Error Bounds for Approximate Solutions to Nonlinear Ordinary Differential Equations

Error bounds are provided for approximate solution of systems of nonlinear ordinary differential equations for cases where there is no known exact solution for comparison. Theorems are proved for problems of heat and mass transfer of a multicomponent system in catalyst particles undergoing chemical reaction. Error bounds are provided for the pointwise error as well as the effectiveness factor. Calculations based on the theorems show the orthogonal collocation method can give results which are proved accurate to 12 digits, thus providing essentially the exact solution. For problems for which the theorems have not yet been proved, the results suggest that the mean-squared residual gives a good indication of the accuracy since the error decreases as the mean-squared residual decreases.

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SCOPE

We study errors arising from the numerical solution of differential equations governing heat and mass transfer, with chemical reaction, in catalyst pellets. In numerical analysis an estimate of the error is obtained by repeating the calculations for various grid spacings and noting the convergence as the grid spacing is reduced. We cannot really say what the error is, however, because we do not know how much the results will change if the grid spacing is reduced further. We wish to obtain exact information about the error without making additional calculations using other grid spacings. For optimum usefulness we are interested in problems which are difficult enough to warrant numerical solution in the first place; that is, no exact solution should be available.

We provide such information for nonlinear ordinary differential equations and use the orthogonal collocation method in the numerical computations. The method for obtaining error bounds employs the concept of the residual, which tells us how well the approximate solution satisfies the differential equation. Theorems relate this residual to the maximum error. Then as the residual becomes smaller the error becomes smaller, too.

The primary importance of such theorems is in the comparison of different methods of solution. We can now take a difficult problem whose solution is unknown, solve the problem using different approximate methods, calculate the maximum error for each solution, and compare the methods and their solutions on a firm basis, since we know exactly how large the error can be. In addition, when we are doing a calculation in which the numerical answer is more important than the methods used, we can examine the residual and calculate the error.

Previous to this time information was available on convergence of the orthogonal collocation method so that we knew the numerical scheme would approximate the exact solution provided we used a sufficiently fine grid spacing. Some results were also available which indicated the rate of convergence, that is, how fast the error decreased as the number of terms was increased. Only limited results were known about error bounds; knowing the error decreased at a certain rate is of no help unless the constants in the expression could be calculated, and oftentimes these depended on the unknown exact solution. Few of the theorems on calculable error bounds are applicable to the problems treated here because of the strong nonlinearity. The paper then gives error bounds for solutions to problems which are of interest to chemical engineers.

CONCLUSION AND SIGNIFICANCE

For many nonlinear problems of reaction in a catalyst pellet it is possible to use the orthogonal collocation method and the error bounds derived here to prove the accuracy of the approximate solution, even though the exact solution is unknown. For examples treated below the first 12 digits of the approximate solution are proved to be exact, so that the method gives, to all intents and purposes, the exact solution. The error in the effectiveness factor is also given. The error bounds illustrate the tremendous power of the orthogonal collocation method in that the error decreases more rapidly than 10^{-N} for the examples treated here. Each additional collocation point ($N \rightarrow N + 1$) gives another digit accuracy. In finite difference methods with a truncation error $0(h^2)$, the error decreases as N^{-2}. Thus at least three times as many grid points ($N \rightarrow 3N$) must be used to reduce the error by a factor of about 10. The error bounds derived here are limited primarily by the necessity to have a small enough Lipschitz constant governing the nonlinear term. Similar bounds can be derived for other problems which have bounded Green's functions and nonlinearities in the reaction rate function.

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In problems for which an error bound has not yet been proved the mean-square residual provides a convenient criterion for judging the solution, since we expect the results obtained here are general: the error bound is proportional to the mean-square residual, and decreases in the residual force a decrease in the error bound.

High-speed digital computers are useful for solving many difficult, nonlinear differential equations arising in engineering. The computations yield an approximation to the exact solution, yet it is difficult to assess the accuracy of that approximation. One method of estimation, useful in finite difference and collocation methods, is to increase the number of grid points or collocation points (N) and repeat the computations until the answer becomes insensitive to N. This approach gives only an estimation of the error, since we usually cannot say how much the results will change if N is increased further. We provide theorems below which permit calculation of error bounds, which are mathematically rigorous upper bounds on the possible error of approximate solutions. We thus leave the realm of speculation on the error and enter the realm of knowing a maximum size of the error. The theorems apply to very general situations, and with several applications we demonstrate the usefulness of such results. For example, for a nonlinear problem which has no known exact solution, we can prove that the approximate solution gives the first 12 significant digits of the exact solution.

The approximate solutions are generated using the collocation method and usually the orthogonal collocation method (Villadsen and Stewart, 1967; Finlayson, 1972). In the orthogonal collocation method we expand the dependent variable in the form

$$\tilde{y}(x) = y(1) + (1 - x^2) \sum_{i=1}^{N} a_i P_{i-1}(x^2) \qquad (1)$$

where the orthogonal polynomials P_i are generated by

$$\int_0^1 w(x^2)\, P_i(x^2)\, P_j(x^2)\, x^{a-1}\, dx = \delta_{ij}; \quad w = 1 \text{ or } 1 - x^2 \qquad (2)$$

We substitute expression (1) into the differential equation and require it to be satisfied at a set of collocation points, which are roots to $P_N(x^2) = 0$. This criterion gives the $\{a_i\}$ while the boundary condition determines $y(1)$. (Equation (1) is already written to satisfy the condition $dy/dx = 0$ at $x = 0$.) The orthogonal collocation method thus gives an approximate solution $\tilde{y}(x)$, which depends on N, and N is increased until the answers converge to within some specified accuracy. Then we can estimate the error in the approximate solution.

To provide error estimates we employ the concept of the residual. Once the approximate solution is generated we can substitute it back into the differential equation, thus obtaining a function of x, which we call the residual $R(x)$. The residual is zero at the collocation points, since that is how the $\{a_i\}$ were determined, and usually oscillates about zero between collocation points. The residual provides an estimate of how good the approximate solution is, since we expect as the differential equation is satisfied at more and more points (by increasing N) the residual becomes smaller and the solution becomes more accurate. The theorems below provide a proof of these conjectures.

It has been suggested by others previously (Yang, 1962; Hulbert, 1965; Finlayson, 1965; Krasnoselskii, 1968) that the residual be used to characterize the accuracy of the approximate solution. Error bounds, which utilize the residual function, have been derived in this way for elliptic and parabolic partial differential equations [see Ferguson (1971) for a listing]. For ordinary differential equations the residual has been used to derive error bounds for linear (Varga, 1966) and nonlinear (Ciarlet et al., 1967) problems. By focusing on equations of interest to chemical engineers we obtain stronger results than provided by these authors.

THEOREMS ON ERROR BOUNDS

Consider the problem of chemical reaction in a catalyst pellet in dimensionless form.

$$\frac{1}{x^{a-1}} \frac{d}{dx}\left(x^{a-1} \frac{dc_j}{dx} \right) = f_j(c_1, c_2, \ldots, c_n) \qquad (3)$$

$$\frac{dc_j}{dx} = 0 \quad \text{at} \quad x = 0 \quad j = 1, 2, \ldots, n \qquad (4)$$

$$\frac{2}{Sh_j} \frac{dc_j}{dx} + c_j = c_{0j} \quad \text{at} \quad x = 1 \qquad (5)$$

The parameter a takes values 1, 2, or 3 depending on whether the catalyst shape is planar, cylindrical, or spherical. The modified Sherwood number in Equation (5) accounts for a mass transfer resistance between the catalyst and external medium. The reaction rate term is denoted by f_j and can depend on concentrations of all species $\{c_i\}$. The coupling between species occurs only through this term. The nonlinear function is assumed to be Lipshitz continuous, that is, there exist constants M_{ji} such that

$$|f_j(c_1, c_2, \ldots, c_n) - f_j(c_1', c_2', \ldots, c_n')| \leq \sum_{i=1}^{n} M_{ji} |c_i - c_i'| \qquad (6)$$

for values of c_i and c_i' between some limits. For a single equation ($n = 1$) the M_{11} can be replaced by

$$\overline{M} = \sup_{0 \leq t \leq 1} \left\{ \int_0^1 \left[\left. \frac{df(u)}{du} \right|_{u = \tilde{c} + t(\tilde{c} - c)} \right]^2 x^{a-1}\, dx \right\}^{1/2} \qquad (7)$$

Even though the exact solution c is not known, a bound can sometimes be found for Equation (7). For some problems the Lipshitz constants M_{ji} are the maximum values of the derivative $|\partial f_j/\partial c_i|$. In Equation (7) df/du can sometimes be bounded if the exact and approximate solutions can be proven to lie between some limits.

There are two types of error bounds of interest. Let $c_j(x)$ be the exact solution to Equations (3) to (5) and $\tilde{c}_j(x)$ be an approximate solution. A mean-square error is defined:

$$||\tilde{c} - c||_2 \equiv \left[\int_0^1 [\tilde{c}(x) - c(x)]^2\, x^{a-1}\, dx \right]^{1/2} \qquad (8)$$

while a pointwise error is defined:

$$||\tilde{c} - c||_\infty \equiv \max_{0 \leq x \leq 1} |\tilde{c}(x) - c(x)| \qquad (9)$$

The following three theorems are proved in the Appendix.

Theorem 1: Assume the existence of a solution to Equations (3) to (5) for functions f_j satisfying Equation (6) or (7) for concentrations satisfying $c_* \leq c(x) \leq c^*$, where c_* and c^* are lower and upper bounds on the exact and approximate solution. Then the mean-square error is bounded by

$$||\tilde{c}_j - c_j||_2 \leq ||G_j||_2 \left\{ ||R_j||_2 + \frac{N_j^{1/2} \left\{ \sum_{i=1}^{n} ||R_i||_2^2 \, ||G_i||_2^2 \right\}^{1/2}}{1 - \left\{ \sum_{i=1}^{n} ||G_i||_2^2 \, N_i \right\}^{1/2}} \right\} \qquad (10)$$

where $N_j \equiv \sum_{i=1}^{n} M_{ji}^2$, G_j is the Green's function for the Laplacian operator in Equation (3),

$$||G_j||_2 = \left[\int_0^1 \int_0^1 G^2(x, t; Sh_j) x^{a-1} \, dx \, t^{a-1} \, dt \right]^{1/2} \qquad (11)$$

and R_j is the residual,

$$R_j \equiv \frac{1}{x^{a-1}} \frac{d}{dx}\left(x^{a-1} \frac{d\tilde{c}_j}{dx} \right) - f(\tilde{c}_1, \tilde{c}_2, \ldots, \tilde{c}_n) \qquad (12)$$

$$||R_j||_2 = \left[\int_0^1 R_j^2 \, x^{a-1} \, dx \right]^{1/2} \qquad (13)$$

and the approximate solutions $\{\tilde{c}_j\}$ satisfy the boundary conditions, Equations (4) and (5). Note that the right-hand side of Equation (10) can be calculated without knowledge of $c_j(x)$.

Theorem 2: Under the conditions of Theorem 1 the pointwise error is bounded by

$$||\tilde{c}_j - c_j||_* \leq K_{2j} ||R_i||_2 + \frac{K_{1j} M_j \sum_{i=1}^{n} K_{2i} ||R_i||_2}{1 - \sum_{i=1}^{n} K_{1i} M_i} \qquad (14)$$

and

$$||\tilde{c}_j - c_j||_* \leq K_{2j} \left[\sum_{i=1}^{n} M_{ji} ||\tilde{c}_i - c_i||_2 + ||R_j||_2 \right] \qquad (15)$$

where

$$K_{1j} = \max_{0 \leq x \leq 1} \int_0^1 G(x, t; Sh_j) \, t^{a-1} \, dt \qquad (16)$$

$$K_{2j}^2 = \max_{0 \leq x \leq 1} \int_0^1 G^2(x, t; Sh_j) \, t^{a-1} \, dt \qquad (17)$$

$$M_j = \max_i |M_{ji}| \qquad (18)$$

The pointwise bounds can be used to obtain error bounds for the effectiveness factor.

Theorem 3: Under the conditions of Theorems 1 and 2 the error in the effectiveness factor is bounded by

$$|\tilde{\eta}_j - \eta_j| \leq \frac{\sum_{i=1}^{n} M_{ji} ||\tilde{c}_i - c_i||_*}{|f_j(c_{10}, c_{20}, \ldots, c_{n0})|}. \qquad (19)$$

The various constants involving Green's functions are listed in Table 1. Note that both the pointwise and mean-square error bounds are proportional to the mean-square residual. As the residual is decreased the error is reduced as well. Note that the error bounds make no reference to the method of solution. Equations (10), (14), (15), and (19) apply to approximate solutions derived using collocation methods, finite difference methods, or any method. The only requirement is that the residual function be piecewise continuous. If a second-order finite difference method is used, in which case $y''(x_i) \sim (y_{i+1} - 2y_i + y_{i-1})/h^2$, for example, the solution must be interpolated between the grid points using a quadratic in x, as suggested by Varga (1966).

A corollary to these theorems is that the solution is unique. Assume there are two solutions c and $\tilde{c}$. Then the residual is zero for $\tilde{c}$ and Equation (14) gives $c = \tilde{c}$. Consequently the assumption is contradicted and the solution is unique.

APPLICATIONS

We present results of computations using these error bounds in order to illustrate their utility. All three exam-

TABLE 1. VARIOUS NUMERICAL VALUES ASSOCIATED WITH THE GREEN'S FUNCTIONS DEFINED BY THE ONE-DIMENSIONAL LAPLACIAN OPERATOR WITH A RADIATION TYPE BOUNDARY CONDITION

Geometry	Planar	Cylindrical	Spherical
$G(x, t; Sh)$ =	$\begin{cases} 1 + \frac{2}{Sh} - x, & t \leq x \\ 1 + \frac{2}{Sh} - t, & t \geq x \end{cases}$	$\begin{cases} \frac{2}{Sh} - \ln(x), & t \leq x \\ \frac{2}{Sh} - \ln(t), & t \geq x \end{cases}$	$\begin{cases} \frac{2}{Sh} + \frac{1}{x} - 1, & t \leq x \\ \frac{2}{Sh} + \frac{1}{t} - 1, & t \geq x \end{cases}$
$\|G\|_2^2$ =	$\frac{1}{6} + \frac{2}{Sh}\left[\frac{2}{Sh} + \frac{2}{3}\right]$	$\frac{1}{32} + \frac{2}{Sh}\left[\frac{1}{4}\left(\frac{2}{Sh}\right) + \frac{1}{8}\right]$	$\frac{1}{90} + \frac{2}{Sh}\left[\frac{1}{9}\left(\frac{2}{Sh}\right) + \frac{2}{4}\right]$
K_1 =	$\frac{1}{2} + \frac{2}{Sh}$	$\frac{1}{4} + \frac{1}{2}\left(\frac{2}{Sh}\right)$	$\frac{1}{6} + \frac{1}{3}\left(\frac{2}{Sh}\right)$
K_2^2 =	$\frac{1}{3} + \left(\frac{2}{Sh}\right) + \left(\frac{2}{Sh}\right)^2$	$\frac{1}{4} + \frac{1}{2}\left(\frac{2}{Sh}\right) + \frac{1}{2}\left(\frac{2}{Sh}\right)^2$	$\frac{1}{3} + \frac{1}{3}\left(\frac{2}{Sh}\right) + \frac{1}{3}\left(\frac{2}{Sh}\right)^2$

ples are for diffusion and reaction in spherical catalyst pellets, and approximate solutions are generated using the orthogonal collocation method and regular collocation method.

Example 1. Consider a second-order, irreversible, isothermal reaction with no mass transfer resistance on the boundary. Then in Equations (3) and (4) $a = 3$, $n = 1$, $Sh = \infty$, and $f(c) = \phi^2 c^2$, and we take $c_0 = 1$. For this problem we can prove $0 \leq c(x) \leq 1$ (Cohen and Laetsch, 1970; Ferguson, 1971), and if the approximate solution obeys $0 \leq \tilde{c}(x) \leq 1$ then

$$\overline{M} = \sup_{0 \leq t \leq 1} \left[\int_0^1 \{\phi^2 2[c + t(\tilde{c} - c)]\}^2 x^2 \, dx \right]^{1/2} \leq \phi^2 \frac{2}{\sqrt{3}} \quad (20)$$

Equations (10) and (15) reduce to

$$||\tilde{c} - c||_2 \leq \frac{||R||_2/\sqrt{90}}{1 - 2\phi^2/\sqrt{270}} \quad (21)$$

$$||\tilde{c} - c||_\infty \leq \frac{1}{\sqrt{3}} \left[\phi^2 \frac{2}{\sqrt{3}} ||\tilde{c} - c||_2 + ||R|| \right] \quad (22)$$

The denominator in Equation (21) must be positive so the error bounds apply only for $\phi < 2.86$. We present results for $\phi = 1$. The collocation method was applied twice, using different trial functions.

$$\tilde{c}_1 = 1 + (1 - x^2) \sum_{i=1}^{N} a_i \cos(i - 1)\pi x \quad (23)$$

$$\tilde{c}_2 = 1 + \sum_{i=1}^{N} b_i (x^{2i} - 1) \quad (24)$$

For $\tilde{c}_1$ the collocation points were taken as the zeros to $\cos(m - 1)\pi x = 0$ and $x = 1$. For $\tilde{c}_2$ the collocation points were $x_j = j/N$. The solutions are tabulated elsewhere (Ferguson, 1971), but the error bounds are listed in Table 2.

We see that the cosine series diverges, since the error gets larger. The residual also gets larger, and both phenomena correctly reveal the nonconvergence of this approximate solution. Elsewhere we show that a least-squares collocation method makes the solution converge when using cosine functions. In the least-squares collocation method we evaluate the residual at more collocation points than we have adjustable constants (N) and choose the constants to minimize the sum of the residuals squared. See Ferguson (1971) for further details.

The power series solution converges rapidly and a six-term approximation is accurate to six digits. The collocation method, plus the error bounds, thus lead to a solution whose accuracy is determined. Note also that as the number of terms is doubled from 3 to 6 the error is reduced by a factor of 150, giving rise to very fast convergence with increasing N. The error bound on the effectiveness factor is 5.1×10^{-7} for $N = 6$ using the power series.

Table 2. Error Bounds for Problem with Second-Order Irreversible Reaction

	Cosine series		Power series	
N	$\|\|\tilde{c} - c\|\|_2 \leq$	$\|\|\tilde{c} - c\|\|_\infty \leq$	$\|\|\tilde{c} - c\|\|_2 \leq$	$\|\|\tilde{c} - c\|\|_\infty \leq$
2	1.55×10^{-2}	0.0846	3.55×10^{-4}	1.94×10^{-3}
3	—	0.2240	—	6.90×10^{-5}
4	5.46×10^{-2}	0.2988	4.52×10^{-7}	2.48×10^{-6}
6	1.19×10^{-1}	0.6513	7.93×10^{-8}	4.35×10^{-7}

Bounds similar to Equations (21) and (22) can also be derived for reactions of other orders as well as for reaction rate expressions of the form $f(c) = \phi^2 c/(1 + \alpha|c|)$, $\alpha \geq 0$. See Ferguson (1971).

Example 2. Consider next a first-order irreversible, non-isothermal reaction. The equations for concentration and temperature can be combined in the standard fashion to yield the problem

$$\frac{1}{x^2} \frac{d}{dx} \left(x^2 \frac{dT}{dx} \right) = f(T) \quad (25)$$

$$\frac{dT}{dx}(0) = 0, \quad T(1) = 1 \quad (26)$$

$$f(T) = \phi^2 [T - (1 + \beta)] \exp\{\gamma - \gamma/|T|\} \quad (27)$$

We assume the existence of a solution to Equations (25) to (27), and a variety of methods can be used to prove $1 \leq T(x) \leq 1 + \beta$. Unfortunately this large range of T causes the Lipschitz constant to be too large (14.6). We thus present a new method to bound the temperature.

We first rephrase the problem as an integral equation by using the Green's function for the Laplacian operator.

$$T(x) = 1 - \int_0^1 G(x, t) f(T(t)) t^2 dt. \quad (28)$$

Here $G(x, t)$ is a positive function (see Table 1) and $f(T)$ is a negative function since $T - (1 + \beta) \leq 0$. Thus, we can replace $f(T)$ by its minimum value to obtain

$$T(x) \leq 1 - \left\{ \min_{1 \leq T \leq 1 + \beta} f(T) \right\} \int_0^1 G(x, t) t^2 dt \quad (29)$$

or

$$T(x) \leq 1 - \left\{ \min_{1 \leq T \leq 1 + \beta} f(T) \right\} \left\{ \frac{1}{6}(1 - x^2) \right\} \quad (30)$$

We next carry out the iterative procedure

$$T(x) \leq T_i; \quad T_1 = 1 + \beta \quad (31)$$

$$T_i = 1 + \frac{1}{6} \max\{\phi^2 \beta, -f(T_{i-1})\} \quad (32)$$

obtained by setting $x = 0$, since the maximum T occurs there by Equation (30). We did calculations for $\phi^2 = 0.25$, $\beta = 0.3$, $\gamma = 18$. The upper bound on T of $1 + \beta = 1.3$ is improved to $T(x) \leq 1.01564$ using the iterative procedure. Then the Lipschitz constant is

$$\overline{M} \leq \frac{1}{\sqrt{3}} \left| \frac{df}{dT} \right|_{T = T_{\text{upper bound}}} = 1.548 \quad (33)$$

Theorems 1 and 2 then simplify to

$$||\tilde{T} - T||_2 \leq \frac{||R||_2}{1 - \overline{M}/\sqrt{90}} \quad (34)$$

$$||\tilde{T} - T||_\infty \leq \frac{1}{\sqrt{3}} \{1.548 ||\tilde{T} - T||_2 + ||R||_2\} \quad (35)$$

We used the orthogonal collocation method and expanded the temperature $\tilde{T}$ in a series, Equation (1), using two different sets of polynomials, those defined by Equa-

Table 3. Error Bounds for Problem with First-Order Irreversible Nonisothermal Reaction

	Polynomials with $w = 1$		Polynomials with $w = 1 - x^2$	
N	$\|\|\tilde{T} - T\|\|_2 \leq$	$\|\|\tilde{T} - T\|\|_\infty \leq$	$\|\|\tilde{T} - T\|\|_2 \leq$	$\|\|\tilde{T} - T\|\|_\infty \leq$
1	3.54×10^{-4}	1.94×10^{-3}	4.39×10^{-4}	2.41×10^{-3}
2	1.59×10^{-5}	8.76×10^{-5}	2.21×10^{-5}	1.21×10^{-5}
3	5.80×10^{-7}	3.18×10^{-6}	8.89×10^{-7}	4.87×10^{-6}
6	1.31×10^{-11}	7.14×10^{-11}	2.54×10^{-11}	1.39×10^{-10}
8	4.01×10^{-15}	2.20×10^{-14}	8.94×10^{-15}	4.90×10^{-14}

Table 4. Pointwise Error Bounds for Parallel Chemical Reactions

	Polynomials with $w = 1$		Polynomials with $w = 1 - x^2$	
N	$\|\|\tilde{c_1} - c_1\|\|_\infty \leq$	$\|\|\tilde{c_2} - c_2\|\|_\infty \leq$	$\|\|\tilde{c_1} - c_1\|\|_\infty \leq$	$\|\|\tilde{c_2} - c_2\|\|_\infty \leq$
1	2.761×10^{-3}	3.405×10^{-3}	3.132×10^{-3}	3.860×10^{-3}
2	1.592×10^{-4}	1.957×10^{-4}	2.179×10^{-4}	2.677×10^{-4}
3	7.815×10^{-6}	9.554×10^{-6}	1.220×10^{-6}	1.491×10^{-4}
6	5.756×10^{-10}	6.999×10^{-10}	1.160×10^{-9}	1.411×10^{-9}
8	8.196×10^{-13}	9.956×10^{-13}	1.859×10^{-12}	2.258×10^{-12}

tion (2) with $w = 1$ and $w = 1 - x^2$. The error bounds can thus be used to tell which polynomials are the best choice. The results are in Table 3 and the polynomials with $w = 1$ consistently yield lower error bounds (by about 50%). In addition the pointwise errors are about six times the value of the mean-square error. The maximum error in the effectiveness factor is 4.6×10^{-13}, using $N = 8$ and polynomials with $w = 1$.

Example 3. The last example considers a system of equations governing the reaction of three species, but only two concentrations are independent. The reaction system is

$$C \rightleftarrows 3A \rightleftarrows B. \tag{36}$$

with the concentration of B and C taken as c_1 and c_2. In Equations (3) to (5) we take

$$f_1 = \alpha_1 c_1 - \alpha_2[1 - 3\,(c_1 + c_2)]^3 \tag{37}$$

$$f_2 = \alpha_3 c_2 - \alpha_4[1 - 3\,(c_1 + c_2)]^3 \tag{38}$$

$$c_{01} = c_{02} = 0.1 \tag{39}$$

$$\alpha_1 = 0.1, \quad \alpha_2 = 1.0, \quad \alpha_3 = 0.2, \quad \alpha_4 = 1.2 \tag{40}$$

Here we assume the solution is positive. Then it can be proved in a fashion similar to Equation (28) that $c_3 \leq 0.4$ (see Ferguson, 1971). The Lipschitz constants are derived from

$$f_j(c_1', c_2') - f_j(c_1, c_2) = \sum_{k=1}^{2} \int_0^1 \left.\frac{\partial f_j}{\partial c_k}\right|_{c_k = c_k + t(c_k' - c_k)} (c_k' - c_k)\, dt \tag{41}$$

using the fact that $c_1 \geq 0.1$, $c_2 \geq 0.2$, and $c_3 \leq 0.4$.

$$M_{11} = 1.54, \quad M_{12} = 1.44, \quad M_{21} = 1.728, \quad M_{22} = 1.928$$

The error bound in Equation (10) is then valid for $Sh_j \geq 3.01$. Calculations were performed using the orthogonal collocation method for $Sh = 7$, and $Sh \to \infty$. The error bounds for the case $Sh \to \infty$ are in Table 4 for two sets of polynomials. Again we see that the polynomials with $w = 1$ have consistently lower error bounds and are thus to be preferred. The effectiveness factor has a maximum error of 7.5×10^{-10} for reaction (1) and 5.9×10^{-11} for reaction (2), using $N = 8$ and polynomials with $w = 1$.

The error decreases very rapidly. Figure 1 illustrates the logarithmic decrease in error for Examples 2 and 3,

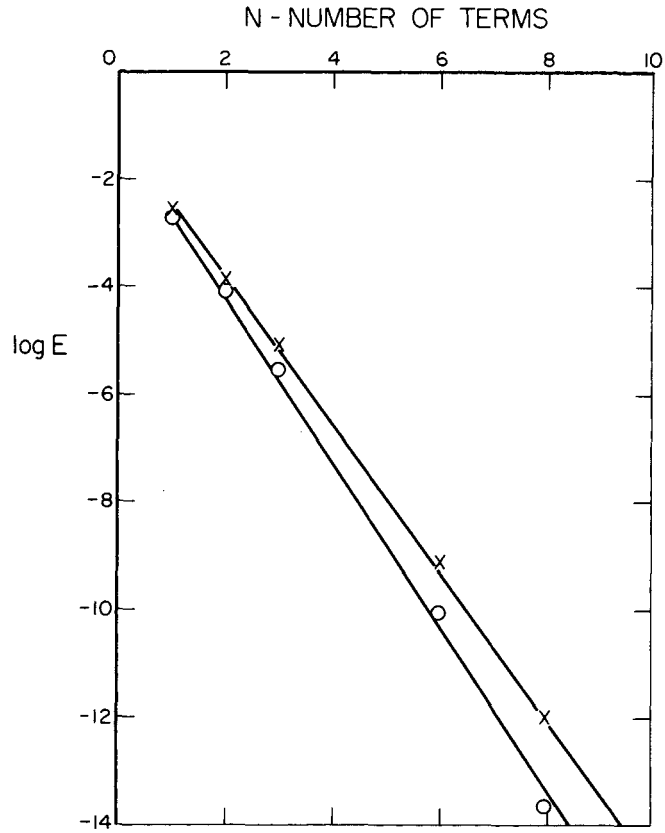

Fig. 1. Variation of error bound with the number of terms in the orthogonal collocation method (0 — Example 2, $E = \|\|\tilde{T} - T\|\|_\infty$; x — Example 3, $E = \|\|\tilde{c_2} - c_2\|\|_\infty$; both for polynomials with $w = 1$.)

which follow the relation

$$\|\tilde{T} - T\|_\infty = 0.1 \times 10^{-1.52N} \tag{42}$$

$$\|\tilde{c_2} - c_2\|_\infty = 0.1 \times 10^{-1.38N} \tag{43}$$

Thus each additional term in the trial function, Equation (1), gives rise to at least a factor 10 decrease in the error.

This rapid convergence should be contrasted with the rate of convergence for usual finite difference methods, which is much slower since they converge as $(1/N)^2$. The computation time associated with the calculation of the error bound is about 50% of the total time (for $N = 8$).

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NOTATION

a = 1, 2, 3 for planar, cylindrical, spherical geometry
a_i = coefficient in trial function, Equation (1) or (23)
b_i = coefficient in trial function, Equation (24)
c = concentration, dimensionless
f_j = jth reaction rate function
G_j = Green's function, listed in Table 1
h = grid spacing in finite difference solution
K_{1j} = constant defined by Equation (16), listed in Table 1
K_{2j} = constant defined by Equation (17), listed in Table 1
M_{ji} = Lipschitz constants obeying Equation (6)
M_j = $\max_i |M_{ji}|$
$\overline{M}$ = Lipschitz constant for single equation, Equation (7)
N = number of interior collocation points
N_j = $\sum_{i=1}^{n} M_{ji}^2$
n = number of independent chemical species
P = orthogonal polynomial
R_j = residual, defined by Equation (12)
Sh_j = modified Sherwood number for jth species
t = position
T = temperature, dimensionless
x = position, dimensionless
y = dummy dependent variable
w = weighting function in Equation (2)

Greek Letters

α = constant in rate expression
β = dimensionless heat of reaction
γ = dimensionless activation energy
δ_{ij} = 1 if $i = j$; 0 if $i \neq j$
ϵ = $\tilde{c} - c$
η = effectiveness factor, defined in Equation (A7)
ϕ = Thiele modulus
$|| \; ||_2$ = Norm defined by Equation (8)
$|| \; ||_\infty$ = Norm defined by Equation (9)

Superscript and Subscripts

$\sim$ = approximate solution
j = jth species
0 = value of quantity outside diffusion film

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APPENDIX A

Proof of Theorem 1.

Write Equations (3) to (5) for the approximate solution, where $R_j(\{\tilde{c}_i\}, x)$ represents the residual, and R_j is a known function of x once the approximate solution is derived.

$$\frac{1}{x^{a-1}} \frac{d}{dx}\left(x^{a-1} \frac{d\tilde{c}_j}{dx} \right) = f_j(\tilde{c}_1, \tilde{c}_2, \ldots, \tilde{c}_n) + R_j(\{\tilde{c}_i\}, x) \tag{A1}$$

$$\frac{d\tilde{c}_j}{dx} = 0 \quad \text{at} \quad x = 0$$

$$\frac{2}{Sh_j} \frac{d\tilde{c}_j}{dx} + \tilde{c}_j = c_{0j} \quad \text{at} \quad x = 1$$

Subtract Equation (3) from Equation (A1) to get

$$\frac{1}{x^{a-1}} \frac{d}{dx}\left[x^{a-1} \frac{d(\tilde{c}_j - c_j)}{dx} \right] = f_j(\{\tilde{c}_i\}) - f_j(\{c_i\}) + R_j \tag{A2}$$

and subtraction of the boundary conditions gives

$$\frac{d(\tilde{c}_j - c_j)}{dx} = 0 \quad \text{at} \quad x = 0$$

$$\frac{2}{Sh_j} \frac{d(\tilde{c}_j - c_j)}{dx} + (\tilde{c}_j - c_j) = 0 \quad \text{at} \quad x = 1$$

The Green's function for the Laplacian operator together with the appropriate boundary conditions gives, in place of Equation (A2),

$$[\tilde{c}_j(x) - c_j(x)]^2 = \left[\int_0^1 G(x, t; Sh_j) \, [R_j + f_j(\tilde{c}) - f_j(c)] \, t^{a-1} \, dt \right]^2$$

Apply Schwartz's inequality to give

$$(\tilde{c}_j(x) - c_j(x))^2 \leq \int_0^1 G^2(x, t; Sh_j) \, t^{a-1} \, dt \int_0^1 [R_j + f_j(\tilde{c}) - f_j(c)]^2 \, t^{a-1} \, dt$$

such that

$$||\epsilon_j||_2 \equiv \left(\int_0^1 (\tilde{c}_j - c_j)^2 t^{a-1}\, dt \right)^{1/2}$$

$$\leq \left[\int_0^1 \int_0^1 G^2(x, t; Sh_j)\, t^{a-1}\, dt\, x^{a-1}\, dx \right]^{1/2}$$

$$\left[\int_0^1 (R_j + (f_j(\tilde{c}) - f_j(c)))^2 t^{a-1}\, dt \right]^{1/2}$$

If we then apply Minkowski's inequality to the last integral of the above inequality,

$$||\epsilon_j||_2 \leq ||G(a; Sh_j)||_2 \left\{ \left[\int_0^1 R_j^2(\tilde{c})\, t^{a-1}\, dt \right]^{1/2} + \left[\int_0^1 (f_j(\tilde{c}) - f_j(c))^2 t^{a-1}\, dt \right]^{1/2} \right\}$$

Since f_j satisfies a Lipschitz condition, Equation (6), the last integral of the above inequality can be bounded in terms of the errors,

$$||\epsilon_j||_2 \leq ||G_j||_2 \left[||R_j||_2 + \left[\sum_{i=1}^n M_{ji}^2 \right]^{1/2} \left[\sum_{i=1}^n \int_0^1 \epsilon_i^2\, t^{a-1}\, dt \right]^{1/2} \right]$$

or

$$||\epsilon_j||_2 \leq ||G_j||_2 \left[|R_j||_2 + \left[\sum_{i=1}^n M_{ji}^2 \right]^{1/2} \left[\sum_{i=1}^n ||\epsilon_i||_2^2 \right]^{1/2} \right] \tag{A3}$$

If there is only a single equation, the Mean Value Theorem can be used to evaluate $f_j(\tilde{c}) - f_j(c)$, and Equation (7) used to arrive at the result, Equation (A3) with $n = 1$ and $M_{11} = \overline{M}$.

Abbreviate $\left[\sum_{i=1}^n M_{ji}^2 \right]$ by N_j; then the result of squaring both sides of Equation (A3), adding over the subscript j, and taking the square root of both sides of the resulting expression is

$$\left[\sum_{j=1}^n ||\epsilon_j||_2^2 \right]^{1/2} \leq \left[\sum_{j=1}^n ||G_j||_2^2 \left[||R_j||_2 + N_j^{1/2} \left[\sum_{i=1}^n ||\epsilon_i||_2^2 \right]^{1/2} \right]^2 \right]^{1/2}$$

$$\leq \left[\sum_{j=1}^n ||G_j||_2^2\, ||R_j||_2^2 \right]^{1/2} + \left[\sum_{i=1}^n ||\epsilon_i||_2^2 \right]^{1/2} \left[\sum_{j=1}^n ||G_j||_2^2\, N_j \right]^{1/2}$$

By solving for $\left[\sum_{j=1}^n ||\epsilon_j||_2^2 \right]^{1/2}$, one can reduce Equation (A3) to the final result, Equation (10).

Proof of Theorem 2. Let $M_j = \max_i [M_{ji}]$. From Equation (A1) and (A2)

$$|\tilde{c}_j(x) - c_j(x)| = \left| \int_0^1 G(x, t; Sh_j) (f_j(\tilde{c}) - f_j(c) + R_j)\, t^{a-1}\, dt \right|$$

$$\leq \int_0^1 G(x, t; Sh_j) (|f_j(\tilde{c}) - f_j(c)| + |R_j|)\, t^{a-1}\, dt$$

$$\leq \int_0^1 G(x, t; Sh_j) \left[M_j \sum_{i=1}^n |\tilde{c}_i(t) - c_i(t)| + |R_j| \right] t^{a-1}\, dt$$

$$= M_j \int_0^1 G(x, t; Sh_j) \sum_{i=1}^n |\tilde{c}_i(t) - c_i(t)|\, t^{a-1}\, dt + \int_0^1 G(x, t; Sh_j) |R_j|\, t^{a-1}\, dt$$

where we have used the fact that the Green's function is nonnegative. Rearranging slightly, and using Schwartz's inequality,

$$|\tilde{c}_j(x) - c_j(x)| \leq M_j \sum_{i=1}^n \int_0^1 G(x, t; Sh_j) |\tilde{c}_i - c_i|\, t^{a-1}\, dt + K_{2j} ||R_j||_2 \tag{A4}$$

$$\leq M_j \sum_{i=1}^n \max_{0 \leq t \leq 1} |\tilde{c}_i(t) - c_i(t)| \int_0^1 G(x, t; Sh_j)\, t^{a-1}\, dt + K_{2j} ||R_j||_2 .$$

Then

$$||\epsilon_j||_\infty \leq K_{1j} M_j \sum_{i=1}^n ||\epsilon_i||_\infty + K_{2j} ||R_j||_2 \tag{A5}$$

We sum this inequality over the subscript j and solve it for $\sum_{i=1}^n ||\epsilon_i||_\infty$.

$$\sum_{i=1}^n ||\epsilon_i||_\infty \leq \frac{\sum_{j=1}^n K_{2j} ||R_j||_2}{1 - \sum_{j=1}^n K_{1j} M_j} \tag{A6}$$

Combination of Equation (A5) and (A6) gives Equation (14). If we use the Schwartz inequality after Equation (A4) we end up with Equation (15).

Proof of Theorem 3. The effectiveness factor is defined as the average rate of reaction with diffusion divided by the average rate of reaction if the concentration were everywhere equal to the bulk stream value. Thus the effectiveness factor includes the effect of both internal and external diffusion. It is (for the jth species and a spherical domain)

$$\eta_j \equiv \frac{3}{f_j(\{c_0\})} \int_0^1 f_j(\{c\}) x^2\, dx \tag{A7}$$

The approximate value is

$$\tilde{\eta}_j = \frac{3}{f_j(\{c_0\})} \int_0^1 f_j(\{\tilde{c}\}) x^2\, dx.$$

Subtracting these two formulas and taking absolute values gives

$$|\tilde{\eta}_j - \eta_j| \leq \frac{3}{|f_j(\{c_0\})|} \int_0^1 |f_j(\{\tilde{c}\}) - f_j(\{c\})|\, x^2\, dx$$

Application of the Lipschitz constant, Equation (6), and use of the pointwise bounds gives

$$|\tilde{\eta}_j - \eta_j| \leq \frac{3}{|f_j(\{c_0\})|} \int_0^1 \sum_{i=1}^n M_{ji} ||\tilde{c}_i - c_i||_\infty\, x^2 dx$$

The final result is then Equation (19).

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