$$S(C, -2\Delta) = \frac{1}{2}\left[S\left[C + S(C, -\Delta)\Delta, -\Delta\right] + \frac{R_A \Delta}{D} \right] \quad (16)$$

The process is continued until the missing initial condition $S(C_S, R)$ is found. The result is a matrix containing concentration gradients as a function of concentration and position. With this information, the concentration profile, effectiveness factor, and effective rate of reaction may be found.

Chu and Hougen (1962) calculated the effectiveness factor for the catalytic oxidation of nitric oxide over a spherical carbon catalyst. They assumed commercial conditions of 56°C and a total pressure of 1.11 atm. The feed contained 1.5% nitric oxide with a dew point of −30°C. The catalyst density was 711 kg/m^3, and an effective diffusion coefficient of 2.20×10^{-6} m^2/s was used. Their rate equation, based on earlier work, was

$$R_A' = \frac{P^2_{NO}\, P_{O_2}}{a + bP^2_{NO} + cP_{NO_2} + wP_{H_2O}} \quad (17)$$

The constants were given as follows:

$a = 0.000181$
$b = 0.916$
$c = 0.00982$
$w = 0.0564$

Using the Runge-Kutta method, they calculated the effectiveness factor for a particle diameter of 3 mm and conversion of 0 to be about 0.32. Equation (12) was programmed for this reaction by using thirty increments of radius and ten increments of concentration. The effectiveness factor was calculated to be 0.33 or about 3% difference. The calculation took about 4 s on an EAI Pacer computer.

This method offers several advantages over previous trial-and-error methods. This straightforward approach should reduce computation time. The indeterminate term in Equation (1) is eliminated. Equation (12) is relatively simple to program, and, once having done so, it is a trivial matter to change the reaction model. Thus, several mechanisms can be investigated in a fairly short time. Also, the concept of invarient imbedding can be applied to many more complicated cases. In this short note, only the case of a single isothermal reaction has been discussed. More complicated mechanisms involving two reactions have been studied by Likins (1970) and the concept should be applicable to nonisothermal cases.

NOTATION

C = concentration, moles/vol.
D = effective diffusion coefficient
r = radial position within particle
R = catalyst effective radius
R_A = rate of reaction, moles/time-vol. catalyst
R_A' = rate of reaction, moles/time-mass catalyst
S = concentration gradient
Δ = increment of radius
δ = increment of concentration

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An Efficient General Purpose Method for the Integration of Stiff Ordinary Differential Equations

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Explicit methods such as the classical fourth-order Runge-Kutta method are known to be unsuitable for the integration of stiff systems, that is, systems with a large spread in the magnitude of the local eigenvalues. Stability of such methods requires that the step length is inversely proportional to the largest eigenvalue throughout the integration, and thus a prohibitively large number of steps is often required.

Simple semi-implicit methods exist which are stable for any step length; however published results with such methods used (Seinfeld et al., 1970; Caillaud and Padmanabhan, 1971) are somewhat disappointing from an accuracy point of view, and recent work (Aiken and Lapidus; 1974) points to singular perturbation methods as preferable alternatives.

Although such methods may be useful in certain extreme cases, they are unattractive as general purpose methods since a large effort is required for their use in each individual case.

It seems, however, that the apparently unsatisfactory behavior of the semi-implicit Runge-Kutta methods is entirely due to an insufficient utilization of their potential.

When used in connection with a simple but efficient step length adjusting procedure, these methods are accurate and efficient and may be used for a spectrum of problems with minimal individual effort from the user.

THE BASIC SEMI-IMPLICIT RUNGE KUTTA METHOD

The method used here is a modified version of the third-order method developed by Caillaud and Padmanabhan (1971).

Let the system to be integrated be

$$\frac{d}{dt}(\mathbf{y}) = \mathbf{f}(\mathbf{y}) \tag{1}$$

$$\text{with initial element } \mathbf{y}(t_n) = \mathbf{y}_n \tag{2}$$

and let the Jacobian $\mathbf{A}$ be given by

$$A_{ij} = (\partial f_i/\partial y_j)_{\mathbf{y}_n} \tag{3}$$

The solution at $t_n + h$, $\mathbf{y}_{n+1}$, is found from

$$\mathbf{k}_1 = h(\mathbf{I} - ha\mathbf{A})^{-1}\,\mathbf{f}(\mathbf{y}_n) \tag{4}$$

$$\mathbf{k}_2 = h(\mathbf{I} - ha\mathbf{A})^{-1}\,\mathbf{f}(\mathbf{y}_n + b_2\mathbf{k}_1) \tag{5}$$

$$\mathbf{k}_3 = (\mathbf{I} - ha\mathbf{A})^{-1}\,(b_{31}\,\mathbf{k}_1 + b_{32}\,\mathbf{k}_2) \tag{6}$$

$$\mathbf{y}_{n+1} = \mathbf{y}_n + R_1\,\mathbf{k}_1 + R_2\,\mathbf{k}_2 + \mathbf{k}_3 \tag{7}$$

where

$$a^3 - 3a^2 + \frac{3}{2}a - \frac{1}{6} = 0, \quad a = 0.4358\ldots$$

$$b_2 = 0.75$$

$$b_{31} = \frac{-1}{6a}(8a^2 - 2a + 1)$$

$$b_{32} = \frac{2}{9a}(6a^2 - 6a + 1)$$

$$R_1 = \frac{11}{27} - b_{31}$$

$$R_2 = \frac{16}{27} - b_{32}$$

The Jacobian $\mathbf{A}$ is evaluated once only, and the value of $\mathbf{f}$ at only one intermediate point is needed. By using LU-decomposition of $(\mathbf{I} - ha\mathbf{A})$, the effort involved is that of solving a set of linear equations equal in dimension to that of the system, with three different right-hand sides.

Application to the trivial problem

$$\frac{d}{dt}y = \lambda y \tag{8}$$

yields

$$y_{n+1} = y_n \cdot \mu(h\lambda) \tag{9}$$

$$\mu(h\lambda) = \frac{1 + (1 - 3a)h\lambda + \left(\frac{1}{2} - 3a + 3a^2\right)(h\lambda)^2}{(1 - ah\lambda)^3} \tag{10}$$

The magnitude of μ is smaller than 1 for all $h\lambda$ with negative real part. Furthermore, $\mu \to 0$ as $h\lambda \to -\infty$. The method is thus strongly A stable. A table of $\mu(h\lambda)$ is given in Caillaud and Padmanabhan (1971) [their ISI3 $(-\infty)$].

Fourth-order methods with similar properties requiring an extra function evaluation are easily developed. Two such methods are described in Michelsen (1976).

EXTRAPOLATION AND STEP LENGTH ADJUSTMENT

A full step—half-step technique is used for step length adjustment. At each selected step length, the problem is first integrated by using the full step length. Let the solution vector be $\mathbf{y}_{n+1}^*(h)$. Next, the same integration is performed in two steps of length 0.5 h. This yields the solution $\mathbf{y}_{n+1}^*(h/2)$.

Subtraction yields

$$\mathbf{e}_{n+1} = \mathbf{y}_{n+1}^*(h/2) - \mathbf{y}_{n+1}^*(h) \tag{11}$$

and the difference vector $\mathbf{e}$ is compared to a prescribed vector of tolerances $\boldsymbol{\varepsilon}$:

$$\text{Let} \quad q = \text{Max}_i \left| \frac{e_i}{\epsilon_i} \right| \tag{12}$$

Provided $q < 1$, the integration result is accepted, and a refined solution vector, where the dominant $O(h^4)$ error term cancels, is found from

$$\mathbf{y}_{n+1} = \mathbf{y}_{n+1}^*(h/2) + \frac{1}{7}\,\mathbf{e}_{n+1} \tag{13}$$

If $q > 1$, the result is not accepted, and the integration from t_n is repeated with steps $h/2$ and $h/4$. Only the result of the two half-step integrations is required as the new full step integration result is available from the first attempt.

Once a step is accepted, the proposed step length for the next step is chosen as

$$h_{n+1} = h_n \cdot \text{Min}\,[(4q)^{-0.25},\ 3] \tag{14}$$

permitting an increase in h when $q < 0.25$ and possibly an acceleration by a factor of 3 when $q << 1$. The factor of 4 in (14) and the empirical restriction on the maximal increase were used as safety margins to avoid selection of too large steps that might be rejected (that is, lead to q values larger than 1). The occurrence of $q^{-0.25}$ is justified by the order of the method.

NUMERICAL TEST EXAMPLES

The first example is a set of rate equations presented in Robertson (1967), Seinfeld et al. (1970), and Caillaud and Padmanabhan (1971):

$$\begin{aligned} \frac{dy_1}{dt} &= -\,0.04\,y_1 + 10^4\,y_2y_3 \\ \frac{dy_2}{dt} &= 0.04\,y_1 - 10^4\,y_2y_3 - 3 \cdot 10^7\,y_2^2 \\ \frac{dy_3}{dt} &= 3 \cdot 10^7\,y_2^2 \end{aligned} \tag{15}$$

$$y_1(0) = 1, \quad y_2(0) = 0, \quad \text{and} \quad y_3(0) = 0$$

The eigenvalue of largest magnitude is rapidly varying, being -0.04 at $t = 0$ and $-2\,450$ at $t = 0.02$. Caillaud and Padmanabhan used for their integration the semi-implicit third-order method with a constant step length, $h = 0.05$.

The results at $t = 10$ and the number of steps using an initial step length of 10^{-4} are given in Table 1.

The table indicates that in comparison to the constant step length method, the accuracy is increased by four orders of magnitude and the computation time reduced by 75%.

The agreement between approximate and exact results at the intermediate times $t = 0.4$, $t = 1$, and $t = 4$ corresponds to that at $t = 10$.

TABLE 1. INTEGRATION OF RATE EQUATIONS

Tolerance vector	No. of steps*	y_1	$10^4 y_2$	y_3
$(10^{-2}, 10^{-4}, 10^{-2})$	15	0.841365	0.16234	0.158619
$(10^{-3}, 10^{-5}, 10^{-3})$	16	0.841368	0.16235	0.158615
$(10^{-2}, 10^{-6}, 10^{-2})$	18	0.841369	0.16235	0.158615
$(10^{-3}, 10^{-7}, 10^{-3})$	24	0.841370	0.16234	0.158614
Constant $h = 0.05$	200	0.851	0.17	0.149
Exact		0.841370	0.16234	0.158614

* Each step of the variable step length method corresponds to three steps of a constant step length method.

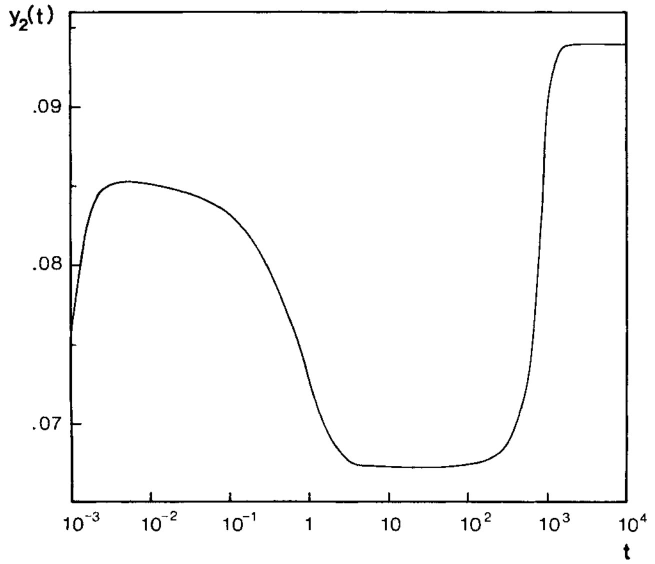

Fig. 1.

TABLE 2. TEMPERATURE AND PARTIAL PRESSURE IN THE PARTICLE PHASE AT $t = 1\,000$

ϵ	No. of steps	y_1	$10^2 y_2$	Computation time IBM 370/165 (s)
10^{-2}	31	703.56	9.0598	0.30
10^{-3}	46	703.83	9.0527	0.40
10^{-4}	64	703.90	9.0507	0.50
Exact ($\epsilon = 10^{-6}$)		703.92	9.0502	

The second example, a dynamic model for a fluid-bed reactor, is taken from Aiken and Lapidus (1974):

$$\begin{aligned}
\frac{dy_1}{dt} &= 1.30(y_3 - y_1) + 1.04 \cdot 10^4 \, k y_2 & y_1(0) &= 759.167 \\
\frac{dy_2}{dt} &= 1.88 \cdot 10^3 (y_4 - y_2(1 + k)) & y_2(0) &= 0 \\
\frac{dy_3}{dt} &= 1\,752 + 266.7 y_1 - 269.3 y_3 & y_3(0) &= 600 \\
\frac{dy_4}{dt} &= 0.1 + 320\, y_2 - 321\, y_4 & y_4(0) &= 0.1
\end{aligned} \tag{16}$$

where $k = 0.0006 \exp\,(20.7 - 15\,000/y_1)$

In this model, y_1 and y_3 represent temperature of the particle phase and the fluid phase, and y_2 and y_4 represent the partial pressure of the reactant in these phases.

Not only is this problem very stiff, the ratio of the magnitude of the largest and smallest eigenvalue being about 10^6, but it is also very parameter sensitive. The equations presented here are in accordance with those of the original reference (Luss and Amundson, 1968) and yield three possible steady state solutions: $y_1(\infty) =$ 691, 759, and 915.

Aiken and Lapidus, however, present as their third equation

$$\frac{dy_3}{dt} = 1\,752 + 267\, y_1 - 269\, y_3 \tag{17}$$

This rounding of the coefficients, however, yields a system with the single steady state solution $y_1(\infty) = 1211$. Presumably these authors have used the full numerical constants, as their solution of the dynamic model is in accordance with ours.

For the actual integration, a new set of variables were chosen:

$$\begin{aligned}
z_1 &= (y_1 - 750)/750 \\
z_2 &= y_2 \\
z_3 &= (y_3 - y_1)/750 \\
z_4 &= y_4 - y_2
\end{aligned} \tag{18}$$

The tolerance vector $\epsilon \cdot (1, 1, 0.1, 0.1)$ and an initial step size of 10^{-4} were used.

The component $y_2(t)$ is shown on Figure 1. Numerical results are given in Table 2.

The solution was also determined at a range of intermediate times, and the accuracy at these times was generally several orders of magnitudes better than the accuracy at $t = 1\,000$, indicating that a different choice of the tolerance vector would be more suitable.

As a final example which will not be presented in detail here (see, for example, Michelsen, 1976), the method was tried on a model for the formation of photochemical smog, presented by Gelinas (1972). This model involves twenty-nine components and sixty-five reactions, with rate constants varying by twenty orders of magnitude. Solution of the full model to a relative accuracy of 10^{-4} for all components requires a computation time of 8 s on the IBM 370/165. A simplified model (sixteen components, twenty-nine reactions), where presumably unimportant components and reactions were eliminated, required a computation time of 1.5 s with a relative accuracy better than 10^{-3} when compared to the full model.

The flexibility of the present method is demonstrated by the fact that these and a variety of other examples taken from Enright et al. (1975) were all solved by using the same computer program and by changing only subprograms for evaluation of the function vector and the Jacobian.

REMARKS AND SUGGESTIONS

A technique which has often been applied to facilitate the solution of stiff problems is the application of the quasi steady state hypothesis. The set of coupled ODE is converted to a set of coupled differential-algebraic equations by replacing the time derivative of certain components of the dependent variables by zero. The set of algebraic equations is then solved for these components, and back substitution in the remaining set of differential equations hopefully results in a more well-behaved problem.

Application of this technique, of course, requires that the quasi steady state hypothesis is valid and that no boundary conditions are violated. To be of any practical value, the resulting set of algebraic equations should furthermore be of such form that explicit elimination of the above-mentioned components is possible. Provided these conditions are satisfied, the main advantage of the technique is that of reducing the dimensionality of the original set. This approach was, for example, utilized in the reduction of our model for the smog formation problem.

If, however, the quasi steady variables cannot be eliminated, the set of differential-algebraic equations must be integrated. This is possible by using a modification of the present method (Michelsen, 1976), but no computational advantage is obtained, and in our opinion it is better in this case to retain the full original set.

NOTATION

$\mathbf{A}$ = Jaoobian matrix of ODE
a, b_i, b_{ij} = Runge-Kutta coefficients, Equations (4) to (6)
$\mathbf{e}$ = deviation vector, Equation (11)
$\mathbf{f}$ = vector function
h = step length
k = rate constant
$\mathbf{k}_i$ = Runge-Kutta vectors
n = step index
q = tolerance parameter
R_i = Runge-Kutta weights, Equation (7)
t = independent variable
$\mathbf{y}$ = vector of dependent variables
$\mathbf{y}^*$ = predictor vectors

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Effectiveness Factors in Gas-Liquid Reactions: The General n^{th} Order Case

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The concept of the effectiveness factor, commonly used in gas-solid catalytic and noncatalytic reactions to account for the effect of diffusion, was extended in an earlier paper (Kulkarni and Doraiswamy, 1975*a*) to include gas-liquid reactions with first-order kinetics. In the present analysis, a general n^{th} order reaction is considered by using the same parameter β defined in our earlier communication to represent the relative contributions to the reaction from the bulk and the film. The effectiveness factor expression for an n^{th} order isothermal gas-solid catalytic reaction obtained by Mehta and Aris (1971) is shown to be a special case of this more general analysis by letting β tend to zero, which represents the condition where the bulk may be regarded as nonexistent. This case is analogous to gas-solid catalytic reactions where the reaction is essentially complete within the catalyst (regarded as film in gas-liquid reactions).

EQUATIONS FOR THE REACTANT CONCENTRATION PROFILE

Let us consider a system in which gas A is absorbed in a liquid and is consumed according to a general n^{th} order reaction. The mass balance equation for A can then be written as

$$D_A \frac{d^2C_A}{dx^2} = k_1 C^n{}_A \qquad (1)$$

with the boundary conditions

$$C_A = C_A^* \quad \text{at} \quad x = 0 \qquad (2a)$$

$$-D_A \frac{dC_A}{dx} = \frac{k_1 C^n{}_{Ao}}{a} \quad \text{at} \quad x = \delta \qquad (2b)$$

Equation (2*b*) represents the kinetic boundary condition explained earlier (1975*a*).

Equations (1) and (2) can be rendered dimensionless to give

$$\frac{d^2w_A}{dy^2} = m^2 w^n{}_A \qquad (3)$$

$$w_A = 1, \quad y = 0 \qquad (4a)$$

$$-\frac{dw_A}{dy} = m^2 \beta w^n{}_{Ao}, \quad y = 1 \qquad (4b)$$

where m is the usual Thiele modulus $\delta\sqrt{k_1/D_A\ C_A{}^{*n-1}}$, and β is the ratio of the area per unit volume in the film to that in the liquid bulk and is given by

$$\beta = \frac{1}{a\delta} \qquad (5)$$

This parameter provides the bridge between gas-solid catalytic and gas-liquid reactions as explained in our earlier communication (1975*a*). It may be noted that the definition of β is based on unit volume of the bulk exclusive of the film volume. This has been done primarily in the interest of mathematical simplicity, but it is also possible to base the definition of β on the total volume of the bulk and the film. As has been subsequently pointed