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11 External Diffusion Effects on Heterogeneous Reactions

Giving up is the ultimate tragedy.

Robert J. Donovan

or

It ain't over 'til it's over.

Yogi Berra

Overview In many industrial reactions, the overall rate of reaction is limited by the rate of mass transfer of reactants between the bulk fluid and the catalytic surface. By mass transfer, we mean any process in which diffusion plays a role. In the rate laws and catalytic reaction steps described in Chapter 10 (diffusion, adsorption, surface reaction, desorption, and diffusion), we neglected the diffusion steps by saying we were operating under conditions where these steps are fast when compared to the other steps and thus could be neglected. We now examine the assumption that diffusion can be neglected. In this chapter we consider the external resistance to diffusion, and in the next chapter we consider internal resistance to diffusion.

We begin with presentation of the fundamentals of diffusion, molar flux, and then write the mole balance in terms of the mole fluxes for rectangular and cylindrical coordinates. Using Fick's law, we write the full equations describing flow, reaction, and diffusion. We consider a few simple geometries and solve the mass flux equations to obtain the concentration gradients and rate of mass transfer. We then discuss mass transfer rates in terms of mass transfer coefficients and correlations for the mass transfer coefficients. Here we include two examples that ask "What if . . ." questions about the system variables. We close the chapter with a discussion on dissolving solids and the shrinking core model, which has applications in drug delivery.

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11.1 Diffusion Fundamentals

The Algorithm
1. Mole balance
2. Rate law
3. Stoichiometry
4. Combine
5. Evaluate

The first step in our CRE algorithm is the mole balance, which we now need to extend to include the molar flux, W_{Az}, and diffusional effects. The molar flow rate of A in a given direction, such as the z direction down the length of a tubular reactor, is just the product of the flux, W_{Az} (mol/m^2 • s), and the cross-sectional area, A_c (m^2), that is,

$$F_{Az} = A_c W_{Az}$$

In the previous chapters we have only considered plug flow in which case

$$W_{Az} = \frac{C_A v}{A_C}$$

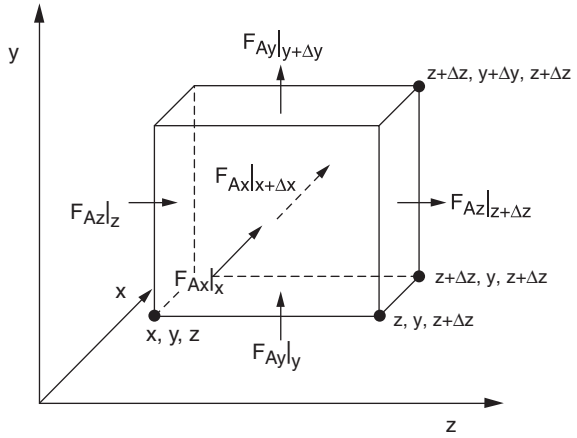
We now will extend this concept to consider diffusion superimposed on the molar average velocity.

11.1.1 Definitions

Diffusion is the spontaneous intermingling or mixing of atoms or molecules by random thermal motion. It gives rise to motion of the species *relative* to motion of the mixture. In the absence of other gradients (such as temperature, electric potential, or gravitational potential), molecules of a given species within a single phase will always diffuse from regions of higher concentrations to regions of lower concentrations. This gradient results in a molar flux of the species (e.g., A), $\mathbf{W}_A$ (moles/area·time), in the direction of the concentration gradient. The flux of A, $\mathbf{W}_A$, is relative to a fixed coordinate (e.g., the lab bench) and is a vector quantity with typical units of mol/m^2·s. In rectangular coordinates

$$\mathbf{W}_A = iW_{Ax} + jW_{Ay} + kW_{Az} \tag{11-1}$$

We now apply the mole balance to species A, which flows and reacts in an element of volume $\Delta V = \Delta x \Delta y \Delta \mathbf{z}$ to obtain the variation of the molar fluxes in three dimensions.



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$$F_{Az} = W_{Az}\Delta x\Delta y$$
$$F_{Ay} = W_{Ay}\Delta x\Delta z$$
$$F_{Ax} = W_{Ax}\Delta z\Delta y$$

$$\left[\begin{array}{c}\text{Molar}\\ \text{flow rate}\\ \text{in}\end{array}\right]_z - \left[\begin{array}{c}\text{Molar}\\ \text{flow rate}\\ \text{out}\end{array}\right]_{z+\Delta z} + \left[\begin{array}{c}\text{Molar}\\ \text{flow rate}\\ \text{in}\end{array}\right]_y - \left[\begin{array}{c}\text{Molar}\\ \text{flow rate}\\ \text{out}\end{array}\right]_{y+\Delta y} +$$

Mole Balance

$$\Delta x\Delta y W_{Az}\big|_z - \Delta x\Delta y W_{Az}\big|_{z+\Delta z} + \Delta x\Delta z W_{Ay}\big|_y - \Delta x\Delta z W_{Ay}\big|_{y+\Delta y} +$$

$$\left[\begin{array}{c}\text{Molar}\\ \text{flow rate}\\ \text{in}\end{array}\right]_x - \left[\begin{array}{c}\text{Molar}\\ \text{flow rate}\\ \text{out}\end{array}\right]_{x+\Delta x} + \left[\begin{array}{c}\text{Rate of}\\ \text{generation}\end{array}\right] = \left[\begin{array}{c}\text{Rate of}\\ \text{accumulation}\end{array}\right]$$

$$\Delta z\Delta y W_{Ax}\big|_x - \Delta z\Delta y W_{Ax}\big|_{x+\Delta x} + r_A\Delta x\Delta y\Delta z = \Delta x\Delta y\Delta z\frac{\partial C_A}{\partial t}$$

Dividing by $\Delta x\Delta y\Delta z$ and taking the limit as they go to zero, we obtain the molar flux balance in rectangular coordinates

$$\boxed{-\frac{\partial W_{Ax}}{\partial x} - \frac{\partial W_{Ay}}{\partial y} - \frac{\partial W_{Az}}{\partial z} + r_A = \frac{\partial C_A}{\partial t}} \tag{11-2}$$

The corresponding balance in cylindrical coordinates with no variation in the rotation about the **z**-axis is

COMSOL

$$\boxed{-\frac{1}{r}\frac{\partial}{\partial r}(rW_{Ar}) - \frac{\partial W_{Az}}{\partial z} + r_A = \frac{\partial C_A}{\partial t}} \tag{11-3}$$

We will now evaluate the flux terms $\mathbf{W}_A$. We have taken the time to derive the molar flux equations in this form because they are now in a form that is consistent with the partial differential equation (PDE) solver COMSOL, which is included on the CD with this textbook.

11.1.2 Molar Flux

The molar flux of A, $\mathbf{W}_A$, is the result of two contributions: $\mathbf{J}_A$, the molecular diffusion flux relative to the bulk motion of the fluid produced by a concentration gradient, and $\mathbf{B}_A$, the flux resulting from the bulk motion of the fluid:

Total flux = diffusion + bulk motion

$$\boxed{\mathbf{W}_A = \mathbf{J}_A + \mathbf{B}_A} \tag{11-4}$$

The bulk flow term for species A is the total flux of all molecules relative to a fixed coordinate times the mole fraction of A, y_A; i.e., $\mathbf{B}_A = y_A \sum \mathbf{W}_i$.

The bulk flow term $\mathbf{B}_A$ can also be expressed in terms of the concentration of A and the molar average velocity **V**:

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$$\mathbf{B}_A = C_A\mathbf{V} \tag{11-5}$$

$$\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} = \frac{\text{mol}}{\text{m}^3} \cdot \frac{\text{m}}{\text{s}}$$

where the molar average velocity is

Molar average velocity

$$\mathbf{V} = \sum y_i \mathbf{V}_i$$

Here $\mathbf{V}_i$ is the particle velocity of species i, and y_i is the mole fraction of species i. By particle velocities, we mean the vector-average velocities of millions of A molecules at a point. For a binary mixture of species A and B, we let $\mathbf{V}_A$ and $\mathbf{V}_B$ be the particle velocities of species A and B, respectively. The flux of A with respect to a fixed coordinate system (e.g., the lab bench), $\mathbf{W}_A$, is just the product of the concentration of A and the particle velocity of A:

$$\mathbf{W}_A = C_A\mathbf{V}_A \tag{11-6}$$

$$\left(\frac{\text{mol}}{\text{dm}^2 \cdot \text{s}}\right) = \left(\frac{\text{mol}}{\text{dm}^3}\right)\left(\frac{\text{dm}}{\text{s}}\right)$$

The molar average velocity for a binary system is

$$\mathbf{V} = y_A\mathbf{V}_A + y_B\mathbf{V}_B \tag{11-7}$$

The total molar flux of A is given by Equation (11-4). $\mathbf{B}_A$ can be expressed either in terms of the concentration of A, in which case

$$\boxed{\mathbf{W}_A = \mathbf{J}_A + C_A\mathbf{V}} \tag{11-8}$$

or in terms of the mole fraction of A:

Binary system of A and B

$$\boxed{\mathbf{W}_A = \mathbf{J}_A + y_A(\mathbf{W}_A + \mathbf{W}_B)} \tag{11-9}$$

We now need to evaluate the molar flux of A, $\mathbf{J}_A$, that is superimposed on the molar average velocity $\mathbf{V}$.

11.1.3 Fick's First Law

Our discussion on diffusion will be restricted primarily to binary systems containing only species A and B. We now wish to determine *how* the molar diffusive flux of a species (i.e., $\mathbf{J}_A$) is related to its concentration gradient. As an aid in the discussion of the transport law that is ordinarily used to describe diffusion, recall similar laws from other transport processes. For example, in conductive heat transfer the constitutive equation relating the heat flux $\mathbf{q}$ and the temperature gradient is Fourier's law:

Experimentation with frog legs led to Fick's first law

$$\mathbf{q} = -k_t\nabla T \tag{11-10}$$

where k_t is the thermal conductivity.

In rectangular coordinates, the gradient is in the form

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Constitutive equations in heat, momentum, and mass transfer

$$\nabla = i\,\frac{\partial}{\partial x} + j\,\frac{\partial}{\partial y} + k\,\frac{\partial}{\partial z} \tag{11-11}$$

The one-dimensional form of Equation (11-10) is

Heat Transfer

$$q_z = -k_t\,\frac{dT}{dz} \tag{11-12}$$

In momentum transfer, the constitutive relationship between shear stress, τ, and shear rate for simple planar shear flow is given by Newton's law of viscosity:

Momentum Transfer

$$\tau = -\mu\,\frac{du}{dz}$$

The mass transfer flux law is analogous to the laws for heat and momentum transport, i.e., for constant total concentration

Mass Transfer

$$\mathbf{J}_{Az} = -D_{AB}\frac{dC_A}{dz}$$

The general 3-dimensional constitutive equation for $\mathbf{J}_A$, the diffusional flux of **A** resulting from a concentration difference, is related to the mole fraction gradient by Fick's first law:

$$\mathbf{J}_A = -cD_{AB}\nabla y_A \tag{11-13}$$

where c is the total concentration (mol/dm^3), D_{AB} is the diffusivity of A in B (dm^2/s), and y_A is the mole fraction of A. Combining Equations (11-9) and (11-13), we obtain an expression for the molar flux of A:

Molar flux equation

$$\boxed{\mathbf{W}_A = -cD_{AB}\nabla y_A + y_A(\mathbf{W}_A + \mathbf{W}_B)} \tag{11-14}$$

In terms of concentration for constant total concentration

Molar flux equation

$$\boxed{\mathbf{W}_A = -D_{AB}\nabla C_A + C_A\mathbf{V}} \tag{11-15}$$

11.2 Binary Diffusion

Although many systems involve more than two components, the diffusion of each species can be treated as if it were diffusing through another single species rather than through a mixture by defining an effective diffusivity. Methods and examples for calculating this effective diffusivity can be found in Hill.[1]

11.2.1 Evaluating the Molar Flux

The task is to now evaluate the bulk flow term.

We now consider four typical conditions that arise in mass transfer problems and show how the molar flux is evaluated in each instance. The first two

[1] C. G. Hill, *Chemical Engineering Kinetics and Reactor Design* (New York: Wiley, 1977), p. 480.

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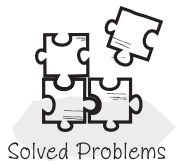
conditions, equal molar counter diffusion (EMCD) and dilute concentration give the same equation for $\mathbf{W}_A$, that is,

$$\mathbf{W}_A = -D_{AB}\nabla C_A$$

The third condition, diffusion through a stagnant film, does not occur as often and is discussed in the summary notes and the solved problems on the CD. The fourth condition is the one we have been discussing up to now for plug flow and the PFR, that is,



$$F_A = vC_A$$

We will first consider equimolar counter diffusion (EMCD).

11.2.1A Equimolar Counter Diffusion. In equimolar counter diffusion (EMCD), for every mole of A that diffuses in a given direction, one mole of B diffuses in the opposite direction. For example, consider a species A that is diffusing at steady state from the bulk fluid to a catalyst surface, where it isomerizes to form B. Species B then diffuses back into the bulk (see Figure 11-1). For every mole of A that diffuses to the surface, 1 mol of the isomer B diffuses away from the surface. The fluxes of A and B are equal in magnitude and flow counter to each other. Stated mathematically,

$$\mathbf{W}_A = -\mathbf{W}_B \tag{11-16}$$

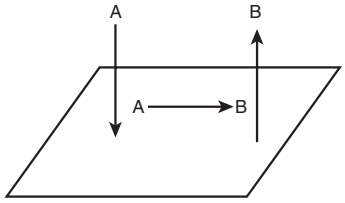


Figure 11-1 EMCD in isomerization reaction.

An expression for $\mathbf{W}_A$ in terms of the concentration of A, C_A, for the case of EMCD can be found by first substituting Equation (11-16) into Equation (11-9):

$$\mathbf{W}_A = \mathbf{J}_A + y_A[\mathbf{W}_A + (-\mathbf{W}_A)] = \mathbf{J}_A + 0$$
$$= \mathbf{J}_A = -cD_{AB}\nabla y_A$$

For constant total molar concentration

EMCD flux equation

$$\boxed{\mathbf{W}_A = \mathbf{J}_A = -D_{AB}\nabla C_A} \tag{11-17}$$

11.2.1B Dilute Concentrations. When the mole fraction of the diffusing solute and the bulk motion in the direction of the diffusion are small, the second term on the right-hand side of Equation (11-14) [i.e., $y_A(\mathbf{W}_A + \mathbf{W}_B)$] can usually be neglected compared with the first term, $\mathbf{J}_A$. Under these conditions,

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together with the condition of constant total concentration, the flux of A is identical to that in Equation (11-16), that is,

Flux at dilute concentrations

$$\boxed{\mathbf{W}_A \simeq \mathbf{J}_A = -D_{AB}\nabla C_A} \tag{11-18}$$

This approximation is almost always used for molecules diffusing within aqueous systems when the convective motion is small. For example, the mole fraction of a 1 *M* solution of a solute *A* diffusing in water whose molar concentration, C_W, is

$$C_W = 55.6 \text{ mol/dm}^3$$

would be

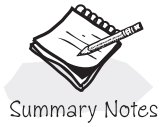
$$y_A = \frac{C_A}{C_W + C_A} = \frac{1}{55.6 + 1} = 0.018$$

Consequently, in most liquid systems the concentration of the diffusing solute is small, and Equation (11-18) is used to relate $\mathbf{W}_A$ and the concentration gradient within the boundary layer.

Equation (11-14) also reduces to Equation (11-17) for porous catalyst systems in which the pore radii are very small. Diffusion under these conditions, known as *Knudsen diffusion*, occurs when the mean free path of the molecule is greater than the diameter of the catalyst pore. Here the reacting molecules collide more often with pore walls than with each other, and molecules of different species do not affect each other. The flux of species A for Knudsen diffusion (where bulk flow is neglected) is

$$\mathbf{W}_A = \mathbf{J}_A = -D_K \nabla C_A \tag{11-19}$$

where D_K is the Knudsen diffusivity.[2]



11.2.1C Diffusion Through a Stagnant Gas ($W_B = 0$). Because this condition only affects mass transfer in a limited number of situations, we will discuss this condition in the *Summary Notes* of the CD-ROM.

11.2.1D Forced Convection. In systems where the flux of A results primarily from forced convection, we assume that the diffusion in the direction of the flow (e.g., axial z direction), J_{Az}, *is small in comparison with the bulk flow* contribution in that direction, $B_{Az}(V_z \equiv U)$,

$$J_{Az} \simeq 0$$

[2] C. N. Satterfield, *Mass Transfer in Heterogeneous Catalysis* (Cambridge: MIT Press, 1970), pp. 41–42, discusses Knudsen flow in catalysis and gives the expression for calculating D_K.

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$$W_{Az} \simeq B_{Az} = C_A V_z \equiv C_A U = \frac{v}{A_c} C_A = \frac{F_A}{A_c}$$

Molar flux of species A when axial diffusion effects are negligible

where A_c is the cross-sectional area and v is the volumetric flow rate. Although the component of the diffusional flux vector of A in the direction of flow, J_{Az}, is neglected, the component of the flux of A in the x direction, J_{Ax}, which is normal to the direction of flow, may not necessarily be neglected (see Figure 11-2).

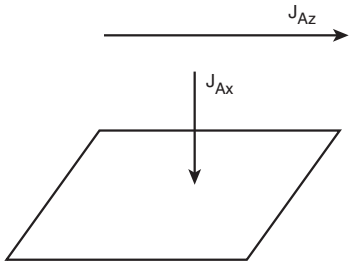

Figure 11-2 Forced axial convection with diffusion to surface.

When diffusional effects can be neglected, F_A can be written as the product of the volumetric flow rate and concentration:

Plug flow

$$F_A = vC_A$$

11.2.1E Diffusion and Convective Transport. When accounting for diffusional effects, the molar flow rate of species A, F_A, in a specific direction **z**, is the product of molar flux in that direction, W_{Az}, and the cross-sectional area normal to the direction of flow, A_c:

$$F_{Az} = A_c W_{Az}$$

In terms of concentration the flux is

$$W_{Az} = -D_{AB}\frac{dC_A}{dz} + C_A U_z$$

The molar flow rate is

$$F_{Az} = W_{Az} A_c = \left[-D_{AB}\frac{dC_A}{dz} + C_A U_z\right] A_c \tag{11-20}$$

Similar expressions follow for W_{Ax} and W_{Az}. Substituting for the flux W_{Ax}, W_{Ay}, and W_{Az} into Equation (11-2), we obtain

Flow, diffusion, and reaction.

This form is used in Comsol Multiphysics.

$$\boxed{D_{AB}\left[\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right] - U_x\frac{\partial C_A}{\partial x} - U_y\frac{\partial C_A}{\partial y} - U_z\frac{\partial C_A}{\partial z} + r_A = \frac{\partial C_A}{\partial t}} \tag{11-21}$$

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COMSOL Equation (11-21) is in a user-friendly form to apply to the PDE solver, COMSOL. For one-dimension at steady state, Equation (11-21) reduces to

$$\boxed{D_{AB}\frac{d^2C_A}{dz^2} - U_z\frac{dC_A}{dz} + r_A = 0} \tag{11-22}$$

In order to solve Equation (11-22) we need to specify the boundary conditions. In this chapter we will consider some of the simple boundary conditions, and in Chapter 14 we will consider the more complicated boundary conditions, such as the Danckwerts' boundary conditions.

We will now use this form of the molar flow rate in our mole balance in the z direction of a tubular flow reactor

$$\frac{dF_{Az}}{dV} = r_A \tag{1-11}$$

However, we first have to discuss the boundary conditions in solving the equation.

11.2.2 Boundary Conditions

The most common boundary conditions are presented in Table 11-1.

TABLE 11-1. TYPES OF BOUNDARY CONDITIONS

1. Specify a concentration at a boundary (e.g., $\mathbf{z} = 0$, $C_A = C_{A0}$). For an instantaneous reaction at a boundary, the concentration of the reactants at the boundary is taken to be zero (e.g., $C_{As} = 0$). See Chapter 14 for the more exact and complicated Danckwerts' boundary conditions at $\mathbf{z} = 0$ and $\mathbf{z} = L$.
2. Specify a flux at a boundary.
   a. No mass transfer to a boundary,

$$W_A = 0 \tag{11-23}$$

   For example, at the wall of a nonreacting pipe,

$$\frac{dC_A}{dr} = 0 \qquad \text{at } r = R$$

   That is, because the diffusivity is finite, the only way the flux can be zero is if the concentration gradient is zero.
   b. Set the molar flux to the surface equal to the rate of reaction on the surface,

$$W_A(\text{surface}) = -r''_A(\text{surface}) \tag{11-24}$$

   c. Set the molar flux to the boundary equal to convective transport across a boundary layer,

$$W_A(\text{boundary}) = k_c(C_{Ab} - C_{As}) \tag{11-25}$$

   where k_c is the mass transfer coefficient and C_{As} and C_{Ab} are the surface and bulk concentrations, respectively.
3. Planes of symmetry. When the concentration profile is symmetrical about a plane, the concentration gradient is zero in that plane of symmetry. For example, in the case of radial diffusion in a pipe, at the center of the pipe

$$\frac{dC_A}{dr} = 0 \qquad \text{at } r = 0$$

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11.2.3 Modeling Diffusion Without Reaction

In developing mathematical models for chemically reacting systems in which diffusional effects are important, the first steps are:

Steps in modeling mass transfer

Step 1: Perform a differential mole balance on a particular species A.
Step 2: Substitute for F_{Az} in terms of W_{Az}.
Step 3: Replace W_{Az} by the appropriate expression for the concentration gradient.
Step 4: State the boundary conditions.
Step 5: Solve for the concentration profile.
Step 6: Solve for the molar flux.

We are now going to apply this algorithm to one of the most important cases, diffusion through a boundary layer. Here we consider the boundary layer to be a hypothetical "stagnant film" in which all the resistance to mass transfer is lumped.

External Mass Transfer

Example 11–1 Diffusion Through a Film to a Catalyst Particle

Species A, which is present in dilute concentrations, is diffusing at steady state from the bulk fluid through a stagnant film of B of thickness δ to the external surface of the catalyst (Figure E11-1.1). The concentration of A at the external boundary is C_{Ab} and at the external catalyst surface is C_{As}, with $C_{Ab} > C_{As}$. Because the thickness of the "hypothetical stagnant film" next to the surface is small with respect to the diameter of the particle (i.e., $\delta << d_p$), we can neglect curvature and represent the diffusion in rectilinear coordinates as shown in Figure E11-1.2.

Determine the concentration profile and the flux of A to the surface using (a) shell balances and (b) the general balance equations.

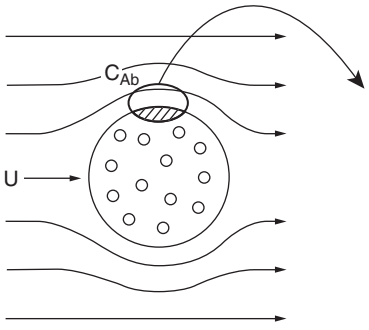

Figure E11-1.1 Transport to a sphere.

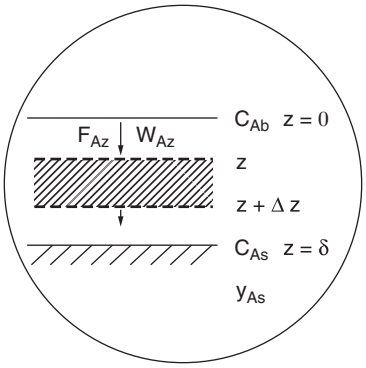

Figure E11-1.2 Boundary layer.

Additional information

$$D_{AB} = 0.01 \text{ cm}^2/\text{s} = 10^{-6} \text{ m}^2/\text{s} \qquad C_{T0} = 0.1 \text{ } kmol/m^3$$

$$y_{Ab} = 0.9$$

$$y_{As} = 0.2$$

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Solution

(a) Shell Balances

Our first step is to perform a mole balance on species A over a differential element of width Δz and cross-sectional area A_c and then arrive at a first-order differential equation in W_{Az} [i.e., Equation (E11-1.2)].

An algorithm
- Mole balance
- Bulk flow = ?
- Differential equation
- Boundary conditions
- Concentration profile
- Molar flux

Following the Algorithm

Step 1: The general **mole balance** equation is

$$\begin{bmatrix}\text{Rate}\\ \text{in}\end{bmatrix} - \begin{bmatrix}\text{Rate}\\ \text{out}\end{bmatrix} + \begin{bmatrix}\text{Rate of}\\ \text{generation}\end{bmatrix} = \begin{bmatrix}\text{Rate of}\\ \text{accumulation}\end{bmatrix}$$

$$F_{Az}|_z - F_{Az}|_{z+\Delta z} + 0 = 0$$

Dividing by $-\Delta z$ gives us

$$\frac{F_{Az}|_{z+\Delta z} - F_{Az}|_z}{\Delta z} = 0$$

and taking the limit as $\Delta z \to 0$, we obtain

$$\frac{dF_{Az}}{dz} = 0 \tag{E11-1.1}$$

Step 2: Next, **substitute** for F_{Az} in terms of W_{Az} and A_c,

$$F_{Az} = W_{Az} A_c$$

Divide by A_c to get

$$\frac{dW_{Az}}{dz} = 0 \tag{E11-1.2}$$

Step 3: To **evaluate the bulk flow term**, we now must relate W_{Az} to the concentration gradient utilizing the specification of the problem statement. For diffusion of almost all solutes through a liquid, the concentration of the diffusing species is considered dilute. For a dilute concentration of the diffusing solute, we have for constant total concentration,

$$W_{Az} = -D_{AB}\frac{dC_A}{dz} \tag{E11-1.3}$$

Differentiating Equation (E11-1.3) for constant diffusivity yields

$$\frac{dW_{Az}}{dz} = -D_{AB}\frac{d^2C_A}{dz^2}$$

However, Equation (E11-1.2) yielded

$$\frac{dW_{Az}}{dz} = 0 \tag{E11-1.4}$$

Therefore, the differential equation describing diffusion through a liquid film reduces to

$$\frac{d^2C_A}{dz^2} = 0 \tag{E11-1.5}$$

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Step 4: The **boundary** conditions are:

$$\text{When } z = 0, \qquad C_A = C_{Ab}$$

$$\text{When } z = \delta, \qquad C_A = C_{A\delta}$$

Step 5: **Solve for the concentration profile.** Equation (E11-1.5) is an elementary differential equation that can be solved directly by integrating twice with respect to z. The first integration yields

$$\frac{dC_A}{dz} = K_1$$

and the second yields

$$C_A = K_1 z + K_2 \tag{E11-1.6}$$

where K_1 and K_2 are arbitrary constants of integration. We now use the boundary conditions to evaluate the constants K_1 and K_2.
At $z = 0$, $C_A = C_{Ab}$; therefore,

$$C_{Ab} = 0 + K_2$$

At $z = \delta$, $C_A = C_{As}$;

$$C_{As} = K_1\delta + K_2 = K_1\delta + C_{Ab}$$

Eliminating K_1 and rearranging gives the following concentration profile:

$$\boxed{\frac{C_A - C_{Ab}}{C_{As} - C_{Ab}} = \frac{z}{\delta}} \tag{E11-1.7}$$

Rearranging (E11-1.7), we get the concentration profile shown in Figure E11-1.3.

$$C_A = C_{Ab} + (C_{As} - C_{Ab})\frac{z}{\delta} \tag{E11-1.8}$$

Concentration profile

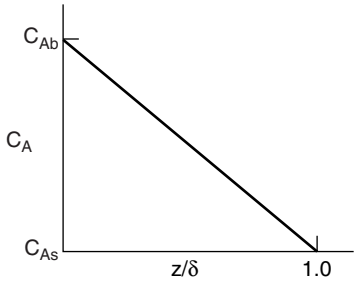

Figure E11-1

Step 6: The next step is to **determine the molar flux** of A diffusing through the stagnant film. For dilute solute concentrations and constant total concentration,

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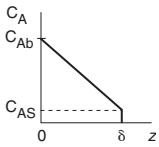
$$W_{Az} = -D_{AB}\left(\frac{dC_A}{dz}\right) \tag{E11-1.3}$$

To determine the flux, differentiate Equation (E11-1.8) with respect to **z** and then multiply by $-D_{AB}$:

$$W_{Az} = (-D_{AB})\frac{d}{dz}\left[C_{Ab} + (C_{As} - C_{Ab})\frac{z}{\delta}\right]$$

$$W_{Az} = -D_{AB}\left(\frac{C_{As} - C_{Ab}}{\delta}\right)$$

$$\boxed{W_{Az} = \frac{D_{AB}}{\delta}(C_{Ab} - C_{As})} \tag{E11-1.9}$$



Equation (E11-1.9) could also be written in terms of mole fractions

$$W_{Az} = \frac{D_{AB}C_{T0}}{\delta}(y_{Ab} - y_{As}) \tag{E11-1.10}$$

If $D_{AB} = 10^{-6}$ m^2/s, $C_{T0} = 0.1$ kmol/m^3, and $\delta = 10^{-6}$ m, $y_{Ab} = 0.9$, and $y_{As} = 0.2$, are substituted into Equation (E11-1.9). Then

EMCD or dilute concentration

$$W_{Az} = \frac{(10^{-6}\text{ m}^2/\text{s})(0.1\text{ kmol/m}^3)(0.9 - 0.2)}{10^{-6}\text{ m}}$$

$$= 0.07\text{ kmol/m}^2\cdot\text{s}$$

(b) General Balance Equations (11-2) and (11-21)

Another method used to arrive at the equation describing flow, reaction, and diffusion for a particular geometry and set of conditions is to use the general balance equations (11-2) and (11-21). In this method, we examine each term and then cross out terms that do not apply. In this example, there is no reaction, $-r_A = 0$, no flux in the x–direction, ($W_{Ax} = 0$) or the y–direction ($W_{Ay} = 0$), and we are at steady state $\left(\frac{\partial C_A}{\partial t} = 0\right)$ so that Equation (11-2) reduces to

$$-\frac{dW_A}{dz} = 0 \tag{E11-1.11}$$

which is the same as Equation (E11-1.4).

Similarly one could apply Equation (11-21) to this example realizing we are at steady state, no reaction, and there is no variation in concentration in either the x–direction or the y–direction

$$\left(\frac{\partial C_A}{\partial x} = 0,\ \frac{\partial^2 C_A}{\partial x^2} = 0\ \text{ and }\ \frac{\partial C_A}{\partial y} = 0,\ \frac{\partial^2 C_A}{\partial y^2} = 0\right)$$

so that Equation (11-21) reduces to

$$D_{AB}\frac{d^2C_A}{dz^2} = 0 \tag{E11-1.12}$$

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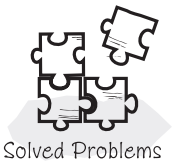


After dividing both sides by the diffusivity, we realize this equation is the same as Equation (E11-1.5).

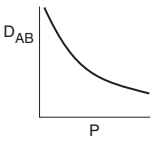
This problem is reworked for diffusion through a stagnant film in the solved example problems on the CD-ROM/web solved problems.

11.2.4 Temperature and Pressure Dependence of D_{AB}

Before closing this brief discussion on mass transfer fundamentals, further mention should be made of the diffusion coefficient.[3] Equations for predicting gas diffusivities are given by Fuller[4] and are also given in Perry's *Handbook*.[5] The orders of magnitude of the diffusivities for gases, liquids,[6] and solids and the manner in which they vary with temperature and pressure are given in Table 11-2. We note that the Knudsen, liquid, and solid diffusivities are independent of total pressure.

It is important to know the magnitude and the T and P dependence of the diffusivity

Gas:



Liquid:

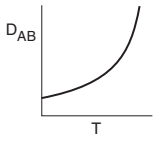


TABLE 11-2. DIFFUSIVITY RELATIONSHIPS FOR GASES, LIQUIDS, AND SOLIDS

	Order of Magnitude		
Phase	cm^2/s	m^2/s	*Temperature and Pressure Dependences*[a]
Gas			
Bulk	10^{-1}	10^{-5}	$D_{AB}(T_2, P_2) = D_{AB}(T_1, P_1)\,\frac{P_1}{P_2}\left(\frac{T_2}{T_1}\right)^{1.75}$
Knudsen	10^{-2}	10^{-6}	$D_A(T_2) = D_A(T_1)\left(\frac{T_2}{T_1}\right)^{1/2}$
Liquid	10^{-5}	10^{-9}	$D_{AB}(T_2) = D_{AB}(T_1)\,\frac{\mu_1}{\mu_2}\left(\frac{T_2}{T_1}\right)$
Solid	10^{-9}	10^{-13}	$D_{AB}(T_2) = D_{AB}(T_1)\,\exp\left[\frac{E_D}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)\right]$

[a] μ_1, μ_2, liquid viscosities at temperatures T_1 and T_2, respectively; E_D, diffusion activation energy.

[3] For further discussion of mass transfer fundamentals, see R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena,* 2nd ed. (New York: Wiley, 2002).

[4] E. N. Fuller, P. D. Schettler, and J. C. Giddings, *Ind. Eng. Chem.*, *58*(5), 19 (1966). Several other equations for predicting diffusion coefficients can be found in B. E. Polling, J. M. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids*, 5th ed. (New York: McGraw-Hill, 2001).

[5] R. H. Perry and D. W. Green, *Chemical Engineer's Handbook*, 7th ed. (New York: McGraw-Hill, 1999).

[6] To estimate liquid diffusivities for binary systems, see K. A. Reddy and L. K. Doraiswamy, *Ind. Eng. Chem. Fund.*, *6*, 77 (1967).

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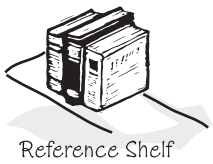
11.2.5 Modeling Diffusion with Chemical Reaction

The method used in solving diffusion problems similar to Example 11-1 is shown in Table 11-3. Also see Cussler.[7]



Expanding the previous six modeling steps just a bit

TABLE 11-3. STEPS IN MODELING CHEMICAL SYSTEMS WITH DIFFUSION AND REACTION

1. Define the problem and state the assumptions. **(See Problem Solving on the CD.)**
2. Define the system on which the balances are to be made.
3. Perform a differential mole balance on a particular species.
4. Obtain a differential equation in W_A by rearranging your balance equation properly and taking the limit as the volume of the element goes to zero.
5. Substitute the appropriate expression involving the concentration gradient for W_A from Section 11.2 to obtain a second-order differential equation for the concentration of A.[a]
6. Express the reaction rate r_A (if any) in terms of concentration and substitute into the differential equation.
7. State the appropriate boundary and initial conditions.
8. Put the differential equations and boundary conditions in dimensionless form.
9. Solve the resulting differential equation for the concentration profile.
10. Differentiate this concentration profile to obtain an expression for the molar flux of A.
11. Substitute numerical values for symbols.

[a]In some instances it may be easier to integrate the resulting differential equation in Step 4 before substituting for W_A.

In $\overset{\text{Move}}{\underset{\longleftarrow}{\longrightarrow}}$ Out of the algorithm (Steps $1 \rightarrow 6$) to generate creative solutions.

The purpose of presenting algorithms (e.g., Table 11-3) to solve reaction engineering problems is to give the readers a starting point or framework with which to work if they were to get stuck. It is expected that once readers are familiar and comfortable using the algorithm/framework, they will be able to move in and out of the framework as they develop creative solutions to nonstandard chemical reaction engineering problems.

11.3 External Resistance to Mass Transfer

11.3.1 The Mass Transfer Coefficient

To begin our discussion on the diffusion of reactants from the bulk fluid to the external surface of a catalyst, we shall focus attention on the flow past a single catalyst pellet. Reaction takes place only on the external catalyst surface and not in the fluid surrounding it. The fluid velocity in the vicinity of the spherical pellet will vary with position around the sphere. The hydrodynamic boundary layer is usually defined as the distance from a solid object to where the fluid velocity is 99% of the bulk velocity U_0. Similarly, the mass transfer boundary layer thickness, δ, is defined as the distance from a solid object to where the concentration of the diffusing species reaches 99% of the bulk concentration.

A reasonable representation of the concentration profile for a reactant A diffusing to the external surface is shown in Figure 11-3. As illustrated, the

[7] E. L. Cussler, *Diffusion Mass Transfer in Fluid Systems*, 2nd ed. (New York: Cambridge University Press, 1997).

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Side Note: Transdermal Drug Delivery

The principles of steady state diffusion have been used in a number of drug delivery systems. Specifically, medicated patches are commonly used to attach to the skin to deliver drugs for nicotine withdrawal, birth control, and motion sickness, to name a few. The U.S. transdermal drug delivery market was $1.2 billion in 2001. Equations similar to Equation 11-26 have been used to model the release, diffusion, and absorption of the drug from the patch into the body. Figure SN11.1 shows a drug delivery vehicle (patch) along with the concentration gradient in the epidermis and dermis skin layers.

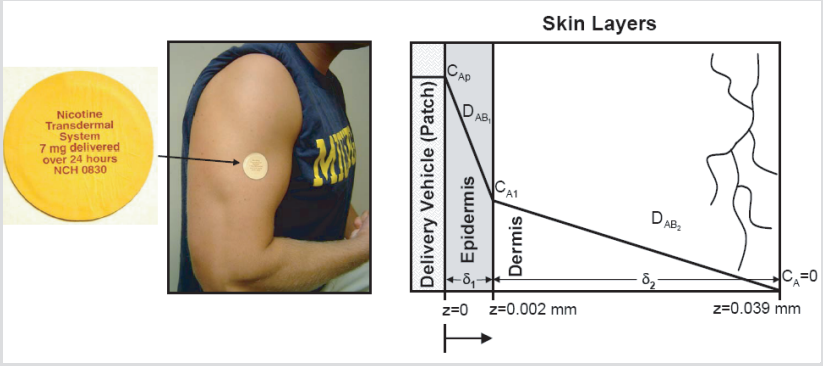

Figure SN 11.1 Transdermal drug delivery schematic.

As a first approximation, the delivery rate can be written as

$$F_A = A_p W_A = \frac{A_p[C_{Ap} - 0]}{R} \tag{1}$$

where

$$R = R_p + \frac{\delta_1}{D_{AB_1}} + \frac{\delta_2}{D_{AB_2}} \tag{2}$$

Where A_p is the area of the patch; C_{Ap}, the concentration of drug in the patch; R, the overall resistance; and R_p, the resistance to release from the patch. There are a number of situations one can consider, such as the patch resistance limits the delivery, diffusion through the epidermis limits delivery, or the concentration of the drug is kept constant in the patch by using solid hydrogels. When diffusion through the epidermis layer limits, the rate of drug delivery rate is

$$F_A = A_p\left[\frac{D_{AB_1}}{\delta_1}\right]C_{Ap} \tag{3}$$

Other models include the use of a quasi-steady analysis to couple the diffusion equation with a balance on the drug in the patch or the zero order dissolution of the hydrogel in the patch.† Problem 11-2(f) explores these situations.

† For further information see: Y. H. Kalia and R. Guy, *Advanced Drug Delivery Reviews 48*, 159 (2001); B. Muller, M. Kasper, C. Surber, and G. Imanidis, *European Journal of Pharmaceutical Science 20,* 181 (2003); *www.drugdeliverytech.com/cgi-bin/articles.cgi?idArticle=143; www.pharmacy.umaryland.edu/faculty/rdalby/Teaching%20Web%20Pages/Teaching.htm*

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change in concentration of A from C_{Ab} to C_{As} takes place in a very narrow fluid layer next to the surface of the sphere. Nearly all of the resistance to mass transfer is found in this layer.

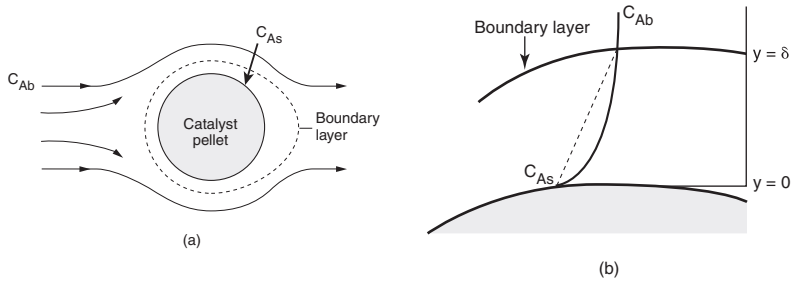

Figure 11-3 Boundary layer around the surface of a catalyst pellet.

11.3.2 Mass Transfer Coefficient

The concept of a hypothetical stagnant film within which all the resistance to external mass transfer exists

A useful way of modeling diffusive transport is to treat the fluid layer next to a solid boundary as a stagnant film of thickness δ. We say that *all* the resistance to mass transfer is found (i.e., lumped) within this hypothetical stagnant film of thickness δ, and the properties (i.e., concentration, temperature) of the fluid at the outer edge of the film are identical to those of the bulk fluid. This model can readily be used to solve the differential equation for diffusion through a stagnant film. The dashed line in Figure 11-3b represents the concentration profile predicted by the hypothetical stagnant film model, while the solid line gives the actual profile. If the film thickness is much smaller than the radius of the pellet, curvature effects can be neglected. As a result, only the one-dimensional diffusion equation must be solved, as was shown in Section 11.1 (see also Figure 11-4).

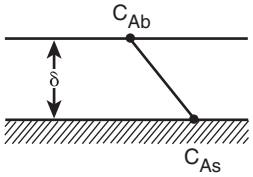

Figure 11-4 Concentration profile for EMCD in stagnant film model.

For either EMCD or dilute concentrations, the solution was shown in Example E11-1 to be in the form

$$W_{Az} = \frac{D_{AB}}{\delta} \cdot [C_{Ab} - C_{As}] \tag{11-26}$$

While the boundary layer thickness will vary around the sphere, we will take it to have a mean film thickness δ. The ratio of the diffusivity D_{AB} to the film thickness δ is the mass transfer coefficient, k_c, that is,

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The mass transfer coefficient

$$\boxed{k_c = \frac{D_{AB}}{\delta}} \tag{11-27}$$

Combining Equations (11-26) and (11-27), we obtain the average molar flux from the bulk fluid to the surface

Molar flux of A to the surface

$$\boxed{W_{Az} = k_c(C_{Ab} - C_{As})} \tag{11-28}$$

In this stagnant film model, we consider all the resistance to mass transfer to be lumped into the thickness δ. The reciprocal of the mass transfer coefficient can be thought of as this resistance

$$\boxed{W_{Az} = \text{Flux} = \frac{\text{Driving force}}{\text{Resistance}} = \frac{C_{Ab} - C_{As}}{(1/k_c)}}$$

11.3.3 Correlations for the Mass Transfer Coefficient

The mass transfer coefficient k_c is analogous to the heat transfer coefficient h. The heat flux q from the bulk fluid at a temperature T_0 to a solid surface at T_s is

$$q_z = h(T_0 - T_s) \tag{11-29}$$

For forced convection, the heat transfer coefficient is normally correlated in terms of three dimensionless groups: the Nusselt number, Nu; the Reynolds number, Re; and the Prandtl number, Pr. For the single spherical pellets discussed here, Nu and Re take the following forms:

$$\text{Nu} = \frac{hd_p}{k_t} \tag{11-30}$$

$$\text{Re} = \frac{U\rho d_p}{\mu} \tag{11-31}$$

The Prandtl number is not dependent on the geometry of the system.

The Nusselt, Prandtl, and Reynolds numbers are used in forced convection heat transfer correlations

$$\text{Pr} = \frac{\mu C_p}{k_t} = \frac{\mu}{\rho}\left(\frac{\rho C_p}{k_t}\right) = \frac{\nu}{\alpha_t} \tag{11-32}$$

where $\alpha_t = k_t/\rho C_p$ = thermal diffusivity, m^2/s

$\nu = \frac{\mu}{\rho}$ = kinematic viscosity (momentum diffusivity), m^2/s

d_p = diameter of pellet, m

U = free-stream velocity, m/s

k_t = thermal conductivity, $J/K \cdot m \cdot s$

ρ = fluid density, kg/m^3

h = heat transfer coefficient, $J/m^2 \cdot s \cdot K$ or $Watts/m^2\ K$

The other symbols are as defined previously.

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The heat transfer correlation relating the Nusselt number to the Prandtl and Reynolds numbers for flow around a sphere is[8]

$$\text{Nu} = 2 + 0.6\text{Re}^{1/2}\text{Pr}^{1/3} \tag{11-33}$$

Although this correlation can be used over a wide range of Reynolds numbers, it can be shown theoretically that if a sphere is immersed in a stagnant fluid (Re = 0), then

$$\text{Nu} = 2 \tag{11-34}$$

and that at higher Reynolds numbers in which the boundary layer remains laminar, the Nusselt number becomes

$$\text{Nu} \simeq 0.6\text{Re}^{1/2}\text{Pr}^{1/3} \tag{11-35}$$

Although further discussion of heat transfer correlations is no doubt worthwhile, it will not help us to determine the mass transfer coefficient and the mass flux from the bulk fluid to the external pellet surface. However, the preceding discussion on heat transfer was not entirely futile, because, for similar geometries, *the heat and mass transfer correlations are analogous*. If a heat transfer correlation for the Nusselt number exists, the mass transfer coefficient can be estimated by replacing the Nusselt and Prandtl numbers in this correlation by the Sherwood and Schmidt numbers, respectively:

Converting a heat transfer correlation to a mass transfer correlation

$$\text{Sh} \longrightarrow \text{Nu}$$

$$\text{Sc} \longrightarrow \text{Pr}$$

The heat and mass transfer coefficients are analogous. The corresponding fluxes are

$$q_z = h(T - T_s) \tag{11-36}$$

$$W_{Az} = k_c(C_A - C_{As})$$

The one-dimensional differential forms of the mass flux for EMCD and the heat flux are, respectively,

For EMCD the heat and molar flux equations are analogous.

$$W_{Az} = -D_{AB}\frac{dC_A}{dz} \tag{E11-1.3}$$

$$q_z = -k_t\frac{dT}{dz} \tag{11-12}$$

If we replace h by k_c and k_t by D_{AB} in Equation (11-30), i.e.,

$$\left.\begin{aligned} h &\longrightarrow k_c \\ k_t &\longrightarrow D_{AB} \end{aligned}\right\} \text{Nu} \longrightarrow \text{Sh}$$

[8] W. E. Ranz and W. R. Marshall, Jr., *Chem. Eng. Prog.*, *48*, 141–146, 173–180 (1952).

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we obtain the mass transfer Nusselt number (i.e., the Sherwood number):

Sherwood number

$$\text{Sh} = \frac{k_c d_p}{D_{\text{AB}}} = \frac{(\text{m/s})(\text{m})}{\text{m}^2/\text{s}} \text{ dimensionless} \tag{11-38}$$

The Prandtl number is the ratio of the kinematic viscosity (i.e., the momentum diffusivity) to the thermal diffusivity. Because the Schmidt number is analogous to the Prandtl number, one would expect that Sc is the ratio of the momentum diffusivity (i.e., the kinematic viscosity), ν, to the mass diffusivity D_{AB}. Indeed, this is true:

$$\alpha_t \longrightarrow D_{\text{AB}}$$

The Schmidt number is

Schmidt number

$$\text{Sc} = \frac{\nu}{D_{\text{AB}}} = \frac{\text{m}^2/\text{s}}{\text{m}^2/\text{s}} \text{ dimensionless} \tag{11-39}$$

The Sherwood, Reynolds, and Schmidt numbers are used in forced convection mass transfer correlations.

Consequently, the correlation for mass transfer for flow around a spherical pellet is analogous to that given for heat transfer [Equation (11-33)], that is,

$$\text{Sh} = 2 + 0.6\text{Re}^{1/2}\text{Sc}^{1/3} \tag{11-40}$$

This relationship is often referred to as the *Frössling correlation*.[9]

11.3.4 Mass Transfer to a Single Particle

In this section we consider two limiting cases of diffusion and reaction on a catalyst particle.[10] In the first case the reaction is so rapid that the rate of diffusion of the reactant to the surface limits the reaction rate. In the second case, the reaction is so slow that virtually no concentration gradient exists in the gas phase (i.e., rapid diffusion with respect to surface reaction).

If rapid reaction, then diffusion limits the overall rate.

Example 11–2 Rapid Reaction on a Catalyst Surface

Calculate the mass flux of reactant A to a single catalyst pellet 1 cm in diameter suspended in a large body of liquid. The reactant is present in dilute concentrations, and the reaction is considered to take place instantaneously at the external pellet surface (i.e., $C_{\text{A}s} \simeq 0$). The bulk concentration of the reactant is 1.0 M, and the free-system liquid velocity is 0.1 m/s. The kinematic viscosity is 0.5 centistoke (cS; 1 centistoke = 10^{-6} m^2/s), and the liquid diffusivity of A is 10^{-10} m^2/s. T = 300K

Solution

For dilute concentrations of the solute the radial flux is

$$W_{\text{A}r} = k_c(C_{\text{A}b} - C_{\text{A}s}) \tag{11-28}$$

[9] N. Frössling, *Gerlands Beitr. Geophys.*, *52*, 170 (1938).

[10] A comprehensive list of correlations for mass transfer to particles is given by G. A. Hughmark, *Ind. Eng. Chem. Fund.*, *19*(2), 198 (1980).

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Because reaction is assumed to occur instantaneously on the external surface of the pellet, $C_{As} = 0$. Also, C_{Ab} is given as 1 mol/dm^3. The mass transfer coefficient for single spheres is calculated from the Frössling correlation:

$$\text{Sh} = \frac{k_c d_p}{D_{AB}} = 2 + 0.6\text{Re}^{1/2}\text{Sc}^{1/3} \tag{11-40}$$

Liquid Phase
Re = 2000
Sc = 5000
Sh = 460
$k_c = 4.6 \times 10^{-6}$ m/s

$$\text{Re} = \frac{\rho d_p U}{\mu} = \frac{d_p U}{\nu} = \frac{(0.01\text{ m})(0.1\text{ m/s})}{0.5 \times 10^{-6}\text{ m}^2/\text{s}} = 2000$$

$$\text{Sc} = \frac{\nu}{D_{AB}} = \frac{5 \times 10^{-7}\text{ m}^2/\text{s}}{10^{-10}\text{ m}^2/\text{s}} = 5000$$

Substituting these values into Equation (11-40) gives us

$$\text{Sh} = 2 + 0.6(2000)^{0.5}(5000)^{1/3} = 460.7 \tag{E11-2.1}$$

$$k_c = \frac{D_{AB}}{d_p}\text{Sh} = \frac{10^{-10}\text{ m}^2/\text{s}}{0.01\text{ m}} \times 460.7 = 4.61 \times 10^{-6}\text{ m/s} \tag{E11-2.2}$$

$$C_{Ab} = 1.0\text{ mol/dm}^3 = 10^3\text{ mol/m}^3$$

Substituting for k_c and C_{Ab} in Equation (11-28), the molar flux to the surface is

$$W_{Ar} = (4.61 \times 10^{-6})\text{ m/s}\,(10^3 - 0)\text{ mol/m}^3 = 4.61 \times 10^{-3}\text{ mol/m}^2\cdot\text{s}$$

Because $W_{Ar} = -r''_{As}$, this rate is also the rate of reaction per unit surface area of catalyst.

$$\boxed{-r''_{As} = 0.0046\text{ mol/m}^2\cdot\text{s} = 0.46\text{ mol/dm}^2\cdot\text{s}}$$

In Example 11-2, the surface reaction was extremely rapid and the rate of mass transfer to the surface dictated the overall rate of reaction. We now consider a more general case. The isomerization

$$\text{A} \longrightarrow \text{B}$$

is taking place on the surface of a solid sphere (Figure 11-5). The surface reaction follows a Langmuir–Hinshelwood single-site mechanism for which the rate law is

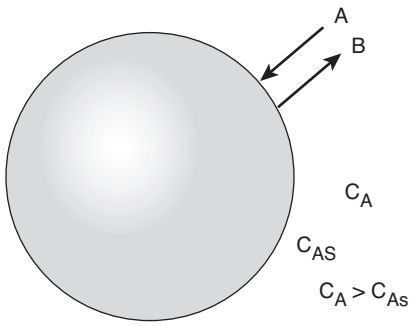

Figure 11-5 Diffusion to, and reaction on, external surface of pellet.

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$$-r''_{As} = \frac{k_r C_{As}}{1 + K_A C_{As} + K_B C_{Bs}} \tag{11-41}$$

The temperature is sufficiently high that we need only consider the case of very weak adsorption (i.e., low surface coverage) of A and B; thus

$$(K_B C_{Bs} + K_A C_{As}) \ll 1$$

Therefore,

$$-r''_{As} = k_r C_{As} \tag{11-42}$$

Using boundary conditions 2b and 2c in Table 11-1, we obtain

$$W_A|_{\text{surface}} = -r''_{As} \tag{11-43}$$

$$W_A = k_c(C_A - C_{As}) = k_r C_{As} \tag{11-44}$$

The concentration C_{As} is not as easily measured as the bulk concentration. Consequently, we need to eliminate C_{As} from the equation for the flux and rate of reaction. Solving Equation (11-44) for C_{As} yields

$$C_{As} = \frac{k_c C_A}{k_r + k_c} \tag{11-45}$$

and the rate of reaction on the surface becomes

Molar flux of A to the surface is equal to the rate of consumption of A on the surface

$$\boxed{W_A = -r''_{As} = \frac{k_c k_r C_A}{k_r + k_c}} \tag{11-46}$$

One will often find the flux to or from the surface as written in terms of an *effective* transport coefficient k_{eff}:

$$W_A = -r''_{As} = k_{\text{eff}} C_A \tag{11-47}$$

where

$$k_{\text{eff}} = \frac{k_c k_r}{k_c + k_r}$$

Rapid Reaction. We first consider how the overall rate of reaction may be increased when the rate of mass transfer to the surface limits the overall rate of reaction. Under these circumstances the specific reaction rate constant is much greater than the mass transfer coefficient

$$k_r \gg k_c$$

and

$$\frac{k_c}{k_r} \ll 1$$

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$$-r''_{As} = \frac{k_c C_A}{1 + k_c/k_r} \approx k_c C_A \tag{11-48}$$

To increase the rate of reaction per unit surface area of solid sphere, one must increase C_A and/or k_c. In this gas-phase catalytic reaction example, and for most liquids, the Schmidt number is sufficiently large that the number 2 in Equation (11-40) is negligible with respect to the second term when the Reynolds number is greater than 25. As a result, Equation (11-40) gives

It is important to know how the mass transfer coefficient varies with fluid velocity, particle size, and physical properties.

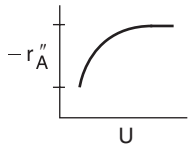
$$k_c = 0.6\left(\frac{D_{AB}}{d_p}\right)\mathrm{Re}^{1/2}\,\mathrm{Sc}^{1/3}$$

$$= 0.6\left(\frac{D_{AB}}{d_p}\right)\left(\frac{U d_p}{\nu}\right)^{1/2}\left(\frac{\nu}{D_{AB}}\right)^{1/3}$$

$$k_c = 0.6 \times \frac{D_{AB}^{2/3}}{\nu^{1/6}} \times \frac{U^{1/2}}{d_p^{1/2}} \tag{11-49}$$

$$k_c = 0.6 \times (\text{Term 1}) \times (\text{Term 2})$$

Mass Transfer Limited

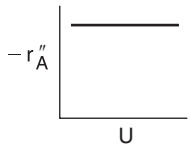


Term 1 is a function of the physical properties D_{AB} and ν, which depend on temperature and pressure only. The diffusivity always increases with increasing temperature for both gas and liquid systems. However, the kinematic viscosity ν increases with temperature ($\nu \propto T^{3/2}$) for gases and decreases exponentially with temperature for liquids. Term 2 is a function of flow conditions and particle size. Consequently, to increase k_c and thus the overall rate of reaction per unit surface area, one may either decrease the particle size or increase the velocity of the fluid flowing past the particle. For this particular case of flow past a single sphere, we see that if the velocity is doubled, the mass transfer coefficient and consequently the rate of reaction is increased by a factor of

$$(U_2/U_1)^{0.5} = 2^{0.5} = 1.41 \text{ or } 41\%$$

Reaction Rate Limited

Slow Reaction. Here the specific reaction rate constant is small with respect to the mass transfer coefficient:



Mass transfer effects are not important when the reaction rate is limiting.

$$k_r \ll k_c$$

$$-r''_{As} = \frac{k_r C_A}{1 + k_r/k_c} \approx k_r C_A \tag{11-50}$$

The specific reaction rate is independent of the velocity of fluid and for the solid sphere considered here, independent of particle size. *However*, for porous catalyst pellets, k_r may depend on particle size for certain situations, as shown in Chapter 12.

Figure 11-6 shows the variation in reaction rate with Term 2 in Equation (11-49), the ratio of velocity to particle size. At low velocities the mass

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transfer boundary layer thickness is large and diffusion limits the reaction. As the velocity past the sphere is increased, the boundary layer thickness decreases, and the mass transfer across the boundary layer no longer limits the rate of reaction. One also notes that for a given velocity, reaction-limiting conditions can be achieved by using very small particles. However, the smaller the particle size, the greater the pressure drop in a packed bed. When one is obtaining reaction rate data in the laboratory, one must operate at sufficiently high velocities or sufficiently small particle sizes to ensure that the reaction is not mass transfer–limited.

When collecting rate law data, operate in the reaction-limited region.

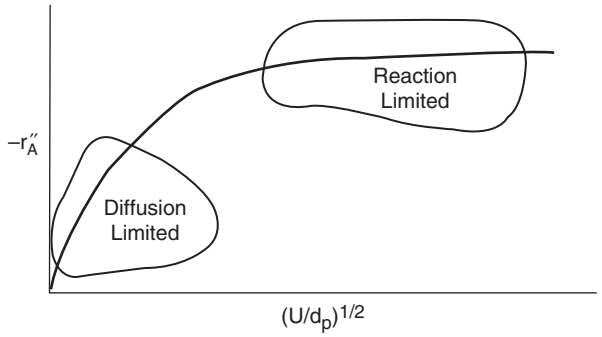

Figure 11-6 Regions of mass transfer–limited and reaction–limited reactions.

11.3.5 Mass Transfer–Limited Reactions in Packed Beds

A number of industrial reactions are potentially mass transfer–limited because they may be carried out at high temperatures without the occurrence of undesirable side reactions. In mass transfer–dominated reactions, the surface reaction is so rapid that the rate of transfer of reactant from the bulk gas or liquid phase to the surface limits the overall rate of reaction. Consequently, mass transfer–limited reactions respond quite differently to changes in temperature and flow conditions than do the rate-limited reactions discussed in previous chapters. In this section the basic equations describing the variation of conversion with the various reactor design parameters (catalyst weight, flow conditions) will be developed. To achieve this goal, we begin by carrying out a mole balance on the following mass transfer–limited reaction:

$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D \tag{2-2}$$

carried out in a packed-bed reactor (Figure 11-7). A steady-state mole balance on reactant A in the reactor segment between $\mathbf{z}$ and $\mathbf{z} + \Delta\mathbf{z}$ is

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$$\begin{bmatrix}\text{Molar}\\ \text{rate in}\end{bmatrix} - \begin{bmatrix}\text{Molar}\\ \text{rate out}\end{bmatrix} + \begin{bmatrix}\text{Molar rate of}\\ \text{generation}\end{bmatrix} = \begin{bmatrix}\text{Molar rate of}\\ \text{accumulation}\end{bmatrix}$$

$$F_{Az}|_z - F_{Az}|_{z+\Delta z} + r''_A a_c (A_c \Delta z) = 0 \qquad (11\text{-}51)$$

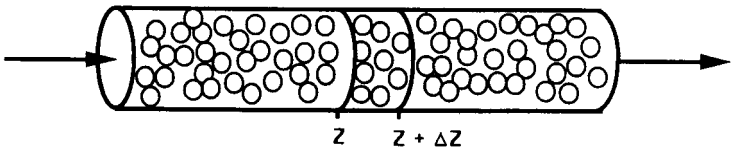

Figure 11-7 Packed-bed reactor.

where r''_A = rate of generation of A per unit catalytic surface area, mol/s·m^2
a_c = external surface area of catalyst per volume of catalytic bed, m^2/m^3
$= 6(1 - \phi)/d_p$ for packed beds, m^2/m^3
ϕ = porosity of the bed (i.e., void fraction)[11]
d_p = particle diameter, m
A_c = cross-sectional area of tube containing the catalyst, m^2

Dividing Equation (11-51) by $A_c \Delta \mathbf{z}$ and taking the limit as $\Delta \mathbf{z} \longrightarrow 0$, we have

$$-\frac{1}{A_c}\left(\frac{dF_{Az}}{dz}\right) + r''_A a_c = 0 \qquad (11\text{-}52)$$

We now need to express $F_{A\mathbf{z}}$ and r''_A in terms of concentration.

The molar flow rate of A in the axial direction is

$$F_{A\mathbf{z}} = A_c W_{A\mathbf{z}} = (J_{A\mathbf{z}} + B_{A\mathbf{z}})A_c \qquad (11\text{-}53)$$

Axial diffusion is neglected.

In almost all situations involving flow in packed-bed reactors, the amount of material transported by diffusion or dispersion in the axial direction is negligible compared with that transported by convection (i.e., bulk flow):

$$J_{A\mathbf{z}} \ll B_{A\mathbf{z}}$$

(In Chapter 14 we consider the case when dispersive effects **must** be taken into account.) Neglecting dispersion, Equation (11-20) becomes

$$F_{A\mathbf{z}} = A_c W_{A\mathbf{z}} = A_c B_{A\mathbf{z}} = U C_A A_c \qquad (11\text{-}54)$$

where U is the superficial molar average velocity through the bed (m/s). Substituting for $F_{A\mathbf{z}}$ in Equation (11-52) gives us

$$-\frac{d(C_A U)}{dz} + r''_A a_c = 0 \qquad (11\text{-}55)$$

For the case of constant superficial velocity U,

[11]In the nomenclature for Chapter 4, for Ergun Equation for pressure drop.

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Differential equation describing flow and reaction in a packed bed

$$\boxed{-U\frac{dC_A}{dz} + r''_A a_c = 0} \tag{11-56}$$

For reactions at steady state, the molar flux of A to the particle surface, W_{Ar} (mol/m$^2\cdot$s) (see Figure 11-8), is equal to the rate of disappearance of A on the surface $-r''_A$ (mol/m$^2\cdot$s); that is,

$$-r''_A = W_{Ar} \tag{11-57}$$

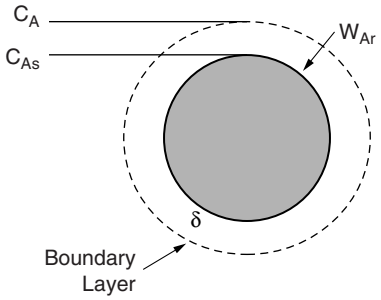
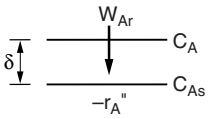


Figure 11-8 Diffusion across stagnant film surrounding catalyst pellet.



From Table 11-1, the boundary condition at the external surface is

$$-r''_A = W_{Ar} = k_c(C_A - C_{As}) \tag{11-58}$$

where k_c = mass transfer coefficient = D_{AB}/δ, (m/s)
C_A = bulk concentration of A (mol/m^3)
C_{As} = concentration of A at the catalytic surface (mol/m^3)

Substituting for r''_A in Equation (11-56), we have

$$-U\frac{dC_A}{dz} - k_c a_c(C_A - C_{As}) = 0 \tag{11-59}$$

In reactions that are completely mass transfer–limited, it is not necessary to know the rate law.

In most mass transfer–limited reactions, the surface concentration is negligible with respect to the bulk concentration (i.e., $C_A \gg C_{As}$):

$$-U\frac{dC_A}{dz} = k_c a_c C_A \tag{11-60}$$

Integrating with the limit, at $\mathbf{z} = 0$, $C_A = C_{A0}$:

$$\boxed{\frac{C_A}{C_{A0}} = \exp\left(-\frac{k_c a_c}{U} z\right)} \tag{11-61}$$

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The corresponding variation of reaction rate along the length of the reactor is

$$-r''_A = k_c C_{A0} \exp\left(-\frac{k_c a_c}{U} z\right) \tag{11-62}$$

The concentration and conversion profiles down a reactor of length L are shown in Figure 11-9.

Reactor concentration profile for a mass transfer–limited reaction

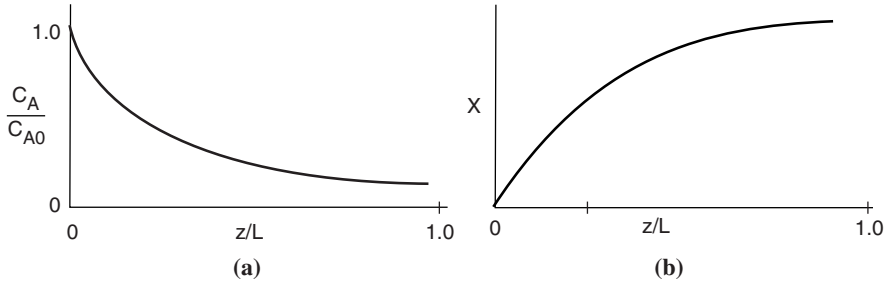

Figure 11-9 Axial concentration (a) and conversion (b) profiles in a packed bed.

To determine the reactor length L necessary to achieve a conversion X, we combine the definition of conversion,

$$X = \frac{C_{A0} - C_{AL}}{C_{A0}} \tag{11-63}$$

with the evaluation of Equation (11-61) at $z = L$ to obtain

$$\boxed{\ln \frac{1}{1-X} = \frac{k_c a_c}{U} L} \tag{11-64}$$

11.3.6 Robert the Worrier

Robert is an engineer who is always worried. He thinks something bad will happen if we change an operating condition such as flow rate or temperature or an equipment parameter such as particle size. Robert's motto is "If it ain't broke, don't fix it." We can help Robert be a little more adventuresome by analyzing how the important parameters vary as we change operating conditions in order to predict the outcome of such a change. We first look at Equation (11-64) and see that conversion depends upon k_c, a_c, U, and L. We now examine how each of these parameters will change as we change operating conditions. We first consider the effects of temperature and flow rate on conversion.

To learn the effect of flow rate and temperature on conversion, we need to know how these parameters affect the mass transfer coefficient. That is, we must determine the correlation for the mass transfer coefficient for the particular geometry and flow field. For flow through a packed bed, the correlation

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given by Thoenes and Kramers[12] for $0.25 < \phi < 0.5$, $40 < \mathrm{Re}' < 4000$, and $1 < \mathrm{Sc} < 4000$ is

$$\mathrm{Sh}' = 1.0(\mathrm{Re}')^{1/2}\mathrm{Sc}^{1/3} \tag{11-65}$$

Thoenes–Kramers correlation for flow through packed beds

$$\left[\frac{k_c d_p}{D_{AB}}\left(\frac{\phi}{1-\phi}\right)\frac{1}{\gamma}\right] = \left[\frac{U d_p \rho}{\mu(1-\phi)\gamma}\right]^{1/2}\left(\frac{\mu}{\rho D_{AB}}\right)^{1/3} \tag{11-66}$$

where $\mathrm{Re}' = \dfrac{\mathrm{Re}}{(1-\phi)\gamma}$

$\mathrm{Sh}' = \dfrac{\mathrm{Sh}\,\phi}{(1-\phi)\gamma}$

d_p = particle diameter (equivalent diameter of sphere of the same volume), m
= $[(6/\pi)$ (volume of pellet)$]^{1/3}$, m

ϕ = void fraction (porosity) of packed bed

γ = shape factor (external surface area divided by πd_p^2)

U = superficial gas velocity through the bed, m/s

μ = viscosity, kg/m·s

ρ = fluid density, kg/m^3

$\nu = \dfrac{\mu}{\rho}$ = kinematic viscosity, m^2/s

D_{AB} = gas-phase diffusivity, m^2/s

For constant fluid properties and particle diameter:

$$k_c \propto U^{1/2} \tag{11-67}$$

We see that the mass transfer coefficient increases with the square root of the superficial velocity through the bed. Therefore, *for a fixed concentration*, C_A, such as that found in a differential reactor, the rate of reaction should vary with $U^{1/2}$:

For diffusion-limited reactions, reaction rate depends on particle size and fluid velocity.

$$-r_A'' \propto k_c C_A \propto U^{1/2}$$

However, if the gas velocity is continually increased, a point is reached where the reaction becomes reaction rate–limited and consequently, is independent of the superficial gas velocity, as shown in Figure 11-6.

Most mass transfer correlations in the literature are reported in terms of the Colburn J factor (i.e., J_D)as a function of the Reynolds number. The relationship between J_D and the numbers we have been discussing is

Colburn J factor

$$J_D = \frac{\mathrm{Sh}}{\mathrm{Sc}^{1/3}\mathrm{Re}} \tag{11-68}$$

Figure 11-10 shows data from a number of investigations for the J factor as a function of the Reynolds number for a wide range of particle shapes and

[12]D. Thoenes, Jr. and H. Kramers, *Chem. Eng. Sci.*, *8*, 271 (1958).

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gas flow conditions. *Note:* There are serious deviations from the Colburn analogy when the concentration gradient and temperature gradient are coupled as shown by Venkatesan and Fogler.[13]

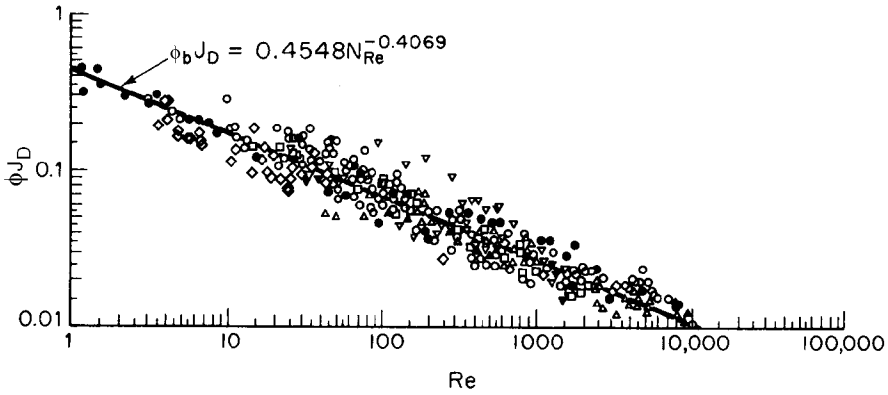


Figure 11-10 Mass transfer correlation for packed beds. $\phi b \equiv \phi$ [Reprinted with permission from P. N. Dwidevi and S. S. Upadhyay, *Ind. Eng. Chem. Process Des. Dev.*, *16*, 157 (1977). Copyright © 1977 American Chemical Society.]

Dwidevi and Upadhyay[14] review a number of mass transfer correlations for both fixed and fluidized beds and arrive at the following correlation, which is valid for both gases ($Re > 10$) and liquids ($Re > 0.01$) in either fixed or fluidized beds:

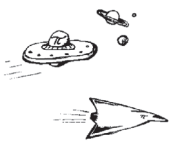
A correlation for flow through packed beds in terms of the Colburn *J* factor

$$\phi J_D = \frac{0.765}{Re^{0.82}} + \frac{0.365}{Re^{0.386}} \tag{11-69}$$

For nonspherical particles, the equivalent diameter used in the Reynolds and Sherwood numbers is $d_p = \sqrt{A_p/\pi} = 0.564\sqrt{A_p}$, where A_p is the external surface area of the pellet.

To obtain correlations for mass transfer coefficients for a variety of systems and geometries, see either D. Kunii and O. Levenspiel, *Fluidization Engineering*, 2nd ed. (Butterworth-Heinemann, 1991), Chap. 7, or W. L. McCabe, J. C. Smith, and P. Harriott, *Unit Operations in Chemical Engineering*, 6th ed. (New York: McGraw-Hill, 2000). For other correlations for packed beds with different packing arrangements, see I. Colquhoun-Lee and J. Stepanek, *Chemical Engineer*, 108 (Feb. 1974).

Actual case history and current application



Example 11–3 Maneuvering a Space Satellite

Hydrazine has been studied extensively for use in monopropellant thrusters for space flights of long duration. Thrusters are used for altitude control of communication satellites. Here the decomposition of hydrazine over a packed bed of alumina-supported

[13]R. Venkatesan and H. S. Fogler, *AIChE J., 50,* 1623 (July 2004).

[14]P. N. Dwidevi and S. N. Upadhyay, *Ind. Eng. Chem. Process Des. Dev.*, *16*, 157 (1977).

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iridium catalyst is of interest.[15] In a proposed study, a 2% hydrazine in 98% helium mixture is to be passed over a packed bed of cylindrical particles 0.25 cm in diameter and 0.5 cm in length at a gas-phase velocity of 15 m/s and a temperature of 750 K. The kinematic viscosity of helium at this temperature is 4.5×10^{-4} m^2/s. The hydrazine decomposition reaction is believed to be externally mass transfer–limited under these conditions. If the packed bed is 0.05 m in length, what conversion can be expected? Assume isothermal operation.

Additional information

$D_{AB} = 0.69 \times 10^{-4}$ m^2/s at 298 K
Bed porosity: 30%
Bed fluidicity: 95.7%

Solution

Rearranging Equation (11-64) gives us

$$\boxed{X = 1 - e^{-(k_c a_c / U)L}} \tag{E11-3.1}$$

(a) Thoenes–Kramers correlation

1. First we find the volume-average particle diameter:

$$d_p = \left(\frac{6V}{\pi}\right)^{1/3} = \left(6\,\frac{\pi D^2}{4}\,\frac{\mathrm{L}}{\pi}\right)^{1/3} \tag{E11-3.2}$$
$$= [1.5(0.0025\text{ m})^2(0.005\text{ m})]^{1/3} = 3.61 \times 10^{-3}\text{ m}$$

2. Surface area per volume of bed:

$$a_c = 6\left(\frac{1-\phi}{d_p}\right) = 6\left(\frac{1-0.3}{3.61\times 10^{-3}\text{ m}}\right) = 1163\text{ m}^2/\text{m}^3 \tag{E11-3.3}$$

3. Mass transfer coefficient:

$$\mathrm{Re} = \frac{d_p U}{\nu} = \frac{(3.61\times 10^{-3}\text{ m})(15\text{ m/s})}{4.5\times 10^{-4}\text{ m}^2/\text{s}} = 120.3$$

For cylindrical pellets,

$$\gamma = \frac{2\pi r L_p + 2\pi r^2}{\pi d_p^2} = \frac{(2)(0.0025/2)(0.005) + (2)(0.0025/2)^2}{(3.61\times 10^{-3})^2} = 1.20 \tag{E11-3.4}$$

$$\mathrm{Re}' = \frac{\mathrm{Re}}{(1-\phi)\gamma} = \frac{120.3}{(0.7)(1.2)} = 143.2$$

Correcting the diffusivity to 750 K using Table 11-2 gives us

$$D_{AB}(750\text{ K}) = D_{AB}(298\text{ K}) \times \left(\frac{750}{298}\right)^{1.75} = (0.69 \times 10^{-4}\text{ m}^2/\text{s})(5.03)$$

Representative values

Gas Phase
Re′ = 143
Sc = 1.3
Sh′ = 13.0
k_c = 3.5 m/s

[15] O. I. Smith and W. C. Solomon, *Ind. Eng. Chem. Fund.*, *21*, 374 (1982).

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$$D_{AB}\,(750\text{ K}) = 3.47\times10^{-4}\text{ m}^2/\text{s} \tag{E11-3.5}$$

$$\text{Sc} = \frac{\nu}{D_{AB}} = \frac{4.5\times10^{-4}\text{ m}^2/\text{s}}{3.47\times10^{-4}\text{ m}^2/\text{s}} = 1.30$$

Substituting Re′ and Sc into Equation (11-65) yields

$$\text{Sh}' = (143.2)^{1/2}(1.3)^{1/3} = (11.97)(1.09) = 13.05 \tag{E11-3.6}$$

$$k_c = \frac{D_{AB}(1-\phi)}{d_p\phi}\,\gamma(\text{Sh}') = \left(\frac{3.47\times10^{-4}\text{ m}^2/\text{s}}{3.61\times10^{-3}\text{ m}}\right)\left(\frac{1-0.3}{0.3}\right)$$
$$\times\,(1.2)(13.05) = 3.52\text{ m/s} \tag{E11-3.7}$$

The conversion is

$$X = 1-\exp\left[-(3.52\text{ m/s})\left(\frac{1163\text{ m}^2/\text{m}^3}{15\text{ m/s}}\right)(0.05\text{ m})\right] \tag{E11-3.8}$$
$$= 1-1.18\times10^{-6} \simeq 1.00 \qquad \text{virtually complete conversion}$$

(b) Colburn J_D factor. Calculate the surface-area-average particle diameter.

For cylindrical pellets the external surface area is

$$A = \pi dL_p + 2\pi\left(\frac{d^2}{4}\right) \tag{E11-3.9}$$

$$d_p = \sqrt{\frac{A}{\pi}} = \sqrt{\frac{\pi dL_p + 2\pi(d^2/4)}{\pi}} \tag{E11-3.10}$$

$$= \sqrt{(0.0025)(0.005) + \frac{(0.0025)^2}{2}} = 3.95\times10^{-3}\text{ m}$$

$$a_c = \frac{6(1-\phi)}{d_p} = 1063\text{ m}^2/\text{m}^3$$

Typical values

Gas Phase
Re = 130
$J_D = 0.23$
Sc = 1.3
Sh = 33
$k_c = 3$ m/s

$$\text{Re} = \frac{d_pU}{\nu} = \frac{(3.95\times10^{-3}\text{ m})(15\text{ m/s})}{4.5\times10^{-4}\text{ m}^2/\text{s}}$$
$$= 131.6$$

$$\phi J_D = \frac{0.765}{\text{Re}^{0.82}} + \frac{0.365}{\text{Re}^{0.386}} \tag{11-69}$$

$$= \frac{0.765}{(131.6)^{0.82}} + \frac{0.365}{(131.6)^{0.386}} = 0.014 + 0.055 \tag{E11-3.11}$$
$$= 0.069$$

$$J_D = \frac{0.069}{0.3} = 0.23 \tag{E11-3.12}$$

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$$\text{Sh} = \text{Sc}^{1/3}\text{Re}(J_D) \tag{E11-3.13}$$

$$= (1.3)^{1/3}(131.6)(0.23) = 33.0$$

$$k_c = \frac{D_{\text{AB}}}{d_p}\,\text{Sh} = \frac{3.47\times10^{-4}}{3.95\times10^{-3}}\,(33) = 2.9\ \text{m/s}$$

Then

$$X = 1 - \exp\left[-(2.9\ \text{m/s})\left(\frac{1063\ \text{m}^2/\text{m}^3}{15\ \text{m/s}}\right)(0.05\ \text{m})\right] \tag{E11-3.14}$$

$$= 1 - 0.0000345$$

$$\simeq 1 \qquad \text{again, virtually complete conversion}$$

If there were such a thing as the **bed fluidicity**, given in the problem statement, it would be a useless piece of information. Make sure that you know what information you need to solve problems, and go after it. Do not let additional data confuse you or lead you astray with useless information or facts that represent someone else's bias, which are probably not well-founded.

11.4 What If . . . ? (Parameter Sensitivity)

J. D. Goddard's

Back of the Envelope

One of the most important skills of an engineer is to be able to predict the effects of changes of system variables on the operation of a process. The engineer needs to determine these effects quickly through approximate but reasonably close calculations, which are sometimes referred to as "back-of-the-envelope calculations."[16] This type of calculation is used to answer such questions as "**What** will happen **if** I decrease the particle size?" "**What if** I triple the flow rate through the reactor?"

We will now proceed to show how this type of question can be answered using the packed-bed, mass transfer–limited reactors as a model or example system. Here we want to learn the effect of changes of the various parameters (e.g., temperature, particle size, superficial velocity) on the conversion. We begin with a rearrangement of the mass transfer correlation, Equation (11-66), to yield

$$k_c \propto \left(\frac{D_{\text{AB}}^{2/3}}{\nu^{1/6}}\right)\left(\frac{U^{1/2}}{d_p^{1/2}}\right) \tag{11-70}$$

Find out how the mass transfer coefficient varies with changes in *physical properties and system properties*

The first term on the right-hand side is dependent on physical properties (temperature and pressure), whereas the second term is dependent on system properties (flow rate and particle size). One observes from this equation that the mass transfer coefficient increases as the particle size decreases. The use of sufficiently small particles offers another technique to escape from the mass transfer–limited regime into the reaction rate–limited regime.

[16]Prof. J. D. Goddard, University of Michigan, 1963–1976. Currently at University of California, San Diego.

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Example 11–4 The Case of Divide and Be Conquered

A mass transfer–limited reaction is being carried out in two reactors of equal volume and packing, connected in series as shown in Figure E11-4.1. Currently, 86.5% conversion is being achieved with this arrangement. It is suggested that the reactors be separated and the flow rate be divided equally among each of the two reactors (Figure E11-4.2) to decrease the pressure drop and hence the pumping requirements. In terms of achieving a higher conversion, Robert is wondering if this is a good idea?

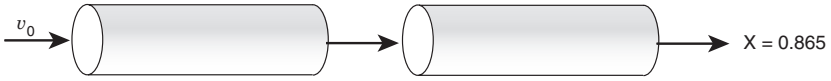

Figure E11-4.1 Series arrangement

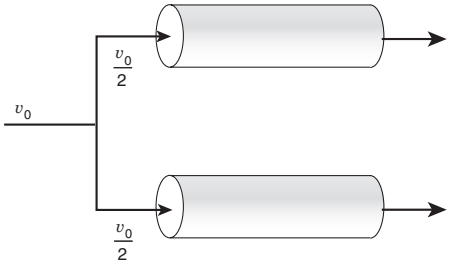

Figure E11-4.2 Parallel arrangement.

Reactors in series versus reactors in parallel

Solution

As a first approximation, we neglect the effects of small changes in temperature and pressure on mass transfer. We recall Equation (11-64), which gives conversion as a function of reactor length. For a mass transfer–limited reaction

$$\ln \frac{1}{1-X} = \frac{k_c a_c}{U} L \tag{11-64}$$

For case 1, the undivided system:

$$\left(\ln \frac{1}{1-X_1}\right) = \frac{k_{c1} a_c}{U_1} L_1 \tag{E11-4.1}$$

$$X_1 = 0.865$$

For case 2, the divided system:

$$\left(\ln \frac{1}{1-X_2}\right) = \frac{k_{c2} a_c}{U_2} L_2 \tag{E11-4.2}$$

$$X_2 = ?$$

We now take the ratio of case 2 (divided system) to case 1 (undivided system):

$$\frac{\ln \dfrac{1}{1-X_2}}{\ln \dfrac{1}{1-X_1}} = \frac{k_{c2}}{k_{c1}} \left(\frac{L_2}{L_1}\right) \frac{U_1}{U_2} \tag{E11-4.3}$$

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The surface area per unit volume a_c is the same for both systems.

From the conditions of the problem statement we know that

$$L_2 = \tfrac{1}{2}L_1$$
$$U_2 = \tfrac{1}{2}U_1$$
$$X_1 = 0.865$$
$$X_2 = ?$$

However, we must also consider the effect of the division on the mass transfer coefficient. From Equation (11-70) we know that

$$k_c \propto U^{1/2}$$

Then

$$\frac{k_{c2}}{k_{c1}} = \left(\frac{U_2}{U_1}\right)^{1/2} \tag{E11-4.4}$$

Multiplying by the ratio of superficial velocities yields

$$\frac{U_1}{U_2}\left(\frac{k_{c2}}{k_{c1}}\right) = \left(\frac{U_1}{U_2}\right)^{1/2} \tag{E11-4.5}$$

$$\ln\frac{1}{1-X_2} = \left(\ln\frac{1}{1-X_1}\right)\frac{L_2}{L_1}\left(\frac{U_1}{U_2}\right)^{1/2} \tag{E11-4.6}$$

$$= \left(\ln\frac{1}{1-0.865}\right)\left[\frac{\frac{1}{2}L_1}{L_1}\left(\frac{U_1}{\frac{1}{2}U_1}\right)^{1/2}\right]$$

$$= 2.00\left(\frac{1}{2}\right)\sqrt{2} = 1.414$$

Solving for X_2 gives us

$$X_2 = 0.76$$

Bad idea!! Robert was right to worry.

Consequently, we see that although the divided arrangement will have the advantage of a smaller pressure drop across the bed, it is a bad idea in terms of conversion. Recall that if the reaction were reaction rate–limited, both arrangements would give the same conversion.

Example 11–5 The Case of the Overenthusiastic Engineers

The same reaction as that in Example 11-4 is being carried out in the same two reactors in series. A new engineer suggests that the rate of reaction could be increased by a factor of 2^{10} by increasing the reaction temperature from 400°C to 500°C, reasoning that the reaction rate doubles for every 10°C increase in temperature. Another engineer arrives on the scene and berates the new engineer with quotations from Chapter 3 concerning this rule of thumb. She points out that it is valid only for a specific activation energy within a specific temperature range. She then

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Robert worries if this temperature increase will be worth the trouble.

suggests that he go ahead with the proposed temperature increase but should only expect an increase on the order of 2^3 or 2^4. What do you think? Who is correct?

Solution

Because almost all surface reaction rates increase more rapidly with temperature than do diffusion rates, increasing the temperature will only increase the degree to which the reaction is mass transfer–limited.

We now consider the following two cases:

Case 1: $T = 400°C$ $X = 0.865$

Case 2: $T = 500°C$ $X = ?$

Taking the ratio of case 2 to case 1 and noting that the reactor length is the same for both cases ($L_1 = L_2$), we obtain

$$\frac{\ln \dfrac{1}{1-X_2}}{\ln \dfrac{1}{1-X_1}} = \frac{k_{c2}}{k_{c1}}\left(\frac{L_2}{L_1}\right)\frac{U_1}{U_2} = \frac{k_{c2}}{k_{c1}}\left(\frac{U_1}{U_2}\right) \tag{E11-5.1}$$

The molar feed rate F_{T0} remains unchanged:

$$F_{T0} = v_{01}\left(\frac{P_{01}}{RT_{01}}\right) = v_{02}\left(\frac{P_{02}}{RT_{02}}\right) \tag{E11-5.2}$$

Because $v = A_c U$, the superficial velocity at temperature T_2 is

$$U_2 = \frac{T_2}{T_1}\,U_1 \tag{E11-5.3}$$

We now wish to learn the dependence of the mass transfer coefficient on temperature:

$$k_c \propto \left(\frac{U^{1/2}}{d_p^{1/2}}\right)\left(\frac{D_{AB}^{2/3}}{\nu^{1/6}}\right) \tag{E11-5.4}$$

Taking the ratio of case 2 to case 1 and realizing that the particle diameter is the same for both cases gives us

$$\frac{k_{c2}}{k_{c1}} = \left(\frac{U_2}{U_1}\right)^{1/2}\left(\frac{D_{AB2}}{D_{AB1}}\right)^{2/3}\left(\frac{\nu_1}{\nu_2}\right)^{1/6} \tag{E11-5.5}$$

The temperature dependence of the gas-phase diffusivity is (from Table 11-2)

$$D_{AB} \propto T^{1.75} \tag{E11-5.6}$$

For most gases, viscosity increases with increasing temperature according to the relation

$$\mu \propto T^{1/2}$$

From the ideal gas law,

$$\rho \propto T^{-1}$$

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Then

$$\nu = \frac{\mu}{\rho} \propto T^{3/2} \tag{E11-5.7}$$

It's really important to know how to do this type of analysis.

$$\frac{\ln \dfrac{1}{1-X_2}}{\ln \dfrac{1}{1-X_1}} = \frac{U_1}{U_2}\left(\frac{k_{c2}}{k_{c1}}\right) = \left(\frac{U_1}{U_2}\right)^{1/2}\left(\frac{D_{AB2}}{D_{AB1}}\right)^{2/3}\left(\frac{\nu_1}{\nu_2}\right)^{1/6} \tag{E11-5.8}$$

$$= \left(\frac{T_1}{T_2}\right)^{1/2}\left[\left(\frac{T_2}{T_1}\right)^{1.75}\right]^{2/3}\left[\left(\frac{T_1}{T_2}\right)^{3/2}\right]^{1/6}$$

$$= \left(\frac{T_1}{T_2}\right)^{1/2}\left(\frac{T_2}{T_1}\right)^{7/6}\left(\frac{T_1}{T_2}\right)^{1/4} = \left(\frac{T_2}{T_1}\right)^{5/12} \tag{E11-5.9}$$

$$= \left(\frac{773}{673}\right)^{5/12} = 1.059$$

$$\ln \frac{1}{1-X_1} = \ln \frac{1}{1-0.865} = 2$$

$$\ln \frac{1}{1-X_2} = 1.059\left(\ln \frac{1}{1-X_1}\right) = 1.059(2) \tag{E11-5.10}$$

$$X_2 = 0.88$$

Bad idea!! Robert was right to worry.

Consequently, we see that increasing the temperature from 400°C to 500°C increases the conversion by only 1.7%. Both engineers would have benefited from a more thorough study of this chapter.

For a packed catalyst bed, the temperature-dependence part of the mass transfer coefficient for a gas-phase reaction can be written as

$$k_c \propto U^{1/2} \quad (D_{AB}^{2/3}/\nu^{1/6}) \tag{11-71}$$

$$k_c \propto U^{1/2} T^{11/12} \tag{11-72}$$

Important concept

Depending on how one fixes or changes the molar feed rate, F_{T0}, U may also depend on the feed temperature. ***As an engineer, it is extremely important that you reason out the effects of changing conditions***, as illustrated in the preceding two examples.

11.5 The Shrinking Core Model

The shrinking core model is used to describe situations in which solid particles are being consumed either by dissolution or reaction and, as a result, the

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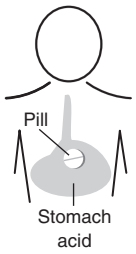

amount of the material being consumed is "shrinking." This model applies to areas ranging from pharmacokinetics (e.g., dissolution of pills in the stomach) to the formation of an ash layer around a burning coal particle, to catalyst regeneration. To design the time release of drugs into the body's system, one must focus on the rate of dissolution of capsules and solid pills injected into the stomach. See PRS11.4. In this section we focus primarily on catalyst regeneration and leave other applications such as drug delivery as exercises at the end of the chapter.

11.5.1 Catalyst Regeneration

Many situations arise in heterogeneous reactions where a gas-phase reactant reacts with a species contained in an inert solid matrix. One of the most common examples is the removal of carbon from catalyst particles that have been deactivated by fouling (see Section 10.7.1). The catalyst regeneration process to reactivate the catalyst by burning off the carbon is shown in Figures 11-11 through 11-13. Figure 11-11 shows a schematic diagram of the removal of carbon from a single porous catalyst pellet as a function of time. Carbon is first removed from the outer edge of the pellet and then in the final stages of the regeneration from the center core of the pellet.

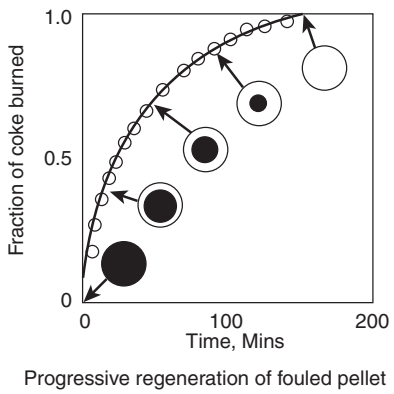

Figure 11-11 Shell progressive regeneration of fouled pellet. [Reprinted with permission from J. T. Richardson, *Ind. Eng. Chem. Process Des. Dev.*, *11*(1), 8 (1972); copyright American Chemical Society.]

As the carbon continues to be removed from the porous catalyst pellet, the reactant gas must diffuse farther into the material as the reaction proceeds to reach the unreacted solid phase. Note that approximately 3 hours was required to remove all of the carbon from the pellets at these conditions. The regeneration time can be reduced by increasing the gas-phase oxygen concentration and temperature.

To illustrate the principles of the shrinking core model, we shall consider the removal of carbon from the catalyst particle just discussed. In Figure 11-12

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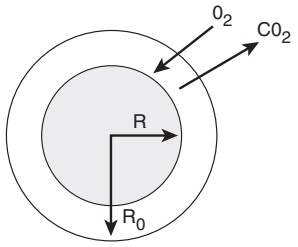


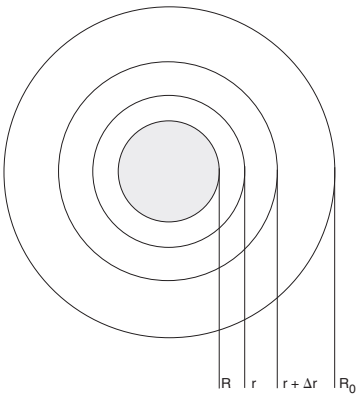
Figure 11-12 Partially regenerated catalyst pellet.

a core of unreacted carbon is contained between $r = 0$ and $r = R$. Carbon has been removed from the porous matrix between $r = R$ and $r = R_0$. Oxygen diffuses from the outer radius R_0 to the radius R, where it reacts with carbon to form carbon dioxide, which then diffuses out of the porous matrix. The reaction

$$C + O_2 \longrightarrow CO_2$$

at the solid surface is very rapid, so the rate of oxygen diffusion to the surface controls the rate of carbon removal from the core. Although the core of carbon is shrinking with time (an unsteady-state process), we assume the concentration profiles at any instant in time to be the steady-state profiles over the distance $(R_0 - R)$. This assumption is referred to as the *quasi-steady state assumption* (QSSA).

QSSA
Use steady-state profiles



Oxygen must diffuse through the porous pellet matrix until it reaches the unreacted carbon core.

Figure 11-13 Sphere with unreacted carbon core of radius R.

To study how the radius of unreacted carbon changes with time, we must first find the rate of diffusion of oxygen to the carbon surface. Next, we perform a mole balance on the elemental carbon and equate the rate of consumption of carbon to the rate of diffusion of oxygen to the gas carbon interface.

In applying a differential oxygen mole balance over the increment Δr located somewhere between R_0 and R, we recognize that O_2 does not react in

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this region and reacts only when it reaches the solid carbon interface located at $r = R$. We shall let species A represent O_2.

Step 1: The mole balance on O_2 (i.e., A) between r and $r + \Delta r$ is

$$\begin{bmatrix}\text{Rate}\\ \text{in}\end{bmatrix} - \begin{bmatrix}\text{Rate}\\ \text{out}\end{bmatrix} + \begin{bmatrix}\text{Rate of}\\ \text{generation}\end{bmatrix} = \begin{bmatrix}\text{Rate of}\\ \text{accumulation}\end{bmatrix}$$

$$W_{Ar}4\pi r^2|_r - W_{Ar}4\pi r^2|_{r+\Delta r} + \quad 0 \quad = \quad 0$$

Dividing through by $-4\pi\Delta r$ and taking the limit gives

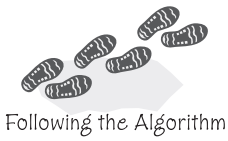
Mole balance on oxygen

$$\lim_{\Delta r\to 0}\frac{W_{Ar}r^2|_{r+\Delta r} - W_{Ar}r^2|_r}{\Delta r} = \frac{d(W_{Ar}r^2)}{dr} = 0 \tag{11-73}$$

Step 2: For every mole of O_2 that diffuses into the spherical pellet, 1 mol of CO_2 diffuses out ($W_{CO_2} = -W_{O_2}$), that is, EMCD. The constitutive equation for constant total molar concentration becomes

$$W_{Ar} = -D_e\frac{dC_A}{dr} \tag{11-74}$$

where D_e is an *effective diffusivity* in the porous catalyst. In Chapter 12 we present an expanded discussion of effective diffusivities in a porous catalyst [cf. Equation (12-1)].



Step 3: Combining Equations (11-73) and (11-74) yields

$$\frac{d}{dr}\left(-D_e\frac{dC_A}{dr}r^2\right) = 0$$

Dividing by $(-D_e)$ gives

$$\boxed{\frac{d}{dr}\left(r^2\frac{dC_A}{dr}\right) = 0} \tag{11-75}$$

Step 4: The boundary conditions are:

At the outer surface of the particle, $r = R_0$: $C_A = C_{A0}$

At the fresh carbon/gas interface, $r = R(t)$: $C_A = 0$ (rapid reaction)

Step 5: Integrating twice yields

$$r^2\frac{dC_A}{dr} = K_1$$

$$C_A = \frac{-K_1}{r} + K_2$$

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Using the boundary conditions to eliminate K_1 and K_2, the concentration profile is given by

$$\boxed{\frac{C_A}{C_{A0}} = \frac{1/R - 1/r}{1/R - 1/R_0}} \tag{11-76}$$

A schematic representation of the profile of O_2 is shown in Figure 11-14 at a time when the inner core is receded to a radius R. The zero on the r axis corresponds to the center of the sphere.

Concentration profile at a given time, t (i.e., core radius, R)

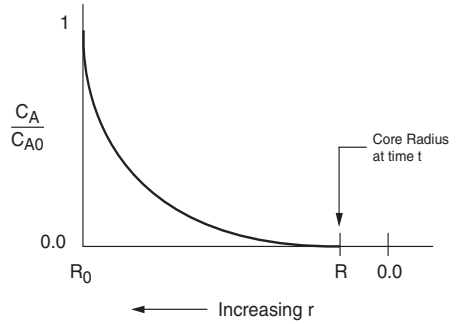

Figure 11-14 Oxygen concentration profile shown from the external radius of the pellet (R_0) to the pellet center. The gas–carbon interface is located at R.

Step 6: The molar flux of O_2 to the gas–carbon interface is

$$W_{Ar} = -D_e \frac{dC_A}{dr} = \frac{-D_e C_{A0}}{(1/R - 1/R_0)\, r^2} \tag{11-77}$$

Step 7: We now carry out an overall balance on elemental carbon. Elemental carbon does not enter or leave the particle.

$$\left[\begin{array}{c}\text{Rate}\\ \text{in}\end{array}\right] - \left[\begin{array}{c}\text{Rate}\\ \text{out}\end{array}\right] + \left[\begin{array}{c}\text{Rate of}\\ \text{generation}\end{array}\right] = \left[\begin{array}{c}\text{Rate of}\\ \text{accumulation}\end{array}\right]$$

Mole balance on shrinking core

$$0 \quad - \quad 0 \quad + \quad r_C'' 4\pi R^2 \quad = \quad \frac{d\left(\frac{4}{3}\pi R^3 \rho_C \phi_C\right)}{dt}$$

where ρ_C is the molar density of the solid carbon and ϕ_C is the volume fraction of carbon in the porous catalyst. Simplifying gives

$$\frac{dR}{dt} = \frac{r_C''}{\phi_C \rho_C} \tag{11-78}$$

Step 8: The rate of disappearance of carbon is equal to the flux of O_2 to the gas–carbon interface:

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$$-r''_C = -W_{Ar}\Big|_{r=R} = \frac{D_e C_{A0}}{R - R^2/R_0} \tag{11-79}$$

The minus sign arises with respect to W_{Ar} in Equation (11-79) because O_2 is diffusing in an inward direction [i.e., opposite to the increasing coordinate (r) direction]:

$$-\frac{dR}{dt} = \frac{D_e C_{A0}}{\phi_C \rho_C}\left(\frac{1}{R - R^2/R_0}\right)$$

Step 9: Integrating with limits $R = R_0$ at $t = 0$, the time necessary for the solid carbon interface to recede inward to a radius R is

$$t = \frac{\rho_C R_0^2 \phi_C}{6 D_e C_{A0}}\left[1 - 3\left(\frac{R}{R_0}\right)^2 + 2\left(\frac{R}{R_0}\right)^3\right] \tag{11-80}$$

We see that as the reaction proceeds, the reacting gas–solid moves closer to the center of the core. The corresponding oxygen concentration profiles at three different times are shown in Figure 11-15.

Concentration profiles at different times at inner core radii

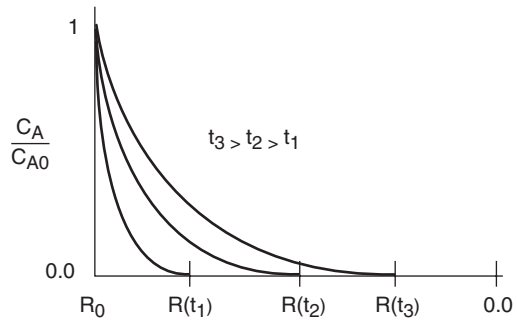

Figure 11-15 Oxygen concentration profile at various times. At t_1, the gas–carbon interface is located at $R(t_1)$; at t_2 it is located at $R(t_2)$.

The time necessary to consume all the carbon in the catalyst pellet is

Time to complete regeneration of the particle

$$t_c = \frac{\rho_C R_0^2 \phi_C}{6 D_e C_{A0}} \tag{11-81}$$

For a 1-cm diameter pellet with a 0.04 volume fraction of carbon, the regeneration time is the order of 10 s.

Variations on the simple system we have chosen here can be found on page 360 of Levenspiel[17] and in the problems at the end of this chapter.

[17]O. Levenspiel, *Chemical Reactor Engineering*, 2nd ed. (New York: Wiley, 1972).

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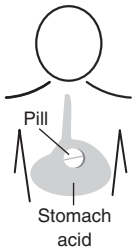
11.5.2 Pharmacokinetics—Dissolution of Monodispersed Solid Particles



We now consider the case where the total particle is being completely consumed. We choose as an example the case where species A must diffuse to the surface to react with solid B at the liquid–solid interface. Reactions of this type are typically zero order in B and first order in A. The rate of mass transfer to the surface is equal to the rate of surface reaction.

$$W_{Ar} = k_c(C_A - C_{As}) = -r''_{As} = k_r C_{As}$$

(Diffusion) (Surface reaction)

Eliminating C_{As}, we arrive at an equation identical to Equation (11-46) for the radial flux:

$$W_{Ar} = -r''_{As} = \frac{k_c k_r}{k_c + k_r} C_A \tag{11-46}$$

For the case of small particles and negligible shear stress at the fluid boundary, the Frössling equation, Equation (11-40), is approximated by

$$\text{Sh} = 2$$

or

$$k_c = \frac{2D_e}{D} \tag{11-82}$$

where D is the diameter of the dissolving particle. Substituting Equation (11-82) into (11-46) and rearranging yields

Diameter at which mass transfer and reaction rate resistances are equal is D^*

$$-r''_{As} = \frac{k_r C_A}{1 + k_r/k_c} = \frac{k_r C_A}{1 + k_r D/2D_e} = \frac{k_r C_A}{1 + D/D^*} \tag{11-83}$$

where $D^* = 2D_e/k_r$ is the diameter at which the resistances to mass transfer and reaction rate are equal.

$D > D^*$	mass transfer controls
$D < D^*$	reaction rate controls

A mole balance on the solid particle yields

Balance on the dissolving solid B

$$\text{In} - \text{Out} + \text{Generation} = \text{Accumulation}$$

$$0 - 0 + \quad r''_{Bs}\pi D^2 = \quad \frac{d(\rho\pi D^3/6)}{dt}$$

where ρ is the molar density of species B. If 1 mol of A dissolves 1 mol of B, then $-r''_{As} = -r''_{Bs}$, and after differentiation and rearrangement we obtain

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Ibuprofen

$$\frac{dD}{dt} = -\left[\frac{2(-r''_{As})}{\rho}\right] = -\frac{2k_r C_A}{\rho}\left(\frac{1}{1+D/D^*}\right)$$

$$\boxed{\frac{dD}{dt} = -\frac{\alpha}{1+D/D^*}} \tag{11-84}$$

where

$$\alpha = \frac{2k_r C_A}{\rho}$$

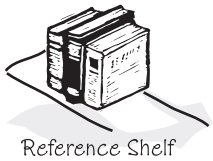
At time $t = 0$, the initial diameter is $D = D_i$. Integrating Equation (11-84) for the case of excess concentration of reactant A, we obtain the following diameter–time relationship:

Excess A

$$D_i - D + \frac{1}{2D^*}(D_i^2 - D^2) = \alpha t \tag{11-85}$$

The time to complete dissolution of the solid particle is

$$t_c = \frac{1}{\alpha}\left(D_i + \frac{D_i^2}{2D^*}\right) \tag{11-86}$$



The dissolution of polydisperse particle sizes is analyzed using population balances and is discussed on the CD-ROM.

Closure. After completing this chapter, the reader should be able to define and describe molecular diffusion and how it varies with temperature and pressure, the molar flux, bulk flow, the mass transfer coefficient, the Sherwood and Schmidt numbers, and the correlations for the mass transfer coefficient. The reader should be able to choose the appropriate correlation and calculate the mass transfer coefficient, the molar flux, and the rate of reaction. The reader should be able to describe the regimes and conditions under which mass transfer–limited reactions occur and when reaction rate limited reactions occur and to make calculations of the rates of reaction and mass transfer for each case. One of the most important areas for the reader to apply the knowledge of this (and other chapters) is in their ability to ask and answer "What if . . ." questions. Finally, the reader should be able to describe the shrinking core model and apply it to catalyst regeneration and pharmacokinetics.

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SUMMARY

1. The molar flux of A in a binary mixture of A and B is

$$\mathbf{W}_A = -cD_{AB}\nabla y_A + y_A(\mathbf{W}_A + \mathbf{W}_B) \tag{S11-1}$$

   a. For equimolar counterdiffusion (EMCD) or for dilute concentration of the solute,

$$\mathbf{W}_A = -cD_{AB}\boldsymbol{\nabla} y_A \tag{S11-2}$$

   b. For diffusion through a stagnant gas,

$$\mathbf{W}_A = cD_{AB}\boldsymbol{\nabla}\ln(1 - y_A) \tag{S11-3}$$

   c. For negligible diffusion,

$$\mathbf{W}_A = y_A\mathbf{W} = C_A\mathbf{V} \tag{S11-4}$$

Representative Values
Liquid Phase
Re ~ 5000
Sc ~ 4000
Sh ~ 500
$k_c = 10^{-2}$ m/s
Gas Phase
Re ~ 500
Sc ~ 1
Sh ~ 10
$k_c = 5$ m/s

2. The rate of mass transfer from the bulk fluid to a boundary at concentration C_{As} is

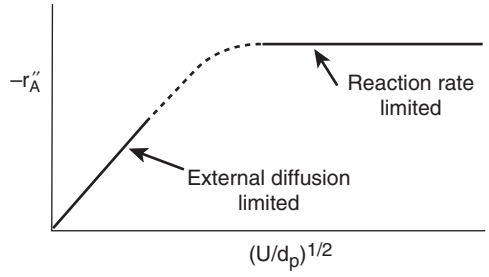
$$W_A = k_c(C_{Ab} - C_{As}) \tag{S11-5}$$

   where k_c is the mass transfer coefficient.
3. The Sherwood and Schmidt numbers are, respectively,

$$\text{Sh} = \frac{k_c d_p}{D_{AB}} \tag{S11-6}$$

$$\text{Sc} = \frac{\nu}{D_{AB}} \tag{S11-7}$$

4. If a heat transfer correlation exists for a given system and geometry, the mass transfer correlation may be found by replacing the Nusselt number by the Sherwood number and the Prandtl number by the Schmidt number in the existing heat transfer correlation.
5. Increasing the gas-phase velocity and decreasing the particle size will increase the overall rate of reaction for reactions that are externally mass transfer–limited.



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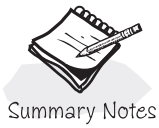
6. The conversion for externally mass transfer–limited reactions can be found from the equation

$$\ln \frac{1}{1-X} = \frac{k_c a_c}{U} L \tag{S11-8}$$

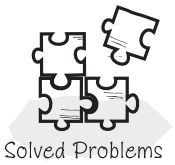
7. Back-of-the-envelope calculations should be carried out to determine the magnitude and direction that changes in process variables will have on conversion. **What if . . .?**
8. The shrinking core model states that the time to regenerate a coked catalyst particle is

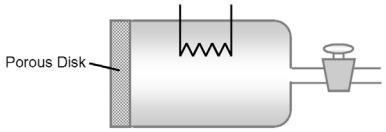
$$t_c = \frac{\rho_C R_0^2 \phi_c}{6 D_e C_{A0}} \tag{S11-9}$$

CD-ROM MATERIAL



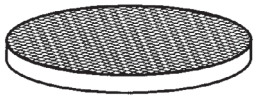
- **Learning Resources**
  1. *Summary Notes*
     Diffusion Through a Stagnant Film
  4. *Solved Problems*
     Example CD11-1 Calculating Steady State Diffusion
     Example CD11-2 Relative Fluxes W_A, B_A, and J_A
     Example CD11-3 Diffusion Through a Stagnant Gas
     Example CD11-4 Measuring Gas-Phase Diffusivities





Example CD11-5 Measuring Liquid-Phase Diffusivities

- **Professional Reference Shelf**
  R11.1. *Mass Transfer-Limited Reactions on Metallic Surfaces*
  A. Catalyst Monoliths
  B. Wire Gauze Reactors



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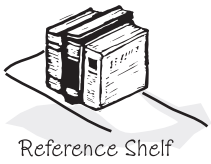
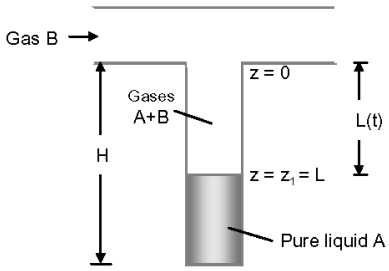
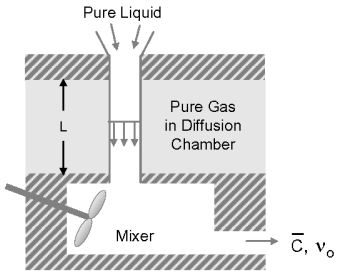


R11.2. *Methods to Experimentally Measure Diffusivities*

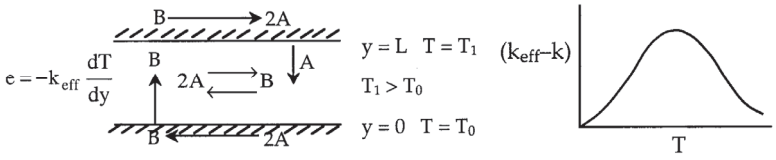


A. Gas-phase diffusivities



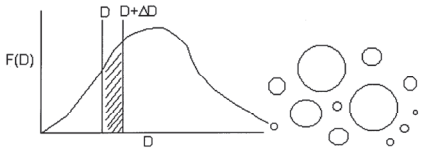
B. Liquid-phase diffusivities

R11.3. *Facilitated Heat Transfer*



Ibuprofen

R11.4. *Dissolution of Polydisperse Solids (e.g., Pills in the stomach)*



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 = ◆◆

P11-1$_A$ Read over the problems at the end of this chapter. Make up an original problem that uses the concepts presented in this chapter. See Problem 4-1$_A$ for the guidelines. To obtain a solution:

(a) Make up your data and reaction.

(b) Use a real reaction and real data.

The journals listed at the end of Chapter 1 may be useful for part (b).

P11-2$_A$ **(a)** **Example 11-1.** Consider the mass transfer–limited reaction

$$A \longrightarrow 2B$$

What would your concentration (mole fraction) profile look like? Using the same values for D_{AB}, and so on, in Example 11-1, what is the flux of A?

(b) **Example 11-2.** How would your answers change if the temperature was increased by 50°C, the particle diameter was doubled, and fluid velocity was cut in half? Assume properties of water can be used for this system.

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(c) **Example 11-3.** How would your answers change if you had a 50–50 mixture of hydrazine and helium? If you increase d_p by a factor of 5?

(d) **Example 11-4**. *What if* you were asked for representative values for Re, Sc, Sh, and k_c for both liquid- and gas-phase systems for a velocity of 10 cm/s and a pipe diameter of 5 cm (or a packed-bed diameter of 0.2 cm)? What numbers would you give?

(e) **Example 11-5**. How would your answers change if the reaction were carried out in the liquid phase where kinematic viscosity varied as

$$v(T_2) = v(T_1)\exp\left[-4000K\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right]?$$

(f) **Side Note**. Derive equations (1) to (3) on page 772. Next consider there are no gradients inside the patch and that the equilibrium solubility in the skin immediately adjacent to the skin is $C_{A0} = HC_{AP}$ where H is a form of Henry's law constant. Write the flux as a function of H, δ_1, D_{AB1}, D_{AB2}, δ_2, and C_{AP}. Finally carry out a quasi-steady analysis, i.e.,

$$V_P\frac{dC_{AP}}{dt} = -\frac{A_P}{R}C_{AP}$$

to predict the drug delivery as a function of time. Compare this result with that where the drug in the patch is in a dissolving solid and a hydro-gel and therefore constant with time. Explore this problem using different models and parameter values.

Additional information

$H = 0.1$, $D_{AB1} = 10^{-6}$ cm^2/s, $D_{AB2} = 10^{-5}$ cm^2/s, $A_p = 5$ cm^2, $V = 1$ cm^3 and $C_{AP} = 10$ mg/dm^3

P11-3$_B$ Pure oxygen is being absorbed by xylene in a catalyzed reaction in the experimental apparatus sketched in Figure P11-3$_B$. Under constant conditions of temperature and liquid composition the following data were obtained:

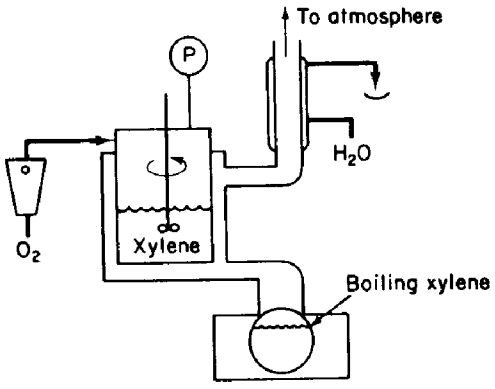

Figure P11-3$_B$

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Stirrer Speed (rpm)	*Rate of Uptake of* O_2 (mL/h) *for System Pressure* (absolute)			
	1.2 atm	1.6 atm	2.0 atm	3.0 atm
400	15	31	75	152
800	20	59	102	205
1200	21	62	105	208
1600	21	61	106	207

No gaseous products were formed by the chemical reaction. What would you conclude about the relative importance of liquid-phase diffusion and about the order of the kinetics of this reaction? **(California Professional Engineers Exam)**

P11-4$_C$ In a diving-chamber experiment, a human subject breathed a mixture of O_2 and He while small areas of his skin were exposed to nitrogen gas. After awhile the exposed areas became blotchy, with small blisters forming on the skin. Model the skin as consisting of two adjacent layers, one of thickness δ_1 and the other of δ_2. If counterdiffusion of He out through the skin occurs at the same time as N_2 diffuses into the skin, at what point in the skin layers is the sum of the partial pressures a maximum? If the saturation partial pressure for the sum of the gases is 101 kPa, can the blisters be a result of the sum of the gas partial pressures exceeding the saturation partial pressure and the gas coming out of the solution (i.e., the skin)?

Before answering any of these questions, derive the concentration profiles for N_2 and He in the skin layers. Hint: See Side Note.

Diffusivity of He and N_2 in the inner skin layer

$= 5 \times 10^{-7}$ cm^2/s and 1.5×10^{-7} cm^2/s, respectively

Diffusivity of He and N_2 in the outer skin layer

$= 10^{-5}$ cm^2/s and 3.3×10^{-4} cm^2/s, respectively

	External Skin Boundary Partial Pressure	*Internal Skin Boundary Partial Pressure*
N_2	101 kPa	0
He	0	81 kPa
δ_1	20 μm	Stratum corneum
δ_2	80 μm	Epidermis

Green engineering

P11-5$_B$ The decomposition of cyclohexane to benzene and hydrogen is mass transfer–limited at high temperatures. The reaction is carried out in a 5-cm-ID pipe 20 m in length packed with cylindrical pellets 0.5 cm in diameter and 0.5 cm in length. The pellets are coated with the catalyst only on the outside. The bed porosity is 40%. The entering volumetric flow rate is 60 dm^3/min.

(a) Calculate the number of pipes necessary to achieve 99.9% conversion of cyclohexane from an entering gas stream of 5% cyclohexane and 95% H_2 at 2 atm and 500°C.

(b) Plot conversion as a function of length.

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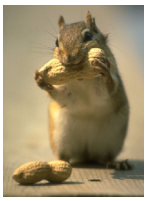
(c) How much would your answer change if the pellet diameter and length were each cut in half?

(d) How would your answer to part (a) change if the feed were pure cyclohexane?

(e) What do you believe is the point of this problem?



P11-6$_B$ Assume the minimum respiration rate of a chipmunk is 1.5 micromoles of O_2/min. The corresponding volumetric rate of gas intake is 0.05 dm^3/min at STP.

(a) What is the deepest a chipmunk can burrow a 3-cm diameter hole beneath the surface in Ann Arbor, Michigan? $D_{AB} = 1.8 \times 10^{-5}$ m/s

(b) In Boulder, Colorado?

(c) How would your answers to (a) and (b) change in the dead of winter when $T = 0$°F?

(d) Critique and extend this problem (e.g., CO_2 poisoning).

P11-7$_C$ Carbon disulfide (A) is evaporating into air (B) at 35°C ($P_{v.p.c.} = 510$ mm Hg) and 1 atm from the bottom of a 1.0 cm diameter vertical tube. The distance from the CS_2 surface to the open end is 20.0 cm, and this is held constant by continuous addition of liquid CS_2 from below. The experiment is arranged so that the vapor concentration of CS_2 at the open end is zero.

(a) Calculate the molecular diffusivity of CS_2 in air (D_{ca}) and its vapor pressure at 35°C. (*Ans.:* $D_{AB} = 0.12$ cm^2/s.)

(b) Find the molar and mass fluxes (W_{Az} and n_c of CS_2) in the tube.

(c) Calculate the following properties at 0.0, 5.0, 10.0, 15.0, 18.0, and 20.0 cm from the CS_2 surface. Arrange columns in the following order on one sheet of paper. (Additional columns may be included for computational purposes if desired.) On a separate sheet give the relations used to obtain each quantity. Try to put each relation into a form involving the minimum computation and the highest accuracy:

(1) y_A and y_B (mole fractions), C_A

(2) V_A, V_B, V*, V (mass velocity)

(3) J_A, J_B

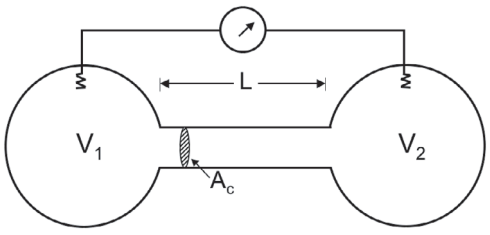
(d) Plot each of the groups of quantities in **(c)(1)**, **(2)**, and **(3)** on separate graphs. Name all variables and show units. Do *not* plot those parameters in parentheses.

(e) What is the rate of evaporation of CS_2 in cm/day?

(f) Discuss the physical meaning of the value of V_A and J_A at the open end of the tube.

(g) Is *molecular* diffusion of air taking place?

P11-8$_B$ A device for measuring the diffusion coefficient of a gas mixture (Figure P11-8$_B$) consists of two chambers connected by a small tube. Initially the chambers contain different proportions of two gases, A and B. The total pressure is the same in each chamber.



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(a) Assuming that diffusion may be described by Fick's law, that the concentration in each flask is uniform, and that the concentration gradient in the *tube* is linear show that

$$\ln(C_{A1} - C_{A2}) = \frac{D_{AB}A_C}{L}\left(\frac{1}{V_1} + \frac{1}{V_2}\right)t + \text{constant}$$

State any other assumptions needed.

(b) B. G. Bray (Ph.D. Thesis, University of Michigan, 1960) used a similar device. The concentration of hydrogen in hydrogen-argon mixtures was determined from measurements of an ionizing current in each chamber. The ionizing current is proportional to concentration. The difference in ionizing currents between chambers one and two is measured (ΔIC). Compute the diffusion coefficient, D_{AB}, for the following data.
769 psia, $T = 35^{\circ}C$, $C_T = 2.033$ mol/dm^3, cell constant,

$$\frac{A_C}{L}\left(\frac{1}{V_1} + \frac{1}{V_2}\right) = 0.01025 \text{ cm}^{-2}$$

Time, min	10	20	33	50	66	83	100	117	133
ΔIC	36.60	32.82	28.46	23.75	19.83	16.60	13.89	11.67	9.79

P11-9$_A$ A spherical particle is dissolving in a liquid. The rate of dissolution is first order in the solvent concentration, C. Assuming that the solvent is in excess, show that the following conversion time relationships hold.

Rate-Limiting Regime	*Conversion-Time Relationship*
Surface reaction	$1 - (1 - X)^{1/3} = \frac{\alpha t}{D_i}$
Mass transfer	$\frac{D_i}{2D^*}[1 - (1 - X)^{2/3}] = \frac{\alpha t}{D_i}$
Mixed	$[1 - (1 - X)^{1/3}] + \frac{D_i}{2D^*}[1 - (1 - X)^{2/3}] = \frac{\alpha t}{D_i}$

P11-10$_C$ A powder is to be completely dissolved in an aqueous solution in a large, well-mixed tank. An acid must be added to the solution to render the spherical particle soluble. The particles are sufficiently small that they are unaffected by fluid velocity effects in the tank. For the case of excess acid, $C_0 = 2\ M$, derive an equation for the diameter of the particle as a function of time when

(a) Mass transfer limits the dissolution: $-W_A = k_c C_{A0}$

(b) Reaction limits the dissolution: $-r''_A = k_r C_{A0}$

What is the time for complete dissolution in each case?

(c) Now assume that the acid is not in excess and that mass transfer is limiting the dissolution. One mole of acid is required to dissolve 1 mol of solid. The molar concentration of acid is 0.1 M, the tank is 100 L, and 9.8 mol of solid is added to the tank at time $t = 0$. Derive an expression

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for the radius of the particles as a function of time and calculate the time for the particles to dissolve completely.

(d) How could you make the powder dissolve faster? Slower?

Additional information:

$$D_e = 10^{-10}\ \text{m}^2/\text{s}, \qquad k = 10^{-18}/\text{s}$$

$$\text{initial diameter} = 10^{-5}\ \text{m}$$

P11-11$_B$ The irreversible gas-phase reaction

$$\text{A} \xrightarrow{\text{catalyst}} \text{B}$$

is carried out adiabatically over a packed bed of solid catalyst particles. The reaction is first order in the concentration of A on the catalyst surface:

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

The feed consists of 50% (mole) A and 50% inerts and enters the bed at a temperature of 300 K. The entering volumetric flow rate is 10 dm^3/s (i.e., 10,000 cm^3/s). The relationship between the Sherwood number and the Reynolds number is

$$\text{Sh} = 100\,\text{Re}^{1/2}$$

As a first approximation, one may neglect pressure drop. The entering concentration of A is 1.0 *M*. Calculate the catalyst weight necessary to achieve 60% conversion of A for

(a) Isothermal operation.

(b) Adiabatic operation.

(c) What generalizations can you make after comparing parts **(a)** and **(b)**?

Additional information:

Kinematic viscosity: $\mu/\rho = 0.02\ \text{cm}^2/\text{s}$
Particle diameter: $d_p = 0.1\ \text{cm}$
Superficial velocity: $U = 10\ \text{cm/s}$
Catalyst surface area/mass of catalyst bed: $a = 60\ \text{cm}^2/\text{g cat.}$
Diffusivity of A: $D_e = 10^{-2}\ \text{cm}^2/\text{s}$
Heat of reaction: $\Delta H^\circ_{\text{Rx}} = -10{,}000\ \text{cal/g mol A}$
Heat capacities:

$$C_{p\text{A}} = C_{p\text{B}} = 25\ \text{cal/g mol}\cdot\text{K}$$

$$C_{p\text{S}}\ (\text{solvent}) = 75\ \text{cal/g mol}\cdot\text{K}$$

$$k'\ (300\ \text{K}) = 0.01\ \text{cm}^3/\text{s}\cdot\text{g cat with } E = 4000\ \text{cal/mol}$$

P11-12$_C$ (*Pills*) An antibiotic drug is contained in a solid inner core and is surrounded by an outer coating that makes it palatable. The outer coating and the drug are dissolved at different rates in the stomach, owing to their differences in equilibrium solubilities.

(a) If $D_2 = 4$ mm and $D_1 = 3$ mm, calculate the time necessary for the pill to dissolve completely.

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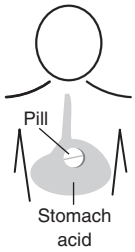

(b) Assuming first-order kinetics ($k_A = 10\ h^{-1}$) for the absorption of the dissolved drug (i.e., in solution in the stomach) into the bloodstream, plot the concentration in grams of the drug in the blood per gram of body weight as a function of time when the following three pills are taken simultaneously:

Pill 1: $D_2 = 5$ mm, $D_1 = 3$ mm

Pill 2: $D_2 = 4$ mm, $D_1 = 3$ mm

Pill 3: $D_2 = 3.5$ mm, $D_1 = 3$ mm

(c) Discuss how you would maintain the drug level in the blood at a constant level using different-size pills?

(d) How could you arrange a distribution of pill sizes so that the concentration in the blood was constant over a period (e.g., 3 hr) of time?

Additional information:

Amount of drug in inner core = 500 mg
Solubility of outer layer at stomach conditions = 1.0 mg/cm^3
Solubility of inner layer at stomach conditions = 0.4 mg/cm^3
Volume of fluid in stomach = 1.2 L
Typical body weight = 75 kg
Sh = 2, $D_{AB} = 6 \times 10^{-4}$ cm^2/min

Green engineering

P11-13$_B$ If disposal of industrial liquid wastes by incineration is to be a feasible process, it is important that the toxic chemicals be completely decomposed into harmless substances. One study carried out concerned the atomization and burning of a liquid stream of "principal" organic hazardous constituents (POHCs) [*Environ. Prog.*, *8*, 152 (1989)]. The following data give the burning droplet diameter as a function of time (both diameter and time are given in arbitrary units):

Time	20	40	50	70	90	110
Diameter	9.7	8.8	8.4	7.1	5.6	4.0

What can you learn from these data?

P11-14$_B$ (*Estimating glacial ages*) The following oxygen-18 data were obtained from soil samples taken at different depths in Ontario, Canada. Assuming that all the ^{18}O was laid down during the last glacial age and that the transport of ^{18}O to the surface takes place by molecular diffusion, estimate the number of years since the last glacial age from the following data. Independent measurements give the diffusivity of ^{18}O in soil as 2.64×10^{-10} m^2/s.

Figure P11-14 Glaciers.

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	(surface)					
Depth (m)	0	3	6	9	12	18
^{18}O *Conc. Ratio* (C/C_0)	0	0.35	0.65	0.83	0.94	1.0

C_0 is the concentration of ^{18}O at 25 m.

JOURNAL ARTICLE PROBLEM

P11J-1 After reading the article "Designing gas-sparged vessels for mass transfer" [*Chem. Eng.*, *89*(24), p. 61 (1982)], design a gas-sparged vessel to saturate 0.6 m^3/s of water up to an oxygen content of 4×10^{-3} kg/m^3 at 20°C. A liquid holding time of 80 s is required.

JOURNAL CRITIQUE PROBLEMS

P11C-1 The decomposition of nitric oxide on a heated platinum wire is discussed in *Chem. Eng. Sci.*, *30*, 781 (1975). After making some assumptions about the density and the temperatures of the wire and atmosphere, and using a correlation for convective heat transfer, determine if mass transfer limitations are a problem in this reaction.

P11C-2 Given the proposed rate equation on page 296 of the article in *Ind. Eng. Chem. Process Des. Dev.*, *19*, 294 (1980), determine whether or not the concentration dependence on sulfur, C_s, is really second-order. Also, determine if the intrinsic kinetic rate constant, K_{2p}, is indeed only a function of temperature and partial pressure of oxygen and not of some other variables as well.

P11C-3 Read through the article on the oxidation kinetics of oil shale char in *Ind. Eng. Chem. Process Des. Dev.*, *18*, 661 (1979). Are the units for the mass transfer coefficient k_m in Equation (6) consistent with the rate law? Is the mass transfer coefficient dependent on sample size? Would the shrinking core model fit the authors' data as well as the model proposed by the authors?

- **Additional Homework Problems**

CDP11-A_A An isomerization reaction that follows Langmuir–Hinshelwood kinetics is carried out on a monolith catalyst. [2nd Ed. P10-11]

CDP11-B_B A parameter sensitivity analysis is required for this problem in which an isomerization is carried out over a 20-mesh gauze screen. [2nd Ed. P10-12]

CDP11-C_C This problem examines the effect of temperature in a catalyst monolith. [2nd Ed. P10-13]

CDP11-D_D A second-order catalytic reaction is carried out in a catalyst monolith. [2nd Ed. P10-14]

CDP11-E_C Fracture acidizing is a technique to increase the productivity of oil wells. Here acid is injected at high pressures to fracture the rock and form a channel that extends out from the well bore. As the acid flows through the channel it etches the sides of the channel to make it larger and thus less resistant to the flow of oil. Derive an equation for the

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concentration profile of acid and the channel width as a function of distance from the well bore.

CDP11-F_C The solid–gas reaction of silicon to form SiO_2 is an important process in microelectronics fabrication. The oxidation occurs at the Si–SiO_2 interface. Derive an equation for the thickness of the SiO_2 layer as a function of time. [2nd Ed. P10-17]

CDP11-G_B Mass transfer limitations in CVD processing to produce material with ferroelectric and piezoelectric properties. [2nd Ed. P10-17]

CDP11-H_B Calculate multicomponent diffusivities. [2nd Ed. P10-9]

CDP11-I_B Application of the shrinking core model to FeS_2 rock samples in acid mine drainage. [2nd Ed. P10-18]

CDP11-J_B Removal of chlorine by adsorption from a packed bed reactor: Vary system parameters to predict their effect on the conversion. [3rd Ed. P11-5_B]

CDP11-K_B The reversible reaction A $\rightleftharpoons$ B is carried out in a PBR. The rate law is

$$-r'_A = k_A \frac{\left(C_A - \frac{1}{K_C}C_B\right)}{\left(1 + \frac{k_A}{k_B K_C}\right)}$$

Green Engineering Problem

[3rd Ed. P11-6_B]

CDP11-L_B Oxidation of ammonia over wire screens. [3rd Ed. P11-7_B]

CDP11-M_B Sgt. Ambercromby on the scene again to investigate foul play. [3rd Ed. P11-13_B]

CDP11-N_B Additional Green Engineering problems can be found on the web at *www.rowan.edu/greenengineering*.

SUPPLEMENTARY READING

1. The fundamentals of diffusional mass transfer can be found in

BIRD, R. B., W. E. STEWART, and E. N. LIGHTFOOT, *Transport Phenomena*, 2nd ed. New York: Wiley, 2002, Chaps. 17 and 18.

CUSSLER, E. L., *Diffusion Mass Transfer in Fluid Systems*, 2nd ed. New York: Cambridge University Press, 1997.

FAHIEN, R. W., *Fundamentals of Transport Phenomena*. New York: McGraw-Hill, 1983, Chap. 7.

GEANKOPLIS, C. J., *Transport Processes and Unit Operations*. Upper Saddle River, N.J.: Prentice Hall, 2003.

HINES, A. L., and R. N. MADDOX, *Mass Transfer: Fundamentals and Applications*. Upper Saddle River, N.J.: Prentice Hall, 1984.

LEVICH, V. G., *Physiochemical Hydrodynamics*. Upper Saddle River, N.J.: Prentice Hall, 1962, Chaps. 1 and 4.

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2. Equations for predicting gas diffusivities are given in Appendix D. Experimental values of the diffusivity can be found in a number of sources, two of which are

PERRY, R. H., D. W. GREEN, and J. O. MALONEY, *Chemical Engineers' Handbook*, 7th ed. New York: McGraw-Hill, 1997.

SHERWOOD, T. K., R. L. PIGFORD, and C. R. WILKE, *Mass Transfer*. New York: McGraw-Hill, 1975.

3. A number of correlations for the mass transfer coefficient can be found in

LYDERSEN, A. L., *Mass Transfer in Engineering Practice*. New York: Wiley-Interscience, 1983, Chap. 1.

MCCABE, W. L., J. C. SMITH, and P. HARRIOTT, *Unit Operations of Chemical Engineering*, 6th ed. New York: McGraw-Hill, 2000, Chap. 17.

TREYBAL, R. E., *Mass Transfer Operations*, 3rd ed. New York: McGraw-Hill, 1980.