Diffusion and Reaction

DVD 12

Research is to see what everybody else sees, and
to think what nobody else has thought.
Albert Szent-Gyorgyi

The concentration in the internal surface of the pellet is less than that of the external surface

Overview This chapter presents the principles of diffusion and reaction. While the focus is primarily on catalyst pellets, examples illustrating these principles are also drawn from biomaterials engineering and microelectronics. In our discussion of catalytic reactions in Chapter 10, we assumed each point on the interior of catalyst surface was accessible to the same concentration. However, we know there are many, many situations where this equal accessibility will not be true. For example, when the reactants must diffuse inside the catalyst pellet in order to react, we know the concentration at the pore mouth must be higher than that inside the pore. Consequently, the entire catalytic surface is not accessible to the same concentration; therefore, the rate of reaction throughout the pellet will vary. To account for variations in reaction rate throughout the pellet, we introduce a parameter known as the effectiveness factor, which is the ratio of the overall reaction rate in the pellet to the reaction rate at the external surface of the pellet. In this chapter we will develop models for diffusion and reaction in two-phase systems, which include catalyst pellets, tissue generation, and chemical vapor deposition (CVD). The types of reactors discussed in this chapter will include packed beds, bubbling fluidized beds, slurry reactors, trickle bed reactors, and CVD boat reactors. After studying this chapter, you will be able to describe diffusion and reaction in two- and three-phase systems, determine when internal diffusion limits the overall rate of reaction, describe how to go about eliminating this limitation, and develop models for systems in which both diffusion and reaction play a role (e.g., tissue growth, CVD).

From *Elements of Chemical Reaction Engineering, Fourth Edition,* by H. Scott Fogler.

In a heterogeneous reaction sequence, mass transfer of reactants first takes place from the bulk fluid to the external surface of the pellet. The reactants then diffuse from the external surface into and through the pores within the pellet, with reaction taking place only on the catalytic surface of the pores. A schematic representation of this two-step diffusion process is shown in Figures 10-6 and 12-1.

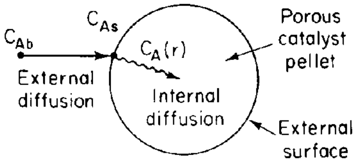

Figure 12-1 Mass transfer and reaction steps for a catalyst pellet.

12.1 Diffusion and Reaction in Spherical Catalyst Pellets

In this section we will develop the internal effectiveness factor for spherical catalyst pellets. The development of models that treat individual pores and pellets of different shapes is undertaken in the problems at the end of this chapter. We will first look at the internal mass transfer resistance to either the products or reactants that occurs between the external pellet surface and the interior of the pellet. To illustrate the salient principles of this model, we consider the irreversible isomerization

$$A \longrightarrow B$$

that occurs on the surface of the pore walls within the spherical pellet of radius R.

12.1.1 Effective Diffusivity

The pores in the pellet are not straight and cylindrical; rather, they are a series of tortuous, interconnecting paths of pore bodies and pore throats with varying cross-sectional areas. It would not be fruitful to describe diffusion within each and every one of the tortuous pathways individually; consequently, we shall define an effective diffusion coefficient so as to describe the average diffusion taking place at any position r in the pellet. We shall consider only radial variations in the concentration; the radial flux W_{Ar} will be based on the total area (voids and solid) normal to diffusion transport (i.e., $4\pi r^2$) rather than void area alone. This basis for W_{Ar} is made possible by proper definition of the effective diffusivity D_e.

The effective diffusivity accounts for the fact that:

1. Not all of the area normal to the direction of the flux is available (i.e., the area occupied by solids) for the molecules to diffuse.

2. The paths are tortuous.
3. The pores are of varying cross-sectional areas.

An equation that relates D_e to either the bulk or the Knudsen diffusivity is

The effective diffusivity

$$D_e = \frac{D_{AB}\phi_p\sigma_c}{\tilde{\tau}} \tag{12-1}$$

where

$$\tilde{\tau} = \text{tortuosity}^1 = \frac{\text{Actual distance a molecule travels between two points}}{\text{Shortest distance between those two points}}$$

$$\phi_p = \text{pellet porosity} = \frac{\text{Volume of void space}}{\text{Total volume (voids and solids)}}$$

σ_c = Constriction factor

The constriction factor, σ_c, accounts for the variation in the cross-sectional area that is normal to diffusion.[2] It is a function of the ratio of maximum to minimum pore areas (Figure 12-2(a)). When the two areas, A_1 and A_2, are equal, the constriction factor is unity, and when $\beta = 10$, the constriction factor is approximately 0.5.

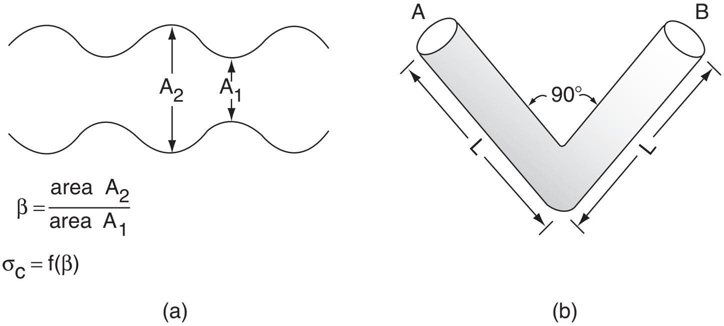

Figure 12-2 (a) Pore constriction; (b) pore tortuosity.

Example 12–1 Finding the Tortuosity

Calculate the tortuosity for the hypothetical pore of length, L (Figure 12-2(b)), from the definition of $\tilde{\tau}$.

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[1] Some investigators lump constriction and tortuosity into one factor, called the tortuosity factor, and set it equal to $\tilde{\tau}/\sigma_c$. C. N. Satterfield, *Mass Transfer in Heterogeneous Catalysis* (Cambridge, Mass.: MIT Press, 1970), pp. 33–47, has an excellent discussion on this point.

[2] See E. E. Petersen, *Chemical Reaction Analysis* (Upper Saddle River, N.J.: Prentice Hall, 1965), Chap. 3; C. N. Satterfield and T. K. Sherwood, *The Role of Diffusion in Catalysis* (Reading, Mass.: Addison-Wesley, 1963), Chap. 1.

Solution

$$\tilde{\tau} = \frac{\text{Actual distance molecule travels from } A \text{ to } B}{\text{Shortest distance between } A \text{ and } B}$$

The shortest distance between points A and B is $\sqrt{2}L$. The actual distance the molecule travels from A to B is $2L$.

$$\tilde{\tau} = \frac{2L}{\sqrt{2}L} = \sqrt{2} = 1.414$$

Although this value is reasonable for $\tilde{\tau}$, values for $\tilde{\tau} = 6$ to 10 are not unknown. Typical values of the constriction factor, the tortuosity, and the pellet porosity are, respectively, $\sigma_c = 0.8$, $\tilde{\tau} = 3.0$, and $\phi_p = 0.40$.

12.1.2 Derivation of the Differential Equation Describing Diffusion and Reaction

First we will derive the concentration profile of reactant A in the pellet.

We now perform a steady-state mole balance on species A as it enters, leaves, and reacts in a spherical shell of inner radius r and outer radius $r + \Delta r$ of the pellet (Figure 12-3). Note that even though A is diffusing inward toward the center of the pellet, the convention of our shell balance dictates that the flux be in the direction of increasing r. We choose the flux of A to be positive in the direction of increasing r (i.e., the outward direction). Because A is actually diffusing inward, the flux of A will have some negative value, such as $-10 \text{ mol/m}^2\cdot\text{s}$, indicating that the flux is actually in the direction of decreasing r.

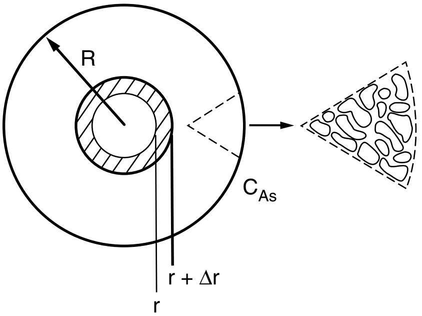

Figure 12-3 Shell balance on a catalyst pellet.

We now proceed to perform our shell balance on A. The area that appears in the balance equation is the total area (voids and solids) *normal* to the direction of the molar flux:

$$\text{Rate of A in at } r = W_{Ar}\cdot\text{Area} = W_{Ar} \times 4\pi r^2\Big|_r \tag{12-2}$$

$$\text{Rate of A out at } (r + \Delta r) = W_{Ar}\cdot\text{Area} = W_{Ar} \times 4\pi r^2\Big|_{r+\Delta r} \tag{12-3}$$

$$\begin{bmatrix}\text{Rate of}\\ \text{generation}\\ \text{of A within a}\\ \text{shell of thickness}\\ \Delta r\end{bmatrix} = \left[\frac{\text{Rate of reaction}}{\text{Mass of catalyst}}\right] \times \left[\frac{\text{Mass catalyst}}{\text{Volume}}\right] \times \left[\text{Volume of shell}\right]$$

$$= \qquad r'_{\text{A}} \qquad \times \qquad \rho_{\text{c}} \qquad \times \qquad 4\pi r_{\text{m}}^2 \Delta r \tag{12-4}$$

Mole balance for diffusion and reaction inside the catalyst pellet

where r_{m} is some mean radius between r and $r + \Delta r$ that is used to approximate the volume ΔV of the shell and ρ_{c} is the density of the pellet.

The mole balance over the shell thickness Δr is

Mole balance

$$\begin{array}{ccccccc} \textbf{(In at } \boldsymbol{r}\textbf{)} & - & \textbf{(Out at } \boldsymbol{r+\Delta r}\textbf{)} & + & \textbf{(Generation within } \boldsymbol{\Delta r}\textbf{)} & = & 0 \\ (W_{\text{A}r}\times 4\pi r^2|_r) & - & (W_{\text{A}r}\times 4\pi r^2|_{r+\Delta r}) & + & (r'_{\text{A}}\,\rho_{\text{c}}\times 4\pi r_{\text{m}}^2\,\Delta r) & = & 0 \end{array} \tag{12-5}$$

After dividing by $(-4\pi\,\Delta r)$ and taking the limit as $\Delta r \to 0$, we obtain the following differential equation:

$$\frac{d(W_{\text{Ar}}r^2)}{dr} - r'_{\text{A}}\rho_{\text{c}}r^2 = 0 \tag{12-6}$$

Because 1 mol of A reacts under conditions of constant temperature and pressure to form 1 mol of B, we have Equimolar Counter Diffusion (EMCD) at constant total molar concentration (Section 11.2.1A), and, therefore,

The flux equation

$$W_{\text{Ar}} = -cD_{\text{e}}\frac{dy_{\text{A}}}{dr} = -D_{\text{e}}\frac{dC_{\text{A}}}{dr} \tag{12-7}$$

where C_{A} is the number of moles of A per dm^3 of open pore volume (i.e., volume of gas) as opposed to (mol/vol of gas and solids). In systems where we do not have EMCD in catalyst pores, it may still be possible to use Equation (12-7) if the reactant gases are present in dilute concentrations.

After substituting Equation (12-7) into Equation (12-6), we arrive at the following differential equation describing diffusion with reaction in a catalyst pellet:

$$\boxed{\frac{d[-D_{\text{e}}(dC_{\text{A}}/dr)r^2]}{dr} - r^2\rho_{\text{c}}r'_{\text{A}} = 0} \tag{12-8}$$

We now need to incorporate the rate law. In the past we have based the rate of reaction in terms of either per unit volume,

$$\boxed{-r_{\text{A}}[=](\text{mol/dm}^3\cdot\text{s})}$$

or per unit mass of catalyst,

$$\boxed{-r'_{\text{A}}\,[=](\text{mol/g cat}\cdot\text{s})}$$

From *Elements of Chemical Reaction Engineering, Fourth Edition,* by H. Scott Fogler.

Inside the Pellet

$-r'_A = S_a(-r''_A)$

$-r_A = \rho_c(-r'_A)$

$-r_A = \rho_c S_a(-r''_A)$

When we study reactions on the internal surface area of catalysts, the rate of reaction and rate law are often based on per unit surface area,

$$\boxed{-r''_A [=] (\text{mol/m}^2 \cdot \text{s})}$$

As a result, the surface area of the catalyst per unit mass of catalyst,

$$S_a [=] (\text{m}^2/\text{g cat.})$$

is an important property of the catalyst. The rate of reaction per unit mass of catalyst, $-r'_A$, and the rate of reaction per unit surface area of catalyst are related through the equation

S_a: 10 grams of catalyst may cover as much surface area as a football field

$$-r'_A = -r''_A S_a$$

A typical value of S_a might be 150 m^2/g of catalyst.

The rate law

As mentioned previously, at high temperatures, the denominator of the catalytic rate law approaches 1. Consequently, for the moment, it is reasonable to assume that the surface reaction is of nth order in the gas-phase concentration of A within the pellet.

$$-r''_A = k''_n C_A^n \tag{12-9}$$

where the units of the rate constants for $-r_A$, $-r'_A$, and $-r''_A$ are

$$-r''_A\text{:}\ k''_n [=] \left(\frac{\text{m}^3}{\text{kmol}}\right)^{n-1} \frac{\text{m}}{\text{s}}$$

Similarly,

For a **first-order** catalytic reaction

per unit Surface Area: $k''_1 = [\text{m/s}]$

per unit Mass of Catalyst: $k'_1 = k''_1 S_a = [m^3/(\text{kg} \cdot \text{s})]$

per unit Volume: $k_1 = k''_1 S_a \rho_c = [\text{s}^{-1}]$

$$-r'_A\text{:}\ k'_n = S_a k''_n [=] \left(\frac{\text{m}^3}{\text{kmol}}\right)^{n-1} \frac{\text{m}^3}{\text{kg} \cdot \text{s}}$$

$$-r_A\text{:}\ k_n = k'_n \rho_c = \rho_c S_a k''_n [=] \left(\frac{\text{m}^3}{\text{kmol}}\right)^{n-1} \frac{1}{\text{s}}$$

Differential equation and boundary conditions describing diffusion and reaction in a catalyst pellet

Substituting the rate law equation (12-9) into Equation (12-8) gives

$$\frac{d[r^2(-D_e dC_A/dr)]}{dr} + r^2 \overbrace{k''_n S_a \rho_c}^{k_n} C_A^n = 0 \tag{12-10}$$

By differentiating the first term and dividing through by $-r^2 D_e$, Equation (12-10) becomes

$$\boxed{\frac{d^2 C_A}{dr^2} + \frac{2}{r}\left(\frac{dC_A}{dr}\right) - \frac{k_n}{D_e} C_A^n = 0} \tag{12-11}$$

The boundary conditions are:

1. The concentration remains finite at the center of the pellet:

$$\boxed{C_A \text{ is finite} \qquad \text{at } r = 0}$$

2. At the external surface of the catalyst pellet, the concentration is C_{As}:

$$\boxed{C_A = C_{As} \qquad \text{at } r = R}$$

12.1.3 Writing the Equation in Dimensionless Form

We now introduce dimensionless variables ψ and λ so that we may arrive at a parameter that is frequently discussed in catalytic reactions, the *Thiele modulus*. Let

$$\psi = \frac{C_A}{C_{As}} \tag{12-12}$$

$$\lambda = \frac{r}{R} \tag{12-13}$$

With the transformation of variables, the boundary condition

$$C_A = C_{As} \qquad \text{at } r = R$$

becomes

$$\psi = \frac{C_A}{C_{As}} = 1 \qquad \text{at } \lambda = 1$$

and the boundary condition

$$C_A \text{ is finite} \qquad \text{at } r = 0$$

becomes

$$\psi \text{ is finite} \qquad \text{at } \lambda = 0$$

We now rewrite the differential equation for the molar flux in terms of our dimensionless variables. Starting with

$$W_{Ar} = -D_e \frac{dC_A}{dr} \tag{11-7}$$

we use the chain rule to write

$$\frac{dC_A}{dr} = \left(\frac{dC_A}{d\lambda}\right)\frac{d\lambda}{dr} = \frac{d\psi}{d\lambda}\left(\frac{dC_A}{d\psi}\right)\frac{d\lambda}{dr} \tag{12-14}$$

Then differentiate Equation (12-12) with respect to ψ and Equation (12-13) with respect to r, and substitute the resulting expressions,

$$\frac{dC_A}{d\psi} = C_{As} \qquad \text{and} \qquad \frac{d\lambda}{dr} = \frac{1}{R}$$

into the equation for the concentration gradient to obtain

$$\frac{dC_A}{dr} = \frac{d\psi}{d\lambda}\frac{C_{As}}{R} \tag{12-15}$$

The flux of A in terms of the dimensionless variables, ψ and λ, is

The total rate of consumption of A inside the pellet, M_A (mol/s)

$$W_{Ar} = -D_e \frac{dC_A}{dr} = -\frac{D_e C_{As}}{R}\left(\frac{d\psi}{d\lambda}\right) \tag{12-16}$$

At steady state, the net flow of species A that enters into the pellet at the external pellet surface reacts completely within the pellet. The overall rate of reaction is therefore equal to the total molar flow of A into the catalyst pellet. The overall rate of reaction, M_A, can be obtained by multiplying the molar flux into the pellet at the outer surface by the external surface area of the pellet, $4\pi R^2$:

All the reactant that diffuses into the pellet is consumed (a black hole)

$$M_A = -4\pi R^2 W_{Ar}\big|_{r=R} = +4\pi R^2 D_e \frac{dC_A}{dr}\bigg|_{r=R} = 4\pi R D_e C_{As}\frac{d\psi}{d\lambda}\bigg|_{\lambda=1} \tag{12-17}$$

Consequently, to determine the overall rate of reaction, which is given by Equation (12-17), we first solve Equation (12-11) for C_A, differentiate C_A with respect to r, and then substitute the resulting expression into Equation (12-17).

Differentiating the concentration gradient, Equation (12-15), yields

$$\frac{d^2C_A}{dr^2} = \frac{d}{dr}\left(\frac{dC_A}{dr}\right) = \frac{d}{d\lambda}\left(\frac{d\psi}{d\lambda}\frac{C_{As}}{R}\right)\frac{d\lambda}{dr} = \frac{d^2\psi}{d\lambda^2}\left(\frac{C_{As}}{R^2}\right) \tag{12-18}$$

After dividing by C_{As}/R^2, the dimensionless form of Equation (12-11) is written as

$$\frac{d^2\psi}{d\lambda^2} + \frac{2}{\lambda}\frac{d\psi}{d\lambda} - \frac{k_n R^2 C_{As}^{n-1}}{D_e}\psi^n = 0$$

Then

Dimensionless form of equations describing diffusion and reaction

$$\boxed{\frac{d^2\psi}{d\lambda^2} + \frac{2}{\lambda}\left(\frac{d\psi}{d\lambda}\right) - \phi_n^2\psi^n = 0} \tag{12-19}$$

where

$$\boxed{\phi_n^2 = \frac{k_n R^2 C_{\mathrm{As}}^{n-1}}{D_{\mathrm{e}}}} \tag{12-20}$$

Thiele modulus

The square root of the coefficient of ψ^n, (i.e., ϕ_n) is called the Thiele modulus. The Thiele modulus, ϕ_n, will always contain a subscript (e.g., n), which will distinguish this symbol from the symbol for porosity, ϕ, defined in Chapter 4, which has no subscript. The quantity ϕ_n^2 is a measure of the ratio of "a" surface reaction rate to "a" rate of diffusion through the catalyst pellet:

$$\boxed{\phi_n^2 = \frac{k_n R^2 C_{\mathrm{As}}^{n-1}}{D_{\mathrm{e}}} = \frac{k_n R C_{\mathrm{As}}^{n}}{D_{\mathrm{e}}[(C_{\mathrm{As}}-0)/R]} = \frac{\text{“a” surface reaction rate}}{\text{“a” diffusion rate}}} \tag{12-20}$$

When the Thiele modulus is large, internal diffusion usually limits the overall rate of reaction; when ϕ_n is small, the surface reaction is usually rate-limiting. If for the reaction

$$\mathrm{A} \longrightarrow \mathrm{B}$$

the surface reaction were rate-limiting with respect to the adsorption of A and the desorption of B, and if species A and B are weakly adsorbed (i.e., low coverage) and present in very dilute concentrations, we can write the apparent first-order rate law

$$-r''_{\mathrm{A}} \simeq k''_1 C_{\mathrm{A}} \tag{12-21}$$

The units of k''_1 are m^3/m^{2}s (= m/s).

For a first-order reaction, Equation (12-19) becomes

$$\boxed{\frac{d^2\psi}{d\lambda^2} + \frac{2}{\lambda}\frac{d\psi}{d\lambda} - \phi_1^2\psi = 0} \tag{12-22}$$

where

$$\boxed{\phi_1 = R\sqrt{\frac{k''_1 \rho_{\mathrm{c}} S_{\mathrm{a}}}{D_{\mathrm{e}}}} = R\sqrt{\frac{k_1}{D_{\mathrm{e}}}}}$$

$$k_1 = k''_1 \rho_{\mathrm{c}} S_{\mathrm{a}} \ [=] \ \left(\frac{\mathrm{m}}{\mathrm{s}} \cdot \frac{\mathrm{g}}{\mathrm{m}^3} \cdot \frac{\mathrm{m}^2}{\mathrm{g}}\right) = 1/\mathrm{s}$$

$$\frac{k_1}{D_{\mathrm{e}}} \ [=] \ \left(\frac{1/\mathrm{s}}{\mathrm{m}^2/\mathrm{s}}\right) = \frac{1}{\mathrm{m}^2}$$

$$\phi_1 = R\sqrt{\frac{k_1}{D_{\mathrm{e}}}} [=] \mathrm{m}\left(\frac{s^{-1}}{\mathrm{m}^2/s}\right)^{1/2} = \frac{1}{1} \quad \text{(Dimensionless)}$$

The boundary conditions are

$$\boxed{\begin{array}{ll}\text{B.C. 1: } \psi = 1 & \text{at } \lambda = 1 \\ \text{B.C. 2: } \psi \text{ is finite} & \text{at } \lambda = 0\end{array}} \qquad \begin{array}{r}(12\text{-}23)\\(12\text{-}24)\end{array}$$

12.1.4 Solution to the Differential Equation for a First-Order Reaction

Differential equation (12-22) is readily solved with the aid of the transformation $y = \psi\lambda$:

$$\frac{d\psi}{d\lambda} = \frac{1}{\lambda}\left(\frac{dy}{d\lambda}\right) - \frac{y}{\lambda^2}$$

$$\frac{d^2\psi}{d\lambda^2} = \frac{1}{\lambda}\left(\frac{d^2y}{d\lambda^2}\right) - \frac{2}{\lambda^2}\left(\frac{dy}{d\lambda}\right) + \frac{2y}{\lambda^3}$$

With these transformations, Equation (12-22) reduces to

$$\frac{d^2y}{d\lambda^2} - \phi_1^2 y = 0 \tag{12-25}$$

This differential equation has the following solution (Appendix A.3):

$$y = A_1 \cosh\phi_1\lambda + B_1 \sinh\phi_1\lambda$$

In terms of ψ,

$$\psi = \frac{A_1}{\lambda}\cosh\phi_1\lambda + \frac{B_1}{\lambda}\sinh\phi_1\lambda \tag{12-26}$$

The arbitrary constants A_1 and B_1 can easily be evaluated with the aid of the boundary conditions. At $\lambda = 0$; $\cosh\phi_1\lambda \to 1$, $(1/\lambda) \to \infty$, and $\sinh\phi_1\lambda \to 0$. Because the second boundary condition requires ψ to be finite at the center (i.e., $\lambda = 0$), therefore A_1 must be zero.

The constant B_1 is evaluated from B.C. 1 (i.e., $\psi = 1$, $\lambda = 1$) and the dimensionless concentration profile is

Concentration profile

$$\boxed{\psi = \frac{C_A}{C_{As}} = \frac{1}{\lambda}\left(\frac{\sinh\phi_1\lambda}{\sinh\phi_1}\right)} \tag{12-27}$$

Figure 12-4 shows the concentration profile for three different values of the Thiele modulus, ϕ_1. Small values of the Thiele modulus indicate surface reaction controls and a significant amount of the reactant diffuses well into the pellet interior without reacting. Large values of the Thiele modulus indicate that the surface reaction is rapid and that the reactant is consumed very close to the external pellet surface and very little penetrates into the interior of the pellet. Consequently, if the porous pellet is to be plated with a precious metal catalyst (e.g., Pt), it should only be plated in the immediate vicinity of the external surface when large values of ϕ_n characterize the diffusion and reaction. That is, it would be a waste of the precious metal to plate the entire pellet when internal diffusion is limiting because the reacting gases are consumed near the outer surface. Consequently, the reacting gases would never contact the center portion of the pellet.

For large values of the Thiele modulus, internal diffusion limits the rate of reaction.

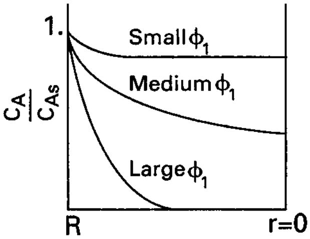

Figure 12-4 Concentration profile in a spherical catalyst pellet.

Example 12–2 Applications of Diffusion and Reaction to Tissue Engineering

The equations describing diffusion and reaction in porous catalysts also can be used to derive rates of tissue growth. One important area of tissue growth is in cartilage tissue in joints such as the knee. Over 200,000 patients per year receive knee joint replacements. Alternative strategies include the growth of cartilage to repair the damaged knee.[3]

One approach currently being researched by Professor Kristi Anseth at the University of Colorado is to deliver cartilage forming cells in a hydrogel to the damaged area such as the one shown in Figure E12-2.1.

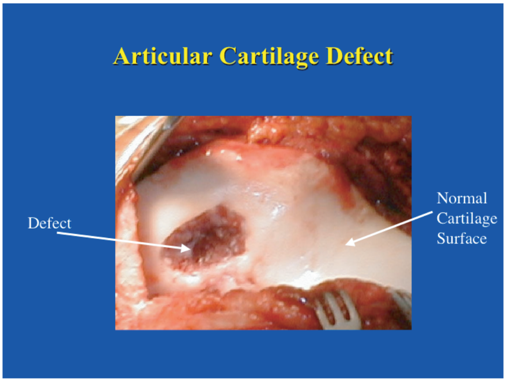

Figure E12-2.1 Damaged cartilage. (Figure courtesy of *Newsweek*, September 3, 2001.)

Here the patient's own cells are obtained from a biopsy and embedded in a hydrogel, which is a cross-linked polymer network that is swollen in water. In order for the cells to survive and grow new tissue, many properties of the gel must be tuned to allow diffusion of important species in and out (e.g., nutrients *in* and cell-secreted extracellular molecules *out*, such as collagen). Because there is no blood flow through the cartilage, oxygen transport to the cartilage cells is primarily by diffusion. Consequently, the design must be that the gel can maintain the necessary rates of diffusion of nutrients (e.g., O_2) into the hydrogel. These rates of exchange in the gel depend on the geometry and the thickness of the gel. To illustrate the application of chemical reaction engineering principles to tissue engineering, we will examine the diffusion and consumption of one of the nutrients, oxygen.

Our examination of diffusion and reaction in catalyst pellets showed that in many cases the reactant concentration near the center of the particle was virtually zero. If this condition were to occur in a hydrogel, the cells at the center would die. Consequently, the gel thickness needs to be designed to allow rapid transport of oxygen.

Let's consider the simple gel geometry shown in Figure E12-2.2.

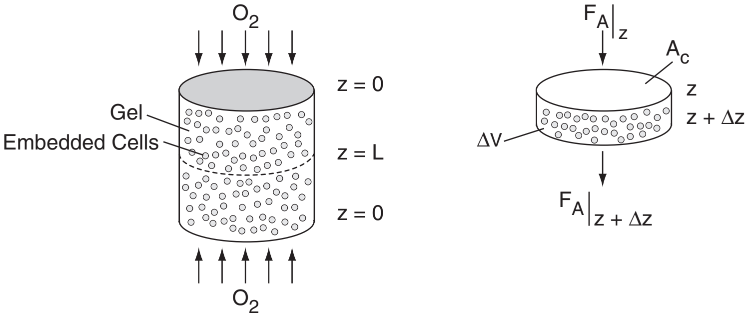

Figure E12-2.2 Schematic of cartilage cell system.

We want to find the gel thickness at which the minimum oxygen consumption rate is 10^{-13} mol/cell/h. The cell density in the gel is 10^{10} cells/dm^3, the bulk concentration of oxygen ($z = 0$) is 2×10^{-4} mol/dm^3, and the diffusivity is 10^{-5} cm^2/s.

Solution

A mole balance on oxygen, A, in the volume $\Delta V = A_c \Delta z$ is

$$F_A\big|_z - F_A\big|_{z+\Delta z} + r_A A_c \Delta z = 0 \qquad \text{(E12-2.1)}$$

Dividing by Δz and taking the limit as $\Delta z \to 0$ gives

$$\frac{1}{A_c}\frac{dF_A}{dz} + r_A = 0 \qquad \text{(E12-2.2)}$$

$$F_A = A_c\left[-D_{AB}\frac{dC_A}{dz} + UC_A\right] \qquad \text{(E12-2.3)}$$

For dilute concentrations we neglect UC_A and combine Equations (E12-2.2) and (E12-2.3) to obtain

$$\boxed{D_{AB}\frac{d^2C_A}{dz^2}+r_A=0} \tag{E12-2.4}$$

If we assume the O_2 consumption rate is zero order, then

$$D_{AB}\frac{d^2C_A}{dz^2}-k=0 \tag{E12-2.5}$$

Putting our equation in dimensionless form using $\psi = C_A/C_{A0}$ and z/L, we obtain

$$\frac{d^2\psi}{d\lambda^2}-\frac{kL^2}{D_{AB}C_{A0}}=0 \tag{E12-2.6}$$

Recognizing the second term is just the ratio of a reaction rate to a diffusion rate for a zero order reaction, we call this ratio the Thiele modulus, ϕ_0. We divide and multiply by two to facilitate the integration:

$$\boxed{\phi_0=\frac{k}{2D_{AB}C_{A0}}L^2} \tag{E12-2.7}$$

$$\boxed{\frac{d^2\psi}{d\lambda^2}-2\phi_0=0} \tag{E12-2.8}$$

The boundary conditions are

At $\lambda = 0$ $\psi = 1$ $C_A = C_{A0}$ (E12-2.9)

At $\lambda = 1$ $\frac{d\psi}{d\lambda} = 0$ Symmetry condition (E12-2.10)

Recall that at the midplane ($z = L$, $\lambda = 1$) we have symmetry so that there is no diffusion across the midplane so the gradient is zero at $\lambda = 1$.

Integrating Equation (E12-2.8) once yields

$$\frac{d\psi}{d\lambda}=2\phi_0\lambda+K_1 \tag{E12-2.11}$$

Using the symmetry condition that there is no gradient across the midplane, Equation (E12-2.10), gives $K_1 = -2\phi_0$:

$$\frac{d\psi}{d\lambda}=2\phi_0(\lambda-1) \tag{E12-2.12}$$

Integrating a second time gives

$$\psi=\phi_0\lambda^2-2\phi_0\lambda+K_2$$

Using the boundary condition $\psi = 1$ at $\lambda = 0$, we find $K_2 = 1$. The dimensionless concentration profile is

$$\boxed{\psi = \phi_0 \lambda(\lambda - 2) + 1} \tag{E12-2.13}$$

Note: The dimensionless concentration profile given by Equation (E12-2.13) is only valid for values of the Thiele modulus less than or equal to 1. This restriction can be easily seen if we set $\phi_0 = 10$ and then calculate ψ at $\lambda = 0.1$ to find $\psi = -0.9$, which is a negative concentration!! This condition is explored further in Problem P12-10$_B$.

Parameter Evaluation

Evaluating the zero-order rate constant, k, yields

$$k = \frac{10^{10}\text{cells}}{\text{dm}^3} \cdot \frac{10^{-13}\text{mole O}_2}{\text{cell} \cdot \text{h}} = 10^{-3}\text{mole /dm}^3 \cdot \text{h}$$

and then the ratio

$$\frac{k}{2C_{A0}D_{AB}} = \frac{10^{-3}\text{mol/dm}^3 \cdot \text{h}}{2 \times 0.2 \times 10^{-3}\text{mol/dm}^3 \cdot 10^{-5}\,\dfrac{\text{cm}^2}{\text{s}} \times \dfrac{3600\text{ s}}{\text{h}}} = 70\text{ cm}^{-2} \tag{E12-2.14}$$

The Thiele modulus is

$$\boxed{\phi_0 = 70\text{ cm}^{-2} L^2} \tag{E12-2.15}$$

(a) Consider the gel to be completely effective such that the concentration of oxygen is reduced to zero by the time it reaches the center of the gel. That is, if $\psi = 0$ at $\lambda = 1$, we solve Equation (E12-2.13) to find that $\phi_0 = 1$

$$\phi_0 = 1 = \frac{70}{\text{cm}^2} L^2 \tag{E12-2.16}$$

Solving for the gel half thickness L yields

$$L = 0.12\text{ cm}$$

Let's critique this answer. We said the oxygen concentration was zero at the center, and the cells can't survive without oxygen. Consequently, we need to redesign so C_{O_2} is not zero at the center.

(b) Now consider the case where the minimum oxygen concentration for the cells to survive is 0.1 mmol/dm^3, which is one half that at the surface (i.e., $\psi = 0.5$ at $\lambda = 1.0$). Then Equation (E12-2.13) gives

$$\phi_0 = 0.5 = \frac{70L^2}{\text{cm}^2} \tag{E12-2.17}$$

Solving Equation (E12-2.17) for L gives

$$\boxed{L = 0.085\text{ cm} = 0.85\text{ mm} = 850\ \mu\text{m}}$$

Consequently, we see that the maximum thickness of the cartilage gel ($2L$) is the order of 1 mm, and engineering a thicker tissue is challenging.

(c) One can consider other perturbations to the preceding analysis by considering the reaction kinetics to follow a first-order rate law, $-r_A = k_A C_A$, or Monod kinetics,

$$-r_A = \frac{\mu_{\max} C_A}{K_S + C_A} \tag{E12-2.18}$$

The author notes the similarities to this problem with his research on wax build-up in subsea pipeline gels.[4] Here as the paraffin diffuses into the gel to form and grow wax particles, these particles cause paraffin molecules to take a longer diffusion path, and as a consequence the diffusivity is reduced. An analogous diffusion pathway for oxygen in the hydrogel containing collagen is shown in Figure E12-2.3.

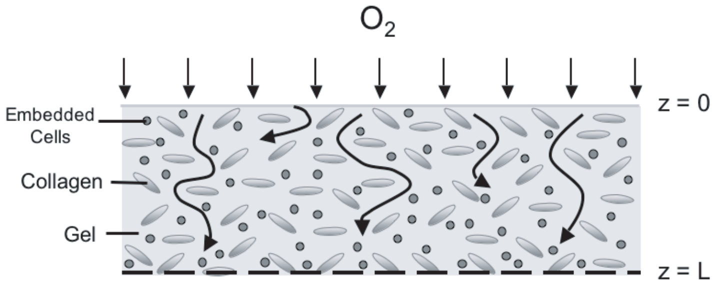

Figure E12-2.3 Diffusion of O_2 around collagen.

$$D_e = \frac{D_{AB}}{1 + \alpha^2 F_w^2/(1 - F_w)} \tag{E12-2.19}$$

where α and F_w are predetermined parameters that account for diffusion around particles. Specifically, for collagen, α is the aspect ratio of the collagen particle and F_w is weight fraction of "solid" collagen obstructing the diffusion.[4] A similar modification could be made for cartilage growth. These situations are left as an exercise in the end-of-the-chapter problems, e.g., P12-2(b).

12.2 Internal Effectiveness Factor

The magnitude of the effectiveness factor (ranging from 0 to 1) indicates the relative importance of diffusion and reaction limitations. The internal effectiveness factor is defined as

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[4] P. Singh, R. Venkatesan, N. Nagarajan, and H. S. Fogler, *AIChE J., 46*, 1054 (2000).

η is a measure of how far the reactant diffuses into the pellet before reacting.

$$\boxed{\eta = \frac{\text{Actual overall rate of reaction}}{\text{Rate of reaction that would result if entire interior surface were exposed to the external pellet surface conditions } C_{\mathrm{As}},\ T_{\mathrm{s}}}} \tag{12-28}$$

The overall rate, $-r'_{\mathrm{A}}$, is also referred to as the observed rate of reaction $[-r_{\mathrm{A}}(\text{obs})]$. In terms of symbols, the effectiveness factor is

$$\boxed{\eta = \frac{-r_{\mathrm{A}}}{-r_{\mathrm{As}}} = \frac{-r'_{\mathrm{A}}}{-r'_{\mathrm{As}}} = \frac{-r''_{\mathrm{A}}}{-r''_{\mathrm{As}}}}$$

To derive the effectiveness factor for a first-order reaction, it is easiest to work in reaction rates of (moles per unit time), M_{A}, rather than in moles per unit time per volume of catalyst (i.e., $-r_{\mathrm{A}}$)

$$\eta = \frac{-r_{\mathrm{A}}}{-r_{\mathrm{As}}} = \frac{-r_{\mathrm{A}} \times \text{Volume of catalyst particle}}{-r_{\mathrm{As}} \times \text{Volume of catalyst particle}} = \frac{M_{\mathrm{A}}}{M_{\mathrm{As}}}$$

First we shall consider the denominator, M_{As}. If the entire surface were exposed to the concentration at the external surface of the pellet, C_{As}, the rate for a first-order reaction would be

$$M_{\mathrm{As}} = \frac{\text{Rate at external surface}}{\text{Volume}} \times \text{Volume of catalyst}$$

$$= -r_{\mathrm{As}} \times \left(\frac{4}{3}\pi R^3\right) = kC_{\mathrm{As}}\left(\frac{4}{3}\pi R^3\right) \tag{12-29}$$

The subscript s indicates that the rate $-r_{\mathrm{As}}$ is evaluated at the conditions present at the **external** surface of the pellet (i.e., $\lambda = 1$).

The actual rate of reaction is the rate at which the reactant diffuses into the pellet at the outer surface. We recall Equation (12-17) for the actual rate of reaction,

The actual rate of reaction

$$M_{\mathrm{A}} = 4\pi R D_{\mathrm{e}} C_{\mathrm{As}} \left.\frac{d\psi}{d\lambda}\right|_{\lambda=1} \tag{12-17}$$

Differentiating Equation (12-27) and then evaluating the result at $\lambda = 1$ yields

$$\left.\frac{d\psi}{d\lambda}\right|_{\lambda=1} = \left(\frac{\phi_1 \cosh \lambda\phi_1}{\lambda \sinh \phi_1} - \frac{1}{\lambda^2}\frac{\sinh \lambda\phi_1}{\sinh \phi_1}\right)_{\lambda=1} = (\phi_1 \coth \phi_1 - 1) \tag{12-30}$$

Substituting Equation (12-30) into (12-17) gives us

$$M_{\mathrm{A}} = 4\pi R D_{\mathrm{e}} C_{\mathrm{As}}(\phi_1 \coth \phi_1 - 1) \tag{12-31}$$

We now substitute Equations (12-29) and (12-31) into Equation (12-28) to obtain an expression for the effectiveness factor:

$$\eta = \frac{M_A}{M_{As}} = \frac{M_A}{(-r_{As})\left(\frac{4}{3}\pi R^3\right)} = \frac{4\pi R D_e C_{As}}{k_1 C_{As}\frac{4}{3}\pi R^3}(\phi_1 \coth\phi_1 - 1)$$

$$= 3\underbrace{\frac{1}{k_1 R^2/D_e}}_{\phi_1^2}(\phi_1 \coth\phi_1 - 1)$$

Internal effectiveness factor for a first-order reaction in a spherical catalyst pellet

$$\boxed{\eta = \frac{3}{\phi_1^2}(\phi_1 \coth\phi_1 - 1)} \tag{12-32}$$

A plot of the effectiveness factor as a function of the Thiele modulus is shown in Figure 12-5. Figure 12-5(a) shows η as a function of the Thiele modulus ϕ_s for a spherical catalyst pellet for reactions of zero, first, and second order. Figure 12-5(b) corresponds to a first-order reaction occurring in three differently shaped pellets of volume V_p and external surface area A_p, and the Thiele modulus for a first-order reaction, ϕ_1, is defined differently for each shape. When volume change accompanies a reaction (i.e., $\varepsilon \neq 0$) the corrections shown in Figure 12-6 apply to the effectiveness factor for a first-order reaction.

If $\phi_1 > 2$

then $\eta \approx \frac{3}{\phi_1^2}[\phi_1 - 1]$

If $\phi_1 > 20$

then $\eta \approx \frac{3}{\phi_1}$

We observe that as the particle diameter becomes very small, ϕ_n decreases, so that the effectiveness factor approaches 1 and the reaction is surface-reaction-limited. On the other hand, when the Thiele modulus ϕ_n is large (~30), the internal effectiveness factor η is small (i.e., $\eta \ll 1$), and the reaction is diffusion-limited within the pellet. Consequently, factors influencing the rate of external mass transport will have a negligible effect on the overall reaction rate. For large values of the Thiele modulus, the effectiveness factor can be written as

$$\eta \simeq \frac{3}{\phi_1} = \frac{3}{R}\sqrt{\frac{D_e}{k_1}} \tag{12-33}$$

To express the overall rate of reaction in terms of the Thiele modulus, we rearrange Equation (12-28) and use the rate law for a first-order reaction in Equation (12-29)

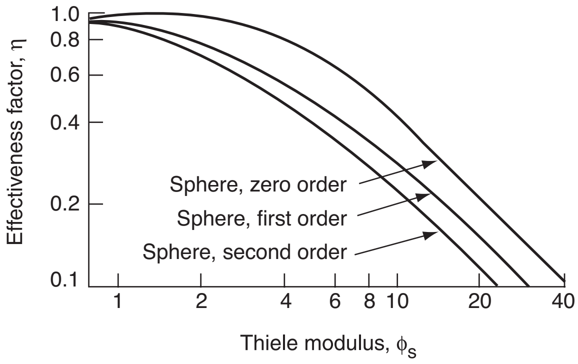
$$-r_A = \left(\frac{\text{Actual reaction rate}}{\text{Reaction rate at } C_{As}}\right) \times (\text{Reaction rate at } C_{As})$$

$$= \eta(-r_{As})$$

$$= \eta(k_1 C_{As}) \tag{12-34}$$

Combining Equations (12-33) and (12-34), the overall rate of reaction for a first-order, internal-diffusion-limited reaction is

$$-r_A = \frac{3}{R}\sqrt{D_e k_1}\, C_{As} = \frac{3}{R}\sqrt{D_e S_a \rho_c k_1''}\, C_{As}$$



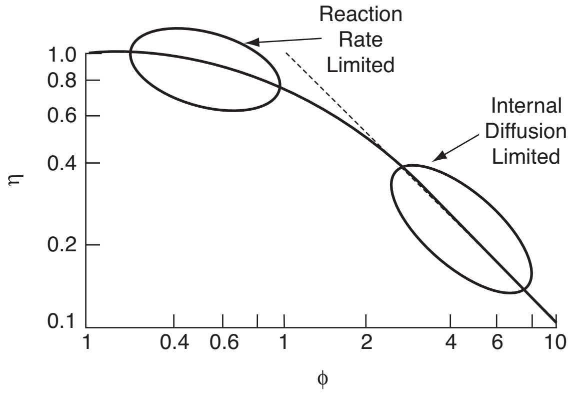
Zero order $\phi_{s0} = R\sqrt{k_0'' S_a \rho_c / D_e C_{A0}} = R\sqrt{k_0 / D_e C_{A0}}$

First order $\phi_{s1} = R\sqrt{k_1'' S_a \rho_c / D_e} = R\sqrt{k_1 / D_e}$

Second order $\phi_{s2} = R\sqrt{k_2'' S_a \rho_c C_{A0} / D_e} = R\sqrt{k_2 C_{A0} / D_e}$

(a)

Internal effectiveness factor for different reaction orders and catalyst shapes



Sphere $\phi_1 = (R/3)\sqrt{k_1'' S_a \rho_c / D_e} = \frac{R}{3}\sqrt{k_1 / D_e}$

Cylinder $\phi_1 = (R/2)\sqrt{k_1'' S_a \rho_c / D_e} = \frac{R}{2}\sqrt{k_1 / D_e}$

Slab $\phi_1 = L\sqrt{k_1'' S_a \rho_c / D_e} = L\sqrt{k_1 / D_e}$

(b)

Figure 12-5 (a) Effectiveness factor plot for *n*th-order kinetics on spherical catalyst particles (from *Mass Transfer in Heterogeneous Catalysis*, by C. N. Satterfield, 1970; reprint edition: Robert E. Krieger Publishing Co., 1981; reprinted by permission of the author). (b) First-order reaction in different pellet geometrics (from R. Aris, *Introduction to the Analysis of Chemical Reactors*, 1965, p. 131; reprinted by permission of Prentice-Hall, Englewood Cliffs, N.J.).

Correction for volume change with reaction (i.e., $\varepsilon \neq 0$)

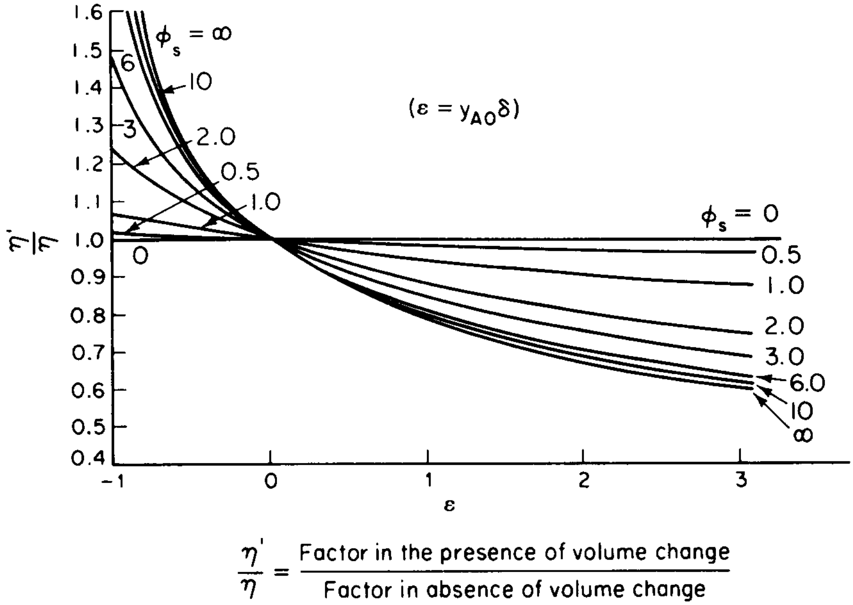


Figure 12-6 Effectiveness factor ratios for first-order kinetics on spherical catalyst pellets for various values of the Thiele modulus of a sphere, ϕ_s, as a function of volume change. [From V. W. Weekman and R. L. Goring, *J. Catal.*, *4*, 260 (1965).]

How can the rate of reaction be increased?

Therefore, to increase the overall rate of reaction, $-r'_A$: (1) decrease the radius R (make pellets smaller); (2) increase the temperature; (3) increase the concentration; and (4) increase the internal surface area. For reactions of order n, we have, from Equation (12-20),

$$\phi_n^2 = \frac{k_n'' S_a \rho_c R^2 C_{As}^{n-1}}{D_e} = \frac{k_n R^2 C_{As}^{n-1}}{D_e} \tag{12-20}$$

For large values of the Thiele modulus, the effectiveness factor is

$$\boxed{\eta = \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{\phi_n} = \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{R} \sqrt{\frac{D_e}{k_n}}\, C_{As}^{(1-n)/2}} \tag{12-35}$$

Consequently, for reaction orders greater than 1, the effectiveness factor decreases with increasing concentration at the external pellet surface.

The preceding discussion of effectiveness factors is valid only for isothermal conditions. When a reaction is exothermic and nonisothermal, the effectiveness factor can be significantly greater than 1 as shown in Figure 12-7. Values of η greater than 1 occur because the external surface temperature of the pellet is less than the temperature inside the pellet where the exothermic reaction is taking place. Therefore, the rate of reaction inside the pellet is greater than the rate at the surface. Thus, because the effectiveness factor is the

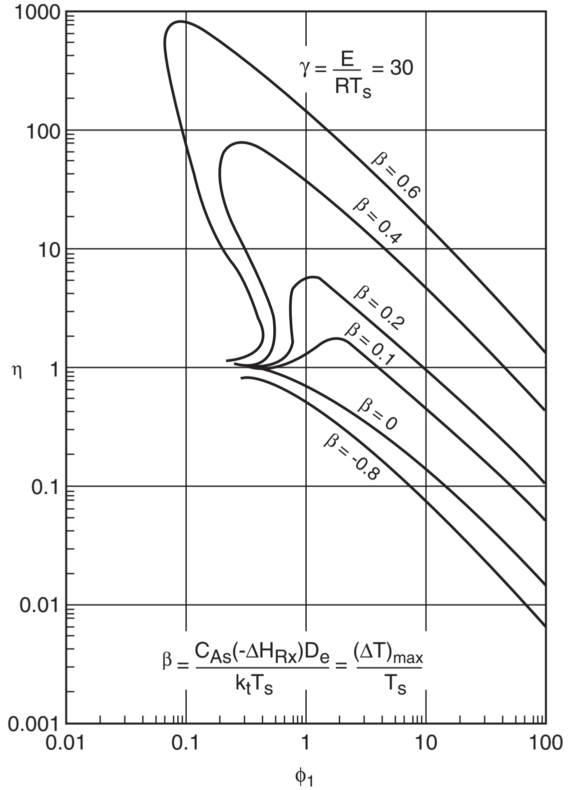


Figure 12-7 Nonisothermal effectiveness factor.

Can you find regions where multiple solutions (MSS) exist?

ratio of the actual reaction rate to the rate at surface conditions, the effectiveness factor can be greater than 1, depending on the magnitude of the parameters β and γ. The parameter γ is sometimes referred to as the Arrhenius number, and the parameter β represents the maximum temperature difference that could exist in the pellet relative to the surface temperature T_s.

$$\gamma = \text{Arrhenius number} = \frac{E}{RT_s}$$

$$\beta = \frac{\Delta T_{\max}}{T_s} = \frac{T_{\max} - T_s}{T_s} = \frac{-\Delta H_{Rx} D_e C_{As}}{k_t T_s}$$

Typical parameter values

(See Problem P12-13$_C$ for the derivation of β.) The Thiele modulus for a first-order reaction, ϕ_1, is evaluated at the external surface temperature. Typical values of γ for industrial processes range from a value of $\gamma = 6.5$ ($\beta = 0.025$, $\phi_1 = 0.22$) for the synthesis of vinyl chloride from HCl and acetone to a value of $\gamma = 29.4$ ($\beta = 6 \times 10^{-5}$, $\phi_1 = 1.2$) for the synthesis of ammonia.[5] The lower the thermal conductivity k_t and the higher the heat of reaction, the greater the temperature difference (see Problems P12-13$_C$ and P12-14$_C$). We observe

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[5] H. V. Hlavacek, N. Kubicek, and M. Marek, *J. Catal.*, *15*, 17 (1969).

Criterion for **no** MSSs in the pellet

from Figure 12-7 that multiple steady states can exist for values of the Thiele modulus less than 1 and when β is greater than approximately 0.2. There will be no multiple steady states when the criterion developed by Luss[6] is fulfilled.

$$\boxed{4(1+\beta)>\beta\gamma} \tag{12-36}$$

12.3 Falsified Kinetics

You may not be measuring what you think you are.

There are circumstances under which the measured reaction order and activation energy are not the true values. Consider the case in which we obtain reaction rate data in a differential reactor, where precautions are taken to virtually eliminate external mass transfer resistance (i.e., $C_{As} = C_{Ab}$). From these data we construct a log-log plot of the measured rate of reaction $-r'_A$ as a function of the gas-phase concentration, C_{As} (Figure 12-8). The slope of this plot is the apparent reaction order n' and the rate law takes the form

$$-r'_A = k'_n C_{As}^{n'} \tag{12-37}$$

Measured rate with apparent reaction order n'

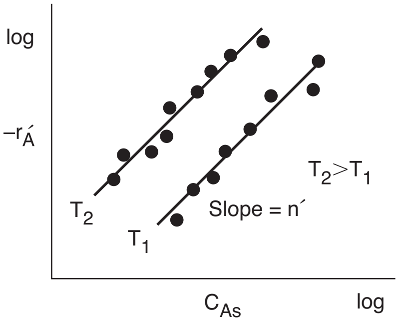

Figure 12-8 Determining the apparent reaction order ($-r_A = \rho_b\,(-r'_A)$).

We will now proceed to relate this measured reaction order n' to the true reaction order n. Using the definition of the effectiveness factor, note that the actual rate $-r'_A$, is the product of η and the rate of reaction evaluated at the external surface, $k_n C_{As}^n$, i.e.,

$$-r'_A = \eta\,(-r'_{As}) = \eta\,(k_n C_{As}^n) \tag{12-38}$$

For large values of the Thiele modulus ϕ_n, we can use Equation (12-35) to substitute into Equation (12-38) to obtain

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[6] D. Luss, *Chem. Eng. Sci.*, *23*, 1249 (1968).

$$-r'_A = \frac{3}{\phi_n}\sqrt{\frac{2}{n+1}} \quad k_n C_{As}^n = \frac{3}{R}\sqrt{\frac{D_e}{k_n}C_{As}^{1-n}}\sqrt{\frac{2}{n+1}}\; k_n C_{As}^n$$

$$= \frac{3}{R}\sqrt{\frac{2D_e}{(n+1)}}\; k_n^{1/2} C_{As}^{(n+1)/2} \tag{12-39}$$

We equate the true reaction rate, Equation (12-39), to the measured reaction rate, Equation (12-37), to get

$$-r'_A = \sqrt{\frac{2}{n+1}}\left(\frac{3}{R}\sqrt{D_e}\; k_n^{1/2} C_{As}^{(n+1)/2}\right) = k'_n C_{As}^{n'} \tag{12-40}$$

We now compare Equations (12-39) and (12-40). Because the overall exponent of the concentration, C_{As}, must be the same for both the analytical and measured rates of reaction, the apparent reaction order n' is related to the true reaction order n by

The true and the apparent reaction order

$$\boxed{n' = \frac{1+n}{2}} \tag{12-41}$$

In addition to an apparent reaction order, there is also an apparent activation energy, E_{App}. This value is the activation energy we would calculate using the experimental data, from the slope of a plot of $\ln(-r'_A)$ as a function of $1/T$ at a fixed concentration of A. Substituting for the measured and true specific reaction rates in terms of the activation energy gives

$$\underbrace{k'_n = A_{App} e^{-E_{App}/RT}}_{\text{measured}} \qquad \underbrace{k_n = A_T e^{-E_T/RT}}_{\text{true}}$$

into Equation (12-40), we find that

$\boxed{n_{true} = 2n_{apparent} - 1}$

$$-r'_A = \left(\frac{3}{R}\sqrt{\frac{2}{n+1}\,D_e}\right) A_T^{1/2}\left[\exp\left(\frac{-E_T}{RT}\right)\right]^{1/2} C_{As}^{(n+1)/2} = A_{App}\left[\exp\left(\frac{-E_{App}}{RT}\right)\right] C_{As}^{n'}$$

Taking the natural log of both sides gives us

$$\ln\left[\frac{3}{R}\sqrt{\frac{2}{n+1}\,D_e}\; A_T^{1/2} C_{As}^{(n+1)/2}\right] - \frac{E_T}{2RT} = \ln(A_{App} C_{As}^{n'}) - \frac{E_{App}}{RT} \tag{12-42}$$

where E_T is the true activation energy.

Comparing the temperature-dependent terms on the right- and left-hand sides of Equation (12-42), we see that the true activation energy is equal to twice the apparent activation energy.

The true activation energy

$$\boxed{E_T = 2E_{App}} \tag{12-43}$$

From *Elements of Chemical Reaction Engineering, Fourth Edition,* by H. Scott Fogler.

This measurement of the apparent reaction order and activation energy results primarily when internal diffusion limitations are present and is referred to as *disguised* or *falsified kinetics*. Serious consequences could occur if the laboratory data were taken in the disguised regime and the reactor were operated in a different regime. For example, what if the particle size were reduced so that internal diffusion limitations became negligible? The higher activation energy, E_T, would cause the reaction to be much more temperature-sensitive, and there is the possibility for *runaway reaction conditions* to occur.

Important industrial consequence of falsified kinetic

12.4 Overall Effectiveness Factor

For first-order reactions we can use an overall effectiveness factor to help us analyze diffusion, flow, and reaction in packed beds. We now consider a situation where external and internal resistance to mass transfer to and within the pellet are of the same order of magnitude (Figure 12-9). At steady state, the transport of the reactant(s) from the bulk fluid to the external surface of the catalyst is equal to the net rate of reaction of the reactant within and on the pellet.

Here, both internal and external diffusion are important.

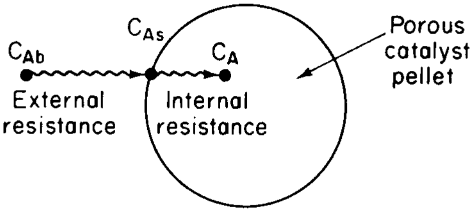

Figure 12-9 Mass transfer and reaction steps.

The molar rate of mass transfer from the bulk fluid to the external surface is

$$\text{Molar rate} = (\text{Molar flux}) \cdot (\text{External surface area})$$

$$M_A = W_{Ar} \cdot (\text{Surface area/Volume})(\text{Reactor volume})$$

$$= W_{Ar} \cdot a_c \Delta V \tag{12-44}$$

where a_c is the external surface area per unit reactor volume (cf. Chapter 11) and ΔV is the volume.

This molar rate of mass transfer to the surface, M_A, is equal to the net (total) rate of reaction *on* **and** *within* the pellet:

$$\boxed{M_A = -r''_A \text{ (External area + Internal area)}}$$

$$\text{External area} = \frac{\text{External area}}{\text{Reactor volume}} \times \text{Reactor volume}$$

$$= a_c \, \Delta V$$

$$\text{Internal area} = \frac{\text{Internal area}}{\text{Mass of catalyst}} \times \frac{\text{Mass of catalyst}}{\text{Volume of catalyst}} \times \frac{\text{Volume of catalyst}}{\text{Reactor volume}} \times \text{Reactor volume}$$

$$= S_a \overbrace{\rho_c (1-\phi)}^{\rho_b} \Delta V$$

$$= S_a \rho_b \, \Delta V$$

ρ_b = Bulk density
= $\rho_c (1 - \phi)$
ϕ = Porosity
nomenclature note
in Example 12-4.

$$\boxed{M_A = -r''_A [a_c \, \Delta V + S_a \rho_b \, \Delta V]} \tag{12-45}$$

Combining Equations (12-44) and (12-45) and canceling the volume ΔV, one obtains

$$W_{Ar} a_c = -r''_A \cdot (a_c + S_a \rho_b)$$

For most catalysts the internal surface area is much greater than the external surface area (i.e., $S_a \rho_b \gg a_c$), in which case we have

$$\boxed{W_{Ar} a_c = -r''_A S_a \rho_b} \tag{12-46}$$

where $-r''_A$ is the overall rate of reaction within and on the pellet per unit surface area. The relationship for the rate of mass transport is

$$M_A = W_{Ar} a_c \, \Delta V = k_c (C_{Ab} - C_{As}) a_c \, \Delta V \tag{12-47}$$

where k_c is the external mass transfer coefficient (m/s). Because internal diffusion resistance is also significant, not all of the interior surface of the pellet is accessible to the concentration at the external surface of the pellet, C_{As}. We have already learned that the effectiveness factor is a measure of this surface accessibility [see Equation (12-38)]:

$$-r''_A = -r''_{As} \eta$$

Assuming that the surface reaction is first order with respect to A, we can utilize the internal effectiveness factor to write

$$-r''_A = \eta k''_1 C_{As} \tag{12-48}$$

We need to eliminate the surface concentration from any equation involving the rate of reaction or rate of mass transfer, because C_{As} cannot be measured by standard techniques. To accomplish this elimination, first substitute Equation (12-48) into Equation (12-46):

$$W_{\mathrm{Ar}} a_c = \eta k_1'' S_a C_{\mathrm{As}} \rho_b$$

Then substitute for $W_{\mathrm{Ar}} a_c$ using Equation (12-47)

$$k_c a_c (C_{\mathrm{Ab}} - C_{\mathrm{As}}) = \eta k_1'' S_a \rho_b C_{\mathrm{As}} \tag{12-49}$$

Solving for C_{As}, we obtain

Concentration at the pellet surface as a function of bulk gas concentration

$$C_{\mathrm{As}} = \frac{k_c a_c C_{\mathrm{Ab}}}{k_c a_c + \eta k_1'' S_a \rho_b} \tag{12-50}$$

Substituting for $C_{\mathrm{A}s}$ in Equation (12-48) gives

$$-r_{\mathrm{A}}'' = \frac{\eta k_1'' k_c a_c C_{\mathrm{Ab}}}{k_c a_c + \eta k_1'' S_a \rho_b} \tag{12-51}$$

In discussing the surface accessibility, we defined the internal effectiveness factor η with respect to the concentration at the external surface of the pellet, C_{As}:

$$\boxed{\eta = \frac{\text{Actual overall rate of reaction}}{\text{Rate of reaction that would result if entire interior surface were exposed to the external pellet surface conditions, } C_{\mathrm{As}}, T_s}} \tag{12-28}$$

Two different effectiveness factors

We now define an overall effectiveness factor that is based on the bulk concentration:

$$\boxed{\Omega = \frac{\text{Actual overall rate of reaction}}{\text{Rate that would result if the entire surface were exposed to the bulk conditions, } C_{\mathrm{Ab}}, T_b}} \tag{12-52}$$

Dividing the numerator and denominator of Equation (12-51) by $k_c a_c$, we obtain the net rate of reaction (total molar flow of A to the surface in terms of the bulk fluid concentration), which is a measurable quantity:

$$-r_{\mathrm{A}}'' = \frac{\eta}{1 + \eta k_1'' S_a \rho_b / k_c a_c} k_1'' C_{\mathrm{Ab}} \tag{12-53}$$

Consequently, the overall rate of reaction in terms of the bulk concentration C_{Ab} is

$$\boxed{-r''_A = \Omega(-r''_{Ab}) = \Omega k''_1 C_{Ab}} \tag{12-54}$$

where

Overall effectiveness factor for a first-order reaction

$$\boxed{\Omega = \frac{\eta}{1 + \eta k''_1 S_a \rho_b / k_c a_c}} \tag{12-55}$$

The rates of reaction based on surface and bulk concentrations are related by

$$-r''_A = \Omega(-r''_{Ab}) = \eta(-r''_{As}) \tag{12-56}$$

where

$$-r''_{As} = k''_1 C_{As}$$
$$-r''_{Ab} = k''_1 C_{Ab}$$

The actual rate of reaction is related to the reaction rate evaluated at the bulk concentration of A. The actual rate can be expressed in terms of the rate per unit volume, $-r_A$, the rate per unit mass, $-r'_A$, and the rate per unit surface area, $-r''_A$, which are related by the equation

$$-r_A = -r'_A \rho_b = -r''_A S_a \rho_b$$

In terms of the overall effectiveness factor for a first-order reaction and the reactant concentration in the bulk

$$-r_A = -r_{Ab}\Omega = -r'_{Ab}\rho_b\Omega = -r''_{Ab} S_a \rho_b \Omega = k''_1 C_{Ab} S_a \rho_b \Omega \tag{12-57}$$

where again

Overall effectiveness factor

$$\Omega = \frac{\eta}{1 + \eta k''_1 S_a \rho_b / k_c a_c}$$

Recall that k''_1 is given in terms of the catalyst surface area ($m^3/m^2 \cdot s$).

12.5 Estimation of Diffusion- and Reaction-Limited Regimes

In many instances it is of interest to obtain "quick and dirty" estimates to learn which is the rate-limiting step in a heterogeneous reaction.

12.5.1 Weisz–Prater Criterion for Internal Diffusion

The Weisz–Prater criterion uses measured values of the rate of reaction, $-r'_A$ (obs), to determine if internal diffusion is limiting the reaction. This criterion can be developed intuitively by first rearranging Equation (12-32) in the form

$$\eta\phi_1^2 = 3(\phi_1 \coth\phi_1 - 1) \tag{12-58}$$

Showing where the Weisz–Prater comes from

The left-hand side is the Weisz–Prater parameter:

$$C_{WP} = \eta \times \phi_1^2 \tag{12-59}$$

$$= \frac{\text{Observed (actual) reaction rate}}{\text{Reaction rate evaluated at } C_{As}} \times \frac{\text{Reaction rate evaluated at } C_{As}}{\text{A diffusion rate}}$$

$$= \frac{\text{Actual reaction rate}}{\text{A diffusion rate}}$$

Substituting for

$$\eta = \frac{-r'_A(\text{obs})}{-r'_{As}} \qquad \text{and} \qquad \phi_1^2 = \frac{-r''_{As} S_a \rho_c R^2}{D_e C_{As}} = \frac{-r'_{As} \rho_c R^2}{D_e C_{As}}$$

in Equation (12-59) we have

$$C_{WP} = \frac{-r'_A(\text{obs})}{-r'_{As}} \left(\frac{-r'_{As} \rho_c R^2}{D_e C_{As}} \right) \tag{12-60}$$

$$\boxed{C_{WP} = \eta\phi_1^2 = \frac{-r'_A(\text{obs})\, \rho_c R^2}{D_e C_{As}}} \tag{12-61}$$

Are there any internal diffusion limitations indicated from the Weisz–Prater criterion?

All the terms in Equation (12-61) are either measured or known. Consequently, we can calculate C_{WP}. However, if

$$\boxed{C_{WP} \ll 1}$$

there are no diffusion limitations and consequently no concentration gradient exists within the pellet. However, if

$$\boxed{C_{WP} \gg 1}$$

internal diffusion limits the reaction severely. Ouch!

Example 12–3 Estimating Thiele Modulus and Effectiveness Factor

The first-order reaction

$$A \longrightarrow B$$

was carried out over two different-sized pellets. The pellets were contained in a spinning basket reactor that was operated at sufficiently high rotation speeds that external mass transfer resistance was negligible. The results of two experimental runs made under identical conditions are as given in Table E12-3.1. **(a)** Estimate the Thiele modulus and effectiveness factor for each pellet. **(b)** How small should the pellets be made to virtually eliminate all internal diffusion resistance?

These two experiments yield an enormous amount of information.

TABLE E12-3.1 DATA FROM A SPINNING BASKET REACTOR[†]

	Measured Rate (obs) (mol/g cat · s) × 10^5	*Pellet Radius* (m)
Run 1	3.0	0.01
Run 2	15.0	0.001

[†] See Figure 5-12(c).

Solution

(a) Combining Equations (12-58) and (12-61), we obtain

$$\frac{-r'_A(\text{obs})R^2\rho_c}{D_e C_{As}} = \eta\phi_1^2 = 3(\phi_1 \coth\phi_1 - 1) \tag{E12-3.1}$$

Letting the subscripts 1 and 2 refer to runs 1 and 2, we apply Equation (E12-3.1) to runs 1 and 2 and then take the ratio to obtain

$$\frac{-r'_{A2}R_2^2}{-r'_{A1}R_1^2} = \frac{\phi_{12}\coth\phi_{12} - 1}{\phi_{11}\coth\phi_{11} - 1} \tag{E12-3.2}$$

The terms ρ_c, D_e, and C_{As} cancel because the runs were carried out under identical conditions. The Thiele modulus is

$$\phi_1 = R\sqrt{\frac{-r'_{As}\rho_c}{D_e C_{As}}} \tag{E12-3.3}$$

Taking the ratio of the Thiele moduli for runs 1 and 2, we obtain

$$\boxed{\frac{\phi_{11}}{\phi_{12}} = \frac{R_1}{R_2}} \tag{E12-3.4}$$

or

$$\phi_{11} = \frac{R_1}{R_2}\phi_{12} = \frac{0.01\text{ m}}{0.001\text{ m}}\phi_{12} = 10\phi_{12} \tag{E12-3.5}$$

Substituting for ϕ_{11} in Equation (E12-3.2) and evaluating $-r'_A$ and R for runs 1 and 2 gives us

$$\left(\frac{15\times10^{-5}}{3\times10^{-5}}\right)\frac{(0.001)^2}{(0.01)^2} = \frac{\phi_{12}\coth\phi_{12} - 1}{10\phi_{12}\coth(10\phi_{12}) - 1} \tag{E12-3.6}$$

$$0.05 = \frac{\phi_{12}\coth\phi_{12} - 1}{10\phi_{12}\coth(10\phi_{12}) - 1} \tag{E12-3.7}$$

We now have one equation and one unknown. Solving Equation (E12-3.7) we find that

$$\boxed{\begin{array}{ll} \phi_{12} = 1.65 & \text{for } R_2 = 0.001\text{ m} \\ \text{Then} & \\ \phi_{11} = 10\phi_{12} = 16.5 & \text{for } R_1 = 0.01\text{ m} \end{array}}$$

The corresponding effectiveness factors are

Given two experimental points, one can predict the particle size where internal mass transfer does not limit the rate of reaction.

$$\boxed{\begin{array}{ll} \text{For } R_2: & \eta_2 = \dfrac{3(\phi_{12}\coth\phi_{12} - 1)}{\phi_{12}^2} = \dfrac{3(1.65\coth 1.65 - 1)}{(1.65)^2} = 0.856 \\ \text{For } R_1: & \eta_1 = \dfrac{3(16.5\coth 16.5 - 1)}{(16.5)^2} \approx \dfrac{3}{16.5} = 0.182 \end{array}}$$

(b) Next we calculate the particle radius needed to virtually eliminate internal diffusion control (say, $\eta = 0.95$):

$$0.95 = \frac{3(\phi_{13}\coth\phi_{13} - 1)}{\phi_{13}^2} \tag{E12-3.8}$$

Solution to Equation (E12-2.8) yields $\phi_{13} = 0.9$:

$$\boxed{R_3 = R_1\frac{\phi_{13}}{\phi_{11}} = (0.01)\left(\frac{0.9}{16.5}\right) = 5.5 \times 10^{-4}\text{ m}}$$

A particle size of 0.55 mm is necessary to virtually eliminate diffusion control (i.e., $\eta = 0.95$).

12.5.2 Mears' Criterion for External Diffusion

The Mears[7] criterion, like the Weisz–Prater criterion, uses the measured rate of reaction, $-r'_A$, (kmol/kg cat·s) to learn if mass transfer from the bulk gas phase to the catalyst surface can be neglected. Mears proposed that when

Is external diffusion limiting?

$$\boxed{\frac{-r'_A\rho_b Rn}{k_c C_{Ab}} < 0.15} \tag{12-62}$$

external mass transfer effects can be neglected.

---

[7] D. E. Mears, *Ind. Eng. Chem. Process Des. Dev.*, *10*, 541 (1971). Other interphase transport-limiting criteria can be found in *AIChE Symp. Ser. 143* (S. W. Weller, ed.), 70 (1974).

where n = reaction order
R = catalyst particle radius, m
ρ_b = bulk density of catalyst bed, kg/m^3
$= (1 - \phi)\rho_c \quad (\phi = \text{porosity})$
ρ_c = solid density of catalyst, kg/m^3
C_{Ab} = bulk reactant concentration, mol/dm^3
k_c = mass transfer coefficient, m/s

The mass transfer coefficient can be calculated from the appropriate correlation, such as that of Thoenes–Kramers, for the flow conditions through the bed. When Equation (12-62) is satisfied, no concentration gradients exist between the bulk gas and external surface of the catalyst pellet.

Mears also proposed that the bulk fluid temperature, T, will be virtually the same as the temperature at the external surface of the pellet when

Is there a temperature gradient?

$$\boxed{\left|\frac{-\Delta H_{Rx}(-r'_A)\rho_b RE}{hT^2R_g}\right| < 0.15} \tag{12-63}$$

where h = heat transfer coefficient between gas and pellet, kJ/m$^2\cdot$s$\cdot$K
R_g = gas constant, 8.314 J/mol$\cdot$K
ΔH_{Rx} = heat of reaction, kJ/mol
E = activation energy, kJ/kmol

and the other symbols are as in Equation (12-62).

12.6 Mass Transfer and Reaction in a Packed Bed

We now consider the same isomerization taking place in a packed bed of catalyst pellets rather than on one single pellet (see Figure 12-10). The concentration C_{Ab} is the bulk gas-phase concentration of A at any point along the length of the bed.

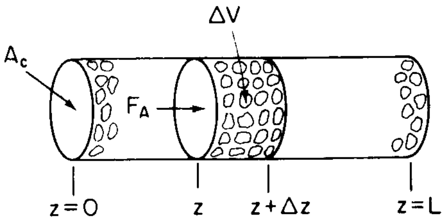

Figure 12-10 Packed-bed reactor.

We shall perform a balance on species A over the volume element ΔV, neglecting any radial variations in concentration and assuming that the bed is operated at steady state. The following symbols will be used in developing our model:

A_c = cross-sectional area of the tube, dm^2
C_{Ab} = bulk gas concentration of A, mol/dm^3
ρ_b = bulk density of the catalyst bed, g/dm^3
v_0 = volumetric flow rate, dm^3/s
U = superficial velocity = v_0/A_c, dm/s

Mole Balance

A mole balance on the volume element ($A_c\Delta z$) yields

$$\begin{array}{ccccccc}[\text{Rate in}] & - & [\text{Rate out}] & + & [\text{Rate of formation of A}] & = & 0\\ A_cW_{Az}|_z & - & A_cW_{Az}|_{z+\Delta z} & + & r_A'\rho_bA_c\Delta z & = & 0\end{array}$$

Dividing by $A_c\ \Delta z$ and taking the limit as $\Delta z \longrightarrow 0$ yields

$$-\frac{dW_{Az}}{dz}+r_A'\rho_b=0 \tag{12-64}$$

Assuming that the total molar concentration c is constant, Equation (11-14) can be expressed as

$$W_{Az}=-D_{AB}\frac{dC_{Ab}}{dz}+y_{Ab}(W_{Az}+W_{Bz})$$

Also, writing the bulk flow term in the form

$$B_{Az}=y_{Ab}(W_{Az}+W_{Bz})=y_{Ab}cU=UC_{Ab}$$

Equation (12-64) can be written in the form

$$D_{AB}\frac{d^2C_{Ab}}{dz^2}-U\frac{dC_{Ab}}{dz}+r_A'\rho_b=0 \tag{12-65}$$

Now we will see how to use η and Ω to calculate conversion in a packed bed.

The term $D_{AB}(d^2C_{Ab}/dz^2)$ is used to represent either diffusion and/or dispersion in the axial direction. Consequently, we shall use the symbol D_a for the dispersion coefficient to represent either or both of these cases. We will come back to this form of the diffusion equation when we discuss dispersion in Chapter 14. The overall reaction rate within the pellet, $-r_A'$, is the overall rate of reaction within and on the catalyst per unit mass of catalyst. It is a function of the reactant concentration within the catalyst. This overall rate can be related to the rate of reaction of A that would exist if the entire surface were exposed to the bulk concentration C_{Ab} through the overall effectiveness factor Ω:

$$-r_A'=-r_{Ab}'\times\Omega \tag{12-57}$$

For the first-order reaction considered here,

$$-r_{Ab}'=-r_{Ab}''S_a=k''S_aC_{Ab} \tag{12-66}$$

Substituting Equation (12-66) into Equation (12-57), we obtain the overall rate of reaction per unit mass of catalyst in terms of the bulk concentration C_{Ab}:

$$-r'_{\text{A}} = \Omega k'' S_{\text{a}} C_{\text{Ab}}$$

Substituting this equation for $-r'_{\text{A}}$ into Equation (12-65), we form the differential equation describing diffusion with a first-order reaction in a catalyst bed:

Flow and first-order reaction in a packed bed

$$\boxed{D_{\text{a}} \frac{d^2 C_{\text{Ab}}}{dz^2} - U \frac{dC_{\text{Ab}}}{dz} - \Omega \rho_{\text{b}} k'' S_{\text{a}} C_{\text{Ab}} = 0} \tag{12-67}$$

As an example, we shall solve this equation for the case in which the flow rate through the bed is very large and the axial diffusion can be neglected. Young and Finlayson[8] have shown that axial dispersion can be neglected when

Criterion for neglecting axial dispersion/diffusion

$$\boxed{\left|\frac{-r'_{\text{A}} \rho_{\text{b}} d_{\text{p}}}{U_0 C_{\text{Ab}}}\right| \ll \left|\frac{U_0 d_{\text{p}}}{D_{\text{a}}}\right|} \tag{12-68}$$

where U_0 is the superficial velocity, d_{p} the particle diameter, and D_{a} is the effective axial dispersion coefficient. In Chapter 14 we will consider solutions to the complete form of Equation (12-67).

Neglecting axial dispersion with respect to forced axial convection,

$$\left|U \frac{dC_{\text{Ab}}}{dz}\right| \gg \left|D_{\text{a}} \frac{d^2 C_{\text{Ab}}}{dz^2}\right|$$

Equation (12-67) can be arranged in the form

$$\frac{dC_{\text{Ab}}}{dz} = -\left(\frac{\Omega \rho_{\text{b}} k'' S_{\text{a}}}{U}\right) C_{\text{Ab}} \tag{12-69}$$

With the aid of the boundary condition at the entrance of the reactor,

$$C_{\text{Ab}} = C_{\text{Ab0}} \qquad \text{at } z = 0$$

Equation (12-69) can be integrated to give

$$C_{\text{Ab}} = C_{\text{Ab0}}\, e^{-(\rho_{\text{b}} k'' S_{\text{a}} \Omega z)/U} \tag{12-70}$$

The conversion at the reactor's exit, $z = L$, is

Conversion in a packed-bed reactor

$$\boxed{X = 1 - \frac{C_{\text{Ab}}}{C_{\text{Ab0}}} = 1 - e^{-(\rho_{\text{b}} k'' S_{\text{a}} \Omega L)/U}} \tag{12-71}$$

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[8] L. C. Young and B. A. Finlayson, *Ind. Eng. Chem. Fund.*, *12*, 412 (1973).

Example 12–4 Reducing Nitrous Oxides in a Plant Effluent

In Section 7.1.4 we saw the role that nitric oxide plays in smog formation and the incentive we would have for reducing its concentration in the atmosphere. It is proposed to reduce the concentration of NO in an effluent stream from a plant by passing it through a packed bed of spherical porous carbonaceous solid pellets. A 2% NO–98% air mixture flows at a rate of 1×10^{-6} m³/s (0.001 dm³/s) through a 2-in.-ID tube packed with porous solid at a temperature of 1173 K and a pressure of 101.3 kPa. The reaction

$$\mathrm{NO} + \mathrm{C} \longrightarrow \mathrm{CO} + \tfrac{1}{2}\mathrm{N}_2$$

is first order in NO, that is,

$$-r'_{\mathrm{NO}} = k''_1 S_a C_{\mathrm{NO}}$$

and occurs primarily in the pores inside the pellet, where

Green chemical reaction engineering

$$S_a = \text{Internal surface area} = 530\ \mathrm{m^2/g}$$

$$k''_1 = 4.42 \times 10^{-10}\ \mathrm{m^3/m^2 \cdot s}$$

Calculate the weight of porous solid necessary to reduce the NO concentration to a level of 0.004%, which is below the Environmental Protection Agency limit.

Additional information:

At 1173 K, the fluid properties are

$$\nu = \text{Kinematic viscosity} = 1.53 \times 10^{-8}\ \mathrm{m^2/s}$$

$$D_{AB} = \text{Gas-phase diffusivity} = 2.0 \times 10^{-8}\ \mathrm{m^2/s}$$

$$D_e = \text{Effective diffusivity} = 1.82 \times 10^{-8}\ \mathrm{m^2/s}$$

Also see Web site *www.rowan.edu/greenengineering*

The properties of the catalyst and bed are

$$\rho_c = \text{Density of catalyst particle} = 2.8\ \mathrm{g/cm^3} = 2.8 \times 10^6\ \mathrm{g/m^3}$$

$$\phi = \text{Bed porosity} = 0.5$$

$$\rho_b = \text{Bulk density of bed} = \rho_c(1-\phi) = 1.4 \times 10^6\ \mathrm{g/m^3}$$

$$R = \text{Pellet radius} = 3 \times 10^{-3}\ \mathrm{m}$$

$$\gamma = \text{Sphericity} = 1.0$$

Solution

It is desired to reduce the NO concentration from 2.0% to 0.004%. Neglecting any volume change at these low concentrations gives us

$$X = \frac{C_{Ab0} - C_{Ab}}{C_{Ab0}} = \frac{2 - 0.004}{2} = 0.998$$

where A represents NO.

The variation of NO down the length of the reactor is given by Equation (12-69)

$$\frac{dC_{\text{Ab}}}{dz} = -\frac{\Omega k'' S_a \rho_b C_{\text{Ab}}}{U} \tag{12-69}$$

Multiplying the denominator on the right and left hand sides of Equation (12-69) by the cross-sectional area, A_c, to get $v_0 = A_c W$ and realizing that the weight of catalyst up to a point z in the bed is

(Mole balance)
+
(Rate law)
+
(Overall effectiveness factor)

$$W = \rho_b A_c z$$

the variation of NO concentration with solids is

$$\frac{dC_{\text{Ab}}}{dW} = -\frac{\Omega k'' S_a C_{\text{Ab}}}{U} \tag{E12-4.1}$$

Because NO is present in dilute concentrations, we shall take $\varepsilon \ll 1$ and set $U = v_0$. We integrate Equation (E12-4.1) using the boundary condition that when $W = 0$, then $C_{\text{Ab}} = C_{\text{Ab0}}$:

$$\boxed{X = 1 - \frac{C_{\text{Ab}}}{C_{\text{Ab0}}} = 1 - \exp\left(-\frac{\Omega k'' S_a W}{v_0}\right)} \tag{E12-4.2}$$

where

$$\Omega = \frac{\eta}{1 + \eta k'' S_a \rho_c / k_c a_c} \tag{12-55}$$

Rearranging, we have

$$\boxed{W = \frac{v_0}{\Omega k'' S_a} \ln \frac{1}{1-X}} \tag{E12-4.3}$$

1. *Calculating the internal effectiveness factor* for spherical pellets in which a first-order reaction is occurring, we obtained

$$\eta = \frac{3}{\phi_1^2}(\phi_1 \coth \phi_1 - 1) \tag{12-32}$$

As a first approximation, we shall neglect any changes in the pellet size resulting from the reactions of NO with the porous carbon. The Thiele modulus for this system is[9]

$$\phi_1 = R\sqrt{\frac{k_1'' \rho_c S_a}{D_e}} \tag{E12-4.4}$$

where

R = pellet radius = 3×10^{-3} m
D_e = effective diffusivity = 1.82×10^{-8} m^2/s
ρ_c = 2.8 g/cm^3 = 2.8×10^6 g/m^3

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[9] L. K. Chan, A. F. Sarofim, and J. M. Beer, *Combust. Flame*, *52*, 37 (1983).

$k_1'' $ = specific reaction rate = 4.42×10^{-10} m³/m²·s

$$\phi_1 = 0.003 \text{ m} \sqrt{\frac{(4.42\times10^{-10} \text{ m/s})(530 \text{ m}^2/\text{g})(2.8\times10^6 \text{ g/m}^3)}{1.82\times10^{-8} \text{ m}^2/\text{s}}}$$

$$\phi_1 = 18$$

Because ϕ_1 is large,

$$\eta \cong \frac{3}{18} = 0.167$$

2. *To calculate the external mass transfer coefficient*, the Thoenes–Kramers correlation is used. From Chapter 11 we recall

$$\text{Sh}' = (\text{Re}')^{1/2}\text{Sc}^{1/3} \tag{11-65}$$

For a 2-in.-ID pipe, $A_c = 2.03 \times 10^{-3}$ m². The superficial velocity is

$$U = \frac{v_0}{A_c} = \frac{10^{-6} \text{ m}^3/\text{s}}{2.03\times10^{-3} \text{ m}^2} = 4.93\times10^{-4} \text{ m/s}$$

Procedure
Calculate
Re′
Sc
Then
Sh′
Then
k_c

$$\text{Re}' = \frac{Ud_p}{(1-\phi)\nu} = \frac{(4.93\times10^{-4} \text{ m/s})(6\times10^{-3} \text{ m})}{(1-0.5)(1.53\times10^{-8} \text{ m}^2/\text{s})} = 386.7$$

Nomenclature note: ϕ with subscript 1, ϕ_1 = Thiele modulus
ϕ without subscript, ϕ = porosity

$$\text{Sc} = \frac{\nu}{D_{AB}} = \frac{1.53\times10^{-8} \text{ m}^2/\text{s}}{2.0\times10^{-8} \text{ m}^2/\text{s}} = 0.765$$

$$\text{Sh}' = (386.7)^{1/2}(0.765)^{1/3} = (19.7)(0.915) = 18.0$$

$$k_c = \frac{1-\phi}{\phi}\left(\frac{D_{AB}}{d_p}\right)\text{Sh}' = \frac{0.5}{0.5}\left(\frac{2.0\times10^{-8} \text{ (m}^2/\text{s)}}{6.0\times10^{-3} \text{ m}}\right)(18.0)$$

$$k_c = 6 \times 10^{-5} \text{ m/s}$$

3. *Calculating the external area per unit reactor volume*, we obtain

$$a_c = \frac{6(1-\phi)}{d_p} = \frac{6(1-0.5)}{6\times10^{-3} \text{ m}} = 500 \text{ m}^2/\text{m}^3 \tag{E12-4.5}$$

4. *Evaluating the overall effectiveness factor*. Substituting into Equation (12-55), we have

$$\Omega = \frac{\eta}{1+\eta k_1'' \; S_a \rho_b / k_c a_c}$$

$$\Omega = \frac{0.167}{1+\dfrac{(0.167)(4.4\times10^{-10}\ \text{m}^3/\text{m}^2\cdot\text{s})(530\ \text{m}^2/\text{g})(1.4\times10^{6}\ \text{g/m}^3)}{(6\times10^{-5}\ \text{m/s})(500\ \text{m}^2/\text{m}^3)}}$$

$$= \frac{0.167}{1+1.83} = 0.059$$

In this example we see that both the external and internal resistances to mass transfer are significant.

5. *Calculating the weight of solid necessary to achieve* 99.8% *conversion*. Substituting into Equation (E12-4.3), we obtain

$$W = \frac{1\times10^{-6}\ \text{m}^3/\text{s}}{(0.059)(4.42\times10^{-10}\ \text{m}^3/\text{m}^2\cdot\text{s})(530\ \text{m}^2/\text{g})} \ln\frac{1}{1-0.998}$$

$$= 450\ \text{g}$$

6. *The reactor length is*

$$L = \frac{W}{A_c \rho_b} = \frac{450\ \text{g}}{(2.03\times10^{-3}\ \text{m}^2)(1.4\times10^{6}\ \text{g/m}^3)}$$

$$= 0.16\ \text{m}$$

12.7 Determination of Limiting Situations from Reaction Data

For external mass transfer-limited reactions in packed beds, the rate of reaction at a point in the bed is

$$-r_A' = k_c a_c C_A \tag{12-72}$$

Variation of reaction rate with system variables

The correlation for the mass transfer coefficient, Equation (11-66), shows that k_c is directly proportional to the square root of the velocity and inversely proportional to the square root of the particle diameter:

$$k_c \propto \frac{U^{1/2}}{d_p^{1/2}} \tag{12-73}$$

We recall from Equation (E12-4.5), $a_c = 6(1-\phi)/d_p$, that the variation of external surface area with catalyst particle size is

$$a_c \propto \frac{1}{d_p}$$

Consequently, for external mass transfer-limited reactions, the rate is inversely proportional to the particle diameter to the three-halves power:

$$-r'_A \propto \frac{1}{d_p^{3/2}} \tag{12-74}$$

From Equation (11-72) we see that for gas-phase external mass transfer-limited reactions, the rate increases approximately linearly with temperature.

Many heterogeneous reactions are diffusion limited.

When internal diffusion limits the rate of reaction, we observe from Equation (12-39) that the rate of reaction varies inversely with particle diameter, is independent of velocity, and exhibits an exponential temperature dependence which is not as strong as that for surface-reaction-controlling reactions. For surface-reaction-limited reactions the rate is independent of particle size and is a strong function of temperature (exponential). Table 12-1 summarizes the dependence of the rate of reaction on the velocity through the bed, particle diameter, and temperature for the three types of limitations that we have been discussing.

Very Important Table

Table 12-1 Limiting Conditions

Type of Limitation	*Variation of Reaction Rate with:*		
	Velocity	*Particle Size*	*Temperature*
External diffusion	$U^{1/2}$	$(d_p)^{-3/2}$	≈Linear
Internal diffusion	Independent	$(d_p)^{-1}$	Exponential
Surface reaction	Independent	Independent	Exponential

The exponential temperature dependence for internal diffusion limitations is usually not as strong a function of temperature as is the dependence for surface reaction limitations. If we would calculate an activation energy between 8 and 24 kJ/mol, chances are that the reaction is strongly diffusion-limited. An activation energy of 200 kJ/mol, however, suggests that the reaction is reaction-rate-limited.

12.8 Multiphase Reactors

Multiphase reactors are reactors in which two or more phases are necessary to carry out the reaction. The majority of multiphase reactors involve gas and liquid phases that contact a solid. In the case of the slurry and trickle bed reactors, the reaction between the gas and the liquid takes place on a solid catalyst surface (see Table 12-2). However, in some reactors the liquid phase is an inert medium for the gas to contact the solid catalyst. The latter situation arises when a large heat sink is required for highly exothermic reactions. In many cases the catalyst life is extended by these milder operating conditions.

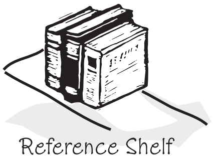

Reference Shelf

The multiphase reactors discussed in this edition of the book are the slurry reactor, fluidized bed, and the trickle bed reactor. The trickle bed reactor, which has reaction and transport steps similar to the slurry reactor, is discussed in the first edition of this book and on the CD-ROM along with the bubbling

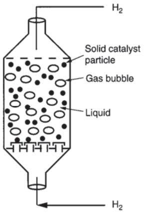
TABLE 12-2. APPLICATIONS OF THREE-PHASE REACTORS

- I. *Slurry reactor*
  - A. Hydrogenation
    - 1. of fatty acids over a supported nickel catalyst
    - 2. of 2-butyne-1,4-diol over a Pd-$CaCO_3$ catalyst
    - 3. of glucose over a Raney nickel catalyst
  - B. Oxidation
    - 1. of C_2H_4 in an inert liquid over a $PdCl_2$-carbon catalyst
    - 2. of SO_2 in inert water over an activated carbon catalyst
  - C. Hydroformation
    - of CO with high-molecular-weight olefins on either a cobalt or ruthenium complex bound to polymers
  - D. Ethynylation
    - Reaction of acetylene with formaldehyde over a $CaCl_2$-supported catalyst
- II. *Trickle bed reactors*
  - A. Hydrodesulfurization
    - Removal of sulfur compounds from crude oil by reaction with hydrogen on Co-Mo on alumina
  - B. Hydrogenation
    - 1. of aniline over a Ni-clay catalyst
    - 2. of 2-butyne-1,4-diol over a supported Cu-Ni catalyst
    - 3. of benzene, α-CH_3 styrene, and crotonaldehyde
    - 4. of aromatics in napthenic lube oil distillate
  - C. Hydrodenitrogenation
    - 1. of lube oil distillate
    - 2. of cracked light furnace oil
  - D. Oxidation
    - 1. of cumene over activated carbon
    - 2. of SO_2 over carbon

Source: C. N. Satterfield, *AIChE J.*, *21*, 209 (1975); P. A. Ramachandran and R. V. Chaudhari, *Chem. Eng.*, *87*(24), 74 (1980); R. V. Chaudhari and P. A. Ramachandran, *AIChE J.*, *26*, 177 (1980).

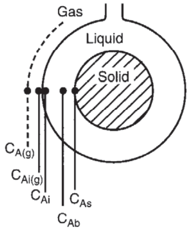


fluidized bed. In slurry reactors, the catalyst is suspended in the liquid, and gas is bubbled through the liquid. A slurry reactor may be operated in either a semibatch or continuous mode.



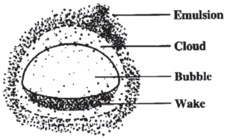
12.8.1 Slurry Reactors

A complete description of the slurry reactor and the transport and reaction steps are given on the CD-ROM, along with the design equations and a number of examples. Methods to determine which of the transport and reaction steps are rate limiting are included. See Professional Reference Shelf R12.1.



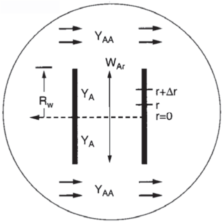
12.8.2 Trickle Bed Reactors

The CD-ROM includes all the material on trickle bed reactors from the first edition of this book. A comprehensive example problem for trickle bed reactor design is included. See Professional Reference Shelf R12.2.



12.9 Fluidized Bed Reactors

The Kunii-Levenspiel model for fluidization is given on the CD-ROM along with a comprehensive example problem. The rate limiting transport steps are also discussed. See Professional Reference Shelf R12.3.



12.10 Chemical Vapor Deposition (CVD)

Chemical Vapor Deposition in boat reactors is discussed and modeled. The equations and parameters which affect wafer thickness and shape are derived and analyzed. This material is taken directly from the second edition of this book. See Professional Reference Shelf R12.4.

Closure After completing this chapter, the reader should be able to derive differential equations describing diffusion and reaction, discuss the meaning of the effectiveness factor and its relationship to the Thiele modulus, and identify the regions of mass transfer control and reaction rate control. The reader should be able to apply the Weisz–Prater and Mears criteria to identify gradients and diffusion limitations. These principles should be able to be applied to catalyst particles as well as biomaterial tissue engineering. The reader should be able to apply the overall effectiveness factor to a packed bed reactor to calculate the conversion at the exit of the reactor. The reader should be able to describe the reaction and transport steps in slurry reactors, trickle bed reactors, fluidized-bed reactors, and CVD boat reactors and to make calculations for each reactor.

SUMMARY

1. The concentration profile for a first-order reaction occurring in a spherical catalyst pellet is

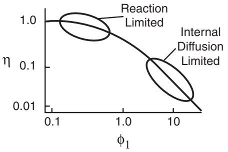
$$\frac{C_A}{C_{As}} = \frac{R}{r}\left[\frac{\sinh(\phi_1 r/R)}{\sinh \phi_1}\right] \tag{S12-1}$$

where ϕ_1 is the Thiele modulus. For a first-order reaction

$$\phi_1^2 = \frac{k_1}{D_e} R^2 \tag{S12-2}$$

2. The effectiveness factors are

$$\begin{array}{c}\text{Internal}\\ \text{effectiveness}\\ \text{factor}\end{array} = \eta = \frac{\text{Actual rate of reaction}}{\begin{array}{c}\text{Reaction rate if entire interior}\\ \text{surface is exposed to concentration}\\ \text{at the external pellet surface}\end{array}}$$



$$\begin{array}{c}\text{Overall}\\\text{effectiveness}\\\text{factor}\end{array} = \Omega = \frac{\text{Actual rate of reaction}}{\begin{array}{c}\text{Reaction rate if entire surface area}\\\text{is exposed to bulk concentration}\end{array}}$$

3. For large values of the Thiele modulus for an n^{th} order reaction,

$$\eta = \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{\phi_n} \tag{S12-3}$$

4. For internal diffusion control, the true reaction order is related to the measured reaction order by

$$n_{\text{true}} = 2n_{\text{apparent}} - 1 \tag{S12-4}$$

The true and apparent activation energies are related by

$$E_{\text{true}} = 2E_{\text{app}} \tag{S12-5}$$

5. A. The Weisz–Prater Parameter

$$C_{\text{WP}} = \phi_1^2 \eta = \frac{-r'_{\text{A}}(\text{observed})\,\rho_c R^2}{D_e C_{\text{As}}} \tag{S12-6}$$

The Weisz–Prater criterion dictates that

If $C_{\text{WP}} \ll 1$ no internal diffusion limitations present

If $C_{\text{WP}} \gg 1$ internal diffusion limitations present

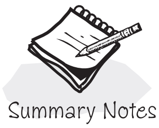
B. Mears Criteria for Neglecting External Diffusion and Heat Transfer

$$\boxed{\frac{-r'_{\text{A}}\rho_b R n}{k_c C_{\text{Ab}}} < 0.15} \tag{S12-7}$$

and

$$\boxed{\left|\frac{-\Delta H_{\text{Rx}}(-r'_{\text{A}})(\rho_b R E)}{h T^2 R_g}\right| < 0.15} \tag{S12-8}$$

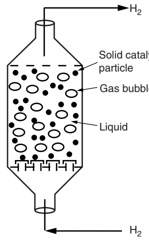
CD-ROM MATERIAL



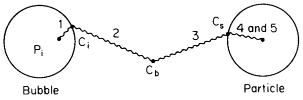
- **Learning Resources**
  1. *Summary Notes*

- **Professional Reference Shelf**

  R12.1. *Slurry Reactors*



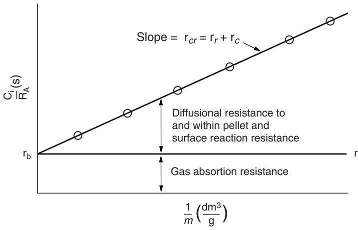
Transport Steps and Resistances

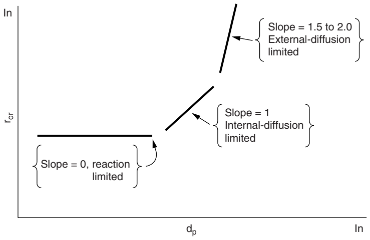


A. Description of Use of Slurry Reactors
   Example R12-1 Industrial Slurry Reactor
B. Reaction and Transport Steps in a Step in Slurry Reactor

$$\boxed{\frac{C_i}{R_A} = \frac{1}{k_b a_b} + \frac{1}{m}\left(\overbrace{\frac{1}{k_b a_b}}^{r_c} + \overbrace{\frac{1}{k\eta}}^{r_r}\right)}$$

C. Determining the Rate-Limiting Step
   1. Effect of Loading, Particle Size and Gas Adsorption
   2. Effect of Shear
      Example R12-2 Determining the Controlling Resistance
D. Slurry Reactor Design

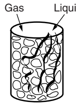


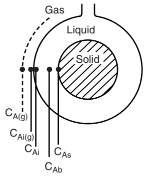


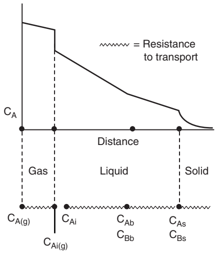
Example R12-3 Slurry Reactor Design

R12.2. *Trickle Bed Reactors*

A. Fundamentals







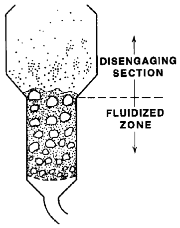
B. Limiting Situations
C. Evaluating the Transport Coefficients

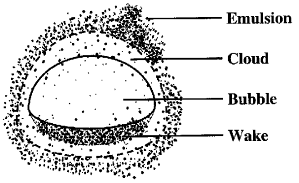
$$\boxed{-r'_A = \frac{1/H}{\underbrace{\frac{(1-\phi)\rho_c}{Hk_ga_i}+\frac{(1-\phi)\rho_c}{k_la_i}+\frac{1}{k_ca_p}+\frac{1}{\eta kC_{\text{B}s}}}_{k_{vg}}}\,C_\text{A}(g) \qquad \frac{\text{mol}}{\text{g cat}\cdot\text{s}}}$$

Reference Shelf

R12.3. *Fluidized-Bed Reactors*

A. Descriptive Behavior of the Kunii-Levenspiel Bubbling Bed Model





B. Mechanics of Fluidized Beds
   Example R12-4 Maximum Solids Hold-Up
C. Mass Transfer in Fluidized Beds
D. Reaction in a Fluidized Bed
E. Solution to the Balance Equations for a First Order Reaction

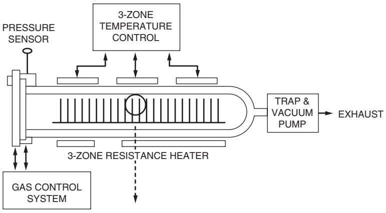
$$\boxed{W = \frac{\rho_c A_c u_b (1-\varepsilon_{mf})(1-\delta)}{k_{cat}K_R}\ln\frac{1}{1-X}}$$

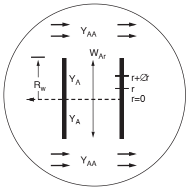
$$\boxed{K_R = \gamma_b + \cfrac{1}{\cfrac{k_{cat}}{K_{bc}} + \cfrac{1}{\gamma_c + \cfrac{1}{\cfrac{1}{\gamma_e} + \cfrac{k_{cat}}{K_{ce}}}}}}$$

   Example R12-5 Catalytic Oxidation of Ammonia
F. Limiting Situations
   Example R12-6 Calculation of the Resistances
   Example R12-7 Effect of Particle Size on Catalyst Weight for a Slow Reaction
   Example R12-8 Effect of Catalyst Weight for a Rapid Reaction

Reference Shelf

R12.4. *Chemical Vapor Deposition Reactors*

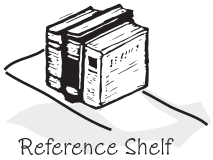


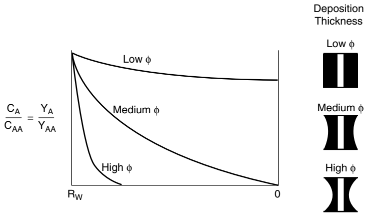


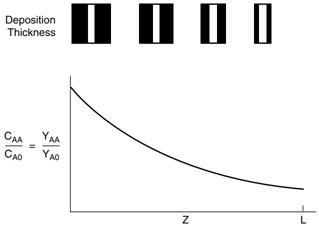
A. Chemical Reaction Engineering in Microelectronic Processing
B. Fundamentals of CVD
C. Effectiveness Factors for Boat Reactors

$$\boxed{\eta = \frac{2I_1(\phi_1)}{\phi_1 I_o(\phi_1)}}$$

Example R12-9 Diffusion Between Wafers
Example R12-10 CVD Boat Reactor







QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

A = ● B = ■ C = ◆ D = ◆◆

P12-1$_C$ Make up an original problem using the concepts presented in Section ______ (your instructor will specify the section). Extra credit will be given if you obtain and use real data from the literature. (See Problem P4-1$_A$ for the guidelines.)

P12-2$_B$ **(a)** **Example 12-1.** *Effective Diffusivity.* Make a sketch of a diffusion path for which the tortuosity is 5. How would your effective gas-phase diffusivity change if the absolute pressure were tripled and the temperature were increased by 50%?

(b) **Example 12-2.** *Tissue Engineering*. How would your answers change if the reaction kinetics were (1) first order in O_2 concentration with $k_1 = 10^{-2}$ h^{-1}? (2) For zero-order kinetics carry out a quasi steady state analysis using Equation (E12-2.19) along with the overall balance

$$\frac{dF_w}{dt} = v_c W_{O_2}\big|_{z=0} A_c$$

to predict the O_2 flux and collagen build-up as a function of time. Sketch ψ versus λ at different times. Sketch λ_c as a function of time. *Hint:* See P12-10$_B$. *Note*: $V = A_cL$. Assume $\alpha = 10$ and the stoichiometric coefficient for oxygen to collagen, v_c, is 0.05 mass fraction of cell/mol O_2. $A_c = 2$ cm^2

(c) **Example 12-3.** (1) What is the percent of the total resistance for internal diffusion and for reaction rate for each of the three particles studied? (2) Apply the Weisz-Prater criteria to a particle 0.005 m in diameter.

(d) **Example 12-4.** *Overall Effectiveness Factor.* (1) Calculate the percent of the total resistance for external diffusion, internal diffusion, and surface reaction. Qualitatively how would each of your percentages change (2) if the temperature were increased significantly? (3) if the gas velocity were tripled? (4) if the particle size were decreased by a factor of 2? How would the reactor length change in each case? (5) What length would be required to achieve 99.99% conversion of the pollutant NO?

What if...

(e) you applied the Mears and Weisz–Prater criteria to Examples 11-4 and 12-4? What would you find? What would you learn if $\Delta H^{\circ}_{\text{Rx}} = -25$ kcal/mol, $h = 100$ Btu/h·ft^2·°F and $E = 20$ kcal/mol?

(f) we let $\gamma = 30$, $\beta = 0.4$, and $\phi = 0.4$ in Figure 12-7? What would cause you to go from the upper steady state to the lower steady state and vice versa?

(g) your internal surface area decreased with time because of sintering. How would your effectiveness factor change and the rate of reaction change with time if $k_d = 0.01\ \text{h}^{-1}$ and $\eta = 0.01$ at $t = 0$? Explain.

(h) someone had used the false kinetics (i.e., wrong E, wrong n)? Would their catalyst weight be overdesigned or underdesigned? What are other positive or negative effects that occur?

Green engineering
Web site
www.rowan.edu/
greenengineering

(i) you were to assume the resistance to gas absorption in CDROM Example R12.1 were the same as in Example R12.3 and that the liquid phase reactor volume in Example R12.3 was 50% of the total, could you estimate the controlling resistance? If so, what is it? What other things could you calculate in Example R12.1 (e.g., selectivity, conversion, molar flow rates in and out)? *Hint:* Some of the other reactions that occur include

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

$$H_2O + CO \longrightarrow CO_2 + H_2$$

(j) the temperature in CDROM Example R12.2 were increased? How would the relative resistances in the slurry reactor change?

(k) you were asked for all the things that could go wrong in the operation of a slurry reactor, what would you say?

P12-3$_B$ The catalytic reaction

$$A \longrightarrow B$$

takes place within a fixed bed containing spherical porous catalyst X22. Figure P12-3$_B$ shows the overall rates of reaction at a point in the reactor as a function of temperature for various entering total molar flow rates, F_{T0}.

(a) Is the reaction limited by external diffusion?

(b) If your answer to part (a) was "yes," under what conditions [of those shown (i.e., T, F_{T0})] is the reaction limited by external diffusion?

(c) Is the reaction "reaction-rate-limited"?

(d) If your answer to part (c) was "yes," under what conditions [of those shown (i.e., T, F_{T0})] is the reaction limited by the rate of the surface reactions?

(e) Is the reaction limited by internal diffusion?

(f) If your answer to part (e) was "yes," under what conditions [of those shown (i.e., T, F_{T0})] is the reaction limited by the rate of internal diffusion?

(g) For a flow rate of 10 g mol/h, determine (if possible) the overall effectiveness factor, Ω, at 360 K.

(h) Estimate (if possible) the internal effectiveness factor, η, at 367 K.

(i) If the concentration at the external catalyst surface is 0.01 mol/dm^3, calculate (if possible) the concentration at $r = R/2$ inside the porous catalyst at 367 K. (Assume a first-order reaction.)

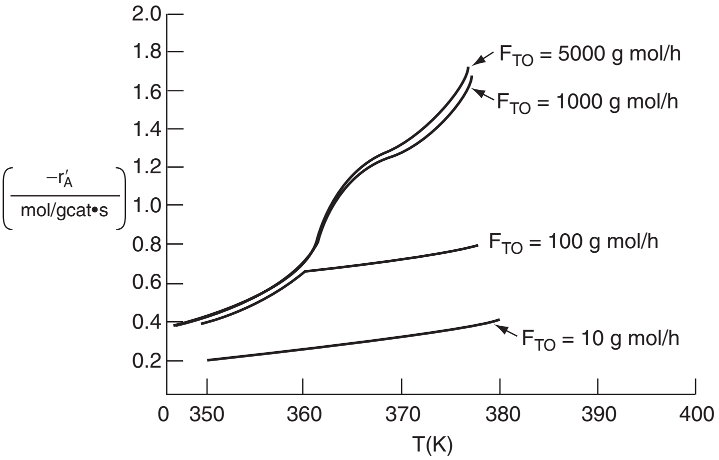


Figure P12-3$_B$ Reaction rates in a catalyst bed.

Additional information:

Gas properties:	**Bed properties:**
Diffusivity: 0.1 cm^2/s	Tortuosity of pellet: 1.414
Density: 0.001 g/cm^3	Bed permeability: 1 millidarcy
Viscosity: 0.0001 g/cm·s	Porosity = 0.3

Member

Hall of Fame

P12-4$_B$ The reaction

$$A \longrightarrow B$$

is carried out in a differential packed-bed reactor at different temperatures, flow rates, and particle sizes. The results shown in Figure P12-4$_B$ were obtained.

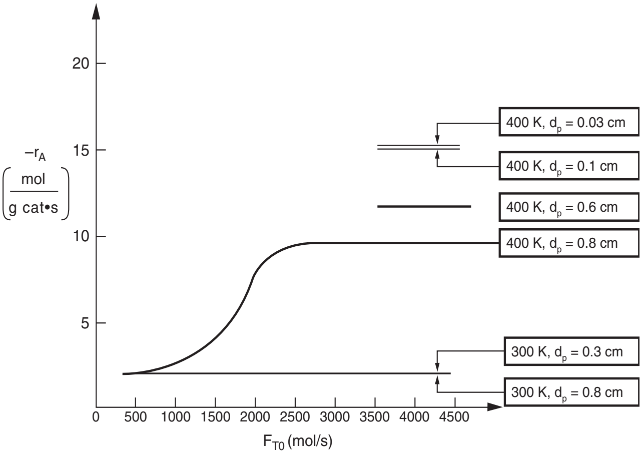


Figure P12-4$_B$ Reaction rates in a catalyst bed.

- **(a)** What regions (i.e., conditions d_p, T, F_{T0}) are external mass transfer-limited?
- **(b)** What regions are reaction-rate-limited?
- **(c)** What region is internal-diffusion-controlled?
- **(d)** What is the internal effectiveness factor at T = 400 K and d_p = 0.8 cm?

P12-5$_A$ Curves A, B, and C in Figure P12-5$_A$ show the variations in reaction rate for three different reactions catalyzed by solid catalyst pellets. What can you say about each reaction?

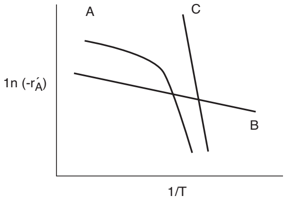


Figure P12-5$_A$ Temperature dependence of three reactions.

P12-6$_B$ A first-order heterogeneous irreversible reaction is taking place within a spherical catalyst pellet which is plated with platinum throughout the pellet (see Figure 12-3). The reactant concentration halfway between the external surface and the center of the pellet (i.e., $r = R/2$) is equal to one-tenth the concentration of the pellet's external surface. The concentration at the external surface is 0.001 g mol/dm^3, the diameter ($2R$) is 2×10^{-3} cm, and the diffusion coefficient is 0.1 cm^2/s.

$$A \longrightarrow B$$

(a) What is the concentration of reactant at a distance of 3×10^{-4} cm in from the external pellet surface? (*Ans.:* $C_A = 2.36 \times 10^{-4}$ mol/dm^3.)

(b) To what diameter should the pellet be reduced if the effectiveness factor is to be 0.8? (*Ans.:* $d_p = 6.8 \times 10^{-4}$ cm. Critique this answer!)

(c) If the catalyst support were not yet plated with platinum, how would you suggest that the catalyst support be plated *after* it had been reduced by grinding?

Application Pending for Problem Hall of Fame

P12-7$_B$ The swimming rate of a small organism [*J. Theoret. Biol.*, *26*, 11 (1970)] is related to the energy released by the hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP). The rate of hydrolysis is equal to the rate of diffusion of ATP from the midpiece to the tail (see Figure P12-7$_B$). The diffusion coefficient of ATP in the midpiece and tail is 3.6×10^{-6} cm^2/s. ADP is converted to ATP in the midsection, where its concentration is 4.36×10^{-5} mol/cm^3. The cross-sectional area of the tail is 3×10^{-10} cm^2.

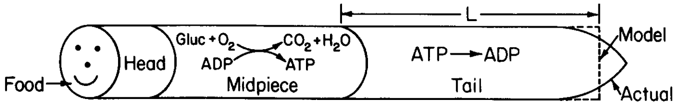


Figure P12-7$_B$ Swimming of an organism.

(a) Derive an equation for diffusion and reaction in the tail.

(b) Derive an equation for the effectiveness factor in the tail.

(c) Taking the reaction in the tail to be of zero order, calculate the length of the tail. The rate of reaction in the tail is 23×10^{-18} mol/s.

(d) Compare your answer with the average tail length of 41 μm. What are possible sources of error?

P12-8$_B$ A first-order, heterogeneous, irreversible reaction is taking place within a catalyst pore which is plated with platinum entirely along the length of the pore (Figure P12-8$_B$). The reactant concentration at the plane of symmetry (i.e., equal distance from the pore mouths) of the pore is equal to one-tenth the concentration at the pore mouth. The concentration at the pore mouth is 0.001 mol/dm^3, the pore length ($2L$) is 2×10^{-3} cm, and the diffusion coefficient is 0.1 cm^2/s.

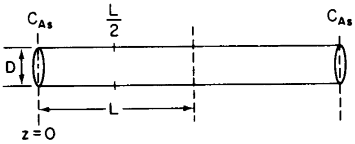


Figure P12-8$_B$ Single catalyst pore.

(a) Derive an equation for the effectiveness factor.
(b) What is the concentration of reactant at $L/2$?
(c) To what length should the pore length be reduced if the effectiveness factor is to be 0.8?
(d) If the catalyst support were not yet plated with platinum, how would you suggest the catalyst support be plated *after* the pore length, L, had been reduced by grinding?

P12-9$_A$ A first-order reaction is taking place inside a porous catalyst. Assume dilute concentrations and neglect any variations in the axial (x) direction.
(a) Derive an equation for both the internal and overall effectiveness factors for the rectangular porous slab shown in Figure P12-9$_A$.
(b) Repeat part (a) for a cylindrical catalyst pellet where the reactants diffuse inward in the radial direction.

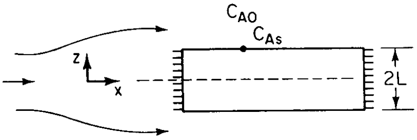


Figure P12-9$_A$ Flow over porous catalyst slab.

P12-10$_B$ The irreversible reaction

$$A \longrightarrow B$$

is taking place in the porous catalyst disk shown in Figure P12-9$_A$. The reaction is zero order in A.
(a) Show that the concentration profile using the symmetry B.C. is

$$\frac{C_A}{C_{As}} = 1 + \phi_0^2 \left[\left(\frac{z}{L} \right)^2 - 1 \right] \qquad \text{(P12-10.1)}$$

where

$$\phi_0^2 = \frac{kL^2}{2D_e C_{As}} \tag{P12-10.2}$$

(b) For a Thiele modulus of 1.0, at what point in the disk is the concentration zero? For $\phi_0 = 4$?

(c) What is the concentration you calculate at $z = 0.1\ L$ and $\phi_0 = 10$ using Equation (P12-10.1)? What do you conclude about using this equation?

(d) Plot the dimensionless concentration profile $\psi = C_A/C_{As}$ as a function of $\lambda = z/L$ for $\phi_0 = 0.5$, 1, 5, and 10. *Hint:* there are regions where the concentration is zero. Show that $\lambda_C = 1 - 1/\phi_0$ is the start of this region where the gradient and concentration are both zero. [L. K. Jang, R. L. York, J. Chin, and L. R. Hile, *Inst. Chem. Engr.*, 34, 319 (2003).] Show that $\psi = \phi_0^2\ \lambda^2 - 2\phi_0(\phi_0 - 1)\ \lambda + (\phi_0 - 1)^2$ for $\lambda_C \leq \lambda < 1$.

(e) The effectiveness factor can be written as

$$\eta = \frac{\int_0^L -r_A A_c\, dz}{-r_{As} A_c L} = \frac{\int_0^{z_C} -r_A A_c\, dz + \int_{z_C}^{L} -r_A A_c\, dz}{-r_{As} A_c L} \tag{P12-10.3}$$

where z_C (λ_C) is the point where both the concentration gradients and flux go to zero and A_c is the cross-sectional area of the disk. Show for a zero-order reaction that

$$\eta = \begin{cases} 1 & \text{for } \phi_0 \leq 1.0 \\ 1 - \lambda_C = \dfrac{1}{\phi_0} & \text{for } \phi_0 \geq 1 \end{cases} \tag{P12-10.4}$$

(f) Make a sketch for η versus ϕ_0 similar to the one shown in Figure 12-5.

(g) Repeat parts (a) to (f) for a spherical catalyst pellet.

(h) What do you believe to be the point of this problem?

P12-11$_C$ The second-order decomposition reaction

$$A \longrightarrow B + 2C$$

is carried out in a tubular reactor packed with catalyst pellets 0.4 cm in diameter. The reaction is internal-diffusion-limited. Pure A enters the reactor at a superficial velocity of 3 m/s, a temperature of 250°C, and a pressure of 500 kPa. Experiments carried out on smaller pellets where surface reaction is limiting yielded a specific reaction rate of 0.05 $m^6/mol \cdot g\ cat \cdot s$. Calculate the length of bed necessary to achieve 80% conversion. Critique the numerical answer.

Additional information:

Effective diffusivity: $2.66 \times 10^{-8}\ m^2/s$
Ineffective diffusivity: $0.00\ m^2/s$
Bed porosity: 0.4
Pellet density: $2 \times 10^6\ g/m^3$
Internal surface area: $400\ m^2/g$

P12-12$_C$ Derive the concentration profile and effectiveness factor for cylindrical pellets 0.2 cm in diameter and 1.5 cm in length. Neglect diffusion through the ends of the pellet.

- **(a)** Assume that the reaction is a first-order isomerization. (*Hint:* Look for a Bessel function.)
- **(b)** Rework Problem P12-11$_C$ for these pellets.

P12-13$_C$ Reconsider diffusion and reaction in a spherical catalyst pellet for the case where the reaction is not isothermal. Show that the energy balance can be written as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 k_t \frac{dT}{dr}\right) + (-\Delta H^\circ_R)(-r_A) = 0 \qquad \text{(P12-13.1)}$$

where k_t is the effective thermal conductivity, cal/s·cm·K of the pellet with $dT/dr = 0$ at $r = 0$ and $T = T_s$ at $r = R$.

- **(a)** Evaluate Equation (12-11) for a first-order reaction and combine with Equation (P12-13.1) to arrive at an equation giving the maximum temperature in the pellet.

$$T_{max} = T_s + \frac{(-\Delta H^\circ_{Rx})(D_e C_{As})}{k_t} \qquad \text{(P12-13.2)}$$

  Note: At T_{max}, $C_A = 0$.
- **(b)** Choose representative values of the parameters and use a software package to solve Equations (12-11) and (P12-13.1) simultaneously for $T(r)$ and $C_A(r)$ when the reaction is carried out adiabatically. Show that the resulting solution agrees qualitatively with Figure 12-7.

P12-14$_C$ Determine the effectiveness factor for a nonisothermal spherical catalyst pellet in which a first-order isomerization is taking place.

Additional information:

$A_i = 100 \text{ m}^2/\text{m}^3$
$\Delta H^\circ_R = -800{,}000$ J/mol
$D_e = 8.0 \times 10^{-8} \text{ m}^2/\text{s}$
$C_{As} = 0.01 \text{ kmol/m}^3$
External surface temperature of pellet, $T_s = 400$ K
$E = 120{,}000$ J/mol
Thermal conductivity of pellet = 0.004 J/m·s·K
$d_p = 0.005$ m
Specific reaction rate = 10^{-1} m/s at 400 K
Density of calf's liver = 1.1 g/dm^3

How would your answer change if the pellets were 10^{-2}, 10^{-4}, and 10^{-5} m in diameter? What are typical temperature gradients in catalyst pellets?

P12-15$_B$ *Extension of Problem P12-8$_B$.* The elementary isomerization reaction

$$A \longrightarrow B$$

is taking place on the walls of a cylindrical catalyst pore. (See Figure P12-8$_B$.) In one run a catalyst poison P entered the reactor together with the reactant A. To estimate the effect of poisoning, we assume that the poison renders the catalyst pore walls near the pore mouth ineffective up to a distance z_1, so that no reaction takes place on the walls in this entry region.

(a) Show that before poisoning of the pore occurred, the effectiveness factor was given by

$$\eta = \frac{1}{\phi} \tanh\phi$$

where

$$\phi = L\sqrt{\frac{2k}{rD_e}}$$

with k = reaction rate constant (length/time)
r = pore radius (length)
D_e = effective molecular diffusivity (area/time)

(b) Derive an expression for the concentration profile and also for the molar flux of A in the ineffective region $0 < z < z_1$, in terms of z_1, D_{AB}, C_{A1}, and C_{As}. Without solving any further differential equations, obtain the new effectiveness factor η' for the poisoned pore.

P12-16$_B$ *Falsified Kinetics*. The irreversible gas-phase dimerization

$$2A \longrightarrow A_2$$

is carried out at 8.2 atm in a stirred contained-solids reactor to which only pure A is fed. There are 40 g of catalyst in each of the four spinning baskets. The following runs were carried out at 227°C:

Total Molar Feed Rate, F_{T0} (g mol/min)	1	2	4	6	11	20
Mole Fraction A in Exit, y_A	0.21	0.33	0.40	0.57	0.70	0.81

The following experiment was carried out at 237°C:

$$F_{T0} = 9 \text{ g mol/min} \qquad y_A = 0.097$$

(a) What are the apparent reaction order and the apparent activation energy?
(b) Determine the true reaction order, specific reaction rate, and activation energy.
(c) Calculate the Thiele modulus and effectiveness factor.
(d) What pellet diameter should be used to make the catalyst more effective?
(e) Calculate the rate of reaction on a rotating disk made of the catalytic material when the gas-phase reactant concentration is 0.01 g mol/L and the temperature is 227°C. The disk is flat, nonporous, and 5 cm in diameter.

Additional information:

Effective diffusivity: 0.23 cm^2/s
Surface area of porous catalyst: 49 m^2/g cat
Density of catalyst pellets: 2.3 g/cm^3
Radius of catalyst pellets: 1 cm
Color of pellets: blushing peach

P12-17$_B$ Derive Equation (12-35). *Hint:* Multiply both sides of Equation (12-25) for *n*th order reaction, that is,

$$\frac{d^2y}{d\lambda^2} - \phi_n^2 y^n = 0$$

by $2dy/d\lambda$, rearrange to get

$$\frac{d}{d\lambda}\left(\frac{dy}{d\lambda}\right)^2 = \phi_n^2 y^n 2\frac{dy}{d\lambda}$$

and solve using the boundary conditions $dy/d\lambda = 0$ at $\lambda = 0$.

JOURNAL ARTICLE PROBLEMS

P12J-1 The article in *Trans. Int. Chem. Eng.*, *60*, 131 (1982) may be advantageous in answering the following questions.
- **(a)** Describe the various types of gas–liquid–solid reactors.
- **(b)** Sketch the concentration profiles for gas absorption with:
  - **(1)** An instantaneous reaction
  - **(2)** A very slow reaction
  - **(3)** An intermediate reaction rate

P12J-2 After reading the journal review by Y. T. Shah et al. [*AIChE J.*, *28*, 353 (1982)], design the following bubble column reactor. One percent carbon dioxide in air is to be removed by bubbling through a solution of sodium hydroxide. The reaction is mass-transfer-limited. Calculate the reactor size (length and diameter) necessary to remove 99.9% of the CO_2. Also specify a type of sparger. The reactor is to operate in the bubbly flow regime and still process 0.5 m^3/s of gas. The liquid flow rate through the column is 10^{-3} m^3/s.

JOURNAL CRITIQUE PROBLEMS

P12C-1 Use the Weisz–Prater criterion to determine if the reaction discussed in *AIChE J.*, *10*, 568 (1964) is diffusion-rate-limited.

P12C-2 Use the references given in *Ind. Eng. Chem. Prod. Res. Dev.*, *14*, 226 (1975) to define the iodine value, saponification number, acid number, and experimental setup. Use the slurry reactor analysis to evaluate the effects of mass transfer and determine if there are any mass transfer limitations.

- **Additional Homework Problems**

CDP12-A$_B$ Determine the catalyst size that gives the highest conversion in a packed bed reactor.

CDP12-B$_B$ Determine the importance of concentration and temperature gradients in a packed bed reactor.

CDP12-C$_B$ Determine the concentration profile and effectiveness factor for the first order gas phase reaction

$$A \rightarrow 3B$$

Slurry Reactors

CDP12-D_B	Hydrogenation of methyl linoleate-comparing catalyst. [3rd Ed. P12-19]
CDP12-E_B	Hydrogenation of methyl linoleate. Find the rate-limiting step. [3rd Ed. P12-20]
CDP12-F_B	Hydrogenation of 2-butyne–1,4-diol to butenediol. Calculate the percent resistance of total for each step and the conversion. [3rd Ed. P12-21]

CVD Boat Reactors

CDP12-G_D	Determine the temperature profile to achieve a uniform thickness. [2nd Ed. P11-18]
CDP12-H_B	Explain how varying a number of the parameters in the *CVD boat reactor* will affect the wafer shape. [2nd Ed. P11-19]
CDP12-I_B	Determine the wafer shape in a CVD boat reactor for a series of operating conditions. [2nd Ed. P11-20]
CDP12-J_C	Model the build-up of a silicon wafer on parallel sheets. [2nd Ed. P11-21]
CDP12-K_C	Rework CVD boat reactor accounting for the reaction $SiH_4 \rightleftarrows SiH_2 + H_2$ [2nd ed. P11-22]

Trickle Bed Reactors

CDP12-L_B	Hydrogenation of an unsaturated organic is carried out in a *trickle bed reactor*. [2nd Ed. P12-7]
CDP12-M_B	The oxidation of ethanol is carried out in a *trickle bed reactor*. [2nd Ed. P12-9]
CDP12-N_C	Hydrogenation of aromatics in a *trickle bed reactor* [2nd Ed. P12-8]

Fluidized Bed Reactors

CDP12-O_C	Open-ended fluidization problem that requires critical thinking to compare the two-phase fluid models with the three-phase bubbling bed model.
CDP12-P_A	Calculate reaction rates at the top and the bottom of the bed for Example R12.3-3.
CDP12-Q_B	Calculate the conversion for A → B in a bubbling fluidized bed.
CDP12-R_B	Calculate the effect of operating parameters on conversion for the reaction-limited and transport-limited operation.
CDP12-S_B	*Excellent Problem* Calculate all the parameters in Example R12-3.3 for a different reaction and different bed.
CDP12-T_B	Plot conversion and concentration as a function of bed height in a bubbling fluidized bed.
CDP12-U_B	Use RTD studies to compare bubbling bed with a fluidized bed.
CDP12-V_B	New problems on web and CD-ROM.
CDP12-W_B	Green Engineering, *www.rowan.edu/greenengineering*.

Green Engineering

SUPPLEMENTARY READING

1. There are a number of books that discuss internal diffusion in catalyst pellets; however, one of the first books that should be consulted on this and other topics on heterogeneous catalysis is

   Lapidus, L., and N. R. Amundson, *Chemical Reactor Theory: A Review*. Upper Saddle River, N.J.: Prentice Hall, 1977.

   In addition, see

   Aris, R., *Elementary Chemical Reactor Analysis*. Upper Saddle River, N.J.: Prentice Hall, 1969, Chap. 6. One should find the references listed at the end of this reading particularly useful.

   Luss, D., "Diffusion—Reaction Interactions in Catalyst Pellets," p. 239 in *Chemical Reaction and Reactor Engineering*. New York: Marcel Dekker, 1987.

   The effects of mass transfer on reactor performance are also discussed in

   Denbigh, K., and J. C. R. Turner, *Chemical Reactor Theory*, 3rd ed. Cambridge: Cambridge University Press, 1984, Chap. 7.

   Satterfield, C. N., *Heterogeneous Catalysis in Industrial Practice*, 2nd ed. New York: McGraw-Hill, 1991.

2. Diffusion with homogeneous reaction is discussed in

   Astarita, G., and R. Ocone, *Special Topics in Transport Phenomena*. New York: Elsevier, 2002.

   Danckwerts, P. V., *Gas–Liquid Reactions*. New York: McGraw-Hill, 1970.

   Gas-liquid reactor design is also discussed in

   Charpentier, J. C., review article, *Trans. Inst. Chem. Eng.*, *60*, 131 (1982).

   Shah, Y. T., *Gas–Liquid–Solid Reactor Design*. New York: McGraw-Hill, 1979.

3. Modeling of CVD reactors is discussed in

   Hess, D. W., K. F. Jensen, and T. J. Anderson, "Chemical Vapor Deposition: A Chemical Engineering Perspective," *Rev. Chem. Eng.*, *3*, 97, 1985.

   Jensen, K. F., "Modeling of Chemical Vapor Deposition Reactors for the Fabrication of Microelectronic Devices," *Chemical and Catalytic Reactor Modeling*, ACS Symp. Ser. 237, M. P. Dudokovic, P. L. Mills, eds., Washington, D.C.: American Chemical Society, 1984, p. 197.

   Lee, H. H., *Fundamentals of Microelectronics Processing*. New York: McGraw-Hill, 1990.

4. Multiphase reactors are discussed in

   Ramachandran, P. A., and R. V. Chaudhari, *Three-Phase Catalytic Reactors*. New York: Gordon and Breach, 1983.

   Rodrigues, A. E., J. M. Colo, and N. H. Sweed, eds., *Multiphase Reactors*, Vol. 1: *Fundamentals*. Alphen aan den Rijn, The Netherlands: Sitjhoff and Noordhoff, 1981.

   Rodrigues, A. E., J. M. Colo, and N. H. Sweed, eds., *Multiphase Reactors*, Vol. 2: *Design Methods*. Alphen aan den Rijn, The Netherlands: Sitjhoff and Noordhoff, 1981.

SHAH, Y. T., B. G. KELKAR, S. P. GODBOLE, and W. D. DECKWER, "Design Parameters Estimations for Bubble Column Reactors" (journal review), *AIChE J.*, *28*, 353 (1982).

TARHAN, M. O., *Catalytic Reactor Design*. New York: McGraw-Hill, 1983.

YATES, J. G., *Fundamentals of Fluidized-Bed Chemical Processes*, 3rd ed. London: Butterworth, 1983.

The following *Advances in Chemistry Series* volume discusses a number of multiphase reactors:

FOGLER, H. S., ed., *Chemical Reactors*, ACS Symp. Ser. 168. Washington, D.C.: American Chemical Society, 1981, pp. 3–255.

5. Fluidization

In addition to Kunii and Levenspiel's book, many correlations can be found in

DAVIDSON, J. F., R. CLIFF, and D. HARRISON, *Fluidization*, 2nd ed. Orlando: Academic Press, 1985.

A discussion of the different models can be found in

YATES, J. G., *Fluidized Bed Chemical Processes.* London: Butterworth-Heinemann, 1983. Also see GELDART, D. ed. *Gas Fluidization Technology.* Chichester: Wiley-Interscience, 1986.