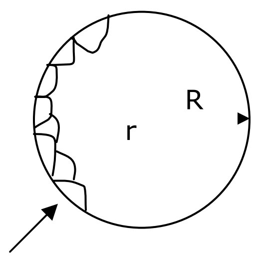
10.37 Chemical and Biological Reaction Engineering, Spring 2007
Prof. K. Dane Wittrup
Lecture 20: Reaction and Diffusion in Porous Catalyst

This lecture covers: Effective diffusivity, internal and overall effectiveness factor, Thiele modulus, and apparent reaction rates

Reaction & Diffusion

-Diffusion in a porous solid phase
Ex. Precious metals on ceramic supports or drug/nutrient delivery through tissues
-Derive steady state material balance accounting for diffusion and reaction in a spherical geometry
-Thiele modulus (ϕ)



$[S]_0$= surface concentration of a growth substrate (ex. glucose and O_2)

Figure 1. Sphere of Cells

Assume pseudo-homogeneous medium and Fick's Law describes diffusion

$Flux = -D\dfrac{d[S]}{dr}$, where $Flux\,[=]\,\dfrac{\#\,molecules}{area \cdot time}$ and $D\,[=]\,\dfrac{length^2}{time}$

$$-r_s = k_n C_s^n$$

$$-r_s = \frac{V_{\max} C_s}{K_s + C_s}$$

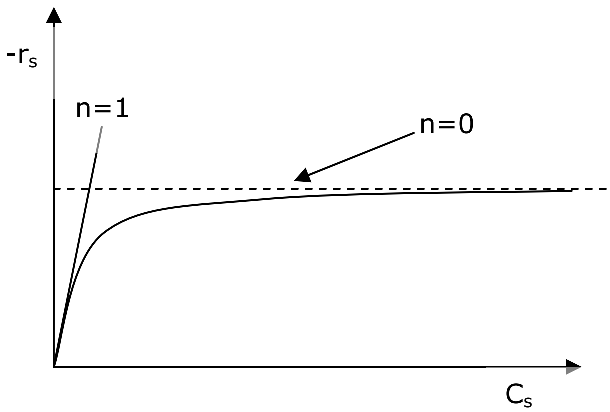


Figure 2. Rate of reaction versus species concentration

$C_s \ll K_s \Rightarrow 1^{st}$ order $\quad r_s \approx \frac{V_{max} C_s}{K_s}$

$C_s \gg K_s \Rightarrow 0^{th}$ order $\quad r_s \approx V_{max}$

Steady-state Shell Balance

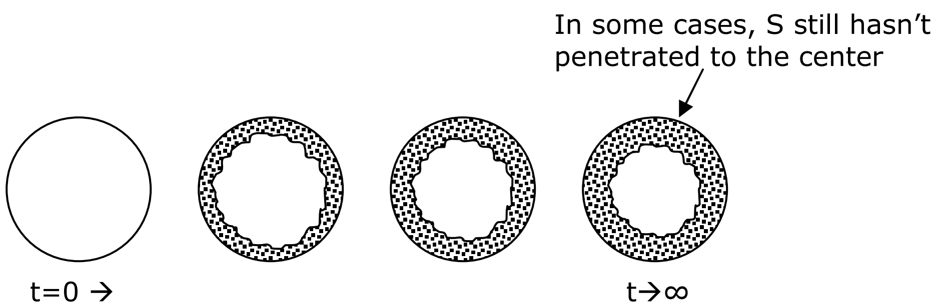


Figure 3. Time progression as species, S, enters the sphere

Thin shell r to (r+Δr)

S_{in} by diffusion $-S_{out}$ by diffusion $-S_{cons}$ by reaction=0

$$Flux \cdot 4\pi r^2\Big|_{r+\Delta r} - Flux \cdot 4\pi r^2\Big|_{r} - k_n C_s^n 4\pi r^2 \Delta r = 0$$

Divide through by $4\pi\Delta r$ and take the limit as Δr→0

$$\frac{d\left(Flux \cdot r^2\right)}{dr} - k_n C_s^n r^2 = 0$$

$$\frac{d}{dr}\left(-D\frac{dC_s}{dr}\cdot r^2\right) - k_n C_s^n r^2 = 0$$

$$\left.\frac{d^2 C_s}{dr^2} + \frac{2}{r}\frac{dC_s}{dr} - \frac{k_n}{D} C_s^n = 0 \right\} \text{2nd order ODE}$$

2 Boundary conditions:

$$C_s\big|_{r=R} = C_{s,0}$$

C_s is finite everywhere, or

$$\left.\frac{dC_s}{dr}\right|_{r=0} = 0$$

Nondimensionalize

$$\rho = \frac{r}{R} \quad S = \frac{C_s}{C_{s,0}}$$

$$\frac{d^2S}{d\rho^2} + \frac{2}{\rho}\frac{dS}{d\rho} - \phi^2 S^n = 0$$

Boundary conditions: S=1 @ $\rho=1$
S is finite everywhere

$$\phi^2 = \frac{k_n R^2 C_{s,0}^{n-1}}{D} = \frac{\left(R^2/D\right)}{\left(1/k_n C_{s,0}^{n-1}\right)} = \frac{\text{characteristic diffusion time}}{\text{characteristic reaction time}}$$

If diffusion is slow → diffusion dominates
If reaction is slow → reaction dominates

If $\phi^2 << 1$ → reaction limited regime
If $\phi^2 >> 1$ → diffusion limited regime

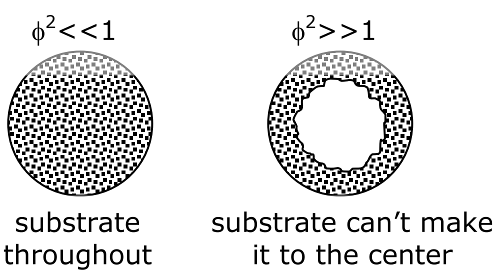


Figure 4. Reaction and diffusion limited regimes

$$S = \frac{1}{\rho}\frac{\sinh(\phi\rho)}{\sinh(\phi)}$$

$$\sinh(z) = \frac{e^z - e^{-z}}{2}$$

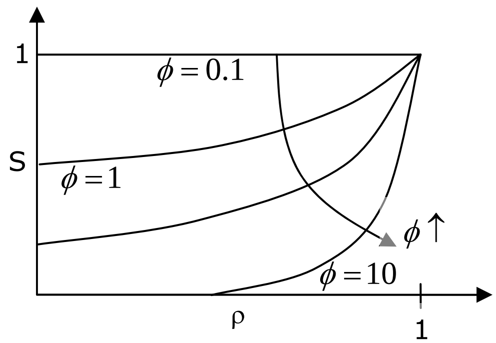


Figure 5. S versus ρ for various values of ϕ

Define "effectiveness factor" η

$$\eta = \frac{\text{overall rate of reaction}}{\text{rate if } C_s = C_{s,0} \text{ everywhere}}$$

overall reaction rate in sphere at steady state = [inward flux @ r=R (ρ=1)]*Area

$$= D\left.\frac{dC_s}{dr}\right|_{r=R} 4\pi R^2$$

$$= 4\pi RDC_{s,0}\left.\frac{dS}{d\rho}\right|_{\rho=1} = 4\pi RDC_{s,0}\left(\phi\coth\phi - 1\right)$$

$$\eta = \frac{3}{\phi^2}\left(\phi\coth\phi - 1\right)$$

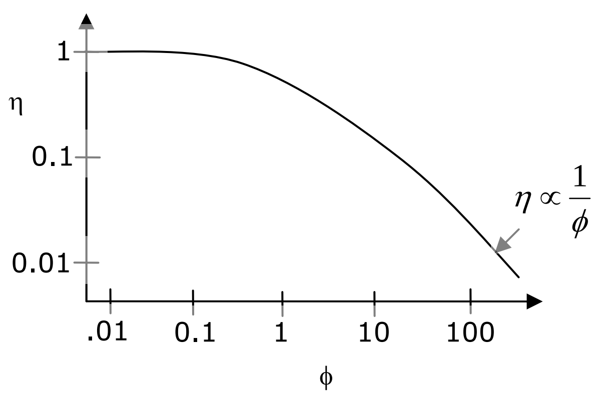


Figure 6. Log-log plot of effectiveness factor versus thiele modulus

Higher values of Thiele modulus → effectiveness goes down

*For a variety of reaction kinetics, geometries and rate laws, plots of η vs ϕ all look the same.

Shrinking Core Model

In cases with noncatalytic and irreversible reaction, diffusion limit is describable by the “shrinking core model”.

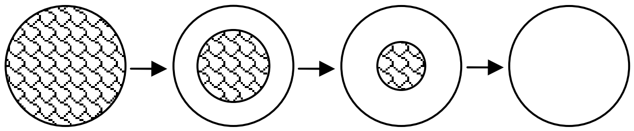


Figure 7. Shrinking core model

Rapid, irreversible reaction limited by rate of diffusion of a reactant from the surface
The following must be written down for the shell balance:
1. Rate of reaction
2. Rate of diffusion
3. Rate of movement of the core