- **Catalysis**

- **Kinetics of Catalytic Reactions**

  - Langmuir-Hinshelwood kinetics

  - Rate-limiting/controlling step

- **Diffusion and Reaction in porous catalysts**

  - External diffusion

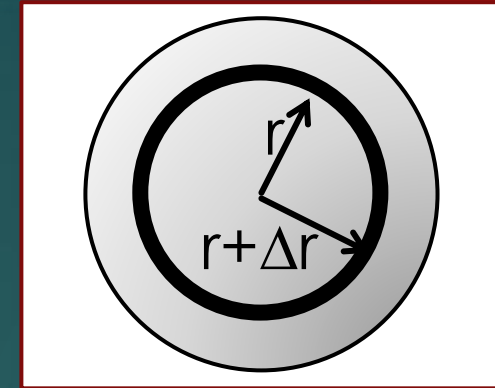 - Internal diffusion (effective diffusivity)

Internal Diffusion and Reaction in Porous Catalysts

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Reaction and Diffusion need to be considered simultaneously for porous catalysts

- J_A is the diffusional flux of A, and $J_A = -D_{eff} \dfrac{dC_A(r)}{dr}$

- Shell balance carried out:

- (Moles of A in)$_{at\ r}$ −(Moles of A out)$_{at\ r+\Delta r}$ + moles of A generated in shell $= 0$

- $\left(J_A \times 4\pi r^2\right)_r - \left(J_A \times 4\pi r^2\right)_{r+\Delta r} +$ moles of A generated in $shell = 0$

- $\begin{bmatrix} moles\ of\ A \\ generated\ in\ shell \end{bmatrix} = \begin{bmatrix} \text{Rate of reaction} \\ \text{Mass of catalyst} \end{bmatrix} \begin{bmatrix} \text{Mass of catalyst} \\ \text{Volume} \end{bmatrix} [\text{Volume of shell}]$

- $\left(J_A \times 4\pi r\right)_r - \left(J_A \times 4\pi r\right)_{r+\Delta r} + r'_A \times \rho_B \times 4\pi r^2 \Delta r = 0$

$$\Rightarrow -\frac{1}{r^2}\frac{d\left(J_A \times r^2\right)}{dr} + r'_A \rho_B = 0 \qquad \Rightarrow \qquad \frac{d^2 C_A(r)}{dr^2} + \frac{2}{r}\frac{dC_A(r)}{dr} - \frac{r'_A \times \rho_B}{D_{eff}} = 0$$

Combined equation in the dimensionless form

▶ Reaction-diffusion equation in spherical pellet: $\frac{d^2 C_A(r)}{dr^2} + \frac{2}{r}\frac{dC_A(r)}{dr} - \frac{r_A' \times \rho_B}{D_{eff}} = 0$

▶ Defining dimensionless parameters as: $\zeta = \frac{C_A(r)}{C_{AS}}$ and $\lambda = \frac{r}{R}$

▶ Boundary conditions are: $\zeta = 1$ at $\lambda = 1$; ζ is finite at $\lambda = 0$

▶ For n^{th} order reaction given by: $-r_A' = k_n' C_A^n$, and $r_A' * \rho_B = k_n C_A^n \rightarrow k_n = \rho_B k_n'$

▶ k_n *is per unit volume* and k_n' *is when rate is per unit mass of catalyst*

▶ Then: $\frac{d^2\zeta(\lambda)}{d\lambda^2} + \frac{2}{\lambda}\frac{d\zeta(\lambda)}{d\lambda} - \frac{k_n R^2 C_{AS}^{n-1}}{D_{eff}}\zeta^n = 0$ and with $\varphi_n^2 = \frac{k_n R^2 C_{AS}^{n-1}}{D_{eff}}$

$$\frac{d^2\zeta(\lambda)}{d\lambda^2} + \frac{2}{\lambda}\frac{d\zeta(\lambda)}{d\lambda} - \varphi_n^2 \zeta^n = 0$$

Thiele modulus – reaction rate and diffusional rate

▶ The dimensionless ODE showing variation of conc with radius:

$$\frac{d^2\zeta(\lambda)}{d\lambda^2} + \frac{2}{\lambda}\frac{d\zeta(\lambda)}{d\lambda} - \varphi_n^2\zeta^n = 0$$

▶ φ_n^2 is the ratio of "a" surface reaction rate to "a" rate of diffusion

$$\varphi_n^2 = \frac{k_n R^2 C_{AS}^{n-1}}{D_{eff}} = \frac{k_n R C_{AS}^n}{D_{eff}\left[(C_{AS} - 0)/R\right]} = \frac{\text{"a" surface reaction rate}}{\text{"a" diffusion rate}}$$

▶ The square root of φ_n^2 is called the Thiele modulus and is dimensionless

○ when Thiele modulus is large, internal diffusion usually limits the overall rate of reaction, and

○ when it is small the surface reaction is usually rate limiting

For 1st order reactions the ODE provides some clues

- For 1st order: $\dfrac{d^2\zeta(\lambda)}{d\lambda^2} + \dfrac{2}{\lambda}\dfrac{d\zeta(\lambda)}{d\lambda} - \varphi_1^2\zeta = 0$ with: $\varphi_1^2 = \dfrac{k_1 R^2}{D_{eff}}$ and $\varphi_1 = R\sqrt{\dfrac{k_1}{D_{eff}}}$

- Using $y = \zeta\lambda$ we have: $\dfrac{d^2 y}{d\lambda^2} - \varphi_1^2 y = 0$

- Which has a solution: $y = A_1\cosh(\varphi_1\lambda) + A_2\sinh(\varphi_1\lambda) = \zeta\lambda$

   where, $\cosh(x) = \dfrac{e^x + e^{-x}}{2}$ and $\sinh(x) = \dfrac{e^x - e^{-x}}{2}$

- Boundary conditions are: at $\lambda = 1, \zeta = 1; \, at \, \lambda = 0, \, \zeta$ is finite

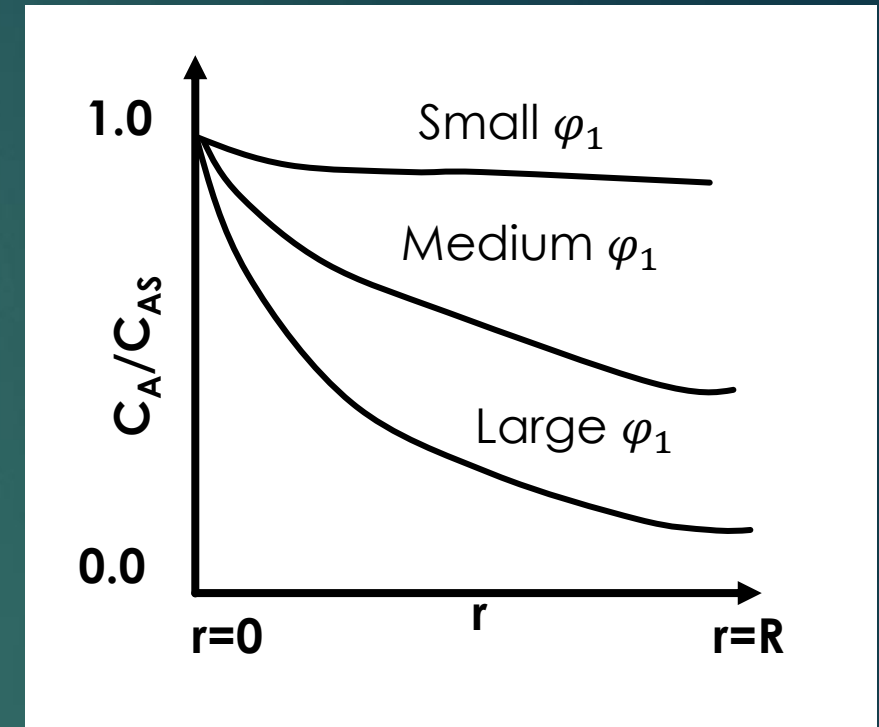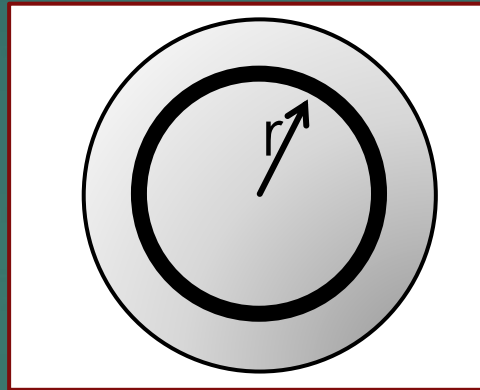   i.e., $A_1\cosh(\varphi_1) + A_2\sinh(\varphi_1) = 1$ & $A_1\cosh(0) + A_2 * 0 = 0 \implies A_1 = 0$

- Thus, $A_2 = \dfrac{1}{\sinh\varphi_1}$, and the change in concentration with radius

$$\zeta = \frac{C_A(r)}{C_{As}} = \frac{1}{\lambda}\frac{\sinh\varphi_1\lambda}{\sinh\varphi_1} = \frac{r}{R}\frac{\sinh(r\varphi_1/R)}{\sinh\varphi_1}$$

Magnitude of the Thiele modulus indicates the existance of concentration gradient

- $C_A(r) = C_{As} \dfrac{r}{R} \dfrac{\sinh(r\varphi_1/R)}{\sinh\varphi_1}$

- The concentration profile are shown for various φ_1
- Small φ_1 indicates surface reaction controls (rapid diffusion)
  - reactants diffuse into pellet interior
- Large φ_1 indicates pore diffusion controls (rapid reaction)
  - reactants consumed close to external surface and very little penetrates

The internal effectiveness factor signifies the effectiveness of creating the porous structure

▶ Ideally there should be no concentration profile, i.e., $C_A(r) = C_{AS}$

  ○ then rates are not affected by diffusion

▶ Due to the concentration profiles shown for different values of φ_1 the rates are affected

  ○ the entire active sites inside the pores may not be effective due to reaction-diffusion $C_A(r) \neq C_{AS}$

▶ Effectiveness factor is a measure of this "effectiveness" and is defined as

$$\eta = \frac{\text{Actual overall rate of reaction (observed rate)}}{\text{reaction rate if the entire interior pore surface was exposed to } C_{AS}}$$

Effectiveness factor for a first order reaction

▶ $\eta = \dfrac{\text{Actuall overall rate of reaction (observed rate)}}{\text{reaction rate with } c_A = c_{AS}} = \dfrac{(-r_A')_{obs}}{(-r_A')_{C_A = C_{AS}}}$

▶ Amount of material reacted is the amount of material diffused into the pores

▶ Thus, $(-r_A)_{obs} \times \text{volume of catalyst particle} = 4\pi R D_{eff} C_{AS} \left(\dfrac{d\varsigma}{d\lambda}\right)_{\lambda=1}$

▶ $\eta = \dfrac{(-r_A)_{obs} \times \text{volume of catalyst particle}}{(-r_A)_{C_A = C_{AS}} \times \text{volume of catalyst particle}} = \dfrac{4\pi R D_{eff} C_{AS}\left(\frac{d\varsigma}{d\lambda}\right)_{\lambda=1}}{k_1 C_{AS}\left(\frac{4}{3}\pi R^3\right)}$

▶ We know: $\varsigma = \dfrac{C_A(r)}{C_{AS}} = \dfrac{1}{\lambda}\dfrac{\sinh(\varphi_1 \lambda)}{\sinh(\varphi_1)} \rightarrow \dfrac{d\varsigma}{d\lambda} = \left(\dfrac{\varphi_1 \cosh(\lambda\varphi_1)}{\lambda \sinh(\varphi_1)} - \dfrac{1}{\lambda^2}\dfrac{\sinh(\lambda\varphi_1)}{\sinh(\varphi_1)}\right)$

$$\left(\dfrac{d\varsigma}{d\lambda}\right)_{\lambda=1} = (\varphi_1 \coth(\varphi_1) - 1)$$

Effectiveness is a function of Thiele modulus

$$\eta = \frac{(-r'_A)_{obs} \times \text{volume of catalyst particle}}{k_1 C_{AS}\left(\frac{4}{3}\pi R^3\right)} = \frac{4\pi R D_{eff} C_{AS}}{k_1 C_{AS}\left(\frac{4}{3}\pi R^3\right)} (\varphi_1 \coth\varphi_1 - 1)$$
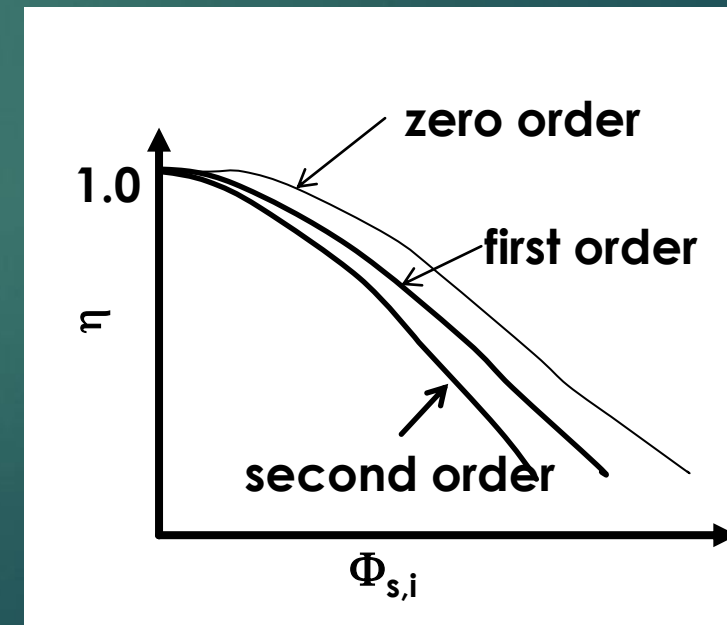
$$\eta = 3\frac{1}{k_1 R^2 / D_{eff}} (\varphi_1 \coth\varphi_1 - 1) = \frac{3}{\varphi_1^2} (\varphi_1 \coth\varphi_1 - 1)$$

▶ η versus Thiele modulus for a spherical particle, φ_1, is plotted for different reaction orders (log-log plot)

▶ Zero order $\Rightarrow \varphi_{s0} = R\sqrt{\dfrac{k_0}{D_{eff} C_{AS}}}$

First order $\Rightarrow \varphi_{s1} = R\sqrt{\dfrac{k_1}{D_{eff}}}$

Second order $\Rightarrow \varphi_{s2} = R\sqrt{\dfrac{k_2 C_{AS}}{D_{eff}}}$
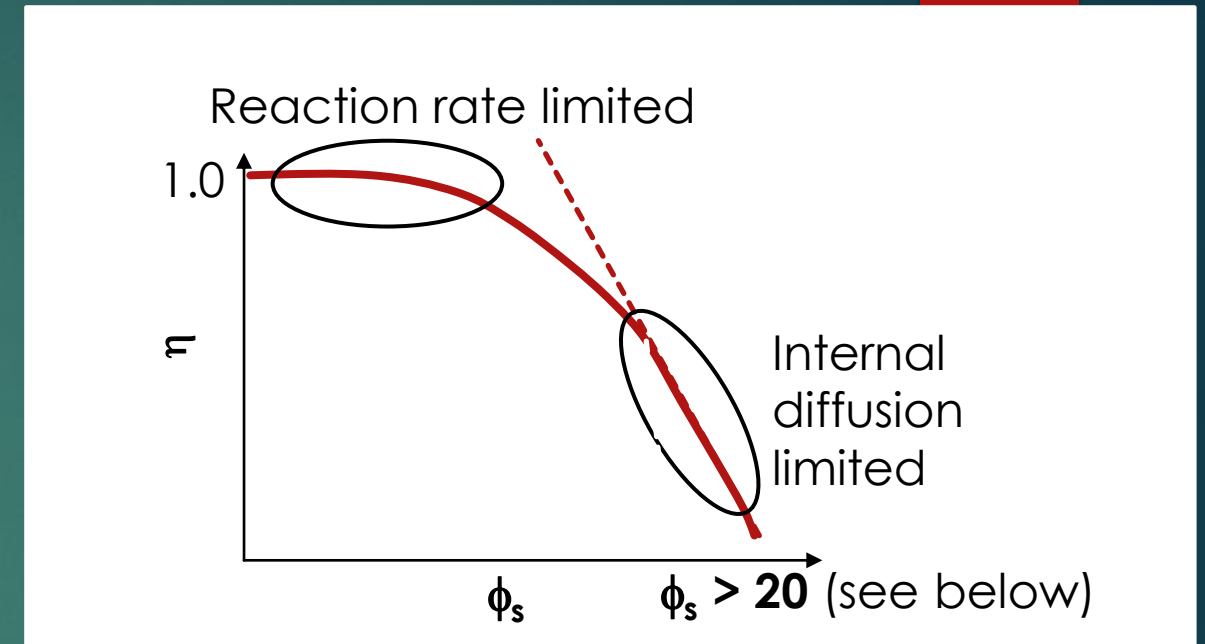
Effectiveness factor for different particle shapes (1st order reaction)

▶ $Sphere \Rightarrow \varphi_{s1} = \dfrac{R}{3}\sqrt{\dfrac{k_1}{D_{eff}}}$

$Cylinder \Rightarrow \varphi_{c1} = \dfrac{R}{2}\sqrt{\dfrac{k_1}{D_{eff}}}$

$Slab/plate \Rightarrow \varphi_{p1} = L\sqrt{\dfrac{k_1}{D_{eff}}}$

▶ For small size particles, φ is small and $\eta \to 1$

▶ For large $\varphi_1 (> 20)$, $\coth\varphi_1 \to 1\ and\ \eta \to 3/\varphi_1;$ $\qquad \eta = \dfrac{3}{R}\sqrt{\dfrac{D_{eff}}{k_1}}$

▶ Thus, $(-r_A)_{obs} = (-r_A)\eta = k_1 C_{AS}\eta$

▶ Depending on η, which depends on φ, the true rate can be determined (other combinations are also possible)

Falsified kinetics can result due to diffusional limited reaction

▶ Thiele modulus for a nth order is given by:
$$\varphi_n^2 = \frac{k_n R^2 C_{AS}^{n-1}}{D_{eff}}$$

▶ For large values of the Thiele modulus:

$$\eta = \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{\varphi_n} = \frac{3}{R}\left(\frac{2D_{eff}(C_{AS})^{1-n}}{(n+1)k_n}\right)^{1/2}$$

▶ We have, $(-r_A)_{obs} = (-r_{As}).\eta = k_n C_{AS}^n \eta$ and substituting for η for large φ

$$(-r_A')_{obs} = k_n C_{AS}^n \eta = \frac{3}{R}\left(\frac{2D_{eff}(C_{AS})^{1-n}}{(n+1)k_n}\right)^{1/2} k_n C_{AS}^n = \frac{3}{R}\left(\frac{2D_{eff}k_n(C_{AS})^{1+n}}{(n+1)}\right)^{1/2}$$

Apparent order will change for large Thiele modulus

▶ We obtained the following expression for the observed reaction rate

▶ $(-r_A)_{obs} = \dfrac{3}{R}\left(\dfrac{2D_{eff}k_n(C_{AS})^{1+n}}{(n+1)}\right)^{1/2}$

▶ Which is in terms of an apparent rate constant, k_n^{app}, and apparent order n'

$(-r_A)_{obs} = k_n^{app} C_{AS}^{n'}$ where $n' = \dfrac{1+n}{2}$

▶ Thus, a true zero order kinetics would appear to be like a ½ order reaction during measurements, and so on

▶ Further, for a true activation energy E_T and true pre-exponential factor A_T

$$k_n = A_T e^{\left(-E_T/RT\right)}$$

▶ Based on apparent values of the observed reaction rate we have

$$k_n^{app} = A_{app} e^{\left(-E_{app}/RT\right)}$$

Activation energy will also change for large Thiele modulus

▶ Substituting for temperature effect of rate constant in the rate of reaction equation

$$(-r'_A)_{obs} = \frac{3}{R} \left(\frac{2 D_{eff} (C_{AS})^{1+n}}{(n+1)} \right)^{1/2} A_T^{1/2} \left[\exp \left(-\frac{E_T}{RT} \right) \right]^{1/2} = A_{app} \left[\exp \left(-\frac{E_{app}}{RT} \right) \right] C_{AS}^{n'}$$

▶ Taking the natural log and comparing the temperature-dependent terms we have: $E_T = 2 E_{app}$

▶ Thus, information in a laboratory scale reactor with small particles (low Thiele modulus) when used for large reactors with large particles (high Thiele modulus) the temperature dependency will be different

The effect of strong diffusional limitations can be estimated

▶ Often it is necessary to obtain estimates of the extent of diffusional limitations in experimental data

▶ For 1ˢᵗ order reaction in a spherical pellet we obtained: $\eta = \frac{3}{\varphi_1^2}(\varphi_1 \coth\varphi_1 - 1)$

▶ Or $\eta\varphi_1^2 = C_{WP} = 3(\varphi_1 \coth\varphi_1 - 1)$, where C_{WP} is the Weisz-Prater parameter

▶ Substituting $\eta = \frac{(-r_A)_{obs}}{(-r_A)_{C_A=C_{AS}}}$ and $\varphi_1^2 = \frac{k_1 R^2}{D_{eff}} = \frac{k_1 R^2 C_{As}}{D_{eff} C_{As}} = \frac{R^2(-r_A)_{C_A=C_{AS}}}{D_{eff} C_{As}}$

▶ We have: $C_{WP} = \frac{(-r_A)_{obs}}{(-r_A)_{C_A=C_{AS}}} * \frac{R^2(-r_A)_{C_A=C_{AS}}}{D_{eff} C_{As}} = \frac{R^2(-r_A)_{obs}}{D_{eff} C_{As}} = \frac{R^2(-r_A')_{obs}\rho_B}{D_{eff} C_{As}}$

▶ All terms associated with determining C_{WP} can be measured

The Weisz-Prater criterion to estimate the presence of mass transfer limitations

▶ $C_{WP} = 3(\varphi_1 \coth\varphi_1 - 1)$ where $C_{WP} = \dfrac{R^2(-r'_A)_{obs}\rho_B}{D_{eff}C_{As}}$

▶ For large $\varphi_1 (> 20)$, $(\varphi_1 \coth\varphi_1 - 1) \to \varphi_1$ and $3\varphi_1 \gg 1$

▶ Thus, if $C_{WP} \gg 1$ then internal diffusion significantly limits the reaction

▶ Further, $\eta\varphi_1^2 = 3(\varphi_1 \coth\varphi_1 - 1) = C_{WP} = \dfrac{R^2(-r'_A)_{obs}\rho_B}{D_{eff}C_{As}}$

▶ For two runs 1 and 2, $-r'_{A1}$ and $-r'_{A2}$, for different radius particles, R_1 and R_2

▶ We have $\dfrac{R_1^2(-r'_{A1})_{obs}}{R_2^2(-r'_{A2})_{obs}} = \dfrac{\varphi_{11} \coth\varphi_{11} - 1}{\varphi_{12} \coth\varphi_{12} - 1}$ For diffusional limited reactions

▶ $\dfrac{R_1^2(-r'_{A1})_{obs}}{R_2^2(-r'_{A2})_{obs}} = \dfrac{\varphi_{11}}{\varphi_{12}} = \dfrac{R_1}{R_2}$ then $\dfrac{(-r'_{A1})_{obs}}{(-r'_{A2})_{obs}} = \dfrac{R_2}{R_1}$ that is $(-r'_{A1})_{obs} \propto 1/R$

Other effects for large diffusional effects also exist

▶ Non-isothermal reactors need additional considerations, another Mears Criteria

▶ 3 new dimensionless parameters introduced

▶ Diffusional effects (large Thiele modulus) may also effect the selectivities of multiple reactions

▶ 3 reaction schemes have been considered

- ○ $A \rightarrow D$ and $X(impurity) \rightarrow Y$

- ○ $A \rightarrow D$ and $A \rightarrow U$

- ○ $A \rightarrow D \rightarrow U$

▶ Temperature effects and selectivity changes are beyond the scope of ChE331A!