ChE 344
Reaction Engineering and Design

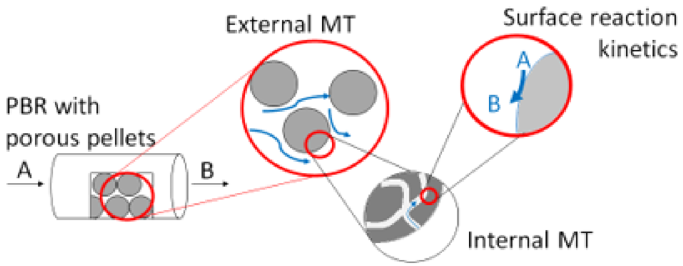
Lecture 25: Thurs, Apr 14, 2022

Catalysis-Internal and external mass transport

Reading for today’s Lecture: Chapter 14-15

Lecture 25: Catalysis-External and internal mass transport
Related Text: Chapter 14/15

In a catalytic gas-phase packed bed reactor, the observed reaction rate (what you would see using the reactor design equations to extract the reaction rate) can be controlled by different reaction regimes, including mass transport (MT). In order for the reaction A → B to occur, the A molecules must flow through the reactor, diffuse through the boundary layer around the catalyst pellet (external diffusion), diffuse through the pores of the porous pellet (internal diffusion), and then react on the surface (through a reaction mechanism, for example, the Langmuir-Hinshelwood mechanism).



By modeling the transport we can get the dependence of the reaction rate (r_A') on different parameters. How the reaction rate changes with these parameters depends on what limits the rate (i.e., which of these three steps is the slowest/limiting). When we say a certain step is limiting, we essentially mean the other steps are at quasi-equilibrium.

*One note, I called the pellet diameter D_p when we discussed the Ergun equation. This is the same as what I call d_p here, the capital vs. lower case is not meant to signify any physical difference.

Limitation	Fluid velocity	Pellet size	Temperature
External	$(\text{Velocity})^{1/2}$	$(d_p)^{-3/2}$	~Linear
Internal	Independent	d_p^{-1}	Exponential(-1/T)
Surface reaction	Independent	Independent	Exponential(-1/T)

There are some useful chemical engineering parameters that are typically used for understanding regimes. One very common one is the Thiele modulus. Here it is for a spherical porous pellet, with a first order reaction:

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

It is used to evaluate whether there are internal diffusion limitations. We also define an internal effectiveness factor:

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

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

At very large values of the Thiele modulus (where internal diffusion is very slow, and so limits the rate):

$$\eta = \frac{3}{\phi_1}$$

There is also a total effectiveness factor term that incorporates both external and internal mass transport, but we did not cover it yet.

On Tuesday we thought about cases where a certain ‘slow’ step controls the rate of reaction

For example, Langmuir-Hinshelwood w/ surface reaction RDS

$$A + * \rightleftharpoons A *$$

$$B + * \rightleftharpoons B *$$

$$A * + B * \rightarrow Product + 2 *$$

$$r_{LH,c} = k_{LH,c} \frac{K_A C_A K_B C_B}{(1 + K_A C_A + K_B C_B)^2}$$

Examples of L-H type behavior

- Ammonia synthesis
- CO oxidation
- Catalytic hydrogenation
- CH_4 reforming

Eley-Rideal:

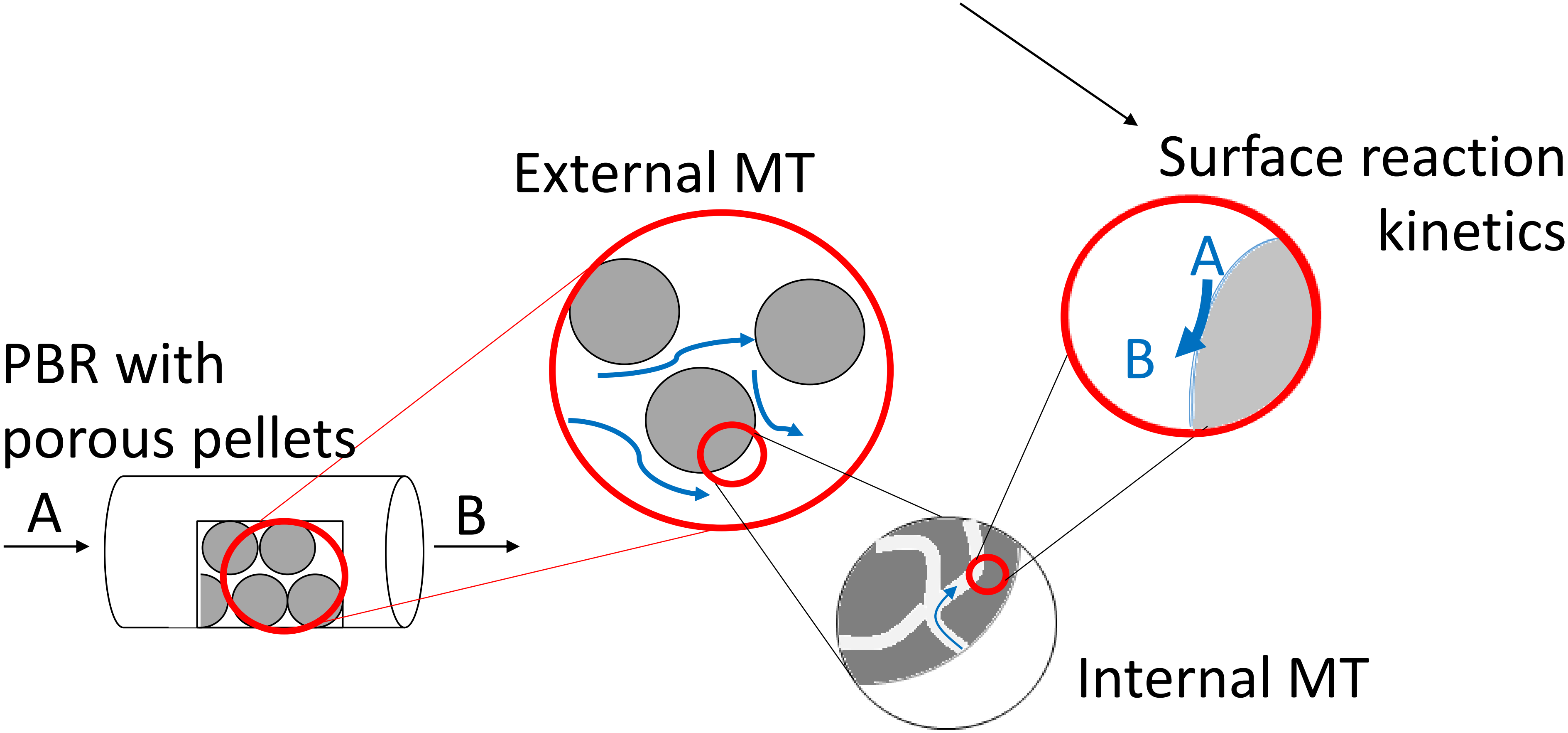
$$A + * \rightleftharpoons A *$$

$$A * + B \xrightarrow{k_1} C$$

$$r = k_1 \frac{K_A C_A}{1 + K_A C_A} C_B$$

Today we will discuss 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



- External mass transfer: bulk fluid to catalyst pellet surface
- Internal mass transfer: Pellet surface to pores inside catalyst pellet
- Reaction at surface: Rate controlled by rate law derived from reaction mechanism (intrinsic kinetics)

<u>What I want you to get out of Lecture today</u>:

- How could you determine from reaction measurements which of the three ‘regimes’ controls the rate? (possible qualitative final questions)
- General terms to be aware of (not on final)
- How to get out of different regimes (not on final)

What we will discuss today is heterogeneous catalysts in porous pellets, but conceptually the idea of mass transport affecting the rate can also apply to enzymes, reactions in solution, surface diffusion

Lets think back again to our resistor-in-series model, but now apply it to include mass transport as well.

External mass transfer

Internal mass transfer

Surface kinetics

A

B

$1/k_c$

$1/\mathfrak{D}_{eff}$

$1/k$

Reactant

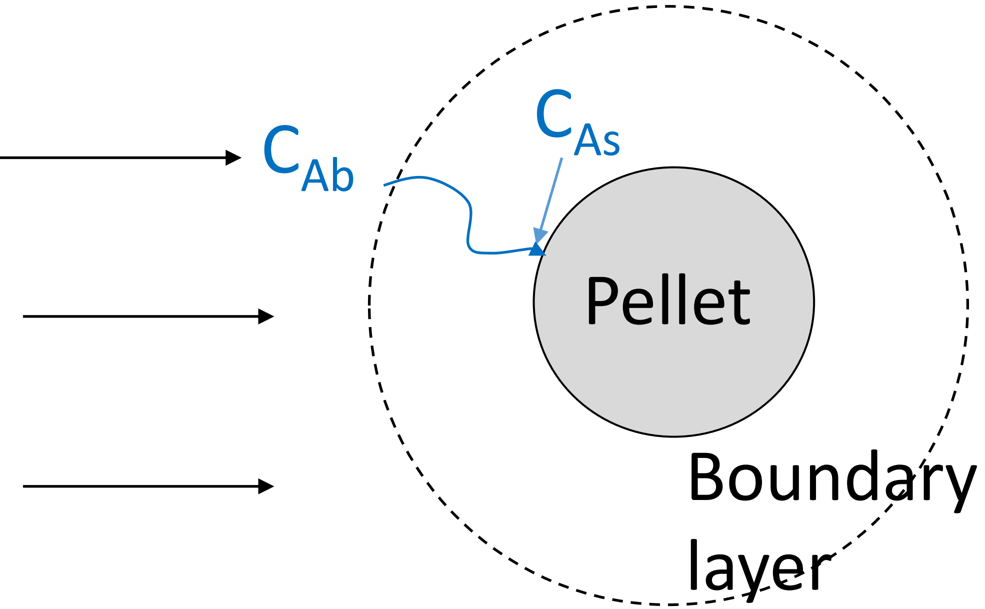
Product

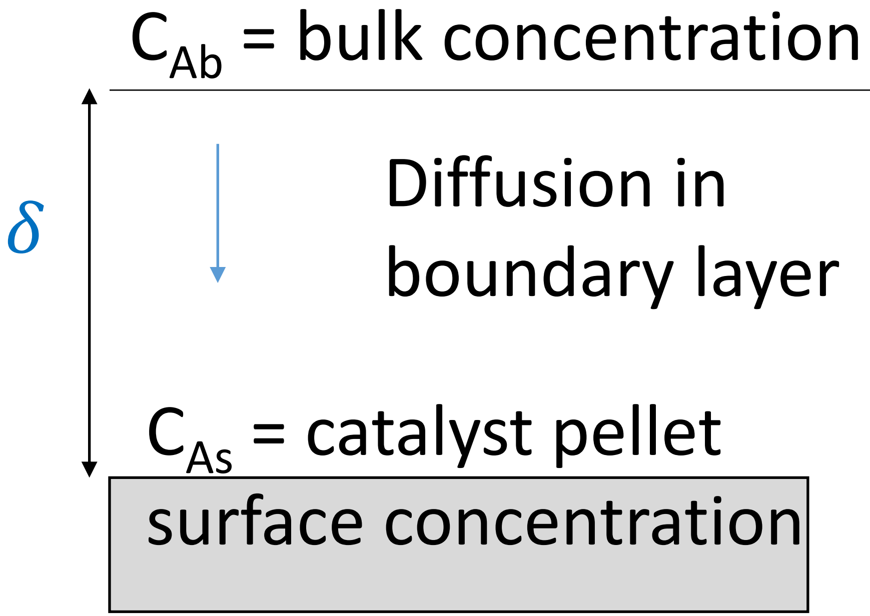
Any or all of these could be controlling the observed rate.

A handy reference for PBRs if first order reaction. The observed rate will have the following dependencies.

Limitation	Fluid velocity	Pellet Size	Temp.
External	$(\text{Velocity})^{1/2}$	$(d_p)^{-3/2 \text{ or } -1/2}$	~Linear
Internal	Independent	$(d_p)^{-1}$	Exp.
Surface rxn	Independent	Independent	Exp.

External mass transport (diffusion)





C_{Ab} = bulk concentration

Diffusion in boundary layer

C_{As} = catalyst pellet surface concentration

Flux from bulk to surface:

$$W_{Az} = \frac{\mathfrak{D}_{AB}}{\delta}[C_{Ab} - C_{As}] = k_c[C_{Ab} - C_{As}]$$

with the mass transfer coefficient k_c

Diffusion coefficient $\mathfrak{D}_{AB}$

Discuss with your neighbors:

You are flowing A through a packed bed and measuring the reaction rate of A→B. As you increase the flow velocity of A, the reaction rate goes up. What can you say about C_{Ab}, C_{As}? Hint: Look at our helpful table from slide 6.

If the flow velocity increases the reaction rate, you are external diff. limited, so there is a gradient across the boundary layer. Since A must be diffusing towards the surface…

A) $C_{Ab} \approx C_{As}$

[✓ B) $C_{Ab} > C_{As}$]

C) $C_{Ab} < C_{As}$

D) $\frac{C_{Ab}}{C_{As}} = 1$

If steady state, the flux to the outside of the pellet is equal to the rate of reaction on pellet surface (for now considering non-porous pellet).

$$W_A a_c = -r_A$$

$$\text{mol/m}^2\text{s}*\text{m}^2/\text{m}^3 \;[=]\; \text{mol/m}^3\text{s}$$

a_c is the external MT area / unit reactor volume [=] (m^2/m^3).

If we say the catalyst pellet is coated in catalyst, the catalyst area is the outer surface area of a sphere with diameter d_p.

$$W_A = -r_A'' = kC_{As}$$

NOT C_{Ab}

1st order kinetic rate constant (k_r in book)

r_A is the rate in mol/s per **volume** of reactor

r_A' is the rate in mol/s per **weight** of catalyst

r_A'' is the rate in mol/s per **surface area** of catalyst

Through a_c

Comparing external flux through boundary layer to surface reaction (here first order):

$$k_c[C_{Ab} - C_{As}] = kC_{As}$$

C_{Ab} is the measureable bulk concentration that we have normally been just calling C_A. For our mechanism analyses, we had been assuming $C_{As} = C_{Ab} = C_A$. But here not the case:

$$W_A = -r_A'' = \frac{k_c k}{k + k_c} C_A = k_{eff} C_A$$

$=C_{Ab}$ but NOT C_{As}

Mathematically and conceptually the same as two resistors in series with resistances $1/k$ and $1/k_c$

To obtain the mass transfer coefficient we can use the following dimensionless numbers

- Sherwood (convective mass transfer rate divided by the diffusive mass transfer rate)
- Reynolds (inertial forces to viscous)
- Schmidt number (momentum diffusivity to mass diffusivity)

$$Sh = \frac{k_c d_p}{\mathfrak{D}_{AB}} \qquad Re = \frac{\rho U d_p}{\mu} \qquad Sc = \frac{\nu}{\mathfrak{D}_{AB}}$$

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}$$

ν is kinematic viscosity

U is velocity

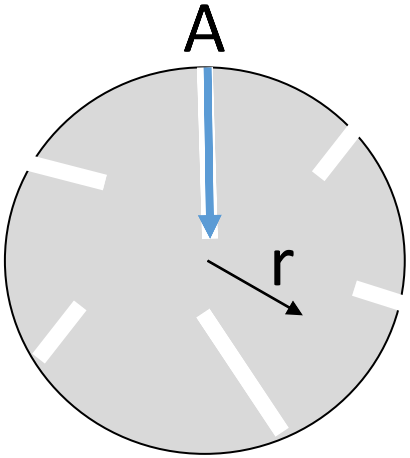
$$Sh \propto Re^{1/2} Sc^{1/3}$$

Chapman Enskog, $\mathfrak{D}_{AB} \propto T^{3/2}$

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

$$k_c \propto T \left(d_p\right)^{-1/2} (U)^{1/2}$$

Internal diffusion: Porous catalyst pellets are often used to increase the number of catalyst sites ($[*]_0$). So the catalyst coats the inside of the porous pellet.



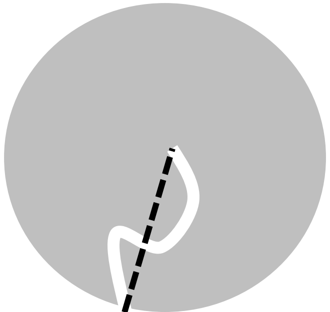
Want to determine the concentration profile in the sphere, $C_A(r)$, but diffusion in pore is different than in boundary layer

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

ϕ_p is the void fraction of the pores (<1).

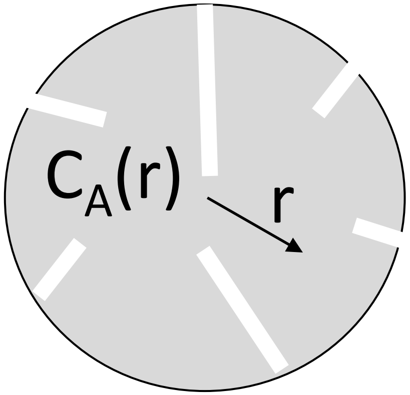
σ_c is the constrictivity, related to molecule size compared to pore diameter (<1). Depends on pore size distribution

$\tilde{\tau}$ is the tortuosity, actual distance traveled/shortest distance (>1).



Discuss with your neighbors:

For the porous catalyst pellet, if the pellet diameter is 2R, what can you say about $C_A(r=R)$ and $C_A(r=0.5R)$ if your reaction is $A \rightarrow B$?



[✓ A) $C_A(r=R) = C_{As} > C_A(r=0.5R)$]

B) $C_A(r=R) = C_{Ab} > C_A(r=0.5R)$

C) $C_A(r=R) = C_{As} < C_A(r=0.5R)$

D) $C_A(r=R) = C_{As} = 2C_A(r=0.5R)$

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

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

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.

Large Thiele modulus means the reaction is internal diffusion limited (rate constant > diffusivity coefficient, deep pores).

- Uniform catalyst sites
- Uniform distribution of sites within catalyst pores
- Uniform $\mathfrak{D}_{Eff}$
- Isothermal

The (internal) 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.

For first order reaction:

$$-r_A = kC_A$$

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

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

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

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(* Plotting η vs. Thiele modulus ϕ *)

In[3]:= η[ϕ_] := 3/ϕ^2 * (ϕ * Coth[ϕ] - 1)

In[4]:= LogLogPlot[η[ϕ], {ϕ, 0, 30}, Frame → True, FrameLabel → {"ϕ", "η"},
         LabelStyle → {Large, Black}, PlotStyle → Red]

Out[4]=
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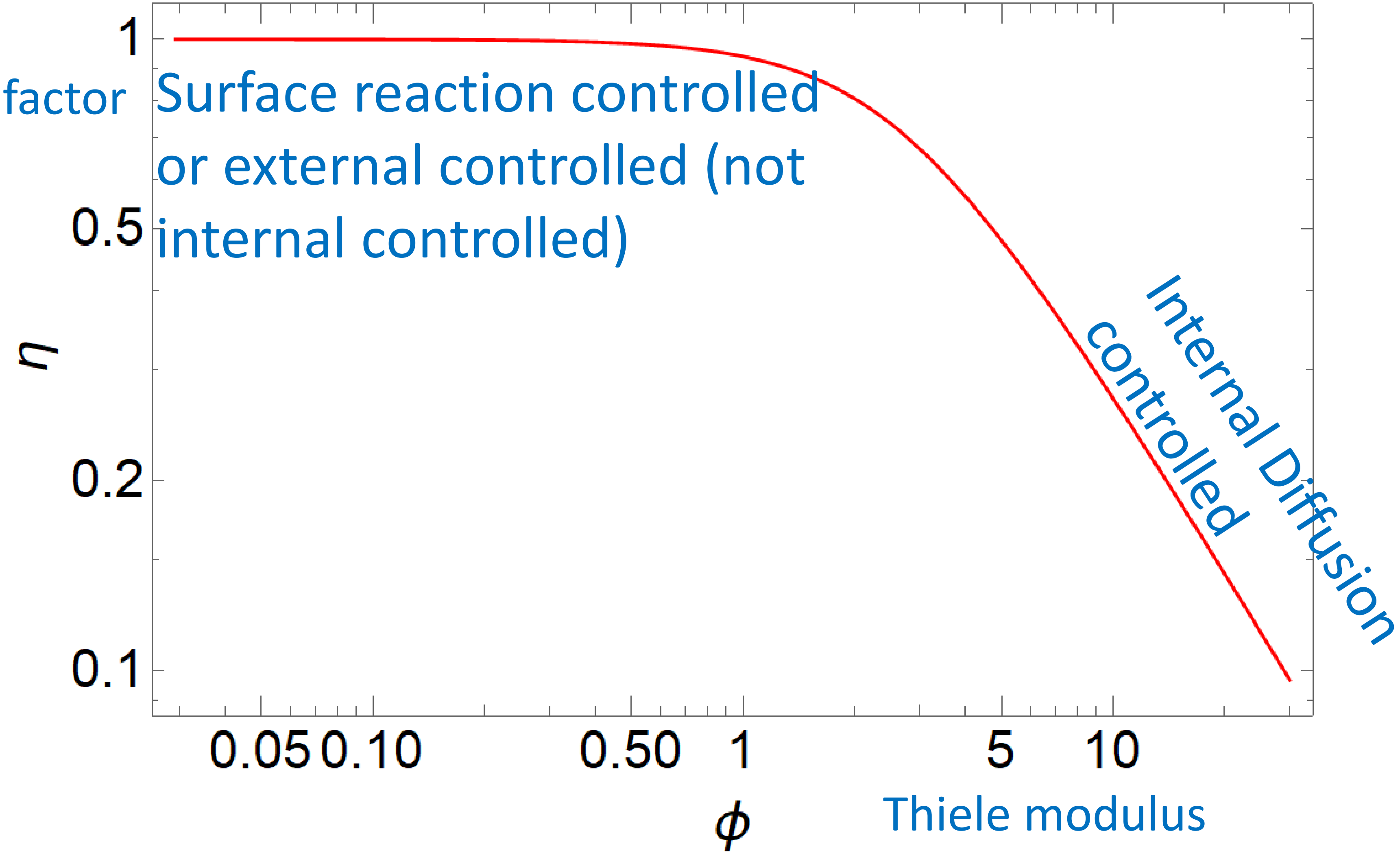


Eff. factor

Surface reaction controlled or external controlled (not internal controlled)

Internal Diffusion controlled

Thiele modulus

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

$$-r_A'' \propto \left(d_p\right)^{-1/2}$$

a_c =Surface area/Volume $\propto \left(d_p\right)^{-1}$

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

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

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

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

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

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 $\propto U^0 d_p^0 e^{-1/T}$)

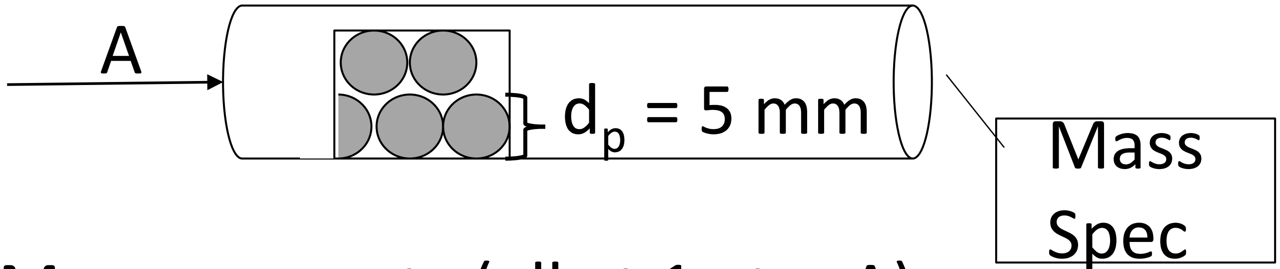
Increase T

Cons: Safety, reduced selectivity

Discuss with your neighbors:

A → B, 1^{st} order

$\Delta P = \Delta T = 0$



Measurements (all at 1 atm A):

$v_0 = 2.5$ mL A/min, $X \approx 0.02$ (2%)

$v_0 = 5$ mL A/min, $X \approx 0.01$ (1%)

$v_0 = 10$ mL A /min, $X \approx 0.005$ (0.5%)

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

Which of the following <u>cannot</u> 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