Radial and Axial Temperature Variations in a Tubular Reactor

Overview. Up to now we neglected gradients in radial concentration, reaction rate and temperature in tubular reactors. This chapter introduces the analysis of reactors with both axial and radial gradients.

- We first discuss diffusion fundamentals in order to develop Partial Differential Equations (PDEs) for the mole balance.
- We next develop the PDE for the energy balance.
- We next solve this set of coupled PDEs numerically.

The solutions to these equations bring us to a secondary goal of this chapter: to introduce the use of computational fluid dynamics (CFD) software to solve CRE problems. We have chosen to use the software program COMSOL to solve PDEs for the concentration and temperature profiles.

15.1 Diffusion Fundamentals

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.

15.1.1 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), \( W_A \) (moles/area·time), in the direction of the concentration gradient. The flux of A, \( W_A \), 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

\[
W_A = iW_{Ax} + jW_{Ay} + kW_{Az} \tag{15-1}
\]

where \( i, j, \) and \( k \) are the coordinate vectors in a Cartesian coordinate system. We now apply the mole balance to species A, which flows and reacts in an element of volume \( \Delta V = \Delta x\Delta y\Delta z \), shown in Figure 15-1, to obtain the variation of the molar fluxes in three dimensions.

![Figure 15-1](Mole balance on a cubical element of volume \( \Delta x\Delta y\Delta z \).)

\[
F_{Az} = W_{Az} \Delta x \Delta y, \quad F_{Ay} = W_{Ay} \Delta x \Delta z, \quad F_{Ax} = W_{Ax} \Delta z \Delta y
\]

Mole Balance

\[
\begin{bmatrix}
\text{Molar flow rate} \\
\text{in} \ z
\end{bmatrix}_{\Delta z} - \begin{bmatrix}
\text{Molar flow rate} \\
\text{out} \ z + \Delta z
\end{bmatrix}_{\Delta z} + \begin{bmatrix}
\text{Molar flow rate} \\
\text{in} \ y
\end{bmatrix}_{\Delta y} - \begin{bmatrix}
\text{Molar flow rate} \\
\text{out} \ y + \Delta y
\end{bmatrix}_{\Delta y}
\]

\[
\Delta x \Delta y W_{Az} \mid z - \Delta x \Delta y W_{Az} \mid z + \Delta z + \Delta x \Delta z W_{Ay} \mid y - \Delta x \Delta z W_{Ay} \mid y + \Delta y
\]
Sec. 15.1 Diffusion Fundamentals

Moving by \( D_x \), \( D_y \), and \( D_z \) and taking the limit as \( D_x \), \( D_y \), and \( D_z \) go to zero, we obtain the molar flux balance in rectangular coordinates

\[
\begin{align*}
&\frac{\partial W_{Ax}}{\partial x} - \frac{\partial W_{Ay}}{\partial y} - \frac{\partial W_{Az}}{\partial z} + r_A = \frac{\partial C_A}{\partial t} \\
&+ \Delta z \Delta y W_{Ax} \mid_x - \Delta z \Delta y W_{Ax} \mid_{x+\Delta x} + r_A \Delta x \Delta y \Delta z = \Delta x \Delta y \Delta z \frac{\partial C_A}{\partial t}
\end{align*}
\]

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

\[
- \frac{\partial W_{Ax}}{\partial x} - \frac{\partial W_{Ay}}{\partial y} - \frac{\partial W_{Az}}{\partial z} + r_A = \frac{\partial C_A}{\partial t}
\]

(15-2)

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

\[
- \frac{1}{r} \frac{\partial}{\partial r}(r W_A) - \frac{\partial W_{Az}}{\partial z} + r_A = \frac{\partial C_A}{\partial t}
\]

(15-3)

We will now evaluate the flux terms \( W_A \). 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.

15.1.2 Molar Flux

The molar flux of \( A \), \( W_A \), is the result of two contributions: \( J_A \), the molecular diffusion flux relative to the bulk motion of the fluid produced by a concentration gradient, and \( B_A \), the flux resulting from the bulk motion of the fluid:

\[
W_A = J_A + B_A
\]

(15-4)

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., \( B_A = y_A \sum W_i \).

The bulk flow term \( B_A \) can also be expressed in terms of the concentration of \( A \) and the molar average velocity \( V \):

\[
B_A = C_A V
\]

(15-5)

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

where the molar average velocity is

\[
V = \sum y_i V_i
\]

Here \( V \) 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 $V_A$ and $V_B$ 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), $W_A$, is just the product of the concentration of A and the particle velocity of A:

$$W_A = C_A V_A$$ (15-6)

The molar average velocity for a binary system is

$$V = y_A V_A + y_B V_B$$ (15-7)

The total molar flux of A is given by Equation (15-4). $B_A$ can be expressed either in terms of the concentration of A, in which case

$$W_A = J_A + C_A V$$ (15-8)

or in terms of the mole fraction of A:

$$W_A = J_A + y_A (W_A + W_B)$$ (15-9)

We now need to evaluate the molar flux of A, $J_A$, that is superimposed on the molar average velocity $V$.

### 15.1.3 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., $J_A$) is related to its concentration gradient. As an aid in the discussion of the transport law used to describe diffusion, recall similar laws from other transport processes. For example, in conductive heat transfer the constitutive equation relating the heat flux $q$ and the temperature gradient is Fourier’s law:

$$q = -k_i \nabla T$$ (15-10)

where $k_i$ is the thermal conductivity.

In rectangular coordinates, the gradient is in the form

$$\nabla = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z}$$

The one-dimensional form of Equation (15-10) is

$$q_z = -k_i \frac{dT}{dz}$$ (15-11)

In momentum transfer, the constitutive relationship between shear stress, $\tau$, and shear rate for simple planar shear flow is given by Newton’s law of viscosity:
Sec. 15.1 Diffusion Fundamentals

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

\[ J_{Az} = -D_{AB} \frac{dC_A}{dz} \] (15-12)

The general 3-dimensional constitutive equation for \( J_A \), the diffusional flux of \( A \) resulting from a concentration difference, is related to the mole fraction gradient by Fick’s first law:

\[ J_A = -cD_{AB} \nabla y_A \] (15-13)

where \( c \) is the total molar 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 (15-9) and (15-13), we obtain an expression for the total molar flux of \( A \):

\[ W_A = -cD_{AB} \nabla y_A + y_A(W_A + W_B) \] (15-14)

In terms of concentration for constant total concentration

\[ W_A = -D_{AB} \nabla C_A + C_AV \] (15-15)

### 15.1.4 Diffusion and Convective Transport.

When accounting for diffusional effects, the molar flow rate of species \( A \), \( F_{Az} \), 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

\[ F_{Az} = W_{Az} A_c = \left[ -D_{AB} \frac{dC_A}{dz} + C_A U_z \right] A_c \] (15-15A)

Similar expressions follow for \( W_{Ax} \) and \( W_{Ay} \). Substituting for the flux \( W_{Ax} \), \( W_{Ay} \), and \( W_{Az} \) into Equation (15-2), we obtain

\[ D_{AB} \left[ \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right] - U_x \frac{\partial C_A}{\partial x} - U_y \frac{\partial C_A}{\partial y} - U_z \frac{\partial C_A}{\partial z} + r_A = \frac{\partial C_A}{\partial t} \] (15-16)
COMSOL  Equation (15-16) is in a user-friendly form directly applicable to the PDE solver, COMSOL. For one-dimension at steady state, Equation (15-16) reduces to

\[
D_{AB} \frac{d^2 C_A}{dz^2} = U_z \frac{dC_A}{dz} + r_A = 0
\]  

In order to solve Equation (15-17) we need to specify the boundary conditions. In this chapter we consider some of the simpler boundary conditions, and in Chapter CD14 on the CD-ROM we 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 (see Chapter 1)

\[
\frac{dF_{Az}}{dV} = r_A
\]  

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

15.1.5 Boundary Conditions

The most common boundary conditions are presented in Table 15-1.

<table>
<thead>
<tr>
<th>TABLE 15-1.  TYPES OF BOUNDARY CONDITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Specify a concentration at a boundary (e.g., z = 0, ( C_A = C_{A0} )). For an instantaneous reaction at a boundary surface, the concentration of the reactants at the boundary is taken to be zero (e.g., ( C_{A1} = 0 )). See CD-ROM Chapter CD14 for the more exact and complicated Danckwerts’ boundary conditions at ( z = 0 ) and ( z = L ).</td>
</tr>
<tr>
<td>2. Specify a flux at a boundary.</td>
</tr>
<tr>
<td>a. No mass transfer to a boundary,</td>
</tr>
<tr>
<td>( W_{A</td>
</tr>
<tr>
<td>For example, at the wall of a nonreacting pipe,</td>
</tr>
<tr>
<td>( \frac{dC_A}{dr} = 0 ) at ( r = R )</td>
</tr>
<tr>
<td>That is, because the diffusivity is finite, the only way the flux can be zero is if the concentration gradient is zero.</td>
</tr>
<tr>
<td>b. Set the molar flux to the surface equal to the rate of reaction on the surface,</td>
</tr>
<tr>
<td>( W_A(\text{surface}) = -r_A(\text{surface}) )</td>
</tr>
<tr>
<td>c. Set the molar flux to the boundary equal to convective transport across a boundary layer,</td>
</tr>
<tr>
<td>( W_A(\text{boundary}) = k_c(C_{Ab} - C_{As}) )</td>
</tr>
<tr>
<td>3. Planes of symmetry. When the concentration profile is symmetrical about a plane, the concentration gradient is zero at the plane of symmetry. For example, in the case of radial diffusion in a pipe, at the center of the pipe</td>
</tr>
<tr>
<td>( \frac{dC_A}{dr} = 0 ) at ( r = 0 )</td>
</tr>
</tbody>
</table>

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15.2 Radial and Axial Variations in a Tubular Reactor

In the previous chapters we have assumed that there were no radial variations in velocity, concentration, temperature, or reaction rate in the tubular and packed-bed reactors. As a result, the axial profiles could be determined using an ordinary differential equation (ODE) solver. In this section we will consider the case where we have both axial and radial variations in the system variables, in which case we will require a partial differential (PDE) solver. A PDE solver such as COMSOL will allow us to solve tubular reactor problems for both the axial and radial profiles, as shown here and on the Web module.

Fogler [2006, p. 15-7]

Go to the COMSOL Web site http://www.comsol.com/ecre to see the tutorial and chemical reaction engineering examples.

We are going to carry out differential mole and energy balances on the differential cylindrical annulus shown in Figure 15-2.

15.2.1 Molar Flux in Radial Coordinates

In order to derive the governing equations, we need to define a couple of terms. The first is the molar flux of species \( i \), \( W_i \) (mol/m² • s). The molar flux has two components, the radial component \( W_{ir} \), and the axial component, \( W_{iz} \). The molar flow rates are just the product of the molar fluxes and the cross-sectional areas normal to their direction of flow. For example, for species \( i \) flowing in the axial (i.e., \( z \)) direction

\[
F_{iz} = W_{iz} A_{cz}
\]

where \( W_{iz} \) is the molar flux in the \( z \) direction (mol/m²/s), and \( A_{cz} \) (m²) is the cross-sectional area of the tubular reactor.

In Chapter CD11 on the CD-ROM we discuss the molar fluxes in some detail, but for now let us just say they consist of a diffusional component, \(-D_e \frac{\partial C_i}{\partial z}\), and a convective flow component, \( U_z C_i \)

\[
W_{iz} = -D_e \frac{\partial C_i}{\partial z} + U_z C_i
\] (15-21)
where \( D_e \) is the effective diffusivity (or dispersion coefficient) (m\(^2\)/s), and \( U_z \) is the axial molar average velocity (m/s). Similarly, the flux in the radial direction is

\[
W_{ir} = -D_e \frac{\partial C_i}{\partial r} + U_r C_i \tag{15-22}
\]

where \( U_r \) (m/s) is the average velocity in the radial direction. For now we will neglect the velocity in the radial direction, i.e., \( U_r = 0 \).

### 15.2.2 Mole Balances on Species A

A mole balance on a cylindrical system volume of length \( \Delta z \) and thickness \( \Delta r \) as shown in Figure 14-2 gives

\[
\begin{align*}
\text{Moles of A in at } r & \quad = W_{Ar} \cdot \left( \text{Cross-sectional area normal to radial flux} \right) = W_{Ar} \cdot 2\pi r \Delta z \\
\text{Moles of A in at } z & \quad = W_{Az} \cdot \left( \text{Cross-sectional area normal to axial flux} \right) = W_{Az} \cdot 2\pi r \Delta r
\end{align*}
\]

\[
\begin{align*}
\text{Moles of A in at } r & \quad - \text{Moles of A out at } (r + \Delta r) + \text{Moles of A in at } z & \quad - \text{Moles of A out at } (z + \Delta z) \\
& \quad + \text{Moles of A formed} & \quad = \text{Moles of A Accumulated}
\end{align*}
\]

\[
W_{Ar} 2\pi r \Delta z \bigg|_r - W_{Ar} 2\pi r \Delta z \bigg|_{r + \Delta r} + W_{Az} 2\pi r \Delta r \bigg|_z - W_{Az} 2\pi r \Delta r \bigg|_{z + \Delta z} + r_A 2\pi r \Delta r \Delta z = \frac{\partial C_A(2\pi r \Delta r \Delta z)}{\partial t}
\]

Dividing by \( 2\pi r \Delta r \Delta z \) and taking the limit as \( \Delta r \) and \( \Delta z \to 0 \)

\[
- \frac{1}{r} \frac{\partial (r W_{Ar})}{\partial r} - \frac{\partial W_{Az}}{\partial z} + r_A = \frac{\partial C_A}{\partial t}
\]

Similarly, for any species \( i \) and steady-state conditions,

\[
- \frac{1}{r} \frac{\partial (r W_{ir})}{\partial r} - \frac{\partial W_{iz}}{\partial z} + r_i = 0 \tag{15-23}
\]

Using Equations (15-21) and (15-22) to substitute for \( W_{iz} \) and \( W_{ir} \) in Equation (15-23) and then setting the radial velocity to zero, \( U_r = 0 \), we obtain

\[
- \frac{1}{r} \frac{\partial}{\partial r} \left[ \left( -D_e \frac{\partial C_i}{\partial r} r \right) \right] - \frac{\partial}{\partial z} \left[ -D_e \frac{\partial C_i}{\partial z} + U_z C_i \right] + r_i = 0
\]
For steady-state conditions and assuming \( U_z \) does not vary in the axial direction,

\[
D_e \frac{\partial^2 C_i}{\partial r^2} + \frac{D_i \partial C_i}{r \partial r} + D_e \frac{\partial^2 C_i}{\partial z^2} - U_z \frac{\partial C_i}{\partial z} + r_i = 0
\]  
(15-24)

This equation is also discussed further in Chapter CD14.

### 15.3 Energy Flux

When we applied the first law of thermodynamics to a reactor to relate either temperature and conversion or molar flow rates and concentration, we arrived at Equation (11-9). Neglecting the work term we have for steady-state conditions

\[
\widetilde{\dot{Q}} + \sum_{i=1}^{m} F_{i0} H_{i0} - \sum_{i=1}^{m} F_i H_i = 0
\]

(15-25)

In terms of the molar fluxes and the cross-sectional area and \( (q = \dot{Q}/A_c) \)

\[\begin{align*}
A_c [q + (\Sigma W_{i0} H_{i0} - \Sigma W_i H_i)] &= 0
\end{align*}\]

(15-26)

The \( q \) term is the heat added to the system and almost always includes a conduction component of some form. We now define an **energy flux vector**, \( \mathbf{e} \), \((\text{J/m}^2 \cdot \text{s})\), to include both the conduction and convection of energy.

\[\mathbf{e} = \text{Conduction} + \text{Convection} \]

\[
\mathbf{e} = q + \Sigma W_i H_i
\]

(15-27)

where the conduction term \( q \) \((\text{J/m}^2 \cdot \text{s})\) is given by Fourier’s law. For axial \((z)\) and radial \((r)\) conduction Fourier’s laws are

\[
q_z = -k_e \frac{\partial T}{\partial z} \quad \text{and} \quad q_r = -k_e \frac{\partial T}{\partial r}
\]

where \( k_e \) is the thermal conductivity \((\text{J/m} \cdot \text{s} \cdot \text{K})\). The energy transfer (flow) is the vector flux times the cross-sectional area, \( A_c \), normal to the energy flux

\[
\text{Energy flow} = \mathbf{e} \cdot A_c
\]

### 15.3.1 Energy Balance

Using the energy flux, \( e \), to carry out an energy balance on our annulus (Figure 15-2) with system volume \( 2\pi r \Delta r \Delta z \), we have

\[
\text{(Energy flow in at } r) = e_r A_{cr} = e_r \cdot 2\pi r \Delta z
\]

\[
\text{(Energy flow in at } z) = e_z A_{cz} = e_z \cdot 2\pi r \Delta r
\]
\[
\left( \text{Energy Flow} \right)_{\text{in at } r} - \left( \text{Energy Flow} \right)_{\text{out at } r + \Delta r} + \left( \text{Energy Flow} \right)_{\text{in at } z} - \left( \text{Energy Flow} \right)_{\text{out at } z + \Delta z} = \left( \text{Accumulation of Energy in Volume} \right) (2\pi r \Delta r \Delta z)
\]

\[
(e_r 2\pi r \Delta z)_{r + \Delta r} - (e_r 2\pi r \Delta z)_{r} + e_z 2\pi r \Delta r|_{z} - e_z 2\pi r \Delta r|_{z + \Delta z} = 0 \tag{15-28}
\]

Dividing by \(2\pi r \Delta r \Delta z\) and taking the limit as \(\Delta r \) and \(\Delta z \to 0\),

\[
- \frac{1}{r} \frac{\partial (r e_r)}{\partial r} - \frac{\partial e_z}{\partial z} = 0 \tag{15-29}
\]

The radial and axial energy fluxes are

\[
e_r = q_r + \sum W_{ir} H_i
\]

\[
e_z = q_z + \sum W_{iz} H_i
\]

Substituting for the energy fluxes, \(e_r\) and \(e_z\),

\[
- \frac{1}{r} \frac{\partial [r(q_r + \sum W_{ir} H_i)]}{\partial r} - \frac{\partial (q_z + \sum W_{iz} H_i)}{\partial z} = 0 \tag{15-30}
\]

and expanding the convective energy fluxes, \(\Sigma W_i H_i\),

Radial:

\[
\frac{1}{r} \frac{\partial (r \Sigma W_{ir} H_i)}{\partial r} = \frac{1}{r} \Sigma H_i \frac{\partial (r W_{ir})}{\partial r} + \Sigma W_{ir} \frac{\partial H_i}{\partial r} \tag{15-31}
\]

Axial:

\[
\frac{\partial (\Sigma W_{iz} H_i)}{\partial z} = \Sigma H_i \frac{\partial W_{iz}}{\partial z} + \Sigma W_{iz} \frac{\partial H_i}{\partial z} \tag{15-32}
\]

Substituting Equations (15-31) and (15-32) into Equation (15-30), we obtain upon rearrangement

\[
- \frac{1}{r} \frac{\partial (rq_r)}{\partial r} - \frac{\partial q_z}{\partial z} - \Sigma H_i \left( \frac{1}{r} \frac{\partial (r W_{ir})}{\partial r} + \frac{\partial W_{iz}}{\partial z} \right) - \Sigma W_{iz} \frac{\partial H_i}{\partial z} = 0
\]

Recognizing that the term in brackets for steady-state conditions is just the rate of formation of species \(i\), \(r_i\), we have

\[
- \frac{1}{r} \frac{\partial (rq_r)}{\partial r} - \frac{\partial q_z}{\partial z} - \Sigma H_i r_i - \Sigma W_{iz} \frac{\partial H_i}{\partial z} = 0 \tag{15-33}
\]

Recalling

\[
q_r = -k_e \frac{\partial T}{\partial r}, \quad q_z = -k_e \frac{\partial T}{\partial z}, \quad \frac{\partial H_i}{\partial z} = C_p \frac{\partial T}{\partial z},
\]
and
\[ r_i = v_i(-r_A) \]
\[ \sum r_i H_i = \Sigma v_i H_i(-r_A) = -\Delta H_{Rx} r_A \]
we have the energy balance in the form
\[
\frac{k_e}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + k_e \frac{\partial^2 T}{\partial z^2} + \Delta H_{Rx} r_A - (\Sigma W_i C_{p_i}) \frac{\partial T}{\partial z} = 0
\]
(15-34)

### 15.4 Some Initial Approximations

**Assumption 1.** Neglect the axial diffusive term [i.e., \(-D_e \frac{\partial C_i}{\partial z}\)] wrt the convective term in the expression involving heat capacities
\[ \Sigma C_{p_i} W_i = \Sigma C_{p_i}(0 + U_z C_i) = \Sigma C_{p_i} C_i U_z \]
With this assumption, Equation (15-34) becomes
\[
\frac{k_e}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{k_e}{r} \frac{\partial^2 T}{\partial z^2} + \Delta H_{Rx} r_A - (U_z \Sigma C_{p_i} C_i) \frac{\partial T}{\partial z} = 0
\]
(15-35)

For laminar flow, the velocity profile is
\[ U_z = 2 U_0 \left[ 1 - \left( \frac{r}{R} \right)^2 \right] \]
(15-36)
where \( U_0 \) is the average velocity inside the reactor and \( R \) is the tabular reactor radius.

**Assumption 2.** Assume that the sum \( C_{p_m} = \Sigma C_{p_i} C_i = C_{A0} \Sigma \theta_i C_{p_i} \) is constant.
The energy balance now becomes
\[
\frac{k_e \partial^2 T}{\partial z^2} + \frac{k_e}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \Delta H_{Rx} r_A - U_z C_{p_m} \frac{\partial T}{\partial z} = 0
\]
(15-37)

Equation (15-36) is the form we will use in the COMSOL problem that follows. In many instances, the term \( C_{p_m} \) is just the product of the solution density and the heat capacity of the solution (J/kg • K).

### 15.5 Heat Exchange Fluid Balance

We also recall that a balance on the coolant gives the variation of coolant temperature with axial distance where \( U_{ht} \) is the overall heat transfer coefficient and \( R \) is the reactor wall radius.
15.6 Boundary and Initial Conditions

A. Initial conditions if other than steady state
\( t = 0, \ C_i = 0, \ T = T_0, \ \text{for } z > 0 \text{ all } r \) (A)

B. Boundary conditions

1) Radial
   (a) At \( r = 0 \), we have symmetry \( \partial T / \partial r = 0 \) and \( \partial C_i / \partial r = 0 \).
   (b) At the tube wall \( r = R \), the temperature flux to the wall on the reaction side equals the convective flux out of the reactor into the shell side of the heat exchanger.
   \[-k_c \frac{\partial T}{\partial r} \bigg|_R = U_h(T(R,z) - T_u) \] (B)
   (c) There is no mass flow through the tube walls
   \[ \partial C_i / \partial r = 0 \text{ at } r = R. \] (C)

2) Axial
   (a) At the entrance to the reactor \( z = 0 \),
   \( T = T_0 \) and \( C_i = C_{i0} \) (D)
   (b) At the exit of the reactor \( z = L \),
   \[ \frac{\partial T}{\partial z} = 0 \text{ and } \frac{\partial C_i}{\partial z} = 0 \] (E)

The following examples will solve the preceding equations using COMSOL. For the exothermic reaction with cooling, the expected profiles are

Example 15-1 Radial Effects in a Tubular Reactor

This example will highlight the radial effects in a tubular reactor, which up until now have been neglected to simplify the calculations. Now, the effects of parameters such as inlet temperature and flow rate will be studied using the software program COMSOL. Follow the step-by-step procedure in the Web Module and on the CD-ROM.
We continue Example 12-3, which discussed the reaction of propylene oxide (A) with water (B) to form propylene glycol (C). The hydrolysis of propylene oxide takes place readily at room temperature when catalyzed by sulfuric acid.

\[ \text{A} + \text{B} \rightarrow \text{C} \]

This exothermic reaction is approximated as a first-order reaction, given that the reaction takes place in an excess of water.

The CSTR in Example 12-3 has been replaced by a tubular reactor 1.0 m in length and 0.2 m in diameter. The feed to the reactor consists of two streams that are mixed just before entering the tubular reactor. One stream is an equivolumetric mixture of propylene oxide and methanol, and the other stream is water containing 0.1 wt % sulfuric acid. The water is fed at a volumetric rate 2.5 times larger than the propylene oxide–methanol feed. The molar flow rate of propylene oxide fed to the tubular reactor is 0.1 mol/s.

There is an immediate temperature rise upon mixing the two feed streams caused by the heat of mixing. In these calculations, this temperature rise is already accounted for, and the inlet temperature of both streams is set to \( T_0 = 312 \) K.

The reaction rate law is

\[ -r_A = kC_A \]  

with

\[ k = Ae^{-E/RT} \]

where \( E = 75,362 \) J/mol and \( A = 16.96 \times 10^{12} \) h\(^{-1}\), which can also be put in the form

\[ k(T) = k_0(T_0) \exp \left( \frac{E}{RT} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right) \]

with \( k_0 = 1.28 \) h\(^{-1}\) at 300 K. The thermal conductivity \( k_e \) of the reaction mixture and the diffusivity \( D_e \) are 0.599 W/m/K and \( 10^{-9} \) m\(^2\)/s, respectively, and are assumed to be constant throughout the reactor. In the case where there is heat exchange between the reactor and its surroundings, the overall heat-transfer coefficient is 1300 W/m\(^2\)/K and the temperature of the cooling jacket temperature is assumed to be constant and is set to 273 K. The other property data are shown in Table E15-1.1.

<table>
<thead>
<tr>
<th>TABLE 15-1.1</th>
<th>PHYSICAL PROPERTY DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Propylene Oxide</strong></td>
<td><strong>Methanol</strong></td>
</tr>
<tr>
<td>Molar weight (g/mol)</td>
<td>58.095</td>
</tr>
<tr>
<td>Density (kg/m(^3))</td>
<td>830</td>
</tr>
</tbody>
</table>
15-14 Radial and Axial Temperature Variations in a Tubular Reactor Chap. 15

Solution

Mole Balances: Recalling Equation (14-24) and applying it to species A

\[ \frac{D_e}{\rho_e} \frac{\partial^2 C_A}{\partial r^2} + \frac{1}{r} \frac{D_e}{\rho_e} \frac{\partial C_A}{\partial r} + \frac{D_e}{\rho_e} \frac{\partial^2 C_A}{\partial z^2} - U_z \frac{\partial C_A}{\partial z} + r_A = 0 \]  
\[ (E15-1.4) \]

Rate Law:

\[ -r_A = k(T_1) \exp \left( \frac{E}{R \cdot T_1} - \frac{1}{T} \right) C_A \]  
\[ (E15-1.5) \]

Stoichiometry: The conversion along a streamline \((r)\) at a distance \(z\) from the reactor entrance

\[ X(r, z) = 1 - \frac{C_A(r, z)}{C_{A0}} \]  
\[ (E15-1.6) \]

The overall conversion at a given distance \(z\) from the reactor entrance is

\[ \bar{X}(z) = 1 - \frac{2 \pi \int_0^R C_A(r, z) U_z r dr}{F_{A0}} \]  
\[ (E15-1.7) \]

The mean concentration at any distance \(z\) from the reactor entrance is

\[ \overline{C_A}(z) = \frac{2 \pi \int_0^R C_A(r, z) U_z r dr}{\pi R^2 U_0} \]  
\[ (E15-1.8) \]

For plug flow, the velocity profile is

\[ U_z = U_0 \]  
\[ (E15-1.9) \]

The laminar flow velocity profile is

\[ U_z = 2 U_0 \left[ 1 - \left( \frac{r}{R} \right)^2 \right] \]  
\[ (E15-1.10) \]

Recalling the Energy Balance

\[ k_e \frac{\partial^2 T}{\partial z^2} + \frac{k_e}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \Delta H_{R_x} r_A - U_z C_p \frac{\partial T}{\partial z} = 0 \]  
\[ (15-37) \]

<table>
<thead>
<tr>
<th></th>
<th>Propylene Oxide</th>
<th>Methanol</th>
<th>Water</th>
<th>Propylene Glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat capacity (J/mol • K)</td>
<td>146.54</td>
<td>81.095</td>
<td>75.36</td>
<td>192.59</td>
</tr>
<tr>
<td>Heat of formation (J/mol)</td>
<td>-154911.6</td>
<td>238,400</td>
<td>-286098</td>
<td>-525676</td>
</tr>
</tbody>
</table>

Table 15-1.1. Physical Property Data (continued)


Assumptions

1. $U_r$ is zero.
2. Neglect axial diffusion/dispersion flux with regard to convective flux when summing the products of the heat capacities and their respective fluxes.
3. Steady state.

Cooling jacket

$$mC_p \frac{\partial T_a}{\partial z} = 2\pi RU_{ht}(T(R,z) - T_a)$$  \hspace{1cm} (15-38)

Boundary conditions

At $r = 0$, then $\frac{\partial C_i}{\partial r} = 0$ and $\frac{\partial T}{\partial r} = 0$  \hspace{1cm} (E15-1.11)

At $r = R$, then $\frac{\partial C_i}{\partial r} = 0$ and $-k_c \frac{\partial T}{\partial r} = U_{ht}(T(R,z) - T_a)$  \hspace{1cm} (E15-1.12)

At $z = 0$, then $C_i = C_{i0}$ and $T = T_0$  \hspace{1cm} (E15-1.13)

These equations were solved using COMSOL for a number of cases including adiabatic and non-adiabatic plug flow and laminar flow; they were also solved with and without axial and radial dispersion. A detailed accounting on how to change the parameter values in the COMSOL program can be found in the COMSOL Instructions section on the Web in screen shots similar to Figure E15-1.1. Figure E15-1.2 gives the data set in SI units used for the COMSOL example.

Color surfaces are used to show the concentration and temperature profiles, similar to the black and white figures shown in Figure E15-1.2. Read through the COMSOL Web module entitled “Radial and Axial Temperature Gradients.” One notes in Figure E15-2.1 that the conversion is lower near the wall because of the cooler fluid temperature. These same profiles can be found in color on the Web and CD-ROM in the Web Modules.
Analysis: One notes the maximum and minimum in these profiles. Near the wall, the temperature of the mixture is lower because of the cold wall temperature. Consequently, the rate will be lower, and thus the conversion will be lower. However, right next to the wall, the velocity through the reactor is almost zero so the reactants spend a long time in the reactor; therefore, a greater conversion is achieved, as noted by the upturn right next to the wall.
Example 15-2 Radial Effects in a Packed-Bed Reactor

One of the common methods to produce phthalic anhydride is from the partial oxidation of o-xylene. This simplified reaction for the formation of phthalic anhydride from o-xylene oxidation will be represented by

\[
C_8H_{10} + 3O_2 \rightarrow C_4H_4O_3 + 3H_2O
\]

In terms of symbols

\[
A + 3B \rightarrow C + 3D
\]

Phthalic anhydride is primarily used in plasticizers and in resins used to make boat hulls, hot tubs, and synthetic marble surfaces. In the partial oxidation of o-xylene reaction, there are several byproducts as well as products of combustion that are formed if the reactor is not optimized. It is desirable to avoid high temperatures in this reactor based on temperature limits on the materials (reactor walls and catalyst) as well as reducing the formation of byproducts. As you would expect, high temperatures will result in the combustion of both the reactant and product, resulting in the formation of CO\(_2\) and H\(_2\)O. Because of the high operating temperatures, this reactor is cooled using molten salt (sodium nitrite-potassium nitrate). For this COMSOL ECRE problem we will only use approximate reaction kinetics for the overall reaction, as well as making an assumption of constant overall flowrate. This assumption must be employed based on the form of the equation given in the COMSOL ECRE package, which uses a constant velocity through the reactor. For safety considerations, the o-xylene is diluted to a mole fraction of 0.012 and fed to the reactor at 610K.

It is desired to make 76 metric tons of phthalic anhydride per year in a packed-bed reactor 1 m in length with a 0.1 m radius. Other parameters are given in Table E15-2.1.

The reaction follows the following rate law based on partial pressures

\[
-r'_A = k'P_A P_{O_2}
\]

**Additional Information**

| TABLE E15-2.1 COMSOL ECRE CONSTANTS |
|-----------------|---------------------------|
| E               | 112971 J/mol             |
| A               | 8.922 mol/m\(^3\) Pa\(^2\) s |
| R               | 8.314 J/mol\(\times\)K   |

\(^1\) Example problem by Professor Robert Hesketh, Department of Chemical Engineering, Rowan University, Glassboro, New Jersey.
TABLE E15-2.1 COMSOL ECRe CONSTANTS (CONTINUED)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T0</td>
<td>610</td>
</tr>
<tr>
<td>FA0</td>
<td>0.02149 mol/s</td>
</tr>
<tr>
<td>FO2_0</td>
<td>0.37155 mol/s</td>
</tr>
<tr>
<td>Ra</td>
<td>0.1 m</td>
</tr>
<tr>
<td>dHrx</td>
<td>-1125924 J/mol</td>
</tr>
<tr>
<td>ke</td>
<td>0.78 J/(m s K)</td>
</tr>
<tr>
<td>Cp</td>
<td>1150 J/(kg K)</td>
</tr>
<tr>
<td>Uht</td>
<td>156 J/(s K m²)</td>
</tr>
<tr>
<td>Ta</td>
<td>620 K</td>
</tr>
<tr>
<td>FT</td>
<td>1.79078 mol/s</td>
</tr>
<tr>
<td>P</td>
<td>1.01325e5 Pa</td>
</tr>
<tr>
<td>π</td>
<td>3.141592654</td>
</tr>
</tbody>
</table>

Construct a model of this reactor and investigate the radial and axial temperature profiles.

(a) Run your model using values of thermal conductivity from 0.1 to 1000 J/(m K s).

(b) Compare this model to the plug flow model for mass and heat transfer. Discuss the overall effect of the value of effective thermal conductivity of the bed on the resulting temperature profile and outlet conversion obtained.

(c) Give a rationale as to why industry does not use tubes of 0.1 m in diameter, but instead uses a smaller tube diameter of 0.0254 m.

**Preliminary Calculations**

To produce 76 metric ton/y during 350 d/y operation

\[
F_C = \frac{76T}{350d} \times \frac{1d}{24h} \times \frac{1h}{3600s} \times \frac{1000kg}{T} \times \frac{1mol}{148g} = 0.17 \text{ mol/s}
\]

For 79% conversion

\[
F_{A0} = \frac{F_C}{\chi} = \frac{0.17}{0.79} = 0.215 \text{ mol/s}
\]

\[
F_T = F_{T0} - F_{A0} = 0.372 \text{ mol/s}
\]

\[
F_C = \pi(0.1m^2) = 0.0314
\]

\[
v_0 = 0.0896 \text{ m}^3/s
\]
Solution
In COMSOL we will use a 2D axis-symmetric model in the r and z directions. This reaction takes place in a packed-bed reactor, where we will assume that the flow is plug flow with no axial or radial diffusion.

Assumptions:
1. $U_r = 0$ (i.e., assume negligible velocity in the radial direction)
2. $U_z$ = constant
3. Neglect axial diffusion/dispersion flux with respect to convective flux
4. Assume constant density and that mean heat capacity of the gas can be approximated by the values of air
5. Steady-state

Mole Balance:
Starting with Equation (15-24)

$$D_e \frac{\partial^2 C_i}{\partial r^2} + \frac{D_e}{r} \frac{\partial C_i}{\partial r} + D_e \frac{\partial^2 C_i}{\partial z^2} - U_z \frac{\partial C_i}{\partial z} + r_i = 0$$  \hspace{1cm} (15-24)

Neglecting diffusion in the axial and radial directions gives the plug flow equation:

$$-U_z \frac{\partial C_i}{\partial z} + r_i = 0 \hspace{1cm} (E15-2.1)$$

Note that the velocity $U_z$ is constant.

Rate Law:

$$-r'_A = k'P_A P_{O_2} \left( \frac{\text{mol}}{\text{kgcat} \cdot \text{Pa}^2 \cdot \text{s}} \right) \hspace{1cm} (E15-2.2)$$

To convert the rate to per reactor volume we multiply by the bulk density of the catalyst bed, $\rho_B$

$$-r_A = -r'_A \rho_B = \rho_B k'P_A P_{O_2} = kP_A P_{O_2} \hspace{1cm} (E15-2.3)$$

For the COMSOL model, the partial pressures need to be converted to concentration using the ideal gas law $C_i = P_i / RT$

$$-r_A = k(RT)^2 C_A C_{O_2} \hspace{1cm} (E15-2.4)$$

with

$$k = A e^{-\frac{E}{RT}} \left( \frac{\text{mol}}{m^3 \cdot \text{Pa}^2 \cdot \text{s}} \right) \hspace{1cm} (E15-2.5)$$

Stoichiometry:
Because of the dilute reactants, $\varepsilon = 0$. We also will neglect changes in volumetric flow rate with temperature and pressure

$$v = v_0$$
Energy Balance:
Starting with the energy balance from Equation 15-37:

$$\begin{align*}
C_A &= \frac{F_A}{v_0}, \quad C_{O_2} = \frac{F_{O_2}}{v_0}, \quad C_C = \frac{F_C}{v_0} \\
\end{align*}$$ (E15-2.6)

$$\begin{align*}
\begin{bmatrix}
    k_e \frac{\partial^2 T}{\partial z^2} + k_e \frac{r}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \Delta H_{R_2} r_A - U_c C_{P_m} \frac{\partial T}{\partial z} &= 0
\end{bmatrix}
\end{align*}$$ (15-37)

The conductivity used in the energy balance will be an effective conductivity of the bed. The conduction in the axial direction is neglected, resulting in the following equation:

$$\begin{align*}
\frac{k_e}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \Delta H_{R_2} r_A - U_c C_{P_m} \frac{\partial T}{\partial z} &= 0
\end{align*}$$ (E15-2.7)

The boundary conditions for these PDEs will be:

(A) \( -k_e \frac{\partial T}{\partial r} \bigg|_{r=R} = U_h \left( T(R, z) - T_0 \right) \) at \( r = R \) and \( 0 \leq z \leq 1 \) m \hfill (E15-2.8)

(B) \( \frac{\partial C_i}{\partial r} = 0 \) and \( \frac{\partial T}{\partial r} = 0 \) at \( r = 0 \) \hfill (E15-2.9)

(C) \( T = T_0 \) and \( C_i = C_{i_0} \) at \( z = 0 \) and \( 0 \leq r \leq R \) \hfill (E15-2.10)

(D) \( \frac{\partial T}{\partial z} = 0 \) and \( \frac{\partial C_j}{\partial z} = 0 \) at \( z = 1.0 \) m and \( 0 \leq r \leq R \) \hfill (E15-2.11)

Findings:

**Figure E15-2.1:** Surface Plot

**Figure E15-2.2:** Temperature Profile in reactor tube for \( k_e = 0.78 \) J/(s m K). Positions: for \( k_e = 0.78 \) J/(s m K) 1) \( r = 0.1 \) m Wall, 2) \( r = 0.08 \) m, 3) \( r = 0.06 \) m, 4) \( r = 0.04 \) m, 5) \( r = 0.00 \) m center.
Results:
A surface plot of the temperatures in the reactor tube is shown in Figure E15-2.1 which shows a noticeable difference in temperatures of the fluid at the end of the reactor starting at about \( z = 0.7 \) m. For this value of thermal conductivity, the wall remains “cold” at approximately the temperature of the molten salt of 720K. This can also be seen in the cross-section plot that is shown in Figure E15-2.2. Each line on this plot represents a radial position within the reactor. In Figure E15-2.3 a cross section plot showing the temperature profile as a function of radial position and axial distance in the reactor is presented. Each line in this figure represents an axial position in the reactor. In this plot, the difference between the wall temperature and the temperature within the reactor is clearly shown. The plug flow condition, in which the temperature profile has been eliminated in the radial direction, is shown in Figure E15-2.4. This result was obtained with a thermal conductivity of 1000 J/(s m K).

![Figure E15-2.3: Temperature Profile in reactor tube for \( k_e = 0.78 \) J/(s m K). Positions: 1) \( z = 0.0 \) m, 2) \( r = 0.2 \) m, 3) \( z = 0.4 \) m, 3) \( z = 0.6 \) m, 4) \( z = 0.8 \) m, 5) \( r = 1.0 \) m This plot shows a large temperature variation in the radial direction.](image1)

![Figure E15-2.4: Temperature Profile in reactor tube for \( k_e = 1000 \) J/(s m K). Positions: 1) \( z = 0.0 \) m, 2) \( r = 0.2 \) m, 3) \( z = 0.4 \) m, 3) \( z = 0.6 \) m, 4) \( z = 0.8 \) m, 5) \( r = 1.0 \) m This plot shows that there is no temperature variation with respect to radial position.](image2)
Table E15-2.2 gives a summary of the output from the COMSOL program.

**Table E15-2.2** Summary of the Results of the Effect of Thermal Conductivity on T and X

<table>
<thead>
<tr>
<th>$ke$ (J/(s m K))</th>
<th>0.1</th>
<th>0.78</th>
<th>10</th>
<th>100</th>
<th>1000</th>
<th>Plug Flow Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T^\ast Ac$ outlet avg (K m$^2$)</td>
<td>22.3</td>
<td>21.9</td>
<td>21.0</td>
<td>20.7</td>
<td>20.7</td>
<td></td>
</tr>
<tr>
<td>$T$ outlet average (K)</td>
<td>711</td>
<td>697</td>
<td>668</td>
<td>659</td>
<td>658</td>
<td></td>
</tr>
<tr>
<td>$X^\ast Ac$</td>
<td>0.00804</td>
<td>0.00726</td>
<td>0.00569</td>
<td>0.00524</td>
<td>0.00519</td>
<td></td>
</tr>
<tr>
<td>$X$ outlet average</td>
<td>0.256</td>
<td>0.231</td>
<td>0.181</td>
<td>0.167</td>
<td>0.165</td>
<td></td>
</tr>
</tbody>
</table>

**Analysis:** From Table E15-2.2 we observe that the removal of heat is effective in lowering the temperature within the reactor. The advantage of the molten salt cooling is that it will help to prevent a runaway reaction in the reactor tubes. As the radial thermal conductivity is increased, the overall rate of heat transfer from the fluid to the reactor walls increases. As you can see from the table, the conversion also decreases.

**SUMMARY**

To obtain the axial or radial temperature and concentration gradients, the following coupled partial differential equations were solved using COMSOL:

\[
D_e \frac{\partial^2 C_i}{\partial r^2} + \frac{D_e}{r} \frac{\partial C_i}{\partial r} + \frac{D_e}{r} \frac{\partial^2 C_i}{\partial z^2} - U_z \frac{\partial C_i}{\partial z} + r_i = 0 \quad (S15-1)
\]

and

\[
k_e \frac{\partial^2 T}{\partial z^2} + \frac{k_e}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{\Delta H_{\text{rx}} r_A}{U_z C_P m} \frac{\partial T}{\partial z} = 0 \quad (S15-2)
\]

**CD-ROM MATERIAL**

- **Learning Resources**
  1. Summary Notes
  2. Web Module COMSOL Radial and Axial Gradients
P15-1c In a diving-chamber experiment, a human subject breathed a mixture of O₂ 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 δ₁ and the other of δ₂. If counterdiffusion of He out through the skin occurs at the same time as N₂ 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 N₂ and He in the skin layers.

Diffusivity of He and N₂ in the inner skin layer

\[ D_1 = 5 \times 10^{-7} \text{ cm}^2/\text{s} \text{ and } 1.5 \times 10^{-7} \text{ cm}^2/\text{s}, \text{ respectively} \]

Diffusivity of He and N₂ in the outer skin layer

\[ D_2 = 10^{-5} \text{ cm}^2/\text{s} \text{ and } 3.3 \times 10^{-4} \text{ cm}^2/\text{s}, \text{ respectively} \]

<table>
<thead>
<tr>
<th>External Skin Boundary Partial Pressure</th>
<th>Internal Skin Boundary Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>101 kPa</td>
</tr>
<tr>
<td>He</td>
<td>0</td>
</tr>
<tr>
<td>δ₁</td>
<td>20 µm</td>
</tr>
<tr>
<td>δ₂</td>
<td>80 µm</td>
</tr>
</tbody>
</table>

P15-2b 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 dm³/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% H₂ at 2 atm and 500°C.

(b) Plot conversion as a function of length.

(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?

P15-3b Assume the minimum respiration rate of a chipmunk is 1.5 micromoles of O₂/min. The corresponding volumetric rate of gas intake is 0.05 dm³/min at STP.

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

(b) In Boulder, Colorado?
(c) How would your answers to (a) and (b) change in the dead of winter when $T = 0^\circ$F?

(d) Critique and extend this problem (e.g., CO$_2$ poisoning).

**P15-4 Instructions:** If you have not installed COMSOL Multiphysics, request a trial version of the software from the Web site [http://www.comsol.com/ecre](http://www.comsol.com/ecre). From this page you can also download model and documentation files required for the COMSOL exercises outlined in this chapter.

Load COMSOL Multiphysics and follow the installation instructions. Double-click on the COMSOL Multiphysics icon on your desktop. In the Model Library, select model denoted “4-Non-Isothermal Reactor II” and click the Dynamic Help icon on the main toolbar. This opens a Help window in the COMSOL desktop presenting the detailed documentation of the specific model. Scroll the side bar to review the model equations. Move further down the documentation to find the step-by-step instructions that guide you through the model-building process. The steps also detail how to solve the model and analyze the results. If you want bypass the model setup process, return to the Model Library dialog and press OK to open a saved model file.

(a) Why is the concentration of A near the wall lower than the concentration near the center?

(b) Where in the reactor do you find the maximum and minimum reaction rates? Why? **Instructions:** Select the “2D Plot Group 1 > Surface 1” node to access the surface plot dialog. Type “–rA” (replace “cA”) in the “Expression” edit field to plot the absolute rate of consumption of A (moles m$^{-3}$ s$^{-1}$).

(c) Increase the activation energy of the reaction by 5%. How do the concentration profiles change? Decrease? **Instructions:** Select the “Global Definitions > Parameters” node. Multiply the value of “E” in the constants list by 1.05 (just type “*1.05” behind the existing value to increase or multiply by 0.95 to decrease). Go to the “Study 1” node and select “Compute.”

(d) Change the activation energy back to the original value. **Instructions:** Select the “Global Definitions > Parameters” node. Remove the factor “0.95” in the constants list.

(e) Increase the thermal conductivity, $k_e$, by a factor of 10 and explain how this change affects the temperature profiles. At what radial position do you find the highest conversion? **Instructions:** Multiply the value of “ke” in the constants lists by 10. Go to the “Study 1” node and select “Compute.”

(f) Increase the coolant flow rate by a factor of 10 and explain how this change affects the conversion.

(g) In two or three sentences, describe your findings when you varied the parameters (for all parts).

(h) What would be your recommendation to maximize the average outlet conversion?

(i) Review Figure E15-1.2 and explain why the temperature profile goes through a maximum and why the conversion profile goes through a maximum and a minimum.

(j) See other problems in the Web Module.
If you have not installed COMSOL Multiphysics, request a trial version of the software from the Web site http://www.comsol.com/ecre and follow the installation instructions as outlined in P15-4.

(a) Before running the program, sketch the radial temperature profile down a PFR for (1) an exothermic reaction for a PFR with a cooling jacket and (2) an endothermic reaction for a PFR with a heating jacket.

(b) Run COMSOL Multiphysics and compare with your results in (a). Double-click on the COMSOL Multiphysics icon on your desktop. In the Model Library, select the model denoted “3-Non-Isothermal I” and press OK. You can use this model to compare your results in (1) and (2), above. Click the Dynamic Help icon on the main toolbar to review the instructions for this model and other models in COMSOL. Change the velocity profile from laminar parabolic to plug flow. Select the “Model 1 > Definitions > Variables 1” node. Change the expression for uz (the velocity) to “u0” (replace the expression “2*u0*(1–(r/Ra) 2)”, which describes the parabolic velocity profile). You can now continue to vary the input data and change the exothermic reaction to an endothermic one. (Hint: Select the “Global Definitions > Parameters” node to access the list of constants. Do not forget “T a0” the jacket temperature at the end of the list.) To run a simulation, go to the “Study 1” node and select “Compute.” Write a paragraph describing your findings.

(c) The thermal conductivity in the reactor, denoted “ke” in Figure E15-1.1, is the molecular thermal conductivity for the solution. In a plug flow reactor, the flow is turbulent. In such a reactor, the apparent thermal conductivity is substantially larger than the molecular thermal conductivity of the fluid. Vary the value of the thermal conductivity “ke” to learn its influence on the temperature and concentration profile in the reactor.

(d) In turbulent flow, the apparent diffusivity is substantially larger than the molecular diffusivity. Increase the molecular diffusivity in the PFR to reflect turbulent conditions and study the influence on the temperature and concentration profiles. Here you can go to the extremes. Find something interesting to turn in to your instructor. See other problems in the Web Module.

(e) See other problems in the Web Module.

SUPPLEMENTARY READING

1. Partial differential equations describing axial and radial variations in temperature and concentration in chemical reactors are developed in

