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Orthogonal Collocation in Chemical Reaction Engineering

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I. INTRODUCTION

The orthogonal collocation method is used to obtain approximate solutions to the differential equations modeling chemical reactors. There are two ways to view applications of the orthogonal collocation method. In one view it is a numerical method for which the convergence to the exact answer can be seen as the approximation is refined in successive calculations by using more collocation points, which are similar to grid points in a finite difference method. Another viewpoint considers only the first approximation, which can often be found analytically, and which gives valuable insight to the qualitative behavior of the solution. The answers, however, are of uncertain accuracy, so that the calculation must be refined to obtain useful numbers. However, with experience and appropriate caution, the first approximation is often sufficient and is easy to obtain. Thus it is very often useful in engineering work, where valid approximations are accepted. We present both viewpoints here: we use the first approximation to gain insight into a problem and we refine the calculations to obtain numerical convergence to the exact result. In this later view the method is similar to and in direct competition with finite difference methods, and some of the references listed in the next section discuss the relative advantages of the orthogonal collocation method.

We apply the method to problems arising in chemical reaction engineering. The presentation begins with a description of the method and then is organized around three case studies. In treating these case studies we give attention to methods by which we can ascertain a priori when certain heat and mass transfer phenomena is important, and then, if it is important, how that complication is incorporated in the orthogonal collocation formulation of the mathe-

matical model. An SO_2 oxidation reactor is treated first since al-
most all steady-state heat and mass transfer phenomena are im-
portant in the particular application. An ammonia reactor is in-
cluded as an example involving countercurrent heat transfer. Finally
a quasi-static model is developed for the reduction of nitric oxide in
automobile exhaust. Since the inlet conditions to the reactor vary
widely with time, it is necessary to consider a transient model.
Several assumptions can simplify the transient model, but even so
the computational requirements are extensive. The orthogonal col-
location method is used to reduce the computation time compared to
finite difference methods. The application of orthogonal collocation
in several other areas is outlined briefly.

II. ORTHOGONAL COLLOCATION METHOD

A. General Features of Method

The orthogonal collocation method was first developed by Villad-
sen and Stewart [1], and it is a special case of the collocation method
and the method of weighted residuals, which are discussed in more
detail elsewhere [2]. In most subsections of this section we con-
sider only one-dimensional problems; that is, the solution depends
on only one position, x, and we treat two-dimensional cases in Sec-
tions II-E and III. The unknown exact solution is expanded in a
series of known functions, $\{y_i(x)\}$ which are chosen to satisfy as
many conditions of the problem as is feasible: symmetry conditions
and possibly boundary conditions. The series of functions is called
a trial function.

$$\text{trial function} = y^*(x) = \sum_{i=1}^{N} a_i y_i(x) \tag{1}$$

The unknown coefficients in the series are to be determined in such
a way that the differential equation is satisfied in some "best" way.
In the collocation method the differential equation is required to be
zero at a set of grid points, called collocation points. The trial func-
tion is substituted into the differential equation, and the result is
called the residual. The residual will be zero throughout space for
the exact solution. For the approximate solution the residual is re-
quired to be zero at the collocation points, and this determines the
unknown coefficients in the trial function. As more terms are in-
cluded in the series, there are more unknown coefficients, and hence
the residual is set to zero at more collocation points. The hope is

that as the number of collocation points goes in infinity, and the residual is zero everywhere, that the approximate solution so generated converges to the exact solution. This can be proven in many problems. There are two basic ideas in the collocation method. One is similar to finite difference methods: the differential equation is satisfied at a set of grid or collocation points. The other idea is that the solution is expanded in a series which gives a continuous representation of the approximate solution over the whole region of space. In finite difference methods the solution is obtained by interpolation between adjacent grid points. In the orthogonal collocation method the continuous representation of the solution over the whole region has important advantages in that it increases the rate of conver-
to the exact solution as the number of collocation points is increased.

In this article we adopt an operational explanation of orthogonal collocation; that is, we show how to apply the method and leave the supporting theory to more extensive treatises [2]. In the orthogonal collocation method we make two improvements to Eq. (1): the trial functions are orthogonal polynomials (which improves the rate of convergence as N increases) and the computer programs are written in terms of the solution at the collocation points, $\{y^*(x_j)\}$, rather than the coefficients $\{a_i\}$. From Eq. (1) we see that since $y_i(x_j)$ are known, knowledge of $\{y^*(x_j)\}$ implies knowledge of $\{a_i\}$ and vice versa. Use of $\{y^*(x_j)\}$, however, simplifies the computer programing.

B. Orthogonal Collocation for Problems with Symmetry

In problems such as diffusion and reaction in a spherical or cylindrical catalyst pellet, or reaction in a cylindrical packed bed reactor, the solution is symmetric about the center of the catalyst pellet or the axis of the packed bed. In those problems the boundary condition is expressed as

$$\frac{dy}{dx}\bigg|_{x=0} = 0$$

For some problems it can be shown that this implies the solution is a function of x^2 rather than just x. In that case it is desirable to include this symmetry in the trial function because it reduces the number of unknowns by a factor of two.

We thus expand the solution in terms of orthogonal polynomials in powers of x^2:

$$y^*(x^2) = b + (1 - x^2)\sum_{i=1}^{N} a_i P_{i-1}(x^2) \tag{2}$$

where N is the number of interior collocation points and the colloca-
tion points are the roots to $P_N(x^2) = 0$. The roots for N from 1 to 6
are listed in Ref. 2, Chap. 5, and information is given there as to
roots for higher N.

The orthogonal collocation method is applied by substituting the
trial function, Eq. (2), into the differential equation, which is set to
zero when evaluated at each collocation point x_j. Derivatives of y^*
at the collocation points can be found in terms of $\{a_i\}$ from Eq. (2),
and hence $\{y^*(x_j^2)\}$. Thus the residual is expressed only in terms
of $y^*(x_j^2)$. To illustrate the procedure, consider the problem of re-
action and diffusion in a catalyst particle:

$$\frac{1}{x^{a-1}} \frac{d}{dx}\left(x^{a-1} \frac{dy}{dx}\right) = \frac{d^2y}{dx^2} + \frac{a-1}{x} \frac{dy}{dx} = \phi^2 f(y(x)) \tag{3}$$

$$\frac{dy}{dx}(0) = 0, \qquad -\frac{dy}{dx}(1) = Bi_m(y(1) - 1) \tag{4}$$

$$\eta \equiv \frac{\int_0^1 \phi^2 f(y(x))x^{a-1} \, dx}{\int_0^1 \phi^2 f(1)x^{a-1} \, dx} \tag{5}$$

where Bi_m is a Biot number for mass transfer. The residuals at the
interior collocation points are simply

$$\sum_{i=1}^{N+1} B_{ji}y_i = \phi^2 f(y_j), \quad j = 1, \ldots, N \tag{6}$$

where the B matrix represents the Laplacian at the collocation
points. It is listed in Table 1, and is derived as indicated in Ref. 2,
p. 100. The first boundary condition is satisfied identically. The
second boundary condition gives

$$-\sum_{i=1}^{N+1} A_{N+1,i}y_i = Bi_m(y_{N+1} - 1) \tag{7}$$

where the A matrix represents the first derivative. Equations (6)
and (7) provide N + 1 equations to solve for the N + 1 values of the
approximate solution at the collocation points, $y_1 \rightarrow y_{N+1}$. The effec-
tiveness factor is then given by

$$\eta = \sum_{i=1}^{N+1} f(y_i)W_i / [f(1) \sum_{i=1}^{N+1} W_i]$$

where W_i are the weighting factors for accurate quadrature formulas.

TABLE 1

Matrices in Orthogonal Collocation Method for $N = 1$[a]

Planar geometry, $a = 1$

$$r = \begin{pmatrix} 0.4472 \\ 1.0000 \end{pmatrix} \qquad W = \begin{pmatrix} 0.8333 \\ 0.1667 \end{pmatrix} \qquad A = \begin{pmatrix} -1.118 & 1.118 \\ -2.500 & 2.500 \end{pmatrix} \qquad B = \begin{pmatrix} -2.5 & 2.5 \\ -2.5 & 2.5 \end{pmatrix}$$

Cylindrical geometry, $a = 2$

$$r = \begin{pmatrix} 0.5774 \\ 1.0000 \end{pmatrix} \qquad W = \begin{pmatrix} 0.375 \\ 0.125 \end{pmatrix} \qquad A = \begin{pmatrix} -1.732 & 1.732 \\ -3.000 & 3.000 \end{pmatrix} \qquad B = \begin{pmatrix} -6 & 6 \\ -6 & 6 \end{pmatrix}$$

Spherical geometry, $a = 3$

$$r = \begin{pmatrix} 0.6547 \\ 1.0000 \end{pmatrix} \qquad W = \begin{pmatrix} 0.2333 \\ 0.1000 \end{pmatrix} \qquad A = \begin{pmatrix} -2.291 & 2.291 \\ -3.500 & 3.500 \end{pmatrix} \qquad B = \begin{pmatrix} -10.5 & 10.5 \\ -10.5 & 10.5 \end{pmatrix}$$

Nonsymmetric polynomials. A: d/dx. B: d^2/dx^2

$$x = \begin{pmatrix} 0.0 \\ 0.5 \\ 1.0 \end{pmatrix} \qquad W = \begin{pmatrix} 1/6 \\ 2/3 \\ 1/6 \end{pmatrix} \qquad A = \begin{pmatrix} -3 & 4 & 1 \\ -1 & 0 & 1 \\ 1 & -4 & 3 \end{pmatrix} \qquad B = \begin{pmatrix} 4 & -8 & 4 \\ 4 & -8 & 4 \\ 4 & -8 & 4 \end{pmatrix}$$

[a]Symmetric polynomials. A, First derivative. B, Laplacian $\dfrac{1}{x^{a-1}} \dfrac{d}{dx} x^{a-1} \dfrac{d}{dx}$

The solution of Eqs. (6) and (7) is usually done on a computer, since the equations are generally nonlinear and complicated for $N > 1$. It is instructive to look at the case $N = 1$, however, since an analytic solution is possible. Take a plane slab, $a = 1$, $f(y) = y^2$, and large Bi_m so that the boundary condition becomes $y(1) = y_{N+1} = 1$. Then for $N = 1$, Eqs. (6) and (7) are

$$-2.5y_1 + 2.5y_2 = \phi^2 y_1{}^2, y_2 = 1$$

where the appropriate values of B have been obtained from Table 1. The solution is

$$y_1 = [-2.5 + (6.25 + 10\phi^2)^{1/2}]/2\phi^2 \tag{8}$$

and the effectiveness factor is

$$\eta = (W_1 y_1{}^2 + W_2 y_2{}^2)/(W_1 + W_2)$$

$$\eta = \tfrac{5}{6} y_1{}^2 + \tfrac{1}{6} \tag{9}$$

Thus we can calculate η vs ϕ using Eqs. (8) and (9). The approxima-

tion is valid provided $\phi < 2$, and the reasons it is not valid for larger ϕ and how one determines the limit of 2 are discussed below.

For an unsteady-state problem,

$$\frac{\partial y}{\partial t} = \frac{1}{x^{a-1}} \frac{\partial}{\partial x}\left(x^{a-1}\frac{\partial y}{\partial x}\right) - \phi^2 f(y(x,t)) \tag{10}$$

with boundary conditions (4), we solve for $y_i(t) = y(x_i,t)$. At any time t,

$$\frac{1}{x^{a-1}} \frac{\partial}{\partial x}\left(x^{a-1}\frac{\partial y}{\partial x}\right)\Bigg|_{x_j} = \sum_{i=1}^{N+1} B_{ji}y_i(t)$$

and at any collocation point x_j,

$$\frac{\partial y(x,t)}{\partial t}\Bigg|_{x_j} = \frac{dy_j}{dt}$$

Thus we collocate at spatial positions x_j to obtain

$$\frac{dy_j}{dt} = \sum_{i=1}^{N+1} B_{ji}y_i - \phi^2 f(y_j), \qquad j = 1, \ldots, N \tag{11}$$

and the boundary condition (7). Equation (11) is integrated using standard techniques for ordinary differential equations.

The application of orthogonal collocation to solve problems such as Eq. (3) or Eq. (10) is relatively straightforward. The collocation points must be known, but are readily available. The matrices B and A are generated using the simple algorithm described in Ref. 2, and the Eq. (6) and (7) or (11) and (7) are solved using standard methods.

It is important, of course, to know a priori if the solution is a function of x or only of x^2. Sometimes this can be deduced by expanding the solution in a power series and deriving a recursion relation:

$$y = \sum_{i=0}^{\infty} a_i x^i$$

First $a_1 = 0$ because of the boundary condition, Eq. (4). Often a_3 depends only on a_1, and $a_1 = 0$ implies $a_3 = 0$. If this process continues so that $a_i = 0$ for all odd i, then the symmetric trial functions of this section can be used. If not, the procedures in the next section can be used. It is worthwhile to use symmetric trial functions if they are

applicable because the number of collocation points, and hence unknowns, is cut in half.

C. Orthogonal Collocation for Problems without Symmetry

When the solution is not a function of x^2 it is necessary to include both even and odd powers of x in the expansion. In place of Eq. (2) we then take

$$y^*(x) = b + cx + x(1 - x) \sum_{i=1}^{N} a_i P_{i-1}(x) \tag{12}$$

The matrices for first and second derivatives are different, but the application is otherwise similar. For large N the matrices can be derived without inverting a matrix by using the procedure given in Ref. 3.

Let us apply the method to a isothermal chemical reactor with axial dispersion:

$$\frac{1}{Pe} \frac{d^2 y}{dx^2} - \frac{dy}{dx} - f(y) = 0 \tag{13}$$

$$\frac{1}{Pe} \frac{dy}{dx} = y - 1, \qquad \text{at } x = 0 \tag{14}$$

$$\frac{dy}{dx} = 0, \qquad \text{at } x = 1 \tag{15}$$

The residuals at the collocation points are

$$\frac{1}{Pe} \sum_{i=1}^{N+2} B_{ji} y_i - \sum_{i=1}^{N+2} A_{ji} y_i - f(y_j) = 0, \qquad j = 2, \ldots, N + 1 \tag{16}$$

$$\frac{1}{Pe} \sum_{i=1}^{N+2} A_{1i} y_i = y_1 - 1 \tag{17}$$

$$\sum_{i=1}^{N+2} A_{N+2,i} y_i = 0 \tag{18}$$

These equations are then solved for the solution $\{y_j\}$, with $y_1 = y(0)$, $y_{N+2} = y(1)$, and y_i, $i = 2, \ldots, N + 1$ being the solution at the interior collocation points, $x_2, \ldots, x_{N+1}$.

D. Integration of Ordinary Differential Equations as Initial Value Problems

Orthogonal collocation can be applied to the integration of ordinary differential equations as initial value problems, too. The procedure was first outlined by Villadsen and Sørensen [4]. The initial condition gives y_1, the solution at the first collocation point. Orthogonal collocation is then applied, as in Eqs. (13) and (16) with Pe $\rightarrow \infty$, except that the residual, Eq. (16), is calculated for $j = 2$, ..., $N + 2$, i.e., including the last collocation point. Further details are given in Ref. 2, p. 107.

E. Two-Dimensional Problems

For two-dimensional problems we merely combine the orthogonal collocation method for each separate dimension. We can do this provided the boundaries of the problem lie along coordinate lines.

Let us illustrate the application by treating the problem of diffusion and reaction in a cylindrical catalyst pellet of finite length:

$$\epsilon^2 \frac{\partial^2 y}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial y}{\partial r}\right) = \phi^2 f(y) \tag{19}$$

$$\frac{\partial y}{\partial r} = 0, \quad \text{at } r = 0, \text{ all } z \tag{20}$$

$$\frac{\partial y}{\partial z} = 0, \quad \text{at } z = 0, \text{ all } r \tag{21}$$

$$-\frac{\partial y}{\partial r} = Bi_m(y - 1), \quad \text{at } r = 1, 0 < z < 1 \tag{22}$$

$$-\frac{\partial y}{\partial z} = Bi_m(y - 1), \quad \text{at } z = 1, 0 < r < 1 \tag{23}$$

where Bi_m is taken as constant around the cylinder. Now we write BR for the matrix B used in Section II-B for cylindrical geometry, and BZ for the matrix B used for plane geometry. If the problem was not symmetric in the z direction, we would use the other matrices from Table 1. Next let $y_{ij} = y(r_i, z_j)$. The residuals at the ij-th collocation points are then

$$\epsilon^2 \sum_{\ell=1}^{NZ+1} BZ_{j\ell} y_{i\ell} + \sum_{\ell=1}^{NR+1} BR_{i\ell} y_{\ell j} = \phi^2 f(y_{ij}), \quad i = 1, \ldots, NR; j = 1, \ldots, NZ \tag{24}$$

The boundary conditions are

$$-\sum_{\ell=1}^{NR+1} AR_{NR+1,\ell} y_{\ell j} = Bi_m(y_{NR+1,j} - 1), \qquad j = 1, \ldots, NZ \qquad (25)$$

$$-\sum_{\ell=1}^{NZ+1} AZ_{NZ+1,\ell} y_{i\ell} = Bi_m(y_{i,NZ+1} - 1), \qquad i = 1, \ldots, NR \qquad (26)$$

The effectiveness factor is given by

$$\eta = \frac{\sum_{i=1}^{NR} \sum_{j=1}^{NZ} f(y_{ij}) WR_i WZ_j}{f(1) \sum_{i=1}^{NR} WR_i \sum_{j=1}^{NZ} WZ_j} \qquad (27)$$

Here we have used orthogonal polynomials that result in $WR_{N+1} = WZ_{N+1} = 0$ (those with $w = 1$ in Chap. 5 of Ref. 2). Then the corner point, $y_{NR+1,NZ+1}$ does not enter the calculation.*

To apply the orthogonal collocation method in two-dimensions, we simply used the matrices derived for one dimension in appropriate combinations. It was not necessary to write down the trial function. If the trial function is desired, though, it can be constructed as the product of the two one-dimensional trial functions, with appropriate renumbering of equations:

$$y(r^2) = b + (1 - r^2) \sum_{i=1}^{NR} a_i P_{i-1}(r^2)$$

$$y(z^2) = b' + (1 - z^2) \sum_{i=1}^{NZ} a_i' P_{i-1}'(z^2)$$

Multiplying these together gives

$$y(r^2)y(z^2) = bb' + (1 - z^2) \sum_{i=1}^{NZ} ba_i' P_{i-1}'(z^2) + (1 - r^2) \sum_{i=1}^{NR} b'a_i P_{i-1}(r^2) +$$

$$(1 - z^2)(1 - r^2) \sum_{i=1}^{NR} \sum_{j=1}^{NZ} a_i a_j' P_i(r^2) P_j(z^2)$$

*The two boundary conditions (22) and (23) are also not applied at the corner, $r = 1$, $z = 1$. If they were to be satisfied, there would be two conditions and only one unknown to choose: $y_{NR+1,NZ+1}$. If it is necessary in some problem to include this corner point, then the degree of each polynomial can be increased by one. Then the set of unknowns is the function at each collocation point and the normal derivatives at the boundary. The residual is evaluated at every collocation point, including the boundary points, and the boundary condition is applied as well at the boundary point.

We rewrite this as

$$y(r^2, z^2) = b + (1 - z^2) \sum_{i=1}^{NZ} c_i P_{i-1}'(z^2) + (1 - r^2) \sum_{i=1}^{NR} d_i P_{i-1}(r^2)$$

$$+ (1 - z^2)(1 - r^2) \sum_{i=1}^{NR} \sum_{j=1}^{NZ} e_{ij} P_i(r^2) P_j'(z^2) \tag{28}$$

We cannot determine b unless the corner point $y(1,1)$ is found.

F. Orthogonal Collocation on Finite Elements

All the previous applications of orthogonal collocation have used trial functions defined over the whole domain. For some problems the interesting features of the solution are confined to a narrow region, perhaps as a boundary layer. The orthogonal collocation points corresponding to the trial function may not be located in those regions where the solution changes rapidly or is of the most interest, thereby deteriorating the approximation. Thus we are led to the desire for a method which permits the arbitrary location of collocation points. We also want to preserve the convenient features of the orthogonal collocation method inasmuch as possible. The method of orthogonal collocation on finite elements meets this requirement.

We present the ideas in the context of a one-dimensional problem of diffusion and reaction in a spherical catalyst, Eqs. (3) and (4) with a = 3. The domain $0 \leq x \leq 1$ is divided into elements, and the k-th element extends from x_k to x_{k+1}. In each element we change the independent variable so that it goes from 0 to 1:

$$u = \frac{x - x_k}{x_{k+1} - x_k} = \frac{x - x_k}{\Delta x_k}$$

The differential equation within the k-th element is then

$$\frac{1}{(\Delta x_k)^2} \frac{d^2 y}{du^2} + \frac{2}{x_k + u \Delta x_k} \frac{1}{\Delta x_k} \frac{dy}{du} = \phi^2 f(y) \tag{29}$$

Applying orthogonal collocation on $0 \leq u \leq 1$ gives

$$\frac{1}{(\Delta x_k)^2} \sum_{i=1}^{N+2} B_{ji} y_i^k + \frac{2}{x_k + u_j \Delta x_k} \frac{1}{\Delta x_k} \sum_{i=1}^{N+2} A_{ji} y_i^k = \phi^2 f(y_j^k),$$

$$j = 2, \ldots, N + 1 \tag{30}$$

for the residual at the interior collocation points of the element,

$u_2, \ldots, u_{N+1}$. The points u_1 and u_{N+2} are the end points of the element. The y_i^k is the solution at the i-th collocation point of the k-th element. Between each element we require that the function and its first derivative be continuous. Thus we set

$$y_{N+2}^{k-1} = y_1^k; \quad y_{N+2}^k = y_1^{k+1} \tag{31}$$

$$\frac{1}{\Delta x_{k-1}}\sum_{i=1}^{N+2}A_{N+2,i}y_i^{k-1} = \frac{1}{\Delta x_k}\sum_{i=1}^{N+2}A_{1i}y_i^k \tag{32}$$

$$\frac{1}{\Delta x_k}\sum_{i=1}^{N+2}A_{N+2,i}y_i^k = \frac{1}{\Delta x_{k+1}}\sum_{i=1}^{N+2}A_{1i}y_i^{k+1} \tag{33}$$

In the solution of these equations, Eq. (31) is satisfied automatically by using the same variable for the solution at the last point of one element and the first point of the next element. The solution vector is written as

$$\bar{y}^T = \left(y_1^1, y_2^1, \ldots, y_{N+2}^1, y_2^2, y_3^2, \ldots, y_{N+2}^2, y_2^3, \ldots, y_{N+2}^{NE}\right)$$

with NE as the total number of elements. This vector is renumbered as

$$\bar{y}^T = (y_1, y_2, \ldots, y_L); \qquad L = NE(N+1) + 1$$

The equations can then be written in the form shown in Fig. 1. The matrix on the left-hand side is a block diagonal matrix and is readily inverted. It is not necessary to store all the zeros in the computer. Methods of solution are discussed in more detail elsewhere [5]

G. Comparison of Methods

The method of orthogonal collocation on finite elements is a combination of orthogonal collocation and finite difference methods. It is instructive to compare the methods to see their advantages. The rate of convergence for the usual second order difference scheme is Δx^2 or $(1/N)^2$, where N is the number of grid points minus one and Δx is the grid spacing. By contrast the orthogonal collocation method, using a continuous polynomial defined over the entire domain, converges as $(1/N)^N$, where N is the number of interior collocation points and provided the exact solution is highly continuous [6]. Clearly for large N the rate of convergence is very fast. The method of orthogonal collocation on finite elements converges as $(\Delta x)^{N+2}$, where Δx is the number of elements and $N + 1$ is the degree of poly-
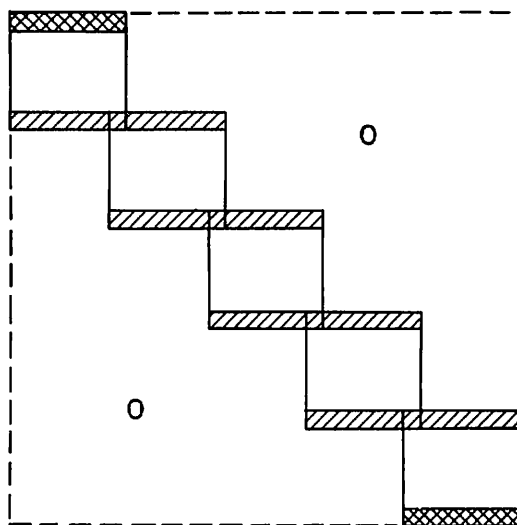
FIG. 1. Matrix structure of orthogonal collocation on finite elements. Cross-hatched area, equations arising from boundary conditions; hatched area, equations arising from continuity of first derivatives at boundaries of elements; clear areas, equations arising from residuals at interior collocation points of each element.

nomial within each element. The function and its first derivative at the end point of each element converge even faster, as $(\Delta x)^{2N}$ when the collocation points are taken as Gaussian quadrature points [7], as is the case when using orthogonal collocation. Douglas [8] has shown for linear problems that the rate of convergence is Δx^{2N} at all the collocation points and Δx^{2+N} globally; that is, at points other than collocation points. Thus we see that the slowest rate of convergence is for the finite difference method, the next highest is for the method of orthogonal collocation on finite elements, and the fastest of all is for orthogonal collocation.

Another feature of interest is the time it takes to solve the resulting equations. Here the advantages are reversed. The finite difference method leads to tridiagonal matrices, which are quickly inverted. The storage requirements are $3N - 2$, where N is the number of grid points. For orthogonal collocation on finite elements the block diagonal matrix illustrated in Fig. 1 is only slightly more time-consuming to invert. Its storage requirements are $NE \times (N + 2)^2$. The orthogonal collocation method leads to a dense matrix, with nearly every value nonzero, which takes the longest time to invert and needs N^2 storage spaces. Of course, since fewer collocation points are needed, the matrix need not be as big. Thus

a priori comparisons of the methods are difficult. In addition, when solving a problem whose solution is a function only of x^2, the orthogonal collocation method automatically requires one-half as many collocation points to achieve the same degree of polynomial in the region. If the solution does not have steep gradients, then orthogonal collocation would be used because of its rapid convergence. If steep gradients are expected, orthogonal collocation on finite elements would be used, again because of its rapid convergence compared to finite difference techniques. It seems that orthogonal collocation on finite elements combines the rapid convergence of the orthogonal collocation method with the relative efficiency of inverting the matrices. Detailed comparisons of computing time and accuracy are given elsewhere [5].

III. SULFUR DIOXIDE OXIDATION REACTOR

A. Introduction

In this chapter we apply the orthogonal collocation method to a particular case—oxidation of SO_2 in a catalytic, packed bed reactor. We discuss the importance of various heat and mass transfer phenomena: radial and axial dispersion, and external and internal resistances to heat and mass transfer. Emphasis is given to deciding when these phenomena are important, and must be included in a mathematical model. The first approximation of the orthogonal collocation method is frequently useful for doing this. Finally, a mathematical model is developed for the SO_2 reactor which includes all the relevant phenomena, and the orthogonal collocation method is applied to this model. The results confirm the importance of the heat and mass transfer resistances.

The reactor in question is a pilot-plant-scale catalytic packed bed reactor for the oxidation of sulfur dioxide to form sulfur trioxide. Results of experimental measurements of temperature and concentration distributions are given in Smith [9]. Reaction rate data are given there as well as in an earlier article by Olson et al. [10]. The reaction rate data was taken in a small reactor, about three particle diameters long. The reactor was assumed to be differential, and conversion and temperature were taken as the average of inlet and outlet values. Olson et al. [10] noticed that interphase resistance was important at the flow rate in question; that is, the particle temperatures differed from the gas stream temperature near the particle. This resistance is called an external resistance to heat transfer since the resistance arises due to the thermal boundary layer developed external to the particle.

The SO_2 reactor which is modeled here was about 50 particle diameters long. The inlet gas stream was preheated to 400°C and entered the packed bed, which was cooled by boiling glycol at 197°C. The average conversion out of the reactor was measured, and the outlet temperature was measured at various radial positions. The reactor was operated several times, with each case having a different length of packing, in order to obtain average concentration and temperature profiles as a function of position down the bed.

A cylindrical packed bed reactor is by its very nature a heterogeneous system. The packing is random and irregular, the void fraction is larger near the wall, and the temperature of the solid and gas need not be the same at nearby positions, and can fluctuate drastically from position to position. We employ here the usual model [11, 12] which treats the reactor as if it were homogeneous, and transport of heat by conduction through the solid and conduction and dispersion through the fluid is modeled by an effective thermal conductivity. Similarly, diffusion and dispersion of mass is included by means of an effective diffusivity. Due to the spatially varying void fraction, the axial velocity also varies with the radius in the bed (see, e.g., Ref. 13 and references cited there). Throughout this paper we employ a plug flow model by assuming the velocity is constant across the cylinder cross section and the effective diffusivities and thermal conductivities are constant. Since the models we use have been discussed in detailed reviews [11, 12], we do not derive the equations, but merely state them.

B. Importance of Radial Dispersion

The equations for concentration of SO_2 and gas temperature in a reactor model including plug flow in the axial direction, radial dispersion, and chemical reaction are

$$\frac{G}{\rho} \frac{\partial C}{\partial z'} = D_r \frac{1}{r'} \frac{\partial}{\partial r'} \left(r' \frac{\partial C}{\partial r'} \right) - \rho_B R(C, T') \tag{34}$$

$$\tilde{C}_p G \frac{\partial T'}{\partial z'} = k_r \frac{1}{r'} \frac{\partial}{\partial r'} \left(r' \frac{\partial T'}{\partial r'} \right) + (-\Delta H_R) \rho_B R(C, T') \tag{35}$$

$$\frac{\partial T'}{\partial r'} = 0, \qquad \frac{\partial C}{\partial r'} = 0 \qquad \text{at } r' = 0 \tag{36}$$

$$-k_r \frac{\partial T'}{\partial r'} = h_w (T' - T_w'), \qquad \frac{\partial C}{\partial r'} = 0, \qquad \text{at } r' = r_0 \tag{37}$$

$$C = C_0, \qquad T' = T_0, \qquad \text{at } z' = 0 \tag{38}$$

For simplicity here we have written the reaction rate expression as if it depended only on the gas concentration and temperature. We also assume here that all physical properties are constant. The generalizations are given below in specific cases where needed.

Next we nondimensionalize these equations using the definitions $z = z'/L$, $r = r'/r_0$, $X = C/C_0$, $T = T'/T_0$, and obtain in place of Eq. (34) to Eq. (38):

$$\frac{\partial X}{\partial z} = \frac{\alpha}{r}\frac{\partial}{\partial r}\left(r\frac{\partial X}{\partial r}\right) - Da_I \Re(X,T) \tag{39}$$

$$\frac{\partial T}{\partial z} = \frac{\alpha'}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + Da_{III}\Re(X,T) \tag{40}$$

$$\frac{\partial T}{\partial r} = 0, \qquad \frac{\partial X}{\partial r} = 0, \qquad \text{at } r = 0 \tag{41}$$

$$-\frac{\partial T}{\partial r} = Bi_w(T - T_w), \qquad \frac{\partial X}{\partial r} = 0, \qquad \text{at } r = 1 \tag{42}$$

$$T = 1, \qquad X = 1, \qquad \text{at } z = 0 \tag{43}$$

The reaction rate term $\Re$ in Eqs. (39) and (40) is a dimensionless version of that appearing in Eqs. (34) and (35). The specific form is left to each case treated below.

When radial dispersion is not important, we expect there to be little variation of X and T in the radial direction. If we average Eqs. (39) and (40) over radius, using

$$\langle f \rangle = \int_0^1 f(r)r \; dr \Big/ \int_0^1 r \; dr$$

and applying the boundary conditions, we get

$$\frac{d\langle X \rangle}{dz} = -Da_I \langle \Re(X,T) \rangle \tag{44}$$

$$\frac{d\langle T \rangle}{dz} = -\frac{2StL}{r_0}(\langle T \rangle - T_w) + Da_{III}\langle \Re(X,T) \rangle \tag{45}$$

If the concentration and temperature do not change in the radial direction, then we can use

$$\langle \Re(X,T) \rangle = \Re(\langle X \rangle, \langle T \rangle) \tag{46}$$

together with the initial conditions

$$\langle X \rangle = 1, \qquad \langle T \rangle = 1, \qquad \text{at } z = 0 \tag{47}$$

Equations (44)-(47) are referred to as the lumped parameter model, since only average quantities are calculated, in contrast with Eqs. (39)-(42), which permit a radial distribution of concentration and temperature, and hence are called a distributed parameter model. The lumped parameter model is easy to solve—hence its wide applicability. We wish to examine the question of whether it is an appropriate simplification.

Orthogonal collocation has been applied to these equations by numerous authors [13-18].* Equations (39) and (40) are similar to Eq. (10) and the application of orthogonal collocation leads to equations similar to Eq. (11):

$$\frac{dX_j}{dz} = \alpha \sum_{i=1}^{N+1} B_{ji} X_i - Da_I \Re(X_j, T_j) \qquad j = 1, \ldots, N \tag{48}$$

$$\frac{dT_j}{dz} = \alpha' \sum_{i=1}^{N+1} B_{ji} T_i + Da_{III} \Re(X_j, T_j) \tag{49}$$

Similarly the boundary conditions give Eq. (7) with $Bi_m = 0$ for the X equation and $Bi_m = Bi_w$ for T.

These equations can be integrated in many different ways. Explicit integration schemes, such as the improved Euler or Runge-Kutta methods, can be used. Then the maximum Δz is limited by stability considerations, and a useful estimate is given by Ref. 2, p. 118:

$$\Delta z \leqslant k / \alpha |\lambda|_{max}$$

$$|\lambda|_{max} < ||B'||_\infty \equiv \overset{max}{j = 1}, \ldots, N \sum_{k=1}^{N} |B_{jk}'|$$

$$B_{jk}' = B_{jk} - B_{j,N+1} A_{N+1,k} / (Bi + A_{N+1,N+1})$$

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*Stewart and Sørensen [18] consider the possibility of using different orthogonal polynomials depending on the Biot number. This is done by using different collocation points, the rest of the analysis being the same. The effect of this change is to sometimes slightly speed convergence to the exact solution as N increases. The present author prefers to use just one set of collocation points for all Bi, namely those with w = 1 in Ref. 2, Chap. 5, in order to simplify the presentation and computer programs.

where the value of k is determined by the integration method. The value of k is 1, 2, and 2.8 for the Euler, modified Euler, and fourth order Runge-Kutta methods, respectively. This estimate gives only a "first guess" for a suitable Δz since the stability of the calculations is also influenced by the reaction rate term, which is not included in the estimate. Crank-Nicolson methods can also be used by writing, e.g.,

$$\frac{T_j^{k+1} - T_j^k}{\Delta z} = \frac{1}{2}\alpha' \sum_{i=1}^{N+1} B_{ji}(T_i^{k+1} + T_i^k) + Da_{III}\Re(X_j^k, T_j^k)$$

Other modifications are also possible. The orthogonal collocation method mentioned in Section II-D has also been found useful for integrating the equations [2, p. 134].

In the first approximation (N = 1, matrices from Table 1) Eqs. (48), (49), and (7) can be rearranged to give

$$\frac{dX_1}{dz} = -Da_I\Re(X_1, T_1) \tag{50}$$

$$\frac{dT_1}{dz} = -\left(\frac{6Bi_w\alpha'}{Bi_w + 3}\right)(T_1 - T_w) + Da_{III}\Re(X_1, T_1) \tag{51}$$

Comparing these equations to Eqs. (44) and (45), we find that they are similar, and in fact the same provided we make the identification

$$\langle X \rangle = X_1, \qquad \langle T \rangle = T_1, \qquad \frac{2StL}{r_0} = \frac{6Bi_w\alpha'}{Bi_w + 3} \tag{52}$$

Now in the first approximation the average conversion is the conversion at the collocation point provided the polynomial used is $P_1(r^2) = 1 - 2r^2$ and the collocation point is $r_1 = 0.707$, rather than 0.577; i.e., the polynomials defined by w = 1 in Ref. 2, Chap. 5. In that case the $6Bi\alpha'/(Bi + 3)$ is replaced by $8Bi\alpha'/(Bi + 4)$ [2, Chap. 5, p. 13]. Notice that Eqs. (50) and (51) refer to the conversion and temperature at a particular radius, when they vary parabolically with r, whereas Eqs. (44) and (45) refer to a conversion and temperature which are constant in r. The dimensional form of Eq. (52) is

$$\frac{1}{U} = \frac{1}{h_w} + \frac{R}{3k_e}, \qquad \text{using } r_1 = 0.577 \tag{53}$$

$$\frac{1}{U} = \frac{1}{h_w} + \frac{R}{4k_e}, \qquad \text{using } r_1 = 0.707 \tag{54}$$

The equivalence (54) has been shown before (see Finlayson [13] for references). In fact, Crider and Foss [19] suggest better comparison with exact results by taking

$$\frac{1}{U} = \frac{1}{h_w} + \frac{R}{3.067k_e} \tag{55}$$

The relative importance of the wall resistance is evident by comparing the two terms in Eq. (53) or (55) with each other. The ratio of $1/h_w$ to $1/U$ or, equivalently, $1/Bi_w + 1/3.067$ gives a measure of the fraction of the thermal resistance which occurs at the wall: e.g., $Bi = 1$, 75%; $Bi = 10$, 23%; $Bi = 20$, 13%. For small Biot numbers, most of the resistance occurs at the wall and only a one-dimensional treatment is necessary. This can be obtained from the orthogonal collocation method using Eqs. (48) and (49) and $N = 1$. For large Biot numbers, radial dispersion becomes more important, and the full two-dimensional treatment is necessary with a larger N.

Numerical computations to test the accuracy of the orthogonal collocation method for various N have confirmed these guidelines. For a case with a severe hot spot, Finlayson [13] found that only $N = 1$ or 2 was needed when $Bi_w = 1$, whereas for $Bi_w = 20$, $N = 5$ was needed for a good approximation. McGreavy and Turner [20] also found that a lumped parameter model was adequate for a case which had $Bi_w = 2$. Mears [21] has presented a criterion which says the error in the average rate of reaction computed by a one-dimensional model is less than 10% provided

$$\frac{Da_{III}}{\alpha'} \frac{E}{R_g T_w} \left(1 + \frac{4}{Bi_w}\right) < 0.8 \tag{56}$$

For the cases treated by Finlayson [13], with $Bi_w = 1$, the left-hand side is 20, but for $Bi_w = 20$ it is 4.8. Thus in both cases radial dispersion is expected to be important. In fact, however, radial dispersion was relatively unimportant for $Bi_w = 1$ when using the overall heat transfer coefficient Eq. (53), and radial dispersion was least important for that case ($Bi_w = 1$) which had the largest left-hand side, in opposition to the criterion. Thus the criterion (56) is only a guideline and computations indicate that the distributed parameter model is important when the Biot number is large (say >3). The case discussed in Section V leads to a different result: the Biot number is large, but the heat of reaction is so small that the reactor is almost isothermal, and a small N suffices. Thus if the Biot number is small (~1) or the reactor is nearly isothermal, the lumped parameter model is suitable. If selectivity among competing reac-

tions is an important consideration, the temperature distribution is important, and a large N (~3 to 5) would be needed for large Biot number. Similar guidelines of needing a distributed parameter model when the Biot number is large are given by Carberry and White [22].

It is instructive to look at the Biot number as a function of Reynolds number. For Reynolds numbers above 200, the Peclet number is approximately constant at a value of 10. Smith [23] summarizes the correlation for heat transfer coefficient as

$$Nu_w = \frac{h_w d_p}{k_f} = 2.58(Re_p Pr)^{0.33} + 0.094 Re_p^{0.8} Pr^{0.4}, \qquad Re_p > 40 \tag{57}$$

We rearrange these equations to give the Biot number

$$Bi_w = \frac{h_w r_0}{k_e} = Nu_w \frac{r_0}{d_p} \frac{Pe}{Pr Re}$$

Using the correlation (57), Pr = 0.7 (common for gases), Pe = 10 gives

$$Bi_w = \frac{r_0}{d_p}(32.7 Re_p^{-2/3} + 1.16 Re_p^{-0.2}) \tag{58}$$

The Biot number decreases as Reynolds number is increased, and the values listed in Table 2 are all small. In an industrial situation the packing diameter is chosen as large as possible in order to minimize pressure drop through the reactor; the tube diameter is chosen

TABLE 2

Biot Number
Dependence on
Reynolds number

Re	Bi[a]
200	4.1
500	2.6
1000	1.8
2000	1.4
5000	1.0

[a]Calculated from
Eq. (58) with r_0/d_p = 3.

small in order to minimize temperature variations across the cross section of the bed (which might have adverse consequences with regard to selectivity), and a high flow rate is used by economic necessity. All of these influences tend to decrease the Biot number, so that in many practical situations the lumped parameter model is adequate. The important parameter deciding that question is the Biot number.

For the SO_2 reactor, we have $r_0 = 0.0262$ m, $d_p = 0.00318$ m, (equivalent diameter of cylindrical packing), Re = 46, and the various correlations for k_e and h_w [11] give Biot numbers ranging from 3.1 to 13. These are high enough that we do not expect the lumped parameter model to suffice, and the detailed calculations shown below demonstrate this. This reactor is a laboratory reactor, operated at a relatively low flow rate, and radial dispersion is important.

C. Importance of Axial Dispersion

To examine the importance of axial dispersion, we study a model involving axial dispersion, but no radial dispersion, with constant physical properties:

$$D_L \frac{\partial^2 C}{\partial z'^2} - \frac{G}{\rho} \frac{\partial C}{\partial z'} - \rho_B R(C,T') = 0 \tag{59}$$

$$k_L \frac{\partial^2 T'}{\partial z'^2} - \tilde{C}_p G \frac{\partial T'}{\partial z'} - \frac{2U}{r_0}(T' - T_w) + (-\Delta H_R)\rho_B R(C,T') = 0$$

$$D_L \frac{\partial C}{\partial z'} = \frac{G}{\rho}(C - C_0), \qquad k_L \frac{\partial T'}{\partial z'} = \tilde{C}_p G(T' - T_0), \qquad \text{at } z' = 0$$

$$\frac{\partial C}{\partial z'} = 0, \qquad \frac{\partial T'}{\partial z'} = 0, \qquad \text{at } z' = L$$

The reaction rate term, R, here has the dimensions of (kg)(mole)/(sec)(kg)(cat). Orthogonal collocation is applied to these equations as illustrated in Eqs. (13)-(18), [2, p. 126].

If the system is isothermal, that is U = 0, $-\Delta H_R = 0$, and $T_w = T_0$, and first order, then $\rho_B R = kC$, where k has dimensions of reciprocal time. Under these conditions a criterion for the importance of axial dispersion is [24-26]

$$\frac{C}{C_p} = 1 + \left(\frac{\rho k}{G}\right)^2 \frac{d_p L}{Pe_{m,z}} \tag{60}$$

where C is the outlet concentration from a reactor of length L with

axial dispersion included, and C_p is the concentration at length from a reactor keeping only the plug flow term, ignoring axial dispersion (setting $D_L = k_L = 0$). As a first approximation we apply Eq. (60) to the SO_2 reactor using a pseudofirst-order rate constant evaluated at the inlet conditions, $k \equiv \rho_B R_0 / C_0 = 4.45 \times 10^4/\text{hr}$, at $T' = 400°C$. Pertinent quantities are listed in Table 3. The results give $C/C_p = 1.04$, so that axial dispersion by this estimate, leads to a small effect.

TABLE 3

Data for SO_2 Reactor

$L = 0.145$ m; $r_0 = 0.0262$ m; $d_p = 0.00318$ m; $\epsilon \simeq 0.43$

$\rho_B = 1030$ (kg)(cat)/m³; $G = 1710$ kg/(m²)(hr); $-\Delta H = 98,000$ kJ/(kg)(mole)

$C_p = 1.00$ kJ/(kg)(°C); $\rho/C_0 = 459$ kg/(kg)(mole); $a_v = 1.05$ m²/(kg)(cat)

$L/d_p = 45.6$; $r_0/d_p = 8.24$; Re $= 46$; $Bi_w = 10$

$Pe_{h,r} = 2.9$; $Pe_{h,z} = 0.95$; $Pe_{m,r} = 9.6$; $Pe_{m,z} = 2$

$\alpha = 0.074$; $\alpha' = 0.22$; $\gamma = 0.010$; $\gamma' = 0.0218$

$Da_I' = 46.4$ (kg)(cat)(hr)/(kg)(mole); $\sigma = 0.730$ (kg)(mole)/(kg)(cat)(hr)

$Da_{III}' = 47.1$ (kg)(cat)(hr)(°K)/(kg)(mole); $\sigma' = 0.00853$ (kg)(mole)/(kg)(cat)(hr)(°K)

$\sigma(X - X_s) = \sigma'(T_s' - T') = R(T_s, X_s)$

$R(T_s, X_s) = \{X_s[1 - 0.167(1 - X_s)]^{1/2} - 2.2(1 - X_s)/K_{eq}\}/[k_1 + k_2(1 - X_s)]^2$

$\left. \begin{array}{l} \ln K_{eg} = -11.02 + 11570/T_s' \\ \ln k_1 = -14.96 + 11070/T_s' \\ \ln k_2 = -1.331 + 2331/T_s' \end{array} \right\}$ T_s' in °K

For reactor used to measure reaction rate

$\alpha' = 0.0209$; $Bi_w = 3.52$; $\gamma' = 0.344$

$\alpha, \gamma, \sigma, \sigma', Da_I', Da_{III}'$ same as above

We next apply the criterion developed by Young and Finlayson[27] for nonisothermal reactors with heating or cooling at the walls. The reason this criterion is different from Eq. (60) is that in an isothermal or adiabatic reactor the concentration always approaches the equilibrium conversion as the length is increased. This is true whether or not axial dispersion is included, so that the effect of axial dispersion is expected to be negligible for long reactors (often the criterion is stated as $L/d_p > 50$ [28, 29]). In a reactor with heating or cooling at the walls, however, the cooling can be so great as to quench the reaction, so that the equilibrium conversion is not reached, no matter how long the reactor is. In this case the temperature distribution is all important, and this is affected by axial dispersion. Young and Finlayson [27] developed a criterion which

says that axial dispersion is important at the inlet of the reactor if the following inequalities are violated:

$$T' - T_p' = \frac{d_p}{Pe_{h,z}} \frac{(-\Delta H_R)\rho_B R(C_0,T_0)}{G\tilde{C}_p} \ll 1 \tag{61}$$

$$\frac{C - C_p}{C_0} = \frac{d_p}{Pe_{m,z}} \frac{\rho\rho_B R(C_0,T_0)}{GC_0} \ll 1 \tag{62}$$

If axial dispersion is important, at the inlet $T'(0)$ may be higher than T_0, thus increasing the reaction rate and affecting the temperature distribution throughout the reactor. If the conversion approaches the equilibrium conversion anyway, then axial dispersion is probably not important. If the temperature reaches a peak and then decreases with length, and the equilibrium conversion is not reached, then axial dispersion should be included if either inequality (61) or (62) is violated. The temperature inequality is the most crucial one in practice. Neither inequality speaks to the question of the importance of axial dispersion at a hot spot interior to the bed, where large axial gradients may develop (see Ref. 27). For the SO_2 reactor using R = 0.0510 (kg)(mole)/(kg)(cat)(hr) at 400°C and zero conversion, application of Eqs. (61) and (62) gives $(C - C_p)/C_0 = 0.022$ and $T' - T_p' = 9.6$°C. The later value is large enough to cause a 60% increase in the reaction rate at the inlet, so axial dispersion is important there. Calculations below show that the equilibrium conversion is not reached, so that axial dispersion must be included in the model.

D. Importance of External Resistance

As a gas stream flows past a catalyst pellet, the reactants must diffuse through a concentration boundary layer near the surface of the catalyst, and energy must also diffuse through a thermal boundary layer. Consequently, the concentration and temperature on the surface of the catalyst are not the same as their bulk stream values due to these resistances to heat and mass transfer. The usual procedure for accounting for this phenomena mathematically is to introduce heat and mass transfer coefficients. By making energy and mass balances around catalyst particles, we are led to the equations

$$k_m a_v(C - C_s) = \rho_B R(C_s,T_s') \tag{63}$$

$$h_p a_v(T_s' - T') = (-\Delta H_R)\rho_B R(C_s,T_s') \tag{64}$$

where $\rho_B R(C_s,T_s')$ is the rate of reaction per unit volume of the bed,

evaluated at the solid concentration and temperature, and a_v is the surface area of catalyst per volume of the bed.

We ask ourselves: Are these external resistances important? Equations (63) and (64) can be solved for C_s and T_s', given C and T', the bulk stream values. For most cases a simple iterative calculation is feasible: substitute C and T' on the right-hand side, solve Eqs. (63) and (64) for C_s and T_s', use these values on the right-hand side, and continue until the desired accuracy is reached. The importance of including the external resistances can be assessed by computing an effectiveness factor

$$\eta = \frac{R(C_s, T_s')}{R(C, T')} \tag{65}$$

This measures the fractional reduction (or increase) of the reaction rate due to external resistance. Since the solution to Eqs. (63) and (64) depends on the bulk stream values, the effectiveness factor will, too. Thus it will vary from position to position in the reactor. We thus calculate η for a range of possible concentrations and temperatures. If the values depart from 1 significantly (say above 1.1 or below 0.9), then external resistances should be included in the model. Mears [21] gives the criterion that the rate neglecting external heat transfer resistances is within 10% of the correct rate provided

$$\frac{(-\Delta H_R)\rho_B R d_p}{2 h_p T_0} \frac{E}{R_g T_0} < 0.15 \tag{66}$$

or

$$\frac{\beta \phi^2}{Bi} \frac{E}{R_g T_0} < 0.15$$

We illustrate two methods of including external resistances in a reactor model including radial dispersion. In place of Eqs. (34) and (35), we use Eqs. (63) and (64) to rewrite the equations in the form

$$\frac{G}{\rho} \frac{\partial C}{\partial z'} = D_r \frac{1}{r'} \frac{\partial}{\partial r'} \left(r' \frac{\partial C}{\partial r'} \right) - k_m a_v (C - C_s) \tag{67}$$

$$\tilde{C}_p G \frac{\partial T'}{\partial z'} = k_r \frac{1}{r'} \frac{\partial}{\partial r'} \left(r' \frac{\partial T'}{\partial r'} \right) + h_p a_v (T_s' - T') \tag{68}$$

At every (r', z') position in the bed where Eqs. (67) and (68) are applied, we must solve Eqs. (63) and (64) since they determine C_s

and T_s'. Another method of introducing the interphase resistances is to use the effectiveness factor. In place of Eqs. (67) and (68) we get

$$\frac{G}{\rho}\frac{\partial C}{\partial z'} = D_r\frac{1}{r'}\frac{\partial}{\partial r'}\ r'\frac{\partial C}{\partial r'}\ -\ \eta\rho_B R(C,T') \tag{69}$$

$$\tilde{C}_p G\frac{\partial T'}{\partial z'} = k_r\frac{1}{r'}\frac{\partial}{\partial r'}\ r'\frac{\partial T'}{\partial r'}\ +\ \eta(-\Delta H_R)\rho_B R(C,T') \tag{70}$$

The reaction rate term is evaluated at the bulk stream values. At first glance this seems to obviate the need to solve Eqs. (63)-(69), but this must be done to find the effectiveness factor η by Eq. (65).

Another feature of interest is the maximum temperature which can be reached in the catalyst, assuming only interphase resistances. Equation (63) can be multiplied by $(-\Delta H_R)$, subtracted from Eq. (64), and the result rearranged to give

$$T_s' + \frac{(-\Delta H_R)k_m}{h_p}C_s = T' + \frac{(-\Delta H_R)k_m}{h_p}C$$

Now for given bulk stream values, C and T', the minimum concentration in the catalyst is zero. Thus the maximum temperature rise is

$$\Delta T_{max}' = \frac{(-\Delta H_R)k_m}{h_p}C \tag{71}$$

This value should also be calculated to assess the importance of external resistances, since it gives an upper bound on T_s', although this temperature may not be reached. The actual T_s' calculated from Eqs. (63) and (64) may be considerably lower so that the calculation of η gives the best insight as to the importance of interphase resistances.

In order to solve Eqs. (63) and (64) or to use Eq. (71), we must have the heat and mass transfer coefficients, h_p and k_m. These are determined from correlations for Nusselt or Sherwood numbers,

$$Nu = \frac{h_p d_p}{k}, \qquad Sh = \frac{k_m d_p}{D} \tag{72}$$

which are given in terms of the j-factors, defined as

$$j_H \equiv Nu Re^{-1}Pr^{-1/3}, \qquad j_M \equiv Sh Re^{-1}Sc^{-1/3}$$

Solving for k_m/h_p and substituting into Eq. (71) gives

$$\Delta T_{max}' = \frac{(-\Delta H_R)}{\rho \tilde{C}_p} \left(\frac{j_M}{j_H}\right)\left(\frac{Pr}{Sc}\right)^{2/3} C$$

Since $j_M = 0.7 j_H$ for a range of Reynolds numbers [9, p. 364], and $Pr \simeq Sc$ for gaseous systems [9, p. 364], this gives

$$\Delta T_{max}' \simeq 0.7(-\Delta H_R)C/(\rho\tilde{C}_p) \tag{73}$$

or a maximum temperature rise of 70% of the adiabatic temperature rise.

For the SO_2 reactor under the stated conditions the adiabatic temperature rise is 214°C, so that Eq. (73) gives $\Delta T_{max}' = 149°C$, which is a significant temperature rise. However, the actual temperature rise is given by Eqs. (63) and (64) which are [27]:

$$X - X_s = 1.37R, \qquad T_s' - T' = 117R$$

where R is given in units of (kg)(mole)/(kg)(cat)(hr)(°K). For T' = 673°K, X = 1.0 (at the inlet) successive application of the suggested iteration gives $X_s = 0.935$ and $T_s' - T' = 5.6°C$. Thus the catalyst would be about 6°C hotter in a place in the reactor where the gas outside was at 400°C and at zero conversion. The effectiveness factor turns out to be $\eta = 0.94$, which is close enough to 1 that it is questionable whether external resistances should be included. However, downstream we find below that the gas temperature rises to 500°C when the conversion is 30%. Under these conditions $T_s' - T'$ = 9.7°K, $X - X_s = 0.11$, and $\eta = 0.57$. Also, the left-hand side of Eq. (66) is 4.0. Thus the external resistance is important here and must be included in the model.

E. Importance of Internal Resistance

After the reactants reach the catalyst particle surface they must diffuse through the pores before reacting. If the rate of diffusion is slow enough, the concentration will be lower near the center than at the boundary of the catalyst. In this case there is also a heat and mass transfer resistance due to intraparticle transport, which is sometimes called an internal resistance. For the SO_2 reactor under consideration, Smith [9, p. 532] indicates the catalyst has only a surface coating of platinum so that no internal resistances are possible. We include the phenomenon here, however, for completeness and indicate how to assess the importance of it.

The equations governing heat and mass transfer in a catalyst particle (assumed here to be spherical) are

$$D_e \frac{1}{s^2} \frac{d}{ds}\left(s^2\frac{dC_s}{ds}\right) = \rho_s R(C_s, T_s') \tag{74}$$

$$k_e \frac{1}{s^2} \frac{d}{ds}\left(s^2\frac{dT_s'}{ds}\right) = -(-\Delta H_R)\rho_s R(C_s, T_s') \tag{75}$$

$$\frac{dC_s}{ds} = 0, \qquad \frac{dT_s'}{ds} = 0, \qquad \text{at } s = 0 \tag{76}$$

$$-D_e \frac{dC_s}{ds} = k_m[C_s - C(r', z')], \qquad \text{at } s = d_p/2 \tag{77}$$

$$-k_e \frac{dT_s'}{ds} = h_p[T_s' - T'(r', z')], \qquad \text{at } s = d_p/2 \tag{78}$$

We have included the external resistance by means of the boundary conditions (77) and (78). If the Biot numbers are large, $Bi_m = k_m d_p/(2D_e)$ or $Bi = h_p d_p/(2k_e)$), then the boundary conditions become

$$C_s(d_p/2) = C(r', z'), \qquad T_s'(d_p/2) = T'(r', z') \tag{79}$$

We must solve Eqs. (74)-(78) for each reactor position (r', z'), since C and T' depend on position in the reactor.

An effectiveness factor can be defined to give the average reaction rate:

$$\eta = \frac{3\int_0^1 R[C_s(u), T_s'(u)]u^2 \, du}{R[C(r', z'), T'(r', z')]} \tag{80}$$

where $u = s/(d_p/2)$. For long cylindrical catalyst pellets the 3 is changed to 2 and $u^2 \, du$ becomes $u \, du$. For plane geometry the corresponding numbers and 1 and du. Notice that this effectiveness factor includes the effect of both external and intraparticle resistance. If it is desirable to separate out those effects, we can define an internal and external effectiveness factor:

$$\eta = \frac{3\int_0^1 R[C_s(u), T_s'(u)]u^2 \, du}{R[C_s(d_p/2), T_s'(d_p/2)]}, \qquad \eta_E = \frac{R[C_s(d_p/2), T_s'(d_p/2)]}{R[C(r', z'), T'(r', z')]}$$

Clearly $\eta = \eta_I \eta_E$. If $\eta_I = 1$ and C_s and $T_s{}'$ are constants inside the catalyst, then $\eta = \eta_E$ is the same effectiveness factor defined in Eq. (65).

The overall effectiveness factor (80) is used in the model. The same equations (69) and (70) are used for the reactor, but the η is determined by Eq. (80) after solution of Eqs. (74)-(78) for each (r', z'). If there is only a single reaction taking place, the problem Eqs. (74)-(78) can be solved for arbitrary C, T', and the solution represented by giving η as an analytic (or graphical) function of the parameters (including C and T'). Then the use of η in the reactor model Eqs. (69) and (70) involves simply an evaluation of this function for the C and T' at each location. Evaluating this function is very much faster than solving the boundary value problem, so that this should be done when possible. If there are multiple reactions and the reactants interact, it becomes more difficult to derive such an analytic representation of η for each reaction, since the η for one reaction depends on the course of the other reaction as well. Then the boundary value problem, expanded for multiple reactions, must be solved, as illustrated below for the NO reduction reactor. The orthogonal collocation method is very useful in reducing the computation time to a minimum (compared to finite difference methods), and this feature is especially welcome since the problem must be solved perhaps thousands of times to model the entire re-actor.

It is convenient to nondimensionalize Eqs. (74)-(78):

$$\nabla^2 X_s = \phi^2 \Re \tag{81}$$

$$\nabla^2 T_s = -\beta \phi^2 \Re \tag{82}$$

$$dX_s/du = 0, \qquad dT_s/du = 0, \qquad \text{at } u = 0 \tag{83}$$

$$-dX_s/du = Bi_m(X_s - X), \qquad \text{at } u = 1 \tag{84}$$

$$-dT_s/du = Bi(T_s - T), \qquad \text{at } u = 1 \tag{85}$$

where $X_s = C_s/C_0$ and $T_s = T_s{}'/T_0$. The Biot numbers are defined in terms of the effective diffusivity and thermal conductivity of the particle, and the particle radius. They are different from the Nus-selt and Sherwood numbers which are defined in terms of the fluid diffusivity and thermal conductivity, and the particle diameter.

1. Effect of Temperature

These equations can be combined [30; 14, p. 234; 2, p. 325] to

$$T_s(u) + \beta X_s(u) = K_2 = T_s(1) + \beta X_s(1) \tag{86}$$

$$K_2 = T + \beta\delta X + \beta X_s(1)[1 - \delta] \tag{87}$$

$$\delta = Bi_m/Bi$$

These equations can be used to give T_s in the concentration equation, so that only a single equation need be solved rather than two coupled equations.

When $\beta > 0$ (exothermic reaction) the minimum X_s (= 0) corresponds to the maximum T_s: $T_{s,max} = K_2$. Since K_2 is a function of the solution $X_s(1)$, however, this is not a useful estimate. When $\delta > 1$, which is the usual case [14, p. 253; 31], then K_2 is a maximum when $X_s(1) = 0$. Thus

$$T_{s,max} = T + \beta\delta X$$

In dimensional notation this is

$$\Delta T_{max}' = \frac{Bi_m}{Bi} \frac{(-\Delta H_R)D_e}{k_e} C \tag{88}$$

If the boundary conditions are Eq. (79), then these carry over with $\delta = 1$. If we have the full boundary conditions (84) and (85), then Eq. (88) simplifies to Eq. (71). Notice also that from Eq. (86) we can derive

$$T_s(0) - T_s(1) = \beta[X_s(1) - X_s(0)]$$

Since the maximum value of $X_s(1) - X_s(0)$ is X, and usually β is small, the maximum temperature rise inside the particle is βX or β when X = 1. The predominate temperature rise occurs outside the particle, as $T_s(1) - T$.

These results can be applied to the SO_2 reactor. Using $D_e = 0.014$ m^2/hr, $k_e = 1.0$ kJ/(m)(hr)(°K),* and $T_0 = 673$°K, we get $\beta = 0.0024$. If the Reynolds number is high enough that there are no external resistances and $\delta = 1$, then the adiabatic temperature rise is $\beta T_0 = 1.6$°K. Clearly the temperature would be almost constant. For the laboratory reactor, however, Bi = 1.2, $Bi_m = 67$, and the temperature rise for this situation is 86°K. Thus the temperature rise across the thermal boundary layer must be accounted for.

2. Effect of Biot Number

Let us next see how the type of solution changes for large versus small Biot numbers. Consider the problem with a zeroth order and isothermal reaction rate, Eqs. (81)-(84) with $\phi^2\mathcal{R} = \phi^2$, $\beta = 0$, and

*The estimation of D_e and k_e is an art in itself. See Ref. 9, Chap. 11.

$X = 1$. Apply orthogonal collocation, $N = 1$, as in Eq. (6) to obtain

$$B_{11}X_1 + B_{12}X_2 = \phi^2$$

$$-(A_{21}X_1 + A_{22}X_2) = Bi_mX_2 - Bi_m$$

where $X_1 = X_s(u_1)$, $X_2 = X_s(u_2) = X_s(1)$. Rearranging these, using $- B_{11} = B_{12} > 0$, $-A_{21} = A_{22} > 0$, and solving for X_1 and X_2 gives

$$X_2 = 1 - \frac{A_{22}\phi^2}{Bi_mB_{12}}$$

$$X_1 = X_2 - \phi^2/B_{12}$$

Now as the $Bi_m \to \infty$ we get $X_2 = 1$ and $X_1 = 1 - 1/B_{12}$. Thus for large Bi_m the boundary concentration equals the external concentration (here 1). For smaller Bi_m there is a difference between the values of the concentration of the bulk gas stream and the boundary of the catalyst (X_2). This difference is increased as the Bi_m is decreased. The concentration change across the boundary, $1 - X_2$, is compared to the total concentration change $1 - X_s(0)$ in Fig. 2 as a function of Bi_m. The function plotted there,

$$\frac{1 - X_2}{1 - X_s(0)} = f(Bi_m) = \frac{1}{1 + Bi_m/2} \tag{89}$$

is the same for all three geometries using orthogonal collocation. Furthermore both the exact and orthogonal collocation solutions to the problem are quadratic polynomial in u, provided $X_s > 0$ everywhere, so the orthogonal collocation solution is exact for $X_s(0) \geqslant 0$, that is for $\phi^2 \leqslant aBi_m/(1 + Bi_m/2)$.

For large Bi_m, as often happens for mass transfer, the boundary concentration is close to 1.0, and the boundary condition might as well be taken as $X_2 = 1.0$. The major change in concentration occurs inside the catalyst and a distributed parameter solution is necessary. For small Bi_m there is a significant change in concentration across the phase boundary so that the external resistance is important and must be included.

When Bi is small, as often happens for heat transfer, it is convenient to lump the thermal resistance by using a one-term collocation solution for temperature. This corresponds to using a heat transfer coefficient defined by Eq. (53) for cylindrical particles and

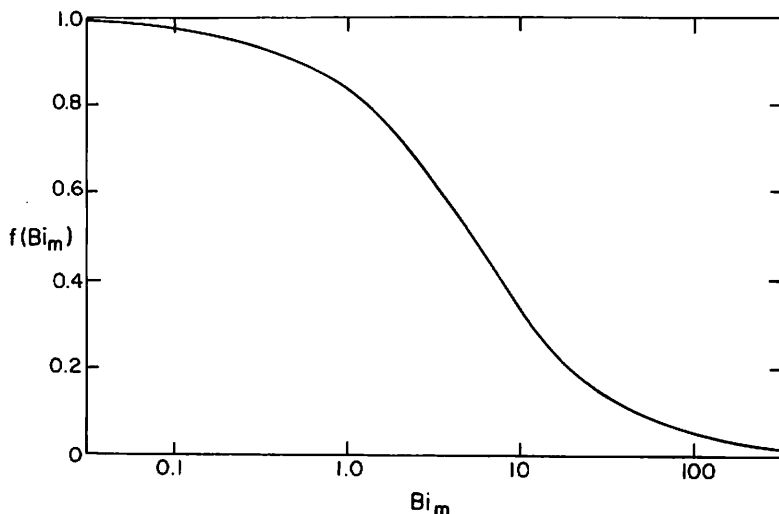$$\frac{1}{U} = \frac{1}{h_w} + \frac{d_p/2}{bk_e} \tag{90}$$

FIG. 2. Function defined by Eq. (89).

with b = 2.5, 3.0, and 3.5 for planar, cylindrical, and spherical geometry, respectively. The analysis is the same as applied to obtain Eq. (51).

3. Effect of Thiele Modulus

We also want to test for the importance of internal diffusion. We do that here using the orthogonal collocation method, $N = 1$, on a problem with no external resistance, Eqs. (81)-(85) with $R = X_s$, $X_s = 1$ at $u = 1$, $\beta = 0$, for a spherical geometry. Applying orthogonal collocation for spherical geometry and using $-B_{11} = B_{12} = 10.5$, we get

$$X_1 = \frac{10.5}{10.5 + \phi^2} \tag{91}$$

The effectiveness factor is

$$\eta = \frac{W_1 X_1 + W_2}{W_1 + W_2} = 0.7 X_1 + 0.3$$

If we define the absence of intraparticle resistances as when $\eta \geq 0.9$, then we need $X_1 \geq 0.857$. Use of Eq. (91) says that $\eta \geq 0.9$ provided $\phi^2 < 1.75$ or $\phi < 1.3$. Since a one-term collocation solution is a good approximation for $\eta \sim 0.9$ (see below), this is expected to be a good estimate. For cylindrical and planar geometries we obtain $\phi < 0.96$ and 0.58, respectively.

F. Effectiveness Factor Calculation

When internal resistances are important, the orthogonal colloca-
tion method applied to Eqs. (81)-(85) gives

$$\sum_{i=1}^{N+1} B_{ji} X_{si} = \phi^2 \mathfrak{R}(X_{sj}, T_{sj}), \qquad j = 1, \ldots, N \tag{92}$$

$$\sum_{i=1}^{N+1} B_{ji} T_{si} = -\beta \phi^2 \mathfrak{R}(X_{sj}, T_{sj}) \tag{93}$$

$$-\sum_{i=1}^{N+1} A_{N+1,i} X_{si} = Bi_m (X_{s,N+1} - X) \tag{94}$$

$$-\sum_{i=1}^{N+1} A_{N+1,i} T_{si} = Bi(T_{s,N+1} - T) \tag{95}$$

$$\eta = \frac{\sum\limits_{i=1}^{N+1} W_i \mathfrak{R}(X_{xi}, T_{si})}{\sum\limits_{i=1}^{N+1} W_i \mathfrak{R}(X, T)} \tag{96}$$

We emphasize that many species and many reactions can be treated,
as is done in Section V, but here we use only a single species for
simplicity in presentation. To solve these equations we first solve
for $X_{s,N+1}$ and $T_{s,N+1}$ from Eqs. (94) and (95) and substitute into
Eqs. (92) and (93), obtaining, for example,

$$\sum_{i=1}^{N} B_{ji}' X_{si} = \phi^2 \mathfrak{R}(X_{sj}, T_{sj}) - B, \qquad j = 1, \ldots, N \tag{97}$$

$$B_{ji}' \equiv B_{ji} - \frac{B_{j,N+1} A_{N+1,i}}{A_{N+1,N+1} + Bi_m}, \qquad B \equiv B_{j,N+1} Bi_m X / (A_{N+1,N+1} + Bi_m) \tag{98}$$

Several methods to solve these equations have been found to be
feasible. Successive substitution is possible for small ϕ^2. A guess
for $\{X_{sj}, T_{sj}\}$ is substituted into the right-hand side of Eq. (97), and
new values are calculated on the left-hand side. These values are
then used on the right-hand side and the process is repeated until
the $\{X_{sj}, T_{sj}\}$ quit changing from one iteration to the next to within
some desired tolerance. For large ϕ^2 such a procedure diverges,
and the limits on ϕ^2 for success depend on R and N. For example,
for N = 1, $Bi_m \to \infty$, and first-order, isothermal irreversible reac-

tion, the successive substitution method converges to the solution provided $\phi^2/B_{12} < 1$. For a spherical catalyst pellet this is $\phi^2 < 10.5$. Furthermore, the rate of convergence is very slow for ϕ^2 close to 10.5. Thus the usable range of ϕ^2 is precisely in the region (small ϕ^2) where the calculation need not be done anyway. Thus we need a better method, applicable for large ϕ^2.

The Newton-Raphson method has been found suitable for a wide range of ϕ^2 including nonisothermal problems with large concentration gradients. In this method the equations are linearized about the k-th iteration

$$F_j \equiv \sum_{i=1}^{N} B_{ji}'X_{si} - \phi^2 \Re(X_{sj}, T_{sj}) - B$$

$$F_j^{k+1} = \sum_{i=1}^{N} B_{ji}'X_{si}^{k+1} - \phi^2\{R\big|_{k,j} + \Re_X\big|_{k,j}(X_{sj}^{k+1} - X_{sj}^{k})$$
$$+ \Re_T\big|_{k,j}(T_{sj}^{k+1} - T_{sj}^{k}) - B$$

The notation $\big|_{k,j}$ means that the term is evaluated for X_{sj}^{k}, T_{sj}^{k}. Similar equations are written for the T_{sj} equations. We desire $F_j^{k+1} = 0$, so set this to be true, rearrange the equations, and solve for $\{X_j^{k+1}, T_j^{k+1}\}$. This process is repeated until numerical convergence is obtained. If the reaction rate expression is too complicated to differentiate analytically, as is often the case for realistic systems, then the derivatives may be obtained numerically. Since the numerical derivatives do not affect the solution, just the numerical process to obtain it, slight errors in evaluating the derivatives in this way are usually inconsequential. If the problem has more than one solution, the solution obtained depends on the initial guess.

The Newton-Raphson method is useful as a general method. The reaction rate expression may have a form that admits other types of iterations as well. For a reaction which is nearly first order, and is isothermal, we can define a first-order reaction rate by

$$\Re(X_{sj}, T_{sj}) = k(X_{sj}, T_{sj})X_{sj}$$

Then the iteration

$$\sum_{i=1}^{N} B_{ji}'X_i^{k+1} = \phi^2 k(X_{sj}^{k}, T_{sj}^{k})X_{sj}^{k+1} - B$$

converges provided k does not change very much. Another case would be when the reaction rate is almost constant. Then the successive substitution method converges. Both of these iterations are found useful in the NO reduction reactor treated in Section V.

If the solution is expected to have a profile which has a very steep boundary layer near u = 1 and takes the equilibrium value elsewhere, then orthogonal collocation on finite elements would be the preferred method of solution. Then the equations can be rearranged to have $\phi^2 \Delta u_\ell^2 R$ on the right-hand side, and a successive substitution method would converge for arbitrary right-hand side provided Δu_ℓ is small enough [5].

It often happens that Bi_m is large and Bi is small [31]. Then we can neglect the external mass transfer resistance and the internal heat transfer resistance. We then use a lumped parameter model for the energy equation, integrating it over the catalyst. This permits the catalyst temperature to be different from the bulk gas temperature, although the temperature is uniform within the catalyst. Such approximations simplify the problem, and the orthogonal collocation method can be applied to the simplified problem as in Eqs. (92)-(96).

1. One-Term Approximations, and Asymptotic Solutions

The application of orthogonal collocation discussed above is useful if one desires very accurate results. However, results of engineering accuracy can be achieved very easily using one of two methods. Both methods use a first approximation, N = 1, for small ϕ. In the first method, for large ϕ the exact asymptotic results are used. In the second method, due to Paterson and Cresswell [30], a revised orthogonal collocation method is used. The first method is illustrated by application to an isothermal, first-order, irreversible reaction, Eqs. (81)-(84), with $\Re = X_s$, $\beta = 0$, in planar geometry. A one-term collocation method, using the fact that $-B_{11} = B_{12}$ and $-A_{21} = A_{22}$, gives

$$\left(1 - \frac{A_{22}}{A_{22} + Bi_m}\right)X_1 = -\frac{\phi^2 X_1}{B_{12}} + \frac{Bi_m}{A_{22} + Bi_m} \tag{99}$$

$$X_2 = \frac{A_{22}X_1 + Bi_m}{A_{22} + Bi_m} \tag{100}$$

$$\eta = \frac{W_1 X_1 + W_2 X_2}{W_1 + W_2}$$

For a plane geometry $A_{22} = 2.5$, $B_{12} = 2.5$, $W_1 = 0.8333$, and $W_2 = 0.1667$. Figure 3 plots η vs ϕ for the one-term approximation when $Bi_m = 10$. The solid line gives the exact solution, and it is clear that the one-term approximation, given by the dotted line, is not valid
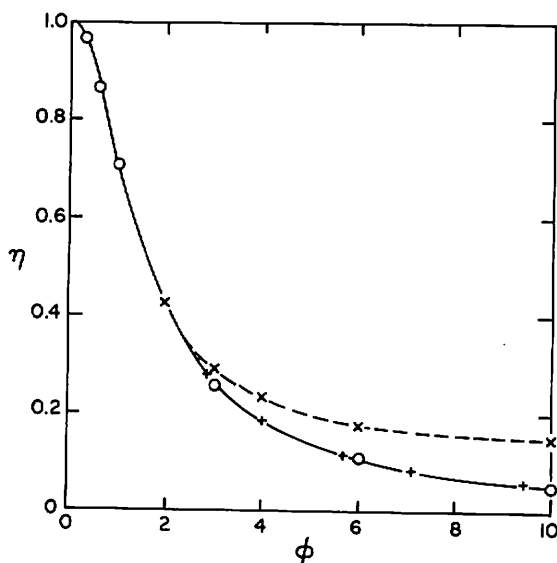
FIG. 3. Effectiveness factor. $\Re(C) = C$, $Bi_m = 10$, $a = 1$.

when $\phi > 2$ or $\eta < 0.4$. This is because for large ϕ the concentration profile can no longer be well represented by the form $a + bu^2$, since the concentration is nearly zero over the inner portion of the catalyst. For large ϕ we use a larger N or the exact asymptotic solution.

Results for large ϕ have been derived by Petersen [32, p. 70]. For the problem (81)–(85) under conditions of large Bi_m and Bi, and $X = 1$, $T = 1$, the boundary conditions are

$$X_s(1) = 1, \quad T_s(1) = 1$$

The effectiveness factor is given by

$$\eta = \frac{\sqrt{2}}{\hat{\phi}} \left[\int_0^1 \Re(y)/\Re(1) \ dy \right]^{1/2}, \qquad \hat{\phi} = \frac{V_p \phi}{A_p d_p/2}$$

where $\hat{\phi}$ is introduced to account for different geometries, and V_p and A_p are the particle volume and external surface area, respectively. The reaction rate depends only on the concentration, X_s, and we use $T_s + \beta X_s = 1 + \beta$ to convert a temperature dependence into a concentration dependence. For the first-order isothermal reaction with large Bi_m, this gives $\eta = 1/\hat{\phi}$.

When the modified Biot number is finite, and a reversible reac-

tion is allowed, a similar perturbation analysis gives

$$\eta = \frac{\sqrt{2}}{\phi} \left[\int_{X_{eq}}^{X_s(1)} \Re(y)/\Re(X) \ dy \right]^{1/2}$$

where $X_s(1)$ is determined from

$$Bi_m[X_s(1) - X] = -\sqrt{2}\phi \left[\int_{X_{eq}}^{X_s(1)} \Re(y)/\Re(X) \ dy \right]^{1/2}$$

and X_{eq} is the value of the concentration at equilibrium and at the center of the catalyst. Now we use Eq. (86) to determine the temperature in terms of the concentration.

For example, for a second-order isothermal reaction in a sphere these equations reduce to

$$\eta = \frac{3}{\phi}\sqrt{\frac{2}{3}}[X_s(1)]^{3/2} \tag{101}$$

$$Bi_m[X_s(1) - 1] = -\sqrt{\frac{2}{3}}\phi[X_s(1)]^{3/2} \tag{102}$$

Now the Thiele modulus can be increased in two ways. Since the reaction rate, and hence ϕ, is much more dependent on temperature than is the mass transfer coefficient as the temperature is increased, then $\phi \rightarrow \infty$ at constant Bi_m. If the radius of the catalyst is increased while keeping the temperature fixed, then $\phi \rightarrow \infty$ at constant ϕ/Bi_m since both ϕ and Bi_m are proportional to the radius. Thus, roughly, changing ϕ at constant Bi_m corresponds to changing the temperature, while changing ϕ at constant ϕ/Bi_m corresponds to changing the radius of the catalyst pellet.

Applying these ideas to Eqs. (101) and (102), for constant Bi_m we find that $X_s(1) \rightarrow 0$ as

$$1 = \frac{\phi}{Bi_m}\sqrt{\frac{2}{3}}[X_s(1)]^{3/2}$$

and

$$\eta = 3Bi_m/\phi^2, \qquad Bi_m = \text{constant}, \qquad \phi \rightarrow \infty$$

If both ϕ and Bi_m get large together, so that ϕ/Bi_m is constant, then $X_s(1)$ is constant, too, and is solved from Eq. (102). Then Eq. (101) shows that

$$\eta = \frac{A}{\phi}, \qquad \frac{\phi}{Bi_m} = \text{constant}, \qquad \phi, Bi_m \rightarrow \infty$$

where the numerical value of A depends on the solution for $X_s(1)$.

Combination of the asymptotic results for large ϕ and the orthogonal collocation results for small ϕ then gives an easy method to calculate η vs ϕ for the whole range of ϕ. This procedure is suitable, provided the η vs ϕ curve has the general shape shown on Fig. 3. For cases when $\eta > 1$, the second method must be used.

2. One-Term Approximations Using Finite Elements

The second method is an adaptation of that presented by Paterson and Cresswell [30]. This approach should be used whenever $\eta > 1$. For small ϕ we again use orthogonal collocation with N = 1. For large ϕ we recognize that the concentration drops to its equilibrium value near the surface of the pellet, and retains that value from there to the center. Thus we introduce the concept of an effective reaction zone, defined by u = b. For $0 < u < b$ the concentration is defined as the equilibrium value. For $b < u < 1$ we approximate the concentration as a second degree polynomial in u using orthogonal collocation. Thus we are using orthogonal collocation on two elements, with the solution constant in one element.

Consider the problem Eqs. (81)-(85) with X = 1, T = 1. This can be reduced to a single equation using Eq. (86). We drop the subscript s for convenience. At the reaction zone we want

$$X(b) = X_{eq}, \qquad \frac{dX}{du}(b) = 0$$

in order that the reaction cease and no mass transfer take place into the unreacting core. The domain is transformed using s = (u − b)/(1 − b) so that s goes from 0 to 1. The differential equations and boundary conditions are then

$$\frac{1}{(1-b)^2} \frac{d^2X}{ds^2} + \frac{a-1}{b+s(1-b)} \frac{1}{(1-b)} \frac{dX}{ds} = \phi^2 R(X,T)$$

$$-\frac{1}{(1-b)} \frac{dX}{ds} = Bi_m(X-1), \qquad \text{at } s = 1$$

$$X = X_{eq}, \qquad \frac{dX}{ds} = 0, \qquad \text{at } s = 0$$

The point s = 0 is the edge of the reaction zone.

We apply orthogonal collocation to this problem. While the problem was symmetric in u (the solution was a function of u^2 only, not u), it is no longer symmetric in s. Thus we must use the matrices and roots from the bottom of Table 1.* We call $X_1 = X(0)$, $X_2 = X(1/2)$, $X_3 = X(1)$, and set $X_1 = X_{eq}$. We thus have three unknowns: X_2, X_3, and b. We assume that X_{eq} is known, and if the reaction is reversible and nonisothermal, the calculations are more complicated. Three equations are obtained by collocation at $s = 1/2$, the boundary condition at $s = 1$, and the zero flux condition at $s = 0$:

$$\frac{1}{(1-b)^2}[B_{21}X_{eq} + B_{22}X_2 + B_{23}X_3] + \frac{a-1}{b + \frac{1}{2}(1-b)}\frac{1}{(1-b)}[A_{21}X_{eq}$$

$$+ A_{22}X_2 + A_{23}X_3] = \phi^2 \mathcal{R}[X_2, X_3]$$

$$-\frac{1}{1-b}[A_{31}X_{eq} + A_{32}X_2 + A_{33}X_3] = Bi_m[X_3 - X]$$

$$A_{11}X_{eq} + A_{12}X_2 + A_{13}X_3 = 0$$

These can be rearranged to give (using the numerical values for B_{ji} and A_{ji}):

$$X_2 = (X_3 + 3X_{eq})/4 \tag{103}$$

$$X_3 = \frac{(1-b)Bi_m X + 2X_{eq}}{2 + (1-b)Bi_m} \tag{104}$$

$$2\left[\frac{1}{(1-b)^2} + \frac{a-1}{1-b^2}\right](X_3 - X_{eq}) = \phi^2 \mathcal{R}(X_2, X_3) \tag{105}$$

The effectiveness factor is

$$\eta = 3(1-b)\{b^2 \int_0^1 \mathcal{R}\ ds + 2b(1-b)\int_0^1 \mathcal{R}s\ ds + (1-b)^2 \int_0^1 \mathcal{R}s^2\ ds\},$$
$$\text{sphere} \tag{106}$$

$$\eta = 2(1-b)\{b\int_0^1 \mathcal{R}\ ds + (1-b)\int_0^1 \mathcal{R}s\ ds\}, \quad \text{cylinder} \tag{107}$$

$$\eta = (1-b)\int_0^1 \mathcal{R}\ ds, \quad \text{slab} \tag{108}$$

*Paterson and Cresswell [30] use symmetric polynomials in s. For spheres they achieve better comparison to exact solutions, without the discontinuities apparent in Figs. 4 and 6. However, the symmetry cannot be justified (in s) for cylinders and spheres. The problem does not arise for planar geometry because of the absence of the $\frac{1}{u}\frac{dX}{du}$ form.

$$\int_0^1 f(s) \ ds \equiv \tfrac{1}{6}(f_1 + f_3) + \tfrac{2}{3}f_2$$

and the quadrature formula is used to evaluate the integrals. Equations (103)-(105) can be used as follows. If Bi_m is given and it is desired to determine η as a function of ϕ, then a value of b is chosen between 0 and 1, X_3 and X_2 are calculated from Eqs. (103) and (104) and then ϕ is calculated from Eq. (105). This procedure is repeated for various b. A value of b close to 1 correspond to large ϕ. A value of b = 0 gives a ϕ which is not zero. For ϕ smaller than this the orthogonal collocation method, N = 1, as illustrated in Eqs. (99) and (100), is used. The value b = 0 corresponds to the case when the center concentration is at equilibrium and the reaction zone fills the whole pellet. The regular orthogonal collocation method corresponds to X(u = 0) > 0. If Bi_m is not constant, but changes with ϕ by ϕ/Bi_m = constant, then Eqs. (103)-(105) must be solved. The author has found a Newton-Raphson method, using Bi_m as the independent variable, works well for this case.

This procedure is applied to the first-order reaction giving the results shown by + in Fig. 3. Clearly the two element orthogonal collocation solution provides an adequate approximation to the exact η vs ϕ curve for the range of η shown.

For a nonisothermal, first-order irreversible reaction we take Eqs. (81)-(85) with $R = X_s \exp[\gamma - \gamma/T_s]$. For the parameter values X = 1, T = 1, γ = 20, β = 0.02, Bi = 5, Bi_m = 250, and δ = 50 we get the curve shown in Fig. 4.

The solution using orthogonal collocation on finite elements used 20 elements, spaced uniformly for $\phi < 9$ and bunched near u = 1 for $\phi > 9$. The integrated mean square residual was calculated and the only solutions accepted had values less than 1, which other calculations [5] indicate would make the error in η less than 0.01%. The curve with Bi_m constant corresponds to changing ϕ by changing the temperature at constant particle size. The effectiveness factor falls initially due to internal mass transfer limitations and then rises abruptly due to external heat transfer limitations. The curve with ϕ/Bi_m constant corresponds to changing the radius at constant temperature. The two-element solution gives a fair approximation of the exact curve. As mentioned above, use of symmetric polynomials (which changes the collocation point in the element) gives better results but is mathematically indefensible.

3. High Order Approximations

The accuracy of the orthogonal collocation solution can also be improved by increasing the number of collocation points. For the same test problem, treated in Fig. 3, we show the accuracy in η as
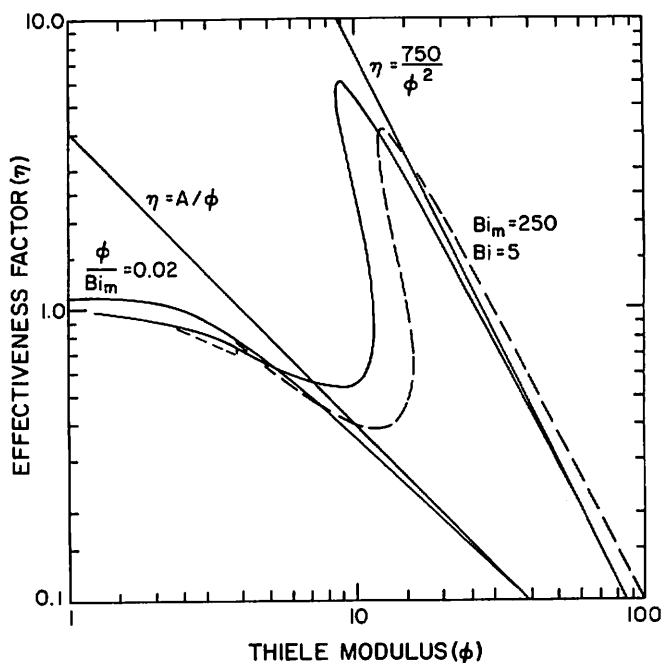
FIG. 4. Effectiveness factor for nonisothermal, first-order, irreversible reaction in a sphere. $\beta = 0.02$, $\gamma = 20$, (———) Orthogonal collocation finite element solution, (- -) one-term orthogonal collocation, or two-element solution. A six-term orthogonal collocation solution gave accuracy of $10^{-4}\%$ for $\phi \leqslant 5$.

a function of N in Fig. 5. We note several features: all the graphs are straight lines, indicating the error is proportional to $(1/N)^{Nb}$ with different b. The error is greater for low η, which corresponds to situations with concentration boundary layers near the edge of the catalyst. For this problem, whenever $\eta > 0.05$, 1% accuracy is achieved with $N \gtrless 3$.

The last conclusion in particular does not generalize to nonisothermal problems. Due to the very steep concentration gradient for large ϕ [for $\phi = 14$, $X \simeq 0$ at $u = 0.997$ and rises to $X \simeq 0.16$ at $u = 1.0$] only a finite element (or finite difference) type of solution is feasible.

Sørensen et al. [33] have applied a two-dimensional orthogonal collocation to diffusion and reaction in a cylindrical catalyst of finite length. The specific equations are handled as in Eqs. (19)-(27). They use N = 6 in each direction and find that for an irreversible, nonisothermal first-order reaction in the region of multiple solutions,
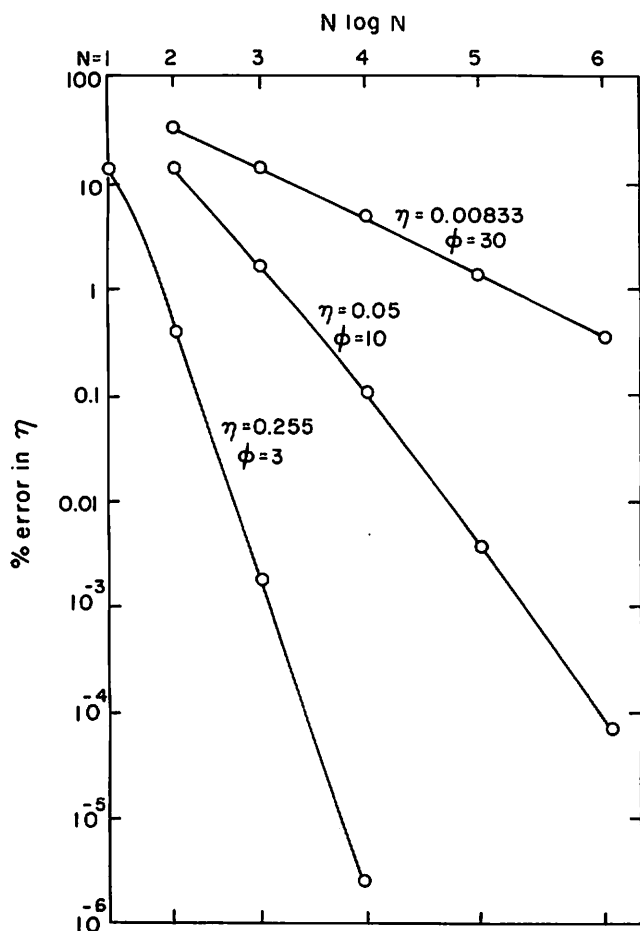
FIG. 5. Accuracy vs N in orthogonal collocation method. Same problem as in Fig. 3, with polynomials defined by w = 1, N = 1 [2, p. 102].

the effectiveness factor is not given very well by the curve for spheres using $\hat{\phi}$. They also found some extraneous solutions which tended to disappear for N = 8. The authors comment that one must be careful in nonlinear problems to test the adequacy of the solution, since extraneous solutions are possible. Ferguson and Finlayson [34] use the residual to derive error bounds for one-dimensional problems, and the residual can also be used to see if the solution is extraneous or accurate.

4. Application to Sulfur Dioxide

We next consider a specific application— the oxidation of SO_2 on a catalyst impregnated with vanadium pentoxide. We use one of the reaction rate expressions discussed by Livbjerg and Villadsen [35] and the parameters given there corresponding to the experimental data. The reaction is

$$SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons SO_3$$
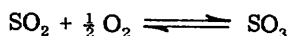
and the differential equations governing the problem are

$$\frac{1}{r'^2} \frac{d}{dr'} \left(r'^2 c_T D_{e,SO_2} \frac{dX_{SO_2}}{dr'} \right) = -\rho_B R \tag{109}$$

$$\frac{1}{r'^2} \frac{d}{dr'} \left(r'^2 c_T D_{e,O_2} \frac{dX_{O_2}}{dr'} \right) = -\tfrac{1}{2} \rho_B R \tag{110}$$

$$\frac{1}{r'^2} \frac{d}{dr'} \left(r'^2 c_T D_{e,SO_3} \frac{dX_{SO_3}}{dr'} \right) = \rho_B R \tag{111}$$

$$\frac{1}{r'^2} \frac{d}{dr'} \left(r'^2 k_e \frac{dT}{dr} \right) = (-\Delta H_e) \rho_B R$$

$$\frac{dX_{SO_2}}{dr'} = \frac{dX_{O_2}}{dr'} = \frac{dX_{SO_3}}{dr'} = \frac{dT}{dr'} = 0, \qquad \text{at } r' = 0$$

$$X_{SO_2} = 0.07, \qquad X_{O_2} = 0.11, \qquad X_{SO_2} = 0, \qquad T = T_b,$$
$$\text{at } r' = d_p/2$$

The experimental data was taken in a small-scale reactor designed to have as little interphase resistance as possible, so that the Biot numbers are taken as infinite. The reaction rate expression and other parameters are listed in Table 4. The experimental data was taken on a 6 mm × 6 mm cylindrical catalyst pellet. We can model the cylindrical catalyst pellet as a spherical catalyst pellet with the same volume to surface ratio, which in this case is the length, 6 mm. Livbjerg and Villadsen [35] report that $D_{e,O_2} = 1.4 D_{e,SO_2}$ and $D_{e,SO_3} = 0.9 D_{e,SO_2}$. Equations (109)-(111) can be combined to show that

$$D_{e,O_2}(X_{O_2} - 0.11) = \tfrac{1}{2} D_{e,SO_2}(X_{SO_2} - 0.07) \tag{112}$$

$$D_{e,SO_3} X_{SO_3} = D_{e,SO_2}(0.07 - X_{e,SO_2}) \tag{113}$$

TABLE 4

Parameters for SO_2 Catalyst Particle Problem

R $= r_1 (1 - B^2)$

B $= p_{SO_3}/(K_p p_{SO_2} p_{O_2}^{1/2})$

r_1 $= k p_{O_2} p_{SO_2}/[1 + p_{SO_2} K_{SO_2} + p_{SO_3} K_{SO_3}]^2$

k $= 3.13 \times 10^{-3}$ at 453.6°C

K_p $= 10^{5000/T - 4.743}$ atm$^{-1/2}$

K_{SO_2} $= \exp[-9.953 + 8619/T]$

K_{SO_3} $= \exp[-71.745 + 52596/T]$

T in °K

ρ_s $= 1310$ kg/m^3, $C_T = 0.0168$ (kg)(mole)/m^3

D_{e,SO_2} $= 0.0149$ m^2/hr; $k_e \cong 1.06$ kJ/(m)(hr)(°C)

The reactor is maintained at 1 atm, so that $X_{SO_2} = P_{SO_2}$. The effective diffusivity was determined by Livbjerg and Villadsen by fitting the calculations to the experimental data.

The equations can be nondimensionalized to give (with $c_T D_{e,SO_2}$ constant)

$$\frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{dX}{dr}\right) = -\frac{\rho_B (d_p/2)^2}{c_T D_{e,SO_2}} R$$

$$Y = 0.07, \quad \text{at } r = 1$$

The mole fractions of O_2 and SO_3 are given from Eqs. (112) and (113) while the temperature is given by Eq. (86). Here we have

$$T = T_b + \frac{(-\Delta H_R) c_T D_{e,SO_2}}{k_e}(0.07 - X_{SO_2})$$

and $(-\Delta H_R) c_T D_{e,SO_2}/k_e = 2.5$°C, so that T is essentially constant, thus justifying the assumption that $c_T D_{e,SO_2}$ is constant. The results of the calculation are shown on Fig. 6, as derived using a six-term collocation solution and a two-element solution. The influence of intraparticle resistance in reducing the reaction rate are clearly evident for the larger particles.

G. Multiplicity and Stability

Figure 4 illustrates the fact that for some conditions it is possible to have more than one effectiveness factor for a given Thiele modulus. When this occurs the concentration profiles corresponding to each
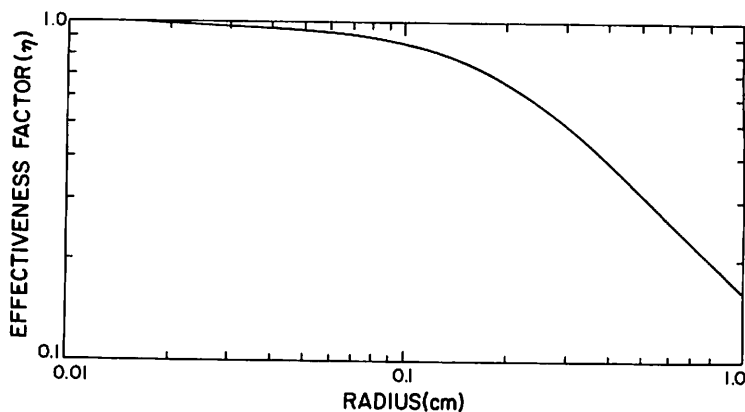
FIG. 6. Effectiveness factor vs sphere radius. SO_2 oxidation; for $r_p' < 0.5$ cm the curve is from a 6-term orthogonal collocation solution while for $r_p' > 0.5$ cm the curve is from a two-element orthogonal collocation solution.

effectiveness factor are different. Thus there are many solutions to the same problem, and the problem is not unique. It is of interest to determine when this is the case.

The general conditions on the reaction rate expression which require a unique solution have been worked out [36, 37]. For example, for a first-order, irreversible reaction with infinite Biot and modified Biot numbers, the solution is unique when $\gamma\beta \le 4(1 + \beta)$. If multiple steady states occur, then it is of interest to determine the range of parameter values for that occurrence. Obviously, if we calculate the entire η versus ϕ curve we can deduce under what conditions, if any, multiple steady states occur. However, we can sometimes use a one-term orthogonal collocation solution to provide an approximation to the conditions.

Stewart and Villadsen [38] have developed a graphical technique for deducing the range of particle sizes, or Thiele moduli, for which multiple steady states occur. Their technique is especially easy to apply when the boundary conditions correspond to infinite Biot numbers, so that the concentration and temperature are known on the boundary. The reaction rate expression is plotted as a function of concentration, and if the problem is nonisothermal the temperature is eliminated as a variable using Eq. (86). A one-term collocation solution is applied to give $(B_{11}X_1 + B_{12})/\phi^2 = \Re(X_1,T_1)$. The left-hand side gives a straight line, vs X_1. Intersections of the two curves give solutions for X_1, and where one line (corresponding to one ϕ^2) intersects the curve more than once, multiple steady states are possible. When $Bi = Bi_m \to \infty$ the maximum dimensionless tempera-

ture rise is β, and β is usually small enough that multiple steady states do not occur in practice. When the Biot numbers are finite, the concentration and temperature on the boundary are not known a priori, but must be determined from the solution. In that case the graphical procedure of Stewart and Villadson is not as simple to apply. Then we turn to the two-element orthogonal collocation solution devised by Paterson and Cresswell [30].

We use the Eqs. (103)-(105) to determine ϕ as a function of b, where b ranges from 0 to 1. Then by using the appropriate equations (106)-(108) to calculate the effectiveness factor, we can trace out the curve of η vs ϕ in the region where multiple steady states are possible. For the nonisothermal, irreversible first-order reaction in a sphere, the results in Fig. 4 show that multiple steady states are possible for $8.6 < \phi < 11.6$ using the detailed, orthogonal collocation on finite element analysis, whereas the one-term Paterson-Cresswell approximation gives multiple steady-states for $12 < \phi < 16$. Clearly the approximate results are well within the accuracy of experimental data for reaction rate constants and effective diffusivity, so that this simple procedure is sufficient for most purposes. Multiplicity can also be examined by solution of the steady-state equations, and Michelsen and Villadsen [39] have used orthogonal collocation to study a problem having 21 solutions.

1. Stability

Once the steady-state solution is derived for reaction and diffusion in a particle, it is sometimes necessary to examine the stability of the steady state. If the steady state is unstable, then a small perturbation of the bulk gas concentration or temperature will lead to large changes in the concentration and temperature profiles within the particle.

The unsteady-state equations for a catalyst particle with a single reaction are

$$\epsilon_s \frac{\partial X}{\partial t} = \nabla^2 X - \phi^2 \mathcal{R}(X,T) \tag{114}$$

$$Le \frac{\partial T}{\partial t} = \nabla^2 T + \beta \phi^2 \mathcal{R}(X,T) \tag{115}$$

$$\frac{\partial X}{\partial r} = 0, \qquad \frac{\partial T}{\partial r} = 0, \qquad r = 0 \tag{116}$$

$$-\frac{\partial X}{\partial r} = Bi_m[X - X_0(t)], \qquad \text{at } r = 1 \tag{117}$$

$$-\frac{\partial T}{\partial r} = Bi[T - T_0(t)], \qquad \text{at } r = 1 \tag{118}$$

These equations can be integrated using orthogonal collocation as illustrated by Eqs. (10) and (11). Ferguson and Finlayson [40] have done this for an extreme case with $\beta = 0.6$. Their example exhibits three steady states, and the transient problem takes the solution from one steady state to another. The stability limitations on step size presented for Eqs. (48) and (49) were developed for this case.

The same problem was also solved using Liu's method; a stable, explicit, finite difference method; and the Crank-Nicolson method. The orthogonal collocation method was from 20 to 40 times as fast as the fastest finite difference solution, for an accuracy of the flux at the catalyst boundary of 3% during the transient and 0.1% at steady state (this was achieved with N = 10 or 12). If the accuracy requirements are relaxed to 7% during the transient and 3% for the steady state, then the orthogonal collocation method was only twice as fast as the finite difference method. This result illustrates a general feature the author has found on several problems. When comparing the orthogonal collocation method to a finite difference method, the orthogonal collocation method looks more and more favorable as the allowable error is decreased. Elnashaie and Cresswell [41] applied both orthogonal collocation and finite difference methods to problems of this type. They found that the orthogonal collocation method was very accurate, required only a few collocation points, and used less than 10% of the computation time of finite difference methods.

Waede Hansen [42] has also integrated these equations and considered various simplifications obtained by averaging the temperature over the catalyst pellet. He solved the nonisothermal, irreversible, first-order reaction for parameter values of Le = 1, $\beta = 0.1$, $\phi = 1$, $\gamma = 40$, Bi = 12.5, $Bi_m = 250$, and $\epsilon_s = 0.5$. For transients induced by step changes in the boundary conditions, he found that a model (his model M3) with external, but not internal, heat transfer resistance did not compare well during the transient to the complete model given by Eqs. (114)-(118). We have repeated the calculations for a heat transfer coefficient calculated using the lumping procedure, Eq. (90). The results shown in Fig. 7 indicate that in transient problems the lumping procedure may not be suitable. Of course, this was for an example with a high Biot number, so that the distributed aspect of the problem would be important.

The time-dependent calculations are time consuming to perform, and the results apply only to the particular transient investigated. Another approach to the stability problem is to linearize the tran-
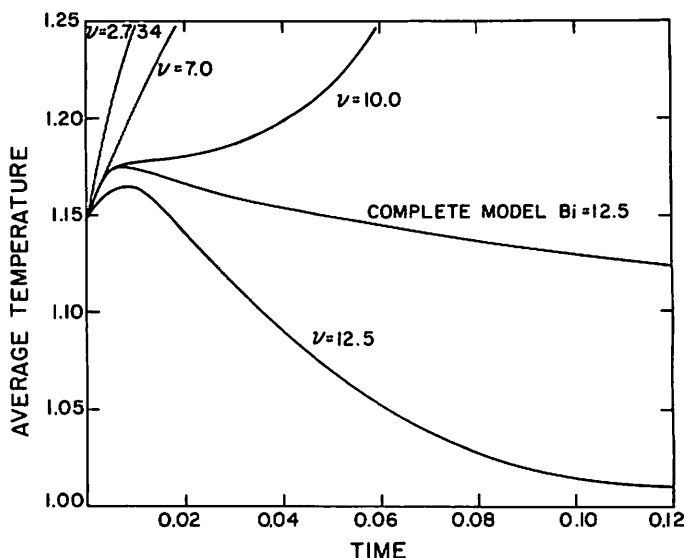
FIG. 7. Average temperature of catalyst during transient. The curves labeled with a value of ν are for a model assuming the catalyst temperature is uniform, although different from the bulk stream value. $\nu = 2.734$ corresponds to the overall heat transfer coefficient predicted by Eq. (90).

sient equations about the steady-state solution. The equations are then

$$\epsilon_s \frac{\partial X}{\partial t} = \nabla^2 X - \phi^2 (\mathcal{R}_T(u)T + \mathcal{R}_X(u)X) \qquad (119)$$

$$Le \frac{\partial T}{\partial t} = \nabla^2 T + \beta\phi^2 (\mathcal{R}_T(u)T + \mathcal{R}_X(u)X) \qquad (120)$$

$$-\frac{\partial X}{\partial u} = Bi_m X, \qquad -\frac{\partial T}{\partial u} = BiT, \quad at \ u = 1 \qquad (121)$$

Here X is the differences between the concentration during the transient and the steady-state value, and a similar definition applies to T. The $\mathcal{R}_s$ and $\mathcal{R}_X$ are known functions of position since they depend on the steady-state solution which has presumably been found using orthogonal collocation or some other method. The orthogonal collocation method is applied to Eqs. (119)-(121) to obtain

$$\frac{dX_j}{dt} = \sum_{i=1}^{N} B_{ji}{}' X_i - \phi^2 [R_T(u_j)T_j + R_X(u_j)X_j], \quad j = 1, \dots, N$$

with a similar equation for $T_j(t)$. The stability of these equations is investigated by substituting $X_j(t) = a_j e^{\lambda t}$ and $T_j(t) = b_j e^{\lambda t}$ and looking for conditions under which the real part of the eigenvalue λ is positive, thus leading to an exponential growth of X and T, or instability. McGowin and Perlmutter [43, 44] used such a technique and obtained good results with five interior points. They treated a reactor with axial dispersion rather than the particle problem.

It is sometimes possible to obtain useful results with a one-term orthogonal collocation solution, and the detailed analysis is given elsewhere [2, p. 123; 45]. It shows that the one-term solution is unstable whenever Q is negative:

$$Q = \frac{10.5}{Le} \frac{Bi}{3.5 + Bi} + \frac{10.5 Bi_m}{3.5 + Bi_m} - \frac{\beta \mathcal{R}_T}{Le} + \mathcal{R}_x \qquad (122)$$

The value of $\mathcal{R}_T$ and $\mathcal{R}_x$ to be used here can be the appropriate values calculated using the approximate one-term collocation steady-state solution.

Calculations by Luss and Lee [46] and Lee et al. [47] indicated that better results could be achieved if the values of $\mathcal{R}_T$ and $\mathcal{R}_x$ are taken as the average values determined by an accurate solution to the steady-state problem. In other words, if orthogonal collocation is used, then one must use a high enough N to achieve an accurate value of the average values of $\mathcal{R}_T$ and $\mathcal{R}_x$. Equation (122) can be rearranged to give

$$Q = \left[\frac{1}{Le} \frac{10.5 Bi}{3.5 + Bi} - \beta \mathcal{R}_T \right] + \left[\frac{10.5 Bi_m}{3.5 + Bi_m} + \mathcal{R}_x \right]$$

The last term is positive when $\mathcal{R}_x$ is positive, as is usually the case, so that if $\mathcal{R}_T$ is small enough the first term is positive, too, and $Q > 0$ for all Lewis number. For larger values of $\mathcal{R}_T$, however, the first term can be negative. In that case Q will still be positive for large Lewis number, but can be negative for small Lewis number.

Luss and Lee [46] present an example in which the strongly reacting steady state is unstable for Le = 0.2, and presumably for smaller Le. The Le_c predicted by Luss and Lee [46] using a special lumping procedure was 0.12. Orthogonal collocation, using the average values of $\mathcal{R}_T$ and $\mathcal{R}_x$ reported by Luss and Lee gave Le_c = 0.21, which would say the case with Le = 0.2 should be unstable, as it was. Orthogonal collocation, using a one-term approximation to compute $\mathcal{R}_T$ and $\mathcal{R}_x$, predicted that the solution would be stable regardless of how small Le become, and this disagrees with the more precise results. Thus when the solution has sharp gradients

it is better to use the average values of $\mathcal{R}_T$ and $\mathcal{R}_X$ computed with a high order approximation. Lee et al. [47] devised a lumping procedure similar to that of Luss and Lee. For the third case in their Table 1, they predict the steady-state solution will be unstable when $\beta/\mathrm{Le} < 1.546$. If orthogonal collocation is used for the lumping, and average values of $\mathcal{R}_X$ and $\mathcal{R}_T$ are used from a precise steady-state solution, then the steady-state should be unstable for $\beta/\mathrm{Le} < 1.32$. In fact, the detailed calculations showed that instability occurred at $\beta/\mathrm{Le} \approx 1.3$. Often it turns out that $\mathrm{Le} < 1$ is required for instability, and the values of Le listed by Hlaváček et al. [48] indicate that $\mathrm{Le} > 1$ for most industrial reactions. Thus these results are not of widespread practical importance, but it is interesting that a one-term collocation method can give a correct qualitative picture of the instability.

H. Results

We now apply these techniques to the sulfur dioxide reactor. A general description of the reactor is given in Section III-A. We have seen that radial and axial dispersion are both expected to be important in this reactor. External resistances to heat and mass transfer are also important.

The dimensionless equations governing this reactor are then

$$\gamma \frac{\partial^2 X}{\partial z^2} - \frac{\partial X}{\partial z} + \frac{\alpha}{r} \frac{\partial}{\partial r}\left(r \frac{\partial X}{\partial r}\right) - \mathrm{Da_I}'\sigma(X - X_s) = 0 \qquad (123)$$

$$\gamma' \frac{\partial^2 T'}{\partial z^2} - \frac{\partial T'}{\partial z} + \frac{\alpha'}{r} \frac{\partial}{\partial r}\left(r \frac{\partial T'}{\partial r}\right) + \mathrm{Da_{III}}'\sigma'(T_s' - T') = 0 \qquad (124)$$

$$\frac{\partial X}{\partial r} = 0, \qquad \frac{\partial T'}{\partial r} = 0, \qquad \text{at } r = 0 \qquad (125)$$

$$\frac{\partial T'}{\partial r} = -\mathrm{Bi_w}(T' - T_w), \frac{\partial X}{\partial r} = 0, \qquad \text{at } r = 1 \qquad (126)$$

$$\gamma \frac{\partial X}{\partial z} = X, \qquad \gamma' \frac{\partial T'}{\partial z} = \tfrac{1}{2}[1 + \sqrt{1 + A_0}](T' - T_0), \qquad \text{at } z = 0 \qquad (127)$$

$$\frac{\partial X}{\partial z} = 0, \qquad \gamma' \frac{\partial T'}{\partial z} = \tfrac{1}{2}[1 - \sqrt{1 + A_1}](T' - T_w), \qquad \text{at } z = 1 \qquad (128)$$

$$A_1 = 24\alpha_1'\gamma_1'\mathrm{Bi_1}/(\mathrm{Bi_1} + 3)$$

The parameters α_i, etc., refer to the inlet (i = 0) and outlet (i = 1) sections. The exact boundary conditions are derived by Young and Finlayson [27], and the approximate boundary conditions are derived there also by using a one-term (in the radial direction) collocation solution in the inlet and outlet portions of the reactor. Various parameter values are listed in Table 3.

The orthogonal collocation formulation of Eq. (123) is

$$\sum_{\ell=1}^{NZ+2} [\gamma BZ_{j\ell} - AZ_{j\ell}]X_{i\ell} + \alpha \sum_{\ell=1}^{NR+1} BR_{i\ell}X_{\ell j} + Da_i'\sigma(X_{sij} - X_{ij}) = 0,$$

$$(129)$$

$$i = 1, \ldots, NR, \quad j = 2, \ldots, NZ + 1$$

$$\gamma \sum_{\ell=1}^{NZ+2} AZ_{1\ell}X_{i\ell} = X_{i1}, \qquad \sum_{\ell=1}^{NZ+2} AZ_{N+2,\ell}X_{i\ell} = 0, \qquad i = 1, \ldots, NR$$

$$\sum_{\ell=1}^{NR+1} AR_{N+1,\ell}X_{\ell j} = 0, \qquad j = 2, \ldots, NZ + 1$$

with similar equations for temperature. The location of collocation points is illustrated in Fig. 8 for NZ = NR = 6. The orthogonal collocation solution results in zero residuals at each interior collocation point, i.e., Eq. (129) is satisfied there, and the inlet (or outlet) boundary conditions are satisfied at the points marked O, while the radial boundary conditions are satisfied at the points marked X. No conditions are applied at the corners (see footnote in Section II-E).
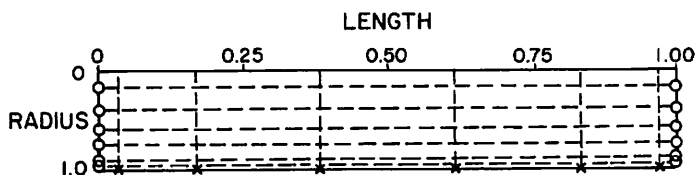

FIG. 8. Grid of collocation points for cylinder. NR = 6, NZ = 6 was used for SO₂ reactor: (o) inlet or outlet axial boundary condition satisfied; (X) radial boundary condition satisfied.

To solve the equations we first solve the boundary conditions for the boundary value of X or T in terms of the other values. These values are substituted into Eq. (129) and give equations having as the unknowns the values of X and T at the NZ × NR interior collocation points. The collocation points are renumbered to represent the unknowns as X_k, k = 1, $\ldots$, NR × NZ rather than as X_{ij}, i = 1, $\ldots$, NR,

$j = 2, \ldots, NZ + 1$. Then the equations are solved using either a Newton-Raphson or a successive substitution method. At each iteration the Newton-Raphson method requires two matrix inversions, and the matrices are $(NR \times NZ)(NR \times NZ)$ in size. The successive substitution method required two matrix inversions on the first iteration only, but required more iterations to converge (12 rather than 5). The net effect was that the Newton-Raphson method took 23 sec* to solve the equations, while the successive substitution method required only 10 sec.* Both estimates are for $NR = NZ = 6$, resulting in 36×36 matrices.

Next consider accuracy. Using the $NR = NZ = 6$ case as the comparison, calculations with $NR = 6$ but $NZ = 4$ and 5 gave outlet conversions within 7 and 1.5% of the solution with $NZ = 6$. The radial model, without axial dispersion, used an improved Euler method of integration and gave values of outlet conversion for 50 and 250 axial steps ($\Delta z = 0.02$ and 0.004) that were within 1.2 and 0.3%, respectively, of the solution with 500 axial steps. Thus using the orthogonal collocation method in the axial direction drastically reduced the number of points needed from 250 to about 6. For a different case, the laboratory reactor of Olson et al., [10] (see Table 3), it was found that the solution was relatively insensitive to NZ for $NZ = 2, 3, 5$, and the outlet conversion varied with NR, having errors of 1.4 and 0.4% for $NR = 2$ and 3, respectively, compared to solutions derived with $NR = 4$ or 5. Using $NR = 4$ and $NZ = 2$ (resulting in 8×8 matrices), the computation time per case, using Newton-Raphson, was 0.4 sec. For this reactor hundreds of calculations were made in order to do a nonlinear least-squares regression analysis of the rate equation.

Next we compare results predicted by different models which include or exclude various heat and mass transfer phenomena. All the models discussed include the external resistance. First we consider a model which leaves out radial mass dispersion ($\alpha = 0$), with radial heat transfer lumped using Eq. (53). These are obtained by using $N = 1$ in the orthogonal collocation formulation, Eq. (129). The results of average conversion and temperature vs length of the reactor are shown in Fig. 9 as Curves N. Clearly this model does not compare well to the experimental data. Next we add in the effects of radial dispersion. The Curves B in Fig. 9 show that for average conversion very good agreement is obtained with experiment when both axial and radial dispersion are included. The difference between Curves N and B also show the effect of increasing the number of radial collocation points from 1 to 6. Finally, we include radial dis-
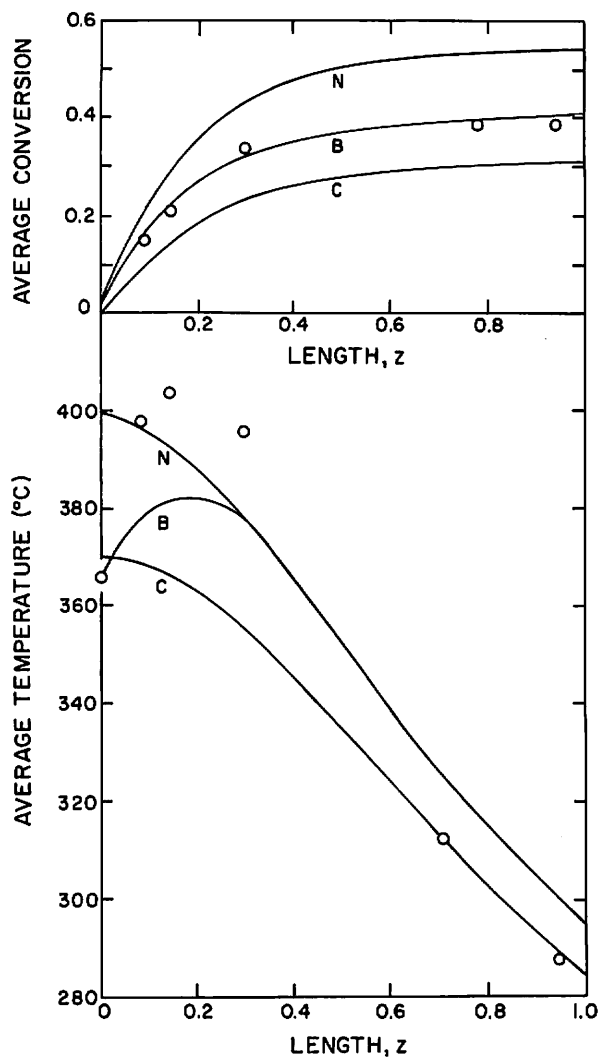
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*CPU time on CDC 6400 computer.

FIG. 9. Average concentration and temperature profiles in SO$_2$ reactor. Axial dispersion models, NZ = 6: B-NR = 6, N-NR = 1; radial model, $\gamma = \gamma' = 0$: C-NR = 6.

persion, but not axial dispersion. The equations are then Eqs. (123) and (124) with $\gamma = \gamma' = 0$, and these are solved using the orthogonal collocation method as illustrated in Eqs. (48) and (49). If the inlet condition is the measured value of 370°C, then the model does not compare as well to the experimental conditions as shown by Curve C

in Fig. 9. Additional calculations are presented elsewhere [27]. We note that the main effect of axial dispersion in this case is to raise the reaction rate at the inlet to the reactor, and the consequences of this increase are felt throughout the bed. Furthermore the radial distribution of temperature near the inlet is very important and affects the outlet conversion.

Thus we see that the orthogonal collocation method is useful for solving the complicated nonlinear equations arising from a laboratory scale packed bed reactor. We apply the method to an industrial reactor in the next chapter.

IV. AMMONIA REACTOR WITH COUNTERCURRENT COOLING

A. Description of Reactor

Industrial reactors are often cooled by the feed stream to the reactor. An example of this is the TVA ammonia reactor represented schematically in Fig. 10. The inlet gas flows up inside a number of tubes which are surrounded by a packed bed of catalyst. At the top of the reactor the gas reverses direction and flows down through the packing. There are also other heat transfer elements of the reactor which are not considered here. Additional details of the reactor can be found in Refs. 49 and 50, and Ref. 50 gives operating and construction details. We are concerned here with the countercurrent nature of the heat transfer. Since the gas stream is heated as it flows up the tubes, the inlet temperature to the reactor bed (i.e., at the top of the reactor) is not known a priori, but depends on the heat transfer that has taken place. The reactor and heat transfer sections must be solved simultaneously in a simulation, as is done below.

First we investigate the various limitations to heat and mass transfer. Radial dispersion is more difficult to analyze here, since the inlet gases flow up the inside of the tubes and then flow down through the packed catalyst bed. Thus the catalyst is on the outside of the tube and the geometry is more complicated. The tubes are located in a hexagonal pattern. We must consider radial temperature gradients due to the cooling tubes as well as at the basket wall. Kjaer [51] estimates the combined heat transfer coefficient between the gas in the cooling tube and the gas in the catalyst bed as 905 kJ/ $(m^2)(hr)(°K)$, based on the outer diameter of the tubes. To calculate a Biot number, we estimate k_e from Pe = 10, giving k_e = 37.2 kJ/ $(m)(hr)(°K)$. To get an effective radius we calculate the catalyst area per tube and figure an equivalent radius assuming a circular cross section. This gives R = 0.054 m, which gives Bi_w = 1.3. If a more precise analysis is desired, we could use the orthogonal collocation
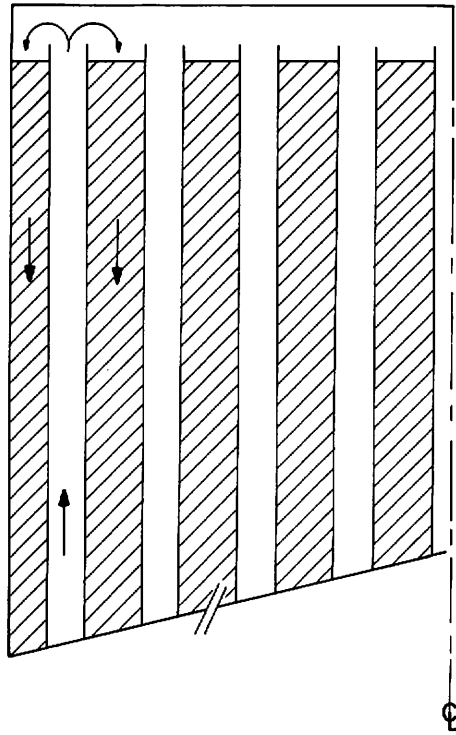
FIG. 10. Schematic of ammonia reactor. Hatched areas are catalyst bed, and clear areas are cooling tubes.

method to solve for the heat transfer in an annulus with a constant rate of heat generation and a zero flux condition at the outer wall. Such an analysis, for N = 1 and a uniform rate of reaction, reveals that for Bi_w = 1 about 70% of the temperature drop occurs at the boundary of the tube and 30% occurs across the packed bed. Thus radial temperature gradients should be small but not necessarily negligible. In fact, Slack et al. [50] reported radial temperature variations, and Refs. 49 and 51 indicate these are probably caused by the fact that the center thermocouple tube replaces a cooling tube, while the off-axis thermocouples are in the middle of an equilateral triangle formed by three cooling tubes. Thus the effective area for cooling is different for a center thermocouple and an off-axis thermocouple, leading to local temperature variations. Here we use a lumped parameter model with an overall heat transfer coefficient.

We next consider axial dispersion and apply the criteria, Eq. (61). We note that the errors introduced by axial dispersion decrease as the flow rate is increased, so that we expect the axial dispersion is not important in this industrial reactor. The criteria give a maximum error at the inlet of 0.1% in the concentration and 0.3°C in the temperature. A maximum of 0.6°C was also found by Eymery [52], who did complete calculations for two models, one including and the other excluding axial dispersion. These values are so small that we neglect axial dispersion. We note, however, that due to the coupling between the reactor section and the heat transfer section, the inclusion of axial dispersion would not add to the computational difficulties, provided we use the orthogonal collocation method or some other method which treats the problem as a boundary value problem.

To examine the importance of external resistances, we apply Eq. (73):

$$\Delta T_{max}' = 0.7(-\Delta H_R 2)(C_{N_2} - C_{N_2,eq})/(\rho C_p) = 390°K$$

The factor 2 is included because the heat of reaction is based on a mole of ammonia, and the concentration is the concentration of nitrogen. This value is so large that we expect the reactor to be operated in such a way that the effectiveness factor is near 1 so that the concentrations of nitrogen and hydrogen do not drop to zero inside the catalyst when the concentrations outside the catalyst are the inlet values. If we use a value of $\rho_B R_0 = 100$(kg)(mole NH_3)/(m^3)(hr) and solve Eqs. (63) and (64), we find the concentration changes 0.1% across the mass boundary layer and the temperature changes 1.2°K. Estimates of Bi and Bi_m give 8 and 170, respectively. Thus external mass transfer limitations are negligible and external heat transfer limitations are small, but could change the rate by 5%. However, the reaction rate data used below were measured under conditions similar to those encountered in the reactor, and include whatever resistances, internal and external, that are important.

B. Equations

The equations are taken from Baddour et al. [49] and represent mass and energy balances on the catalyst bed and the cooling tubes:

$$\frac{dX}{dz} = \Re(X,T) \frac{(1 + X)^2}{(1 + X_0)}$$

$$f(X)\frac{dT}{dz} = -A_1(T - TT) + (A_2 + A_3 T)\Re(X,T)$$

$$\frac{dTT}{dz} = A_1(TT - T)$$

The variables are defined in the notation and Table 5. The heat capacity and heat of reaction are permitted to vary with temperature in a linear fashion.

TABLE 5

Parameters for TVA Ammonia Reactor[a]

D_{basket} = 1.10 m; d_p = 5.18 mm (mesh sizes 3-6); number of tubes = 84; L = 5.18 m; D_{to} = 0.0508 m; D_{ti} = 0.0381 m

Re = 1640; Pr = 0.7; Sc = 0.4; ϵ = 0.4; $-\Delta H_R$ = 46,200 kJ/(kg)(mole)

C_{po} = 30.7 kJ/(kg)(mole)($^\circ$K); ΔC_p = 13.6 kJ/(kg)(mole)($^\circ$K)

$$f(X) = 1 - \frac{\Delta C_p(X - X_0)}{C_{po}(1 + X)}$$

$$\mathcal{R}(X,T) = \frac{A}{T_0 V_0} \frac{1}{T} \exp[-\gamma/T] g(X,T)$$

$$g(X,T) = (K_p p)^2 \mathcal{A}(\beta - y)^{1.5} (\mathcal{C} - y)/y - (\mathcal{D} y/(\beta - y)^{1.5}$$

$\mathcal{A} = (1.5 - X_{H_{2,0}})/(1 + X_0)^{2.5}/3$

$\mathcal{B} = (X_{H_{2,0}} + 1.5 X_0)/(1.5 - X_{H_{2,0}})$

$\mathcal{C} = (X_{N_{2,0}} + 0.5 X_0)/(0.5 - X_{N_{2,0}})$

$\mathcal{D} = (1 + X_0)/(1.5 - X_{H_{2,0}})^{1.5}$

A = 359 × 1.75 × 10^{16} $p^{-0.5}$

γ = $E/R_g T_0$ = 20,300 $^\circ$K/T_0

ln K_p = −13.02 + 11.96/T

T_0 = 501°K; V_0 = 13,800 hr^{-1}

A_1 = 1.354; A_2 = 2.738; A_3 = $\Delta C_p/C_{po}$ = 0.444

Inlet mole fraction: H_2, 0.6375; N_2, 0.2125; NH_3, 0.05; inert, 0.10

---

[a]In the ammonia reactor X is mole fraction.

It is clear that if we knew the value of T and TT at the point z = 0, we could integrate these equations as initial value problems using any of several methods, such as the Runge–Kutta method. This is what Baddour et al. [49] did. In our case, however, we want to solve the simulation problem where the boundary conditions are

X = X_0,   T = TT,   at z = 0

TT = T_0,   at z = 1

Since the boundary conditions are at both ends, we cannot integrate

the equations as initial value problems. This factor complicates the solution. We apply orthogonal collocation by writing

$$\sum_{i=1}^{N+2} A_{ji}X_i = \Re(X_j, T_j)(1 + X_j)^2/(1 + X_0), \qquad j = 2, \ldots, N + 2 \tag{130}$$

$$f(X_j)\sum_{i=1}^{N+2} A_{ji}T_i = -A_1(T_j - TT_j) + (A_2 + A_3T_j)\Re(X_j, T_j)$$
$$j = 2, \ldots, N + 2 \tag{131}$$

$$\sum_{i=1}^{N+2} A_{ji}TT_i = A_1(TT_j - T_j), \qquad j = 1, \ldots, N + 1 \tag{132}$$

together with the boundary conditions

$$X_1 = X_0, \qquad T_1 = TT_1, \qquad TT_{N+2} = T_0$$

Note that we collocate at $j = 1$ ($z = 0$) for the tube temperature, since the corresponding boundary condition is at $j = N + 2$ ($z = 1$).

The equations are solved by a successive substitution method. First the boundary conditions are included in Eq. (130)-(132) and the equations are rearranged:

$$\sum_{i=2}^{N+2} A_{ji}X_i^{k+1} = \Re_j^k(1 + X_j^k)^2/(1 + X_0) - A_{j1}X_0$$

$$\sum_{i=1}^{N+1} A_{ji}TT_i^{k+1} = A_1(TT_j^{k+1} - T_j^k) - A_{j,N+2}T_0$$

$$f(X_j^k)\sum_{i=2}^{N+2} A_{ji}T_i^{k+1} = -A_1(T_j^{k+1} - TT_j^k) + (A_2 + A_3T_j^k)\Re_j^k$$
$$- f(X_j^k)A_{j1}TT_1^{k+1}$$

The two matrices are inverted only once at the onset of the calculation. Since at each iteration only matrix multiplication is necessary, the calculations are efficient even for a large N. The new iteration is then determined using a relaxation factor of RF = 0.5, e.g.,

$$\overline{X}^{k+1} = X^k + RF(X^{k+1} - X^k)$$

C. Results

The results of the calculation are compared in Fig. 11 to the experimental data reported by Baddour et al. [49]. The calculated curve is slightly different from the actual curve, probably due to
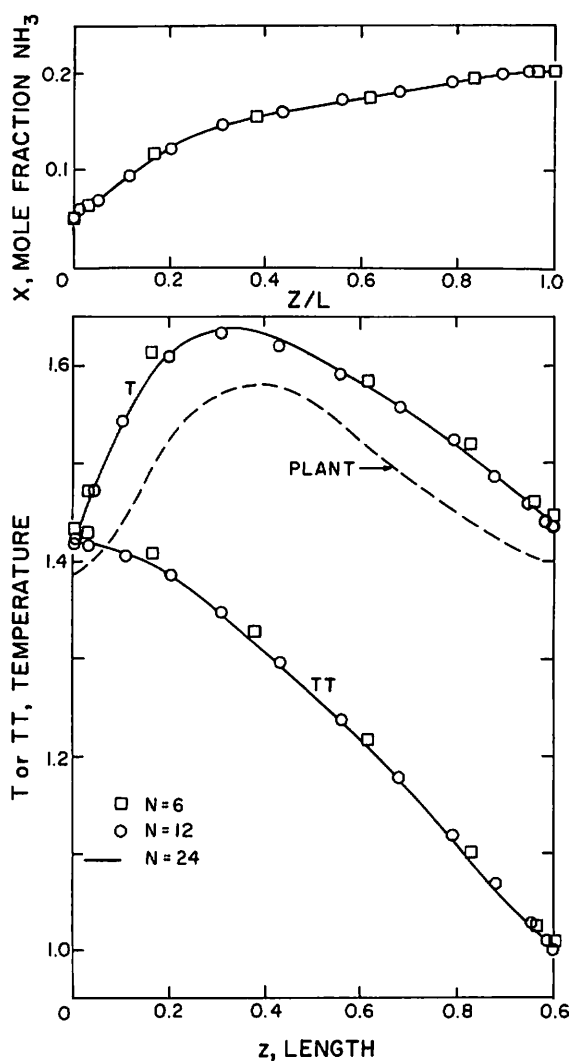
FIG. 11. Temperature and ammonia mole fraction as a function of reactor length.

inaccuracies in the application of the rate expression, the activity, or heat transfer coefficients. We note that Baddour et al. [49] adjusted the coefficients for heat transfer between the reactor and cooling sections in order to obtain agreement with the actual results. The results for N = 6, 12, and 24 show that N = 12 is adequate to solve this problem.

V. REDUCTION OF NITRIC OXIDE IN AUTOMOBILE EXHAUST

A. Introduction

We next consider the removal of nitric oxide which is emitted to the atmosphere from automobile exhaust. The exhaust stream contains carbon monoxide and hydrogen, and the nitric oxide can be reduced by means of the reactions

$$NO + CO = \tfrac{1}{2}N_2 + CO_2$$

$$NO + H_2 = \tfrac{1}{2}N_2 + H_2O$$
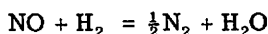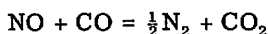
We leave out the side reaction of NO with hydrogen to form ammonia and water due to the unavailability of reaction rate data.

The reactor configuration is very flat and only a few particle diameters long ($L/d_p = 15$). The dimensions were chosen based on the suggestion of Baker and Doerr [53] that about 2.8×10^{-3} m^3 of catalyst would be required, and the length to diameter ratio (1/6) is that described by Wei [54]. This gives a diameter of 0.28 m and a length of 0.046 m. Thus the reactor is more of a pan shape with axial flow. The unusual geometry is a result of the desire to have as small a pressure drop as possible.

The bed is packed with catalyst with a 0.0032-m particle diameter. The rate expressions were measured on copper chromate catalysts and are used here as typical examples and because data were available. The transient operation of the reactor is of primary importance, since the pollution standards for automobiles are based on operation of the vehicle at a range of speeds and driving conditions. Thus one important feature of the analysis is which time-dependent effects must be included and which can be neglected. We find below that internal mass transfer resistances are important, but that the particle problem can be solved at steady-state corresponding to the instantaneous catalyst temperature. This means that the reaction rate can be evaluated at the conditions of the gas stream, provided a formula exists for the effectiveness factor. Unfortunately, there are two reactions, since the nitric oxide can be reduced by both carbon monoxide and hydrogen. The reaction rate expressions for each of these reactions depends on the concentration of nitric oxide, so that the effectiveness factor for each reaction is not a unique function of the conditions for that reaction alone, but depends on the other reaction, too. Thus we felt it was impractical to determine the effectiveness factors a priori, so that they must be calculated throughout the transient. In such a case the orthogonal collocation method is especially useful, since the boundary value problem can

be accurately and efficiently solved using the orthogonal collocation method. Since this calculation must be performed thousands of times during the transient, any computational savings achieved by using orthogonal collocation is welcome.

B. Important Heat and Mass Transfer Phenomena

We first examine the radial dispersion, which might be expected to be important due to the large radius. Using a Peclet number of 10 and Eq. (57) to calculate the Nusselt number, and hence the heat transfer coefficient, we obtain a Biot number of 50 for a case with a flow rate of 50 SCFM (85 m^3/hr). Since the heat transfer coefficient and effective thermal conductivity of the bed depend on flow rate, the Biot number will, too. However, this value is so large that it suggests that the major resistance to heat transfer is inside the bed and a distributed parameter model must be used to account for radial temperature and concentration variations. Calculations for the steady state were made using two models—one a distributed parameter model taking account of radial variations, Eqs. (39)-(43), and the other a lumped parameter model, Eqs. (44) and (45) [55]. The results show that while the temperature difference between the center and the wall of the bed was from 6 to 18°C, the radial variation of NO concentration was less than 3%. Consequently, it was decided to use a lumped parameter model, with a temperature averaged radially in the bed. Of course it is necessary to use an overall heat transfer coefficient calculated using Eq. (53) since the major resistance is not the heat transfer coefficient at the wall, h_w, but is inside the bed, acting through k_s. If we had used just the wall heat transfer coefficient for a problem with such a large Biot number, we would have grossly overestimated the rate of cooling. For example, h_w is 225 kJ/(hr)(m^2)(°C) while U is 16 kJ/(hr)(m^2)(°C).

Axial dispersion might be expected to play a major role in such a short bed since it is essentially isothermal. To investigate this possibility we apply Eqs. (61) and (62). For estimations of the reaction rate we consider a case of 1000 ppm NO, 1% CO, and 200°C, which gives $\rho_B R = 3.7$ (kg)(mole)/(hr)(m^2). Under these conditions we obtain a temperature increase of 2°C at the inlet to the bed and a concentration decrease of 0.01% due to the inclusion of axial dispersion. Furthermore the reactor is almost isothermal, so axial dispersion would be even less important away from the inlet. Thus we neglect axial dispersion.

Next consider the external heat and mass transfer resistances. Equation (71) predicts a maximum temperature increase in the catalyst of 7°C, while Eqs. (63) and (64) predicts a 1°C temperature change and a 15% concentration change. External mass transfer re-

sistance has a small effect, and we are tempted to say external heat transfer resistance is unimportant. However, Eq. (64) is based on a steady state, and in this transient situation we cannot use it to deduce whether we can take $T_s' = T'$. In fact, we see below that the slowest response of the system is the time for heat transfer between the gas and catalyst. To examine the intraparticle resistance we calculate typical values of Biot and modified Biot numbers, obtaining $Bi_m = 130$ and $Bi = 0.8$. These values indicate that a lumped parameter model is adequate for heat transfer in the particle, and that the major mass transfer resistance is inside the particle, rather than at the film outside the particle. To find the effect of η vs ϕ, consider the following simplifications. For large CO concentrations the reaction is essentially first order in NO concentration. Since the temperature increases are so small, let us estimate the importance of internal resistances by using the results for an irreversible, first-order isothermal reaction. Using a pseudofirst reaction rate constant $k' = \rho_s R/C_0 = 4.1 \times 10^5$/hr gives a Thiele modulus of 8 and an effectiveness factor of about 0.4. Thus intraparticle mass transfer resistances are important and must be included in the model.

C. Quasi-Static Model

We model the reactor as a series of four mixing cells. While this introduces some axial dispersion, the effect is not great and the number of mixing cells is not crucial. The advantage of doing this is to reduce the number of grid points in the axial direction compared to direct integration of equations such as (50) and (51).

The mathematical model applied here is a quasi-static model which accounts for the fact that some of the transient phenomena occur extremely rapidly and some transient phenomena are very slow. The slowest time-response of the system is for heat transfer between the gas and the catalyst with a time constant $\tau_4 = (\rho C_p)_s d_p/$ $(6h_p)$. When the residence time in a mixing cell, $\tau_3 = \epsilon V/F$, is less than τ_4, Ferguson and Finlayson [56] suggest the accumulation terms can be dropped in the fluid mass balance. Here $\tau_4/\tau_3 = 5000$. When the volumetric heat capacity ratio, $C_r = \epsilon \rho C_p/[(1 - \epsilon)(\rho C_p)_s]$, is less than 0.002, then the accumulation terms can be dropped from the fluid energy balance [56]. Here $C_r = 0.0002$. When the time constant for mass transfer in the particle, $\tau_1 = \epsilon_s R_p^2/D_e$, is smaller than τ_4, the accumulation term can be neglected in the particle mass balance. Here $\tau_1/\tau_4 = 0.02$. Also, due to the small Biot number, the particle energy balance can be lumped. With these assumptions the dimensionless equations used by Ferguson and Finlayson are

$$0 = \nabla^2 X_s - \frac{\rho_s d_p^2}{4D_{e,NO}} (R_1 + R_2) \tag{133}$$

$$\frac{\partial X_s}{\partial r} = Bi_m(X - X_s), \qquad \text{at } r = 1 \tag{134}$$

$$\tau_4 \frac{dT_s}{dt} = T - T_s + \frac{d_p \rho_s}{2h_p}[-\Delta H_1\langle R_1 \rangle - \Delta H_2\langle R_2 \rangle] \tag{135}$$

$$0 = X_{in}(t) - X + \frac{6}{d_p}\frac{K_{m,NO}(1 - \epsilon)V}{F}[X_s - X] \tag{136}$$

$$0 = T_{in}(t) - T + \frac{6}{d_p}\frac{h_p(1 - \epsilon)V}{F\rho C_p}[T_s - T] \tag{137}$$

where X is the nitric oxide concentration, and similar equations are written for CO, while H_2 is determined by stoichiometry. The brackets here refer to integrals over the volume, $\langle R_1 \rangle = \int_0^1 R_1 r^2 \, dr$. Equation (137) can be solved for T and substituted into the Eq. (135) to eliminate the fluid temperature T from the equation. A similar manipulation eliminates X from Eq. (134), giving

$$\frac{\partial X_s}{\partial r} = \frac{Bi_m}{1 + A}[X_{in}(t) - X_s(1,t)], \qquad \text{at } r = 1 \tag{138}$$

$$A = \frac{6k_{m,NO}(1 - \epsilon)V}{d_p F}$$

We have found in other calculations [55], as have Elnashaie and Cresswell [41], that better results are achieved if we integrate Eq. (133) to obtain

$$\frac{\partial X_s}{\partial r}\bigg|_{r=1} = \frac{\rho_s d_p^2}{4D_{e,NO}} (\langle R_1 \rangle + \langle R_2 \rangle)$$

and write the boundary condition as

$$\frac{\rho_s d_p^2}{4D_{e,NO}} (\langle R_1 \rangle + \langle R_2 \rangle) = \frac{Bi_m}{1 + A}[X_{in}(t) - X_s(1,t)] \tag{139}$$

Orthogonal collocation is applied to this equation using the quadrature formula

$$\frac{\rho_s d_p^2}{4D_{e,NO}} \sum_{i=1}^{N+1} W_i(R_{1i} + R_{2i}) = \frac{Bi_m}{1 + A}[X_{in}(t) - X_{s,N+1}] \tag{140}$$

Orthogonal collocation is then applied to Eq. (133) as in Eqs. (97) and (98), and if we use polynomials defined by $w = 1$ [2, p. 102] so that $W_{N+1} = 0$ for $N > 2$, we obtain

$$\sum_{i=1}^{N} B_{ji}X_{si} = \frac{\rho_s d_p^2}{4D_{e,NO}} (R_{1j} + R_{2j}) - B_{j,N+1}X_{s,N+1} \qquad (141)$$

with $X_{s,N+1}$ determined from Eq. (140). This equation is solved by assuming the NO equation is first order and using the iteration scheme outlined in Section III-F. The CO equation is solved by successive substitution, which works here because CO is in great excess and the concentration changes only slightly. We thus integrate Eq. (135) in time, using an improved Euler scheme, and solve Eqs. (140) and (141) at each time step. The physical properties are permitted to vary as their dependence on inlet temperature dictates. Detailed calculations have shown that using $N = 3$ was adequate, giving results within a few percent of those obtained with $N = 6$. The time step for the integration varied between 1 to 4 sec.

D. Results

The calculations were done by Ferguson [55] for inlet conditions simulating the Federal Test Procedure for testing automobile pollution levels. Typical inlet and outlet nitric oxide concentrations are shown in Fig. 12. More information on the effect of changing catalyst properties and details on other models are given elsewhere [56].

This application of the orthogonal collocation method to a transient problem used a cell model. Other applications [16, 18, 57] used a continuum model, such as the time-dependent version of Eqs. (34)-(38). Waede Hansen [57] handles the quasi-static model by using the fully dynamic model (without neglecting accumulation terms) for a small interval and then using the quasi-static model. Calculations by Ferguson and Finlayson [56] indicate this is not necessary here.

In this application the orthogonal collocation method was useful because the effectiveness factor problem could be solved efficiently using $N = 3$. While a cell model was used here, if continuum models were used the orthogonal collocation method could be applied to those aspects of the problem, too, as was done in Sections III-IV.

VI. OTHER APPLICATIONS

We have seen how to apply orthogonal collocation to three diverse reactors. There are other possible reactor models, too. In the model proposed by deWasch and Froment [58] the reactor continuum is
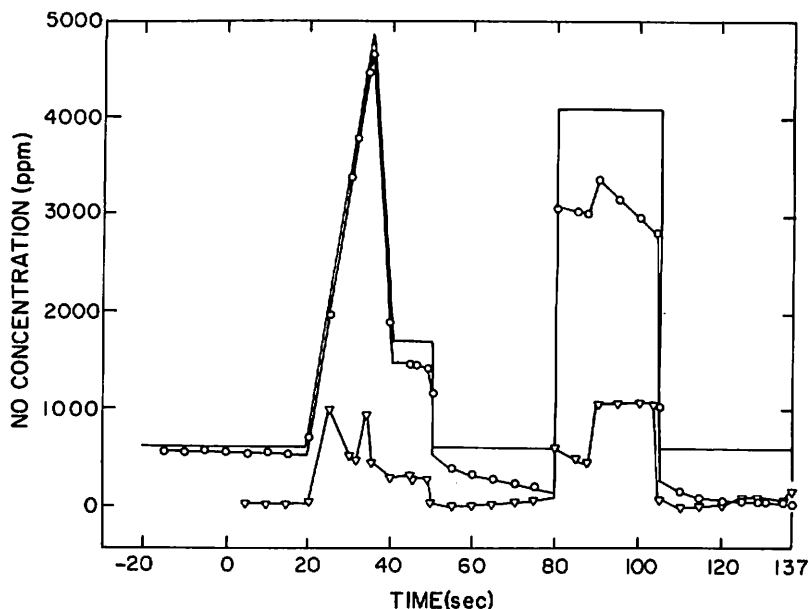
FIG. 12. Nitric oxide concentration (——) inlet value, (○) outlet from reactor during the first cycle, (▽) outlet during the seventh cycle of Federal Test Procedure.

divided into two phases, the catalyst and fluid phases, but radial conduction is permitted to occur in the solid phase, and radial dispersion in the fluid phase is only due to conduction through the fluid and convection. Orthogonal collocation can be applied to such models, too, using the same ideas outlined in Section II-C.

Orthogonal collocation can also be used when the concentration and temperature gradients are steeper than those shown here. In other (unpublished) work, Mr. Larry C. Young has used orthogonal collocation for a steady-state reactor with radial and axial dispersion. Both space dimensions were treated using orthogonal collocation, and the iteration was performed using the Newton-Raphson method. The cases treated had a severe hot spot, with the temperature rising to the adiabatic temperature. Thus the axial temperature and concentration profiles were very steep and as many as 40 terms were included in the axial direction. When using this many collocation points the matrices for first and second derivatives were calculated using a revised version of the scheme outlined in Ref. 3. In a problem such as this, orthogonal collocation on finite elements is also a candidate method, and sufficient experience has not yet been obtained to give guidelines between the choices of a

global expansion, valid over the entire reactor length, or expansions only on finite elements for this problem.

One reactor configuration being considered for catalytic mufflers is a monolith in which the reactants enter a honeycomb and flow down small, long tubes. Catalyst coats the walls and the reaction occurs there. One model of such a device [59] formulated the Graetz problem for heat transfer in a duct. If this is solved for arbitrary wall temperature and wall heat flux, then the chemically reacting case can be reformulated as an integral equation involving only properties on the solid walls, and the eigenvalues and various constants from the Graetz problem can account for the diffusion and convection of heat and mass in the fluid. Such a formulation is simpler to solve than the combined multidimensional equations in the wall and fluid. The orthogonal collocation method is used to solve the Graetz problem, giving the necessary eigenvalues and parameters, and orthogonal collocation can be applied when solving the integral equation, too.

The orthogonal collocation method has only recently been applied in the field of control. Michelsen et al. [60] considered a reactor with convection but no radial or axial dispersion. For control purposes the equations were linearized around a steady state. Orthogonal collocation was applied in the axial direction to reduce the problem to a set of ordinary differential equations in time. Laplace transform methods were then applied to these equations and the various transfer functions examined. Up to 12 collocation points were used with good results. In a companion paper the formulation was applied to a control and estimation problem [61].

The author believes that the full potential of the orthogonal collocation method to reduce the dimensionality of a control problem (reduce the number of ordinary differential equations in time) has not yet been fully realized and utilized. This would seem to be an important area for further applications.

VII. CONCLUSIONS

The orthogonal collocation method is a versatile technique for solving models of chemical reactors. The method has been applied to the full range of situations: steady state and transient, continuum and cell models, radial and axial dispersion, internal and external resistances to heat and mass transfer. While all combinations have not been done, the methods are clear and a combination of those outlined here. Early papers in the field, which began only in 1967, expounded on the method and compared it with other techniques (in particular finite difference methods) while later papers involved

application to specific situations. The orthogonal collocation method has proved to be a very efficient tool for chemical reaction engineering and will be used increasingly in the future.

SYMBOLS

a	1, 2, or 3 for planar, cylindrical, or spherical geometry
a_i	constants in trial function
a_v	surface area of catalyst/bed volume, m^{-1}
A_{ji}	matrix representing first derivative
b	length of effective reaction zone in catalyst
Bi	Biot number for catalyst, $h_p d_p/(2k_e)$
Bi_m	Biot number for mass transfer, $k_m d_p/(2D_e)$
Bi_w	Biot number for packed bed, $h_w r_0/k_r$
B_{ji}	matrix representing Laplacian operator or second derivative
C	gas concentration, (kg)(mole)/m^3
C_T	total concentration, (kg)(mole)/m^3
C_p	heat capacity, kJ/(kg)(°C)
C_r	ratio of volumetric heat capacities of fluid and solid, $\epsilon\rho\tilde{C}_p/(1-\epsilon)(\rho\tilde{C}_p)_s$
d_p	catalyst particle diameter, based on sphere with equivalent volume/area, m
D	gas diffusivity, m^2/hr
D_e	effective diffusivity in catalyst, m^2/hr
D_r	radial effective diffusivity in packed bed, m^2/hr
D_z	axial effective diffusivity in packed bed, m^2/hr
Da_I	Damköler Group I, $\rho_B\rho LR(C_0,T_0)/(GC_0)$
Da_{III}	Damköler Group III, $(-\Delta H_R)\rho_B LR(C_0,T_0)/(G\tilde{C}_p T_0)$
Da_I'	$\rho\rho_B L/(G\tilde{C}_0) = Da_I/R_0$, (kg)(cat)(hr)/(kg)(mole)
Da_{III}'	$\rho_B(-\Delta H_R)L/(G\tilde{C}_p) = Da_{III}T_0/R_0$, (kg)(cat)(hr)(°K)/(kg)(mole)
E	activation energy, kJ/(kg)(mole)
f	dimensionless reaction rate in Section II
F	volumetric flow rate, m^3/hr
G	mass flux based on empty tube area, kg/(m^2)(hr)
h_p	heat transfer coefficient for transfer between fluid and catalyst, kJ/(m^2)(hr)(°C)
h_w	heat transfer coefficient at reactor wall, kJ/(m^2)(hr)(°C)
$-\Delta H_R$	heat of reaction, kJ/(kg)(mole)
j_H	j-factor for heat transfer, Nu $Re_p^{-1}Pr^{-1/3}$
j_M	j-factor for mass transfer, Sh $Re_p^{-1}Sc^{-1/3}$
k	reaction rate constant, (kg)(mole)/(hr)(kg)(cat)(atm^2)
k	also dimensionless reaction rate constant
k	also gas thermal conductivity, kJ/(m)(hr)(°C)

k_e	effective thermal conductivity in catalyst, kJ/(m)(hr)(°C)
k_m	mass transfer coefficient, m/hr
k_r	radial effective thermal conductivity in packed bed, kJ/(m)(hr)(°C)
k_z	axial effective thermal conductivity in packed bed, kJ/(m)(hr)(°C)
K_1	constant appearing in rate equation, atm^{-1}
K_2	constant defined by Eq. (87)
L	reactor length, m
Le	Lewis number, $\rho \tilde{C}_p D_e / k_e$
N	number of interior collocation points
NE	number of elements
NR	number of interior radial collocation points
NZ	number of interior axial collocation points
Nu	Nusselt number, $h_p d_p / k$
Nu_w	Nusselt number, $h_w d_p / k$
p_i	partial pressure of i-th component, atm
P_i	i-th order orthogonal polynomial
Pr	Prandtl number, $\tilde{C}_p \mu / k$
$Pe_{h,r}$	radial heat Peclet number, $d_p G \tilde{C}_p / k_r$
$Pe_{h,z}$	axial heat Peclet number, $d_p G \tilde{C}_p / k_z$
$Pe_{m,r}$	radial mass Peclet number, $d_p G / (\rho D_r)$
$Pe_{m,z}$	axial heat Peclet number, $d_p G / (\rho D_z)$
r	radial position, r'/r_0
r_0	radius of packed bed, m
r'	radial position in packed bed, m
R	reaction rate, (kg)(mole)/(hr)(kg)(cat)
R_g	gas constant, kJ/(kg)(mole)(°K)
Re_p	Reynolds number, $d_p G / \mu$
$\mathfrak{R}$	reaction rate, dimensionless
$\mathfrak{R}_X$	$\partial R(X,T)/\partial X$
$\mathfrak{R}_T$	$\partial R(X,T)/\partial T$
s	radial position in catalyst, m or $(u-b)/(1-b)$
Sc	Schmidt number, $\rho D / \mu$
Sh	Sherwood number, $k_m d_p / D$
St	Stanton number, $U/(G C_p)$
t	time, hr
T	temperature, T'/T_0
T'	temperature, °K
TT	cooling tube temperature, dimensionless
u	normalized position in catalyst particle, $2s/d_p$
u	shifted coordinate in finite element
V	volume of mixing cell, m^3
W_i	weighting factor in quadrature formula
x	spatial position

x_k location of k-th element
X   normalized concentration, C/C_0
X   mole fraction of ammonia in Section IV
y_i trial function
y_i value of y at i-th collocation point
z   axial position, z'/L
z' axial position, m

Greek Letters

α $\rho D_r L/(G r_0^2)$ or $d_p L/(r_0^2 Pe_{m,r})$
α' $k_r L/(G\tilde{C}_p r_0^2)$ or $d_p L/(r_0^2 Pe_{h,r})$
β $(-\Delta H_R)D_e C_0/(k_e T_0)$
γ $E/R_g T_0$ and $\rho D_z/(GL) = d_p/(LPe_{m,z})$
γ' $k_z/(LGC_p) = d_p/(LPe_{n,z})$
δ Bi_m/Bi
ϵ catalyst bed void fraction
ϵ aspect ratio in Section II-E
ϵ_s catalyst void fraction
η effectiveness factor, defined by Eq. (85)
λ eigenvalue in stability analysis
μ viscosity of gas, kg/(m)(sec)
ν dimensionless overall heat transfer coefficient
ρ gas density, kg/m³
ρ_s catalyst density, (kg)(cat)/(cat)(vol)(m³)
ρ_B bulk catalyst density, (kg)(cat)/(vol of bed)(m³)
σ $k_m a_v C_0/\rho_B$
σ' $h_p a_v/(-\Delta H_R \rho_B)$
τ_4 characteristic time for heat transfer between catalyst
             and gas $(\rho\tilde{C}_p)_s d_p/(6h_p)$, hr
τ_1 characteristic time for mass transfer in catalyst, $\epsilon_s d_p^2/(4D_e)$, hr
τ_3 residence time in mixing cell, $\epsilon V/F$
ϕ^2 Thiele modulus squared, $(d_p/2)^2 \rho_B R/(C_0 D_e)$
ϕ $2V_p\phi/(A_p d_p)$

Subscripts and Superscripts

$'$ dimensional variable; also thermal variable in SO_2 reactor
eq   equilibrium value
0   inlet or reference value
i,j   i-th or j-th collocation point
p   result from plug flow model without axial dispersion

s   value in solid (catalyst)
w   value on wall
~   per mass

Acknowledgments

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