ChE 344
Reaction Engineering and Design

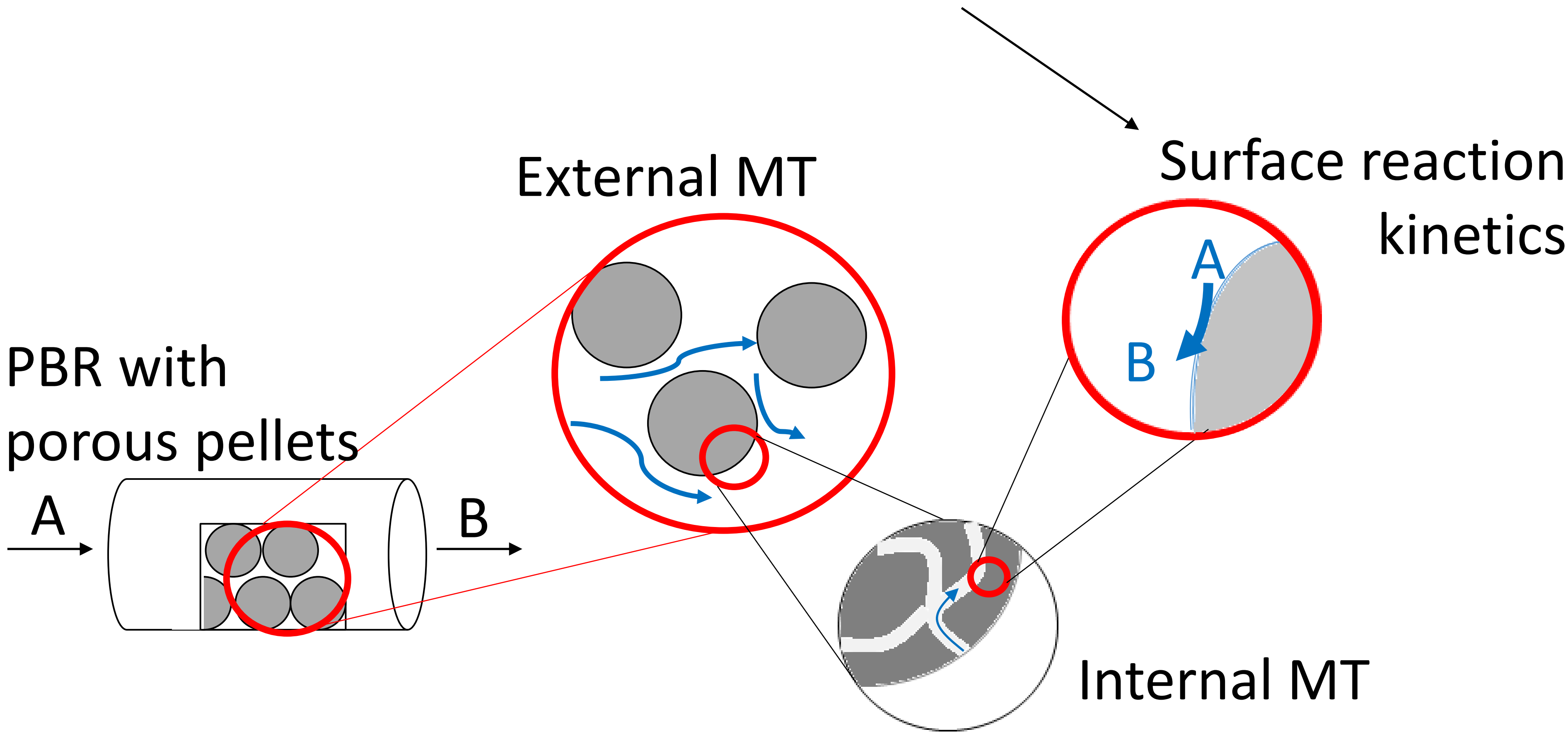
Lecture 26: Tues, Apr 19, 2022

Overall effectiveness factor

Reading for today's Lecture: Chapter 14-15

What controls the overall rate when we consider **mass transport**

From rate law derived from mechanism.
However, concentrations (e.g., C_A) into that rate law are the concentration near the surface



Limiting cases of reaction rate for first order catalytic PBR:

External transport limited (fast internal transport ($\eta = 1$), fast surface reaction)

$$-r_A'' \propto k_c \propto \left(\frac{\rho U}{\mu d_p}\right)^{1/2} (\nu)^{1/3} (\mathfrak{D}_{AB})^{2/3}$$

But rate with respect to catalyst surface area vs. wrt catalyst mass (or reactor volume) are related through a_c

$$-r_A'' \propto (d_p)^{-1/2} \qquad a_c = \text{Surface area/Volume} \propto (d_p)^{-1}$$

$$-r_A' \propto (d_p)^{-3/2}$$

$$-r_A \propto (d_p)^{-3/2}$$

Rate has a non-exponential T dependence, depends on flow rate and pellet diameter.

Internal transport limited: Diffusion in the pores of the pellet is slow relative to external diffusion and surface reaction

$$\eta \neq 1, \phi_1\ large, \frac{\mathfrak{D}_{Eff}}{k}\ small$$

$$k_c\ large, C_{Ab} = C_{As}$$

Because ϕ_1 is large

$$-r_A = \eta k C_{Ab}$$

$$\eta = \frac{3}{{\phi_1}^2}(\phi_1 \coth \phi_1 - 1) = \frac{3}{\phi_1}$$

$$\phi_1 = \sqrt{\frac{k}{\mathfrak{D}_{Eff}}}R$$

R is related to pellet diameter (radius of pellet)

$$r_A \propto \sqrt{\frac{\mathfrak{D}_{Eff}}{k}}R^{-1}k \propto (k)^{1/2}\left(\mathfrak{D}_{Eff}\right)^{1/2}R^{-1}$$

$$\mathfrak{D}_{Eff} = \frac{\mathfrak{D}_{AB}\phi_p\sigma_c}{\tau}$$

Ignoring linear portion of T dependence, assume T-dependence is dominated by exponential

$$r_A \propto (k)^{1/2}\left((T)^{1/2}\right)^{1/2} R^{-1} \propto \exp\left(-\frac{E_a/_2}{RT}\right) U^0 {d_p}^{-1}$$

Internal diffusion limited is the trickiest one for measuring rates. In addition to usually giving a lower apparent activation barrier, can also lead to incorrect reaction orders! n=2 will appear to be 3/2, n=0 will appear to be ½ (not discussed in class but good to know)

Surface reaction limited (surface reaction 'slowest')

Internal is fast:

$\eta = 1, \phi_1\ small, \frac{\mathfrak{D}_{Eff}}{k}\ large$, $C_A(r) = C_{As}$

External is fast:

k_c is large, $C_{Ab} = C_{As}$

Rate dependence as we expect (unless pressure drop shows up!)

$$r_A \propto \exp\left(-\frac{E_a}{RT}\right) U^0 {d_p}^0$$

Would measure the 'true' activation barrier. Can tell you are here if flow rate and pellet size do not affect rate. NOT ENOUGH to see an Arrhenius behavior, because other two ALSO are dependent on T!

Ways to help with different limiting regimes:

External (observed rate $\propto U^{1/2} d_p^{-3/2} T$)
Increase feed velocity
Cons: Higher ΔP, lower spacetime

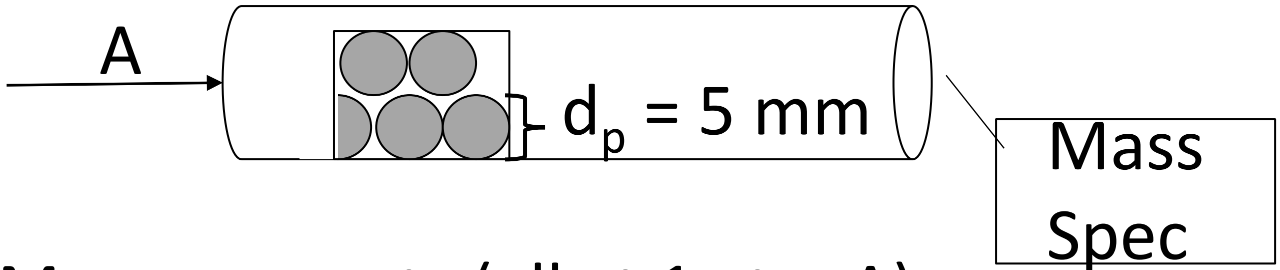
Internal (observed rate $\propto U^{0} d_p^{-1} e^{-1/T}$)
Decrease particle (pellet) size
Cons: Higher ΔP

Surface reaction (observed rate $\propto U^{0} d_p^{0} e^{-1/T}$)
Increase T
Cons: Safety, reduced selectivity

Discuss with your neighbors:

$A \rightarrow B$, 1st order

$\Delta P = \Delta T = 0$



Measurements (all at 1 atm A):

v_0 = 2.5 mL A/min, X ≈ 0.02 (2%)

v_0 = 5 mL A/min, X ≈ 0.01 (1%)

v_0 = 10 mL A /min, X ≈ 0.005 (0.5%)

$$F_{A0}\frac{dX}{dV} = v_0 C_{A0}\frac{dX}{dV} = -r_A$$

$$v_0 C_{A0}\frac{\Delta X}{\Delta V} = -r_A$$

Which of the following cannot be the limiting regime?

Reaction rate is independent of fluid velocity, noting the conversion is not the rate!

$$v_0 = UA_{CS}$$

$v_0 X$ is constant with U or v_0

A) External mass transport

B) Internal mass transport

C) Internal + surface reaction

D) Surface reaction

For a porous pellet:

The flux to the outside of the pellet is equal to the rate of reaction inside and on pellet (ignoring surface of pellet for reaction here compared to larger inner area).

$$W_A a_c = -r_A$$

a_c is the external MT area / unit reactor volume. Units mol/m^{2}s*m^2/m^3 = mol/m^{3}s

$$W_A a_c = -r_A''[S\rho_c(1-\phi_b) + \cancel{a_c}]$$
$$W_A a_c = -\eta r_A''(C_{As})[S\rho_c(1-\phi_b)]$$

r_A'' is the rate in mol/s per surface area of catalyst
ϕ_b is porosity of the catalyst bed
S is the area per mass of catalyst pellet
ρ_c is density of catalyst

S = 500-700 m^2 /g for zeolite, 500-2500 m^2/g activated carbon, 5 mm diameter sphere is 0.0006 m^2/g assuming density = 1 g/mL (so for many porous pellets there is much more area of the catalyst inside the pellet than on the outer surface area!)

$$W_A a_c = -\eta r_A''(C_{As})[S\rho_c(1-\phi_b)]$$

For first order reaction: $r_A''(C_A) = -kC_A$

$$k_c[C_{Ab} - C_{As}]\, a_c = \eta k C_{As}[S\rho_c(1-\phi_b)]$$

$$\frac{k_c[C_{Ab}]a_c}{\eta k S\rho_c(1-\phi_b) + k_c a_c} = C_{As}$$

$$r_A'' = -\eta k C_{As}$$

Observed! That is, what goes into a reactor design equation

Reaction rates with mass transport considerations

$$-r_A'' = \underbrace{\boxed{\frac{\eta k_c a_c}{kS\rho_c(1-\phi_b)\eta + k_c a_c}}}_{\Omega} kC_{Ab}$$

Ω is the external +internal (total) effectiveness factor

$$r_A = r_A'' S\rho_c(1-\phi_b)$$

$$Sh \sim Re^{1/2} Sc^{1/3}$$

$$\frac{k_c d_p}{\mathfrak{D}_{AB}} \propto \left(\frac{\rho u}{\mu}\right)^{1/2} (d_p)^{1/2} (\nu)^{1/3} (\mathfrak{D}_{AB})^{-1/3}$$

-1/2

+2/3

I would not recommend looking beyond this unless you are interested in deriving the internal effectiveness factor

Balance:

In - Out + Generation-Consumed = Accumulation

Convection term, diffusion term, reaction term, accumulation

$$-\nabla \cdot (C_i u) - \nabla \cdot (J) + r_i = \frac{dC_i}{dt}$$

u is fluid velocity, C_i is concentration, *J* is flux

Fick's Law:

$$\mathfrak{D} \nabla C_i = -J$$

Combine mass balance with Fick's:

$$-\nabla \cdot (C_i u) + \mathfrak{D} \nabla^2 C_i + r_i = \frac{dC_i}{dt}$$

$$\nabla \cdot (C_i u) = C_i \nabla \cdot (u) + u \nabla \cdot (C_i)$$

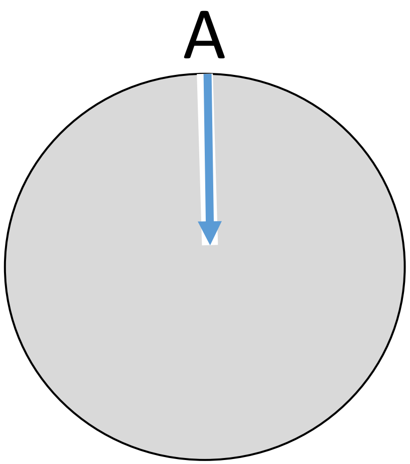
Continuity equation says divergence of flow velocity is zero if density is unchanging with time. For incompressible flow (density does not change with time): $\nabla \cdot (u) = 0$, so

$$-u \nabla \cdot (C_i) + \mathfrak{D} \nabla^2 C_i + r_i = \frac{dC_i}{dt}$$

Example in z-direction using Cartesian coordinates:

$$-u \frac{dC_i}{dz} + \mathfrak{D} \frac{d^2 C_i}{dz^2} + r_i = \frac{dC_i}{dt}$$

Internal mass transport: Diffusion into pore



Want to determine the concentration profile in the sphere:

$C_A(r)$

$C_A(R)=C_{A,s}$ (surface concentration)

A → B, first-order

$$\mathfrak{D}_{Eff}\nabla^2 C_A - u\nabla\cdot(C_A) + r_A = \frac{dC_A}{dt}$$

Assume steady state, no flow (no convection).

$$\mathfrak{D}_{Eff}\nabla^2 C_A + r_A = 0$$

Use only r-part:

$$\mathfrak{D}_{Eff}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dC_A}{dr}\right) - kC_A = 0$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dC_A}{dr}\right) - \overbrace{\frac{k}{\mathfrak{D}_{Eff}}}^{a^2}C_A = 0$$

$$\frac{1}{r^2}[2rC_A' + r^2C_A''] - a^2C_A = 0$$

$$C_A'' + \frac{2}{r}C_A' - a^2C_A = 0$$

To solve this start with assuming:

$$C_A(r) = \frac{U(r)}{r}$$

$$C_A'(r) = -\frac{U}{r^2} + \frac{U'}{r}$$

$$C_A''(r) = 2\frac{U}{r^3} - \frac{U'}{r^2} - \frac{U'}{r^2} + \frac{U''}{r} = \frac{2U}{r^3} - \frac{2U'}{r^2} + \frac{U''}{r}$$

Try out solutions by substituting into pore diffusion equation:

$$\frac{2U}{r^3} - \frac{2U'}{r^2} + \frac{U''}{r} + \frac{2}{r}\left(-\frac{U}{r^2} + \frac{U'}{r}\right) - a^2\frac{U}{r} = 0$$

$$\frac{U''}{r} - a^2\frac{U}{r} = 0$$

$$U'' - a^2 U = 0$$

One solution for U is:

$$U = A\exp(br)$$

Plug in solution:

$$Ab^2\exp(br) - a^2A\exp(br) = 0$$

$$b^2 - a^2 = 0$$

$$b = \pm a$$

$$\sinh ar = \frac{e^{ar} - e^{-ar}}{2} \qquad \cosh ar = \frac{e^{ar} + e^{-ar}}{2}$$

$$U(r) = A\sinh ar + B\cosh ar$$

Conditions $\quad C_A(R) = C_{A,s} \Rightarrow \frac{U(R)}{R} = C_{A,s}$

$$C_A(0) = finite \Rightarrow \lim_{r\to 0}\frac{U(r)}{r} = finite$$

$$\sinh ar = \frac{e^{ar} - e^{-ar}}{2} \xrightarrow{Taylor\ Series}$$

$$\frac{\left(1 + ar + \frac{(ar)^2}{2} + \cdots\right) - \left(1 + (-ar) + \frac{(-ar)^2}{2} + \cdots\right)}{2}$$

$$\sinh ar \xrightarrow[\lim_{r\to 0}]{Taylor\ Series} \frac{1 - 1 + ar - (-ar) + r^3 terms}{2} = \frac{2ar}{2}$$

$$= ar$$

$$\lim_{r\to 0} \frac{\sinh ar}{r} = a$$

$$\lim_{r\to 0} \frac{\cosh ar}{r} = \infty$$

$$U(r) = A \sinh ar + \cancel{B \cosh ar}$$

$$C_A(r) = \frac{A \sinh ar}{r}$$

Apply Boundary Conditions:

$$C_A(R) = \frac{A \sinh aR}{R} = C_{A,s}$$

$$A = \frac{C_{A,s} R}{\sinh aR}$$

$$C_A(r) = \frac{C_{A,s} R}{\sinh aR} \frac{\sinh ar}{r} = \frac{C_{A,s} R}{r} \frac{\sinh ar}{\sinh aR}$$

Recall:

$$\sqrt{\frac{k}{\mathfrak{D}_{Eff}}} = a$$

And now we define (for a sphere, first order reaction) the Thiele modulus:

$$\phi_1 = aR = \sqrt{\frac{k}{\mathfrak{D}_{Eff}}}R$$

Thiele modulus indicates whether reaction rate or diffusion rate is rate-limiting. The Thiele modulus expression will be different depending on the conditions (geometry) and also reaction order.

The effectiveness factor, or the ratio of the observed rate to the rate in absence of internal diffusional limitations is:

$$\eta \equiv \frac{r_{A,observed}}{r_A(C_{A,s})}$$

Effectiveness factor is related to the Thiele modulus:

$$C_A(r) = \frac{C_{A,s}R}{r}\frac{\sinh ar}{\sinh \underbrace{aR}_{\phi}}$$

So for first order reaction:

$$r_A = kC_A$$

$$\eta \equiv \frac{r_{A,observed}}{r_A(C_{A,s})}$$

$$\eta = \frac{\int_0^R r_{A,observed} r^2 dr}{\int_0^R r_A(C_{A,s}) r^2 dr}$$

In spherical coordinates, take the integral over the entire volume (radius) of pellet.

$$\eta = \frac{\int_0^R \cancel{-k} C_A r^2 dr}{\int_0^R \cancel{-k} C_{A,s} r^2 dr}$$

$$\eta = \frac{\int_0^R \frac{C_{A,s} R}{r} \frac{\sinh ar}{\sinh aR} r^2 dr}{\int_0^R C_{A,s} r^2 dr}$$

$$\eta = \frac{\frac{C_{A,s}R}{\sinh aR}\int_0^R \frac{1}{r}\frac{\sinh ar}{1} r^2 dr}{C_{A,s}\int_0^R r^2 dr}$$

$$\eta = \frac{\frac{C_{A,s}R}{\sinh aR}\int_0^R \sinh ar\, r dr}{C_{A,s}\, R^3/3}$$

In[8]:=
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Integrate[Sinh[a*r]*r, {r, 0, R}]
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Out[8]=

$$\frac{a\,R\,\text{Cosh}[a\,R] - \text{Sinh}[a\,R]}{a^2}$$

$$\eta = \frac{\frac{C_{A,s}R}{\sinh aR}\left[\frac{aR\cosh aR - \sinh aR}{a^2}\right]}{C_{A,s}\,{R^3}/_3}$$

$$\eta = \frac{3}{R^2}\left(\frac{aR\cosh aR - \sinh aR}{a^2\sinh aR}\right) = \frac{3}{a^2R^2}(aR\coth aR - 1)$$

Recall aR = ϕ_n (Thiele modulus) in this case.

$$\eta = \frac{3}{{\phi_1}^2}(\phi_1\coth\phi_1 - 1)$$

$$\coth\phi_1 \to 1 \text{ as } \phi_1 increases$$