

**TRANSPORT EFFECTS IN
HETEROGENEOUS CATALYTIC
SYSTEMS**

(CHE 512)

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GAS-SOLID AND LIQUID-SOLID SYSTEMS: A PRIMER

1. INTRODUCTION

In homogeneous systems reaction occurs in a single phase such as gas or liquid. The rate of reaction of say reactant A, which may be the result of a sequence of mechanistic elementary steps that all occur in the single phase present, then quantifies how many moles of A react per unit time and unit volume of the system as a function of the local composition (concentrations) and temperature. For example, for a reaction $A \rightarrow P$ that follows an n-th order irreversible reaction the rate of reaction of A is given by

$$(-R_A) = k_o e^{-E/RT} C_A^n \text{ (mol/m}^3\text{s)} \quad (1)$$

If we know that the order of reaction is 2 ($n = 2$) and that $k_o = 10^{16} \left(\left(\frac{\text{mol}}{\text{m}^3} \right)^{-1} \frac{1}{\text{s}} \right)$ and the activation energy is $E = 30,000 \text{ cal/mol}$, then if the local concentration is $C_A = 10 \text{ (mol/m}^3\text{)}$ and local temperature is $T = 350^\circ \text{ K (} 77^\circ \text{ C)}$ we know that the rate of reaction of A at such conditions is $-R_A = 10^{16} e^{-30,000/1.987 \times 350} \times 10^2 = 0.184 \text{ (mol/m}^3\text{s)}$.

In order to relate the rate of reaction to production rate we have to know how the local concentration and temperature vary through the reactor, i.e. what flow and mixing pattern we have in the reactor. Therefore, for an isothermal continuous flow stirred tank reactor, CSTR, operated at constant temperature of 350° K , feed concentration of $C_{A_o} = 100 \text{ (mol/m}^3\text{)}$ and at 90% conversion for a constant density system, the rate of reaction of A is $0.184 \text{ (mol/m}^2\text{s)}$, since C_A at 90% conversion is 10 mol/m^3 everywhere in the reactor. The reaction rate at the exit conditions is the same as the average rate in the whole reactor since the composition and temperature in the whole reactor is the same as at the exit conditions. In contrast, in a plug flow reactor, PFR, that operates with the same feed and at 90% exit conversion, even if we succeed to keep it isothermal at $T = 350^\circ \text{ C}$, the rate of reaction varies from the inlet to the exit since the concentration varies from inlet to exit. The rate at the inlet is $18.4 \text{ (mol/m}^3\text{s)}$ and $0.184 \text{ (mol/m}^3\text{s)}$ at the exit.

The average rate of reaction for the PFR can be readily obtained from the mass balance of A on the whole reactor, i.e.

(moles of A fed)-(moles of A removed unreacted)=(average reaction rate of A)× (reactor volume)

$$Q (C_{A_o} - C_A) = (-\bar{R}_A) V \quad (2)$$

However, from the differential mass balance on A the PFR design equation results in:

$$\tau = \frac{V}{Q} = \int_{C_A}^{C_{A0}} \frac{d C_A}{(-R_A)} \quad (3)$$

Substituting for volume from eq. (3) into eq. (2) and solving for the average rate yields

$$-\bar{R}_A = \frac{C_{A0} - C_A}{\int_{C_A}^{C_{A0}} \frac{d C_A}{-R_A}} \quad (4)$$

We now apply eq. (4) to our isothermal PFR for the rate expression of eq. (1) with $n = 2$ and with the feed at $C_{A0} = 100 \text{ (mol/m}^3\text{)}$ and exit conversion of 90% ($C_A = C_{A0} (1 - x_A) = 100 (1 - 0.9) = 10 \text{ (mol/m}^3\text{)}$).

The rate constant at 350° K is $1.84 \times 10^{-3} \left(\frac{\text{m}^3}{\text{mol s}} \right)$.

The average rate of reaction in such a PFR then is:

$$\left(-\bar{R}_A \right) = \frac{100 - 10}{\frac{1}{1.84 \times 10^{-3}} \int_{10}^{100} \frac{d C_A}{C_A^2}} = \frac{90 \times 1.84 \times 10^{-3}}{\frac{1}{10} - \frac{1}{100}} = 1.84 \text{ (mol/m}^3\text{s)} \quad (5)$$

Hence, as we well know, plug flow (PFR) is more efficient (higher average rate) than a CSTR for an n-th order reaction.

Now consider the situation when the reaction occurs on the surfaces of a solid phase (catalyst). In order to calculate properly the average reaction rates in such situations we must know, in addition to the reactor flow pattern, also the effect of transport on the concentrations and temperatures that the catalyst actually experiences locally!

2. OBJECTIVES

Present the methodology needed to evaluate reaction rates in solid catalyzed reaction systems where reactants and products are in either gas or liquid phase.

Specifically, show how to handle systems with nonporous catalysts and porous catalysts.

3. TRANSPORT EFFECTS FOR NONPOROUS CATALYSTS

The catalyst is now on a solid surface which is impenetrable to the fluid that surrounds it. This surface may be that of a plane, channel wall, sphere, or pellet of any form and shape. The fluid containing the reactants and products flows past that surface which is catalytically active. In order for reaction to occur, reactant molecules must be transported to the solid surface and product molecules must be transported away from the surface. Due to the finite rate of such transport the concentration of reactants and products locally at the solid surface may be different than such concentrations slightly removed from the surface. The same can be said of the temperature which can be different locally at the solid surface and in the fluid phase slightly removed from the surface. The words “slightly removed from” are of course, scientifically imprecise. They are, however, conveying a certain physical picture of the situation, which envisions turbulent flow and vigorous mixing in the fluid which leaves thin boundary layers (films) close to the surface of the catalyst. It is this film theory that we will exploit to present an approximate picture of the situation related both to mass and heat transfer. Due to reaction on the surface and the heat of reaction, heat must either be supplied to the surface (for endothermic reactions) or removed from the surface (for exothermic ones) and, hence, the surface temperature and the local fluid temperature may be different.

Our task then is to develop the procedure by which if we know the local fluid concentrations and temperature close to the catalyst surface we can calculate the local surface concentrations and temperature at the catalyst surface and, hence, evaluate the local rate of reaction on the catalyst surface. We will start with the simplest situations first and build from there.

3.1. Isothermal Situation, First order Irreversible Reaction

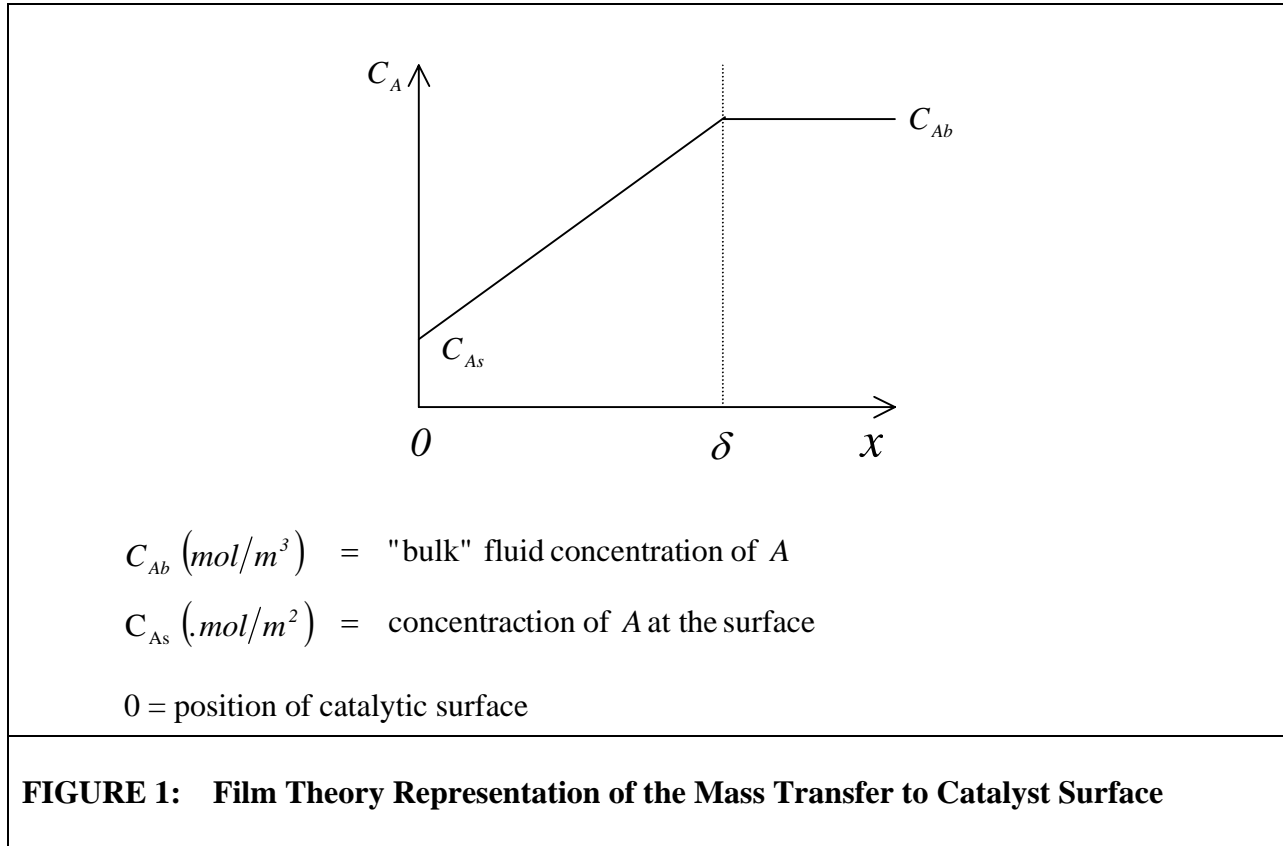
Let us assume that a first order irreversible reaction occurs at the catalyst surface and the heat of reaction is negligible so that we have an essentially isothermal situation and $T_s = T_b$ in the fluid film surrounding the surface where T_s is the local surface temperature and T_b is the local fluid temperature. The rate of reaction is then given by

$$-R'_A = k' C_A \text{ (mol/m}^2\text{s)} \quad (6)$$

One should note that since reaction occurs only on the surface it is proper to measure the rate as moles converted per unit time and unit catalyst surface area.

We focus now our attention at a point of the catalyst surface. Say we have a catalytic sphere that, either alone or in a packed bed, is exposed to the flow of fluid. We consider a point on the surface of the sphere and draw a normal to it into the fluid. This gives us our x-axis in Figure 1. As the ordinate we plot the concentration of A. We see that the concentration of A consists of a straight line profile within the boundary layer B.L., i.e. for $x \leq \delta$, and of a horizontal line for $x > \delta$. This implies that close to the solid surface we always have a diffusional boundary layer of thickness δ which is very thin ($\delta \ll d_p$ where d_p is pellet diameter). Outside that boundary layer the reactant concentration takes the bulk fluid value, C_{Ab} , which is still very close to the

catalyst particle on the characteristic distance scale of the equipment. The concentration at the solid surface is some constant but unknown value C_{As} . This picture is adequate for turbulent flow situations and can be properly modified for laminar flows.



Since inside the B.L. only diffusion takes place, the steady state diffusion equation reduces to

$$\frac{d^2 C_A}{dx^2} = 0 \tag{7}$$

with boundary condition

$$x = 0 \quad C_A = C_{As} \tag{8a}$$

$$x = \delta \quad C_A = C_{Ab} \tag{8b}$$

The solution is a straight line expression of Figure 1:

$$C_A = \frac{C_{Ab} - C_{As}}{\delta} x + C_{As} \tag{9}$$

The flux of A arriving to the surface at $x = 0$, $-\dot{N}_A|_{x=0}$ ($\text{mol A}/\text{m}^2\text{s}$), is by definition

$$-\dot{N}_A|_{x=0} = -\left(-D \frac{dC_A}{dx}\right)_{x=0} = \frac{D}{\delta} (C_{Ab} - C_{As}) \quad (10)$$

where D is the diffusivity of A. We now define the film mass transfer coefficient as

$$k_m = \frac{D}{\delta} \left(\frac{m}{s}\right) \quad (11)$$

and rewrite the flux in terms of k_m

$$-\dot{N}_A|_{x=0} = k_m (C_{Ab} - C_{As}) = \frac{C_{Ab} - C_{As}}{\frac{1}{k_m}} \quad (12)$$

The driving force for this transport of A towards the catalyst surface is clearly the concentration difference that exists across the B.L., i.e. $(C_{Ab} - C_{As})$. The mass transfer resistance $1/k_m$ is the reciprocal of the mass transfer coefficient.

At steady state the flux of A to the catalyst surface, i.e. the number of moles of A transported to the surface per unit time and unit area, must equal the reaction rate of A at the surface, i.e. the number of moles of A reacted per unit time and unit surface. This equality allows us to calculate the unknown surface concentration C_{As} and evaluate the actual reaction rate which is $(-R'_A) = k' C_{As}$.

Hence, since at steady state there can be no reactant accumulation at the catalyst surface:

$$-\dot{N}_A|_{x=0} = -R'_A \quad (13a)$$

$$k_m (C_{Ab} - C_{As}) = k' C_{As} \quad (13b)$$

$$C_{As} = \frac{C_{Ab}}{1 + \frac{k'}{k_m}} \quad (14)$$

It is customary to define a Damhohler number for surface reactions as

$$Da = \frac{(\text{characteristic time for mass transfer})}{(\text{characteristic surface reaction time})} = \frac{(\text{mass transfer resistance})}{(\text{kinetic resistance})} \quad (15)$$

$$= \frac{(\text{kinetic rate at bulk conditions})}{(\text{maximum mass transfer rate})}$$

In our case of a first order surface reaction that is:

$$Da = k'/k_m \quad (15a)$$

As we by now know, characteristic time is a measure of resistance. The larger the characteristic time the larger the resistance. So when mass transfer resistance is negligible compared to the kinetic resistance, $Da \rightarrow 0$, $C_{As} \approx C_{Ab}$ and our concentration profile in Figure 1 is flat. When $Da = O(1)$ and the mass transfer and kinetic resistance are comparable, the concentration profile looks somewhat like that depicted in Figure 1. However, when mass transfer resistance becomes many orders of magnitude larger than kinetic resistance, $Da \rightarrow \infty$, and $C_{As} \approx 0$.

One should keep in mind that since the kinetic constant is an exponential function of temperature while the mass transfer coefficient is a weak function of temperature, the Damhohler number will tend to rise rapidly with temperature.

Substitution of eq. (14) into the rate expression evaluated at the surface concentration yields the actual rate of reaction

$$(-R'_A) = k' C_{As} = \frac{k' C_{Ab}}{1 + \frac{k'}{k_m}} = \frac{C_{Ab}}{\frac{1}{k'} + \frac{1}{k_m}} \quad (16)$$

The actual reaction rate is proportional to the overall driving force, which is the reactant concentration in the bulk, and inversely proportional to the overall resistance, which is the sum of two parts, the kinetic resistance $1/k'$ and the mass transfer resistance, $1/k_m$. When $Da \rightarrow 0$, $\frac{1}{k_m} \ll \frac{1}{k'}$, the true kinetic rate, $k' C_{Ab}$, is observed and only the kinetic resistance is present. In

contrast, when $Da \rightarrow \infty$, $\frac{1}{k_m} \gg \frac{1}{k'}$, only mass transfer resistance remains, the process is mass transfer controlled, and the actual reaction rate is given by the maximum mass transfer rate $k_m C_{Ab}$.

The above findings are often represented with the help of the effectiveness factor, $\bar{\eta}$, which is defined as follows:

$$\bar{\eta} = \frac{(\text{actual reaction rate})}{(\text{kinetic rate at bulk conditions})} \quad (17)$$

The actual reaction rate is given by eq. (16) while the kinetic rate at bulk conditions is eq. (6) evaluated at $C_A = C_{Ab}$. Substitution of these two expressions into eq (17) upon some rearrangement yields:

$$\bar{\eta} = \frac{1}{1 + \frac{k'}{k_m}} = \frac{1}{1 + Da} \quad (18)$$

As $Da \rightarrow 0$, kinetics controls the rate, $\bar{\eta} = 1$ and the observed rate is $k' C_{Ab}$. For Da of order one and larger, the effectiveness factor is as given by Eq (18) and the actual reaction rate is:

$$(-R'_A)_{actual} = \bar{\eta} k' C_{Ab} = \frac{k' C_{Ab}}{1 + Da} = \frac{C_{Ab}}{\frac{1}{k'} + \frac{1}{k_m}} \quad (16a)$$

As $Da \gg 1$, $\bar{\eta} \rightarrow 0$ and mass transfer controls the rate so that the actual rate becomes equal to the maximum rate of mass transfer $k_m C_{Ab}$.

3.2. Isothermal Situation, n-th Order Irreversible Reaction

The physical picture depicted by Figure 1 still holds but finding the unknown surface concentration C_{As} now involves the solution of a nonlinear equation as $-R'_A = k' C_A^n$. Thus the requirement given by eq (13a) still holds

$$-\dot{N}_A \Big|_{x=0} = (-R'_A) \quad (13a)$$

and becomes

$$k_m (C_{Ab} - C_{As}) = k' C_{As}^n \quad (19)$$

We now introduce a dimensionless concentration $a = C_A/C_{Ab}$ so that $a_s = C_{As}/C_{Ab}$. The Damhohler number for an n-th order reaction is:

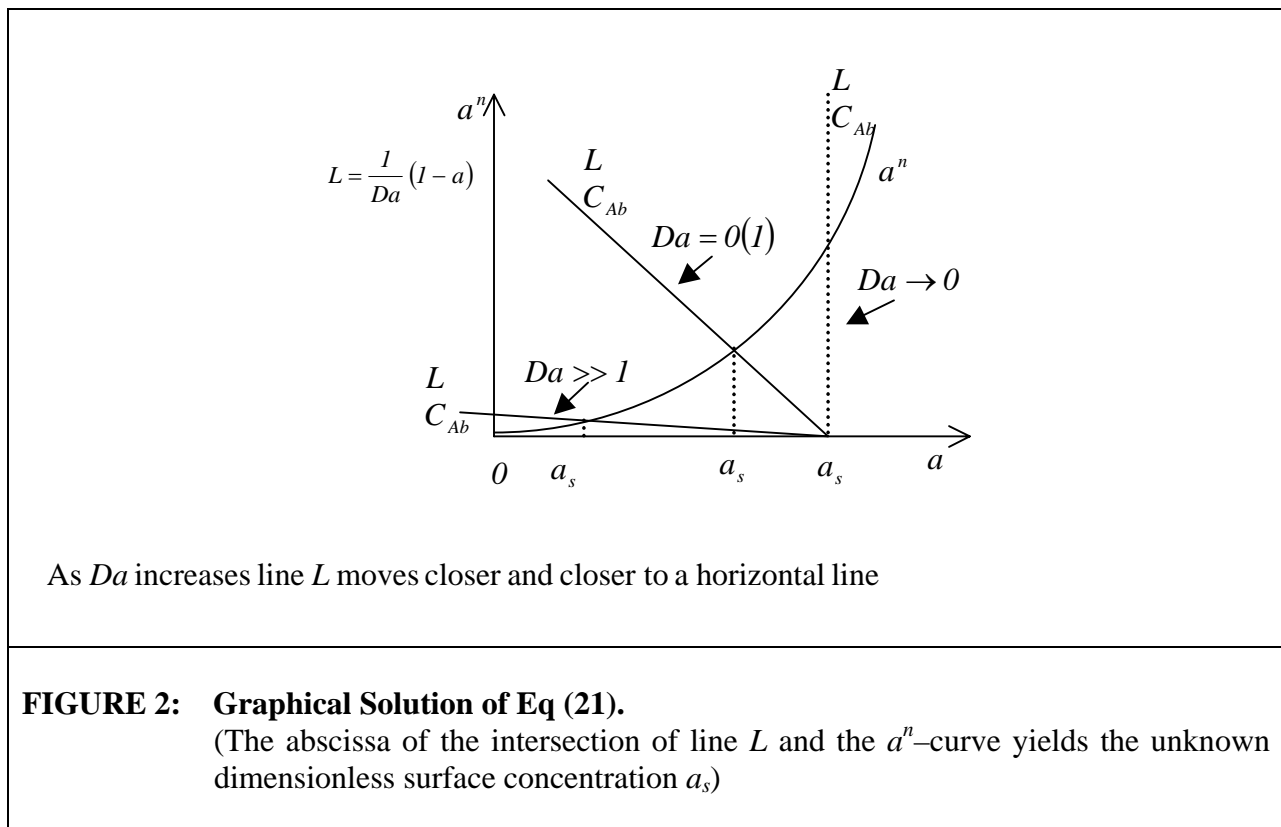
$$Da = \frac{k' C_{Ab}^{n-1}}{k_m} \quad (20)$$

so that equation (19) becomes:

$$\frac{1}{Da} (1 - a_s) = a_s^n = \bar{\eta} \quad (21)$$

The solution for the unknown dimensionless surface concentration a_s is found by solving equation (21) by trial and error. The actual rate of reaction is then given by $k' a_s^n C_{Ab}^n = \bar{\eta} k' C_{Ab}^n$.

Graphical representation of the solution to eq (21) is outlined in Figure 2. Clearly as $Da \rightarrow 0$, $a_s = 1$ and $\bar{\eta} = 1$. For $Da \gg 1$, as Da increases, a_s becomes closer and closer to 0 and as $a_s \rightarrow 0$, mass transfer controls the rate and $(-R'_A) = k_m C_{Ab}$.



Clearly analytical solution of eq (21) is possible for selected values of n .

3.3. Isothermal Situation, Other Rate Forms

The same procedure can be applied with appropriate rate form used in equation (13a) to evaluate the unknown surface concentration.

3.4. Transport Effects for n-th Order Reaction and Non-Isothermal Situation

The energy balance at steady state requires that the rate of heat transfer from (to) the surface be matched by the rate of heat release (use) by reaction on the surface which can be expressed by equation (24).

$$h(T_s - T_b) = (-\Delta H_{rA}) k_o' e^{-E/RT_s} C_{As}^n \quad (24)$$

where h is the heat transfer coefficient and ΔH_{rA} is the heat of reaction per mole of A reacted. We also recall that using the definition of the effectiveness factor, $\bar{\eta}$, we can represent the actual (observed) reaction rate, which is the kinetic rate evaluated at surface conditions i.e. $T = T_s$, $C_A = C_{As}$, as a product of the effectiveness factor and the kinetic rate evaluated at bulk conditions of $T = T_b$, $C_A = C_{Ab}$.

Hence

$$(-R_A)_{actual} = k_o' e^{-E/RT_s} C_{As}^n = \bar{\eta} k_o' e^{-E/RT_b} C_{Ab}^n \quad (25)$$

By utilizing the following dimensionless groups

$$Da = \frac{k_o' e^{-E/RT_b} C_{Ab}^{n-1}}{k_m} = \frac{\text{(kinetic rate at bulk conditions)}}{\text{(maximum mass transfer rate)}} \quad (26)$$

$$\gamma = \frac{E}{RT_b} = \text{dimensionless activation energy} \quad (26b)$$

$$\beta_s = \frac{k_m (-\Delta H_{rA}) C_{Ab}}{h T_b} = \frac{\text{(maximum heat generation rate in mass transfer controlled regime)}}{\text{(maximum heat transfer rate)}} \quad (26c)$$

equations (23) and (24) can be reduced to

$$C_{As} = (1 - \bar{\eta} Da) C_{Ab} \quad (27)$$

$$T_s = (1 + \beta_s \bar{\eta} Da) T_b \quad (28)$$

with

$$\bar{\eta} = e^{\gamma \left(1 - \frac{T_b}{T_s}\right)} \left(\frac{C_{As}}{C_{Ab}}\right)^n \quad (29)$$

Substitution of eqs (27) and (28) into eq (29) yields the final expression for the effectiveness factor, $\bar{\eta}$,

$$\bar{\eta} = e^{\gamma \left(1 - \frac{1}{1 + \beta_s \bar{\eta} Da} \right)} (1 - \bar{\eta} Da)^n \quad (30)$$

The above manipulations have reduced the two nonlinear equations (23) and (24) for the surface concentration, C_{As} , and surface temperature, T_s into a single nonlinear equation (30) for the effectiveness factor $\bar{\eta}$. Once $\bar{\eta}$ is calculated, the actual rate of reaction can be obtained from equation (25) and, if necessary, the surface concentration and surface temperature can be calculated from eqs (27) and (28), respectively.

The following two types of problems arise in general.

- I. The kinetics is known, i.e. n , k_o , E are known as well as ΔH_{rA} . The bulk conditions C_{Ab} , T_b are known as well as the local mean velocity of fluid flow past the surface. One needs to calculate C_{As} and T_s and predict the actual rate of reaction that will be obtained at these conditions.

With the use of the physical properties for the system under consideration, as well as by considering the geometry of the catalyst and the equipment, the appropriate Reynolds, Re , Schmidt, Sc , Prandtl, Pr , numbers can be calculated and the needed mass, k_m , and heat transfer, h , coefficients determined from appropriate correlations. These are usually Sherwood and Nusselt number correlations of the type

$$Sh = \frac{k_m L}{D} = F_m (Re, Sc) \quad (31a)$$

$$Nu = \frac{h L}{\lambda} = F_h (Re, Pr) \quad (31b)$$

where λ is thermal conductivity of the fluid and L is the characteristic linear dimension of the system (e.g. particle diameter, d_p). Mass and heat transfer coefficient can also be evaluated from j_D , j_H type of correlations.

$$j_D = \frac{k_m}{U} Sc^{2/3} = f_m (Re) \quad (32a)$$

$$j_H = \frac{h}{U \rho C_p} Pr^{2/3} = f_h (Re) \quad (32b)$$

Appropriate correlation form must be sought in transport books or in Perry's Engineering Handbook.

Once k_m , h are determined, all the needed parameters γ , β_s , Da and n are calculated based on available information and $\bar{\eta}$ is calculated by trial and error from equation (30).

- II. The second type of problem arises when one has some ideas about n , E and ΔH_{R_A} and has collected some rate data $(-R'_A)_{obs}$ under well defined bulk conditions of C_{Ab} , T_b . Now one needs to assess whether the observed (measured) rate $(-R'_A)_{obs}$ is the kinetic rate or is masked by transport effects.

It is useful to note that the product $\bar{\eta} Da$ is now a known or estimable quantity since

$$\bar{\eta} Da = \frac{(-R'_A)_{obs}}{k_m C_{Ab}} \quad (33)$$

This means that after h and k_m are estimated, the effectiveness factor $\bar{\eta}$ can be calculated directly (without trial and error) from equation (30) by substituting in it equation (33) for $\bar{\eta} Da$.

From the above it is clear that when $\bar{\eta} Da \ll 1$, kinetics controls the rate and $\bar{\eta} = 1$. On the other hand when $\bar{\eta} Da \rightarrow 1$, mass transfer controls the rate. The magnitude of heat transfer effects depends on the magnitude of $T_s - T_b$ and activation energy. It is worth noting that since temperature affects the rate more than concentration, the effectiveness factor $\bar{\eta}$ for exothermic reactions can be larger than one when heat transfer effects are significant. Moreover, if the effectiveness factor, $\bar{\eta}$, is plotted as a function of Damhohler number, Da , with β_s and γ as parameters, for exothermic reactions ($\beta_s > 0$), multiple solutions are possible for $\bar{\eta}$ in an intermediate range of Da -numbers.

Often even for reactions conducted on nonporous catalysts we will express the rate of reaction per unit volume of the reaction mixture $-R_A$ ($mol A/m^3 s$). The relationship to the surface reaction rate is simple and involves catalyst surface area per unit volume of the reaction mixture, a (m^2/m^3) so that $-R_A = (-R'_A) a$.

ADDENDUM TO SECTION 3:

TRANSPORT EFFECTS FOR NONPOROUS CATALYSTS

Selected figures from various papers are enclosed to illustrate the effectiveness factor plots.

Definitions of symbols used are indicated on the figures.

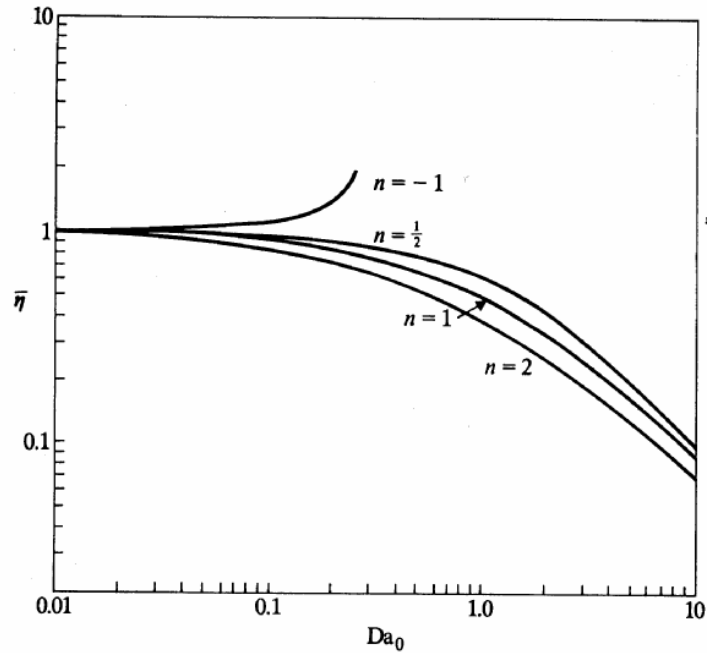


FIGURE 1: Isothermal external catalytic effectiveness for reaction order n . (G. Cassiere and J.J. Carberry, *Chem. Eng. Educ.*, Winter, 1973: 22).

$$\begin{aligned}
 k \left(\left(\frac{\text{mol}}{\text{m}^3} \right)^{1-n} \frac{1}{\text{s}} \right) &= \text{rate constant} \\
 k_m (\text{m/s}) &= \text{mass transfer coefficient} \\
 n &= \text{reaction order} \\
 \bar{\eta} = \frac{(-R_A)_{\text{observed}}}{(-R_A)_{\text{bulk conditions}}} &= \left(\frac{C_{A_s}}{C_{A_b}} \right)^n \\
 Da_o &= \frac{k C_{A_b}^{n-1}}{k_m a} \\
 C_{A_s} \left(\frac{\text{mol}}{\text{m}^3} \right) &= \text{surface concentration} \\
 C_{A_b} \left(\frac{\text{mol}}{\text{m}^3} \right) &= \text{bulk concentration} \\
 a \left(\frac{\text{m}^2}{\text{m}^3} \right) &= \text{catalyst area per unit volume}
 \end{aligned}$$

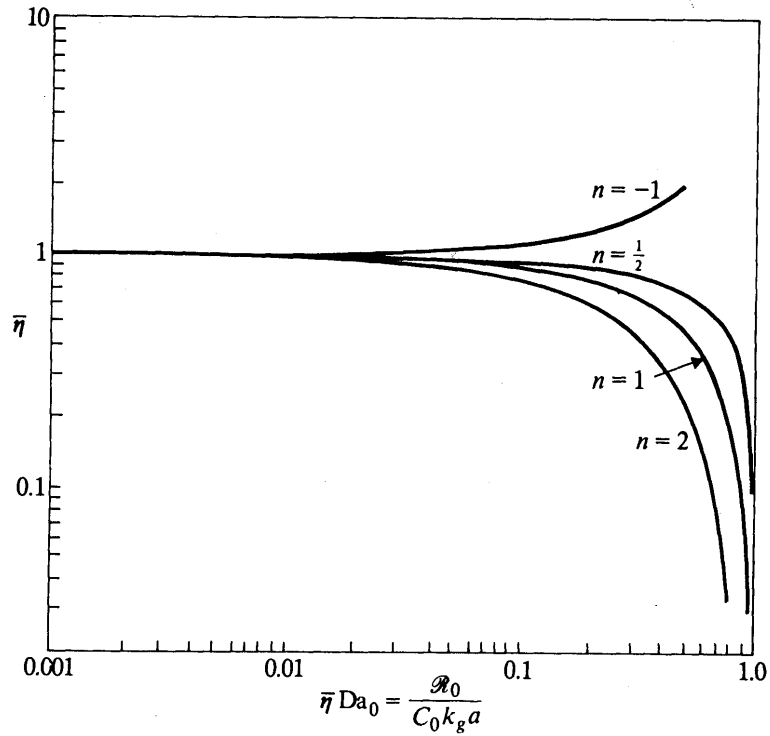


FIGURE 2: Isothermal external catalytic effectiveness in terms of observable for order n . (G. Cassiere and J.J. Carberry, *Chem. Eng. Educ.*, Winter, 1973: 22).

$k \left(\left(\frac{\text{mol}}{\text{m}^3} \right)^{1-n} \frac{1}{\text{s}} \right)$	= rate constant
$k_m (\text{m/s})$	= mass transfer coefficient
n	= reaction order
$\bar{\eta} = \frac{(-R_A)_{\text{observed}}}{(-R_A)_{\text{bulk conditions}}}$	= $\left(\frac{C_{A_s}}{C_{A_b}} \right)^n$
Da_o	= $\frac{k C_{A_b}^{n-1}}{k_m a}$
$C_{A_s} \left(\frac{\text{mol}}{\text{m}^3} \right)$	= surface concentration
$C_{A_b} \left(\frac{\text{mol}}{\text{m}^3} \right)$	= bulk concentration
$a \left(\frac{\text{m}^2}{\text{m}^3} \right)$	= catalyst area per unit volume
$R_o = (-R_A)_{\text{observed}} = (-R_A)_{\text{surf. cond.}}$	= $k C_{A_s}^n$
$k_g a \equiv k_m a$	= volumetric mass transfer coefficient
$C_o \equiv C_{A_o}$	

$$\bar{\beta} = \beta = \frac{(-\Delta H_{r_A}) C_{A_0}}{\rho C_p T_0}$$

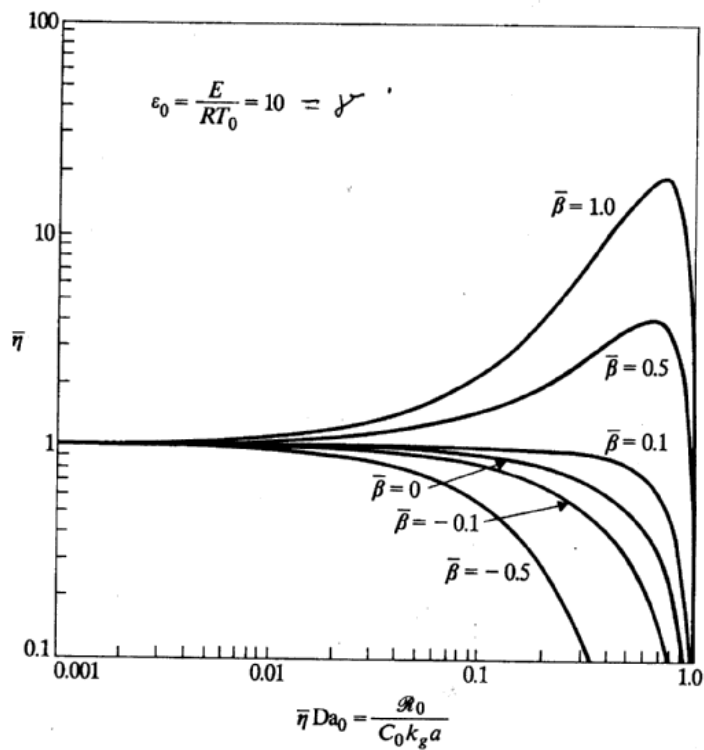


FIGURE 3: External nonisothermal $\bar{\eta}$ versus observable (first order, $\epsilon_0 = 10$). [J.J. Carberry and A.A. Kulkarni, *J. Catal.*, **31**:41 (1973).]

$$\bar{\beta} = \beta = \frac{(-\Delta H_{rA}) C_{A0}}{\rho C_p T_0}$$

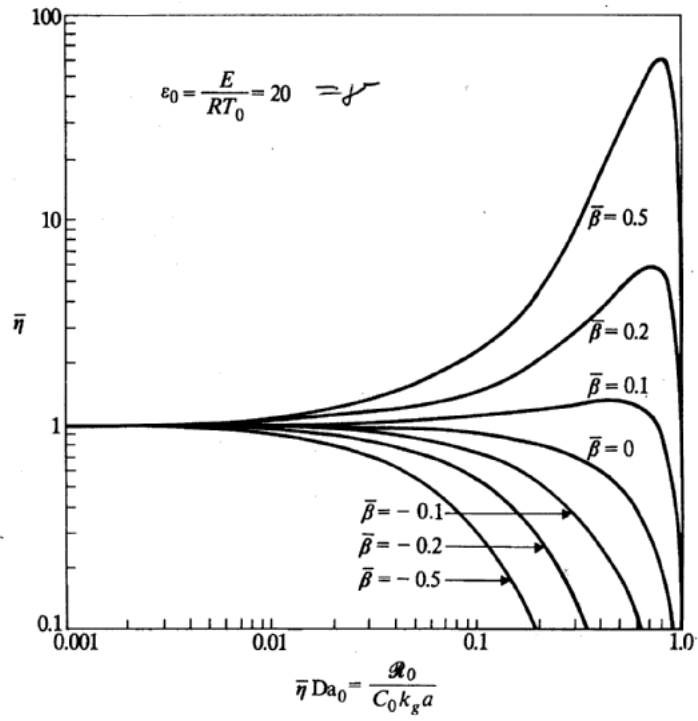


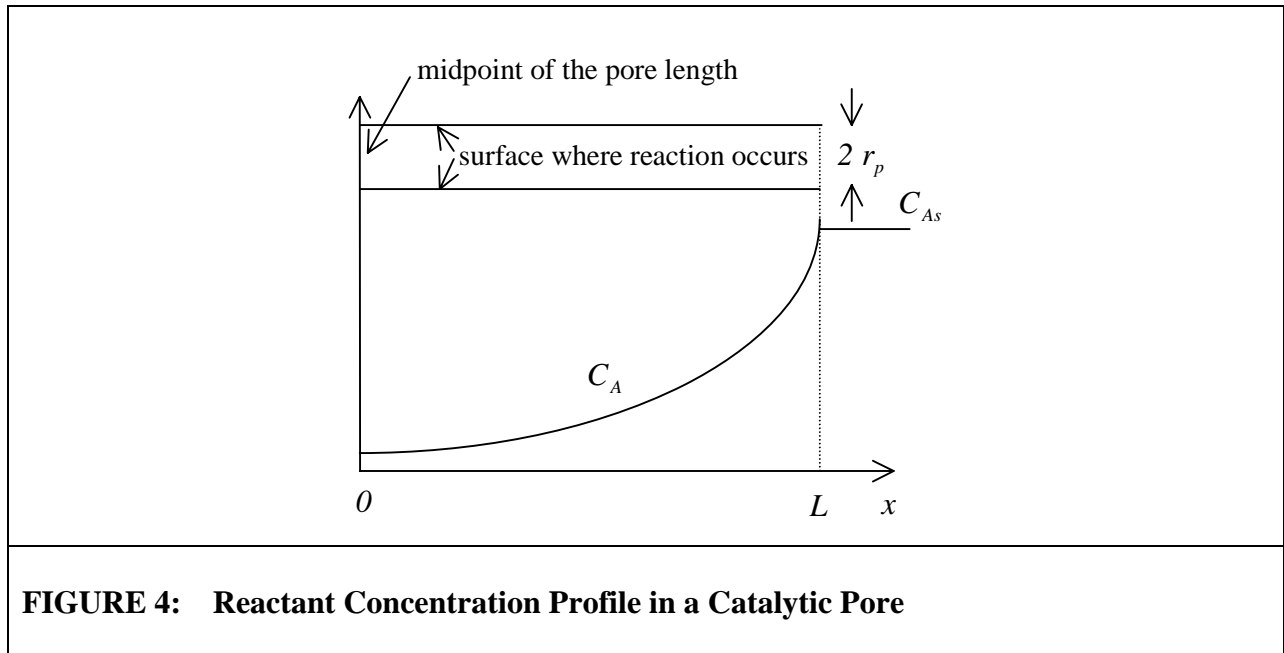
FIGURE 3:

4. TRANSPORT EFFECTS IN POROUS CATALYSTS

4.1. INTERNAL DIFFUSIONAL EFFECTS

4.1.1. First Order Reaction

Let us consider an isothermal pore in a catalyst particle and assume that a first order irreversible reaction takes place on the walls of the pore, i.e., $-R'_A = k' C_A$. Let us further assume that the pore is cylindrical of uniform radius, r_p , and that the length of the pore $2L$ far exceeds its diameter, i.e., $L/d_p \gg 1$. Then we can neglect the concentration variation in the radial direction in the pore and consider only the concentration variation in the longitudinal direction along the length of the pore. Due to diffusion, the concentration along the pore may be different than at the outside pore mouth where it equals the concentration on the outside catalyst surface C_{As} . Our goal is to find the actual rate of reaction in the pore and compare it to the rate that we would have obtained if all the interior pore surface could have been exposed to the concentration at the pore mouth, C_{As} . Figure 4 illustrates this physical situation.



A steady state mass balance on reactant A for an element of length Δx of the pore can be written as:

$$\left(\begin{array}{c} \text{input} \\ \text{by} \\ \text{diffusion} \end{array} \right)_x - \left(\begin{array}{c} \text{output} \\ \text{by} \\ \text{diffusion} \end{array} \right)_{x+\Delta x} - \left(\begin{array}{c} \text{loss by} \\ \text{reaction in} \\ \text{element } \Delta x \end{array} \right) = 0 \quad (34)$$

The diffusion flux (in the positive x direction) is $-D \frac{d C_A}{dx}$ and multiplied by the cross-sectional area of the pore, πr_p^2 , yields the input and output terms. The loss by reaction term is the product of the reaction rate per unit surface, $k' C_A$, and the surface area of the pore element of length Δx on which reaction occurs, which is $2\pi r_p \Delta x$.

Hence, eq (34) can be written as:

$$\left(-D \pi r_p^2 \frac{d C_A}{dx}\right)_x - \left(-D \pi r_p^2 \frac{d C_A}{dx}\right)_{x+\Delta x} - 2\pi r_p \Delta x k' \tilde{C}_A = 0 \quad (34a)$$

where $C_A/x < \tilde{C}_A < C_A/x+\Delta x$. Dividing by Δx , taking the limit as $\Delta x \rightarrow 0$ and remembering that D and r_p are constant (i.e., not functions of x) yields:

$$\frac{d^2 C_A}{dx^2} - \frac{2 k'}{D r_p} C_A = 0 \quad (35)$$

The proper boundary conditions, B.C., are:

$$\text{At the pore mouth:} \quad x = L \quad C_A = C_{As} \quad (36)$$

$$\text{At the center of the pore:} \quad x = 0 \quad \frac{d C_A}{dx} = 0 \quad (37)$$

First, it is customary to define a rate constant for a reaction based per unit volume of pore space, i.e., $k C_A \pi r_p^2 L = k' C_A 2\pi r_p L$, so that

$$k = \frac{2 k'}{r_p} \quad (38)$$

Moreover, by defining a dimensionless distance, $\xi = x/L$, we note that equation (35) becomes

$$\frac{d^2 C_A}{d \xi^2} - \phi^2 C_A = 0 \quad (39)$$

and the B.C. become:

$$\xi = 1 \quad C_A = C_{As} \quad (40a)$$

$$\xi = 0 \quad \frac{d C_A}{d \xi} = 0 \quad (40b)$$

where

$$\phi^2 = \frac{k L^2}{D} = \frac{L^2/D}{l/k} = \frac{\text{characteristic diffusion time}}{\text{characteristic kinetic time}} = \frac{\text{kinetic rate at outside surface conditions}}{\text{maximum diffusion rate into pore}} \quad (41)$$

The dimensionless group ϕ (denoted as m in Levenspiel's text) is the celebrated Thiele modulus. It represents the ratio of the diffusional and reaction resistance (actually the square root of that ratio).

The solution of eq (39) is the sum of two exponentials. The elimination of the two arbitrary constants with the use of BC (40a and b) yields:

$$C_A = C_{As} \frac{\cosh(\phi \xi)}{\cosh \phi} \quad (42)$$

For $\phi \ll 1$, diffusional resistance is negligible compared to the kinetic resistance and the concentration profile would be flat in Figure 4. Expanding eq (42) for small ϕ yields:

$$C_A \approx C_{As} \left[\frac{1 + \frac{\phi^2}{2} \xi^2}{1 + \frac{\phi^2}{2}} \right] = C_{As} \left[1 - \frac{\phi^2}{2} (1 - \xi^2) \right] \quad (43)$$

Hence, for very small ϕ , $C_A \approx C_{As}$ everywhere.

For $\phi \gg 1$, diffusional resistance is very large compared to the kinetic resistance and unreacted A has difficulty penetrating into the pore. Hence, C_A decays exponentially from C_{As} to zero close to the pore mouth. Expanding eq (42) for large ϕ yields:

$$C_A \sim C_{As} \frac{e^{\phi \xi}}{e^{\phi}} \sim C_{As} e^{-\phi(1-\xi)} \quad (44)$$

Remember in Levenspiel's text the modulus ϕ is called m .

Now we are not interested as much in the reactant concentration profile in the pore but in the reaction rate that we will obtain in the pore. Moreover, we define an effectiveness factor, η , to account for internal diffusional effects.

$$\eta = \frac{\text{(actual rate)}}{\left(\begin{array}{c} \text{kinetic rate} \\ \text{evaluated at pore} \\ \text{mouth conditions} \end{array} \right)} \quad (45)$$

The actual rate in the pore is the rate in a differential element dx , $k C_A \pi r_p^2 dx$, summed up (integrated) over the whole length of the pore. To obtain the effectiveness factor that actual rate in the whole pore must be divided by $k C_{As} \pi r_p^2 L$, which is the rate in the pore that would be obtained at pore mouth conditions, i.e., in absence of diffusional effects.

$$\begin{aligned}\eta &= \frac{k \int_0^L C_A dx}{k C_{As} L} = \int_0^1 \frac{\cosh(\phi \xi)}{\cosh \phi} d\xi \\ &= \frac{\sinh(\phi \xi) \Big|_0^1}{\phi \cosh \phi} = \frac{\sinh \phi}{\phi \cosh \phi} = \frac{\tanh \phi}{\phi}\end{aligned}\quad (46)$$

This is the celebrated formula for the Thiele effectiveness factor. For $\phi \ll 1$, $\eta = 1$, kinetics controls the rate. For $\phi \gg 1$, $\eta \sim \frac{1}{\phi}$ and there are strong pore diffusional effects.

We can extend this development to a catalyst particle of any shape. For a first order reaction we define the generalized (with respect to catalyst shape) modulus, Λ , as:

$$\Lambda^2 = \left(\frac{V_p}{S_{ex}} \right)^2 \frac{k}{D_{eff}} \quad (47)$$

where

V_p (cm^3) = is the volume of the catalyst particle

S_{ex} (cm^2) = is the external geometric area of the catalyst particle, i.e., the area that engulfs volume V_p , across which the reactant is supplied by diffusion.

D_{eff} (cm^2/s) = is the effective diffusivity in the catalyst

k ($1/s$) = is the first order rate constant based on unit volume of the catalyst (note it is not any more based on unit volume of pore space)

Then the effectiveness factor is approximately given by an equation equivalent to eq (46), i.e.,

$$\eta = \frac{\tanh \Lambda}{\Lambda} \quad (48)$$

From eq (48) we recognize that for small values of the modulus, Λ , *i.e.*, $\Lambda \ll 1$ small kinetic resistance compared to diffusional resistance, $\eta = 1$. This implies that

$$(-R_A)_{obs} = \eta (-R_A)_{bulk} = (-R_A)_{bulk} = k C_{A_b} \quad (49)$$

Hence, in this kinetically controlled regime the observed rate of reaction is independent of particle diameter. If we can show that the rate is kinetically controlled on particles of diameter, d_{pt} , then it must be kinetically controlled at the same reaction conditions on the same catalyst for all catalyst particles of diameter $d_p \leq d_{pt}$. [Note that for a spherical particle $\Lambda = d_p/6$].

When the modulus Λ is very large ($\Lambda > 6$ or so), $\eta \sim \frac{1}{\Lambda}$ and

$$(-R_A)_{obs} = \eta (-R_A)_{bulk} = \frac{1}{\Lambda} k C_{A_b} = \sqrt{k D_{eff}} \left(\frac{S_{ex}}{V_p} \right) C_{A_b} \quad (50)$$

Since $(V_p/S_{ex}) \propto d_p$, it is clear that in the regime of strong pore diffusional resistance the observed rate of reaction is inversely proportional to the particle diameter.

We also learn from eqs (48) and (50) that in the kinetic regime the apparent rate constant is equal to the true kinetic constant, k , and, hence, the observed activation energy in the kinetic regime equals the true kinetic activation energy. In contrast, in the strong pore diffusional regime, as evident from eq (50), the apparent rate constant is proportional to $\sqrt{k D_{eff}}$. Since the effective diffusivity is a weak function of temperature, while the kinetic rate constant changes exponentially, it is clear that the apparent activation energy in this regime is about $E/2$, where E is the true kinetic activation energy.

It should be noted that reaction engineering textbooks offer different expressions for the effectiveness factor for different shape catalyst particles such as infinite slabs, infinitely long cylinders and spheres. The formula given by eq (48) deviates by at most 11% from these other expressions and produces maximum errors for moduli of order one. Since actual catalyst particles are not infinite cylinders or spheres, it is sufficient to use eq (48) for all types of preliminary investigations. In more precise calculations, if needed, the effectiveness factor can be computed for actual catalyst shapes numerically.

We also need to discuss the meaning and computation of the effective diffusivity, D_{eff} . It is defined in such a way that the dot product of the gradient of concentration, with the normal to the surface, multiplied by effective diffusivity and evaluated at the exterior catalyst surface, and integrated over the whole surface yields the total reactant supply per unit time to the catalyst pellet.

$$\left(\begin{array}{l} \text{moles of A supplied to the} \\ \text{catalyst pellet per unit time} \end{array} \right) = \oint_S D_{eff} \nabla C_A \cdot \underline{n} ds \quad (51)$$

or simply put, the flux of A into the pellet per unit exterior catalyst surface is:

$$-\dot{N}_A|_{ext} \left(\frac{mol A}{cm^2 s} \right) = D \left. \frac{\partial C_A}{\partial n} \right|_{S_{ext}} \quad (52)$$

where n is the coordinate in the direction normal to the local exterior surface along which the flux is evaluated.

If, and only if, the pore size distribution in the catalyst is unimodal and narrow, effective diffusivity can be defined as:

$$D_{eff} = D \frac{\varepsilon_p}{\tau_p} \quad (53)$$

where ε_p is the porosity of the pellet and τ_p is the tortuosity factor which usually assumes values of 2 to 4 but could be higher. It can either be calculated from a model of the pore structure or obtained experimentally. The diffusivity, D , is a “composite” diffusivity meaning

$$\frac{1}{D} = \frac{1}{D_m} + \frac{1}{D_k} \quad (54)$$

where D_m is a molecular diffusivity and D_k is Knudsen diffusivity. If dealing with binary mixtures, or dilute components in a dominant carrier, then D_m can be calculated by the usual formulas for molecular diffusivity. If one deals with multicomponent mixture of similar mole fractions of various components, more sophisticated methods are required (e.g., Stefan-Maxwell equation). D_k is Knudsen diffusivity which can be calculated by:

$$D_k (cm^2/s) = 9700 r_p \sqrt{\frac{T}{M}} \quad (55)$$

where r_p (cm) is the mean pore radius, T (°K) is the absolute temperature, and M is the molecular weight of the diffusing gas. (Since Knudsen diffusion is important only when the molecular free path is much larger than the pore radius, it is clear that it cannot occur in liquids).

When more complicated pore structures (such as bimodal ones) are present in catalyst pellets, alternative, more complex models are needed and eq (53) is not recommended under such conditions.

4.1.2. Extension to n-th Order Reaction

Using slab geometry and asymptotic methods one can extend the formula for the effectiveness factor, eq (48)

$$\eta = \frac{\tanh \Lambda}{\Lambda} \quad (48)$$

to n-th order reactions by defining the modulus as:

$$\Lambda = \frac{V_p}{S_{ex}} \sqrt{\frac{k (n+1) C_{As}^{n-1}}{2 D_{eff}}} \quad (56)$$

and to any rate form by defining the modulus as:

$$\Lambda = \frac{V_p}{S_{ex}} \frac{(-R_A)_s}{\sqrt{2 D_{eff}}} \left[\int_0^{C_{As}} (-R_A) d C_A \right]^{-1/2} \quad (57)$$

where $(-R_A)_s$ is the reaction rate evaluated at the concentration C_{As} , which is the concentration at the pore mouth.

4.2. INTERNAL HEAT TRANSFER EFFECTS

The above developed formulas for the effectiveness factor are only valid if the particle is isothermal. As engineers, we would like to estimate what maximum temperature differences can develop across a catalyst particle. Here, Prater's development (Dwain Prater worked for Mobil Oil) is most helpful.

Consider, only the region R , in which reaction occurs, and the surface ∂R surrounding it over which reactant is supplied as well as heat is exchanged with the surrounding fluid. Mass and energy balances for a differential element in R yield:

$$D_{eff} \nabla^2 C_A - (-R_A) = 0 \quad \text{in } R \quad (58)$$

$$\lambda_{eff} \nabla^2 T + (-\Delta H_{rA})(-R_A) = 0 \quad \text{in } R \quad (59)$$

Here, we assume that effective diffusivity D_{eff} and effective conductivity, λ_{eff} are approximately constant as well as the heat of reaction. While equations (58) and (59) are valid anywhere in R , on the outside surface we have

$$\text{on } \partial R \quad C_A = C_{As} \quad \text{and} \quad T = T_s \quad (60)$$

Multiplying eq (58) by $(-\Delta H_{rA})$ and adding it to eq (59) yields:

$$(-\Delta H_{rA}) D_{eff} \nabla^2 C_A + \lambda_{eff} \nabla^2 T = 0 \quad (61a)$$

$$\nabla^2 [(-\Delta H_{rA}) D_{eff} C_A + \lambda_{eff} T] = 0 \quad (61b)$$

$$\nabla^2 u = 0 \quad (61c)$$

We get eq (61b) from (61a) by the virtue that the Laplacian operation, ∇^2 , is a linear operator and heat of reaction, effective diffusivity and conductivity are assumed constant.

Then we define

$$u = D_{eff} (-\Delta H_{rA}) C_A + \lambda_{eff} T \quad (62)$$

to generate eq (61c) from eq (61b).

Considering the B.C., eq (60), we see that

$$\text{on } \partial R \quad u = u_s = D_{eff} (-\Delta H_{rA}) C_{As} + \lambda_{eff} T_s \quad (61d)$$

The solution of the partial differential equation (61c) with B.C. given by eq (61d) is $u = u_s$ everywhere in region R . By substituting what u and u_s are, we see that this means that everywhere in the catalyst particle the reactant concentration and temperature are tied by the linear equation below

$$D_{eff} (-\Delta H_{rA}) C_A + \lambda_{eff} T = D_{eff} (-\Delta H_{rA}) C_{As} + \lambda_{eff} T_s$$

so that

$$T - T_s = \frac{D_{eff} (-\Delta H_{rA}) (C_{As} - C_A)}{\lambda_{eff}} \quad (63)$$

The maximum temperature difference then between any point in the particle and the outside surface is obtained when one assumes $C_A = 0$ at that point and substitutes the zero value in eq (63). Hence,

$$\Delta T_{\text{pellet max}} = (T_{\text{max}} - T_s) = \frac{D_{eff} (-\Delta H_{rA}) C_{As}}{\lambda_{eff}} \quad (64)$$

The dimensionless quantity $\frac{\Delta T_{\text{pellet max}}}{T_s} = \frac{D_{\text{eff}} (-\Delta H_{rA}) C_{As}}{D_{\text{eff}} T_s}$ should be called Prater number.

We now conclude, by observing eq (64), that the maximum pellet temperature difference in liquids will be negligibly small (due to very low effective diffusivity, $D_{\text{eff}} < 10^{-5} \text{ cm}^2/\text{s}$ and high effective conductivity). $\Delta T_{\text{pellet max}}$ typically cannot exceed 1 °C. In gases, however, due to high D_{eff} and low λ_{eff} , large temperature differences could develop for some systems with large heats of reaction. However, these temperature differences will only materialize when we have strong pore diffusional resistances so that $C_A \rightarrow 0$ in the pellet. In the kinetic regime $C_A \approx C_{As}$ so that large catalyst particle internal temperature differences cannot develop.

Therefore, for all applications to liquid systems and most gaseous systems the isothermal effectiveness factor formula can be used. When the pellet is internally nonisothermal, approximate formulas or numerical solution must be sought.

4.3 EXTERNAL MASS AND HEAT TRANSFER EFFECTS

For catalyst particles at steady state both the mass and energy balance must be satisfied, which leads to the two equations that determine surface concentration and temperature. These equations for a single, first order reaction are:

$$k_m (C_{Ab} - C_{As}) = \eta k_o e^{-E/RT_s} C_{As} V_p / S_{ex} \quad (65)$$

$$h (T_s - T_b) = (-\Delta H_{rA}) \eta k_o e^{-E/RT_s} C_{As} V_p / S_{ex} \quad (66)$$

One should note that eqs (65) and (66), which define the surface concentration C_{As} and surface temperature, T_s , look very much like their counterparts for the nonporous catalyst. The difference is now that the right hand side has to be multiplied with the (V_p / S_{ex}) ratio since the rate is given per unit volume of the catalyst, not unit surface as for a nonporous catalyst. The right hand side also contains the particle internal effectiveness factor, η , which accounts for the possible diffusional and internal heat transfer effects. Thus, for our first order reaction

$$\eta = \frac{(-R_A)_{obs}}{(-R_A)_{C_{As}, T_s}} = \frac{(-R_A)_{obs}}{k_o e^{-E/RT_s} C_{As}} \quad (67)$$

The local bulk fluid concentration is C_{Ab} and local fluid bulk temperature is T_b . Hence, one can define the overall effectiveness factory by:

$$\eta_o = \frac{(-R_A)_{obs}}{(-R_A)_{C_{Ab}, T_b}} = \frac{(-R_A)_{obs}}{k_o e^{-E/RT_b} C_{Ab}} \quad (68)$$

Thus, while the particle effectiveness factor, η , accounts only for the internal transport effects the overall particle effectiveness factor, η_o , accounts for both external and internal effects.

Again two types of problems arise. In a design situation (Type I problem), at a point in the reactor where C_{Ab} , T_b are known one needs to estimate the actual rate of reaction $(-R_A)_{act} = (-R_A)_{obs} = \eta_o (-R_A)_b$ where $(-R_A)_b$ is the rate evaluated at C_{Ab} , T_b . To do this we must assume T_s , C_{As} , evaluate the Thiele modulus at these conditions, check for particle internal isothermality and calculate η . Then one solves eqs (65) and (66) for C_{As} and T_s and develops an iteration scheme (really a relaxation scheme) to correct these values until convergence is obtained. At that point η , η_o , T_s , and C_{As} can all be calculated.

In Type II problem the experimentally observed rate of reaction is known and one needs to estimate how significant are the transport effects. Film mass transfer effect can now be estimated from eq (65) which leads to the form below.

$$\frac{C_{Ab} - C_{As}}{C_{Ab}} = \frac{(-R_A)_{obs} V_p / S_{ex}}{k_m C_{Ab}} \quad (69)$$

If the right hand side (RHS) of eq (69) is very small $C_{As} \approx C_{Ab}$, then there are no film mass transfer effects. In contrast, if the RHS of eq (69) approaches unity, film mass transfer effects are dominant, $C_{As} \approx 0$ and the observed reaction rate is controlled by the external mass transfer rate.

The external film temperature difference can be estimated from eq (66) which is written as:

$$\Delta T_{ext} = T_s - T_b = \frac{(-\Delta H_{rA})(-R_A)_{obs} V_p / S_{ex}}{h} \quad (70)$$

It should be noted that for gases this external ΔT can be large even when internally the particle is isothermal.

The magnitude of the internal diffusional effects can be obtained by calculating the value of the Weisz modulus defined by

$$\Phi = \frac{(-R_A)_{obs} (V_p / S_{ex})^2}{D_{eff} C_{As}} \quad (71)$$

It can readily be shown that the Weisz modulus, Φ , is the product of the particle internal effectiveness factor, η , and Thiele modulus squared, Λ^2 . Hence,

$$\Phi = \eta \Lambda^2 = \Lambda \tanh \Lambda \quad (72)$$

Knowing the value of Φ , we can calculate Λ and get the value of the effectiveness factor from eq (48).

$$\eta = \frac{\tanh \Lambda}{\Lambda} \quad (48)$$

Now we only have to assure that the particle is internally isothermal. We do that by looking at

$$\Delta T_{\text{pellet}} = \frac{D_{\text{eff}} (-\Delta H_{rA}) C_{As} \left(1 - \frac{1}{\cosh \Lambda}\right)}{\lambda_{\text{eff}}} \quad (73)$$

A recipe as to how to handle Type I and Type II problems, presented by O. Levenspiel in his Omnibook, and the pertinent section is attached.

**Reactions at a fluid non-porous solid
interface
(CHE 512)**

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ChE 512: Topic 1
Reactions at a fluid non-porous solid interface

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OUTLINE

- *External Transport: Film Concept*
- *Mass transfer coefficients*
- *Effect of transport on reaction*
- *Simultaneous heat and mass transfer*
- *Multicomponent diffusion*
- *Computer simulation*
- *Examples:*

Film Concept Near a Solid

Near the gas-solid interface, there exists a region of relatively slow moving gas.

Gas velocity becomes zero at the solid surface (No slip condition)

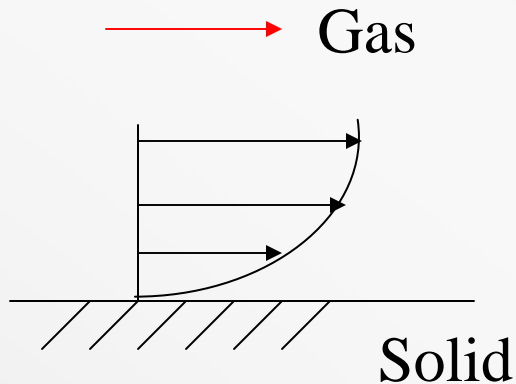
Hydrodynamic boundary layer

If the solid surface is at a different concentration then a concentration boundary layer exists.

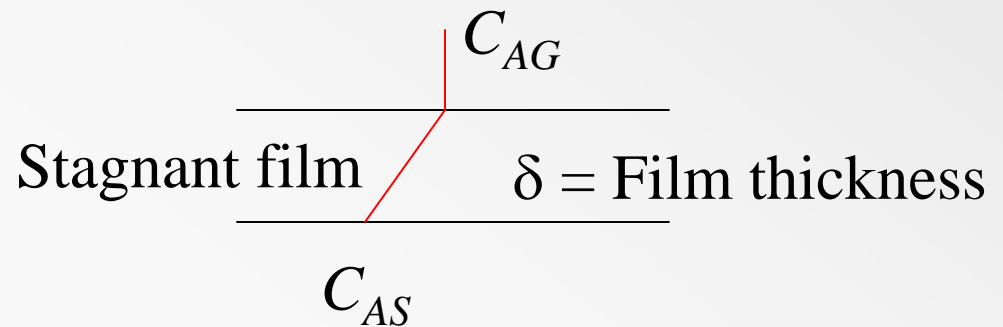
Diffusion-convection transport in this boundary layer is

Represented by a stagnant region near the solid “film”.

Film Model: Schematics



Concentration Profile

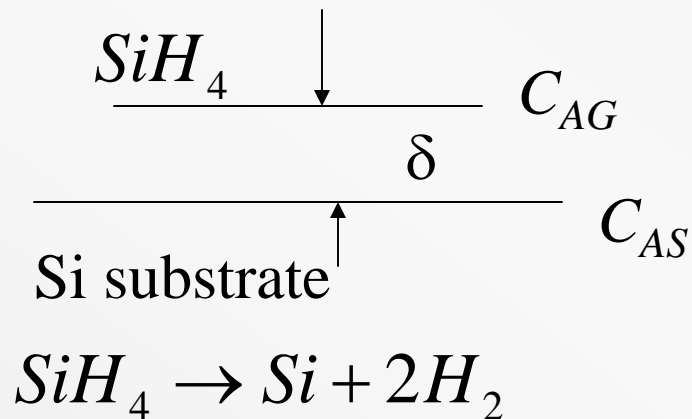


Film Representation

$$\text{Diffusive Flux to Surface} = \frac{D_A}{\delta} (C_{AG} - C_{AS}) = k_{mA} (C_{AG} - C_{AS})$$

$$k_{mA} = \text{mass transfer coefficient} = \frac{D_A}{\delta}$$

Effect of Reaction: First Order



Rate of transport to surface

$$(-J_A) = k_{mA} (C_{AG} - C_{AS})$$

Rate of reaction at surface

$$(-R_A) = k_s C_{AS}$$

$(-R_A)$ is mole/m²s. Surface area is used as a measure.

Rate of reaction: First Order

At steady state, species produced at the surface (per unit area) must balance the flux from the surface.

$$-R_A = -J_A$$

$$k_S C_{AS} = k_m (C_{AG} - C_{AS})$$

$$C_{AS} = \frac{k_m C_{AG}}{k_S + k_m}$$

$$(-R_A) = k_S C_{AS} = \frac{k_S k_m}{k_S + k_m} C_{AG}$$

Effectiveness factor (Non-porous)

$$\frac{-R_A}{k_S C_{AG}} = \eta_{ext} = \frac{k_m}{k_S + k_m} = \frac{\text{actual rate}}{\text{rate at bulk conditions}}$$

$$-R_A = \frac{C_{Ab}}{\frac{1}{k_S} + \frac{1}{k_m}} \quad \text{For first order reaction}$$

$\frac{1}{k_S}$ = resistance due to surface reaction

$\frac{1}{k_m}$ = resistance due to mass transfer

Also $\bar{\eta}_{ext} = \frac{1}{1 + Da}$ **FIRST ORDER**

$$Da = \frac{k_S}{k_m} = \frac{\text{mass transfer resistance}}{\text{kinetic resistance}}$$


Effect of Reaction: Second Order

The physical picture still holds but

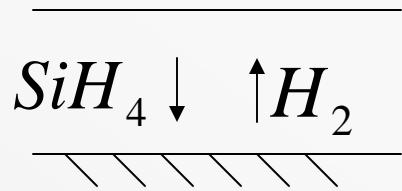
$$(-R_A) = k_{S2} C_{AS}^2$$

$$k_m (C_{AG} - C_{AS}) = k_{S2} C_{AS}^2$$

Let $a = \frac{C_{AS}}{C_{AG}}$ and $Da = k_{S2} \frac{C_{AG}}{k_m}$


$$\frac{1}{Da} (1 - a_s) = a_s^2 = \eta_{ext} \quad \text{Resistances in series do not hold.}$$
$$\eta Da + \sqrt{\eta} - 1 = 0$$

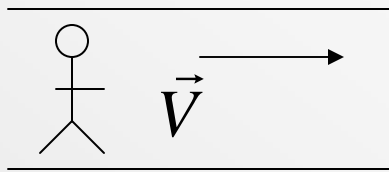
Effect of product counterdiffusion



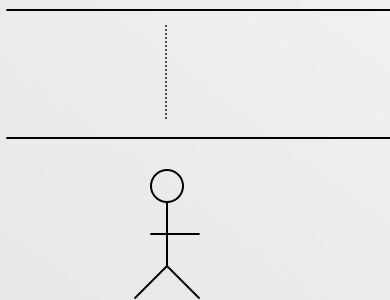
2 moles diffusive in opposite direction for every one mole.



Net velocity is non-zero.



Ficks law: Moving reference



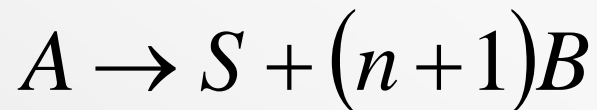
Stationary frame

Need to add convective transport

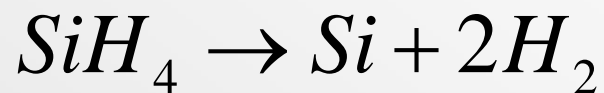
Molar Flux: Stationary Frame

$$\vec{N}_A = \vec{J}_A + C_A \vec{V}$$

$$N_A = -CD \frac{dy_A}{dz} + y_A N_t$$



$$N_B = -(n+1)N_A$$



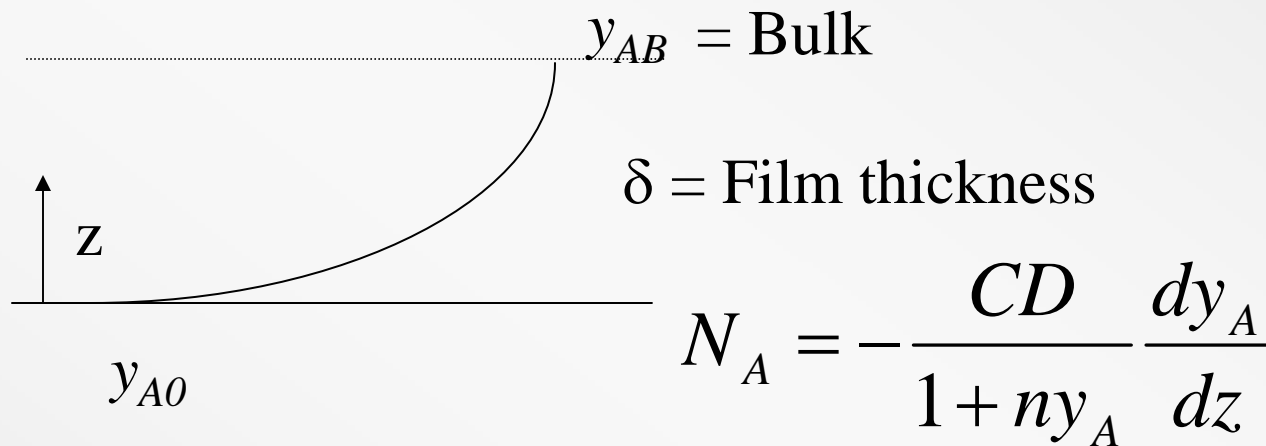
$$N_t = N_A + N_B = -nN_A$$

$$N_A = \frac{-CD}{(1+ny_A)} \frac{dy_A}{dz}$$

$$N_t = C_t V$$

$$y_i = \frac{C_i}{C_t}$$

Effect of counterdiffusion: first order reaction

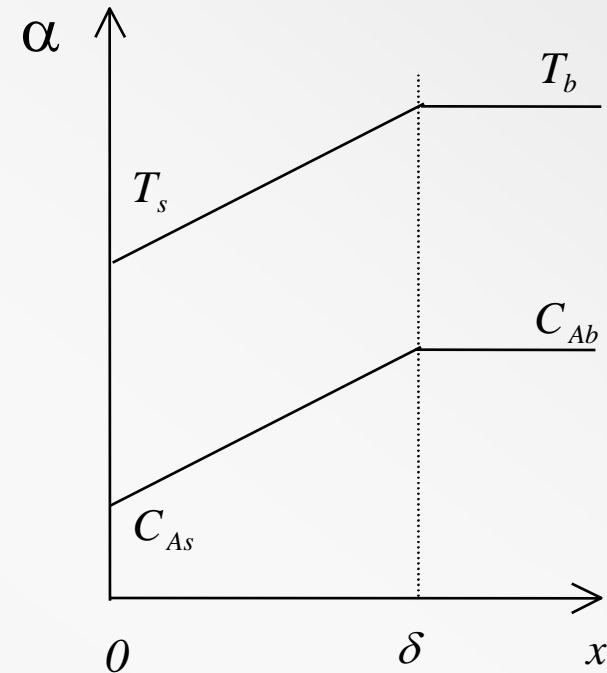
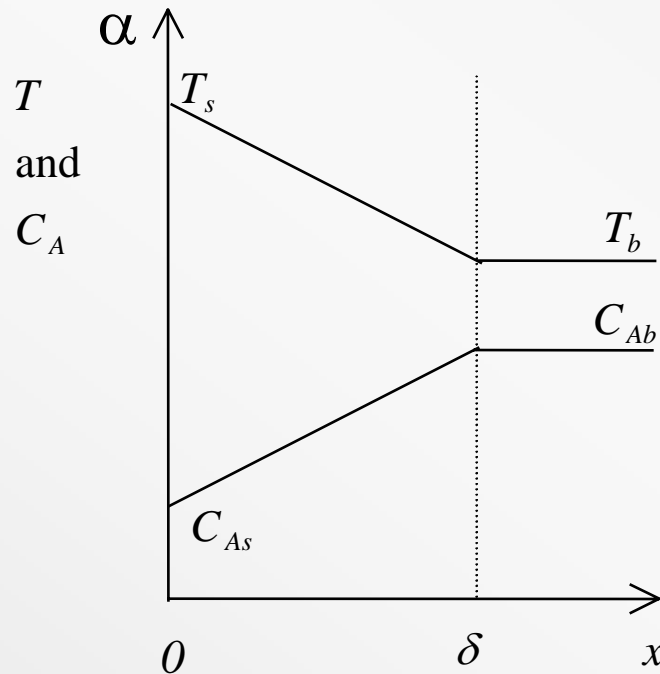


$$\text{B.C. at } z = 0 \quad N_A = R_A = -k_S C y_{A0}$$

$$\text{B.C. at } z = \delta \quad y_A = y_{AB}$$

$$\eta_{ext} = \frac{N_A}{k_S C y_{AB}} = \frac{D/k_S \delta}{\eta y_{AB}} \ln \frac{1 + \eta y_{AB}}{1 + \eta y_{AB} \eta_{ext}}$$

Non-porous system: effect of heat transfer



Schematic representation of the temperature and reactant concentration profiles for

Exothermic reaction

Endothermic reaction

Non-porous system: effect of heat transfer

$$(-R'_A) = k_S e^{-E/RT} C_A^n \text{ (mol/m}^2\text{s)}$$

$$k_m (C_{Ab} - C_{As}) = k_S e^{-E/RT_s} C_{As}^n$$

$$h (T_s - T_b) = (-\Delta H_{rA}) k_S e^{-E/RT_s} C_{As}^n$$

Solve for both C_s and T_s .

$$(-R'_A)_{actual} = k_S e^{-E/RT_s} C_{As}^n = \bar{\eta} k_S e^{-E/RT_b} C_{Ab}^n$$

can be rearranged to a non-linear equation for η_{ext}

Multicomponent Systems

- Transport is described by Stefan-Maxwell Equations

$$\nabla y_i = \sum_{j=1}^n \frac{1}{cD_{ij}} (y_i N_j - y_j N_i)$$

where D_{ij} are the binary pair diffusivity for i - j pair

D_{ij} can be calculated for instance by Chapman-Enskog equation

Note $D_{ij} = D_{ji}$

If $n=3$, then we need three binary pair diffusivities D_{12} , D_{13} and D_{23}

Boundary Conditions

At $z = 0$, $N_i = R_i = f(cy_1, cy_2 \text{ etc.})$

At $z = \delta$, $y_i = y_{i\delta}$ (Bulk values)

$R_i =$ Rate of production by chemical reaction

$$= \sum_{r=1}^{nr} \nu_{ri} r_r$$

*where, $\nu_{ri} =$ stoichiometric coefficient of species i
in the r^{th} reaction*

$r_r =$ rate function for the r^{th} reaction

Numerical solution is usually required (Treat y_i and N_i both as variables)

For a simpler problem see *BSL*, Example 18.5

Pseudo-Binary Diffusivity

This is defined as though Fick's law holds:

$$N_i = -cD_{im} \nabla y_i + y_i \sum_{j=1}^N N_j$$

D_{im} = Pseudo-binary diffusivity of i in the mixture

Rearranging Stefan-Maxwell equation we find:

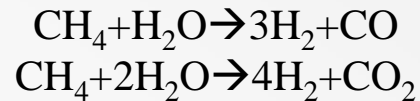
$$\frac{1}{cD_{im}} = \frac{\sum_{i=1}^n \frac{1}{cD_{ij}} (y_j N_i - y_i N_j)}{N_i - y_i \sum_{j=1}^n N_j}$$

In general D_{im} are dependent on positions.

An average value or a constant value can be used as an approximation.

System Invariants

Example: Steam Reforming of Methane



System invariants can be found using MATLAB. Choosing methane and water as the key components:

$$nu = \begin{array}{cccccc} -1 & -1 & 3 & 1 & 0 \\ -1 & -2 & 4 & 0 & 1 \end{array}$$

Use function *rref* to reduce it to an echelon form: *rref*(*nu*)

$$ans = \begin{array}{cccccc} 1 & 0 & -2 & -2 & 1 \\ 0 & 1 & -1 & 1 & -1 \end{array}$$

The invariants are the column vectors for each species

$$\begin{aligned}N_{H_2} &= -2N_{CH_4} - N_{H_2O} \\ N_{CO} &= -2N_{CH_4} + N_{H_2O} \\ N_{CO_2} &= N_{CH_4} - N_{H_2O}\end{aligned}$$

Only two molar fluxes are independent and the rest are tied to these by the relations shown above

Examples

- Chemical Vapor deposition
- Reaction on non-porous surfaces

ChE 512: Topic 2

Reactions in a porous catalyst

(CHE 512)

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ChE 512: Topic 2
Reactions in a porous catalyst

Pore Diffusion and Implications

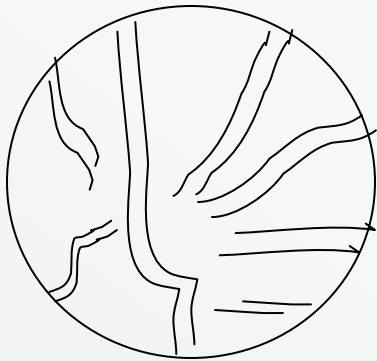
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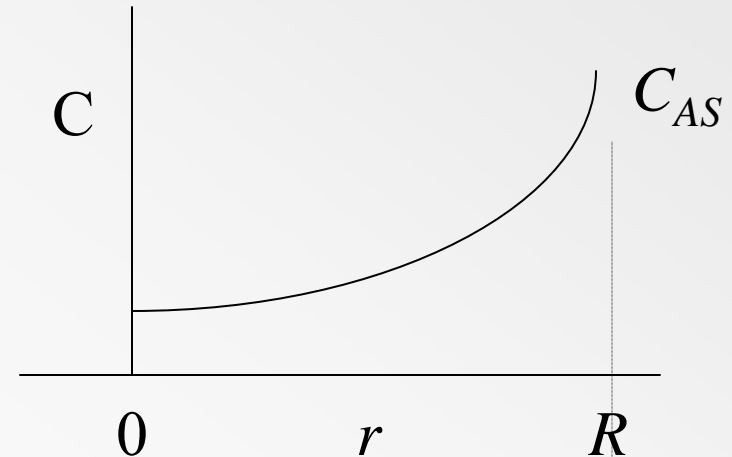
Outline

- Pore diffusion, Effect of pore structure
- Diffusion + Reaction in a porous catalyst
- Effectiveness factor
- Multiple Reactions; Effect of diffusion on rate, selectivity, temperature rise etc
- Numerical Methods

Internal Transport



Schematic of a porous catalyst



Typical concentration profiles within the catalyst

Diffusive flux in the catalyst $= -D_{eA} \frac{dC}{dr}$

D_{eA} = effective or intraparticle diffusion coefficient of species A in the catalyst.

A medium property; not a unique species property

Catalyst Properties

- Mean Diameter = d_p
= $6 \times \text{Volume} / \text{External area}$
- Surface area (internal) per unit mass, S_{int}
- Solid density, ρ_s
- Bulk density, ρ_B
- Average porosity, $\varepsilon_p = 1 - \rho_B / \rho_s$
- Pore volume, $\text{m}^3/\text{kg. catalyst}$

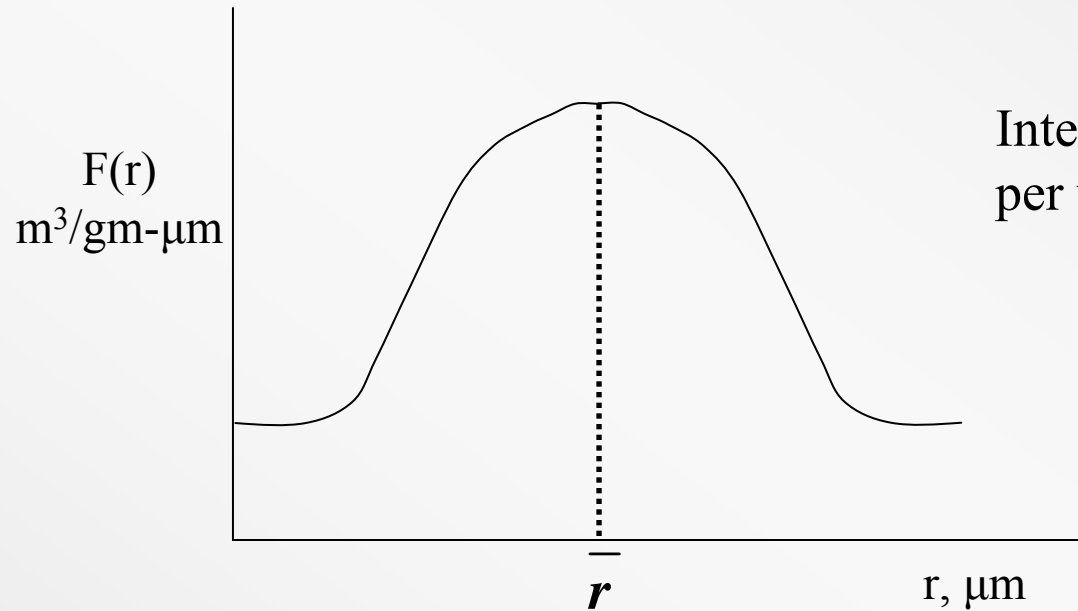
Pore Size Distribution

- Distribution function $F(r)$ defines the pore volume and can be measured by techniques such as Hg porosimetry.
- Volume of pores (per unit mass) in the size r to $r + dr$ is $F(r)dr$.

Units of $F(r)$ is volume/mass / length

- Total volume and average pore radius can be calculated from this distribution function.

Pore Size (Unimodal Case)



Integral under the curve = Pore volume per unit mass of catalyst

Mean Radius:

$$\bar{r} = \int rF(r)dr / \int F(r)dr$$

Bulk Density:

$$1/\rho_B = 1/\rho_s + V$$

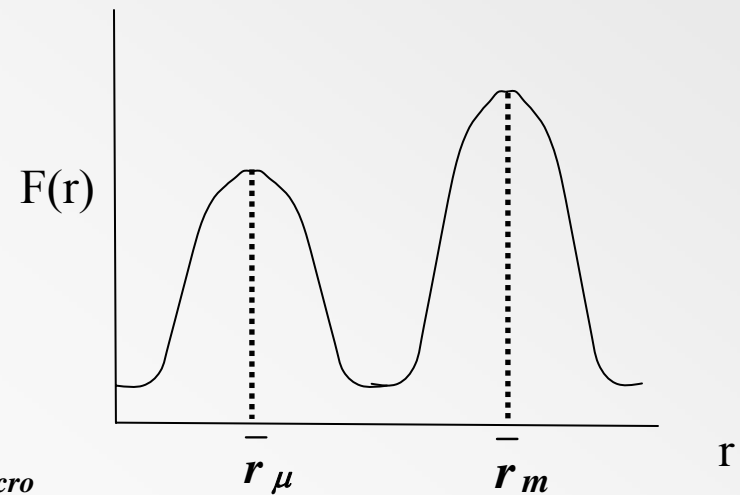
$$\text{Surface area per unit mass} = 2V/\bar{r}$$

(assuming cylindrical pores)

Pore sizes (Bimodal Case)

- Macro-pore volume, V_{macro}
- Micro-pore volume, V_{micro}
- Micropore average size, \bar{r}_{μ}
- Macropore average size, \bar{r}_m
- Bulk density, $1/\rho_B = 1/\rho_s + V_{macro} + V_{micro}$
- Surface area (Total)

$$S = \frac{2V_{macro}}{\bar{r}_{macro}} + \frac{2V_{micro}}{\bar{r}_{micro}} = S_{macro} + S_{micro}$$



Diffusion Mechanisms

- Pore radius \gg mean free path of molecules.
 - Molecular diffusion within the pores
 - Diffusion takes place by molecule to molecule collisions (Ordinary diffusion)
 - No collision with the pore walls
 - Diffusivity in a single pore same as the (pseudo-binary) molecular diffusivity of A in the mixture,
- Pore radius comparable to mean free path
 - Collision with the pore walls predominant mode of transport
 - Knudsen diffusivity in a single pore is given as:

$$D_K = \frac{2}{3} r_e V_A$$

$$V_A = \text{Average speed of A} \\ = (8RT / \pi M_1)^{1/2}$$

$$D_K = 97 r_e (T / M_1)^{1/2}$$

$$D_M = D_{A-mix}$$

Models based on pore size distribution

- Unimodal pore

$$\frac{1}{D_{A,e}} = \frac{1}{D_{M,eff}} + \frac{1}{D_{K,eff}}$$

$$D_{M,eff} = D_M \frac{\varepsilon}{\tau}; \quad D_{K,eff} = D_K \frac{\varepsilon_P}{\tau}$$

$$\tau = \textit{Tortuosity} \cong \frac{1}{\varepsilon_P}$$

- Bimodal pore (macro+micro pores) **Wakao-Smith Model**

$$D_e = \varepsilon_M^2 D_M + \varepsilon_\mu^2 \frac{(1 + 3\varepsilon_M)}{(1 - \varepsilon_M)} D_\mu$$

$$D_{M \text{ or } \mu} = \frac{D_m D_K}{(D_m + D_K)}$$

Governing Differential Equation

Consider a spherical shell located between r and $r + dr$

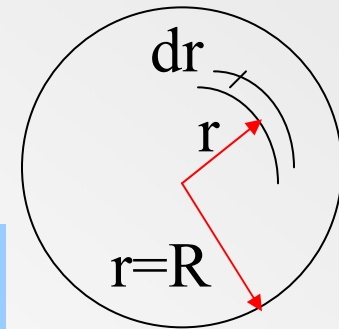
In – Out = - Generation

$$\left(-4\pi r^2 D_e \frac{dC}{dr} \right)_r - \left(-4\pi r^2 D_e \frac{dC}{dr} \right)_{r+\Delta r} = 4\pi r^2 \Delta r k_v C$$

$$\frac{D_e}{r^2} \frac{d}{dr} \left(r^2 \frac{dC}{dr} \right) = k_v C$$

k_v = volumetric reaction rate constant

Rate based on catalyst volume.



Solution for concentration profiles

Transformation $y = cr$ reduces D.E. to a simpler form

$$\text{B.C. at } r = 0 \quad \frac{dC}{dr} = 0$$

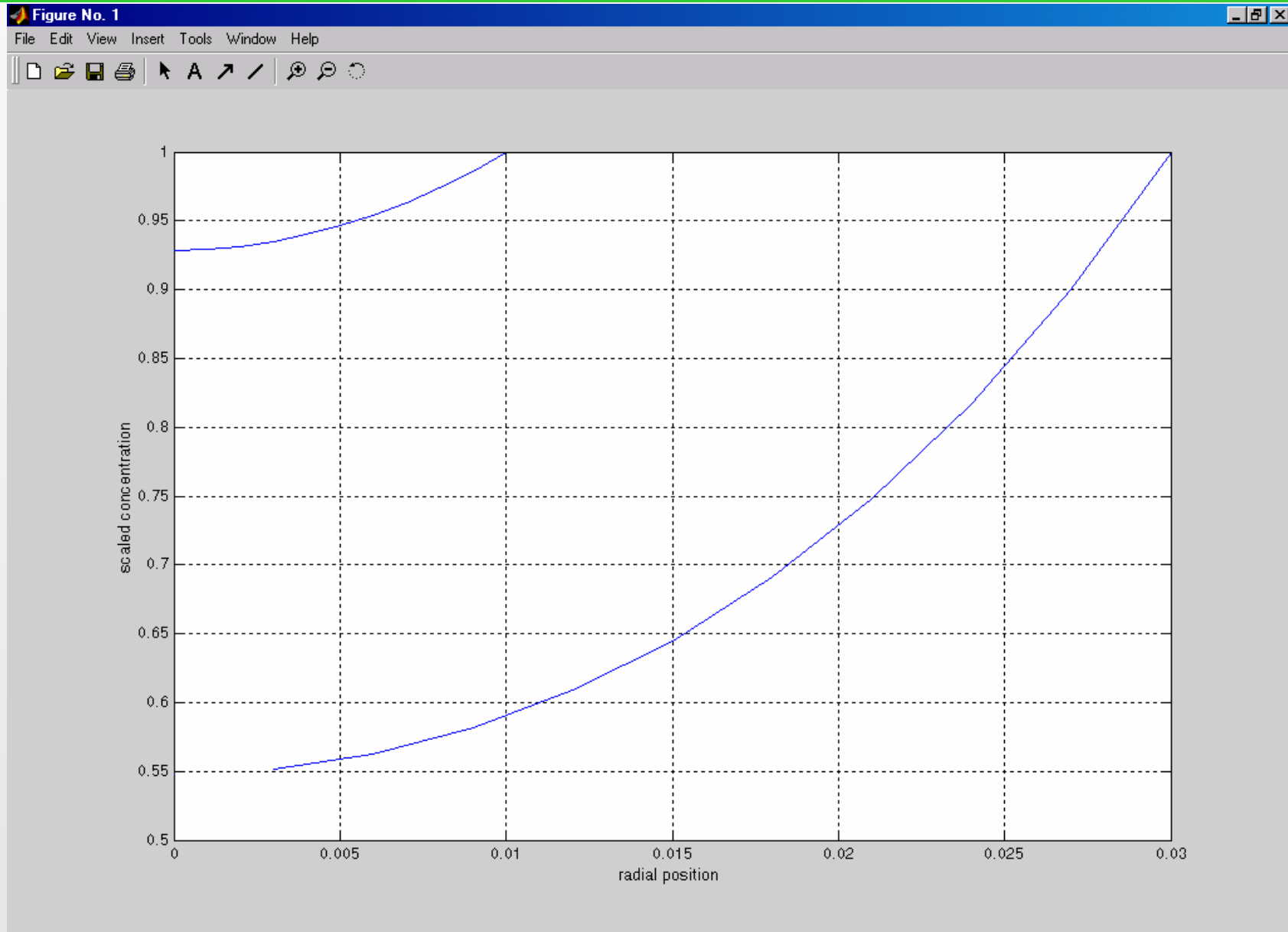
$$\text{B.C. at } r = R \quad C = C_{AS}$$

$$\frac{C_A}{C_{AS}} = \frac{\sinh\left(3\phi \frac{r}{R}\right)}{\frac{r}{R} \sinh(3\phi)}$$

$$\phi = \frac{R}{3} \left(\frac{k_v}{D_{eA}} \right)^{1/2} = \text{Thiele modulus}$$

A measure of relative ratio of particle diffusion time to reaction time.

Concentration profiles within the catalyst



Catalyst Effectiveness

Catalyst effectiveness factor

$$\eta_c = \frac{1}{\phi} \left(\coth(3\phi) - \frac{1}{3\phi} \right)$$

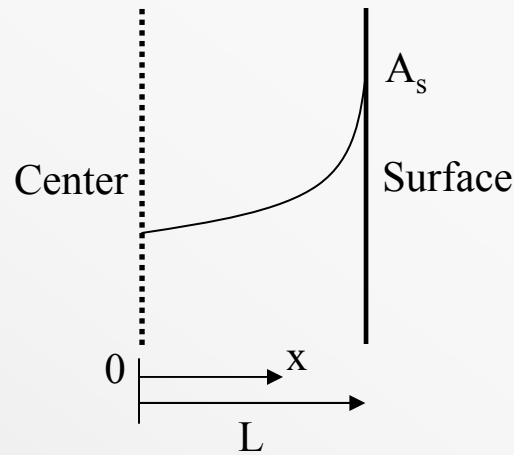
Rate per unit volume of catalyst = $k_v C_{AS} \eta_c$

$$\eta_c = \frac{\text{actual rate}}{\text{rate based on surface concentration}}$$

Actual rate = $\int_0^R 4\pi r^2 k_v C dr$ = An integral average rate

Actual rate from flux = $4\pi R^2 D_e \left(\frac{dc}{dr} \right)_{r=R}$

Slab Model: General Kinetics



$L = \text{Half slab thickness} = V_p/S_p$

$$D_{e,A} \frac{d^2 A}{dx^2} = k_v A \quad (\text{First order reaction})$$

$$\text{Thiele Modulus} = L \sqrt{\frac{k}{D_{e,A}}}; \quad \eta_c = \frac{\tanh \phi}{\phi}$$

General Kinetics:

$$D_{e,A} \frac{d^2 A}{dx^2} = k_v A^m \quad \text{or} \quad f(A)$$

Numerical Solutions or approximate asymptotic solution

Multiple Reactions:

$$D_{e,i} \frac{d^2 A_i}{dx^2} = \sum_{j=1}^{nr} \nu_{ji} r_j$$

Shape Normalization

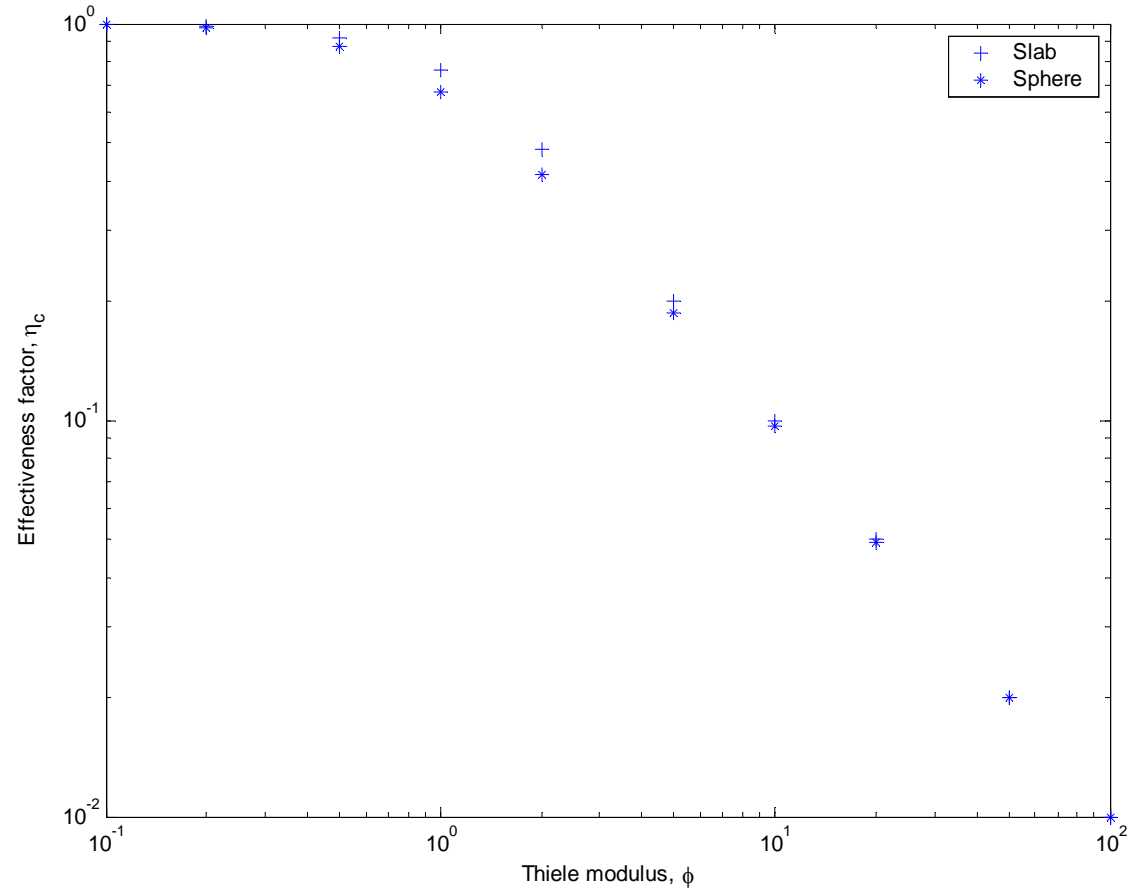
$$L = \frac{V_p}{S_p} = \frac{R}{3}$$

For a sphere

Thiele Modulus =

$$L \sqrt{\frac{k}{D_e}}$$

$$\eta_c = \frac{\tanh \phi}{\phi}$$



Problem 1: Rate for larger size given kinetics

Rate of reaction over a finely crushed catalyst of radius of 0.5 mm was measured as 10.0 mole/sm³ catalyst.

Temperature is 400 K and
pressure is 10⁵ Pa and
mole fraction of reactant in the gas is 0.1.

Find the rate for a catalyst of pellet radius of 3mm.

Solution to Problem 1

Assume $\eta_c = 1$ for small catalyst.

$$C_{Ag} = \frac{yP}{RT} = \frac{0.1 \times 10^5}{8.314 \times 400} = 3.007 \frac{\text{mol}}{\text{m}^3}$$

$$\text{Rate} = kC_{Ag} \quad \text{Hence} \quad k = \frac{\text{Rate}}{C_{Ag}} \quad k = \frac{10 \text{ mol} / \text{m}^3 \text{ s}}{3.007 \text{ mol} / \text{m}^3} = 3.3256 \text{ s}^{-1}$$

To find rate for larger catalyst, we need an estimate of intraparticle diffusion coefficient.

Let $D_e = 4 \times 10^{-6} \text{ m}^2/\text{s}$ (a reasonable estimate)

Then

$$\phi = \frac{R}{3} \sqrt{\frac{k}{D_e}} = 0.9118 \quad \eta_c = 0.7051$$

$$\text{Rate} = \eta_c k C_{Ag} = 7.05 \text{ mole} / \text{m}^3 \text{ s}$$

Diagnositics: The Weisz Modulus

Given the measured rate, establish if there is significant pore diffusion resistance.

$$M_w = \text{Weisz Modulus} = \frac{L^2 (-R_A)_{obs}}{C_{Ag} D_e}$$

where $L = R / 3 =$ characteristic length scale

If Weisz modulus (Wagner modulus) < 0.15 , then the concentration profile in the pellet is nearly uniform.

Note $M_w = \eta_c \phi^2$

Problem 2: Test for pore resistance

A rate of 10^5 mole/hr m^3 cat is observed for a gas concentration of A of 20 mole/ m^3 . The catalyst particle diameter is 2.4 mm.

An independently measured value is needed to solve this problem. Let us assume effective diffusivity is 5×10^{-5} m^2 /hr.

Is there a strong pore diffusion resistance?

Solution to Problem 2

$$L = R / 3 = 4 \times 10^{-4} \text{ mm}$$

$$\text{Wagner modulus} = M_T = \frac{L^2(-R_A)}{D_e C_{Ag}} = 16$$

Strong pore resistance

The measured data are not representative of true or “intrinsic” kinetics.

Problem 3: Intrinsic kinetics

In Problem 2, find the effectiveness factor and the true rate constant.

Solution

$$\text{rate} = k\eta C_{Ag} \rightarrow k\eta = \frac{\text{rate}}{C_{Ag}} = 5000 \text{ hr}^{-1}$$

Since η depends on k , we used a trial and error solution. We expect η to be small. Let us assume some value, say 0.01.

Then $k = \frac{5000}{\eta} = 5 \times 10^5$

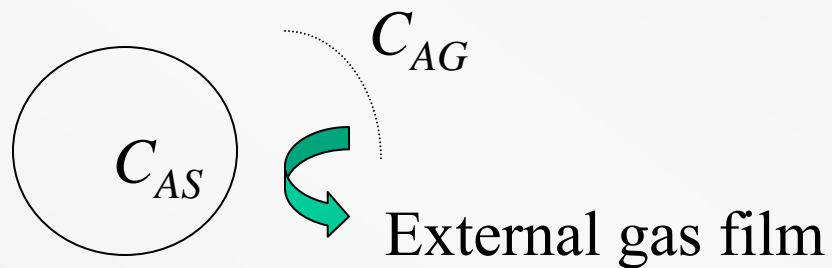
$$\text{Thiele modulus} = L \sqrt{\frac{k}{D_e}} = 40$$

$$\eta = \frac{\tanh \phi}{\phi} = 0.025$$

Solution to Problem 3 con't

η assumed	$k=5000/\eta$	Thiele	η equation
0.01	5×10^5	40	0.025
0.03	1.67×10^5	23	0.0433
0.063	7.93×10^4	15.9	0.0627

External + Internal Transport



$$\begin{aligned}(-R_A) &= 4\pi R^2 k_m (C_{AG} - C_{AS}) \\ &= 4\pi R^3 k \eta_c C_{AS}\end{aligned}$$

Overall effectiveness factor

$$\eta_o = \frac{\text{actual rate}}{\text{rate based on bulk conditions}}$$

Overall effectiveness factor

First order reaction

$$\eta_o = \eta_c \frac{C_{AS}}{C_{AG}}$$

$$\frac{C_{AS}}{C_{AG}} = \frac{1}{1 + \phi^2 \frac{\eta_c}{Bi_M}}$$

where $Bi_M = k_m \frac{R}{D_e} = \text{Biot number for mass transfer}$

$$\eta_o = \frac{\eta_c Bi_M}{Bi_M + \phi^2 \eta_c}$$

$$\frac{1}{\eta_o} = \frac{1}{\eta_c} + \frac{\phi^2}{Bi_M}$$

- Addition of resistances.
- More complex for other orders (nonlinear kinetics) but the concept is the same.
- Thiele modulus is a function of surface concentration for non-linear kinetics.

**Matlab solution to diffusion-reaction
problems
(CHE 512)**

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1 Matlab solution to diffusion-reaction problems

Diffusion-Reaction problems are very common in chemical reaction engineering and often numerical solutions are needed. Here we look at using matlab to obtain such solutions and get results of design interest. Consider a model problem represented as:

$$\frac{d^2c}{dx^2} = f(c) \quad (1)$$

which is a dimensionless form of the diffusion with reaction problem. Here $f(c)$ is a measure of the reaction rate; For example, $f(c) = \phi^2c$ for a first order reaction where ϕ is the Thiele modulus. The variable x is a dimensionless distance along the pore. The point $x = 0$ is taken as the pore mouth and $x = 1$ pore end. The boundary conditions are taken as follows:

At $x = 0$, the dimensionless concentration, $c = 1$.

At $x = 1$, the gradient of the concentration, $dc/dx = 0$.

We use the matlab program `bvp4c` to solve this problem. This requires that the Eqn. (1) be written as two first order equations rather than as a single second order differential equation. This can be done as follows: Consider a solution vector \vec{y} with components y_1 and y_2 defined as follows:

$$y_1 = c \text{ and } y_2 = dc/dx \quad (2)$$

Eqn. (1) is then equivalent to the following two first order equations.

$$\frac{dy_1}{dx} = y_2 (= dc/dx) \quad (3)$$

and

$$\frac{dy_2}{dx} = f(y_1) = (d^2c/dx^2) \quad (4)$$

The boundary conditions are as follows:

$$\text{at } x=0; y_1 = 1 \text{ Pore mouth} \quad (5)$$

and

$$\text{at } x=1 y_2 = 0 \text{ Pore end} \quad (6)$$

The solution for the concentration profile and also for the local values of the gradient can then be obtained using the function `bvp4c` in matlab. The effectiveness factor is related to the gradient at the pore mouth and is calculated as:

$$\eta = -y_2(0)/\phi^2 \quad (7)$$

(verify)

The sample code for solving this problem is as follows:

```
-----  
% program calculates the concentration profiles and the effectiveness  
% factor for m-th order reaction in a slab geometry.  
global phi m phi2 n  
global eta  
  
% user actions, Specify parameters, a guess function for trial solution, a
```

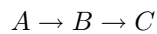
```

% a function odes to define the set of first order differential equations
% and a function bcs to specify the boundary conditions.
% Also define a function to provide initial starting solutions.
phi = 2.0 ; % thiele modulus for first reaction
m =2.0 ; % order of reaction
nmesh = 21 % intial mesh
nplot = nmesh ; % meshes for plotting the result.
% solution block.
x = linspace ( 0, 1, nmesh ) ;
solinit =bvpinit ( x , @guess ) % trial solution given by guess function
sol = bvp4c (@odes, @bcs, solinit) % bvp solved,
% post processing. plot concentration profiles, find eta
x = linspace ( 0, 1, nplot ) ;
y = deval(sol, x) ;
y(1,:) % concentration profiles displayed
plot ( x, y(1,:) ) ; % these are plotted.
eta = -y(2,1) / phi^2
%-----
function yinit = guess (x)
% provides a trial solution to start off
global phi m phi2 n
y1= exp(-phi*x)
y2= 0. * y1
yinit = [y1
         y2 ] ;
%-----
function dydx = odes ( x, y )
% defines the rhs of set of first order differential equations
global phi m phi2 n

dydx = [ y(2)
         phi^2 * y(1)^m
         ] ;
%-----
function res = bcs ( ya , yb)
% provides the boundary conditions at the end points a and b
res = [ ya(1) - 1
       yb(2) ] ;
%-----

```

It is fairly easy to extend the code to multiple reactions. As an example consider a series reaction represented as:



The governing equations are as follows assuming both reactions to be first order.

$$\frac{d^2 c_A}{dx^2} = \phi_1^2 c_A \quad (8)$$

$$\frac{d^2 c_B}{dx^2} = -\phi_1^2 c_A + \phi_2^2 c_B \quad (9)$$

The boundary condition at $x = 0$ (pore mouth) depend on the bulk concentrations of A and B. The boundary condition at $x = 1$ (pore end) is the no flux condition for both A and B.

The solution vector y has size of four and consists of:

$$\vec{y} = \begin{pmatrix} y_1 = c_A \\ y_2 = dc_A/dx \\ y_3 = c_B \\ y_4 = dc_B/dx \end{pmatrix} \quad (10)$$

The system is now formulated as four first order ODEs for the four components of the solution vector and solved by `bvp4c` in exactly the same way. Details are left out as homework problem.

An important consideration in this type of problem is how the selectivity is affected by pore diffusion. The yield of B is defined as:

$$\text{Yield} = \text{flux of B out of the pore mouth} / \text{flux of A into the pore}$$

which can be stated as:

$$\text{Yield} = -(dc_b/dx)_{x=0} / (dc_a/dx)_{x=0} \quad (11)$$

The relative concentration gradients of A and B at the pore mouth determines the local yield of B. A smaller catalyst size is favorable to B production. A larger particle traps B in the interior of the pores allowing it to react further and form C. This reduces the yield.

Maximum yield = $(k_1 C_{A0} - k_2 C_{B0}) / k_1 C_{A0}$ which is also equal to

$$\text{maximum yield} = 1 - \frac{k_2 C_{B0}}{k_1 C_{A0}}$$

with C_{A0} and C_{B0} representing the pore mouth concentrations.

Pore diffusion resistance causes the yield to decrease from the above maximum value. Maximum yield is realized only at low values of the Thiele parameters.

Example simulated with matlab for a particular case illustrates this point.).

Consider $\phi_1 = 2$ and $\phi_2 = 1$. Also $c_{a0} = 1$ and $c_{b0} = 0$ which may correspond to the inlet of the reactor (with no recycle), Yield is found as 0.8067.

Now let the catalyst size be reduced to one half the original size. Then both ϕ_1 and ϕ_2 decrease. The new value of yield is found to be 0.8764. Maximum yield is 1 for both of these cases. The pore diffusion resistance has decreased the yield but the reduction is even more for the larger particles.. Students should verify these using matlab.

2 Asymptotic Solution to diffusion-reaction problems

For a single non-linear reaction problem, a solution can be obtained analytically for large values of Thiele modulus. This asymptotic solution can then be used to define a generalized Thiele modulus and can be extended to obtain approximate analytical solutions even for low Thiele modulus. This avoids solution by numerical methods and is useful in reactor design where repeated calculation of the effectiveness factor at different points in the reactor is often needed. The procedure is illustrated below.

Consider a model problem represented as:

$$D_e \frac{d^2 c}{dx^2} = f(C) \quad (12)$$

where $f(C)$ is the rate (dimensional) of consumption of species. The order of the differential equation can be reduced by one by using the transformation $p = dC/dx$. Noting that

$$\frac{d^2C}{dx^2} = p \frac{dp}{dC} \quad (13)$$

we find that Eq. (12) can be written as

$$D_e p \frac{dp}{dC} = f(C) \quad (14)$$

The above equation can be solved by separation of variables. Two limits are needed to obtain the value of the concentration gradient at the surface, p_s . At the pore end, the value of the gradient p is zero. Also for large values of Thiele modulus the concentration drops to nearly zero at some interior point in the catalyst. Hence the concentration can be set as zero at the pore end. Thus we can set $C = 0$ at $p = 0$ as one of the limits for integration of Eqn. (14). Let the surface gradient be designated as p_s and the concentration at the surface as C_s . This sets another limit for integration of Eqn 13 which can be now be written as:

$$D_e \int_0^{p_s} p dp = \int_0^{C_s} f(C) dC \quad (15)$$

Integrating and rearranging

$$p_s = - \left[2/D_e \left(\int_0^{C_s} f(C) dC \right) \right]^{1/2} \quad (16)$$

The minus sign is used for the square root since the concentration is decreasing with increase in x . The effectiveness factor is given by the ratio of the actual rate to that based on surface concentration.

$$\text{Actual rate} = -D_e p_s S_p \quad (17)$$

by Ficks law applied at the surface. Hence the effectiveness factor is given by:

$$\eta = -D_e p_s S_p / V_p f(C_s) \quad (18)$$

Using the Eq. 16 for p_s we find

$$\eta = (S_p/V_p) f(C_s) \left[2D_e \int_0^{C_s} f(C) dC \right]^{1/2} \quad (19)$$

The above result is applicable for any kinetics provided we are in the asymptotic region. For a first order reaction $\eta = 1/\Lambda$ for large Thiele modulus. In order to make the results in the same format it is convenient to define a Thiele modulus for any kinetics as:

$$\Lambda = (V_p/S_p) f(C_s) \left[2D_e \int_0^{C_s} f(C) dC \right]^{-1/2} \quad (20)$$

which is known as the generalized Thiele modulus. Now we have $\eta = 1/\Lambda$ for any kinetics but only in the asymptotic case. The expression for η is now generalized as:

$$\eta = \frac{\tanh(\Lambda)}{\Lambda} \quad (21)$$

The above expression is strictly valid only in the asymptotic region where $\tanh(\Lambda)$ tend one but is used for the entire range of Λ values as an approximate solution.

Problems on asymptotic solution

1. What form does the Thiele modulus take for an m -th reaction? What is the effect of surface concentration of the Thiele modulus? What is the effect of surface concentration on the effectiveness factor in the asymptotic region for (a) second order reaction, (b) half order reaction?
2. What form does the expression for the generalized Thiele modulus take for a L-H kinetics of the form

$$f(C) = kC/(1 + KC)$$

Write an analytical expression for the effectiveness factor for such reactions. Express the result in terms of the two dimensionless groups: (i) kL^2/D_e and (ii) KC_s . Find the values of η for some chosen values of these parameters and compare it with the numerical solution generated using matlab. Find the region where the errors are maximum. What is the order of maximum error in the approximate analytical solution?

3. Zero order kinetics have special features. The effectiveness factor is equal to 1 up to a value of Thiele modulus at which the concentration at the center of catalyst becomes zero. Find this critical Thiele modulus. What are the operational implications of this result?

3 Effective Diffusion Coefficient

The pore diffusion rate plays an important role in affecting the rate of gas-solid reactions as shown in the earlier sections. The effective diffusivity in the pore D_e is however a medium properly and some models are useful to estimate these in the absence of actual data. The diffusion within the catalyst proceed by two mechanisms: (1) Bulk diffusion within the pores.(2) Bombardment with the walls of the pore if the pore radius is small. The second mechanism is known as Knudsen diffusion.

The bulk diffusion within the pores is a result of gas-gas collision and for a single pore the diffusivity is the same as the gas phase binary diffusivity (for ab binary pair). This value of diffusivity is corrected for the pore structure by incorporating two factors (1) porosity, ε which accounts for the reduced area accessible for diffusion and (2) tortuosity, τ which accounts for the non-straight path for diffusion.

$$D_{b, eff} = D_{12} \frac{\varepsilon}{\tau}$$

Knudsen diffusion occurs when the size is the pores of the order of mean free path of the diffusivity molecule. The molecules now collide more frequently with the pore walls rather than with other molecules. the Knudsen diffusion coefficient in a cylindrical pore is given as:

$$D_K = \frac{2}{3} r_e V_1$$

where r_e = is the effective pore radius and V_1 is the average molecular speed of species 1. This is given from the kinetic theory of gases as:

$$V_1 = \left(\frac{8 RT}{\pi M_1} \right)^{1/2}$$

Substituting the values of gas constants, we find the following dimensional equation for the Knudsen diffusion coefficient for species 1:

$$D_{K,1} = 97 r_e \left(\frac{T}{M_1} \right)^{1/2} \quad (22)$$

in m^2/s with r_e in m and T in Kelvins.

The Knudsen diffusion coefficient in the actual pore is then corrected for the porosity and tortuosity and is given by:

$$D_{K, eff} = \frac{\varepsilon}{\tau} D_K$$

The phenomena of ordinary diffusion and Knudsen diffusion, may be occurring simultaneously. The two can be combined by the following formula:

$$\frac{1}{D_{1, eff}} = \frac{1}{D_{b, eff}} + \frac{1}{D_{K, eff}}$$

Additional mechanism is the surface diffusion where the adsorbed species migrates along the surface. The effects are often ignored if the pores are relatively large. This phenomena may be of importance in monolith type of catalysts.

4 Diffusion in bidisperse media

Catalysts often have a bimodal pore size distribution with micropores and macropores. The model of Wakao-Smith is useful for predicting the effective diffusion coefficients in such systems. According to their model, the effective diffusivity is given as:

$$D_e = \varepsilon_M^2 D_M + \varepsilon_\mu^2 \frac{(1 + 3\varepsilon_M)}{(1 - \varepsilon_M)} D_\mu \quad (23)$$

where ε_M is the void fraction associated with the macropores and D_M is the diffusivity associated with it. Similarly, the term ε_μ is the void fraction associated with the micropores. The term, D_μ in the above equation is the diffusion coefficient associated with the micropores. The diffusivities are calculated by combining the molecular and Knudsen contributions in parallel as:

$$D_{M \text{ or } \mu} = D_m D_K / (D_m + D_K) \quad (24)$$

where D_m is the molecular diffusivity and D_K is the Knudsen diffusivity calculated according to Eqn. (22). The macropore radius, r_M and micropore radius, r_μ are needed for the Knudsen calculations.

Surface area of catalyst associated with pores depend on the pore radius and can be represented as:

$$S_{in} = 2\varepsilon_M/r_M + 2\varepsilon_\mu/r_\mu \quad (25)$$

where S_{in} is the internal surface area per unit catalyst volume. The above expression assumes that the pores are cylindrical. The rate is generally proportional to the surface area. Thus if k_s is the rate constant per unit surface area, then the rate constant k_v based on the catalyst volume is:

$$k_v = k_s S_{in} \quad (26)$$

The Thiele modulus for a first order reaction defined earlier as;

$$\Lambda = (V_p/S_p)(k_s S_{in}/D_e)^{1/2} \quad (27)$$

is thus a complex function of the pore structure. Qualitatively speaking, the micropores increase the area but have lower diffusivity. The macropores have the opposite effect. They are easily accessible (larger diffusivity) but contribute less to the rate constant since they have lower surface area per volume. Hence there is an optimum catalyst structure for a given reaction that gives the best effectiveness factor. The above considerations provide a simple basis to optimize the pore structures of the catalysts.

5 Stefan-Maxwell model for multicomponent diffusion

Mass transport in isothermal multicomponent systems in the gas phase is described by the following constitutive equation.

$$-\frac{dC_i}{dx} = \sum_{j=1}^n \frac{y_j N_i - y_i N_j}{D_{ij}} \quad (28)$$

where n is the number of components and D_{ij} is the binary pair diffusivity in the gas phase.

For porous catalysts the equation is modified by including both Knudsen and bulk diffusion.

$$-\frac{dC_i}{dx} = \frac{N_i}{D_{Ke,i}} + \sum_{j=1}^n \frac{y_j N_i - y_i N_j}{D_{ij,e}} \quad (29)$$

The mass balance for a differential control volume (for a 1-D slab geometry) gives

$$\frac{dN_i}{dx} = \sum_i^{nr} \nu_{ji} r_j \quad (30)$$

where the RHS is the total rate of production of species i from the various reactions. The term r_j is the rate function for the j -th reaction which is the function of the local concentrations of the various species. Eqn. (29 and 30 have to be integrated together now.

Note that Eqn. 29 can be written in terms of the component partial pressures as:

$$-\frac{1}{R_G T} \frac{dp_i}{dx} = \frac{N_i}{D_{Ke,i}} + \sum_{j=1}^n \frac{p_j N_i - p_i N_j}{P_t D_{ij,e}} \quad (31)$$

where P_t is the total pressure and R_G is the gas constant. Since the rates of reactions are usually correlated as a function of partial pressures, the above form is often more convenient. The viscous contribution to flow is neglected in these equations. It does not mean that the catalyst pellets are isobaric; pressure gradients can exist in the pellets and they are implicitly accounted for by the use of the constitutive equations in terms of the partial pressures rather than in terms of component mole fractions.

A structure of a matlab program for solving these equations is presented here.

```
function StefanMaxwell ()
% program calculates the concentration profiles and the effectiveness
% factor based on Stefan-Maxwell model.
% 3-07-05 written by P. A. Ramachandran
% test problem 1 in the paper by Haynes
% user actions, Specify parameters, a guess function for trial solution, a
% function odes to define the set of first order differential equations
% and a function bcs to specify the boundary conditions.
% also define rate in the function ratemodel.

global ns neq
ns = 4 % four species
neq = 8 % 4*2 equations
% Eight variables Y(1) to y(4) are the concentrations of CO, H2O, CO2 and
```

```

% H2, y(5) to y(8) are the flux values.
% parameters used are as follows:

global temp pressure
global ctot
temp = 400+273.;
pressure = 25.0 ; % atm
Rgas = 82.06 % gas constant in cm^3 atm /g-mole K
ctot = pressure/Rgas/temp; % total concentration mole/c.c

% surface (pore mouth) mole fraction
global ys
ys(1) = 0.1; ys(2) = 0.6; ys(3) = 0.08; ys(4) = 0.22 ;
ys = ys * ctot % surface molar concentrations.

% rate and other parameters
global k rhop Keq
k = 2.05e-04 ;
rhop = 1.84 ;
Keq = 12.0

% diffusion parameters; dk = knudsen ; db = binary pair (a matrix)
global dk db
dk(1) = 0.00649;
dk(2) = 0.00494 ;
dk(3) = 0.0098;
dk(4) = 0.0231;
% **** add db values for binary pairs
% catalyst properties
length = 0.1588 ;
rate_s = reactionrate(ys) ; % rate based on surface values
nmesh = 21 % initial mesh
nplot = nmesh ; % meshes for plotting the result.
% solution block.
x = linspace ( 0, 1, nmesh ) ;
solinit =bvpinit ( x , @guess ) % trial solution generated by guess function
sol = bvp4c (@odes, @bcs, solinit) % bvp solved,
% post processing. plot concentration profiles, find eta
x = linspace ( 0, length, nplot) ;
y = deval(sol, x) ;
% concentration profiles of various components.
y(1,:);
y(3,:);
y(2,:);
y(4,:);
plot ( x, y(1,:) , '-+' ) ;% hold on ; plot ( x, y(2,:), '-+' ) % these are plotted.
% flux values for the four species.
y(5,1)

```

```

y(6,1)
y(7,1)
y(8,1)
rate_s
eta = y(5,1)/rate_s /0.1588
%-----
function yinit = guess (x)
global phi m phi2 n
global ys
global k rhop Keq
% find rate based on surface values and use it as trial value for flux
%rate=rhop* k * ys(1)^0.9 * ys(2)^0.3 * ys(3)^(-0.6) * (1.- ys(3) * ys(4)/Keq/ys(1) /ys(2) )
rate= reactionrate(ys) ;
yinit = [ys(1)
         ys(2)
         ys(3)
         ys(4)
         -rate
         -rate
         rate
         rate      ] ; % guess values here
%-----
function dydx = odes ( x, y )

global ns neq
global ctot
global k rhop Keq
global dk db
rate = reactionrate(y);
% bulk diffusion terms to be added. Currently set as zero
bulkterm = zeros (ns,1);
dydx = [- y(5) /dk(1) + bulkterm(1)
        - y(6)/dk(2)
        -y(7)/dk(3)
        -y(8)/dk(4)
        -rate
        -rate
        rate
        rate ] ;
%-----
function res = bcs ( ya , yb)
global a0 b0
global ys
res = [ ya(1) - ys(1)
        ya(2) - ys(2)
        ya(3) - ys(3)
        ya(4) - ys(4)
        yb(5)

```

```

        yb(6)
        yb(7)
        yb(8) ] ;
%-----
function ratemodel = reactionrate(y)
global k rhop Keq
global temp pressure
global ctot
p = y*82.06*temp % species partial pressures
ratemodel =rhop* k * p(1)^0.9 * p(2)^0.3 * p(3)^(-0.6) * (1.- p(3) * p(4)/Keq/p(1) /p(2) ) ;

```

6 Temperature Effects

The simultaneous transport of heat and mass in a porous catalyst can be represented by the following set of equations.

$$D_e \frac{d^2 C}{dx^2} = f(C, T) \quad (32)$$

$$k_e \frac{d^2 T}{dx^2} = (\Delta H) f(C, T) \quad (33)$$

where k_e is the effective conductivity of the catalyst and ΔH is the heat of reaction. The local rate (of disappearance) $f(C, T)$ is now a function of both the pore concentration and the temperature at any point in the pellet.

The boundary conditions are specified as follows: No flux condition is imposed at the pore end ($x = 0$) for both heat and mass.

$$\text{at } x=0 \quad dC/dx = 0; \quad dT/dx = 0$$

At the pore mouth ($x = L$) the flux into the pellet must match the transport through the gas film. This leads to the following boundary conditions.

For mass transport

$$D_e \left(\frac{dC}{dx} \right)_{x=L} = k_m (C_g - C_{x=L})$$

For heat transport

$$k_e \left(\frac{dT}{dx} \right)_{x=L} = h (T_g - T_{x=L})$$

The equations can be put in terms of dimensionless variables by scaling the concentration and temperature by reference values. The bulk concentration and temperature can be used as the reference values if the particle scale model is being analyzed. For reactor scale models, the inlet feed conditions can be used as reference.

The dimensionless mass and heat transport equations are then as follows:

$$\frac{d^2 c}{d\xi^2} = \frac{f(C_{ref}, T_{ref}) L^2}{D_e C_{ref}} [f^*(c, \theta)] \quad (34)$$

where ξ is dimensionless distance x/L and f^* is a dimensionless rate defined as:

$$f^* = f(C, T) / [f(C_{ref}, T_{ref})]$$

The first term on the RHS of 34 can be identified as a Thiele parameter

$$\text{Let } \phi^2 = \frac{f(C_{ref}, T_{ref}) L^2}{D_e C_{ref}}$$

Then the mass balance equation is:

$$\frac{d^2 c}{d\xi^2} = \phi^2 f^*(c, \theta) \quad (35)$$

The heat balance equation can be represented as:

$$\frac{d^2 \theta}{d\xi^2} = -\beta \phi^2 f^*(c, \theta) \quad (36)$$

where β is the dimensionless parameter (thermicity group) defined as:

$$\beta = \frac{(-\Delta H)D_e C_{ref}}{k_e T_{ref}} \quad (37)$$

Note the β takes a positive value for exothermic reactions and a negative value for endothermic reactions.

The boundary conditions can be normalized as:

$$\text{at } \xi = 0 \quad dc/d\xi = 0; \quad d\theta/d\xi = 0$$

and the conditions at $\xi = 1$ can be related to the Biot numbers for heat and mass

$$\left(\frac{dc}{d\xi}\right)_s = Bi_m(c_g - c_s)$$

$$\left(\frac{d\theta}{d\xi}\right)_s = Bi_h(\theta_g - \theta_s)$$

where the subscript s is used for the $\xi = 1$ i.e., the surface values. Here we define

$$Bi_m = k_m L / D_e$$

and

$$Bi_h = hL / k_e$$

The magnitude of the internal temperature gradient can be assessed by combining the above two equations without even actually solving the equations. The mass and heat transport equations 35 and 36 can be combined as:

$$\frac{d^2\theta}{d\xi^2} + \beta \frac{d^2c}{d\xi^2} \quad (38)$$

Hence the integration of the above equation twice leads to

$$\theta - \theta_s = \beta(c_s - c) \quad (39)$$

The maximum value of the temperature occurs for an exothermic reaction when the center concentration drops to zero. This occurs in the strong pore diffusion resistance for mass transfer. Hence an estimate of the internal gradients is:

$$\text{Max } \theta_c - \theta_s = \beta c_s = O(\beta) \quad (40)$$

where θ_c is the center temperature and the symbol O means 'of the order of'.

Also the magnitudes of the external gradients can be estimated by the following procedure: Here we introduce the overall effectiveness factor η_0 defined as: $\eta_0 = \text{actual rate} / \text{rate based on reference conditions}$

Rate of transport to the surface is equal to $S_p k_m (C_g - C_s)$

Rate of reaction is $V_p f(C_{ref}, T_{ref}) \eta_0$.

Equating the two and using the dimensionless groups we find as estimate of the external concentration gradients.

$$c_g - c_s = \frac{\phi^2 \eta_0}{Bi_m} \quad (41)$$

Note that $\phi^2\eta_0$ is the same as the Weisz modulus and can be directly calculated if the measured data is available. The value of η_0 need not be explicitly evaluated in order to use the above equation for diagnostic purposes.

$$\phi^2\eta_0 = (-R_{measured})L^2/(D_eC_{ref}) \quad (42)$$

Similar analysis equating the heat transport in the film to the total heat released from the reaction leads to an estimate the film temperature difference.

$$\theta_s - \theta_g = \frac{\beta\phi^2\eta_0}{Bi_h} \quad (43)$$

The above relations enables a rapid determination or the relative importance of external and internal temperature gradients. It can be, for instance, used to determine if the pellet is operating under near isothermal conditions or whether a temperature correction to the data is necessary.

The temperature rise in the pellet can be assessed as follows: Combining 41 and 43 we find:

$$\theta_c - \theta_s = c_g\beta \left(1 - \frac{\phi^2\eta_0}{Bi_m}\right) \quad (44)$$

which is a closer estimate of the pellet temperature rise than the earlier equation based on the surface concentration.

7 Numerical Solutions

Numerical solution for a first order reaction is indicated in this section. The dimensionless rate for a first order reaction can be expressed as:

$$f^* = c \exp[\gamma(1 - 1/\theta)] \quad (45)$$

where $\gamma = E/R_gT_{ref}$. The governing equations and the boundary conditions shown in the earlier section are summarized for convenience here: The mass balance:

$$\frac{d^2c}{d\xi^2} = \phi^2c \exp[\gamma(1 - 1/\theta)] \quad (46)$$

The heat balance:

$$\frac{d^2\theta}{d\xi^2} = -\beta\phi^2c \exp[\gamma(1 - 1/\theta)] \quad (47)$$

The boundary conditions are:

$$\text{at } \xi = 0 \quad dc/d\xi = 0; \quad d\theta/d\xi = 0$$

and $\xi = 1$

$$\begin{aligned} \left(\frac{dc}{d\xi}\right)_s &= Bi_m(c_g - c_s) \\ \left(\frac{d\theta}{d\xi}\right)_s &= Bi_h(\theta_g - \theta_s) \end{aligned}$$

For the particle problem (local particle scale model) we set c_g and θ_g as one.

We find that even for this simple first order reaction, the overall effectiveness factor is a function of five parameters: ϕ , β , γ , Bi_m and Bi_h .

An illustrative plot of the effectiveness factor vs Thiele modulus is shown in Fig 1 based on the work of Aris and Hatfield. It is clear that the behavior is complex and multiple steady states are observed. For one case in the fig we see two distinct regions of multiple solutions. The region at low Thiele modulus is caused by intraparticle gradients while the second one is due to interparticle gradients. The two regions may overlap producing five steady states as seen in the second case shown in Fig 1.

Sample result was simulated using the matlab program for the following value of the parameters.
 $\phi = 0.5$, $\beta = 1/3$, $\gamma = 27$, $Bi_m = 300$ and $Bi_h = 100$.

Model for Isothermal Pellet

An useful simplification is to assume that there are no internal gradients for temperature. The temperature changes are confined only to the gas film. This simplifies the calculations since the only the intraparticle concentration profiles need to be solved. Approximate analytical solutions shown earlier can be used for the internal effectiveness factor. The particle temperature is not known and has to be solved iteratively. The calculation procedure is indicated below for a first order reaction.

The Thiele modulus is defined on the basis of the surface temperature

$$\psi = \phi \exp[\gamma/2.(1 - 1/\theta_s)] \quad (48)$$

where ϕ is the Thiele modulus based on reference conditions. The catalytic effectiveness factor is then equal to:

$$\eta_c = \frac{\tanh \psi}{\psi} \quad (49)$$

and overall effectiveness factor for a first order reaction was shown earlier as:

$$\eta_0 = \frac{\eta_c Bi_m}{\eta_c \psi^2 + Bi_m} \exp[\gamma(1 - 1/\theta_s)] \quad (50)$$

The surface temperature is related to the gas phase temperature by the equation shown earlier which is reproduced below for completeness.

$$\theta_s = \theta_0 + \frac{\beta \phi^2 \eta_0}{Bi_h} \quad (51)$$

The above equations are solved simultaneously or by trial and error to obtain the overall effectiveness factor and the surface temperature.

Example : Calculate the effectiveness factor for the following conditions;

$\phi = 2.$, $\beta = 0.05$, $\gamma = 20$, $Bi_m = 200$ and $Bi_h = 20$.

Solution: Since β is small let us assume that all the temperature drop is confined to the gas film. To start off the calculations assume a particle temperature of 1.05 Then the following set of results can be obtained.

$\psi = 3.2119$; $\eta_c = 0.32$; $\eta_0 = 0.7899$ and $\theta_s = 1.007$. This is not close to the trial value of 1.05 and the calculations are repeated.

The final value of the surface temperature is calculated using 51 as:

$\theta_s = 1.005$; and $\eta_c = 0.4617$ and $\eta_0 = 0.5049$. The overall effectiveness factor is greater than the catalytic value since it is based on the bulk temperature and not the surface temperature.