
CHAPTER 8

REAL TUBULAR REACTORS IN LAMINAR FLOW

Piston flow is a convenient approximation of a real tubular reactor. The design equations for piston flow are relatively simple and are identical in mathematical form to the design equations governing batch reactors. The key to their mathematical simplicity is the assumed absence of any radial or tangential variations within the reactor. The dependent variables a, b, \dots, T, P , change in the axial, down-tube direction but are completely uniform across the tube. This allows the reactor design problem to be formulated as a set of ordinary differential equations in a single independent variable, z . As shown in previous chapters, such problems are readily solvable, given the initial values $a_{in}, b_{in}, \dots, T_{in}, P_{in}$.

Piston flow is an accurate approximation for some practical situations. It is usually possible to avoid tangential (θ -direction) dependence in practical reactor designs, at least for the case of premixed reactants, which we are considering throughout most of this book. It is harder, but sometimes possible, to avoid radial variations. A long, highly turbulent reactor is a typical case where piston flow will be a good approximation for most purposes. Piston flow will usually be a bad approximation for laminar flow reactors since radial variations in composition and temperature can be large.

Chapters 8 and 9 discuss design techniques for real tubular reactors. By “real,” we mean reactors for which the convenient approximation of piston flow is so inaccurate that a more realistic model must be developed. By “tubular,” we mean reactors in which there is a predominant direction of flow and a reasonably high aspect ratio, characterized by a length-to-diameter ratio, L/d_i , of 8 or more, or its equivalent, an L/R ratio of 16 or more. Practical designs include straight and coiled tubes, multitubular heat exchangers, and packed-bed reactors. Chapter 8 starts with isothermal laminar flow in tubular reactors that have negligible molecular diffusion. The complications of significant molecular diffusion, nonisothermal reactions with consequent diffusion of heat, and the effects of temperature and composition on the velocity profile are subsequently introduced. Chapter 9 treats turbulent reactors and packed-bed reactors of both the laminar and turbulent varieties. The result of these two chapters is a comprehensive design methodology that is applicable to many design problems

in the traditional chemical industry and which forms a conceptual framework for extension to nontraditional industries. The major limitation of the methodology is its restriction to reactors that have a single mobile phase. Reactors with two or three mobile phases, such as gas-liquid reactors, are considered in Chapter 11, but the treatment is necessarily less comprehensive than for the reactors of Chapters 8 and 9 that have only one mobile phase.

8.1 ISOTHERMAL LAMINAR FLOW WITH NEGLIGIBLE DIFFUSION

Consider isothermal laminar flow of a Newtonian fluid in a circular tube of radius R , length L , and average fluid velocity \bar{u} . When the viscosity is constant, the axial velocity profile is

$$V_z(r) = 2\bar{u} \left[1 - \frac{r^2}{R^2} \right] \quad (8.1)$$

Most industrial reactors in laminar flow have pronounced temperature and composition variations that change the viscosity and alter the velocity profile from the simple parabolic profile of Equation (8.1). These complications are addressed in Section 8.7. However, even the profile of Equation (8.1) presents a serious complication compared with piston flow. There is a velocity gradient across the tube, with zero velocity at the wall and high velocities near the centerline. Molecules near the center will follow high-velocity streamlines and will undergo relatively little reaction. Those near the tube wall will be on low-velocity streamlines, will remain in the reactor for long times, and will react to near-completion. Thus, a gradient in composition develops across the radius of the tube. Molecular diffusion acts to alleviate this gradient but will not completely eliminate it, particularly in liquid-phase systems with typical diffusivities of 1.0×10^{-9} to 1.0×10^{-10} for small molecules and much lower for polymers.

When diffusion is negligible, the material moving along a streamline is isolated from material moving along other streamlines. The streamline can be treated as if it were a piston flow reactor, and the system as a whole can be regarded as a large number of piston flow reactors in parallel. For the case of straight streamlines and a velocity profile that depends on radial position alone, concentrations along the streamlines at position r are given by

$$V_z(r) \frac{\partial a}{\partial z} = \mathcal{R}_A \quad (8.2)$$

This result is reminiscent of Equation (1.36). We have replaced the average velocity with the velocity corresponding to a particular streamline. Equation (8.2) is written as a partial differential equation to emphasize the fact that the concentration $a = a(r, z)$ is a function of both r and z . However, Equation (8.2) can be integrated as though it were an ordinary differential equation. The inlet boundary

condition associated with the streamline at position r is $a(r, 0) = a_{in}(r)$. Usually, a_{in} will be same for all values of r , but it is possible to treat the more general case. The outlet concentration for a particular streamline is found by solving Equation (8.2) and setting $z = L$. The outlet concentrations for the various streamlines are averaged to get the outlet concentration from the reactor as a whole.

8.1.1 A Criterion for Neglecting Diffusion

The importance of diffusion in a tubular reactor is determined by a dimensionless parameter, $\mathcal{D}_A \bar{t} / R^2 = \mathcal{D}_A L / (\bar{u} R^2)$, which is the molecular diffusivity of component A scaled by the tube size and flow rate. If $\mathcal{D}_A \bar{t} / R^2$ is small, then the effects of diffusion will be small, although the definition of small will depend on the specific reaction mechanism. Merrill and Hamrin¹ studied the effects of diffusion on first-order reactions and concluded that molecular diffusion can be ignored in reactor design calculations if

$$\mathcal{D}_A \bar{t} / R^2 < 0.003 \quad (8.3)$$

Equation (8.3) gives the criterion for neglecting diffusion. It is satisfied in many industrial-scale, laminar flow reactors, but may not be satisfied in laboratory-scale reactors since they operate with the same values for \mathcal{D}_A and \bar{t} but generally use smaller diameter tubes. Molecular diffusion becomes progressively more important as the size of the reactor is decreased. The effects of molecular diffusion are generally beneficial, so that a small reactor will give better results than a large one, a fact that has proved distressing to engineers attempting a scaleup. For the purposes of scaleup, it may be better to avoid diffusion and accept the composition gradients on the small scale so that they do not cause unpleasant surprises on the large scale. One approach to avoiding diffusion in the small reactor is to use a short, fat tube. If diffusion is negligible in the small reactor, it will remain negligible upon scaleup. The other approach is to accept the benefit of diffusion and to scaleup at constant tube diameter, either in parallel or in series as discussed in Chapter 3. This will maintain a constant value for the dimensionless diffusivity, $\mathcal{D}_A \bar{t} / R^2$.

The Merrill and Hamrin criterion was derived for a first-order reaction. It should apply reasonably well to other simple reactions, but reactions exist that are quite sensitive to diffusion. Examples include the decomposition of free-radical initiators where a few initial events can cause a large number of propagation reactions, and coupling or cross-linking reactions where a few events can have a large effect on product properties.

8.1.2 Mixing-Cup Averages

Suppose Equation (8.2) is solved either analytically or numerically to give $a(r, z)$. It remains to find the average outlet concentration when the flows from all the

streamlines are combined into a single stream. This average concentration is the *convected-mean* or *mixing-cup average concentration*. It is the average concentration, $a_{mix}(L)$, of material leaving the reactor. This material could be collected in a bucket (a mixing cup) and is what a company is able to sell. It is not the spatial average concentration inside the reactor, even at the reactor outlet. See Problem 8.5 for an explanation of this distinction.

The convected mean at position z is denoted by $a_{mix}(z)$ and is found by multiplying the concentration on a streamline, $a(r, z)$, by the volumetric flow rate associated with that streamline, $dQ(r) = V_z(r)dA_c$, and by summing over all the streamlines. The result is the molar flow rate of component A. Dividing by the total volumetric flow, $Q = \bar{u}A_c$, gives the convected-mean concentration:

$$a_{mix}(z) = \frac{1}{\bar{u}A_c} \iint_{A_c} a V_z dA_c = \frac{1}{\bar{u}R^2} \int_0^R a(r, z) V_z(r) 2r dr \quad (8.4)$$

The second integral in Equation (8.4) applies to the usual case of a circular tube with a velocity profile that is a function of r and not of θ . When the velocity profile is parabolic,

$$a_{mix}(z) = \frac{4}{R^2} \int_0^R a(r, z) \left[1 - \frac{r^2}{R^2} \right] r dr = 4 \int_0^1 a(\zeta, z) [1 - \zeta^2] \zeta d\zeta \quad (8.5)$$

where $\zeta = r/R$ is the dimensionless radius.

The mixing-cup average outlet concentration $a_{mix}(L)$ is usually denoted just as a_{out} and the averaging is implied. The averaging is necessary whenever there is a radial variation in concentration or temperature. Thus, Equation (8.4) and its obvious generalizations to the concentration of other components or to the mixing-cup average temperature is needed throughout this chapter and much of Chapter 9. If in doubt, calculate the mixing-cup averages. However, as the next example suggests, this calculation can seldom be done analytically.

Example 8.1: Find the mixing-cup average outlet concentration for an isothermal, first-order reaction with rate constant k that is occurring in a laminar flow reactor with a parabolic velocity profile as given by Equation (8.1).

Solution: This is the simplest, nontrivial example of a laminar flow reactor. The solution begins by integrating Equation (8.2) for a specific streamline that corresponds to radial position r . The result is

$$a(r, z) = a_{in} \exp \left[\frac{-kz}{V_z(r)} \right] \quad (8.6)$$

where k is the first-order rate constant. The mixing-cup average outlet concentration is found using Equation (8.5) with $z = L$:

$$a_{out} = a_{mix}(L) = 4a_{in} \int_0^1 \exp\left[\frac{-kL}{2\bar{u}(1-z^2)}\right] [1-z^2] z \, dz$$

This integral can be solved analytically. Its solution is a good test for symbolic manipulators such as Mathematica or Maple. We illustrate its solution using classical methods. Differentiating Equation (8.1) gives

$$z \, dz = -\frac{dV_z}{4\bar{u}}$$

This substitution allows the integral to be expressed as a function of V_z :

$$a_{out} = \frac{a_{in}}{2\bar{u}^2} \int_0^{2\bar{u}} \exp[-kL/V_z] V_z \, dV_z$$

A second substitution is now made,

$$t = L/V_z \quad (8.7)$$

to obtain an integral with respect to t . Note that t ranges from $\bar{t}/2$ to ∞ as V_z ranges from $2\bar{u}$ to 0 as z ranges from 0 to 1. Some algebra gives the final result:

$$\frac{a_{out}}{a_{in}} = \int_{\bar{t}/2}^{\infty} \exp(-kt) \frac{\bar{t}^2}{2t^3} dt \quad (8.8)$$

This integral is a special function related to the incomplete gamma function. The solution can be considered to be analytical even though the function may be unfamiliar. Figure 8.1 illustrates the behavior of Equation (8.8) as compared with CSTRs, PFRs, and laminar flow reactors with diffusion.

Mixing-cup averages are readily calculated for any velocity profile that is axisymmetric—i.e., has no θ -dependence. Simply use the appropriate functional form for V_z in Equation (8.4). However, analytical integration as in Example 8.1 is rarely possible. Numerical integration is usually necessary, and the trapezoidal rule described in Section 8.3.4 is recommended because it converges $\mathbf{O}(\Delta r^2)$, as do the other numerical methods used in Chapters 8 and 9. Example 8.3 includes a sample computer code. Use of the rectangular rule (see Figure 2.1) is not recommended because it converges $\mathbf{O}(\Delta r)$ and would limit the accuracy of other calculations. Simpson's rule converges $\mathbf{O}(\Delta r^3)$ and

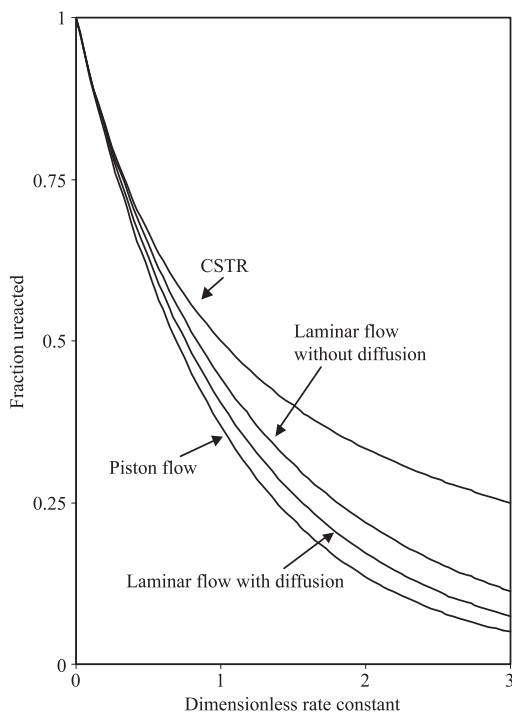


FIGURE 8.1 Fraction unreacted versus dimensionless rate constant for a first-order reaction in various isothermal reactors. The case illustrated with diffusion is for $\mathcal{D}_A \bar{t}/R^2 = 0.1$.

will calculate \bar{u} exactly when the velocity profile is parabolic, but ceases to be exact for the more complex velocity profiles encountered in real laminar flow reactors. The use of Simpson's rule then does no harm but offers no real advantage. The convergence order for a complex calculation is determined by the most slowly converging of the computational components.

The double integral in Equation (8.4) is a fairly general definition of the mixing-cup average. It is applicable to arbitrary velocity profiles and noncircular cross sections but does assume straight streamlines of equal length. Treatment of curved streamlines requires a precise and possibly artificial definition of the system boundaries. See Nauman and Buffham.²

8.1.3 A Preview of Residence Time Theory

Example 8.1 derived a specific example of a powerful result of *residence time theory*. The residence time associated with a streamline is $t = L/V_z$. The outlet concentration for this streamline is $a_{batch}(t)$. This is a general result applicable to diffusion-free laminar flow. Example 8.1 treated the case of a

first-order reaction where $a_{batch}(t) = \exp(-kt)$. Repeating Example 8.1 for the general case gives

$$a_{out} = \int_{\bar{t}/2}^{\infty} a_{batch}(t) \frac{\bar{t}^2}{2t^3} dt \quad (8.9)$$

Equation (8.9) can be applied to any reaction, even a complex reaction where $a_{batch}(t)$ must be determined by the simultaneous solution of many ODEs. The restrictions on Equation (8.9) are isothermal laminar flow in a circular tube with a parabolic velocity profile and negligible diffusion.

The condition of negligible diffusion means that the reactor is *completely segregated*. A further generalization of Equation (8.9) applies to any completely segregated reactor:

$$a_{out} = \int_0^{\infty} a_{batch}(t) f(t) dt \quad (8.10)$$

where $f(t)$ is the *differential distribution function of residence times*. In principle, $f(t)$ is a characteristic of the reactor, not of the reaction. It can be used to predict conversions for any type of reaction in the same reactor. Chapter 15 discusses ways of measuring $f(t)$. For a parabolic velocity profile in a diffusion-free tube,

$$\begin{aligned} f(t) &= 0 & t &\leq \bar{t}/2 \\ f(t) &= \frac{\bar{t}^2}{2t^3} & t &> \bar{t}/2 \end{aligned} \quad (8.11)$$

8.2 CONVECTIVE DIFFUSION OF MASS

Molecules must come into contact for a reaction to occur, and the mechanism for the contact is molecular motion. This is also the mechanism for diffusion. Diffusion is inherently important whenever reactions occur, but there are some reactor design problems where diffusion need not be explicitly considered, e.g., tubular reactors that satisfy the Merrill and Hamrin criterion, Equation (8.3). For other reactors, a detailed accounting for molecular diffusion may be critical to the design.

Diffusion is important in reactors with unmixed feed streams since the initial mixing of reactants must occur inside the reactor under reacting conditions. Diffusion can be a slow process, and the reaction rate will often be limited by diffusion rather than by the intrinsic reaction rate that would prevail if the reactants were premixed. Thus, diffusion can be expected to be important in tubular reactors with unmixed feed streams. Its effects are difficult to calculate, and normal design practice is to use premixed feeds whenever possible.

With premixed reactants, molecular diffusion has already brought the reacting molecules into close proximity. In an initially mixed batch reactor, various portions of the reacting mass will start at the same composition, will react at the same rate, and will thus have the same composition at any time. No concentration gradients develop, and molecular diffusion is unimportant during the reaction step of the process even though it was important during the premixing step. Similarly, mechanical mixing is unnecessary for an initially mixed batch reactor, although mixing must be good enough to eliminate temperature gradients if there is heating or cooling at the wall. Like ideal batch reactors, CSTRs lack internal concentration differences. The agitator in a CSTR brings fluid elements into such close contact that mixing is complete and instantaneous.

Tubular reactors are different. They must have concentration gradients in the axial direction since the average concentration changes from a_{in} to a_{out} along the length of the reactor. The nonisothermal case will have an axial temperature gradient as well. Piston flow reactors are a special case of tubular reactor where radial mixing is assumed to be complete and instantaneous. They continue to have axial gradients.

Laminar flow reactors have concentration and temperature gradients in both the radial and axial directions. The radial gradient normally has a much greater effect on reactor performance. The diffusive flux is a vector that depends on concentration gradients. The flux in the axial direction is

$$J_z = -\mathcal{D}_A \frac{\partial a}{\partial z}$$

As a first approximation, the concentration gradient in the axial direction is

$$\frac{\partial a}{\partial z} \approx \frac{a_{out} - a_{in}}{L}$$

and since L is large, the diffusive flux will be small and can be neglected in most tubular reactors. Note that the piston flow model ignores axial diffusion even though it predicts concentration gradients in the axial direction.

The flux in the radial direction is

$$J_r = -\mathcal{D}_A \frac{\partial a}{\partial r}$$

A first approximation to the radial concentration gradient is

$$\frac{\partial a}{\partial r} \approx \frac{a_{wall} - a_{in}}{R} \approx \frac{-a_{in}}{R}$$

where we have assumed component A to be consumed by the reaction and to have a concentration near zero at the tube wall. The concentration differences in the radial and axial directions are similar in magnitude, but the length scales are very different. It is typical for tubular reactors to have $L/R \gg 1$.

The relatively short distance in the radial direction leads to much higher diffusion rates. In most of what follows, axial diffusion will be ignored.

To account for molecular diffusion, Equation (8.2), which governs reactant concentrations along the streamlines, must be modified to allow diffusion between the streamlines; i.e., in the radial direction. We ignore axial diffusion but add a radial diffusion term to obtain

$$V_z(r) \frac{\partial a}{\partial z} = \mathcal{D}_A \left[\frac{1}{r} \frac{\partial a}{\partial r} + \frac{\partial^2 a}{\partial r^2} \right] + \mathcal{R}_A \quad (8.12)$$

A derivation of this equation is given in Appendix 8.1.

Equation (8.12) is a form of the *convective diffusion equation*. More general forms can be found in any good textbook on transport phenomena, but Equation (8.12) is sufficient for many practical situations. It assumes constant diffusivity and constant density. It is written in cylindrical coordinates since we are primarily concerned with reactors that have circular cross sections, but Section 8.4 gives a rectangular-coordinate version applicable to flow between flat plates.

Equation (8.12) is a partial differential equation that includes a first derivative in the axial direction and first and second derivatives in the radial direction. Three boundary conditions are needed: one axial and two radial. The axial boundary condition is

$$a(r, 0) = a_{in}(r) \quad (8.13)$$

As noted earlier, a_{in} will usually be independent of r , but the numerical solution techniques that follow can easily accommodate the more general case. The radial boundary conditions are

$$\frac{\partial a}{\partial r} = 0 \text{ at the wall,} \quad r = R \quad (8.14)$$

$$\frac{\partial a}{\partial r} = 0 \text{ at the centerline,} \quad r = 0 \quad (8.15)$$

The wall boundary condition applies to a solid tube without transpiration. The centerline boundary condition assumes symmetry in the radial direction. It is consistent with the assumption of an axisymmetric velocity profile without concentration or temperature gradients in the θ -direction. This boundary condition is by no means inevitable since gradients in the θ -direction can arise from natural convection. However, it is desirable to avoid θ -dependency since appropriate design methods are generally lacking.

A solution to Equation (8.12) together with its boundary conditions gives $a(r, z)$ at every point in the reactor. An analytical solution is possible for the special case of a first-order reaction, but the resulting infinite series is cumbersome to evaluate. In practice, numerical methods are necessary.

If several reactive components are involved, a version of Equation (8.12) should be written for each component. Thus, for complex reactions involving N components, it is necessary to solve N simultaneous PDEs (partial differential equations). For batch and piston flow reactors, the task is to solve N simultaneous ODEs. Stoichiometric relationships and the reaction coordinate method can be used to eliminate one or more of the ODEs, but this elimination is not generally possible for PDEs. Except for the special case where all the diffusion coefficients are equal, $\mathcal{D}_A = \mathcal{D}_B = \dots$, stoichiometric relationships should not be used to eliminate any of the PDEs governing reaction with diffusion. When the diffusion coefficients are unequal, the various species may separate due to diffusion. Overall stoichiometry, as measured by $a_{in} - a_{out}$, $b_{in} - b_{out}, \dots$ is preserved and satisfies Equation (2.39). However, convective diffusion does not preserve local stoichiometry. Thus, the reaction coordinate method does not work locally; and if N components affect reaction rates, then all N simultaneous equations should be solved. Even so, great care must be taken with multicomponent systems when the diffusivities differ significantly in magnitude unless there is some dominant component, the “solvent,” that can be assumed to distribute itself to satisfy a material balance constraint such as constant density. The general case of multicomponent diffusion remains an area of research where reliable design methods are lacking.³

8.3 NUMERICAL SOLUTION TECHNIQUES

Many techniques have been developed for the numerical solution of partial differential equations. The best method depends on the type of PDE being solved and on the geometry of the system. Partial differential equations having the form of Equation (8.12) are known as parabolic PDEs and are among the easiest to solve. We give here the simplest possible method of solution, one that is directly analogous to the marching-ahead technique used for ordinary differential equations. Other techniques should be considered (but may not be much better) if the computing cost becomes significant. The method we shall use is based on finite difference approximations for the partial derivatives. Finite element methods will occasionally give better performance, although typically not for parabolic PDEs.

The technique used here is a variant of *the method of lines* in which a PDE is converted into a set of simultaneous ODEs. The ODEs have z as the independent variable and are solved by conventional means. We will solve them using Euler’s method, which converges $\mathbf{O}(\Delta z)$. Higher orders of convergence, e.g., Runge-Kutta, buy little for reasons explained in Section 8.3.3. The ODEs obtained using the method of lines are very stiff, and computational efficiency can be gained by using an ODE-solver designed for stiff equations. However, for a solution done only once, programming ease is usually more important than computational efficiency.

8.3.1 The Method of Lines

Divide the tube length into a number of equally sized increments, $\Delta z = L/J$, where J is an integer. A finite difference approximation for the partial derivative of concentration in the axial direction is

$$\frac{\partial a}{\partial z} \approx \frac{a(r, z + \Delta z) - a(r, z)}{\Delta z} \quad (8.16)$$

This approximation is called a *forward difference* since it involves the forward point, $z + \Delta z$, as well as the central point, z . (See Appendix 8.2 for a discussion of finite difference approximations.) Equation (8.16) is the simplest finite difference approximation for a first derivative.

The tube radius is divided into a number of equally sized increments, $\Delta r = R/I$, where I is an integer. For reasons of convergence, we prefer to use a second-order, *central difference* approximation for the first partial derivative:

$$\frac{\partial a}{\partial r} \approx \frac{a(r + \Delta r, z) - a(r - \Delta r, z)}{2 \Delta r} \quad (8.17)$$

which is seen to involve the $r + \Delta r$ and $r - \Delta r$ points. For the second radial derivative we use

$$\frac{\partial^2 a}{\partial r^2} \approx \frac{a(r + \Delta r, z) - 2a(r, z) + a(r - \Delta r, z)}{\Delta r^2} \quad (8.18)$$

The approximations for the radial derivatives are substituted into the governing PDE, Equation (8.12), to give

$$\frac{\partial a}{\partial z} = Aa(r + \Delta r, z) + Ba(r, z) + Ca(r - \Delta r, z) + \mathcal{R}_A/V_z(r) \quad (8.19)$$

where

$$\begin{aligned} A &= \mathcal{D}_A[1/(2r \Delta r) + 1/\Delta r^2]/V_z(r) \\ B &= \mathcal{D}_A[-2/\Delta r^2]/V_z(r) \\ C &= \mathcal{D}_A[-1/(2r \Delta r) + 1/\Delta r^2]/V_z(r) \end{aligned} \quad (8.20)$$

Equation (8.19) is identical to Equation (8.12) in the limit as $\Delta r \rightarrow 0$ and is a reasonable approximation to it for small but finite Δr . It can be rewritten in terms of the index variable i . For $i = 1, \dots, I - 1$,

$$\frac{da(i, z)}{dz} = A(i)a(i + 1, z) + B(i)a(i, z) + C(i)a(i - 1, z) + \mathcal{R}_A/V_z(i) \quad (8.21)$$

In this formulation, the concentrations have been discretized and are now given by a set of ODEs—a typical member of the set being Equation (8.21), which

applies for $i = 1$ to $i = I - 1$. As indicated by the notation in Equation (8.21), A , B , and C depend on i since, as shown by Equation (8.20), they depend on $r = i \Delta r$. Special forms, developed below, apply at the centerline where $i = 0$ and at the wall where $i = I$.

Equation (8.12) becomes indeterminate at the centerline since both r and $\partial a / \partial r$ go to zero. Application of L'Hospital's rule gives a special form for $r = 0$:

$$\frac{\partial a}{\partial z} = \frac{\mathcal{D}_A}{V_z(0)} \left[2 \frac{\partial^2 a}{\partial z^2} \right] + \frac{\mathcal{R}_A}{V_z(0)} \quad \text{at } r = 0$$

Applying the difference approximation of Equation (8.18) and noting that $a(1, z) = a(-1, z)$ due to the assumed symmetry at the centerline gives

$$\frac{da}{dz} = A(0) a(1, z) + B(0) a(0, z) + (\mathcal{R}_A)_0 / V_z(0) \quad \text{at } r = 0 \quad (8.22)$$

where

$$\begin{aligned} A(0) &= \mathcal{D}_A [4 / \Delta r^2] / V_z(0) \\ B(0) &= \mathcal{D}_A [-4 / \Delta r^2] / V_z(0) \end{aligned} \quad (8.23)$$

The concentration at the wall, $a(I)$, is found by applying the zero flux boundary condition, Equation (8.14). A simple way is to set $a(I) = a(I - 1)$ since this gives a zero first derivative. However, this approximation to a first derivative converges only $\mathbf{O}(\Delta r)$ while all the other approximations converge $\mathbf{O}(\Delta r^2)$. A better way is to use

$$a_{\text{new}}(I) = \frac{4a_{\text{new}}(I - 1) - a_{\text{new}}(I - 2)}{3} \quad (8.24)$$

which converges $\mathbf{O}(\Delta r^2)$. This result comes from fitting $a(i)$ as a quadratic in i in the vicinity of the wall. The constants in the quadratic are found from the values of $a(I - 1)$ and $a(I - 2)$ and by forcing $\partial a / \partial r = 0$ at the wall. Alternatively, Equation (8.24) is obtained by using a second-order, forward difference approximation for the derivative at $r = R$. See Appendix 8.2.

Equations (8.21) and (8.22) constitute a set of simultaneous ODEs in the independent variable z . The dependent variables are the $a(i)$ terms. Each ODE is coupled to the adjacent ODEs; i.e., the equation for $a(i)$ contains $a(i - 1)$ and $a(i + 1)$. Equation (8.24) is a special, degenerate member of the set, and Equation (8.22) for $a(0)$ is also special because, due to symmetry, there is only one adjacent point, $a(1)$. The overall set may be solved by any desired method. Euler's method is discussed below and is illustrated in Example 8.5. There are a great variety of commercial and freeware packages available for solving simultaneous ODEs. Most of them even work. Packages designed for stiff equations are best. The stiffness arises from the fact that $V_z(i)$ becomes very small near the tube wall. There are also software packages that will handle the discretization automatically.

8.3.2 Euler's Method

Euler's method for solving the above set of ODEs uses a first-order, forward difference approximation in the z -direction, Equation (8.16). Substituting this into Equation (8.21) and solving for the forward point gives

$$a_{\text{new}}(i) = A(i)\Delta z a_{\text{old}}(i+1) + [1 + B(i)\Delta z]a_{\text{old}}(i) + C(i)\Delta z a_{\text{old}}(i-1) + (\mathcal{R}_A)_i \Delta z / V_z(i) \quad \text{for } i = 1 \text{ to } I-1 \quad (8.25)$$

where A , B , and C are given by Equation (8.20). The equation for the centerline is

$$a_{\text{new}}(0) = A(0)\Delta z a_{\text{old}}(1) + [1 + B(0)\Delta z]a_{\text{old}}(0) + (\mathcal{R}_A)_0 \Delta z / V_z(0) \quad (8.26)$$

where A and B are given by Equation (8.23). The wall equation finishes the set:

$$a_{\text{new}}(I) = \frac{4a_{\text{new}}(I-1) - a_{\text{new}}(I-2)}{3} \quad (8.27)$$

Equations (8.25) through (8.27) allow concentrations to be calculated at the "new" axial position, $z + \Delta z$, given values at the "old" position, z . If there is no reaction, the new concentration is a weighted average of the old concentrations at three different radial positions, $r + \Delta r$, r , and $r - \Delta r$. In the absence of reaction, there is no change in the average composition, and any concentration fluctuations will gradually smooth out. When the reaction term is present, it is evaluated at the old i th point. Figure 8.2 shows a diagram of the computational scheme. The three circled points at axial position z are used to calculate the new value at the point $z + \Delta z$. The dotted lines in Figure 8.2 show how the radial position r can be changed to determine concentrations for the various values of i . The complete radial profile at $z + \Delta z$ can be found from knowledge of the profile at z . The profile at $z = 0$ is known from the inlet boundary condition, Equation (8.13). The marching-ahead procedure can be used to find the profile at $z = \Delta z$, and so on, repeating the procedure in a stepwise manner until the end of the tube is reached. Colloquially, this solution technique can be called marching ahead with a sideways shuffle. It is worth noting that the axial step size Δz can be changed as the calculation proceeds. This may be necessary if the velocity profile changes during the course of the reaction, as discussed in Section 8.7.

Equations (8.25), (8.26), and (8.27) use the dimensioned independent variables, r and z , but use of the dimensionless variables, \bar{z} and \bar{r} , is often preferred. See Equations (8.56), (8.57), and (8.58) for an example.

A marching-ahead solution to a parabolic partial differential equation is conceptually straightforward and directly analogous to the marching-ahead method we have used for solving ordinary differential equations. The difficulties associated with the numerical solution are the familiar ones of accuracy and stability.

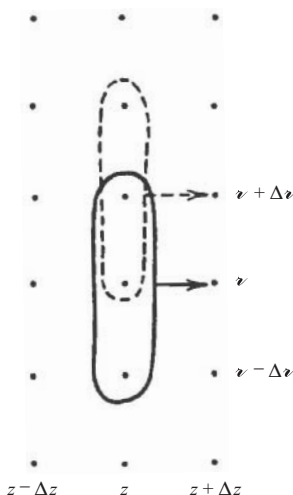


FIGURE 8.2 Computational template for marching-ahead solution.

8.3.3 Accuracy and Stability

The number of radial increments can be picked arbitrarily. A good approach is to begin with a small number, $I=4$, for debugging purposes. When the program is debugged, the value for I is successively doubled until a reasonable degree of accuracy is achieved or until computational times become excessive. If the latter occurs first, find a more sophisticated solution method or a faster computer.

Given a value for I and the corresponding value for Δr , it remains to determine Δz . The choice for Δz is not arbitrary but is constrained by stability considerations. One requirement is that the coefficients on the $a_{old}(i)$ and $a_{old}(0)$ terms in Equations (8.25) and (8.26) cannot be negative. Thus, the *numerical* (or *discretization*) *stability criterion* is

$$[1 + B(i)\Delta z] \geq 0 \quad \text{for} \quad i = 0 \text{ to } I - 1 \quad (8.28)$$

where $B(i)$ is obtained from Equations (8.20) or (8.23). Since $B(i)$ varies with radial position—i.e., with i —the stability criterion should be checked at all values of i . Normal velocity profiles will have $V_z(R)=0$ due to the zero-slip condition of hydrodynamics. For such profiles, the near-wall point, $r = R - \Delta r$, will generally give the most restrictive—i.e., smallest—value for Δz .

$$\Delta z_{max} = \frac{\Delta r^2 V_z(R - \Delta r)}{2\mathcal{D}_A} \quad (8.29)$$

This stability requirement is quite demanding. Superficially, it appears that Δz_{max} decreases as Δr^2 , but $V_z(R - \Delta r)$ is also decreasing, in approximate proportion to Δr . The net effect is that Δz_{max} varies as Δr^3 . Doubling the number of

radial points will increase the number of axial points by a factor of 8 and will increase the computation time by a factor of 16. The net effect is that Δz quickly becomes so small that the convergence order of the ODE-solver ceases to be important.

Equation (8.29) provides no guarantee of stability. It is a necessary condition for stability that is imposed by the discretization scheme. Practical experience indicates that it is usually a sufficient condition as well, but exceptions exist when reaction rates (or heat-generation rates) become very high, as in regions near thermal runaway. There is a second, *physical stability* criterion that prevents excessively large changes in concentration or temperature. For example, Δa , the calculated change in the concentration of a component that is consumed by the reaction, must be smaller than a itself. Thus, there are two stability conditions imposed on Δz : numerical stability and physical stability. Violations of either stability criterion are usually easy to detect. The calculation blows up. Example 8.8 shows what happens when the numerical stability limit is violated.

Regarding accuracy, the finite difference approximations for the radial derivatives converge $\mathbf{O}(\Delta r^2)$. The approximation for the axial derivative converges $\mathbf{O}(\Delta z)$, but the stability criterion forces Δz to decrease at least as fast as Δr^2 . Thus, the entire computation should converge $\mathbf{O}(\Delta r^2)$. The proof of convergence requires that the computations be repeated for a series of successively smaller grid sizes.

8.3.4 The Trapezoidal Rule

The final step in the design calculations for a laminar flow reactor is determination of mixing-cup averages based on Equation (8.4). The trapezoidal rule is recommended for this numerical integration because it is easy to implement and because it converges $\mathbf{O}(\Delta r^2)$ in keeping with the rest of the calculations.

For I equally sized increments in the radial direction, the general form for the trapezoidal rule is

$$\int_0^R F(r) dr \approx \Delta r \left[\frac{F(0)}{2} + \frac{F(I)}{2} + \sum_{i=1}^{I-1} F(i) \right] \quad (8.30)$$

For the case at hand,

$$F(r) = 2\pi r a(r) V_z(r) = 2\pi i \Delta r a(i) V_z(i) \quad (8.31)$$

Both $F(0)$ and $F(R)$ vanish for a velocity profile with zero slip at the wall. The mixing-cup average is determined when the integral of $F(r)$ is normalized by $Q = \pi R^2 \bar{u}$. There is merit in using the trapezoidal rule to calculate Q by integrating $dQ = 2\pi r V_z dr$. Errors tend to cancel when the ratio is taken.

The next few examples show the various numerical methods for a simple laminar flow reactor, gradually adding complications.

Example 8.2: An isothermal reactor with $L = 2$ m, $R = 0.01$ m is being used for a first-order reaction. The rate constant is 0.005 s^{-1} , and $\bar{u} = 0.01 \text{ m/s}$. Estimate the outlet concentration, assuming piston flow.

Solution: For piston flow, $a_{out} = a_{in} \exp(-kL/\bar{u})$ and $Y = a_{in}/a_{out} = \exp(-1) = 0.3679$.

Example 8.3: The reactor of Example 8.2 is actually in laminar flow with a parabolic velocity profile. Estimate the outlet concentration ignoring molecular diffusion.

Solution: Example 8.1 laid the groundwork for this case of laminar flow without diffusion. The mixing-cup average is

$$Y = \frac{a_{mix}(L)}{a_{in}} = \frac{\int_0^R 2\pi r V_z(r) \exp[-kL/V_z(r)] dr}{Q}$$

The following Excel macro illustrates the use of the trapezoidal rule for evaluating both the numerator and denominator in this equation.

```
DefDbl A-H, K-L, P-Z
DefLng I-J, M-O
Sub Exp8_3()
```

```
L=2
Ro=0.01
U=0.01
k=0.005
Itotal=2
```

```
For jj=1 To 8 'This outer loop varies the radial grid
                'size to test convergence
```

```
    Itotal=2 * Itotal
    dr=Ro/Itotal
    Range("A"& CStr(jj)).Select
    ActiveCell.FormulaR1C1=Itotal
```

```
    Fsum=0 'Set to F(0)/2+F(R)/2 for the general
            'trapezoidal rule
    Qsum=0 'Set to Q(0)/2+Q(R)/2 for the general
            'trapezoidal rule
```

```
    For i=1 To Itotal-1
        r=i * dr
        Vz=2 * U * (1-r ^ 2/Ro ^ 2)
```

```

Q=r * Vz 'Factor of 2*Pi omitted since it will
          'cancel in the ratio
F=Q * Exp( - k * L/Vz)
Fsum=Fsum + F * dr
Qsum=Qsum + Q * dr
Next i
aout=Fsum/Qsum

Range("B"& CStr(jj)).Select
ActiveCell.FormulaR1C1=aout

Next jj

End Sub

```

The results are

I	a_{out}/a_{in}
4	0.46365
8	0.44737
16	0.44413
32	0.44344
64	0.44327
128	0.44322
256	0.44321
512	0.44321

The performance of the laminar flow reactor is appreciably worse than that of a PFR, but remains better than that of a CSTR (which gives $Y=0.5$ for $k\bar{t}=1$). The computed value of 0.4432 may be useful in validating more complicated codes that include diffusion.

Example 8.4: Suppose that the reactive component in the laminar flow reactor of Example 8.2 has a diffusivity of $5 \times 10^{-9} \text{ m}^2/\text{s}$. Calculate the minimum number of axial steps, J , needed for discretization stability when the radial increments are sized using $I=4, 8, 16, 32, 64$, and 128. Also, suggest some actual step sizes that would be reasonable to use.

Solution: Begin with $I=4$ so that $\Delta r=R/I=0.0025 \text{ m}$. The near-wall velocity occurs at $r=R-\Delta r=0.0075 \text{ m}$:

$$V_z = 2\bar{u}[1 - r^2/R^2] = 0.02[1 - 0.0075^2/(0.01)^2] = 0.00875 \text{ m/s}$$

$$\Delta z_{max} = \Delta r^2 V_z (R - \Delta r) / [2\mathcal{D}_A] = (0.0025)^2 (0.00875) / (2/5 \times 10^{-9}) = 5.47 \text{ m}$$

$J_{min} = L/\Delta z_{max} = 2/5.47 = 0.3656$, but this must be rounded up to an integer. Thus, $J_{min}=1$ for $I=4$. Repeating the calculations for the other

values of I gives

I	J_{min}	J_{used}
4	1	2
8	3	4
16	22	32
32	167	256
64	1322	2048
128	10527	16384

The third column represents choices for J that are used in the examples that follow. For $I=8$ and higher, they increase by a factor of 8 as I is doubled.

Example 8.5: Use the method of lines combined with Euler's method to determine the mixing-cup average outlet for the reactor of Example 8.4.

Solution: For a first-order reaction, we can arbitrarily set $a_{in} = 1$ so that the results can be interpreted as the fraction unreacted. The choices for I and J determined in Example 8.4 will be used. The marching-ahead procedure uses Equations (8.25), (8.26), and (8.27) to calculate concentrations. The trapezoidal rule is used to calculate the mixing-cup average at the end of the reactor. The results are

I	J	a_{out}/a_{in}
4	1	0.37363
8	4	0.39941
16	32	0.42914
32	256	0.43165
64	2048	0.43175
128	16384	0.43171

These results were calculated using the following Excel macro:

```

DefDbl A-H, K-L, P-Z
DefLng I-J, M-O
Sub Fig8_1()
Dim aold(256), anew(256), Vz(256)
Dim A(256), B(256), C(256), D(256)

ain=1
Da=0.000000005
L=2
R=0.01
U=0.01
k=0.005
Itotal=2

```

```

For jj=1 To 7 'This outer loop varies Itotal to check
               'convergence

    Itotal=2 * Itotal
    If Itotal=4 Then JTotal=2
    If Itotal=8 Then JTotal=4
    If Itotal > 8 Then JTotal=8 * JTotal
    dr=R/Itotal
    dz=L/JTotal

'Set constants in Equation 8.26
    A(0)=4 * Da/dr ^ 2 * dz/2/U
    B(0)=-4 * Da/dr ^ 2 * dz/2/U
    D(0)=-k * dz/2/U
    aold(0)=1

'Set constants in Equation 8.25
    For i=1 To Itotal - 1
        Vz(i)=2 * U * (1 - (i * dr) ^ 2/R ^ 2)
        A(i)=Da * (1/(2 * dr ^ 2 * i) + 1/dr ^ 2) * dz/Vz(i)
        B(i)=Da * (-2/dr ^ 2) * dz/Vz(i)
        C(i)=Da * (-1/(2 * dr ^ 2 * i) + 1/dr ^ 2) * dz/Vz(i)
        D(i)=-k * dz/Vz(i)
        aold(i)=1
    Next

'Set the initial conditions
    For i=0 To Itotal
        aold(i)=ain
    Next

'March down the tube
    For j=1 To JTotal
        anew(0)=A(0) * aold(1) + (1+B(0)) * aold(0)
        +D(0) * aold(0)

'This is the sideways shuffle
    For i=1 To Itotal-1
        x=A(i) * aold(i+1) + (1+B(i)) * aold(i)
        anew(i)=x+C(i) * aold(i-1) +D(i) * aold(i)
    Next j
    Next i

'Apply the wall boundary condition, Equation 8.27

```

```

anew(Itotal) = 4 * anew(Itotal - 1) / 3 - anew(Itotal - 2) / 3
'March a step forward
  For i = 0 To Itotal
    aold(i) = anew(i)
  Next i
'Calculate the mixing cup average
  F = 0
  Q = 0
  For i = 1 To Itotal - 1
    F = F + 2 * dr * i * Vz(i) * anew(i)
    Q = Q + 2 * dr * i * Vz(i)
  Next i
  Y = F / Q

'Output results for this mesh size
Range("A"& CStr(jj)).Select
ActiveCell.FormulaR1C1 = Itotal
Range("B"& CStr(jj)).Select
ActiveCell.FormulaR1C1 = JTotal
Range("C"& CStr(jj)).Select
ActiveCell.FormulaR1C1 = Y

Next jj

End Sub

```

Example 8.5 has $\mathcal{D}_A \bar{t} / R^2 = 0.01$. Since this is larger than 0.003, diffusion should have some effect according to Merrill and Hamrin. The diffusion-free result for $k\bar{t} = 1$ was found to be $Y = 0.4432$ in Example 8.3. The Example 8.5 result of 0.4317 is closer to piston flow, as expected.

8.3.5 Use of Dimensionless Variables

Example 8.5 used the natural, physical variables and the natural dimensions of the problem. A good case can be made for this practice. It is normal in engineering design since it tends to keep the physics of the design transparent and avoids errors, particularly when using physical property correlations. However, it is desirable to use dimensionless variables when results are being prepared for general use, as in a literature publication or when the calculations are so lengthy that rerunning them would be cumbersome. The usual approach in the chemical engineering literature is to introduce scaled, dimensionless independent variables quite early in the analysis of a problem.

The use of dimensionless variables will be illustrated using Equation (8.12) but with an added term for axial diffusion:

$$V_z(r) \frac{\partial a}{\partial z} = \mathcal{D}_A \left[\frac{\partial^2 a}{\partial z^2} + \frac{1}{r} \frac{\partial a}{\partial r} + \frac{\partial^2 a}{\partial r^2} \right] + \mathcal{R}_A \quad (8.32)$$

There are two independent variables, z and r . Both are lengths. They can be scaled separately using two different characteristic lengths or they can be scaled using a single characteristic length. We use two different lengths and define new variables $\mathcal{z} = z/L$ and $\mathcal{r} = r/R$ so that they both have a range from 0 to 1. Substituting the new variables into Equation (8.32) and doing some algebra gives

$$\frac{\partial a}{\partial \mathcal{z}} = \left(\frac{\mathcal{D}_A L}{R^2 V_z} \right) \left[\left(\frac{R^2}{L^2} \right) \frac{\partial^2 a}{\partial \mathcal{z}^2} + \frac{1}{\mathcal{r}} \frac{\partial a}{\partial \mathcal{r}} + \frac{\partial^2 a}{\partial \mathcal{r}^2} \right] + \mathcal{R}_A L / V_z \quad (8.33)$$

When expressed in the scaled variables, the $\partial^2 a / \partial \mathcal{z}^2$ and $\partial^2 a / \partial \mathcal{r}^2$ terms have the same magnitude, but the $\partial^2 a / \partial \mathcal{z}^2$ term is multiplied by a factor of R^2/L^2 that will not be larger than 0.01. Thus, this term, which corresponds to axial diffusion, may be neglected, consistent with the conclusion in Section 8.2.

The velocity profile is scaled by the mean velocity, \bar{u} , giving the dimensionless profile $\mathcal{V}_z(\mathcal{r}) = V_z(r)/\bar{u}$. To complete the conversion to dimensionless variables, the dependent variable, a , is divided by its nonzero inlet concentration. The dimensionless version of Equation (8.12) is

$$\mathcal{V}_z(\mathcal{r}) \frac{\partial a^*}{\partial \mathcal{z}} = \left(\frac{\mathcal{D}_A \bar{t}}{R^2} \right) \left[\frac{1}{\mathcal{r}} \frac{\partial a^*}{\partial \mathcal{r}} + \frac{\partial^2 a^*}{\partial \mathcal{r}^2} \right] + \mathcal{R}_A \bar{t} / a_{in} \quad (8.34)$$

where $\bar{t} = L/\bar{u}$. Equation (8.34) contains the dimensionless number $\mathcal{D}_A \bar{t} / R^2$ that appears in Merrill and Hamrin's criterion, Equation (8.3), and a dimensionless reaction rate, $\mathcal{R}_A \bar{t} / a_{in}$. Merrill and Hamrin assumed a first-order reaction, $\mathcal{R}_A = -ka$, and calculated $a_{out} = a_{mix}(L)$ for various values of $\mathcal{D}_A \bar{t} / R^2$. They concluded that diffusion had a negligible effect on a_{out} when Equation (8.3) was satisfied.

The stability criterion, Equation (8.29), can be converted to dimensionless form. The result is

$$\Delta \mathcal{z}_{max} = I / J_{min} = \frac{\Delta z_{max}}{L} = \frac{\Delta \mathcal{z}^2 \mathcal{V}_z(1 - \Delta \mathcal{z})}{2[\mathcal{D}_A \bar{t} / R^2]} \quad (8.35)$$

and for the special case of a parabolic profile,

$$\Delta \mathcal{z}_{max} = \frac{\Delta \mathcal{z}^3 [2 - \Delta \mathcal{z}]}{2[\mathcal{D}_A \bar{t} / R^2]} \quad (8.36)$$

Example 8.6: Generalize Example 8.5 to determine the fraction unreacted for a first-order reaction in a laminar flow reactor as a function of the dimensionless groups $\mathcal{D}_A \bar{t}/R^2$ and $k\bar{t}$. Treat the case of a parabolic velocity profile.

Solution: The program of Example 8.5 can be used with minor modifications. Set U , R , and L all equal to 1. Then $\mathcal{D}_A \bar{t}/R^2$ will be equal to the value assigned to Da and $k\bar{t}$ will be equal to the value assigned to k . It is necessary to use the stability criterion to determine J . Example 8.5 had $\mathcal{D}_A \bar{t}/R^2 = 0.01$, and larger values for $\mathcal{D}_A \bar{t}/R^2$ require larger values for J .

Figure 8.1 includes a curve for laminar flow with $\mathcal{D}_A \bar{t}/R^2 = 0.1$. The performance of a laminar flow reactor with diffusion is intermediate between piston flow and laminar flow without diffusion, $\mathcal{D}_A \bar{t}/R^2 = 0$. Laminar flow reactors give better conversion than CSTRs, but do not generalize this result too far! It is restricted to a parabolic velocity profile. Laminar velocity profiles exist that, in the absence of diffusion, give reactor performance far worse than a CSTR.

Regardless of the shape of the velocity profile, radial diffusion will improve performance, and the case $\mathcal{D}_A \bar{t}/R^2 \rightarrow \infty$ corresponds to piston flow.

The thoughtful reader may wonder about a real reactor with a high level of radial diffusion. Won't there necessarily be a high level of axial diffusion as well and won't the limit of $\mathcal{D}_A \bar{t}/R^2 \rightarrow \infty$ really correspond to a CSTR rather than a PFR? The answer to this question is "yes, but . . ." The "but" is based on the restriction that $L/R > 16$. For reasonably long reactors, the effects of radial diffusion dominate those of axial diffusion until extremely high values of $\mathcal{D}_A \bar{t}/R^2$. If reactor performance is considered as a function of $\mathcal{D}_A \bar{t}/R^2$ (with $k\bar{t}$ fixed), there will be an interior maximum in performance as $\mathcal{D}_A \bar{t}/R^2 \rightarrow \infty$. This is the piston flow limit illustrated in Figure 8.3. There is another limit, that of a perfectly mixed flow reactor, which occurs at much higher values of $\mathcal{D}_A \bar{t}/R^2$ than those shown in Figure 8.3. The tools needed to quantify this idea are developed in Chapter 9. See Problem 9.11, but be warned that the computations are difficult and of limited utility.

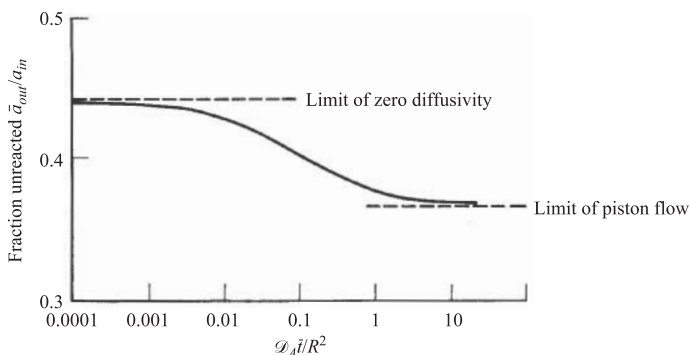


FIGURE 8.3 First-order reaction with $k\bar{t} = 1$ in a tubular reactor with a parabolic velocity profile.

8.4 SLIT FLOW AND RECTANGULAR COORDINATES

Results to this point have been confined to tubular reactors with circular cross sections. Tubes are an extremely practical geometry that is widely used for chemical reactors. Less common is slit flow such as occurs between closely spaced parallel plates, but practical heat exchangers and reactors do exist with this geometry. They are used when especially good mixing is needed within the cross section of the reactor. Using spiral-wound devices or stacked flat plates, it is practical to achieve slit heights as small as 0.003 m. This is far smaller than is feasible using a conventional, multitubular design.

Figure 8.4 illustrates pressure-driven flow between flat plates. The downstream direction is z . The cross-flow direction is y , with $y=0$ at the centerline and $y=\pm Y$ at the walls so that the channel height is $2Y$. Suppose the slit width (x -direction) is very large so that sidewall effects are negligible. The velocity profile for a laminar, Newtonian fluid of constant viscosity is

$$V_z(y) = 1.5\bar{u} \left[1 - \frac{y^2}{Y^2} \right] \quad (8.37)$$

The analog of Equation (8.12) in rectangular coordinates is

$$V_z(y) \frac{\partial a}{\partial z} = \mathcal{D}_A \left[\frac{\partial^2 a}{\partial y^2} \right] + \mathcal{R}_A \quad (8.38)$$

The boundary conditions are

$$\begin{aligned} a &= a_{in}(y) & \text{at } z &= 0 \\ \partial a / \partial y &= 0 & \text{at } y &= 0 \\ \partial a / \partial y &= 0 & \text{at } y &= \pm Y \end{aligned} \quad (8.39)$$

The zero slope boundary condition at $y=0$ assumes symmetry with respect to the centerline. The mathematics are then entirely analogous to those for the tubular geometries considered previously. Applying the method of lines gives

$$\frac{\partial a(y, z)}{\partial z} = Aa(y + \Delta y, z) + Ba(y, z) + C(y - \Delta y, z) + \frac{\mathcal{R}_A}{V_z(y)} \quad (8.40)$$

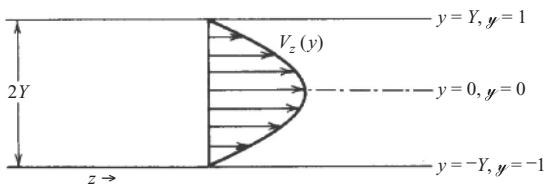


FIGURE 8.4 Pressure driven flow between parallel plates with both plates stationary.

$$\begin{aligned}
 A &= \frac{\mathcal{D}_A}{V_z} \left[\frac{1}{\Delta y^2} \right] \\
 B &= \frac{\mathcal{D}_A}{V_z} \left[\frac{-2}{\Delta y^2} \right] \\
 C &= \frac{\mathcal{D}_A}{V_z} \left[\frac{1}{\Delta y^2} \right] = A
 \end{aligned}
 \tag{8.41}$$

With these revised definitions for A , B , and C , the marching-ahead equation for the interior points is identical to that for cylindrical coordinates, Equation (8.25). The centerline equation is no longer a special case except for the symmetry boundary condition that forces $a(-1) = a(1)$. The centerline equation is thus

$$a_{\text{new}}(0) = 2A(0) \Delta z a_{\text{old}}(1) + [1 + B(0) \Delta z] a_{\text{old}}(0) + (\mathcal{R}_A)_0 \Delta z / V_z(0) \tag{8.42}$$

The wall boundary condition is unchanged, Equation (8.27).

The near-wall stability condition is

$$\Delta z_{\text{max}} = \frac{\Delta y^2 V_z(Y - \Delta y)}{2\mathcal{D}_A} \tag{8.43}$$

Mixing-cup averages are calculated using

$$F(i) = a(i) V_z(i) \tag{8.44}$$

instead of Equation (8.31), and Q can be obtained by integrating $dQ = V_z(y) dy$.

Example 8.7: Determine the flat-plate equivalent to Merrill and Hamrin's criterion.

Solution: Transform Equation (8.38) using the dimensionless independent variables $\mathcal{y} = z/L$ and $y = y/Y$:

$$\mathcal{V}_z(\mathcal{y}) \frac{\partial a}{\partial \mathcal{y}} = \left(\frac{\mathcal{D}_A \bar{t}}{Y^2} \right) \left[\frac{\partial^2 a}{\partial y^2} \right] + \mathcal{R}_A \bar{t} \tag{8.45}$$

Comparing this equation with Equation (8.34) shows that $\mathcal{D}_A \bar{t} / Y^2$ is the flat-plate counterpart of $\mathcal{D}_A \bar{t} / R^2$. We thus seek a value for $\mathcal{D}_A \bar{t} / Y^2$ below which diffusion has a negligible effect on the yield of a first-order reaction.

For comparison purposes, set $k\bar{t} = 1$ and compute $a_{\text{out}}/a_{\text{in}}$ for the tubular case with $\mathcal{D}_A \bar{t} / R^2 = 0$ and with $\mathcal{D}_A \bar{t} / R^2 = 0.003$. The results using the programs in Examples 8.3 and 8.5 with $I = 128$ are 0.44321 and 0.43849, respectively. Thus, Merrill and Hamrin considered the difference between 0.44321 and 0.43849 to be negligible.

Turn now to the flat-plate geometry. The coefficients A , B , and C , and the mixing-cup averaging technique must be revised. This programming exercise is left to the reader. Run the modified program with $k\bar{t} = 1$ but without

diffusion to give $a_{out}/a_{in}=0.41890$ for $I=128$ and $J=16382$. The flat-plate geometry gives better performance than the tube. Why?

To ensure an apples-to-apples comparison, reduce $k\bar{t}$ until a_{out}/a_{in} matches the value of 0.44321 achieved in the tube. This is found to occur at $k\bar{t}=0.9311$. Diffusion is now added until $a_{out}/a_{in}=0.43849$ as in the case of a circular tube with $\mathcal{D}_A\bar{t}/R^2=0.003$. This is found to occur at about $\mathcal{D}_A\bar{t}/Y^2=0.008$. Thus, the flat-plate counterpart to the Merrill and Hamrin criterion is

$$\mathcal{D}_A\bar{t}/Y^2 < 0.008 \quad (8.46)$$

8.5 SPECIAL VELOCITY PROFILES

This section considers three special cases. The first is a flat velocity profile that can result from an extreme form of fluid rheology. The second is a linear profile that results from relative motion between adjacent solid surfaces. The third special case is for motionless mixers where the velocity profile is very complex, but its net effects can sometimes be approximated for reaction engineering purposes.

8.5.1 Flat Velocity Profiles

Flow in a Tube. Laminar flow with a flat velocity profile and slip at the walls can occur when a viscous fluid is strongly heated at the walls or is highly non-Newtonian. It is sometimes called *toothpaste flow*. If you have ever used Stripe[®] toothpaste, you will recognize that toothpaste flow is quite different than piston flow. Although $V_z(r)=\bar{u}$ and $\mathcal{V}_z(z)=1$, there is little or no mixing in the radial direction, and what mixing there is occurs by diffusion. In this situation, the centerline is the critical location with respect to stability, and the stability criterion is

$$\Delta z_{max} = \frac{\Delta r^2 \bar{u}}{4\mathcal{D}_A} \quad (8.47)$$

and Δz_{max} varies as Δr^2 . The flat velocity profile and Equation (8.47) apply to the packed-bed models treated in Chapter 9. The marching-ahead equations are unchanged from those presented in Section 8.3.1, although the coefficients must be evaluated using the flat profile.

Toothpaste flow is an extreme example of non-Newtonian flow. Problem 8.2 gives a more typical example. Molten polymers have velocity profiles that are flattened compared with the parabolic distribution. Calculations that assume a parabolic profile will be conservative in the sense that they will predict a lower conversion than would be predicted for the actual profile. The changes in velocity profile due to variations in temperature and composition are normally much more important than the fairly subtle effects due to non-Newtonian behavior.

In this example, an initial steady-state solution with $a=0$ is propagated downstream. At the fourth axial position, the concentration in one cell is increased to 16. This can represent round-off error, a numerical blunder, or the injection of a tracer. Whatever the cause, the magnitude of the upset decreases at downstream points and gradually spreads out due to diffusion in the y -direction. The total quantity of injected material (16 in this case) remains constant. This is how a real system is expected to behave. The solution technique conserves mass and is stable.

Now consider a case where A violates the stability criterion. Pick $A=1$ to give

$$a_{\text{new}}(i) = a_{\text{old}}(i+1) - a_{\text{old}}(i) + a_{\text{old}}(i-1)$$

The solution now becomes

0	0	0	0	0	0	0	0	16
0	0	0	0	0	0	0	16	-80
0	0	0	0	0	0	16	-64	240
0	0	0	0	0	16	-48	160	-480
0	0	0	0	16	-32	96	-256	720
0	0	0	16	-16	48	-112	304	-816
0	0	0	0	16	-32	96	-256	720
0	0	0	0	0	16	-48	160	-480
0	0	0	0	0	0	16	-64	240
0	0	0	0	0	0	0	16	-80
0	0	0	0	0	0	0	0	16

This equation continues to conserve mass but is no longer stable. The original upset grows exponentially in magnitude and oscillates in sign. This marching-ahead scheme is clearly unstable in the presence of small blunders or round-off errors.

8.5.2 Flow Between Moving Flat Plates

Figure 8.5 shows another flow geometry for which rectangular coordinates are useful. The bottom plate is stationary but the top plate moves at velocity $2\bar{u}$.

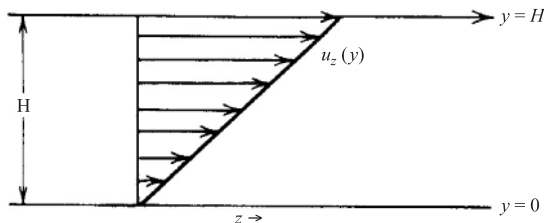


FIGURE 8.5 Drag flow between parallel plates with the upper plate in motion and no axial pressure drop.

The plates are separated by distance H , and the y -coordinate starts at the bottom plate. The velocity profile is linear:

$$V_z = \frac{2\bar{u}y}{H} \quad (8.51)$$

This velocity profile is commonly called drag flow. It is used to model the flow of lubricant between sliding metal surfaces or the flow of polymer in extruders. A pressure-driven flow—typically in the opposite direction—is sometimes superimposed on the drag flow, but we will avoid this complication. Equation (8.51) also represents a limiting case of Couette flow (which is flow between coaxial cylinders, one of which is rotating) when the gap width is small. Equation (8.38) continues to govern convective diffusion in the flat-plate geometry, but the boundary conditions are different. The zero-flux condition applies at both walls, but there is no line of symmetry. Calculations must be made over the entire channel width and not just the half-width.

8.5.3 Motionless Mixers

Most motionless or static mixers consist of tubes or ducts in which stationary vanes (elements) have been installed to promote radial flow. There are many commercial types, some of which are shown in Figure 8.6. Similar results can be achieved in deep laminar flow by using a series of helically coiled tubes where the axis of each successive coil is at a 90° angle to the previous coil axis.⁴ With enough static mixing elements or helical coils in series, piston flow can be approached. The flow geometry is complex and difficult to analyze. Velocity profiles, streamlines, and pressure drops can be computed using programs for *computational fluid dynamics* (CFD), such as Fluent[®], but these computations have not yet become established and verified as design tools. The axial dispersion model discussed in Chapter 9 is one approach to data correlation. Another approach is to use Equation (8.12) for segments of the reactor but to periodically reinitialize the concentration profile. An empirical study⁵ on Kenics-type static mixers found that four of the Kenics elements correspond to one zone of complete radial mixing. The computation is as follows:

1. Start with a uniform concentration profile, $a(z) = a_m$ at $z = 0$.
2. Solve Equation (8.12) using the methods described in this chapter and ignoring the presence of the mixing elements.
3. When an axial position corresponding to four mixing elements is reached, calculate the mixing-cup average composition a_{mix} .
4. Restart the solution of Equation (8.12) using a uniform concentration profile equal to the mixing-cup average, $a(z) = a_{mix}$.
5. Repeat Steps 2 through 4 until the end of the reactor is reached.

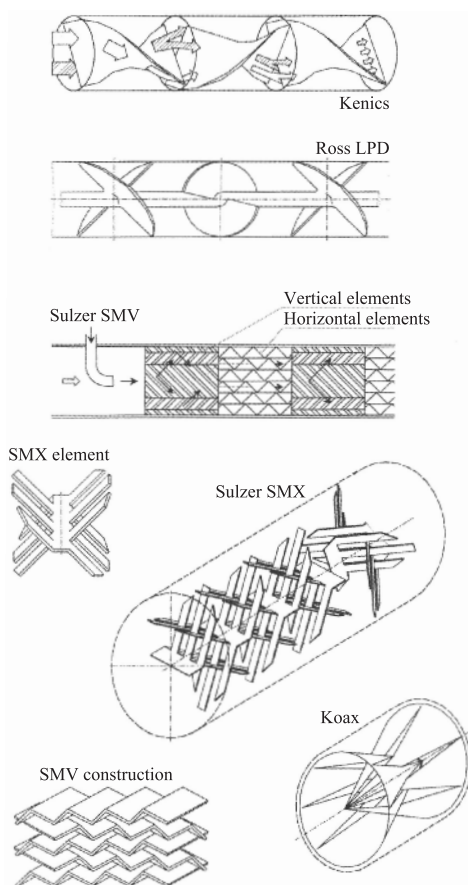


FIGURE 8.6 Commercial motionless mixers. (Drawing courtesy of Professor Pavel Dittl, Czech Technical University.)

This technique should give reasonable results for isothermal, first-order reactions. It and other modeling approaches are largely untested for complex and nonisothermal reactions.

8.6 CONVECTIVE DIFFUSION OF HEAT

Heat diffuses much like mass and is governed by similar equations. The temperature analog of Equation (8.12) is

$$V_z(r) \frac{\partial T}{\partial z} = \alpha_T \left[\frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} \right] - \frac{\Delta H_R \mathcal{R}}{\rho C_P} \quad (8.52)$$

where α_T is the thermal diffusivity and $\Delta H_R \mathcal{R}$ follows the summation convention of Equation (5.17). The units on thermal diffusivity are the same as those on molecular diffusivity, m^2/s , but α_T will be several orders of magnitude larger than \mathcal{D}_A . The reason for this is that mass diffusion requires the actual displacement of molecules but heat can be transferred by vibrations between more-or-less stationary molecules or even between parts of a molecule as in a polymer chain. Note that $\alpha_T = \lambda/(\rho C_P)$, where λ is the thermal conductivity. Equation (8.52) assumes constant α_T and ρ . The assumption of constant density ignores expansion effects that can be significant in gases that are undergoing large pressure changes. Also ignored is viscous dissipation, which can be important in very high-viscosity fluids such as polymer melts. Standard texts on transport phenomena give the necessary embellishments of Equation (8.52).

The inlet and centerline boundary conditions associated with Equation (8.52) are similar to those used for mass transfer:

$$T = T_{in}(r) \quad \text{at} \quad z = 0 \quad (8.53)$$

$$\partial T / \partial r = 0 \quad \text{at} \quad r = 0 \quad (8.54)$$

The usual wall boundary condition is

$$T = T_{wall}(z) \quad \text{at} \quad r = R \quad (8.55)$$

but the case of an insulated wall,

$$\partial T / \partial r = 0 \quad \text{at} \quad r = R$$

is occasionally used.

Equation (8.52) has the same form as Equation (8.12), and the solution techniques are essentially identical. Replace a with T , \mathcal{D}_A with α_T , and \mathcal{R}_A with $-\Delta H_R \mathcal{R}/(\rho C_P)$, and proceed as in Section 8.3.

The equations governing the convective diffusion of heat and mass are coupled through the temperature and composition dependence of the reaction rates. In the general case, Equation (8.52) is solved simultaneously with as many versions of Equation (8.12) as there are reactive components. The method of lines treats a single PDE as $I - 1$ simultaneous ODEs. The general case has $N + 1$ PDEs and thus is treated as $(N + 1)(I - 1)$ ODEs. Coding is easiest when the same axial step size is used for all the ODEs, but this step size must satisfy the most restrictive of the stability criteria. These criteria are given by Equation (8.29) for the various chemical species. The stability criterion for temperature is identical except that α_T replaces the molecular diffusivities and α_T is much larger, which leads to smaller step sizes. Thus, the step size for the overall program will be imposed by the stability requirement for the temperature equation. It may be that accurate results require very small axial steps and excessive computer time. Appendix 8.3 describes alternative finite difference approximations that eliminate the discretization stability condition. Algorithms exist where $\Delta z \sim \Delta r$ rather than $\Delta z \sim \Delta r^2$ (flat profile) or $\Delta z \sim \Delta r^3$ (parabolic

profile) so that the number of computations increases by a factor of only 4 (rather than 8 or 16) when Δr is halved. The price for this is greater complexity in the individual calculations.

The equations governing convective diffusion of heat in rectangular-coordinate systems are directly analogous to those governing convective diffusion of mass. See Sections 8.4 and 8.5. The wall boundary condition is usually a specified temperature, and the stability criterion for the heat transfer equation is usually more demanding (smaller Δz_{max}) than that for mass transfer. Also, in slit flow problems, there is no requirement that the two walls be at the same temperature. When the wall temperatures are different, the marching-ahead equations must be applied to the entire slit width, and not just the half-width, since the temperature profiles (and the corresponding composition profiles) will not be symmetric about the centerline. There are no special equations for the centerline. Instead, the ordinary equation for an interior point e.g., Equation (8.40), is used throughout the interior with $a(y) \neq a(-y)$ and $T(y) \neq T(-y)$.

8.6.1 Dimensionless Equations for Heat Transfer

Transformation of the independent variables to dimensionless form uses $\bar{z} = r/R$ and $\bar{y} = z/L$. In most reactor design calculations, it is preferable to retain the dimensions on the dependent variable, temperature, to avoid confusion when calculating the Arrhenius temperature dependence and other temperature-dependent properties. The following set of marching-ahead equations are functionally equivalent to Equations (8.25)–(8.27) but are written in dimensionless form for a circular tube with temperature (still dimensioned) as the dependent variable. For the centerline,

$$T(0, \bar{y} + \Delta \bar{y}) = \left[1 - 4 \left(\frac{\bar{u} \alpha_T \bar{t}}{\mathcal{V}_z(0) R^2} \right) \frac{\Delta \bar{y}}{\Delta \bar{z}^2} \right] T(0, \bar{y}) + 4 \left(\frac{\bar{u} \alpha_T \bar{t}}{\mathcal{V}_z(0) R^2} \right) \frac{\Delta \bar{y}}{\Delta \bar{z}^2} T(\Delta \bar{z}, \bar{y}) - \frac{\Delta H_R \mathcal{R} \bar{t} \bar{u}}{\rho C_P \mathcal{V}_z(0)} \Delta \bar{y} \quad (8.56)$$

For interior points,

$$T(\bar{z}, \bar{y} + \Delta \bar{y}) = \left[1 - 2 \left(\frac{\bar{u} \alpha_T \bar{t}}{\mathcal{V}_z(\bar{z}) R^2} \right) \frac{\Delta \bar{y}}{\Delta \bar{z}^2} \right] T(\bar{z}, \bar{y}) + \left(\frac{\bar{u} \alpha_T \bar{t}}{\mathcal{V}_z(\bar{z}) R^2} \right) \frac{\Delta \bar{y}}{\Delta \bar{z}^2} \left[1 + \frac{\Delta \bar{z}}{2 \bar{z}} \right] T(\bar{z} + \Delta \bar{z}, \bar{y}) + \left(\frac{\bar{u} \alpha_T \bar{t}}{\mathcal{V}_z(\bar{z}) R^2} \right) \frac{\Delta \bar{y}}{\Delta \bar{z}^2} \left[1 - \frac{\Delta \bar{z}}{2 \bar{z}} \right] T(\bar{z} - \Delta \bar{z}, \bar{y}) - \frac{\Delta H_R \mathcal{R} \bar{t} \bar{u}}{\rho C_P \mathcal{V}_z(\bar{z})} \Delta \bar{y} \quad (8.57)$$

At the wall,

$$T_{wall}(\mathcal{Y} + \Delta\mathcal{Y}) = \frac{4T(1 - \Delta z, \mathcal{Y} + \Delta\mathcal{Y}) - T(1 - 2\Delta z, \mathcal{Y} + \Delta\mathcal{Y})}{3} \quad (8.58)$$

The more restrictive of the following stability criteria is used to calculate $\Delta\mathcal{Y}_{max}$:

$$\frac{\Delta\mathcal{Y}}{\Delta z^2} \leq \frac{\mathcal{V}_z(z)R^2}{2\bar{u}\alpha_T\bar{t}} \quad \Delta z \leq z \leq 1 - \Delta z \quad (8.59)$$

$$\frac{\Delta\mathcal{Y}}{\Delta z^2} \leq \frac{\mathcal{V}_z(0)R^2}{4\bar{u}\alpha_T\bar{t}} \quad z = 0 \quad (8.60)$$

When the heat of reaction term is omitted, these equations govern laminar heat transfer in a tube. The case where T_{in} and T_{wall} are both constant and where the velocity profile is parabolic is known as the Graetz problem. An analytical solution to this linear problem dates from the 19th century but is hard to evaluate and is physically unrealistic. The smooth curve in Figure 8.7 corresponds to the analytical solution and the individual points correspond to a numerical solution found in Example 8.9. The numerical solution is easier to obtain but, of course, is no better at predicting the performance of a real heat exchanger. A major cause for the inaccuracy is the dependence of viscosity on temperature that causes changes in the velocity profile. Heating at the wall improves heat transfer while cooling hurts it. Empirical heat transfer

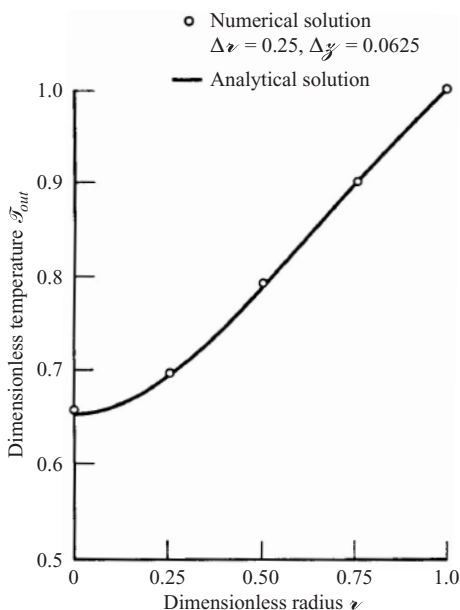


FIGURE 8.7 Numerical versus analytical solutions to the Graetz problem with $\alpha_T\bar{t}/R^2 = 0.4$.

correlations include a viscosity correction factor, e.g., the $(\mu_{bulk}/\mu_{wall})^{0.14}$ term in Equation (5.37). Section 8.7 takes a more fundamental approach by calculating $V_z(r)$ as it changes down the tube.

Example 8.9: Find the temperature distribution in a laminar flow, tubular heat exchanger having a uniform inlet temperature T_{in} and constant wall temperature T_{wall} . Ignore the temperature dependence of viscosity so that the velocity profile is parabolic everywhere in the reactor. Use $\alpha_T \bar{t}/R^2 = 0.4$ and report your results in terms of the dimensionless temperature

$$\mathcal{T} = (T - T_{in})/(T_{wall} - T_{in}) \quad (8.61)$$

Solution: A transformation to dimensionless temperatures can be useful to generalize results when physical properties are constant, and particularly when the reaction term is missing. The problem at hand is the classic Graetz problem and lends itself perfectly to the use of a dimensionless temperature. Equation (8.52) becomes

$$\mathcal{V}_z(z) \frac{\partial \mathcal{T}}{\partial \mathcal{Z}} = \left(\frac{\alpha_T \bar{t}}{R^2} \right) \left[\frac{1}{z} \frac{\partial \mathcal{T}}{\partial z} + \frac{\partial^2 \mathcal{T}}{\partial z^2} \right] + \frac{\Delta H_R \mathcal{R}_A(\mathcal{T}) \bar{t}}{a_{in} \rho C_p (T_{wall} - T_{in})} \quad (8.62)$$

but the heat of reaction term is dropped in the current problem. The dimensionless temperature ranges from $\mathcal{T} = 0$ at the inlet to $\mathcal{T} = 1$ at the walls. Since no heat is generated, $0 \leq \mathcal{T} \leq 1$ at every point in the heat exchanger. The dimensionless solution, $\mathcal{T}(z, \mathcal{Z})$, depends only on the value of $\alpha_T \bar{t}/R^2$ and is the same for all values of T_{in} and T_{wall} . The solution is easily calculated by the marching-ahead technique.

Use $\Delta z = 0.25$. The stability criterion at the near-wall position is obtained from Equation (8.36) with α_T replacing \mathcal{D}_A , or from Equation (8.59) evaluated at $z = 1 - \Delta z$. The result is

$$\Delta \mathcal{Z}_{max} = \frac{\Delta z^2 (2 \Delta z - \Delta z^2)}{(\alpha_T \bar{t}/R^2)} = 0.0684$$

which gives $J_{min} = 15$. Choose $J = 16$ so that $\Delta \mathcal{Z} = 0.0625$.

The marching-ahead equations are obtained from Equations (8.56)–(8.58). At the centerline,

$$\mathcal{T}(0, \mathcal{Z} + \Delta \mathcal{Z}) = 0.2000 \mathcal{T}(0, \mathcal{Z}) + 0.8000 \mathcal{T}(0.25, \mathcal{Z})$$

At the interior points,

$$\mathcal{T}(0.25, \mathcal{Z} + \Delta \mathcal{Z}) = 0.5733 \mathcal{T}(0.25, \mathcal{Z}) + 0.3200 \mathcal{T}(0.50, \mathcal{Z}) + 0.1067 \mathcal{T}(0, \mathcal{Z})$$

$$\mathcal{T}(0.50, \mathcal{Z} + \Delta \mathcal{Z}) = 0.4667 \mathcal{T}(0.50, \mathcal{Z}) + 0.3333 \mathcal{T}(0.75, \mathcal{Z}) + 0.2000 \mathcal{T}(0.25, \mathcal{Z})$$

$$\mathcal{T}(0.75, \mathcal{Z} + \Delta \mathcal{Z}) = 0.0857 \mathcal{T}(0.75, \mathcal{Z}) + 0.5333 \mathcal{T}(1, \mathcal{Z}) + 0.3810 \mathcal{T}(0.5, \mathcal{Z})$$

At the wall,

$$\mathcal{T}(1, \mathcal{Y} + \Delta\mathcal{Y}) = 1.0$$

Note that the coefficients on temperatures sum to 1.0 in each equation. This is necessary because the asymptotic solution, $\mathcal{Y} \gg 1$, must give $\mathcal{T} = 1$ for all z . Had there been a heat of reaction, the coefficients would be unchanged but a generation term would be added to each equation.

The marching-ahead technique gives the following results for \mathcal{T} :

\mathcal{Y}	$z = 0$	$z = 0.25$	$z = 0.50$	$z = 0.75$	$z = 1.0$
0	0	0	0	0	1.0000
0.0625	0	0	0	0.5333	1.0000
0.1250	0	0	0.1778	0.5790	1.0000
0.1875	0	0.0569	0.2760	0.6507	1.0000
0.2500	0.0455	0.1209	0.3571	0.6942	1.0000
0.3125	0.1058	0.1884	0.4222	0.7289	1.0000
0.3750	0.1719	0.2544	0.4377	0.7567	1.0000
0.4375	0.2379	0.3171	0.5260	0.7802	1.0000
0.5000	0.3013	0.3755	0.5690	0.8006	1.0000
0.5625	0.3607	0.4295	0.6075	0.8187	1.0000
0.6250	0.4157	0.4791	0.6423	0.8349	1.0000
0.6875	0.4664	0.5246	0.6739	0.8496	1.0000
0.7500	0.5129	0.5661	0.7206	0.8629	1.0000
0.8125	0.5555	0.6041	0.7287	0.8749	1.0000
0.8750	0.5944	0.6388	0.7525	0.8859	1.0000
0.9375	0.6299	0.6705	0.7743	0.8960	1.0000
1.0000	0.6624	0.6994	0.7941	0.8960	1.0000

Figure 8.7 shows these results for $\mathcal{Y} = 1$ and compares them with the analytical solution. The numerical approximation is quite good, even for a coarse grid with $I=4$ and $J=16$. This is the exception rather than the rule. Convergence should be tested using a finer grid size.

The results for $\mathcal{Y} = 1$ give the outlet temperature distribution for a heat exchanger with $\alpha_T \bar{t}/R^2 = 0.4$. The results at $\mathcal{Y} = 0.5$ give the outlet temperature distribution for a heat exchanger with $\alpha_T \bar{t}/R^2 = 0.2$. There is no reason to stop at $\mathcal{Y} = 1.0$. Continue marching until $\mathcal{Y} = 2$ and you will obtain the outlet temperature distribution for a heat exchanger with $\alpha_T \bar{t}/R^2 = 0.8$.

8.6.2 Optimal Wall Temperatures

The method of lines formulation for solving Equation (8.52) does not require that T_{wall} be constant, but allows $T_{wall}(z)$ to be an arbitrary function of axial position. A new value of T_{wall} may be used at each step in the calculations, just as a new $\Delta\mathcal{Y}$ may be assigned at each step (subject to the stability criterion). The design engineer is thus free to pick a $T_{wall}(z)$ that optimizes reactor performance.

Reactor performance is an issue of selectivity, not of conversion. Otherwise, just push T_{wall} to its maximum possible value. Good selectivity results from an optimal trajectory of time versus temperature for all portions of the reacting fluid, but uniform treatment is difficult in laminar flow due to the large difference in residence time between the wall and centerline. No strategy for controlling the wall temperature can completely eliminate the resultant nonuniformity, but a good strategy for $T_{wall}(z)$ can mitigate the problem. With preheated feed, initial cooling at the wall can help compensate for long residence times. With cold feed, initial heating at the wall is needed to start the reaction, but a switch to cooling can be made at some downstream point. A good general approach to determining the optimal $T_{wall}(z)$ is to first find the best single wall temperature, then find the best two-zone strategy, the best three-zone strategy, and so on. The objective function for the optimization can be as simple as the mixing-cup outlet concentration of a desired intermediate. It can also be based on the concept of *thermal time distributions* introduced in Section 15.4.3.

Optimization requires that $\alpha_T \bar{t}/R^2$ have some reasonably high value so that the wall temperature has a significant influence on reactor performance. There is no requirement that $\mathcal{D}_A \bar{t}/R^2$ be large. Thus, the method can be used for polymer systems that have thermal diffusivities typical of organic liquids but low molecular diffusivities. The calculations needed to solve the optimization are much longer than those needed to solve the ODEs of Chapter 6, but they are still feasible on small computers.

8.7 RADIAL VARIATIONS IN VISCOSITY

Real fluids have viscosities that are functions of temperature and composition. This means that the viscosity will vary across the radius of a tubular reactor and that the velocity profile will be something other than parabolic. If the viscosity is lower near the wall, as in heating, the velocity profile will be flattened compared with the parabolic distribution. If the viscosity is higher near the wall, as in cooling, the velocity profile will be elongated. These phenomena can be important in laminar flow reactors, affecting performance and even operability. Generally speaking, a flattened velocity profile will improve performance by more closely approaching piston flow. Conversely, an elongated profile will usually hurt performance. This section gives a method for including the effects of variable viscosity in a reactor design problem. It is restricted to low Reynolds numbers, $Re < 100$, and is used mainly for reactions involving compounds with high molecular weights, such as greases, waxes, heavy oils, and synthetic polymers. It is usually possible to achieve turbulence with lower molecular weight compounds, and turbulence eliminates most of the problems associated with viscosity changes.

Variable viscosity in laminar tube flows is an example of the coupling of mass, energy, and momentum transport in a reactor design problem of practical significance. Elaborate computer codes are being devised that recognize this

coupling in complex flow geometries. These codes are being verified and are becoming design tools for the reaction engineer. The present example is representative of a general class of single-phase, variable-viscosity, variable-density problems, yet it avoids undue complications in mathematical or numerical analysis.

Consider axisymmetric flow in a circular tube so that $V_\theta = 0$. Two additional assumptions are needed to treat the variable-viscosity problem in its simplest form:

1. The momentum of the fluid is negligible compared with viscous forces.
2. The radial velocity component V_r is negligible compared with the axial component V_z .

The first of these assumptions drops the momentum terms from the equations of motion, giving a situation known as *creeping flow*. This leaves V_r and V_z coupled through a pair of simultaneous, partial differential equations. The pair can be solved when circumstances warrant, but the second assumption allows much greater simplification. It allows V_z to be given by a single, ordinary differential equation:

$$0 = -\frac{dP}{dz} + \frac{1}{r} \frac{d}{dr} \left[\mu r \frac{dV_z}{dr} \right] \quad (8.63)$$

Note that pressure is treated as a function of z alone. This is consistent with the assumption of negligible V_r . Equation (8.63) is subject to the boundary conditions of radial symmetry, $dV_z/dr = 0$ at $r = 0$, and zero slip at the wall, $V_z = 0$ at $r = R$.

The key physical requirements for Equation (8.63) to hold are that the fluid be quite viscous, giving a low Reynolds number, and that the viscosity must change slowly in the axial direction, although it may change rapidly in the radial direction. In essence, Equation (8.63) postulates that the velocity profile $V_z(r)$ is in dynamic equilibrium with the radial viscosity profile $\mu(r)$. If $\mu(r)$ changes as a function of z , then $V_z(r)$ will change accordingly, always satisfying Equation (8.63). Any change in V_z will cause a change in V_r ; but if the changes in $\mu(r)$ are slow enough, the radial velocity components will be small, and Equation (8.63) will remain a good approximation.

Solution of Equation (8.63) for the case of constant viscosity gives the parabolic velocity profile, Equation (8.1), and Poiseuille's equation for pressure drop, Equation (3.14). In the more general case of $\mu = \mu(r)$, the velocity profile and pressure drop are determined numerically.

The first step in developing the numerical method is to find a "formal" solution to Equation (8.63). Observe that Equation (8.63) is variable-separable:

$$r(dP/dz)dr = d[\mu r(dV_z/dr)]$$

This equation can be integrated twice. Note that dP/dz is a constant when integrating with respect to r . The constants of integration are found using the

boundary conditions. The result is

$$V_z(r) = \frac{1}{2} \left[\frac{-dP}{dz} \right] \int_r^R \frac{r_1}{\mu} dr_1 \quad (8.64)$$

where r_1 is a dummy variable of integration. Dummy variables are used to avoid confusion between the variable being integrated and the limits of the integration. In Equation (8.64), V_z is a function of the variable r that is the lower limit of the integral; V_z is not a function of r_1 . The dummy variable is “integrated out” and the value of the integral would be the same if r_1 were replaced by any other symbol.

Equation (8.64) allows the shape of the velocity profile to be calculated (e.g., substitute $\mu = \text{constant}$ and see what happens), but the magnitude of the velocity depends on the yet unknown value for dP/dz . As is often the case in hydrodynamic calculations, pressure drops are determined through the use of a continuity equation. Here, the continuity equation takes the form of a constant mass flow rate down the tube:

$$W = \pi R^2 \bar{u}_{in} \bar{\rho}_{in} = \pi R^2 \bar{u} \bar{\rho} = \int_0^R 2\pi r \rho V_z dr \quad (8.65)$$

Substituting Equation (8.64) into (8.65) allows $(-dP/dz)$ to be determined.

$$-\frac{dP}{dz} = \frac{W}{\pi \int_0^R \rho r \int_r^R (r_1/\mu) dr_1} = \frac{R^2 \bar{u}_{in} \bar{\rho}_{in}}{\int_0^R \rho r \int_r^R (r_1/\mu) dr_1} \quad (8.66)$$

This is the local pressure gradient. It is assumed to vary slowly in the z -direction. The pressure at position z is

$$P = P_{in} + \int_0^z \left[\frac{dP}{dz} \right] dz \quad (8.67)$$

Substituting Equation (8.66) into Equation (8.64) gives

$$V_z(r) = \frac{R^2 \bar{u}_{in} \bar{\rho}_{in}}{2} \frac{\int_r^R (r_1/\mu) dr_1}{\int_0^R \rho r \int_r^R (r_1/\mu) dr_1 dr} \quad (8.68)$$

A systematic method for combining the velocity and pressure calculations with the previous solutions techniques for composition and temperature starts with known values for all variables and proceeds as follows:

1. Take one axial step and compute new values for a, b, \dots, T .
2. Use physical property correlations to estimate new values for μ and ρ .

3. Update $V_z(r)$ using Equation (8.68).
4. Calculate P at the new position using Equation (8.65).
5. Recalculate Δz_{max} using Equation (8.29) and change the actual Δz as required.
6. Repeat Steps 1–5 until $z = L$.

A numerical methodology for calculating $V_z(r)$ is developed in Example 8.10.

Example 8.10: Given tabulated data for $\mu(z)$ and $\rho(z)$, develop a numerical method for using Equation (8.68) to find the dimensionless velocity profile $\mathcal{V}_z(z) = V_z/\bar{u}$.

Solution: The numerical integration techniques require some care. The inlet to the reactor is usually assumed to have a flat viscosity profile and a parabolic velocity distribution. We would like the numerical integration to reproduce the parabolic distribution exactly when μ is constant. Otherwise, there will be an initial, fictitious change in \mathcal{V}_z at the first axial increment. Define

$$G_1(z) = \int_z^1 (z_1/\mu) dz_1$$

and

$$G_2 = \int_0^1 (\rho/\bar{\rho}_m) z G_1(z) dz$$

When μ is constant, the G_1 integrand is linear in z and can be integrated exactly using the trapezoidal rule. The result of the G_1 integration is quadratic in z , and this is increased to cubic in z in the G_2 integrand. Thus, G_2 cannot be integrated exactly with the trapezoidal rule or even Simpson's rule. There are many possible remedies to this problem, including just living with the error in G_2 since it will decrease $O(\Delta z^2)$. In the Basic program segment that follows, a correction of $\Delta z^3/8$ is added to G_2 , so that the parabolic profile is reproduced exactly when μ is constant.

```
'Specify the number of radial increments, Itotal, and
'the values for visc(i) and rho(i) at each radial
'position. Also, the average density at the reactor
'inlet, rho_in, must be specified.
```

```
dr=1/Itotal
```

```
'Use the trapezoidal rule to evaluate G1
G1(Itotal)=0
```

```

For i=1 To Itotal
  m=Itotal-i
  G1(m)=G1(m+1) + dr^2/2* ((m+1)/visc(m+1)
+      +m/visc(m) ) *dr
Next

'Now use it to evaluate G2
G2=0
For i=1 To Itotal-1
  G2=G2+i * dr * rho(i)/rhoIn * G1(i) * dr
Next
G2=G2+rho(Itotal)/rhoIn * G1(Itotal) * dr/2

'Apply a correction term to G2
G2=G2+dr ^ 3/8

'Calculate the velocity profile
For i=0 To Itotal
  Vz(i)=G1(i)/G2/2
Next i

```

The following is an example calculation where the viscosity varies by a factor of 50 across the tube, giving a significant elongation of the velocity profile compared with the parabolic case. The density was held constant in the calculations.

i	$\mu(i)$	Calculated $\bar{V}_z(i)$	Parabolic $\bar{V}_z(i)$
0	1.0	3.26	2.00
1	1.6	2.98	1.97
2	2.7	2.36	1.88
3	4.5	1.72	1.72
4	7.4	1.16	1.50
5	12.2	0.72	1.22
6	20.1	0.40	0.88
7	33.1	0.16	0.47
8	54.6	0.00	0.00

These results are plotted in Figure 8.8.

8.8 RADIAL VELOCITIES

The previous section gave a methodology for calculating $V_z(r)$ given $\mu(r)$ and $\rho(r)$. It will also be true that both μ and ρ will be functions of z . This will cause no difficulty provided the changes in the axial direction are slow.

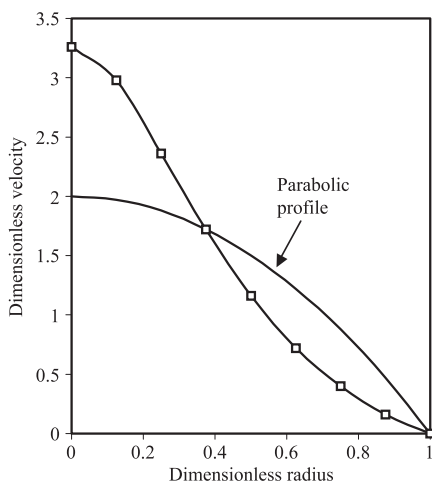


FIGURE 8.8 Elongated velocity profile resulting from a factor of 50 increase in viscosity across the tube radius.

The formulation of Equation (8.68) gives the fully developed velocity profile, $V_z(r)$, which corresponds to the local values of $\mu(r)$ and $\rho(r)$ without regard to upstream or downstream conditions. Changes in $V_z(r)$ must be gradual enough that the adjustment from one axial velocity profile to another requires only small velocities in the radial direction. We have assumed V_r to be small enough that it does not affect the equation of motion for V_z . This does not mean that V_r is zero. Instead, it can be calculated from the fluid continuity equation,

$$\partial(\rho V_z)/\partial z + (1/r)\partial(r\rho V_r)/\partial r = 0 \quad (8.69)$$

which is subject to the symmetry boundary condition that $V_r(0)=0$. Equation (8.69) can be integrated to give

$$V_r = \frac{-1}{\rho r} \int_0^r r_1 \frac{\partial(\rho V_z)}{\partial z} dr_1 \quad (8.70)$$

Radial motion of fluid can have a significant, cumulative effect on the convective diffusion equations even when V_r has a negligible effect on the equation of motion for V_z . Thus, Equation (8.68) can give an accurate approximation for V_z even though Equations (8.12) and (8.52) need to be modified to account for radial convection. The extended versions of these equations are

$$V_z \frac{\partial a}{\partial z} + V_r \frac{\partial a}{\partial r} = \mathcal{D}_A \left[\frac{1}{r} \frac{\partial a}{\partial r} + \frac{\partial^2 a}{\partial r^2} \right] + \mathcal{R}_A \quad (8.71)$$

$$V_z \frac{\partial T}{\partial z} + V_r \frac{\partial T}{\partial r} = \alpha_T \left[\frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} \right] - \frac{\Delta H_R \mathcal{R}}{\rho C_p} \quad (8.72)$$

The boundary conditions are unchanged. The method of lines solution continues to use a second-order approximation for $\partial a / \partial r$ and merely adds a V_r term to the coefficients for the points at $r \pm \Delta r$.

The equivalent of radial flow for flat-plate geometries is V_y . The governing equations are similar to those for V_r . However, the various corrections for V_y are seldom necessary. The reason for this is that the distance Y is usually so small that diffusion in the y -direction tends to eliminate the composition and temperature differences that cause V_y . That is precisely why flat-plate geometries are used as chemical reactors and for laminar heat transfer.

It is sometimes interesting to calculate the paths followed by nondiffusive fluid elements as they flow through the reactor. These paths are called *streamlines* and are straight lines when the V_z profile does not change in the axial direction. The streamlines curve inward toward the center of the tube when the velocity profile elongates, as in cooling or polymerization. They curve outward when the velocity profile flattens, as in heating or depolymerization. Example 13.10 treats a case where they initially curve inward as the viscosity increases due to polymerization but later curve outward as the reaction goes to completion and diffusion mitigates the radial gradient in polymer concentration.

If desired, the streamlines can be calculated from

$$\int_0^{r_{in}} \rho r_1 V_z(r_1, 0) dr_1 = \int_0^r \rho r_1 V_z(r_1, z) dr_1 \quad (8.73)$$

This mass balance equation shows that material that is initially at radial position r_{in} will move to radial position r for some downstream location, $z > 0$. A worked example of radial velocities and curved streamlines is given in Chapter 13, Example 13.10.

8.9 VARIABLE PHYSICAL PROPERTIES

The treatment of viscosity variations included the possibility of variable density. Equations (8.12) and (8.52) assumed constant density, constant \mathcal{D}_A , and constant α_T . We state here the appropriate generalizations of these equations to account for variable physical properties.

$$\frac{1}{A_c} \frac{\partial (A_c V_z a)}{\partial z} = \frac{\partial}{\partial z} \left[\mathcal{D}_A \frac{\partial a}{\partial z} \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[\mathcal{D}_A r \frac{\partial a}{\partial r} \right] + \mathcal{R}_A \quad (8.74)$$

$$V_z \rho \frac{\partial H}{\partial z} = \frac{\partial}{\partial z} \left[\lambda \frac{\partial T}{\partial z} \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[\lambda r \frac{\partial T}{\partial r} \right] - \Delta H_R \mathcal{R} \quad (8.75)$$

For completeness, axial diffusion and variable cross-section terms were included in Equations (8.74) and (8.75). They are usually dropped. Also, the variations in \mathcal{D}_A and λ are usually small enough that they can be brought outside the derivatives. The primary utility of these equations, compared with Equations (8.12) and (8.52), is for gas-phase reactions with a significant pressure drop.

8.10 SCALEUP OF LAMINAR FLOW REACTORS

Chapter 3 introduced the basic concepts of scaleup for tubular reactors. The theory developed in this chapter allows scaleup of laminar flow reactors on a more substantive basis. *Model-based scaleup* supposes that the reactor is reasonably well understood at the pilot scale and that a model of the proposed plant-scale reactor predicts performance that is acceptable, although possibly worse than that achieved in the pilot reactor. So be it. If you trust the model, go for it. The alternative is *blind scaleup*, where the pilot reactor produces good product and where the scaleup is based on general principles and high hopes. There are situations where blind scaleup is the best choice based on business considerations; but given your druthers, go for model-based scaleup.

Consider the scaleup of a small, tubular reactor in which diffusion of both mass and heat is important. As a practical matter, the same fluid, the same inlet temperature, and the same mean residence time will be used in the small and large reactors. Substitute fluids and *cold-flow models* are sometimes used to study the fluid mechanics of a reactor, but not the kinetics of the reaction.

The goal of a scaleup is to achieve similar product quality at a higher rate. The throughput scaleup factor is S . This determines the flow rate to the large system; and the requirement of constant \bar{t} fixes the volume of the large system. For scaleup of flow in an open tube, the design engineer has two basic variables, R and T_{wall} . An exact scaleup requires that $\mathcal{D}_A \bar{t} / R^2$ and $\alpha_T \bar{t} / R^2$ be held constant, and the only way to do this is to keep the same tube diameter. Scaling in parallel is exact. Scaling in series may be exact and is generally conservative for incompressible fluids. See Section 3.2. Other forms of scaleup will be satisfactory only under special circumstances. One of these circumstances is isothermal laminar flow when $\mathcal{D}_A \bar{t} / R^2$ is small in the pilot reactor.

8.10.1 Isothermal Laminar Flow

Reactors in isothermal laminar flow are exactly scaleable using geometric similarity if diffusion is negligible in the pilot reactor. Converting Equation (8.2) to

dimensionless form gives

$$\mathcal{V}_z(z) \frac{\partial a}{\partial \mathcal{V}} = \mathcal{R}_A \bar{t} \quad (8.76)$$

The absolute reactor size as measured by R and L does not appear. Using the same feed composition and the same \bar{t} in a geometrically similar reactor will give a geometrically similar composition distribution; i.e., the concentration at the point (z, \mathcal{V}) will be the same in the large and small reactors. Similarly, the viscosity profile will be the same when position is expressed in dimensionless form, and this leads to the same velocity profile, pressure drop, and mixing-cup average composition. These statements assume that diffusion really was negligible on the small scale and that the Reynolds number remains low in the large reactor. Blind scaleup will then give the same product from the large reactor as from the small. If diffusion was beneficial at the small scale, reactor performance will worsen upon scaleup. The Reynolds number may become too high upon scaleup for the creeping flow assumption of Section 8.7 to remain reasonable, but the probable consequence of a higher Reynolds number is improved performance at the cost of a somewhat higher pressure drop.

It may not be feasible to have an adequately low value for $\mathcal{D}_A \bar{t}/R^2$ and still scale using geometric similarity. Recall that reactor scaleups are done at constant \bar{t} . The problem is that the pilot reactor would require too high a flow rate and consume too much material when $\mathcal{D}_A \bar{t}/R^2$ is small enough (i.e., R is large enough) and L/R is large enough for reasonable scaleup. The choice is to devise a model-based scaleup. Model the pilot reactor using the actual value for $\mathcal{D}_A \bar{t}/R^2$. Confirm (and adjust) the model based on experimental measurements. Then model the large reactor using the appropriately reduced value for $\mathcal{D}_A \bar{t}/R^2$. If the predicted results are satisfactory, go for it. If the predictions are unsatisfactory, consider using motionless mixers in the large reactor. These devices lower the effective value for $\mathcal{D}_A \bar{t}/R^2$ by promoting radial mixing. The usual approach to scaling reactors that contain motionless mixers is to start with geometric similarity but to increase the number of mixing elements to compensate for the larger tube diameter. For mixers of the Kenics type, an extra element is needed each time the tube diameter is doubled.

8.10.2 Nonisothermal Laminar Flow

The temperature counterpart of $\mathcal{D}_A \bar{t}/R^2$ is $\alpha_T \bar{t}/R^2$; and if $\alpha_T \bar{t}/R^2$ is low enough, then the reactor will be adiabatic. Since $\alpha_T \gg \mathcal{D}_A$, the situation of an adiabatic, laminar flow reactor is rare. Should it occur, then $T(z, \mathcal{V})$ will be the same in the small and large reactors, and blind scaleup is possible. More commonly, $\alpha_T \bar{t}/R^2$ will be so large that radial diffusion of heat will be significant in the small reactor. The extent of radial diffusion will lessen upon scaleup, leading to the possibility of thermal runaway. If model-based scaleup predicts a reasonable outcome, go for it. Otherwise, consider scaling in series or parallel.

PROBLEMS

- 8.1. Polymerizations often give such high viscosities that laminar flow is inevitable. A typical monomer diffusivity in a polymerizing mixture is 1.0×10^{-10} m/s (the diffusivity of the polymer will be much lower). A pilot-scale reactor might have a radius of 1 cm. What is the maximum value for the mean residence time before molecular diffusion becomes important? What about a production-scale reactor with $R = 10$ cm?
- 8.2. The velocity profile for isothermal, laminar, non-Newtonian flow in a pipe can sometimes be approximated as

$$V_z = V_0[1 - (r/R)^{(\eta+1)/\eta}]$$

where η is called the flow index, or power law constant. The case $\eta = 1$ corresponds to a Newtonian fluid and gives a parabolic velocity profile. Find a_{out}/a_{in} for a first-order reaction given $k\bar{t} = 1.0$ and $\eta = 0.5$. Assume negligible diffusion.

- 8.3. Repeat Example 8.1 and obtain an analytical solution for the case of first-order reaction and pressure-driven flow between flat plates. Feel free to use software for the symbolic manipulations, but do substantiate your results.
- 8.4. Determine whether the sequence of a_{out}/a_{in} versus I in Example 8.5 is converging as expected. What is your prediction for the calculated value that would be obtained if the program is run with $I = 256$, and $J = 131,072$. Run the program to test your prediction.
- 8.5. Equation (8.4) defines the average concentration, a_{out} , of material flowing from the reactor. Omit the $V_z(r)$ term inside the integral and normalize by the cross-sectional area, $A_c = \pi R^2$, rather than the volumetric flow rate, Q . The result is the spatial average concentration $a_{spatial}$, and is what you would measure if the contents of the tube were frozen and a small disk of the material was cut out and analyzed. In-line devices for measuring concentration may measure $a_{spatial}$ rather than a_{out} . Is the difference important?
 - (a) Calculate both averages for the case of a parabolic velocity profile and first-order reaction with $k\bar{t} = 1.0$.
 - (b) Find the value of $k\bar{t}$ that maximizes the difference between these averages.
- 8.6. Determine the equivalent of Merrill and Hamrin's criterion for a tubular reactor when the reaction is:
 - (a) Second order of the form $2A \rightarrow P$.
 - (b) Half-order: $A \rightarrow P$, $\mathcal{R}_A = -ka^{1/2}$. Be sure to stop the reaction if the concentration of A drops to zero. It will go to zero at some locations in the reactor when $\mathcal{D}_A \bar{t}/R^2 = 0$. Does it still fall to zero when $\mathcal{D}_A \bar{t}/R^2$ is just large enough to affect a_{out} ?

- 8.7. Consider an isothermal, laminar flow reactor with a parabolic velocity profile. Suppose an elementary, second-order reaction of the form $A + B \rightarrow P$ with rate $\mathcal{R} = kab$ is occurring with $ka_{in} \bar{t} = 2$. Assume $a_{in} = b_{in}$. Find a_{out}/a_{in} for the following cases:
 (a) $\mathcal{D}_A \bar{t}/R^2 = \mathcal{D}_B \bar{t}/R^2 = 0.01$.
 (b) $\mathcal{D}_A \bar{t}/R^2 = 0.01$, $\mathcal{D}_B \bar{t}/R^2 = 0.001$.
- 8.8. Which is better for isothermal chemical reactions, pressure driven flow or drag flow between flat plates? Assume laminar flow with first-order chemical reaction and compare systems with the same values for the slit width ($2Y=H$), length, mean velocity, and reaction rate constant.
- 8.9. Free-radical polymerizations tend to be highly exothermic. The following data are representative of the thermal (i.e., spontaneous) polymerization of styrene:

$$\lambda = 0.13 \text{ J}/(\text{m} \cdot \text{s} \cdot \text{K})$$

$$\mathcal{D}_A = 1.0 \times 10^{-9} \text{ m}^2/\text{s}$$

$$\Delta H = -8 \times 10^4 \text{ J/g-mol}$$

$$C_P = 1.9 \times 10^3 \text{ J}/(\text{kg} \cdot \text{K})$$

$$\rho = 950 \text{ kg/m}^3$$

$$a_{in} = 9200 \text{ g-mol/m}^3$$

$$L = 7 \text{ m}$$

$$\bar{t} = 1 \text{ h}$$

$$k = 1.0 \times 10^{10} \exp(-10,000/T) \text{ h}^{-1}$$

$$T_{in} = 120^\circ\text{C}$$

$$T_{wall} = 120^\circ\text{C}$$

Assume laminar flow and a parabolic velocity distribution. Calculate the temperature and composition profiles in the reactor. Start with $I=4$ and double until your computer cries for mercy. Consider two cases: (a) $R=0.01 \text{ m}$; (b) $R=0.20 \text{ m}$.

- 8.10. Suppose the consecutive reactions $A \xrightarrow{k_I} B \xrightarrow{k_{II}} C$ are elementary with rate constants $k_I = 4.5 \times 10^{11} \exp(-10,000/T) \text{ h}^{-1}$ and $k_{II} = 1.8 \times 10^{12} \exp(-12,000/T) \text{ h}^{-1}$. The reactions are occurring in a tube in laminar flow with $a_{in}=1$, $b_{in}=c_{in}=0$. Both reactions are exothermic with $-\Delta H_I a_{in}/(\rho C_P) = -\Delta H_{II} a_{in}/(\rho C_P) = 50 \text{ K}$. The reactor is operated with $\bar{t} = 1 \text{ h}$, $T_{in} = 400 \text{ K}$, and $T_{wall} = 400 \text{ K}$. Assume $\alpha_T \bar{t}/R^2 = 0.1$. Determine a_{out} , b_{out} , and c_{out} given
 (a) $\mathcal{D}_A \bar{t}/R^2 = 0.01$ $\mathcal{D}_B \bar{t}/R^2 = 0.01$
 (b) $\mathcal{D}_A \bar{t}/R^2 = 0.01$ $\mathcal{D}_B \bar{t}/R^2 = 0.001$
- 8.11. Determine the opposite of the Merrill and Hamlin criterion. That is, find the value of $\mathcal{D}_A \bar{t}/R^2$ above which a laminar flow reactor closely

approximates a piston flow reactor for a first-order reaction. Make the comparison at $k\bar{t} = 1$.

- 8.12.** An unreconstructed cgs'er messed up your viscosity correlation by reporting his results in centipoise rather than pascal seconds. How does this affect the sample velocity profile calculated in Example 8.10? What does the term "unreconstructed cgs'er" mean?
- 8.13.** Suppose you are marching down the infamous tube and at step j have determined the temperature and composition at each radial point. A correlation is available to calculate viscosity, and it gives the results tabulated below. Assume constant density and $\text{Re} = 0.1$. Determine the axial velocity profile. Plot your results and compare them with the parabolic distribution.

r/R	Isothermal μ	Cooling μ	Heating μ
1.000	1.0	54.6	0.018
0.875	1.0	33.1	0.030
0.750	1.0	20.1	0.050
0.625	1.0	12.2	0.082
0.500	1.0	7.4	0.135
0.375	1.0	4.5	0.223
0.250	1.0	2.7	0.368
0.125	1.0	1.6	0.607
0	1.0	1.0	1.000

- 8.14.** Derive the equations necessary to calculate $V_z(y)$ given $\mu(y)$ for pressure-driven flow between flat plates.
- 8.15.** The stated boundary condition associated with Equation (8.69) is that $V_r(0) = 0$. This is a symmetry condition consistent with the assumption that $V_\theta = 0$. There is also a zero-slip condition that $V_r(R) = 0$. Prove that both boundary conditions are satisfied by Equation (8.70). Are there boundary conditions on V_z ? If so, what are they?
- 8.16.** Stepwise condensation polymerizations can be modeled as a second-order reaction of the functional groups. Let a be the concentration of functional groups so that $\mathcal{R}_A = -ka^2$. The following viscosity relationship

$$\mu/\mu_0 = 1 + 100[1 - (a/a_{in})^3]$$

is reasonable for a condensation polymer in a solvent. Determine a_{out}/a_{in} for a laminar flow reactor with $k\bar{t} = 2$ and with negligible diffusion. Neglect the radial velocity component V_r .

- 8.17.** Rework Problem 8.16 including the V_r ; i.e., solve Equation (8.70). Plot the streamlines. See Example 13.10 for guidance.

REFERENCES

1. Merrill, L. S., Jr. and Hamrin, C. E., Jr., "Conversion and temperature profiles for complex reactions in laminar and plug flow," *AIChE J.*, **16**, 194–198 (1970).
2. Nauman, E. B. and Buffham, B. A., *Mixing in Continuous Flow Systems*, Wiley, New York, 1983, pp. 31–33.
3. Nauman, E. B. and Savoca, J. T., "An engineering approach to an unsolved problem in multicomponent diffusion," *AIChE J.*, **47**, 1016–1021 (2001).
4. Nigam, K. D. P. and Saxena, A. K., "Coiled configuration for flow inversion and its effects on residence time distribution," *AIChE J.*, **30**, 363–368 (1984).
5. Nauman, E. B., "Reactions and residence time distributions in motionless mixers," *Can. J. Chem. Eng.*, **60**, 136–140 (1982).

SUGGESTIONS FOR FURTHER READING

The convective diffusion equations for mass and energy are given detailed treatments in most texts on transport phenomena. The classic reference is

Bird, R. B., Stewart, W. E., and Lightfoot, E. N., *Transport Phenomena*, Wiley, New York, 1960.

Practical applications to laminar flow reactors are still mainly in the research literature. The first good treatment of a variable-viscosity reactor is

Lynn, S. and Huff, J. E., "Polymerization in a Tubular Reactor," *AIChE J.*, **17**, 475–481 (1971).

A detailed model of an industrially important reaction, styrene polymerization, is given in

Wyman, C. E. and Carter, L. F., "A Numerical Model for Tubular Polymerization Reactors," *AIChE Symp. Ser.*, **72**, 1–16 (1976).

See also Chapter 13 of this book.

The appropriateness of neglecting radial flow in the axial momentum equation yet of retaining it in the convective diffusion equation is discussed in

McLaughlin, H. S., Mallikarjun, R., and Nauman, E. B., "The Effect of Radial Velocities on Laminar Flow, Tubular Reactor Models," *AIChE J.*, **32**, 419–425 (1986).

Gas-phase reactors are often in laminar flow but have such high diffusivities that radial concentration gradients tend to be unimportant. Combustion reactions are fast enough to be exceptions. See

Roesler, J. F., "An Experimental and Two-Dimensional Modeling Investigation of Combustion Chemistry in a Laminar Non-Plug-Flow Reactor," *Proc. 27th Symp. (Int.) Combust.*, **1**, 287–293 (1998).

The usefulness of your training in solving PDEs need not be limited to classic chemical engineering. For a potentially more remunerative application, see

Clewlow, L. and Strickland, C., *Implementing Derivatives Models*, Wiley, New York, 1998.

The derivatives are the financial type, e.g., option spreads. The methods used are implicit finite difference techniques. See Appendix 8.3.

APPENDIX 8.1: THE CONVECTIVE DIFFUSION EQUATION

This section derives a simple version of the convective diffusion equation, applicable to tubular reactors with a one-dimensional velocity profile $V_z(r)$. The starting point is Equation (1.4) applied to the differential volume element shown in Figure 8.9. The volume element is located at point (r, z) and is in the shape of a ring. Note that θ -dependence is ignored so that the results will not be applicable to systems with significant natural convection. Also, convection due to V_r is neglected. Component A is transported by radial and axial diffusion and by axial convection. The diffusive flux is governed by Fick's law. The various terms needed for Equation (1.4) are

$$\text{Radial diffusion in} = -\mathcal{D}_A \left[\frac{\partial a}{\partial r} \right]_r [2\pi r \Delta z]$$

$$\text{Axial diffusion in} = -\mathcal{D}_A \left[\frac{\partial a}{\partial z} \right]_z [2\pi r \Delta r]$$

$$\text{Axial convection in} = V_z(z)a(z)[2\pi r \Delta r]$$

$$\text{Radial diffusion out} = -\mathcal{D}_A \left[\frac{\partial a}{\partial r} \right]_{r+\Delta r} [2\pi(r + \Delta r) \Delta z]$$

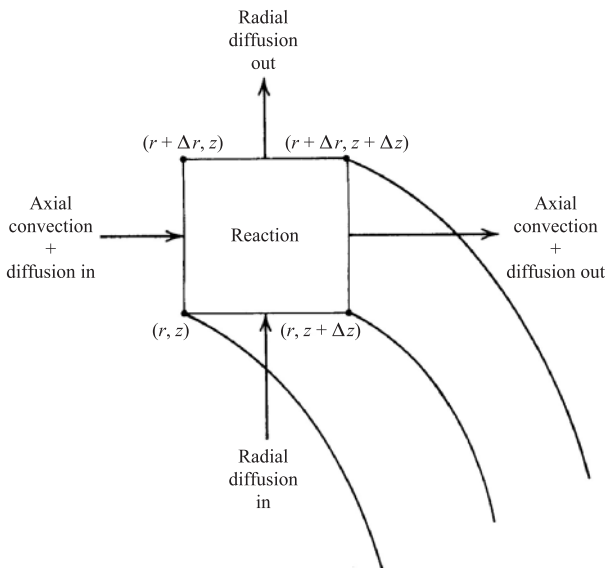


FIGURE 8.9 Differential volume element in cylindrical coordinates.

$$\text{Axial diffusion out} = -\mathcal{D}_A \left[\frac{\partial a}{\partial z} \right]_{z+\Delta z} [2\pi r \Delta r]$$

$$\text{Axial convection out} = V_z(z)a(z+\Delta z)[2\pi r \Delta r]$$

$$\text{Formation of A by reaction} = \mathcal{R}_A [2\pi r \Delta r \Delta z]$$

$$\text{Accumulation} = \frac{\partial a}{\partial t} [2\pi r \Delta r \Delta z]$$

Applying Equation (1.2), dividing everything by $[2\pi r \Delta r \Delta z]$, and rearranging gives

$$\begin{aligned} \frac{\partial a}{\partial t} + \frac{V_z(z+\Delta z)a(z+\Delta z) - V_z(z)a(z)}{\Delta z} &= \frac{\mathcal{D}_A(\partial a/\partial z)_{z+\Delta z} - \mathcal{D}_A(\partial a/\partial z)_z}{\Delta z} \\ &+ \frac{\mathcal{D}_A(\partial a/\partial r)_{r+\Delta r} - \mathcal{D}_A(\partial a/\partial r)_r}{\Delta r} + \mathcal{D}_A \frac{\partial a}{\partial r} \frac{1}{r} + \mathcal{R}_A \end{aligned}$$

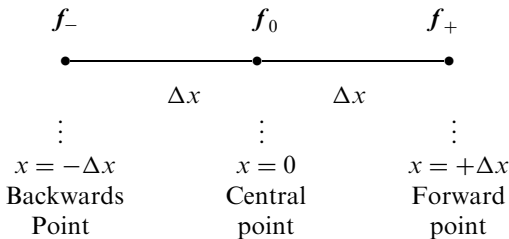
The limit is now taken as $\Delta z \rightarrow 0$ and $\Delta r \rightarrow 0$. The result is

$$\frac{\partial a}{\partial t} + \frac{\partial(V_z a)}{\partial z} = \frac{\partial(\mathcal{D}_A(\partial a/\partial z))}{\partial z} + \frac{\partial(\mathcal{D}_A(\partial a/\partial r))}{\partial r} + \frac{\mathcal{D}_A}{r} \frac{\partial a}{\partial r} + \mathcal{R}_A \quad (8.77)$$

which is a more general version of Equation (8.12). Assume steady-state operation, V_z independent of z , and constant diffusivity to obtain Equation (8.12).

APPENDIX 8.2: FINITE DIFFERENCE APPROXIMATIONS

This section describes a number of finite difference approximations useful for solving second-order partial differential equations; that is, equations containing terms such as $\partial^2 f/\partial x^2$. The basic idea is to approximate f as a polynomial in x and then to differentiate the polynomial to obtain estimates for derivatives such as $\partial f/\partial x$ and $\partial^2 f/\partial x^2$. The polynomial approximation is a local one that applies to some region of space centered about point x . When the point changes, the polynomial approximation will change as well. We begin by fitting a quadratic to the three points shown below.



The quadratic has the form

$$f = A + Bx + Cx^2$$

Writing it for the three points gives

$$f_- = A - B \Delta x + C \Delta x^2$$

$$f_0 = A$$

$$f_+ = A + B \Delta x + C \Delta x^2$$

These equations are solved for A , B , and C to give

$$f = f_0 + \left(\frac{f_+ - f_-}{2 \Delta x} \right) x + \left(\frac{f_+ - 2f_0 + f_-}{2 \Delta x^2} \right) x^2$$

This is a *second-order approximation* and can be used to obtain derivatives up to the second. Differentiate to obtain

$$\frac{df}{dx} = \left(\frac{f_+ - f_-}{2 \Delta x} \right) + \left(\frac{f_+ - 2f_0 + f_-}{\Delta x^2} \right) x$$

and

$$\frac{d^2f}{dx^2} = \frac{f_+ - 2f_0 + f_-}{\Delta x^2}$$

The value of the first derivative depends on the position at which it is evaluated. Setting $x = +\Delta x$ gives a *second-order, forward difference*:

$$\left[\frac{df}{dx} \right]_+ \approx \frac{3f_+ - 4f_0 + f_-}{2 \Delta x}$$

Setting $x = 0$ gives a *second-order, central difference*:

$$\left[\frac{df}{dx} \right]_0 \approx \frac{f_+ - f_-}{2 \Delta x}$$

Setting $x = -\Delta x$ gives a *second-order, backward difference*:

$$\left[\frac{df}{dx} \right]_- \approx \frac{-f_+ + 4f_0 - 3f_-}{2 \Delta x}$$

The second derivative is constant (independent of x) for this second-order approximation. We consider it to be a *central difference*:

$$\left[\frac{d^2f}{dx^2} \right]_0 \approx \frac{f_+ - 2f_0 + f_-}{\Delta x^2}$$

All higher derivatives are zero. Obviously, to obtain a nontrivial approximation to an n th derivative requires at least an n th-order polynomial. The various nontrivial derivatives obtained from an n th order polynomial will converge $\mathbf{O}(\Delta x^n)$.

Example 8.11: Apply the various second-order approximations to $f = x \exp(x)$.

Solution: $f_+ = \Delta x \exp(\Delta x)$, $f_0 = 0$, $f_- = -\Delta x \exp(-\Delta x)$. The various derivative approximations are

$$\left[\frac{df}{dx} \right]_+ = \frac{3 \exp(\Delta x) - \exp(-\Delta x)}{\Delta x}$$

$$\left[\frac{df}{dx} \right]_0 = \frac{\exp(\Delta x) + \exp(-\Delta x)}{2 \Delta x}$$

$$\left[\frac{df}{dx} \right]_- = \frac{-\exp(\Delta x) + 3 \exp(-\Delta x)}{2}$$

$$\left[\frac{d^2f}{dx^2} \right]_0 = \frac{\exp(\Delta x) - \exp(-\Delta x)}{\Delta x}$$

Evaluating them as a function of Δx gives

Δx	$\left[\frac{df}{dx} \right]_+$	Δ	$\left[\frac{df}{dx} \right]_0$	Δ	$\left[\frac{df}{dx} \right]_-$	Δ	$\left[\frac{d^2f}{dx^2} \right]$	Δ
1	3.893		1.543		-0.807		2.350	
		1.723		0.415		-0.892		0.266
1/2	2.170		1.128		0.805		2.084	
		0.633		0.096		-0.441		0.063
1/4	1.537		1.031		0.526		2.021	
		0.279		0.024		-0.231		0.016
1/8	1.258		1.008		0.757		2.005	
		0.131		0.006		-0.120		0.004
1/16	1.127		1.002		0.877		2.001	
		0.0064		0.002		0.0061		0.002
1/32	1.063		1.000		0.938		2.000	
∞	1		1		1		2	

It is apparent that the central difference approximations converge $\mathbf{O}(\Delta x^2)$. The forward and backward approximations to the first derivative converge $\mathbf{O}(\Delta x)$. This is because they are really approximating the derivatives at the points $x = \pm \Delta x$ rather than at $x = 0$.

For a *first-order approximation*, a straight line is fit between the points $x=0$ and x to get the *first-order, forward difference approximation*

$$\left[\frac{df}{dx} \right]_{+\Delta x/2} \approx \frac{f_+ - f_0}{\Delta x}$$

and between the points $x = -\Delta x$ and $x=0$ to get the *first-order, backward difference approximation*:

$$\left[\frac{df}{dx} \right]_{-\Delta x/2} \approx \frac{f_0 - f_-}{\Delta x}$$

These both converge $\mathbf{O}(\Delta x)$.

APPENDIX 8.3: IMPLICIT DIFFERENCING SCHEMES

The method of lines is called an *explicit* method because the “new” value $T(r, z + \Delta z)$ is given as an explicit function of the “old” values $T(r, z), T(r - \Delta r, z), \dots$. See, for example, Equation (8.57). This explicit scheme is obtained by using a first-order, forward difference approximation for the axial derivative. See, for example, Equation (8.16). Other approximations for dT/dz are given in Appendix 8.2. These usually give rise to *implicit* methods where $T(r, z \pm \Delta z)$ is not found directly but is given as one member of a set of simultaneous algebraic equations. The simplest implicit scheme is known as *backward differencing* and is based on a first-order, backward difference approximation for $\partial T / \partial z$. Instead of Equation (8.57), we obtain

$$\begin{aligned} \left[1 - 2 \left(\frac{\bar{u} \alpha_T \bar{t}}{V_z(\bar{z}) R^2} \right) \frac{\Delta \bar{z}}{\Delta \bar{z}^2} \right] T(\bar{z}, \bar{z}) - \left(\frac{\bar{u} \alpha_T \bar{t}}{V_z(\bar{z}) R^2} \right) \frac{\Delta \bar{z}}{\Delta \bar{z}^2} \left[1 + \frac{\Delta \bar{z}}{2 \bar{z}} \right] T(\bar{z} + \Delta \bar{z}, \bar{z}) \\ - \left(\frac{\bar{u} \alpha_T \bar{t}}{V_z(\bar{z}) R^2} \right) \frac{\Delta \bar{z}}{\Delta \bar{z}^2} \left[1 - \frac{\Delta \bar{z}}{2 \bar{z}} \right] T(\bar{z} - \Delta \bar{z}, \bar{z}) \\ = T(\bar{z}, \bar{z} - \Delta \bar{z}) - \left[\frac{\Delta H_R \mathcal{R} \bar{t} \bar{u}}{\rho C_P V_z(\bar{z})} \right]_{\bar{z} - \Delta \bar{z}} \Delta \bar{z} \end{aligned} \quad (8.78)$$

Here, the temperatures on the left-hand side are the new, unknown values while that on the right is the previous, known value. Note that the heat sink/source term is evaluated at the previous location, $\bar{z} - \Delta \bar{z}$. The computational template is backwards from that shown in Figure 8.2, and Equation (8.78) cannot be solved directly since there are three unknowns. However, if a version of Equation (8.78) is written for every interior point and if appropriate special forms are written for the centerline and wall, then as many equations are

obtained as there are unknown temperatures. The resulting algebraic equations are linear and can be solved by matrix inversion. The backward differencing scheme is stable for all Δz and $\Delta \mathcal{J}$ so that $I = 1/\Delta z$ and $J = 1/\Delta \mathcal{J}$ can be picked independently. This avoids the need for extremely small $\Delta \mathcal{J}$ values that was encountered in Example 8.5. The method converges $\mathbf{O}(\Delta z^2, \Delta \mathcal{J})$.

Example 8.12: Use the backward differencing method to solve the heat transfer problem of Example 8.3. Select $\Delta z = 0.25$ and $\Delta \mathcal{J} = 0.0625$.

$$\mathcal{T}(1, \mathcal{J}) = 1.0$$

$$\begin{aligned} -0.5333\mathcal{T}(1, \mathcal{J}) + 1.9143\mathcal{T}(0.75, \mathcal{J}) - 0.3810\mathcal{T}(0.5, \mathcal{J}) &= \mathcal{T}(0.75, \mathcal{J} - \Delta \mathcal{J}) \\ -0.3333\mathcal{T}(0.75, \mathcal{J}) + 1.5333\mathcal{T}(0.50, \mathcal{J}) - 0.2000\mathcal{T}(0.25, \mathcal{J}) &= \mathcal{T}(0.50, \mathcal{J} - \Delta \mathcal{J}) \\ -0.3200\mathcal{T}(0.50, \mathcal{J}) + 1.4267\mathcal{T}(0.25, \mathcal{J}) - 0.1067\mathcal{T}(0, \mathcal{J}) &= \mathcal{T}(0.25, \mathcal{J} - \Delta \mathcal{J}) \\ -0.8000\mathcal{T}(0.25, \mathcal{J}) - 1.800\mathcal{T}(0, \mathcal{J}) &= \mathcal{T}(0, \mathcal{J} - \Delta \mathcal{J}) \end{aligned}$$

In matrix form

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ -0.5333 & 1.9143 & -0.3810 & 0 & 0 \\ 0 & -0.3333 & 1.5333 & -0.2000 & 0 \\ 0 & 0 & -0.3200 & 1.4267 & -0.1067 \\ 0 & 0 & 0 & -0.8000 & 1.8000 \end{bmatrix} \begin{bmatrix} \mathcal{T}(1, \mathcal{J}) \\ \mathcal{T}(0.75, \mathcal{J}) \\ \mathcal{T}(0.50, \mathcal{J}) \\ \mathcal{T}(0.25, \mathcal{J}) \\ \mathcal{T}(0, \mathcal{J}) \end{bmatrix} = \begin{bmatrix} 1 \\ \mathcal{T}(0.75, \mathcal{J} - \Delta \mathcal{J}) \\ \mathcal{T}(0.50, \mathcal{J} - \Delta \mathcal{J}) \\ \mathcal{T}(0.25, \mathcal{J} - \Delta \mathcal{J}) \\ \mathcal{T}(0, \mathcal{J} - \Delta \mathcal{J}) \end{bmatrix}$$

This system of equations is solved for each \mathcal{J} , beginning with the inlet boundary:

$$\begin{bmatrix} 1 \\ \mathcal{T}(0.75, \mathcal{J} - \Delta \mathcal{J}) \\ \mathcal{T}(0.50, \mathcal{J} - \Delta \mathcal{J}) \\ \mathcal{T}(0.25, \mathcal{J} - \Delta \mathcal{J}) \\ \mathcal{T}(0, \mathcal{J} - \Delta \mathcal{J}) \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

Results are

\bar{y}	$z = 0$	$z = 0.25$	$z = 0.5$	$z = 0.75$	$z = 1$
0	0	0	0	0	1.0000
0.0625	0.0067	0.0152	0.0654	0.2916	1.0000
0.1250	0.0241	0.0458	0.1487	0.4605	1.0000
0.1875	0.0525	0.0880	0.2313	0.5652	1.0000
0.2500	0.0901	0.1372	0.3068	0.6349	1.0000
0.3125	0.1345	0.1901	0.3737	0.6846	1.0000
0.3740	0.1832	0.2440	0.4326	0.7223	1.0000
0.4375	0.2338	0.2972	0.4844	0.7523	1.0000
0.5000	0.2848	0.3486	0.5303	0.7771	1.0000
0.5625	0.3349	0.3975	0.5712	0.7982	1.0000
0.6250	0.3832	0.4437	0.6079	0.8166	1.0000
0.6875	0.4293	0.4869	0.6410	0.8327	1.0000
0.7500	0.4728	0.5271	0.6710	0.9471	1.0000
0.8125	0.5135	0.5645	0.6982	0.8601	1.0000
0.8750	0.5515	0.5991	0.7230	0.8718	1.0000
0.9375	0.5869	0.6311	0.7456	0.8824	1.0000
1.0000	0.6196	0.6606	0.7664	0.8921	1.0000

The backward differencing method requires the solution of $I + 1$ simultaneous equations to find the radial temperature profile. It is *semi-implicit* since the solution is still marched-ahead in the axial direction. *Fully implicit* schemes exist where $(J + 1)(I + 1)$ equations are solved simultaneously, one for each grid point in the total system. Fully implicit schemes may be used for problems where axial diffusion or conduction is important so that second derivatives in the axial direction, $\partial^2 a / \partial z^2$ or $\partial^2 T / \partial z^2$, must be retained in the partial differential equation. An alternative approach for this case is the shooting method described in Chapter 9. When applied to partial differential equations, shooting methods are usually implemented using an implicit technique in the radial direction. This gives rise to a tridiagonal matrix that must be inverted at each step in axial marching. The *Thomas algorithm* is a simple and efficient way of performing this inversion. Some finite difference approximations combine forward and backward differencing. One of these, *Crank-Nicholson*, is widely used. It is semi-implicit, unconditionally stable (at least for the linear case), and converges $O(\Delta r^2, \Delta z^2)$.