Which, if any, of the conditions shown (flow rates, T, and d_p) is the reaction limited by **the surface reaction?**

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.

The graph below shows the reaction rates obtained when the irreversible, liquid-phase, catalytic reaction A→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 **the surface reaction?**

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):**

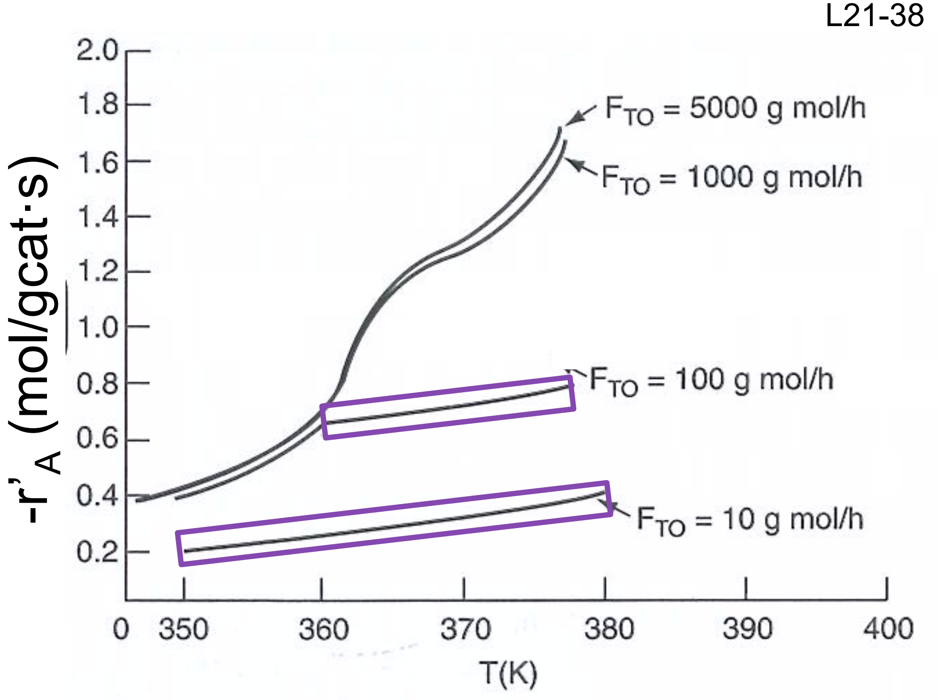
T = 400K, d_p= 0.1 cm & F_{T0}= 3500 mol/h, T = 400K, d_p= 0.05 cm & F_{T0}= 3500 mol/h,

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

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 external diffusion?



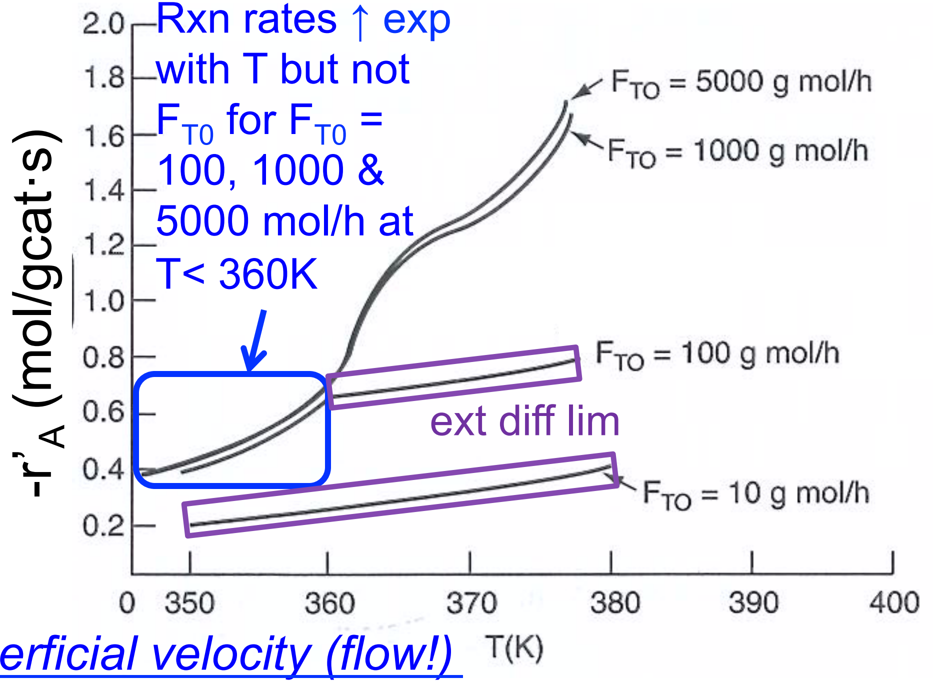
External diffusion limited where $-r'_A$↑ linearly when T↑

Type of Limitation	Variation of Reaction Rate with:		
	Superficial velocity	**Particle size**	**Temperature**
External	$U^{1/2}$	$d_p^{-3/2}$	Linear
Internal	Independent	d_p^{-1}	Exponential
Surface reaction	Independent	Independent	Exponential

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

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 surface reaction rate?



Rxn rates ↑ exp with T but not F_{T0} for F_{T0} = 100, 1000 & 5000 mol/h at T< 360K

ext diff lim

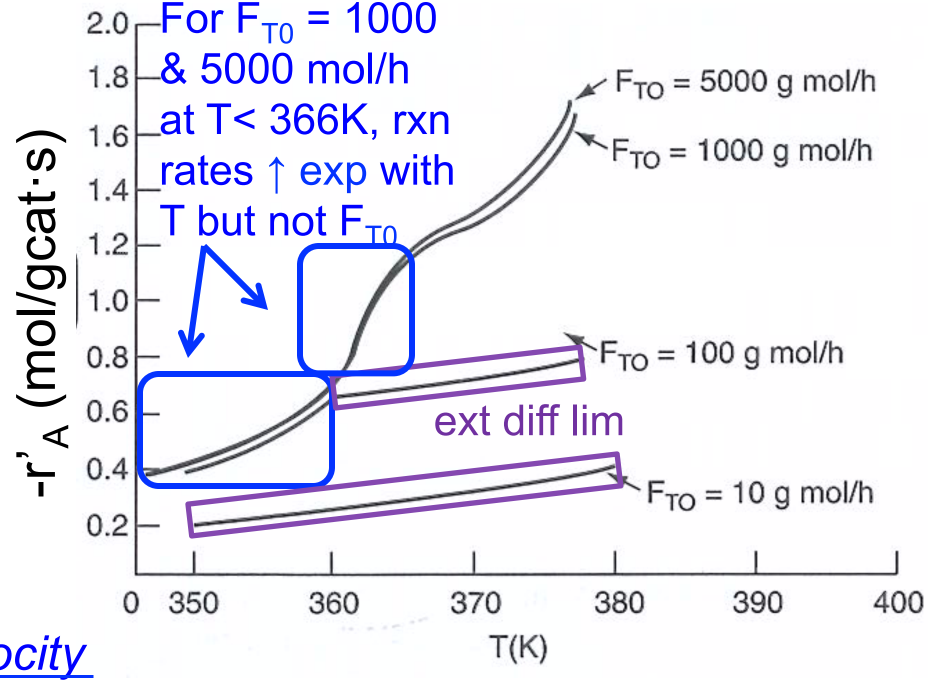
Surface rxn limited when $-r'_A$ increases exponentially with T↑ *but independent of superficial velocity (flow!)*

Type of Limitation	Variation of Reaction Rate with:		
	Superficial velocity	**Particle size**	**Temperature**
External	$U^{1/2}$	$d_p^{-3/2}$	Linear
Internal	Independent	d_p^{-1}	Exponential
Surface reaction	Independent	Independent	Exponential

For conditions F_{T0} = 100, 1000 & 5000 mol/h at T< 360K, rxn rate is independent of F_{T0} but exponentially dependent on T→ surface reaction limited

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 surface reaction rate?



For F_{T0} = 1000 & 5000 mol/h at T< 366K, rxn rates ↑ exp with T but not F_{T0}

ext diff lim

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

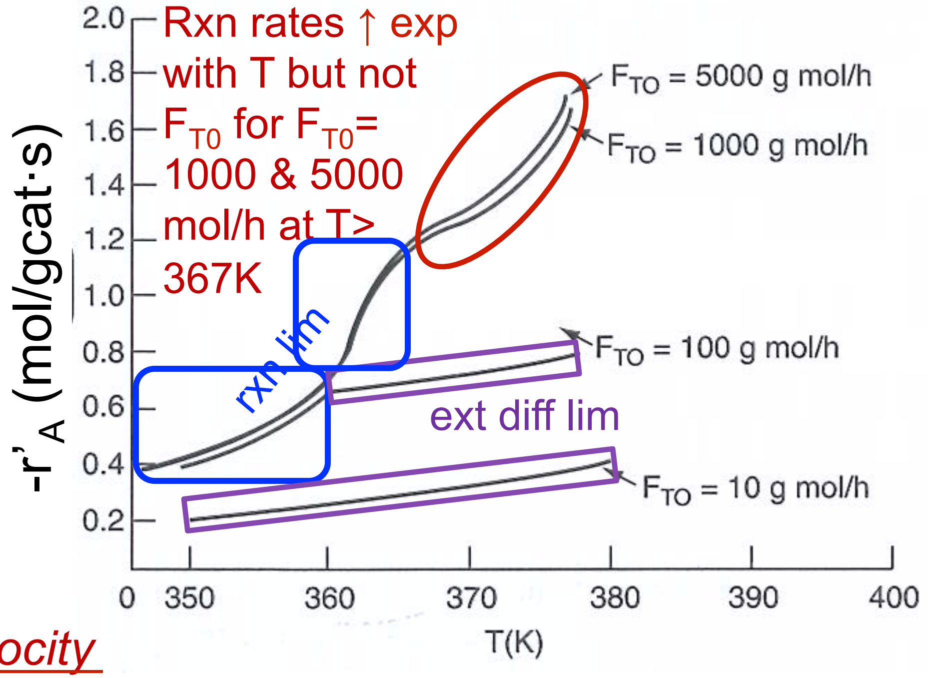
Type of Limitation	Variation of Reaction Rate with:		
	Superficial velocity	**Particle size**	**Temperature**
External	$U^{1/2}$	$d_p^{-3/2}$	Linear
Internal	Independent	d_p^{-1}	Exponential
Surface reaction	Independent	Independent	Exponential

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

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?


Rxn rates ↑ exp with T but not F_{T0} for F_{T0}= 1000 & 5000 mol/h at T> 367K

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

Type of Limitation	Variation of Reaction Rate with:		
	Superficial velocity	**Particle size**	**Temperature**
External	$U^{1/2}$	$d_p^{-3/2}$	Linear
Internal	Independent	d_p^{-1}	Exponential
Surface reaction	Independent	Independent	Exponential

For F_{T0} = 1000 & 5000 mol/h at T> 367K, rxn rate is roughly independent of F_{T0} but exponentially dependent on T. The reaction rate is internal diffusion limited at T> 370K for F_{T0} = 1000 & 5000 mol/h

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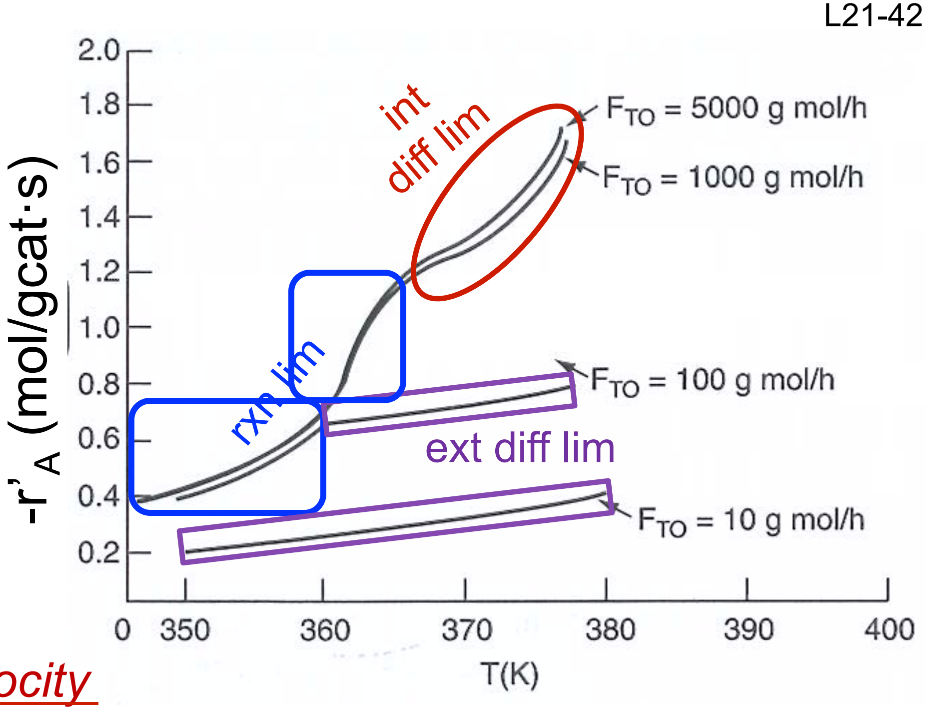

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Surface reaction	Independent	Independent	Exponential

How do we know it's not surface rxn limited at F_{T0}=1000 & 5000 mol/h & T>367K?

As T↑, the specific rate constant k↑, the rate of the surface rxn & consumption of reactant ↑. Thus the reactant is more likely to be consumed before it reaches the core.

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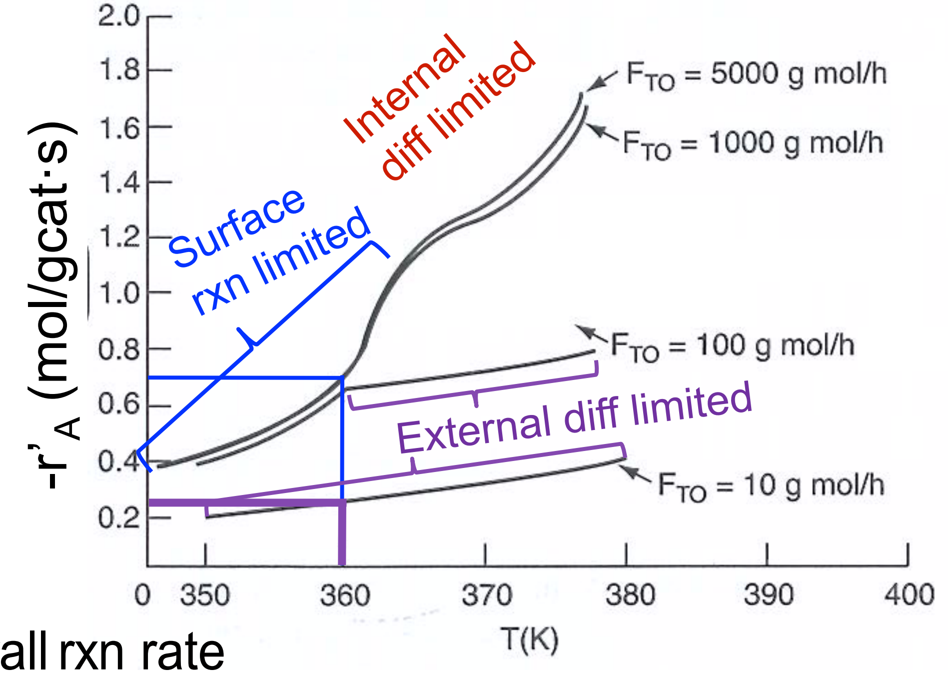
The catalytic reaction A→B takes place in a fixed bed reactor containing spherical porous catalyst X22. The overall rxn rates at a point in the reactor are shown in the graph below. For a flow rate of 10 g mol/h, determine the overall effectiveness factor Ω at 360K



$$\Omega = \underbrace{\frac{\text{actual overall rxn rate}}{\text{rxn rate if entire interior surface were exposed to the bulk conditions}}}_{\text{Rxn w/out diffusion limitations}}$$

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

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

Use the rxn rate obtained under surface reaction limited conditions

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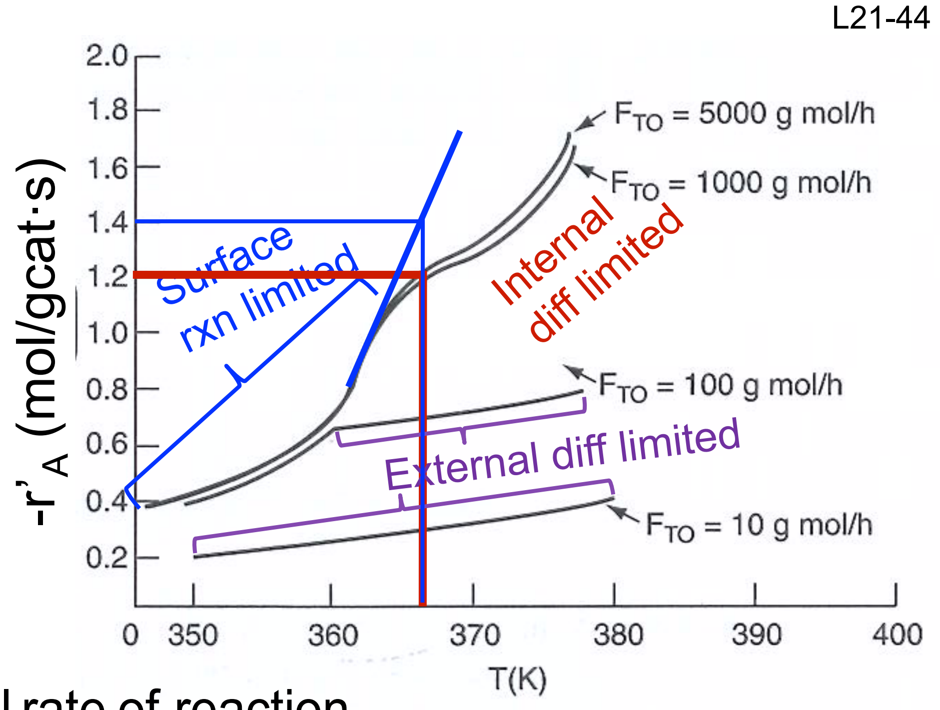
The catalytic reaction A→B takes place in a fixed bed reactor containing spherical porous catalyst X22. The overall rxn rates at a point in the reactor are shown in the graph below. For F_{T0}= 5000 g mol/h, estimate the internal effectiveness factor η at 367K



$$\eta = \underbrace{\frac{\text{actual overall rate of reaction}}{\text{rate of rxn if entire interior surface were exposed to the external surface conditions}}}_{\text{Rxn w/out internal diffusion limitations}}$$

$$\eta = \frac{-r''_A}{-r''_{As}} \rightarrow \eta = \frac{1.2}{1.4} \rightarrow \eta = 0.86$$

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_{T0} = 5000 mol/h plot to estimate the rxn rate that would be obtained without internal diffusion

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$X_{A1}=0.632$ for d_p, z, & υ_0 $\quad\quad$ $X_{A2}=?$ for $d_{p1}/3$, $1.5z_1$, and $4\upsilon_{0,1}$

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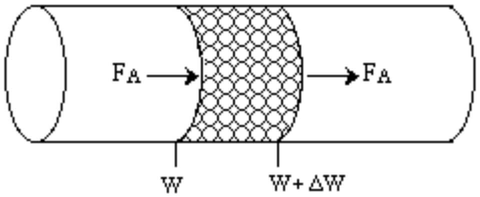
Need to relate X_A to reactor length in the presence of an external diffusion limit

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 :

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

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: $F_{\mathbf{Az}} = W_{\mathbf{Az}} A_c = (\cancel{J_{\mathbf{Az}}} + B_{\mathbf{Az}}) A_c$

Axial diffusion is negligible compared to bulk flow (convection)

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

Substitute into the mass balance

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

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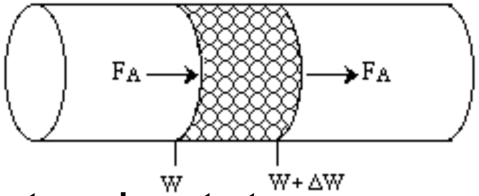
Review: Mass Transfer Limited Rxn in PBR (continued)



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

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

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

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

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

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

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

a_c: external surface area of catalyst per catalyst bed volume

ϕ: porosity of bed

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

In terms of X_A:

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

Express X_A at 2 reaction conditions as a ratio:

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

Relate U to υ_0 & a_c to d_p

$$\frac{a_{c1}}{a_{c2}} = \frac{\dfrac{\cancel{6(1-\phi)}}{d_{p1}}}{\dfrac{\cancel{6(1-\phi)}}{d_{p2}}} \rightarrow \frac{a_{c1}}{a_{c2}} = \frac{d_{p2}}{d_{p1}}$$

$U = \upsilon_0/A_c$ where A_c = cross-sectional area of PBR

$$\frac{U_1}{U_2} = \frac{\upsilon_{0,1}/A_c}{\upsilon_{0,2}/A_c} \rightarrow \frac{U_1}{U_2} = \frac{\upsilon_{0,1}}{\upsilon_{0,2}}$$

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$$\frac{\ln(1-X_{A1})}{\ln(1-X_{A2})} = \frac{k_{c1}a_{c1}zU_2}{k_{c2}a_{c2}(1.5z)U_1} \qquad \frac{a_{c1}}{a_{c2}} = \frac{d_{p2}}{d_{p1}} \qquad \frac{U_1}{U_2} = \frac{\upsilon_{0,1}}{\upsilon_{0,2}}$$

How are k_{c1} and k_{c2} related?

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

Typically the 2 is negligible so

$$\rightarrow k_c = \frac{D_{AB}}{d_p}(0.6)\left(\frac{Ud_p}{\nu}\right)^{1/2}\left(\frac{\nu}{D_{AB}}\right)^{1/3} \rightarrow k_c = 0.6\frac{D_{AB}^{2/3}}{\nu^{1/6}}\frac{U^{1/2}}{d_p^{1/2}}$$

$$\frac{k_{c1}}{k_{c2}} = \frac{\cancel{0.6}}{\cancel{0.6}}\,\frac{\cancel{\dfrac{D_{AB}^{2/3}}{\nu^{1/6}}}\,\dfrac{U_1^{1/2}}{d_{p,1}^{1/2}}}{\cancel{\dfrac{D_{AB}^{2/3}}{\nu^{1/6}}}\,\dfrac{U_2^{1/2}}{d_{p,2}^{1/2}}} \rightarrow \frac{k_{c1}}{k_{c2}} = \left(\frac{U_1^{1/2}}{d_{p,1}^{1/2}}\right)\left(\frac{d_{p,2}^{1/2}}{U_2^{1/2}}\right)$$

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

$$\rightarrow\frac{\ln(1-X_{A1})}{\ln(1-X_{A2})}=\frac{k_{c1}}{k_{c2}}\left(\frac{a_{c1}}{a_{c2}}\right)\left(\frac{z}{1.5z}\right)\frac{U_2}{U_1}$$

$$\boxed{\frac{a_{c1}}{a_{c2}}=\frac{d_{p2}}{d_{p1}}}\qquad\boxed{\frac{U_1}{U_2}=\frac{\upsilon_{0,1}}{\upsilon_{0,2}}}\qquad\boxed{\frac{k_{c1}}{k_{c2}}=\left(\frac{U_1^{1/2}}{d_{p,1}^{1/2}}\right)\left(\frac{d_{p,2}^{1/2}}{U_2^{1/2}}\right)}$$

$$\rightarrow\frac{\ln(1-X_{A1})}{\ln(1-X_{A2})}=\left(\frac{U_1^{1/2}}{d_{p,1}^{1/2}}\right)\left(\frac{d_{p,2}^{1/2}}{U_2^{1/2}}\right)\left(\frac{d_{p2}}{d_{p1}}\right)\left(\frac{\cancel{z}}{1.5\cancel{z}}\right)\frac{\upsilon_{0,2}}{\upsilon_{0,1}}$$

$$\rightarrow\frac{\ln(1-X_{A1})}{\ln(1-X_{A2})}=\left(\frac{U_1^{1/2}}{U_2^{1/2}}\frac{d_{p,2}^{3/2}}{d_{p,1}^{3/2}}\right)\left(\frac{1}{1.5}\right)\frac{\upsilon_{0,2}}{\upsilon_{0,1}}\quad\rightarrow\frac{\ln(1-X_{A1})}{\ln(1-X_{A2})}=\left(\frac{\cancel{\upsilon_{0,1}}^{1/2}}{\cancel{\upsilon_{0,2}}^{1/2}}\frac{d_{p,2}^{3/2}}{d_{p,1}^{3/2}}\right)\left(\frac{1}{1.5}\right)\cancel{\frac{\upsilon_{0,2}}{\upsilon_{0,1}}}$$

$$\rightarrow\frac{\ln(1-X_{A1})}{\ln(1-X_{A2})}=\left(\frac{\upsilon_{0,2}^{1/2}d_{p,2}^{3/2}}{\upsilon_{0,1}^{1/2}d_{p,1}^{3/2}}\right)\left(\frac{1}{1.5}\right)\quad\rightarrow\frac{\ln(1-0.632)}{\ln(1-X_{A2})}=\left(\frac{4\upsilon_{0,1}^{1/2}\left(d_{p,1}/3\right)^{3/2}}{\upsilon_{0,1}^{1/2}d_{p,1}^{3/2}}\right)\left(\frac{1}{1.5}\right)$$

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$$\rightarrow \frac{\ln(1-0.632)}{\ln(1-X_{A2})} = \left(\frac{4\upsilon_{0,1}{}^{1/2}\left(d_{p,1}/3\right)^{3/2}}{\upsilon_{0,1}{}^{1/2}d_{p,1}{}^{3/2}}\right)\left(\frac{1}{1.5}\right) \rightarrow \frac{\ln(1-0.632)}{\ln(1-X_{A2})} = 2(1/3)^{3/2}0.667$$

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

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

$$\rightarrow \boxed{X_{A2} = 0.98}$$

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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 υ to make sure that the process is not instead slowed down by the surface reaction, but without slowing down external diffusion?

Type of Limitation	**Variation of Reaction Rate with:**		
	Superficial velocity	**Particle size**	**Temperature**
External	$U^{1/2}$	$d_p^{-3/2}$	Linear
Internal	Independent	d_p^{-1}	Exponential
Surface reaction	Independent	Independent	Exponential

- 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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Hint: How does changing C_A and υ 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

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

- Increasing the volumetric flow rate υ_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. $X_{A,\text{mass x-fer}} \propto k_c \propto \upsilon_0^{1/2}$ but $X_{A,\text{reaction}} \propto \tau \propto \upsilon_0^{-1}$ so the increase in υ_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 υ_0 is a good idea.

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