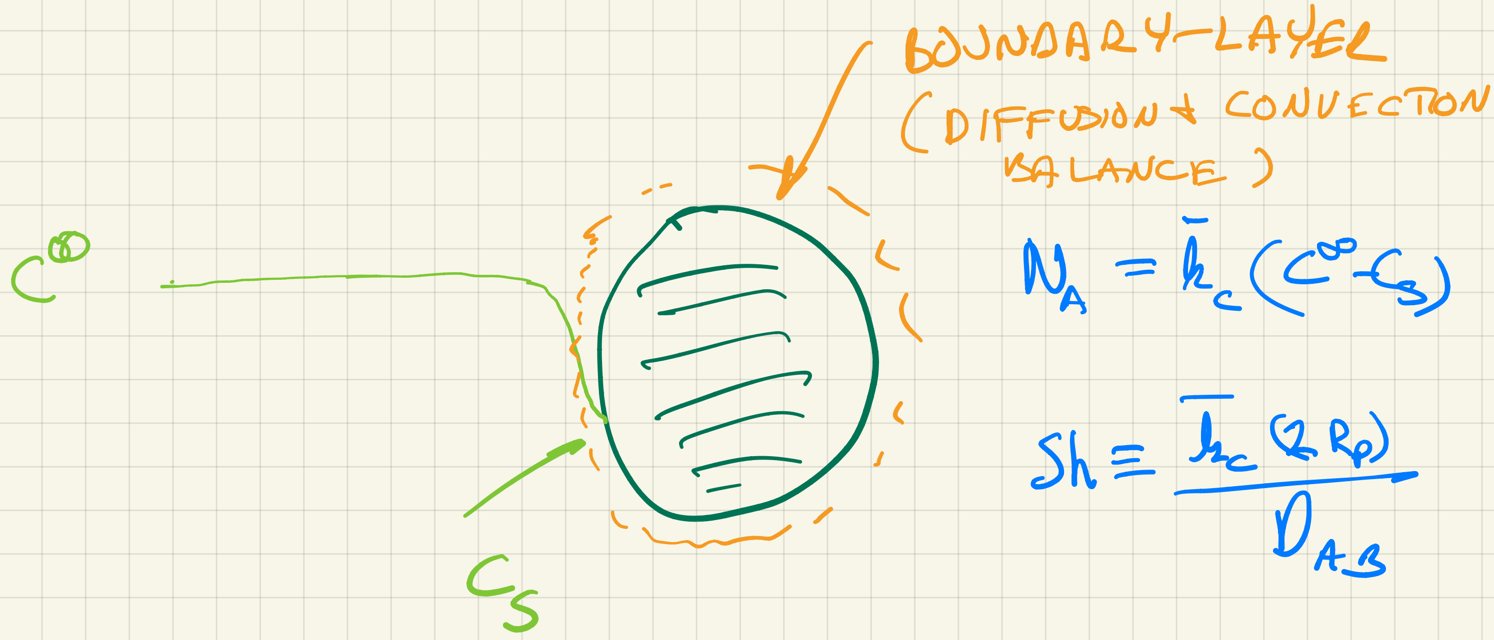
# CBE 40445

9/23/20

## MASS TRANSFER EFFECTS IN HETEROGENOUS CATALYSIS

MASS TRANSFER RESISTANCE EXTERNAL TO CATALYST




$$N_A = \bar{k}_c (C^{\infty} - C_S)$$

$$Sh = \frac{\bar{k}_c (2 R_p)}{D_{AB}}$$

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

NEEDS CONSIDERATION FOR CATALYSTS OF ALL SIZES...

FOR OUR REACTION EXAMPLE, AT STEDY STATE REACTION MATCH MATCHES FLUX:

$$r = N_A = k_s C_{As} = \bar{k}_c (C_A^{\infty} - C_{As})$$

$$C_{As} = \frac{\bar{k}_c C_A^{\infty}}{k_s + \bar{k}_c}$$

$$r = k_s C_{As} = \frac{k_s \bar{k}_c C_A^{\infty}}{k_s + \bar{k}_c}$$

$$= \frac{C_A^{\infty}}{\frac{1}{k_s} + \frac{1}{\bar{k}_c}}$$

SUM OF RESISTANCES

IF $k_s >> \bar{k}_c$

$$r = \bar{k}_c C_A^{\infty}$$

NO EFFECT OF REACTION

SO, AS EXPECTED WE WILL USE DIMENSIONLESS GROUPS...

$$Sh = \frac{\bar{k}_c (2R_p)}{D_{AB}}$$

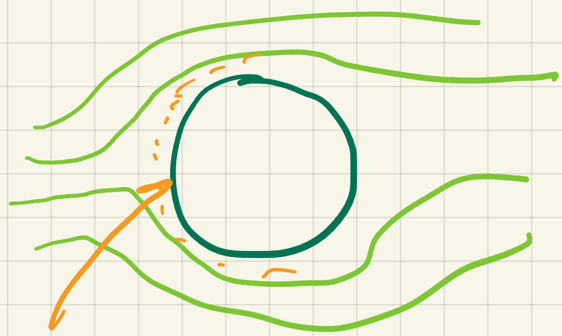
SHERWOOD NUMBER

ENHANCEMENT OF MASS TRANSFER BY FLUID FLOW

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

PURE DIFFUSION

INCREASE CAUSED BY FLUID FLOW



POWERS ON Re + Sc COME FROM SCALING ANALYSIS

IF $Sc \gg 1$,

BALANCE OF CONVECTION + DIFFUSION REQUIRES:

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

STAGNATION POINT HERE, BUT OTHERWISE, THINNING OF BOUNDARY-LAYER IN FRONT OF SPHERE

IT IS INSTRUCTIVE TO DETERMINE HOW MASS TRANSFER COEFFICIENT VARIES

$$\bar{k}_c \sim \frac{(D_{AB})^{2/3}\, u^{1/2}\, \rho^{1/6}}{(R_p)^{1/2}\,(\bar{\mu})^{1/6}}$$

"STIR FASTER" ~ BUT SMALL PARTICLES FOLLOW STREAMLINES

(NEED A DENSITY DIFFERENCE)

HEAT TRANSFER IS ANALOGOUS

"GREATEST" EQUATION FOR HEAT TRANSFER

$$q = h_t (T^{\infty} - T_s)$$

CONDUCTION

NATURAL CONVECTION

FORCED CONVECTION

REACTION RATE WITH $\Delta H_{RXN}$ INCLUDED

$\boxed{\text{ENDO THERMIC RXN}}$

$$r_{obs}(\Delta H_r) = h_t (T^{\infty} - T_s)$$

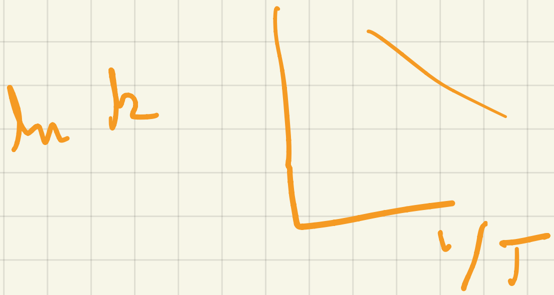
$$k_c (C_A^{\infty} - C_{AS}) \Delta H_r = h_t (T^{\infty} - T_b)$$

ENERGY BALANCE AT STEADY STATE.

# INTERNAL MASS TRANSFER RESISTANCE

ALWAYS NEEDS CONSIDERATION

AS T ↑ MORE IMPORTANT.




$E_a \sim 5$ kCAL/MOLE

↑

NOT REACTION-LIMITED

TO GET SURFACE AREAS OF $10^3\ m^2/g$

EXTENSIVE INTERNAL PORES!!

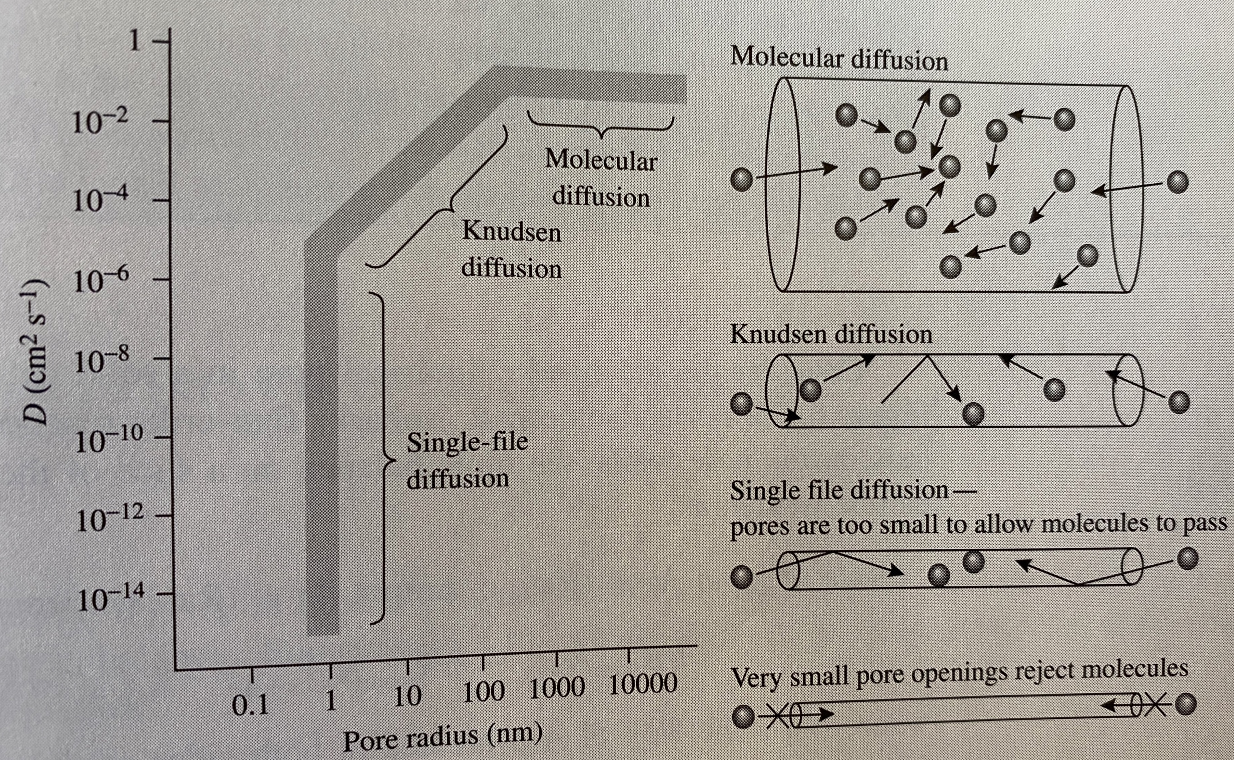
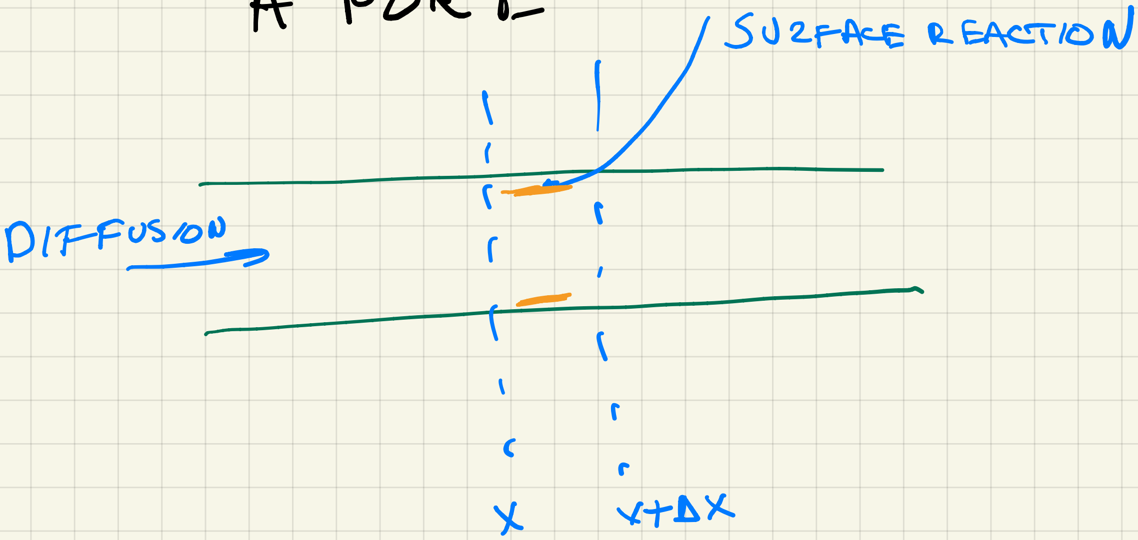



**Figure 6.3.1** | Influence of pore size on diffusivity of gas-phase molecules.

$$D_{KA} = (9.7 \times 10^3)\, R_{PORE} \left(\frac{T}{M_A}\right)^{1/2} \ cm^2/s$$

REACTION WILL BE OCCURING INSIDE CATALYST.

LET'S CONSIDER REACTION & DIFFUSION TOGETHER IN A PORE




MASS BALANCE

RATE OF ACCUMULATION = RATE AT WHICH A FLOWS INTO SLICE AT X=X − RATE AT WHICH A FLOWS OUT OF SLICE AT X=X+ΔX + RATE AT WHICH A IS CREATED BY REACTION

$$0 = N_A\Big|_x \pi R_p^2 - N_A\Big|_{x+\Delta x} \pi R_p^2 - k_s C_A \underbrace{(2\pi R_p)\Delta x}_{\text{SURFACE AREA INSIDE PORE}}$$

SURFACE RATE CONST

$\left(\frac{l}{TIME}\right)$

$$-\frac{dN_A}{dx} = \frac{2k_s}{R_{pore}} C_A$$

S-M EQ'S . . . IF WE USE A MODIFIED DIFFUSIVITY

$$\frac{1}{D_{TA}} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}}$$

$$\frac{dC_A}{dx} = \frac{-N_A}{\left(\frac{1}{D_{AB}} + \frac{1}{D_{KA}}\right)^{-1}}$$

OR

$$N_A = \left(-D_{TA} \frac{dC_A}{dx}\right)$$

IF NOT A FUNCTION OF POSITION

$$\frac{d}{dx}\left(D_{TA} \frac{dC_A}{dx}\right) = \frac{2k_s}{R_{pore}} C_A$$

$$\frac{d^2C_A}{dx^2} - \frac{2k_s}{D_{TA} R_{pore}} = 0$$

WE WOULD LIKE REACTION RATE BASED ON PORE VOLUME BEFORE WE INTEGRATE

(WILL ALLOW GENERALIZATION TO CATALYST PELLET)

$$k_s \, 2\pi R_p \, \Delta x = k \, \pi R_p^2 \, \Delta x$$

SURFACE RATE IN PORE AT SURFACE

SAME RATE BUT ASSUMING A VOLUMETRIC BASIS

$$k = \frac{2 k_s}{R_p}$$

THIS GIVES

$$\frac{d^2 C_A}{dx^2} - \frac{k}{D_{TA}} C_A = 0$$

THIS IS WORTH NONDIMENSIONALIZING

$$\chi = \frac{x}{L}, \qquad \Theta = \frac{C_A}{C_{As}}$$

$$x = L\chi$$

$$dx = L\,d\chi$$

$$dx^2 = L^2\,d\chi^2$$

$$C_A = C_{As}\Theta$$

$$d^2C_A = C_{As}\,d^2\Theta$$

$$\frac{C_{As}}{L^2}\frac{d^2\Theta}{d\chi^2} - \frac{k}{D_{TA}}C_{As}\Theta = 0$$

$$\frac{d^2\Theta}{d\chi^2} - \frac{kL^2}{D_{TA}}\Theta = 0$$

DEFINE

$$\phi^2 \equiv \frac{kL^2}{D_{TA}}$$

THIELE MODOLUS

**Standard Oil company [Indiana]** announced the retirement of **Dr. Ernest W. Thiele** after 35 years with the oil company's research and development department. Dr. Thiele, who has been assistant director and associate director of research, will be a visiting professor of chemical engineering at the University of Notre Dame in September.

Thiele

# Relation between Catalytic Activity and Size of Particle

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Standard Oil Company (Indiana), Whiting, Ind.

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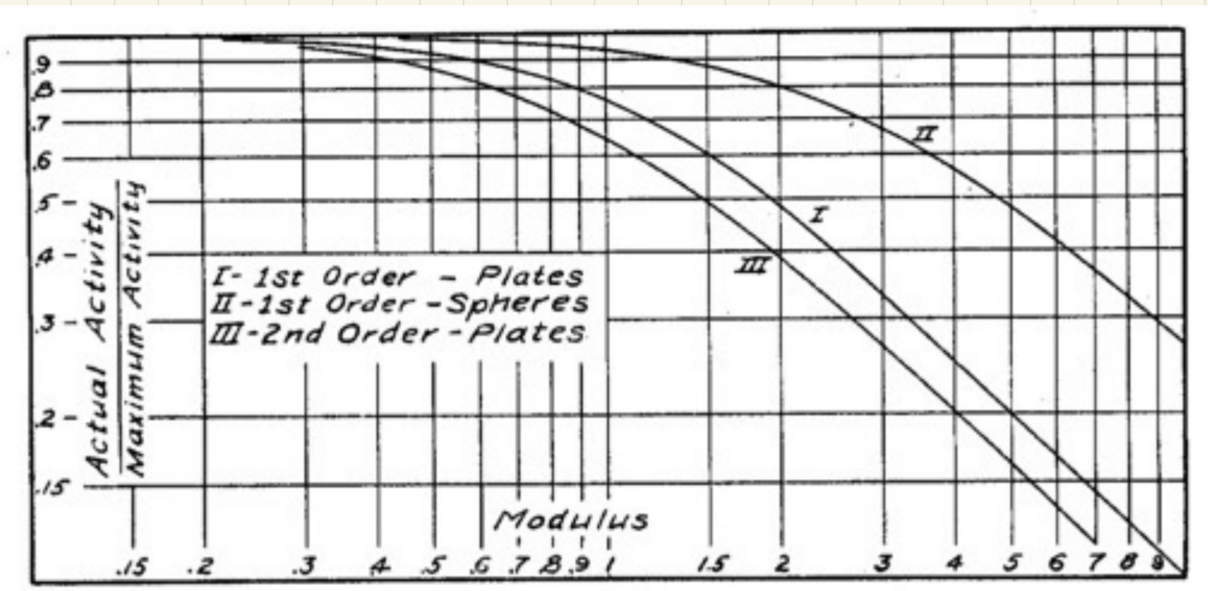
If the reaction is kinetically of the first order, the ratio in question depends on the dimensionless modulus, $x_s \sqrt{(c/kr)}$,

where $x_s$ = some linear dimension fixing the grain size (for example, the radius of the equivalent sphere)
$k$ = coefficient of diffusion of the reactants through the fluid
$r$ = average area of pore cross section per unit length of perimeter of pore cross section (hydraulic radius of pores)
$c$ = activity of the pore surface




Equating the two quantities:

$$d/dx\,(dy/dx) = cy/kr$$
$$d^2y/dx^2 = cy/kr = h^2y$$

At the center of the pore the flow by diffusion must be zero by symmetry. Therefore $dy/dx = 0$ when $x = 0$. Also $y = y_s$ when $x = x_s$. With these conditions the solution of the above differential equation is:

$$y = y_s \left(\frac{e^{hx} + e^{-hx}}{e^{hx_s} + e^{-hx_s}}\right) = y_s \frac{\cosh (hx)}{\cosh (hx_s)}$$

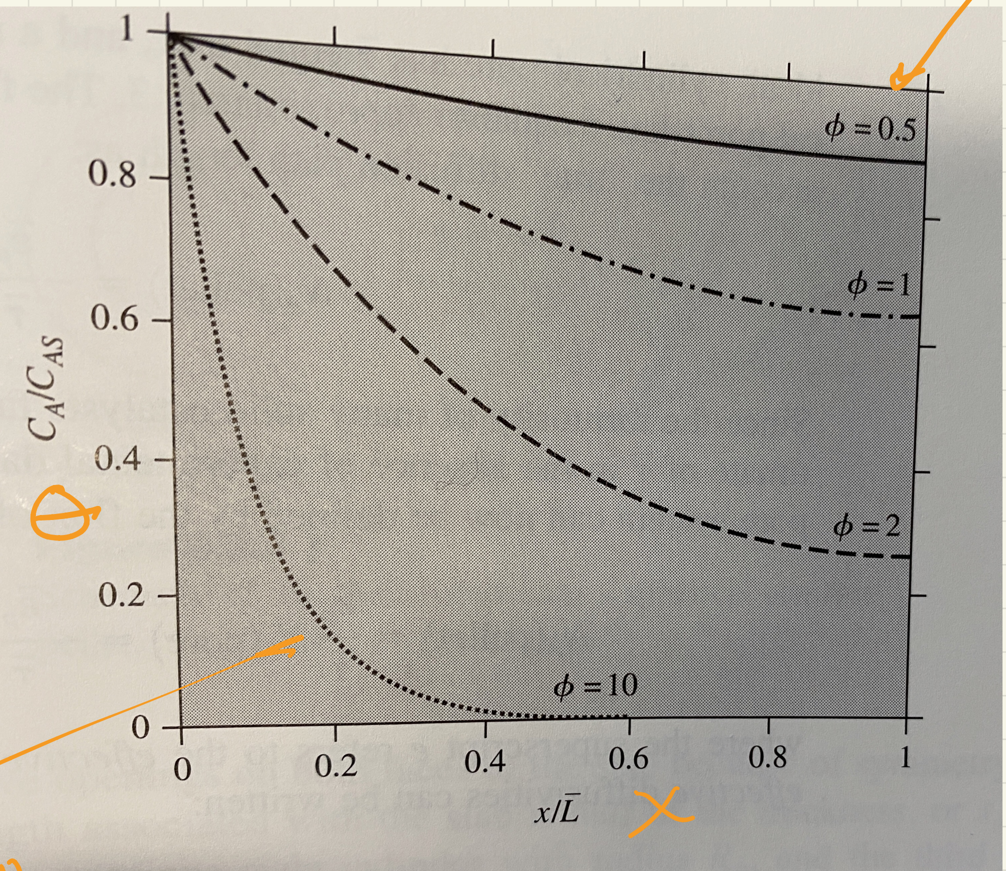
BACK TO $\dfrac{d^2\theta}{dx^2} - \phi^2 \theta = 0$

$\theta = 1 \ @ \ x = 0$

$\dfrac{d\theta}{dx} = 0 \ @ \ x = 1$

$$\theta = \frac{\cosh(\phi(1-x))}{\cosh \phi}$$

SLOW REACTION




FAST REACTION

**Figure 6.3.4 |**
Effect of Thiele modulus on the normalized concentration profiles in a catalyst pore with first-order surface reaction.

$$\phi^2 = \frac{kL^2}{D_{TA}} = \frac{k C_A}{\frac{D_{TA} C_A}{L^2}} \quad \frac{\text{REACTION RATE}}{\text{DIFFUSION RATE}}$$

WE CAN ADAPT THIS TO A POROUS SOLID PARTICLE

$\bar{\varepsilon}_p \Rightarrow$ FRACTION OF PARTICLE THAT IS POROUS

$\sim .3 - .7$

FRACTION AVAILABLE FOR DIFFUSION + REACTION

$\tilde{\tau} \rightarrow$ TORTUOSITY MEASURE OF INCREASED DISTANCE ALONG A PORE COMPARED TO "X" OR RADIUS

THIS DECREASES $D_{TA}$

$$D_{TA}^{e} = \frac{\bar{\varepsilon}_p}{\tilde{\tau}} D_{TA}$$

THE RESULT FOR A SINGLE PORE, WITH A SINGLE, STRAIGHT COORDINATE DIMENSION IS QUITE GENERAL.

THE ANALYSIS FOR A SPHERICAL PARTICLE HAS ALL OF THE SAME PHYSICS/CHEMISTRY AND IS ONLY SLIGHTLY DIFFERENT QUANTITATIVELY

EQUIMOLAR COUNTER-DIFFUSION IN A SPHERE

$$N_A = -D_{TA}^{e} \frac{dC_A}{d\bar{r}}$$

MASS BALANCE IN SPHERICAL COORDINATES

$$-\frac{d}{dr}\left(\bar{r}^2 N_A\right) - \bar{r}^2 k C_A = 0$$

$$\frac{1}{r^n}\frac{d(r^n N_A)}{dr} - kC_A = 0$$

$n=0$ SLAB (RECTANGULAR COORD)

$n=1$ CYLINDER (CYLINDICAL COORD)

$n=2$ SPHERE (SPHERICAL COORD)

FOR $n = 2$

$$\frac{d}{dr}\left(r^2\left(-D^e_{TA}\frac{dC_A}{dr}\right)\right) - r^2 kC_A = 0$$

$$D^e_{TA}\left[\frac{d^2C_A}{dr^2} + \frac{2}{r}\frac{dC_A}{dr}\right] - kC_A = 0$$

$$\psi \equiv \frac{C_A}{C_{AS}}, \qquad w = \frac{r}{R_p}$$

$$\phi = \sqrt{\frac{R_p^2 k}{D^e_{TA}}}$$

$\psi(1) = 1 \qquad w = 1$

$\frac{d\psi}{dw} = 0 \qquad w = 0$

$$\eta = \frac{\sinh(\phi w)}{w \sinh(\phi)}$$



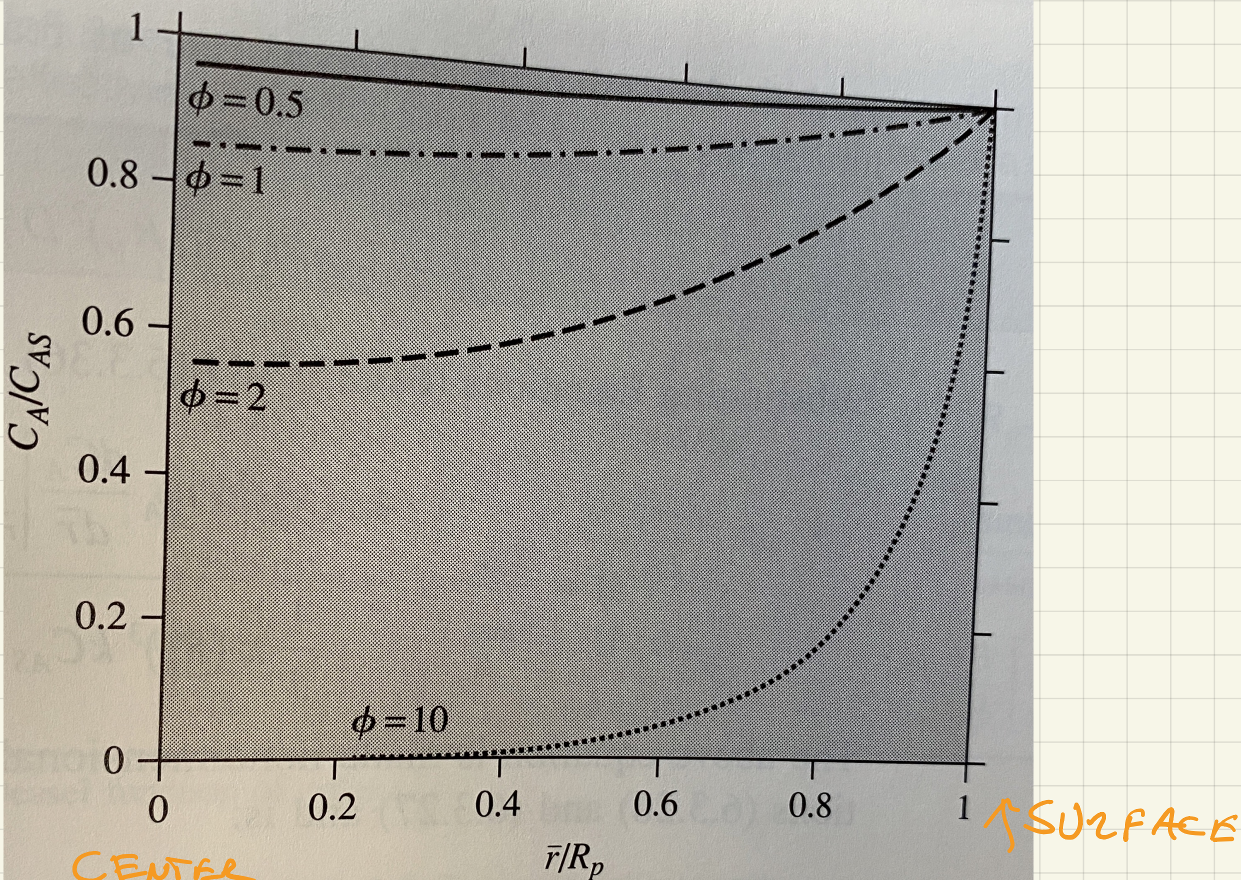



**Figure 6.3.7 |**
Effect of Thiele modulus on the normalized concentration profiles in a spherical catalyst particle with first-order reaction. The external surface of the particle is located at

TO QUANTIFY THE LIMITATION ON REACTION THAT DIFFUSION CAUSES (BECAUSE $C_A(r) < C_{AS}$)

WE DEFINE

EFFECTIVENESS FACTOR:

$$\eta \equiv \frac{r_{OBS}}{r_{MAX}} = \frac{\int_0^{V_p} r(C_A)\,dV}{V_p\, r(C_{AS})}$$

$$= \frac{\int_0^{R_p} r(C_A)\, 4\pi \bar{r}^2 d r}{V_p\, r(C_{AS})} = \frac{S_p \int r(C_A)\left(\frac{\bar{r}}{R_p}\right)^2 dr}{V_p\, r(C_{AS})}$$

$$r_{MAX} = \frac{4}{3}\pi R_p^3 C_{AS}$$

TO GET THE ACUAL RATE, THE EASIEST WAY TO GET IT IS TO CALCULATE THE FLUX OF A AT $\bar{r} = R_p$

$$r_{OBS} = 4\pi R_p^2 D_{TA}^e \underbrace{\left.\frac{dC_A}{d\bar{r}}\right|_{\bar{r}=R_p}}_{\text{SURFACE FLUX}}$$

$$\eta = \frac{3}{\phi^2} \left.\frac{d\psi}{d\omega}\right|_{\omega=1}$$

$$\eta = \frac{3}{\phi}\left[\frac{1}{\tanh\phi} - \frac{1}{\phi}\right]$$

illustrates the relationship between the effectiveness fact
lus for a spherical catalyst pellet.

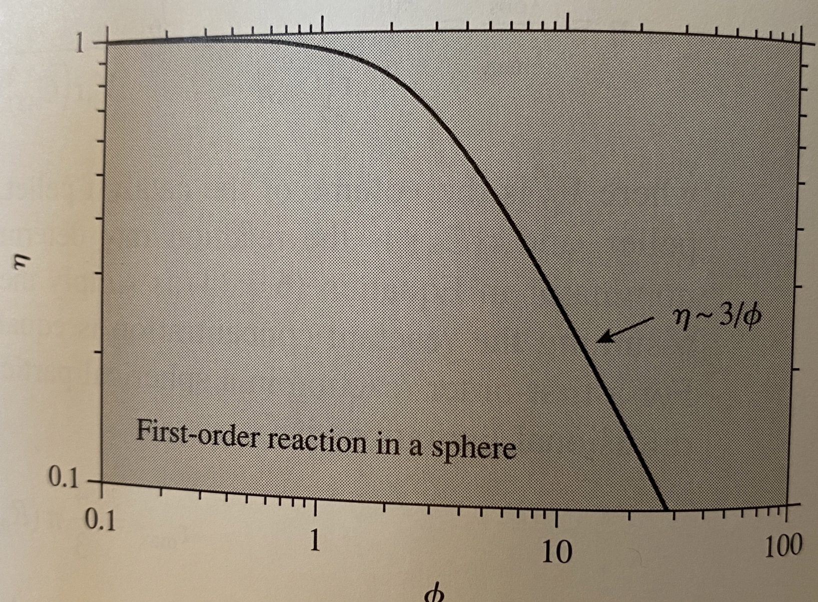



**Figure 6.3.8** |
Effectiveness factor for a first-order reaction in a sphere
as a function of the Thi

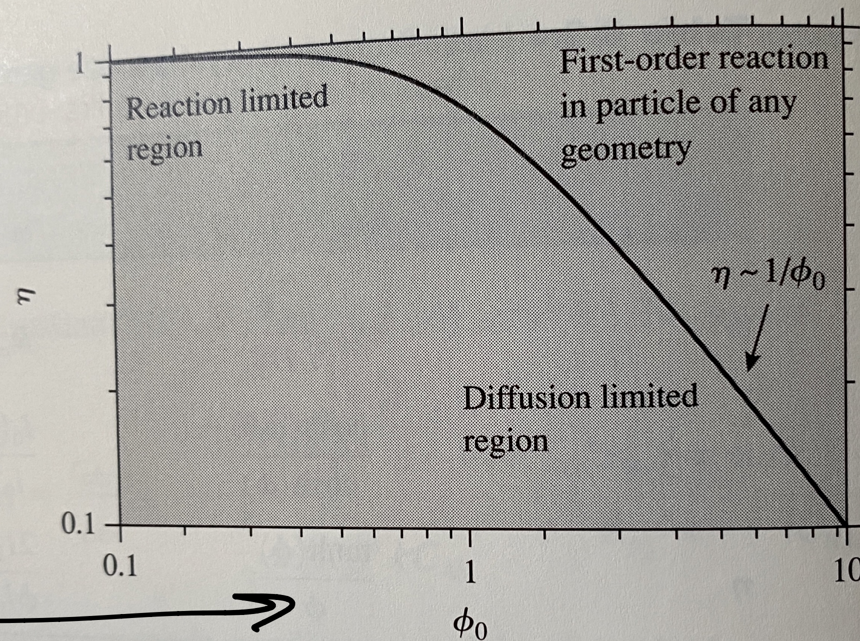
**Table 6.3.1** | Influence of catalyst particle geometry on concentration profile and effectiveness factor for a first-order, isothermal, isobaric reaction.

| | Slab ($\omega = x/x_p$) | Cylinder[a] ($\omega = \bar{r}/R_p$) | Sphere ($\omega = \bar{r}/R_p$) |
|---|---|---|---|
| $\phi$ | $x_p\sqrt{\dfrac{k}{D^e_{TA}}}$ | $R_p\sqrt{\dfrac{k}{D^e_{TA}}}$ | $R_p\sqrt{\dfrac{k}{D^e_{TA}}}$ |
| $\psi = C_A/C_{AS}$ | $\dfrac{\cosh(\phi\omega)}{\cosh(\phi)}$ | $\dfrac{I_0(\phi\omega)}{I_0(\phi)}$ | $\dfrac{\sinh(\phi\omega)}{\omega\sinh(\phi)}$ |
| $\eta$ | $\dfrac{\tanh(\phi)}{\phi}$ | $\dfrac{2I_1(\phi)}{\phi I_0(\phi)}$ | $\dfrac{3}{\phi}\left[\dfrac{1}{\tanh(\phi)} - \dfrac{1}{\phi}\right]$ |

[a] $I_i$ is a modified Bessel function of order $i$.

**Table 6.3.2** | Characteristic length parameters of common pellet shapes.

| | $L_p$ |
|---|---|
| Slab | Length of pore, $x_p$ |
| Cylinder | $R_p/2$ |
| Sphere | $R_p/3$ |




SMALLER PARTICLE: LESS DIFFUSION RESISTANCE

**Figure 6.3.9** |
Effectiveness factor $[\eta = \tanh(\phi_0)/\phi_0]$ for a first-order reaction in a catalyst as a function of the Thiele modulus with generalized length parameter.

o the above definitions the effecti... for any

THE TEXT DOES SOME
EXAMPLES USING THESE
RESULTS