Advanced Reactor Design

Week 9

Internal Diffusion

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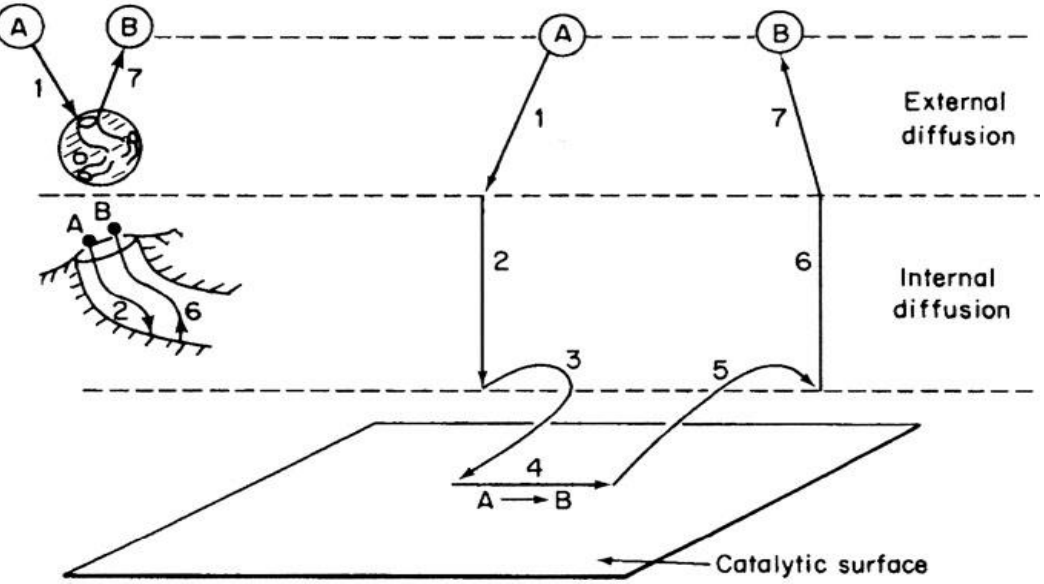
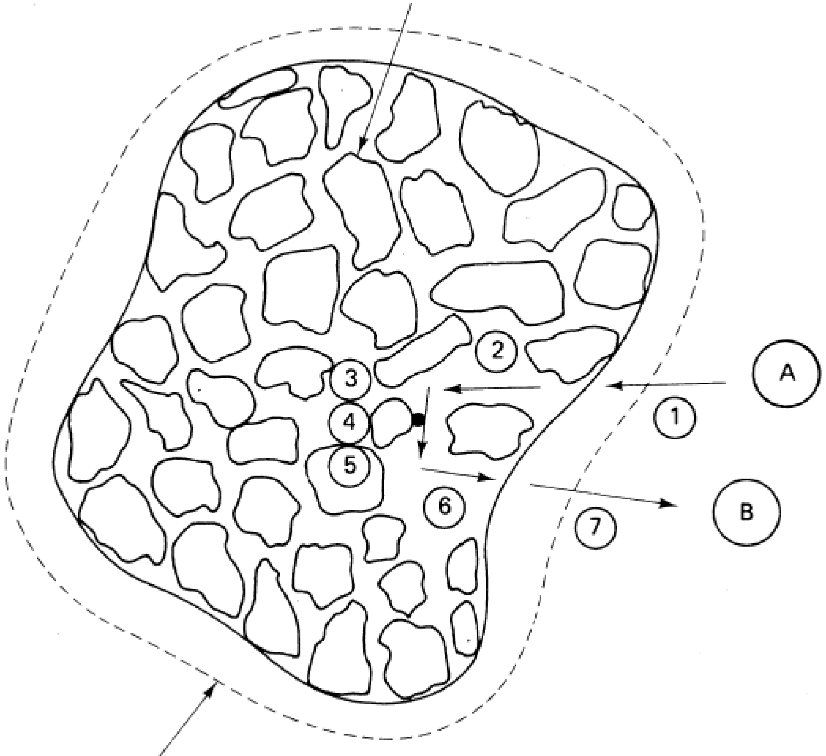
Review: Heterogeneous Catalyst

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





Review: Types of Boundary Conditions

1. Concentration at the boundary (i.e., catalyst particle surface) is specified:
   - If a specific reactant concentration is maintained or measured at the surface, use the specified concentration
   - When an instantaneous reaction occurs at the boundary, then $C_{As} \approx 0$
2. **Flux at the boundary (i.e., catalyst particle surface) is specified:**
   a) **No mass transfer at surface (nonreacting surface)**

$$\left.W_A\right|_{\text{surface}} = 0$$

   b) **Reaction that occurs at the surface is at steady state: set the molar flux on the surface equal to the rate of reaction at the surface**

$$\left.W_A\right|_{\text{surface}} = -r_A''$$

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

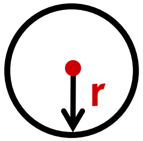
   c) **Convective transport across the boundary layer occurs**

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

3. Planes of symmetry: concentration profile is symmetric about a plane
   - Concentration gradient is zero at the plane of symmetry

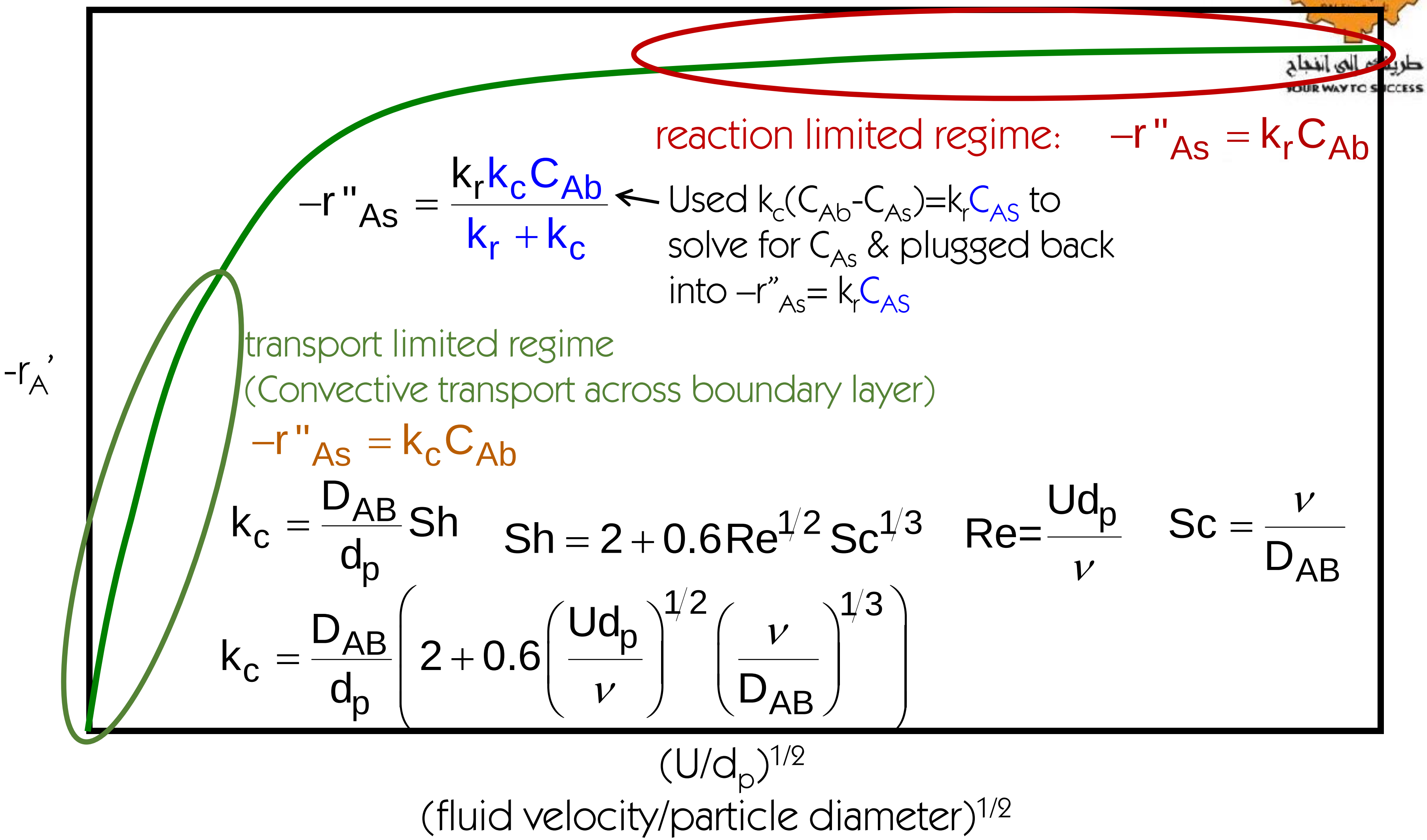
Radial diffusion in a tube:

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



Radial diffusion in a sphere

Review: Transport & Rxn Limited Rates



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

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

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

transport limited regime
(Convective transport across boundary layer)

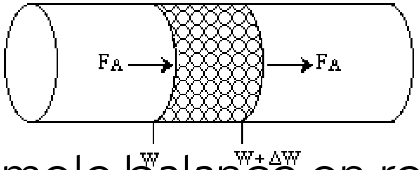
$$-r''_{As} = k_c C_{Ab}$$

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

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

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

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 ($mol/s \cdot m^2$)

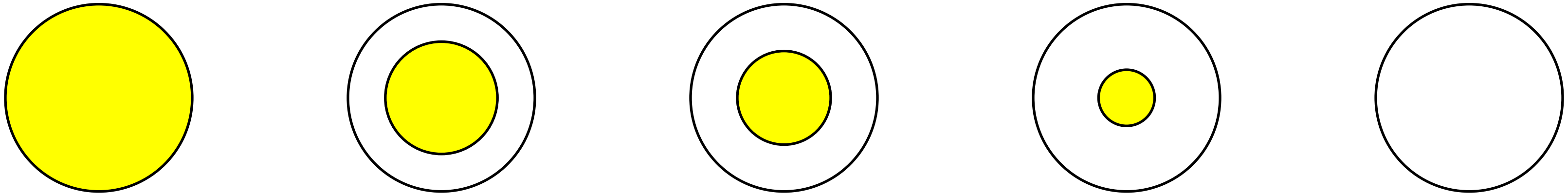
A_c: cross-sectional area of tube containing catalyst (m^2)

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

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

Shrinking Core Model

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

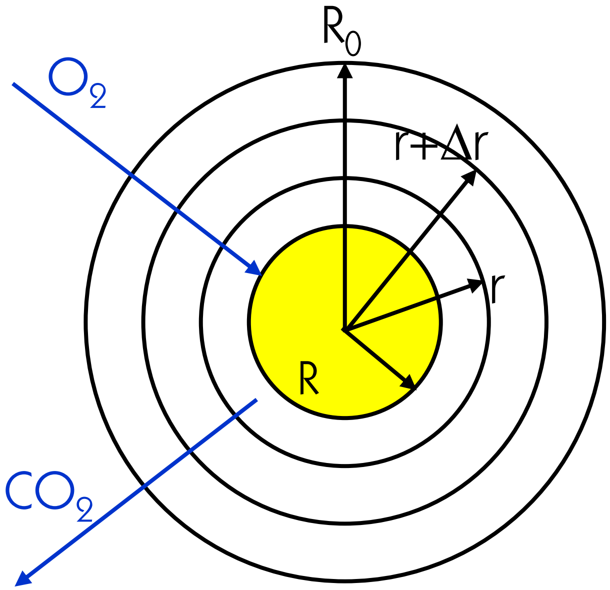


- Regeneration of catalyst by burning off carbon coke in the presence of O_2
- Begins at the surface and proceeds to the core
- Because the amount of carbon that is consumed (burnt off) is proportional to the surface area, and the amount of carbon that is consumed decreases with time

Catalyst Regeneration

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

$$C + O_2 \rightarrow CO_2$$



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

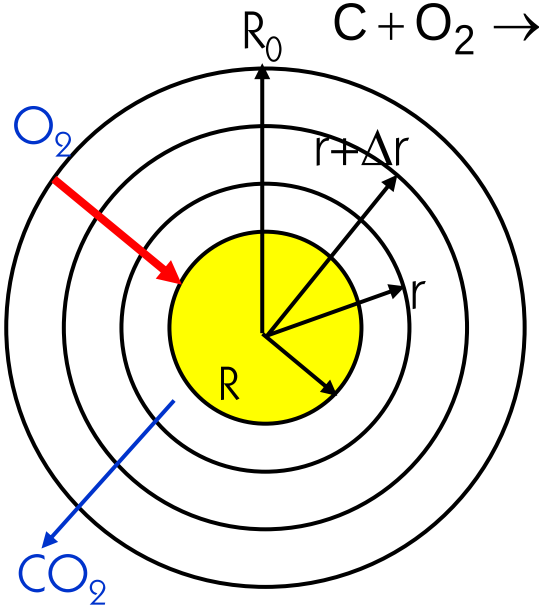
r : radius R_0:outer radius of particle   R: radius of unreacted core   r = 0 at core

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

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

Mole Balance on O_2 From r to r+Δr

$C + O_2 \rightarrow CO_2$



Rate in - rate out + gen = accum

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

Oxygen reacts at the surface, not in this region

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

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

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

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

D_e: effective diffusivity

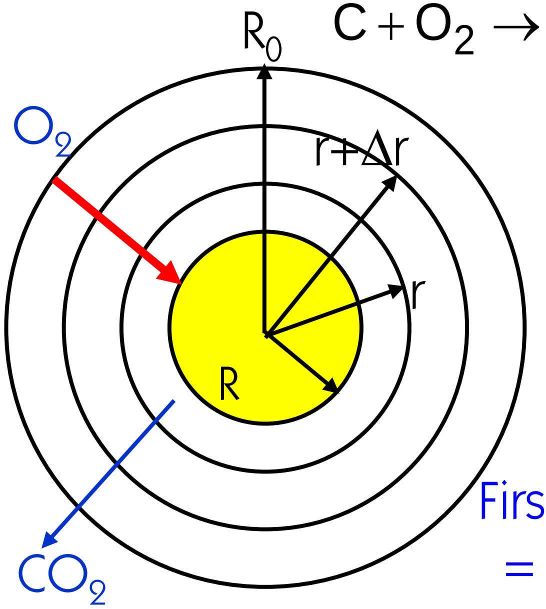
For every mole of O_2 that enters, a mol of CO_2 leaves → W_{O2}=-W_{CO2} $\rightarrow \mathbf{W}_A = -D_e\dfrac{dC_A}{dr}$

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

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

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

طريقك إلى النجاح
YOUR WAY TO SUCCESS



$$C + O_2 \rightarrow CO_2$$

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

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

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

At r = R_0, $C_A = C_{A0}$ and at r = R, $C_A = 0$

First use C_A=0 when r = R to determine K_2

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

For any r:

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

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

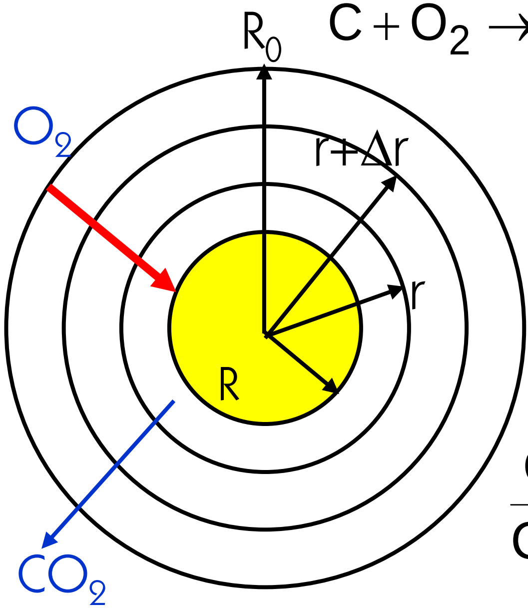
$$C_{A0} = -\frac{K_1}{R_0} + \frac{K_1}{R} \quad \rightarrow C_{A0} = K_1\left(\frac{1}{R} - \frac{1}{R_0}\right)$$

Take the ratio to determine C_A/C_{A0}

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

Oxygen Concentration Profile & Flux

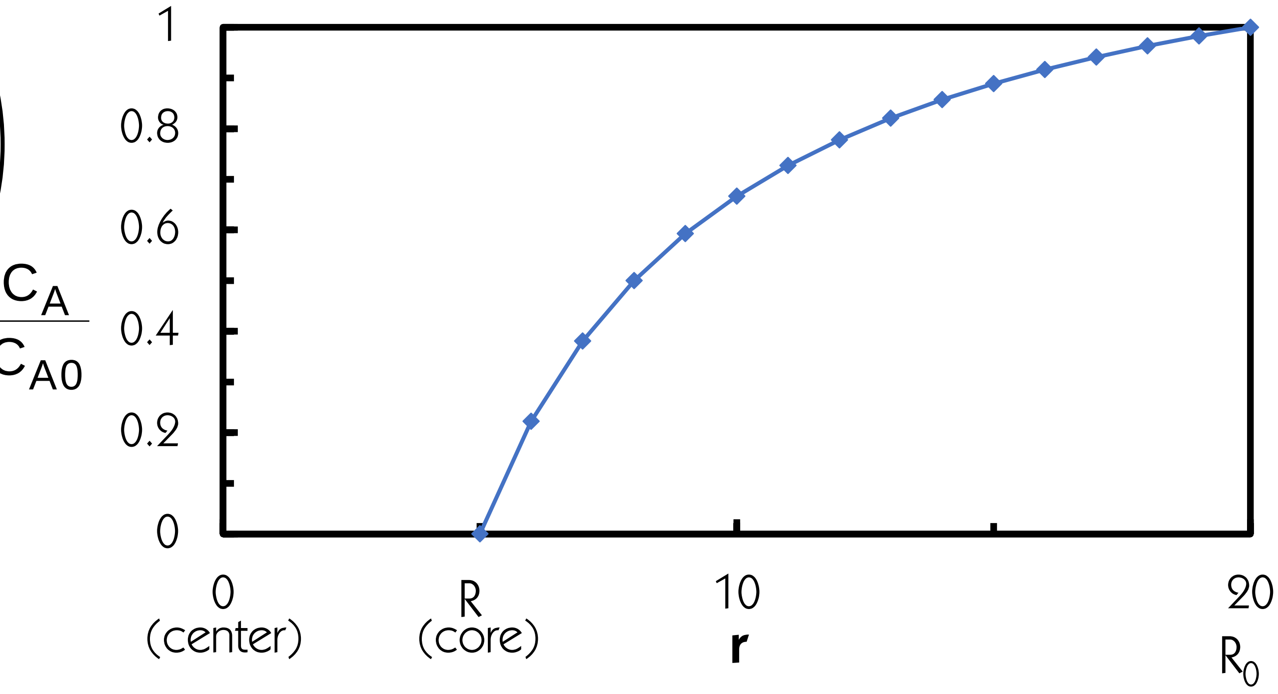
$C + O_2 \rightarrow CO_2$



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

C_A: oxygen concentration
$C_{Ab} = C_{A0}$

Oxygen concentration Profile at time t

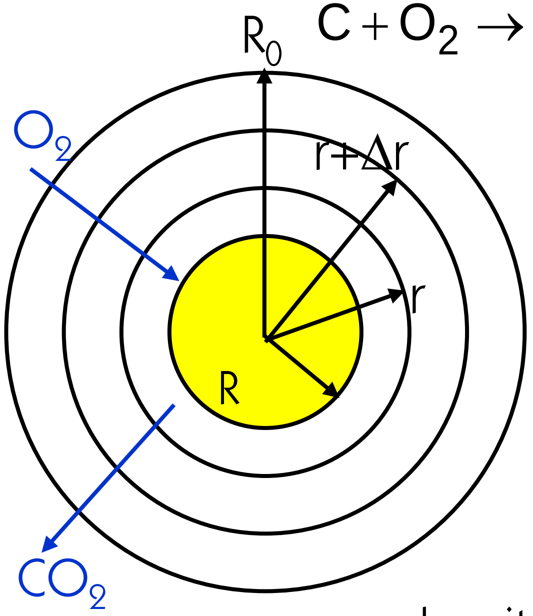


Finally determine the flux of oxygen to the surface of the core:

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

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

Mass Balance on Carbon (C)



$$C + O_2 \rightarrow CO_2$$

In – out + gen = accumulation

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

Elemental C does not enter or leave the surface

Change in the mass of the carbon core

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

ρ$_C$: density of solid C

φ$_C$: fraction of the volume of the core that is C

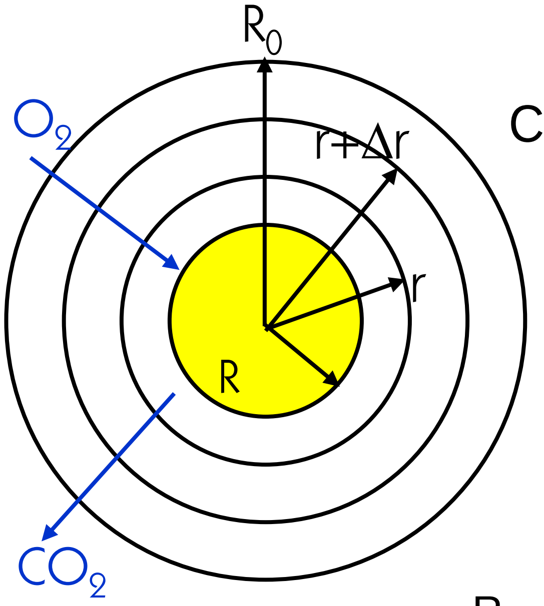
Simplify mass balance:

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

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

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

Time Required to Shrink Core to Radius R



$$C + O_2 \rightarrow CO_2$$

$$\frac{dR}{dt} = \frac{r''_c}{\rho_C \phi_C}$$

$$-r''_c = \frac{D_e C_{A0}}{R - R^2/R_0}$$

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

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

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

Integrate over 0 to t & R_0 to R

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

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

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

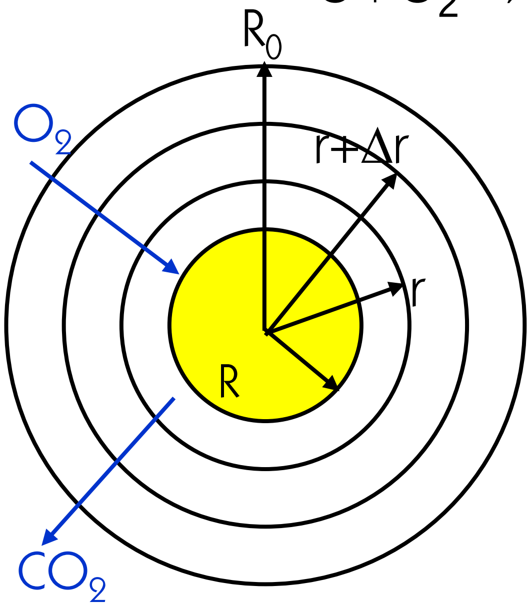
Get common denominators

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

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

Time Required to Shrink Core to Radius R

$$C + O_2 \rightarrow CO_2$$



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

Solve for t:

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

Factor out $R_0^2/6$

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

Factor out -1

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

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

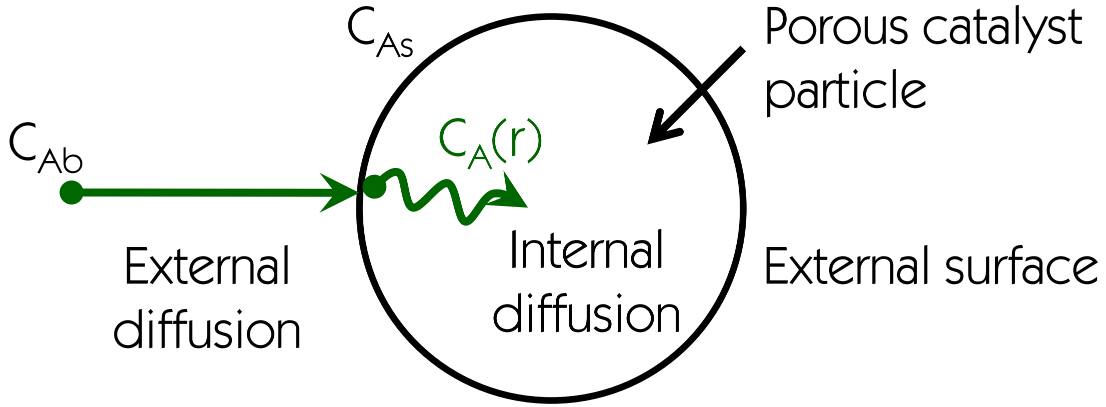
$$\rightarrow t = \left(1 - 3\left(\frac{0}{R_0}\right)^2 + 2\left(\frac{0}{R_0}\right)^3\right)\frac{\rho_C\phi_C R_0^2}{6D_eC_{A0}} \quad \rightarrow \boxed{t = \frac{\rho_C\phi_C R_0^2}{6D_eC_{A0}}}$$

Complete regeneration

Internal Diffusion Effects in Spherical Catalyst Particles

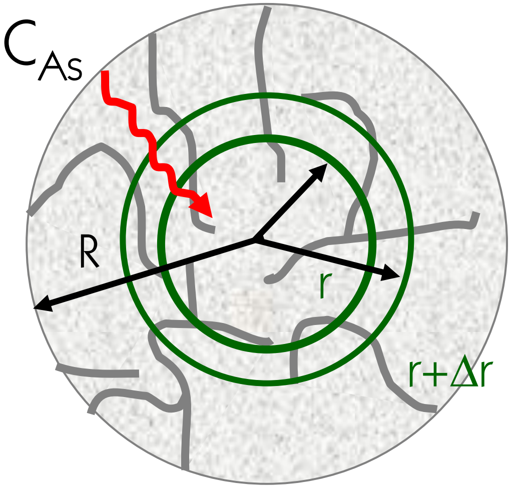
Internal diffusion: diffusion of the reactants or products from the external pellet surface (pore mouth) to the interior of the pellet. (Chapter 12)

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



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

Basic Molar Balance for Differential Element



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

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

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

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

The mole balance over the shell thickness Δr is:

IN - OUT + GEN =ACCUM

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

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

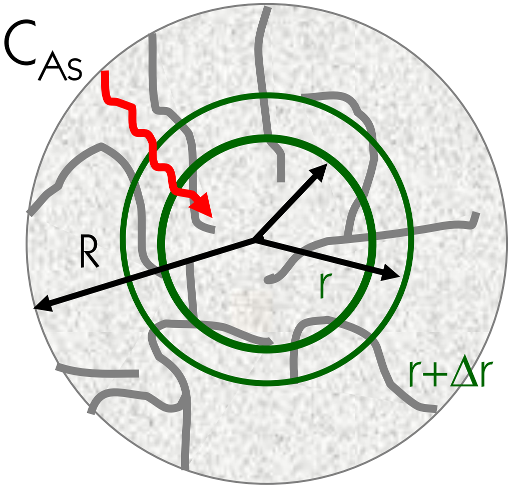
ρ_c: mass of catalyst per unit volume of catalyst (catalyst density)

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

Divide by -4πΔr & take limits 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

Diffusion Equation (Step 2)



IN - OUT + GEN =ACCUM

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

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

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

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

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

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

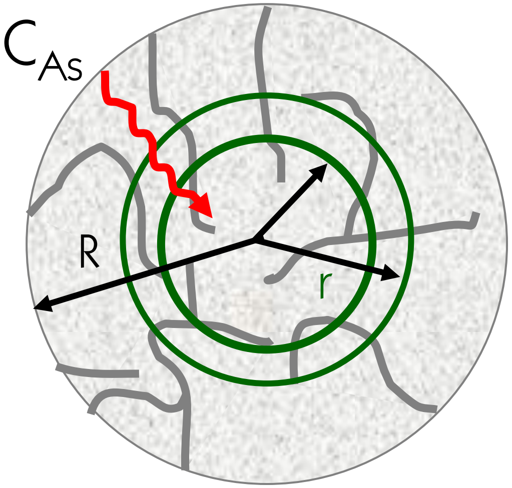
D_A bulk diffusivify

ϕ_p pellet porosity ($V_{\text{void space}}/V_{\text{void \& solid}}$) (typical ~ 0.4)

σ constriction factor (typical ~ 0.8)

$\tilde{\tau}$ tortuosity (distance molecule travels between 2 pts/actual distance between those 2 pts) (typical ~ 3.0)

Diffusion & Rxn in a Spherical Catalyst



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

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

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

Write the rate law based on surface area:

$$-r''_A = k''_n C_A^n \qquad \frac{\text{mol}}{m^2\cdot s}$$

Relate r'_A to r''_A by:

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

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

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

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

Boundary Conditions:

C_A finite at r=0 $\qquad$ $C_A = C_{As}$ at r =R

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

Dimensionless Variables

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

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

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

Boundary Conditions:

Ψ =1 at λ=1 Ψ =finite at λ=0

Thiele modulus for rxn of nth order ≡ ϕ_n

Subscript n = reaction order

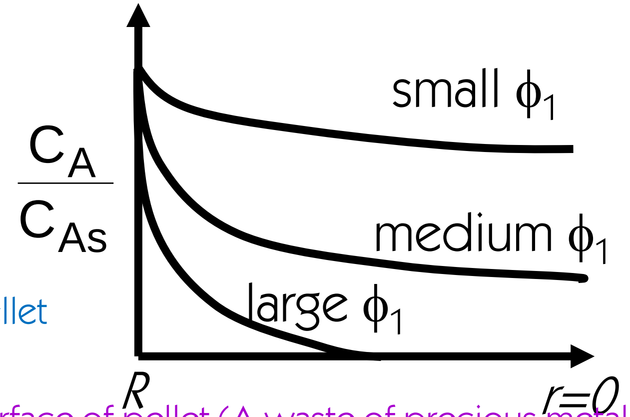
$$\phi_n{}^2=\frac{\text{"a" surface rxn rate}}{\text{"a" diffusion rate}}$$

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)

Internal Effectiveness Factor, η

Internal effectiveness factor:

(1) the relative importance of diffusion and reaction limitations

(2) a measurement of how far the reactant diffuses into the pellet before reacting

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

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

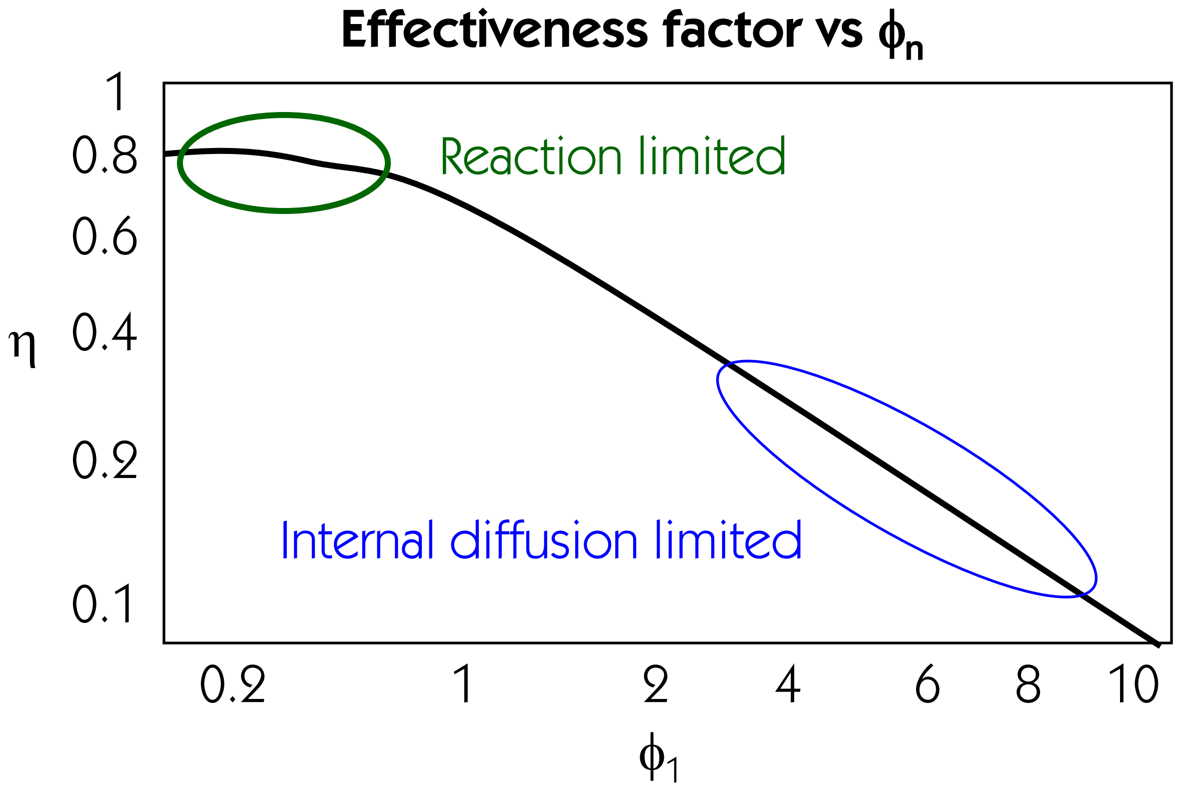
For example, when n=1 (1st order kinetics, $-r''_{As}$)

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

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

Internal Diffusion & Overall Rxn Rate

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


Effectiveness factor vs ϕ_n

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

As particle diameter ↑, ϕ_n ↑, $\eta \rightarrow 0$, rxn is diffusion limited

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

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: $\eta \cong \frac{3}{\phi_1} = \frac{3}{R}\sqrt{\frac{D_e}{k_1 \rho_c S_a}}, << 1$

ϕ_1 is large, diffusion-limited reaction inside the pellet (external diffusion will have a negligible effect on the overall rxn rate because internal diffusion limits the rxn rate)

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

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

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

Overall rate for 1st-order rxn

Clicker Question

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

Overall rate for
1st-order rxn

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

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

(a) decreasing the radius R of the particle
(b) increasing the concentration of the reactant
(c) increasing the temperature
(d) increasing the internal surface area
[✓ (e) Both a and b]

Total Rate of Consumption of A in Pellet, M_A (mol/s)

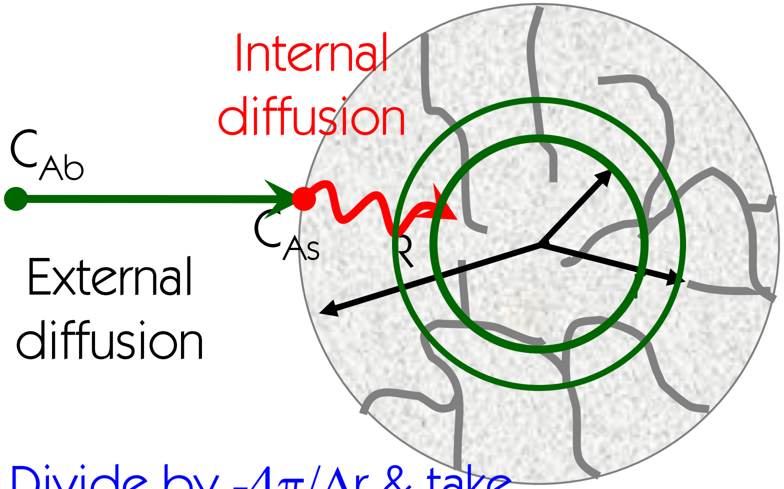
- At steady state, net flow of A into pellet at the external surface completely reacts within the pellet
- Overall molar rxn rate = total molar flow of A into catalyst pellet
- M_A = (external surface area of pellet) x (molar flux of A into pellet at external surface)
- M_A =the net rate of reaction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

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

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

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 Δr 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

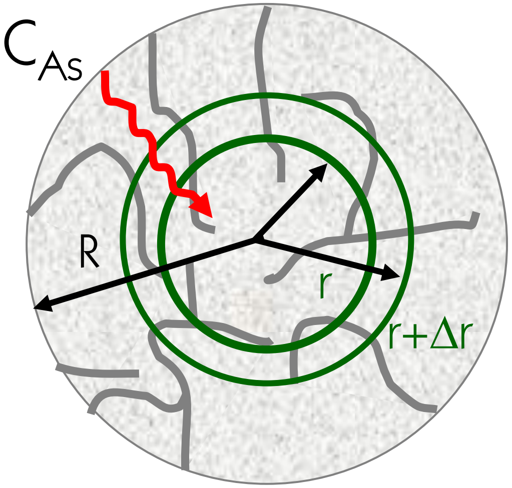
r_m: mean radius between r and $r - \Delta r$

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

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

Differential BMB in spherical catalyst particle

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)

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

Rate law:

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

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

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 Ψ =finite at λ=0

Thiele modulus for rxn of nth order ≡ ϕ_n

Subscript n = reaction order

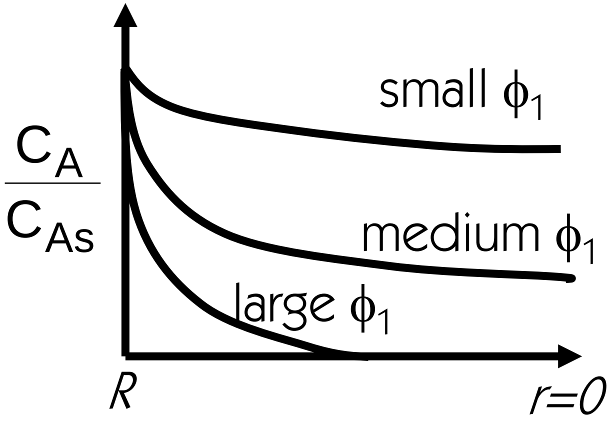
$$\phi_n{}^2=\frac{\text{"a" surface rxn rate}}{\text{"a" diffusion rate}}$$

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)

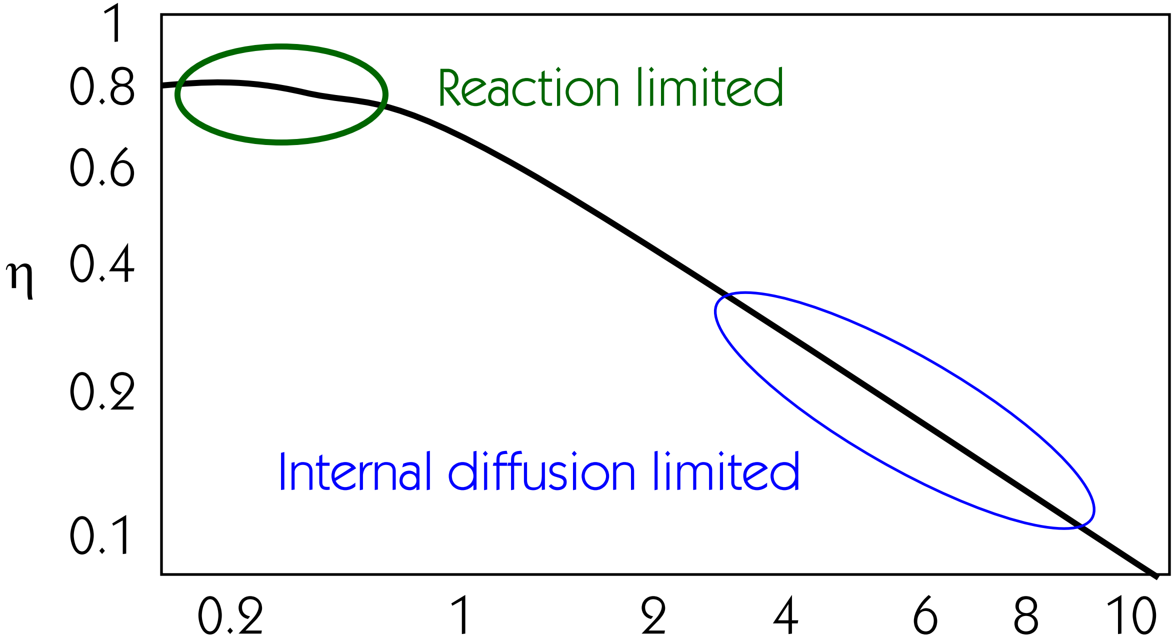
Review: Internal Effectiveness Factor, η

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

eta

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

Effectiveness factor vs ϕ_n



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

- As particle diameter ↓, ϕ_n ↓, $\eta \to 1$, rxn is surface rxn limited
- As particle diameter ↑, ϕ_n ↑, $\eta \to 0$, rxn is diffusion limited

Review: Effectiveness Factor & Rxn Rate

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

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

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

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)

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

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

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

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

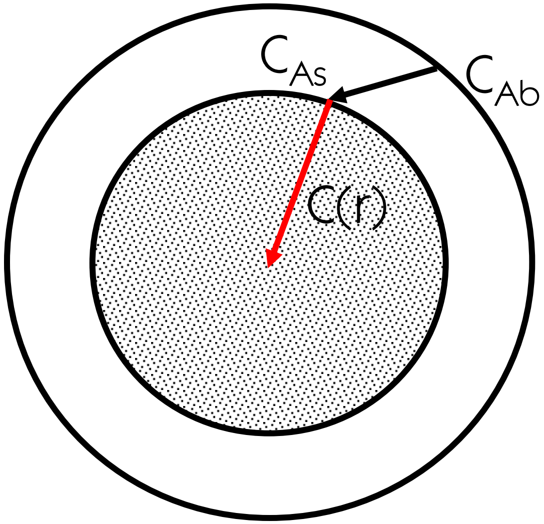
(4) increase the internal surface area

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

reactor volume

external surface area per unit reactor volume

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

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

Basic Molar Balance at Pellet Surface

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

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

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

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

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}

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

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

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

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
(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

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

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

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

Put into design eq to account for internal & external diffusion

Rxn Rate Variation vs Reactor Conditions

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

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

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

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: $$-r''_{Ab}=kC_{Ab}\quad\rightarrow -r'_A=kC_{Ab}\Omega S_a$$

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: $$C_{Ab}=C_{Ab0}\left(1-X_A\right)\rightarrow F_{A0}\frac{dX_A}{dW}=k\Omega S_aC_{Ab0}\left(1-X_A\right)$$

6. Integrate: $$\rightarrow\frac{dX_A}{dW}=\frac{k\Omega S_aC_{Ab0}\left(1-X_A\right)}{F_{A0}}$$

$$\rightarrow\int_0^{X_A}\frac{dX_A}{\left(1-X_A\right)}=\int_0^{W}\frac{k\Omega S_aC_{Ab0}}{F_{A0}}dW$$

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 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.

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:

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

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

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

Are these equations the same?

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

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

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