The background features a large, stylized blue and grey buffalo mascot. The buffalo is facing forward with its mouth open, showing its teeth. Below the buffalo's head, the word "BUFFALO" is written in a large, bold, white, italicized font with a grey outline. The entire graphic is centered on the page.

A First Course on Kinetics and Reaction Engineering

Class 40 on Unit 37

Where We're Going

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
- **Part III - Chemical Reaction Engineering**
 - ▶ A. Ideal Reactors
 - ▶ B. Perfectly Mixed Batch Reactors
 - ▶ C. Continuous Flow Stirred Tank Reactors
 - ▶ D. Plug Flow Reactors
 - ▶ E. Matching Reactors to Reactions
- **Part IV - Non-Ideal Reactions and Reactors**
 - ▶ **A. Alternatives to the Ideal Reactor Models**
 - 33. Axial Dispersion Model
 - 34. 2-D and 3-D Tubular Reactor Models
 - 35. Zoned Reactor Models
 - 36. Segregated Flow Model
 - **37. Overview of Multi-Phase Reactors**
 - ▶ **B. Coupled Chemical and Physical Kinetics**
 - **38. Heterogeneous Catalytic Reactions**
 - **39. Gas-Liquid Reactions**
 - **40. Gas-Solid Reactions**

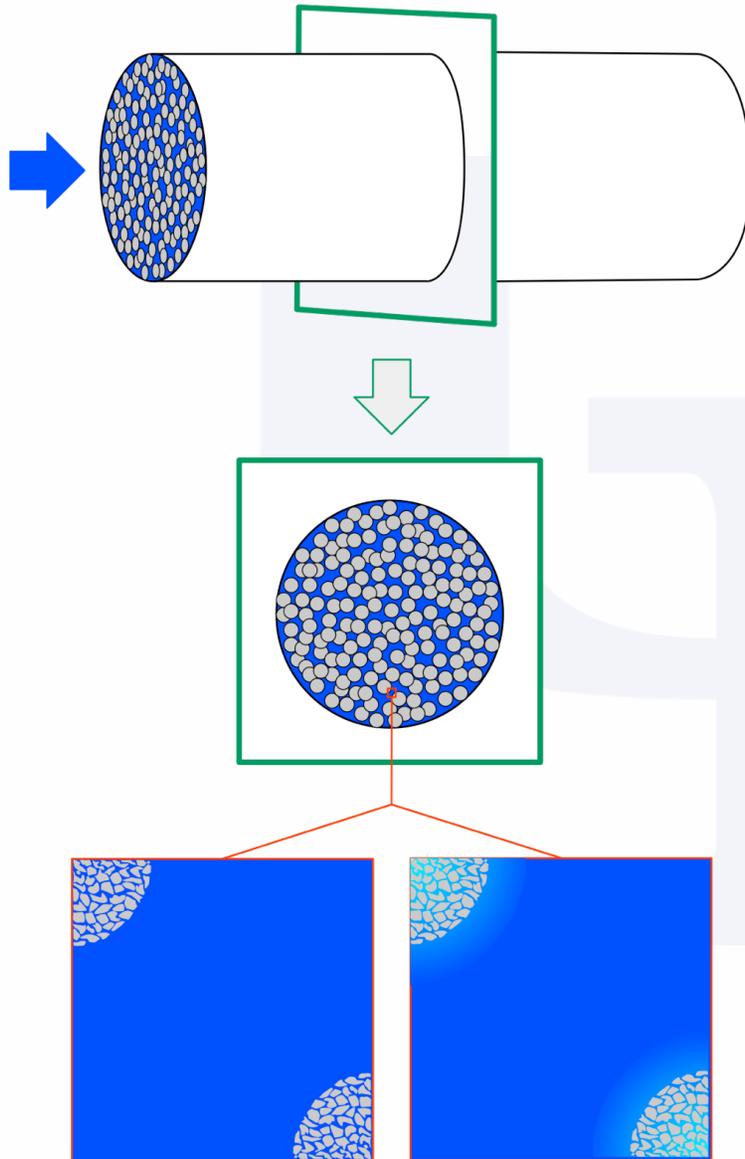


Reactors Other Than CSTRs and PFRs

- For gas-solid or solid-catalyzed gas phase reactions
 - ▶ fluidized bed reactors
 - ▶ riser reactors
- For solid-catalyzed gas-liquid reactions
 - ▶ trickle bed reactors
 - ▶ slurry reactors (also for solid-catalyzed liquid reactions)
- For gas-liquid reactions
 - ▶ spray tower reactors
 - ▶ bubble column reactors
- Laminar flow reactors
- Combined reaction and separation
 - ▶ Reactive distillation columns
 - ▶ Membrane reactors



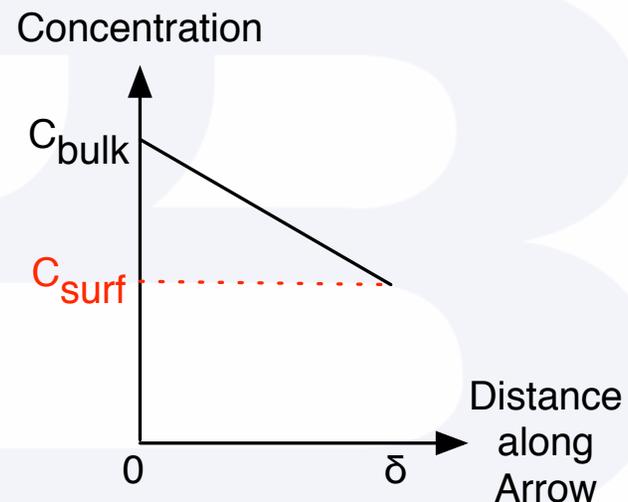
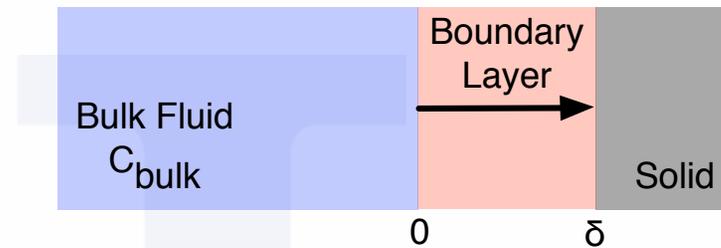
Testing Homogeneity Assumptions



- The PFR reactor model assumes that the fluid in any radial cross section is uniform in temperature and composition
 - ▶ When the reactor contains a packed bed of solid catalyst particles temperature and/or concentration gradients can exist
 - between the bulk fluid and the external surface of the particles
 - within the pores of the particles
- If kinetics data are generated using a packed bed, plug flow tubular reactor model tests must be performed to verify that such gradients do not exist
 - ▶ If they do, the ideal PFR model cannot be used to analyze the kinetics data
- There are two kinds of tests
 - ▶ Experimental
 - ▶ Computational

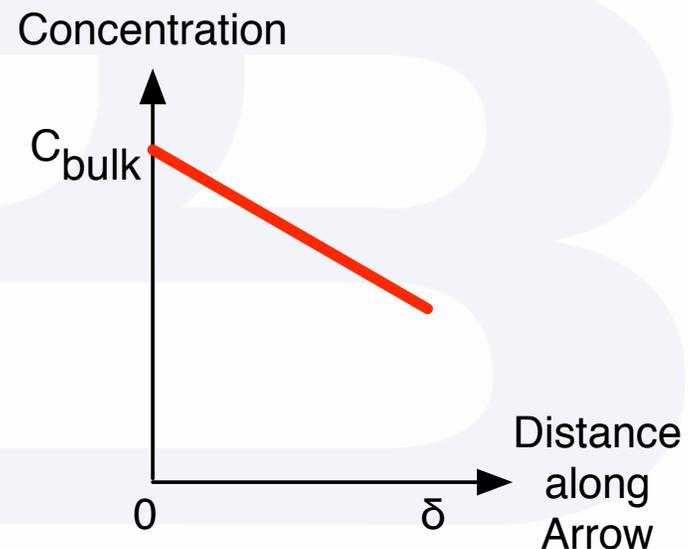
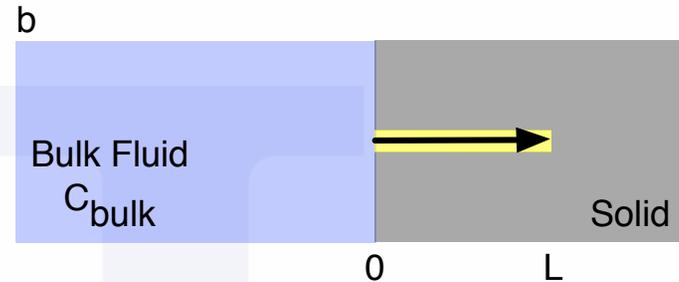
Boundary Layers

- When fluid flows past solid surfaces, such as catalyst particles, a boundary layer forms
- Reactants must diffuse through the boundary layer
 - ▶ This requires that a concentration gradient exists across the boundary layer
- Since the reaction requires the catalyst, no reaction takes place until the solid surface is reached
- The concentration at the solid surface is less than the C_{bulk}
 - ▶ The concentration is equal to C_{surf} where the reaction is taking place
 - ▶ The ideal PFR model assumes the concentration is equal to C_{bulk} , not C_{surf}
- Conditions must be chosen so the gradient is very small
 - ▶ Typical criterion is less than 5% difference between C_{bulk} and C_{surf}



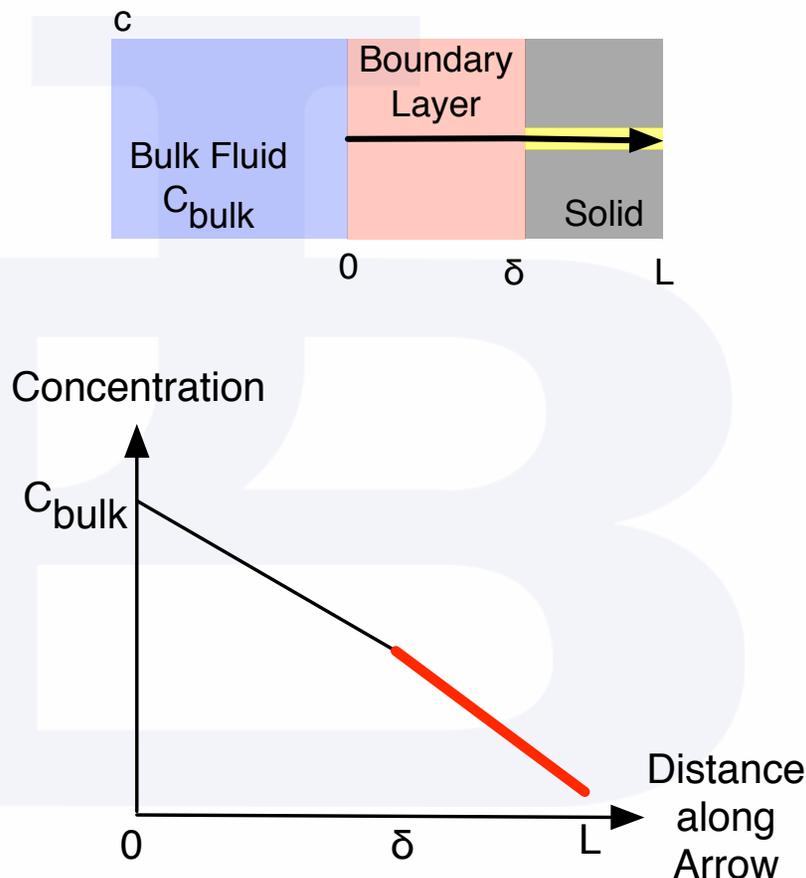
Catalyst Pores

- Many catalysts are porous, and most of the active sites are within the pores
- There isn't any convective flow within the pores
 - ▶ Reactants must diffuse along their length
 - ▶ This requires that a concentration gradient exists along the length of the pores
- Unlike diffusion through a boundary layer, reaction can take place at any point along the diffusion path
 - ▶ Ignoring any boundary layer effects the concentration where the reaction occurs can have a range of values less than or equal to C_{bulk}
- There is no single concentration at which reaction is occurring
 - ▶ In most of the pore, however, $C < C_{\text{bulk}}$
 - ▶ The PFR model assumes $C = C_{\text{bulk}}$ everywhere along the pore
- Conditions must be chosen so the gradient is small



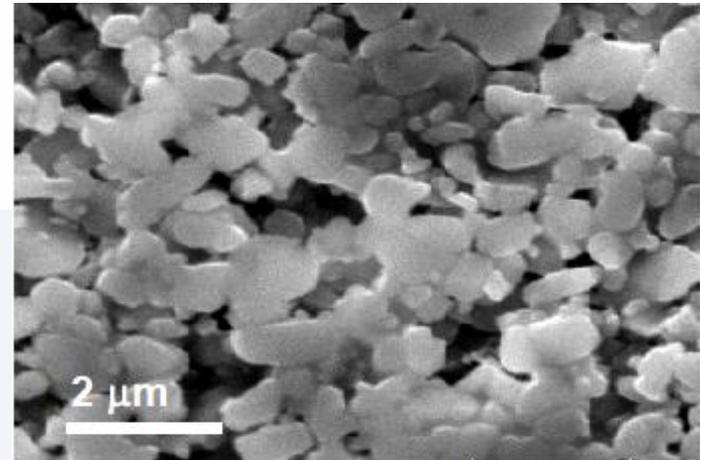
Internal and External Transport Limitations

- Real catalytic reactors can have gradients in both the boundary layer and the catalyst pores
- If these gradients are significant, they reduce, or limit, the rate of reaction compared to what it would be in the absence of the gradients
- Limitations caused by gradients between the bulk fluid and the catalyst surface are called external transport limitations
- Limitations caused by gradients along the pores of the catalyst are called internal transport limitations
- Separate tests are used for internal transport limitations and external transport limitations
 - ▶ In both cases, tests can be experimental and computational



Models for Porous Catalysts

- Catalyst pores are not straight tubes with circular cross-sections
 - ▶ Not only do they have varying cross-sectional shape and average dimensions
 - ▶ They also are connected randomly
- Generally the geometry of the pores is random and unknown
- Therefore, it is virtually impossible to formulate diffusion equations to exactly model the diffusion of species into the pores
- As a result, simplified models are used to represent the pore structure of the catalyst
 - ▶ The objective in formulating a model for the pore structure is to be able to model the diffusion and reaction within a catalyst particle, and to obtain results that agree reasonably with experiment
 - ▶ Different kinds of pore models have proven to be effective
- Here we will consider three kinds of pore models: (1) pseudo-continuum models, (2) defined structure pore models and (3) network models



**Al₂O₃-5wt%SiO₂-5wt% carbonate
1300 °C, 1 h, (62.4 %TD)**

PowerPoint from Composite Material Engineering Technology (COMET)
for Spacecraft Applications Workshop, October 16th-17th, 2007

Pseudo-Continuum Pore Models

- Simplest model is to completely ignore the pore structure

- ▶ Treat a catalyst particle as a single, homogeneous phase
- ▶ Reactants and products diffuse radially (for a spherical particle)
 - Obey Fick's law
 - Requires use of an effective diffusivity
 - Flux equation

- for slab geometry

$$N_A = -D_{eA} \frac{dC_A}{dz}$$

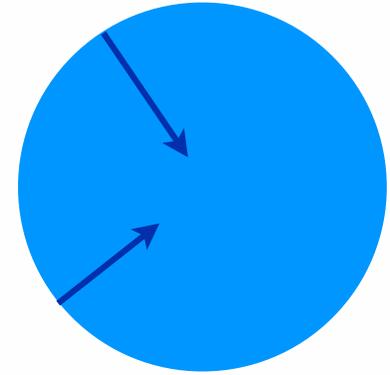
- for sphere geometry

$$N_A = -D_{eA} \left(\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right)$$

- Effective diffusivity is used to account for

- ▶ Diffusion
- ▶ Only a fraction of the cross sectional area (perpendicular to flux) is available for diffusion
 - Assume fraction available is equal to fraction of volume that is void, ϵ
- ▶ Real diffusion path is longer than straight line radial path
 - Real pores twist and turn, fold back in opposite direction
 - Called the tortuosity of the pore, τ

$$D_{eA} = \frac{\epsilon D_A}{\tau}$$



Reactions within Catalyst Pores

- Example Assuming Spherical Catalyst Particles

- ▶ Assume

- spherical catalyst particle
- isothermal catalyst particle
- diffusion can be represented using
 - Fick's first law (pseudo-homogeneous model)
 - Constant effective diffusion coefficient (not affected by composition)
- single irreversible reaction
 - single reactant, A
 - reaction rate is first order with respect to C_A
- steady state

- ▶ Consider a differentially thin spherical shell within the catalyst particle

- transport in and out by diffusion
- reaction within the shell

- ▶ Mass balance on A (assuming rate per catalyst mass)

$$D_{eA} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_A}{dr} \right) = \rho_s k C_A$$

- ▶ Boundary conditions

$$C_A(r = R_p) = C_A^s \quad \left. \frac{dC_A}{dr} \right|_{r=0} = 0$$



The Reaction Rate for the Catalyst Pellet

- ▶ Define the Thiele modulus as

$$- \phi = R_p \sqrt{\frac{k \rho_s}{D_{eA}}}$$

- ▶ Solve for $C_A(r)$

$$- \frac{C_A}{C_A^s} = \frac{\sinh\left(\phi \frac{r}{R_p}\right)}{\left(\frac{r}{R_p}\right) \sinh\phi}$$

- Two ways to calculate the overall rate of reaction for the whole pellet

- ▶ Knowing $C_A(r)$, integrate the rate over the entire volume of the pellet (i. e. as a fcn of r)
- ▶ Recognize that at steady state, the flux at $r = R_p$ must equal the rate of reaction

$$- \text{rate} = N_A = 4\pi R_p^2 D_{eA} \left(-\frac{dC_A}{dr} \right) \Big|_{r=R_p}$$

- substituting $C_A(r)$

$$\text{rate} = N_A = 4\pi\phi R_p D_{eA} C_A^s \left(\frac{1}{\tanh\phi} - \frac{1}{\phi} \right)$$



The Effectiveness Factor

- The concentration of A within the catalyst particle is less than the concentration of A in the bulk fluid outside the catalyst particle
 - ▶ As a consequence, the rate of reaction within the catalyst particle decreases steadily as one moves toward the center of the catalyst particle starting from its external surface
 - ▶ The relative rates of reaction versus diffusion dictate how much the rate changes as a function of distance into the particle
- The effectiveness factor is used to quantify this effect
 - ▶ It is defined as the rate that is actually observed divided by the rate that would have resulted if there was no radial concentration gradient within the particle (i. e. C_A is equal to C_A^s at all values of r)

$$\eta = \frac{N_A}{\frac{4}{3}\pi R_p^3 \rho_s k C_A^s} = \frac{3}{\phi} \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right)$$

- Limiting behavior
 - ▶ as $\phi \rightarrow 0$, $\eta \rightarrow 1$
 - ▶ as $\phi \rightarrow \infty$, $\eta \rightarrow 3/\phi$
- Generally one would prefer to operate a reactor at a Thiele modulus around 1 or below



The Effectiveness Factor Simplifies Reaction Engineering

- The use of the effectiveness factor greatly simplifies reactor design equations

- ▶ e. g. for a PFR,

$$\frac{d}{dz}(u_s C_A) = \eta r_A$$

- ▶ but analytical expression for η as a function of ϕ and the definition of ϕ only apply for the one case considered
 - spherical isothermal particle, Fick's law diffusion with constant effective diffusivity, single first-order reaction with single reactant
 - development of analytical expressions only works for relatively simple cases

- Numerical calculation of the effectiveness factor

- ▶ Retain all the previous assumptions except allow any mathematical form for the rate expression, $r_A(C_A)$
- ▶ Mass balance on A (assuming rate per catalyst mass)

$$D_{eA} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_A}{dr} \right) = \rho_s r_A(C_A) \quad \Rightarrow \quad \frac{d^2 C_A}{dr^2} + \frac{2}{r} \frac{dC_A}{dr} = \frac{\rho_s}{D_{eA}} r_A(C_A)$$

- ▶ Boundary conditions

$$C_A(r = R_p) = C_A^s \quad \left. \frac{dC_A}{dr} \right|_{r=0} = 0$$



Other Cases

- Geometries
 - ▶ infinite and semi-infinite slab and cylinder are common; changes mass balance and boundary conditions, but similar to sphere
- Reactions/rate expressions with multiple reactants and reversible reactions
 - ▶ Many approaches possible
 - ▶ One possibility: assume each species diffuses according to Fick's law with constant effective diffusion coefficients (not necessarily equal to each other) and each species unaffected by diffusion of the others
 - Total pressure will vary within the pellet
 - This possibility might be justified in the case of Knudsen diffusion in a binary system with equimolar counterdiffusion or if one species is present in very great excess
- Reactions with a change in the total number of moles
 - ▶ When effective diffusivities are constant (as above) there is a pressure gradient in the particle
 - ▶ Otherwise, there is a net molar flow in or out of the catalyst particle



Combined External and Internal Effects

- Illustrate for slab geometry, first order reaction

- ▶ Continuity equation and one boundary condition are the same

$$D_{eA} \frac{d^2 C_{sA}}{dy^2} - k \rho_s C_{sA} = 0 \qquad \left. \frac{dC_{sA}}{dy} \right|_{y=0} = 0$$

- ▶ But don't know external surface concentration (at $y = L$)
- ▶ Instead equate flux at external surface to flux through boundary layer

$$D_{eA} \left. \frac{dC_{sA}}{dy} \right|_{y=L} = k_g (C_A - C_{sA}^s)$$

- ▶ Now solution gives internal concentration in terms of bulk fluid concentration instead of external surface concentration

$$C_{sA}(y) = C_A \frac{\cosh\left(\frac{\phi y}{L}\right)}{\cosh(\phi) + \frac{D_{eA}\phi}{Lk_g} \sinh(\phi)}$$

- ▶ And then can define a global effectiveness factor (actual rate / rate if C_A at bulk fluid value at all points in pore)

$$\eta_G = \frac{\frac{\tanh(\phi)}{\phi}}{1 + \frac{D_{eA}\phi}{Lk_g} \tanh(\phi)}$$



Heterogeneous Catalysis Effectiveness Factors

- External concentration gradients (a at right) can be included in kinetics by using mass transfer coefficients

$$N_A = k_c (C_{A,bulk} - C_{A,surf})$$

- for first order reactions

$$-r_A = k' C_{A,bulk} \quad \frac{1}{k'} = \frac{1}{k} + \frac{1}{k_c}$$

- Internal gradients only (b) can be included in kinetics using an effectiveness factor

- for first order reactions & spherical catalyst

$$\phi = R_{part} \sqrt{\frac{k \rho_s}{D_{eA}}} \quad \eta = \frac{3}{\phi} \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right)$$

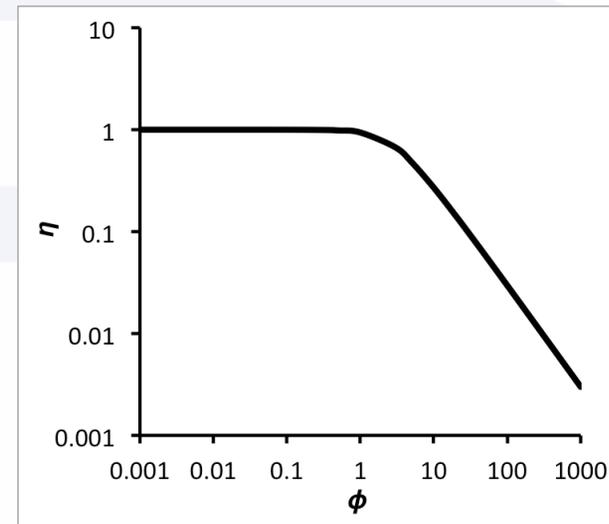
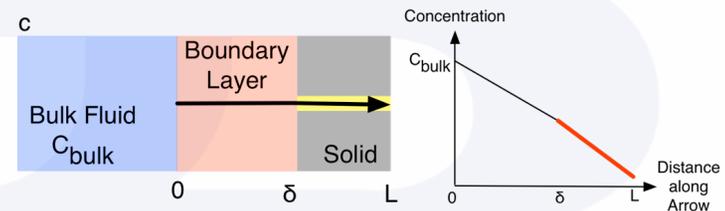
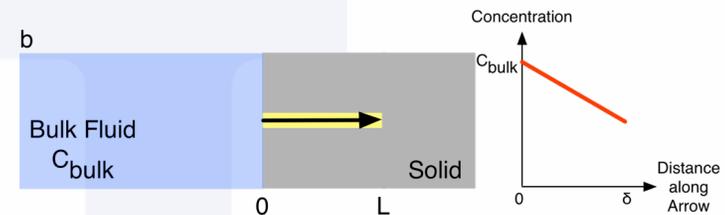
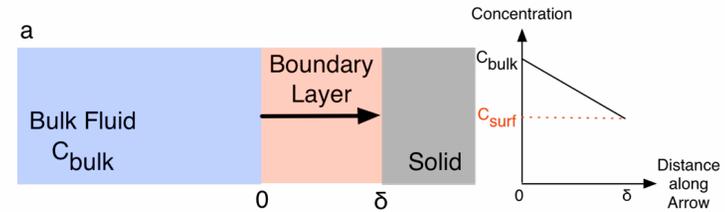
$$-r_A = \eta k C_{A,bulk}$$

- The effectiveness factor is the actual rate divided by the rate that would be observed in the absence of all gradients

- for first order kinetics in spherical particles it depends upon the Thiele modulus as shown at the right, bottom
- it is preferred to operate at a Thiele modulus less than ca. 1

- Combined internal and external gradients (c) can be included in kinetics using a global effectiveness factor

$$\eta_G = \frac{3}{\phi} \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right) \frac{\gamma \tanh \phi}{\phi + (\gamma - 1) \tanh \phi}; \quad \gamma = \frac{k_c R_{part}}{D_{eA}}$$



Questions?



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