

TRANSPORT EFFECTS IN HETEROGENEOUS CATALYTIC SYSTEMS

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) \times (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

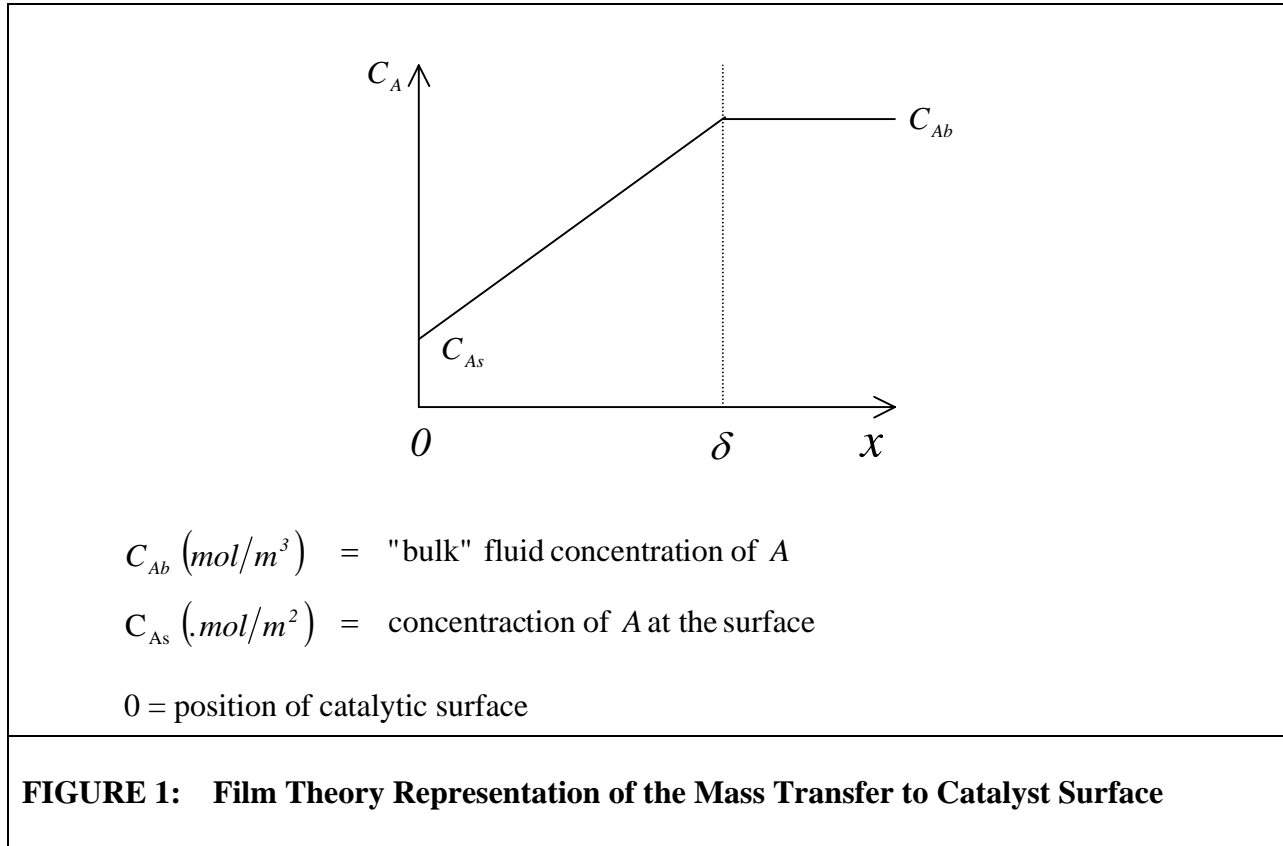
Let us assume that a first order irreversible reaction occurs at the catalyst surface and the heat of reaction is negligible so that we have an essentially isothermal situation and $T_s = T_b$ in the fluid film surrounding the surface where T_s is the local surface temperature and T_b is the local fluid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

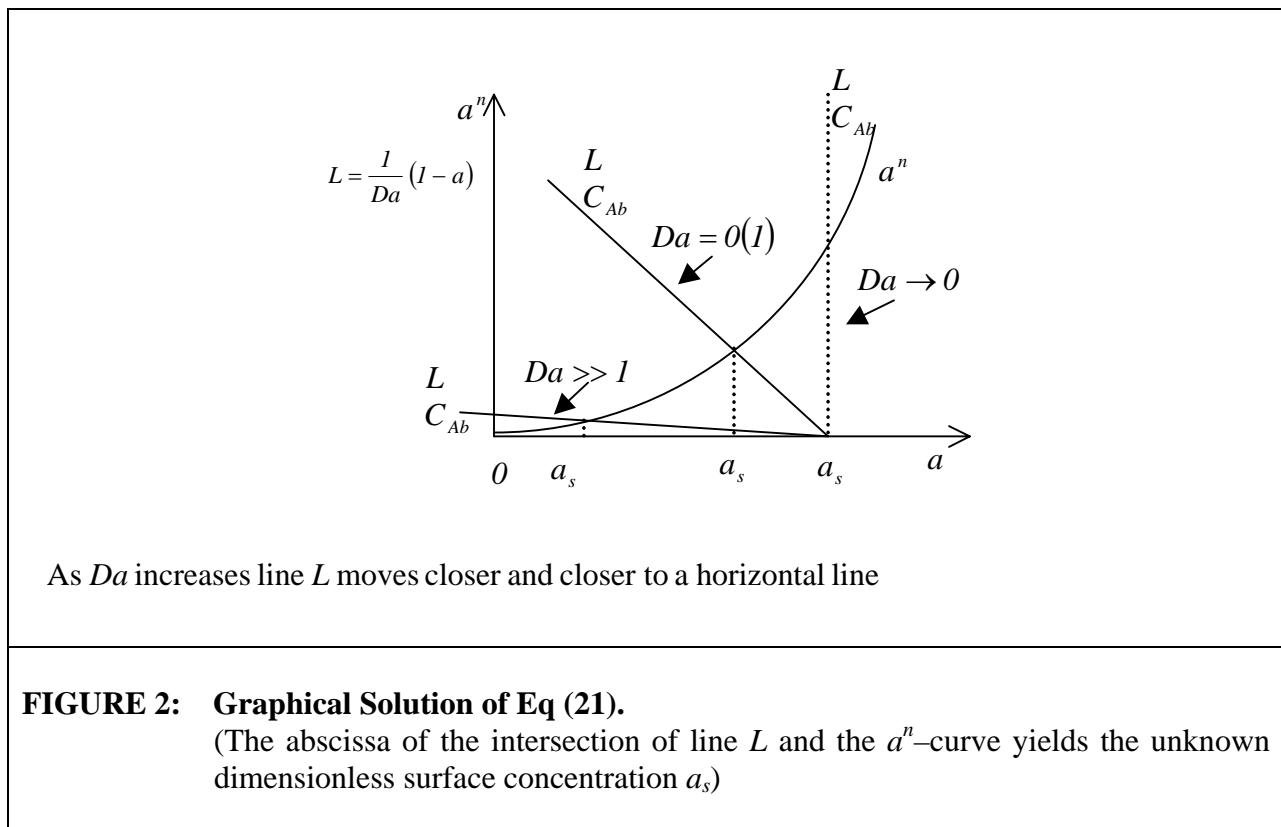
$$Da = \frac{k' C_{Ab}^{n-1}}{k_m} \quad (20)$$

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.

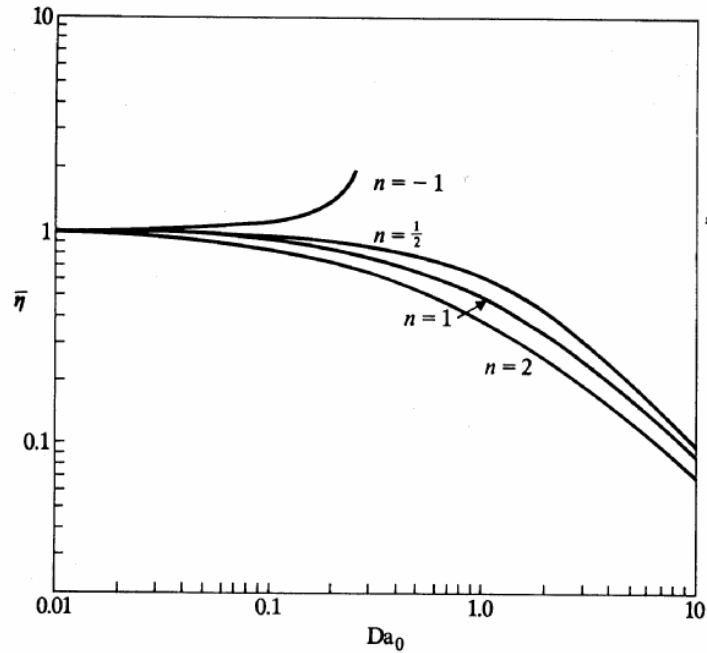


FIGURE 1: Isothermal external catalytic effectiveness for reaction order n . (G. Cassiere and J.J. Carberry, *Chem. Eng. Educ.*, Winter, 1973: 22).

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

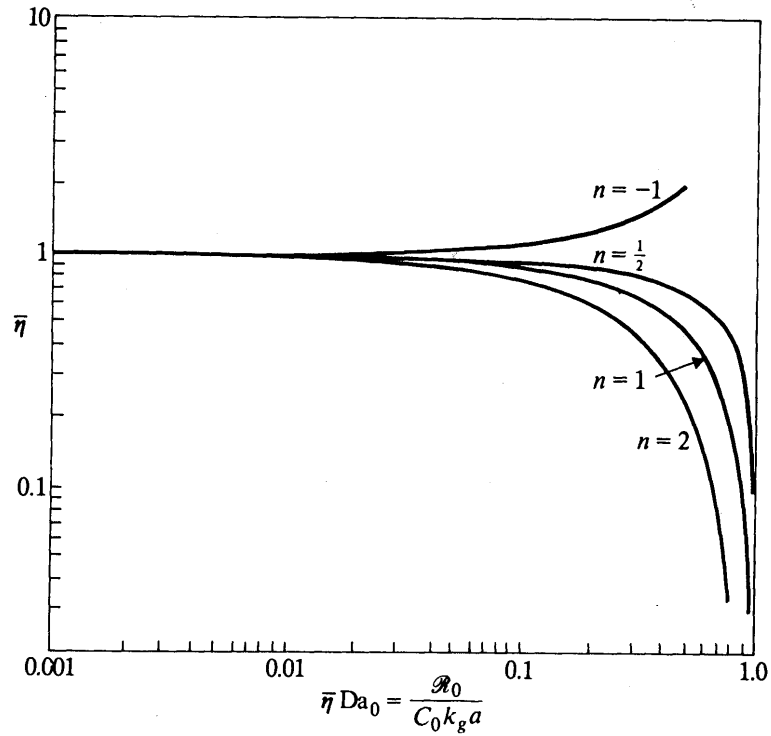


FIGURE 2: Isothermal external catalytic effectiveness in terms of observable for order n . (G. Cassiere and J.J. Carberry, *Chem. Eng. Educ.*, Winter, 1973: 22).

| | |
|--|--|
| $k \left(\left(\frac{\text{mol}}{\text{m}^3} \right)^{1-n} \frac{1}{\text{s}} \right)$ | = 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 |
| $C_o \equiv C_{A_o}$ | |

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

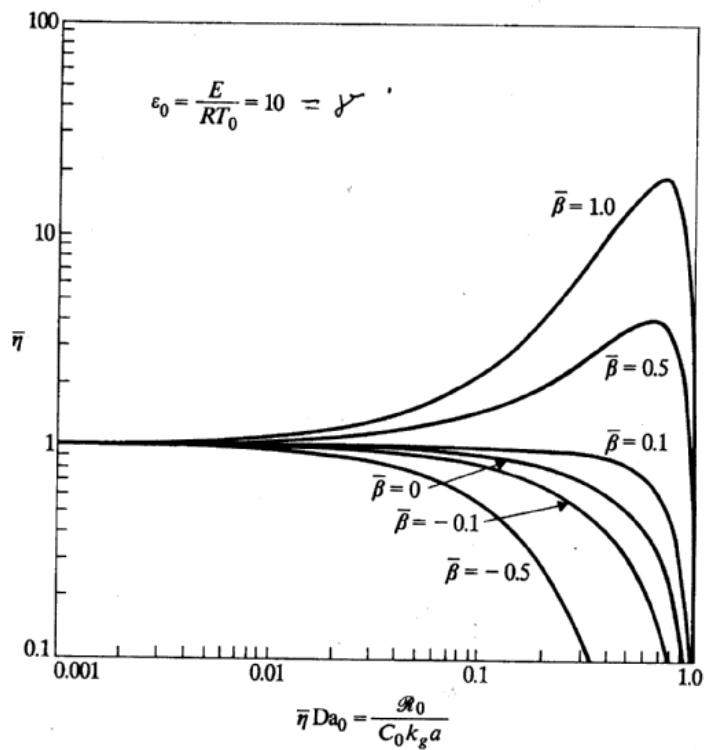


FIGURE 3: External nonisothermal $\bar{\eta}$ versus observable (first order, $\varepsilon_0 = 10$). [*J.J. Carberry and A.A. Kulkarni, J. Catal., 31:41 (1973).*]

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

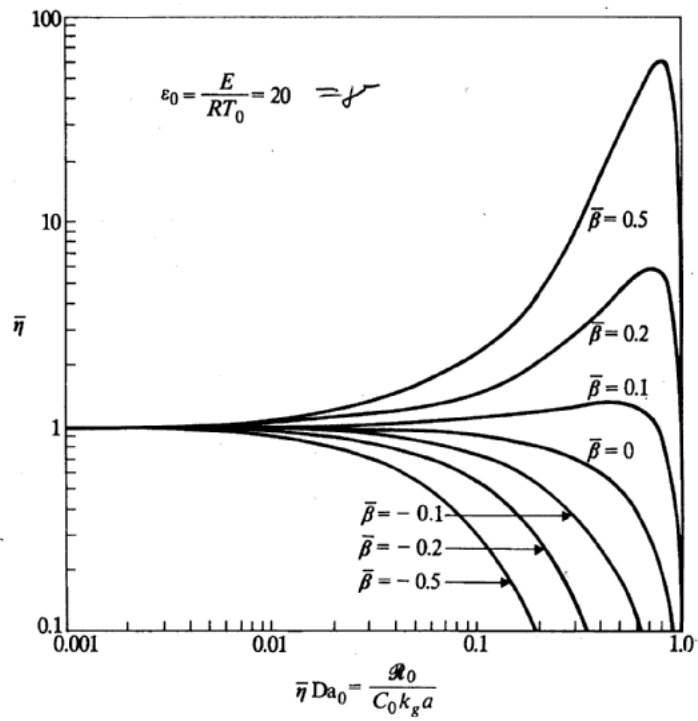


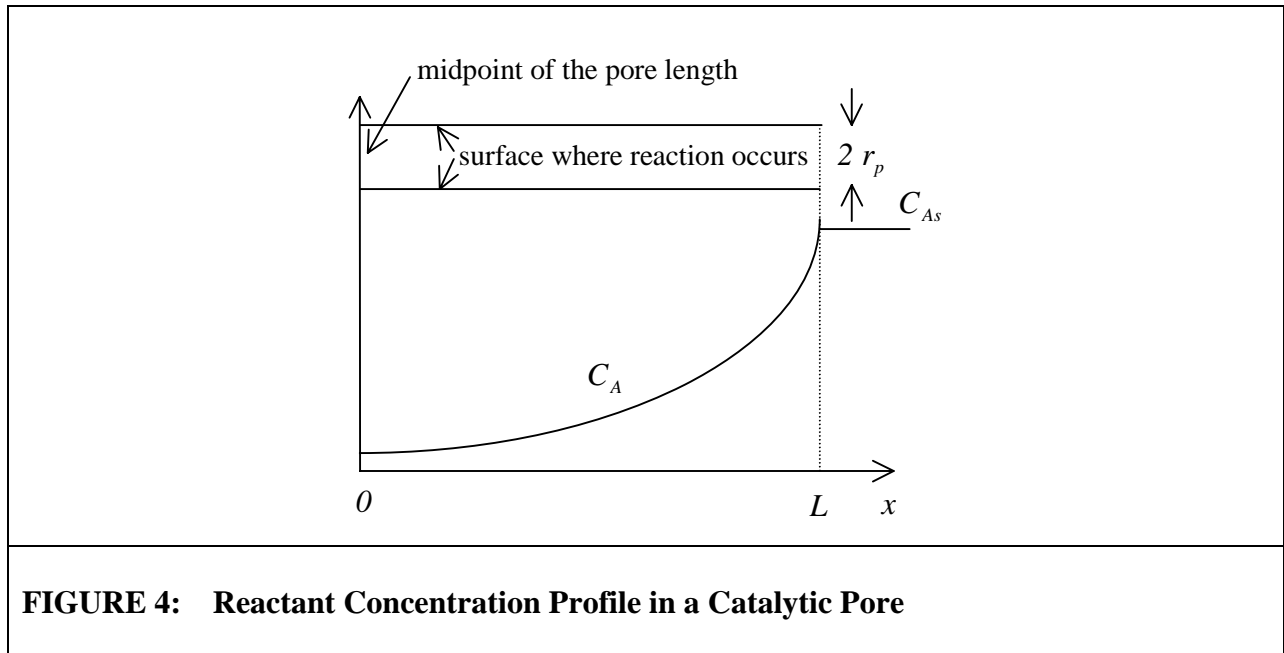
FIGURE 3:

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 diffusional resistance compared to kinetic 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.