pressure loss, presumably reflecting the high tensile stress in the converging flow field. To develop this relation more explicitly, we perform a momentum balance between the orifice entrance and a section of the emerging jet far enough downstream that all stresses are identically zero. This yields

$$\overline{T}_{11} = \rho v_o^2 \left[1 - \frac{R_o^2}{R_\infty^2} \right] - \overline{\tau}_w \frac{2L_o}{R_o} \qquad (1)$$

where $\overline{T}_{11}$ is the average tensile stress at the orifice entrance, v_o the average velocity in the orifice, R_o and L_o the orifice radius and length, respectively, and R_∞ is the final radius of the emerging jet. $\overline{\tau}_w$ is the average wall shear stress existing within the orifice. Equation (1) assumes the velocity profile at the orifice entrance to be flat, a reasonable assumption in light of Figure 1 (see also Metzner, Uebler, and Chan Man Fong 1969; Metzner and Metzner 1970).

By following Metzner et al. (1969), $\overline{T}_{11}$ may be equated to the extensional normal stress difference $N_E = T_{11} - T_{22}$, minus the pressure in the recirculating region P_R:

$$T_{11} \cong N_E - P_R \qquad (2)$$

Combining Equations (1) and (2), we get

$$N_E = P_R + \underbrace{\rho v_o^2 \left[1 - \frac{R_o^2}{R_\infty^2} \right]}_{\text{a.}} \underbrace{- \overline{\tau}_w \frac{2L_o}{R_o}}_{\text{b.}} \qquad (3)$$

Visual observations as well as thrust measurements of the emerging jet indicate that term a. is negligible; R_o and R_∞ are equal within our limits of measurement. An upper bound on the magnitude of term b. may be obtained from the work of Collins and Schowalter (1963) on the entry region flow of Newtonian and power law fluids in tubes. Using their Figure 8, we find that this term is never more than about 20% of P_R in magnitude and decreases in relative importance with increasing velocity. It follows that to a good degree of approximation

$$N_E \cong P_R \qquad (4)$$

The stretch rate or rate of extension at the orifice is given by (Metzner and Metzner, 1970)

$$d_{11} = \frac{Q \sin^3 \Phi}{\pi R_o^3 (1 - \cos \Phi)} \qquad (5)$$

where Φ is the half angle of the converging region of fluid. Values of d_{11} are listed in Table 1. From Equations (4) and (5) we may obtain an expression for the extensional viscosity $\overline{\eta}$:

$$\overline{\eta} = \frac{N_E}{d_{11}} \qquad (6)$$

Calculated values of $\overline{\eta}$ in Table 1 vary from 3.7 to 7.3 Ns/m², or approximately 1 500 to 3 000 times the shear viscosity! These values are similar in magnitude to those reported by Metzner and Metzner (1970) for a 100 p.p.m. by weight solution of Separan AP 30, a lower molecular weight polyacrylamide.

RECOIL

By suddenly plugging the orifice, we observed the behavior illustrated in Figures 1 to 6, a slow but very pronounced recoil, not seen at all with Newtonian fluids. This effect could also be observed at a concentration level of 10 p.p.m. by weight. To our knowledge, the only other published report of this effect is by Bagley and Birks (1960) on low-density polyethylene. This phenomenon offers dramatic qualitative support for the concept that high tensile stresses are present in the converging region.

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Problem Approximation for Stiff Ordinary Differential Equations

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The m dimensional set of ordinary differential equations

$$\frac{dz(t)}{dt} = \dot{\mathbf{z}} = \mathbf{F}(\mathbf{z}) \qquad (1)$$

for which the local Jacobian $\partial \mathbf{F}/\partial \mathbf{z}$ has at least one eigenvalue that does not contribute significantly over most of the domain of interest, so-called *stiff systems,* presents severe requirements for stable and accurate numerical integration. Although there exist numerical methods that are stable for any step size (A stable), these methods are usually not accurate enough to simulate the large eigenvalues unless very small steps are taken. In fact, for the most common class of multistep linear methods, Dahlquist (1963) has proven that second order is the highest accuracy that an A stable technique may achieve. Second-order accuracy may suffice for the nonstiff problem, but for the stiff problem higher accuracy is needed to simulate the large eigenvalues in the region of the domain in which they significantly contribute to the solution, this domain usually occurring initially in kinetic problems. The accuracy problem can be analyzed by using a linear version of (1), that is, $\mathbf{F}(\mathbf{z}) = \mathbf{A}\mathbf{z}(t)$, as illustrated by Lapidus and Seinfeld (1971). The main feature is how well the principal characteristic roots of a numerical algorithm approximate the eigenvalues of (in the linear case) $\exp[h\mathbf{A}]$, where h is a step size. The larger the (absolute value of the) eigenvalues, the poorer will be the accuracy of the numerical approximation. The solution of the linear version of (1) may be written in component form as

$$z_i(t) = \sum_{j=1}^{m} C_{ij} \exp(\lambda_j t) \tag{2}$$

where $\mathbf{C}$ is a matrix of constants depending on the initial conditions and the j eigenvectors corresponding to each eigenvalue λ_j. Often for problems in chemical kinetics, only a few variables (the stiff variables) of the m set have significant contributions from the large eigenvalues. For these variables there will generally be an initial region of the solution over which the large eigenvalues must be accurately simulated; otherwise, errors incurred in that region may propagate and render the remainder of the transient meaningless. While the eigenvalues and eigenvectors in (2) are determined by the model Equations (1), $\mathbf{C}$ is also dependent on the problem, that is, the model plus initial or boundary conditions. For some problems, then, it is conceivable that there may be small factors multiplying each exponential of a stiff eigenvalue, so that there are no stiff variables, even though there is a great disparity in the magnitudes of the largest and smallest (local) eigenvalue.

CHOICE OF INITIAL CONDITIONS TO ELIMINATE STIFFNESS

If a problem does contain stiff variables, the stiff contribution dies out early in the solution, after which the transient will be dictated entirely by the remaining eigenvalues. Thus, the initial conditions on these variables have virtually no effect on the solution and may be chosen freely. The best choice for the initial conditions is that which eliminates any contribution from the stiff eigenvalues, so that high accuracy is not required. This choice results from applying the well-known pseudo-steady-state-approximation (pssa) initially. If (1) is split into stiff variables (y) and nonstiff variables (x), then

$$\frac{d\mathbf{x}}{dt} = \mathbf{f}(\mathbf{x}, \mathbf{y}) \tag{3a}$$

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{x}, \mathbf{y}) \tag{3b}$$

The pssa is applied to the stiff variables, initially giving

$$0 = \mathbf{g}[\mathbf{x}(0), \mathbf{y}_o(0)] \tag{4}$$

where $\mathbf{x}(0)$ are given initial conditions, and $\mathbf{y}_o(0)$ are the zero$^{\text{th}}$ order initial conditions that result from the pssa. We take

$$\mathbf{y}(0) = \mathbf{y}_o(0) \tag{5}$$

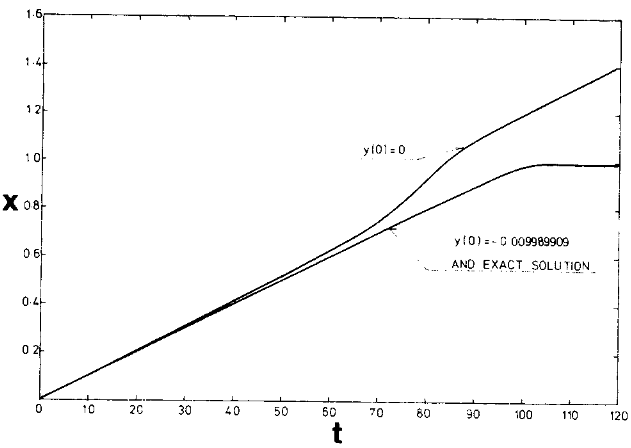

Fig. 1. Problem approximation to linear example.

Aiken and Lapidus (1975) have shown that initially to the zero$^{\text{th}}$ order

$$\mathbf{Y}_o(t) = \mathbf{Y}_o(0) \exp[\partial \mathbf{g}/\partial \mathbf{y}\ \mathbf{x}(0), \mathbf{y}(0)] \tag{6a}$$

$$\mathbf{Y}_o(0) = \mathbf{y}(0) - \mathbf{y}_o(0) \tag{6b}$$

where $\mathbf{Y}_o$ is responsible for most of the initial solution contribution from the large eigenvalues. Equation (5) eliminates this contribution to yield a nonstiff problem. This procedure may be preferred over use of the pssa throughout the transient when (4) is difficult to solve. It also allows standard integration packages to be used without modification.

APPLICATIONS

To illustrate the principles involved, consider first the constant coefficient linear system

$$\frac{dx}{dt} = \dot{x} = \lambda_1 x \quad \text{with } x(0)$$
$$\frac{dy}{dt} = \dot{y} = ax + \lambda_2 y \quad \text{with } y(0) \tag{7}$$

with the analytic solution ($\lambda_2 << \lambda_1 < 0$)

$$x(t) = x(0) \exp[\lambda_1 t]$$

$$y(t) = C_1 \exp[\lambda_1 t] + C_2 \exp[\lambda_2 t]$$

where $C_1 = ax(0)/(\lambda_1 - \lambda_2)$

$C_2 = y(0) - C_1$

The pssa applied initially yields

$$0 = ax(0) + \lambda_2 y_o(0)$$

so rather than use the given $y(0)$ we use

$$y_o(0) = -ax(0)/\lambda_2 \tag{8}$$

With this choice of initial condition, the coefficient of the large eigenvalue C_2 becomes $C_1(\lambda_1/\lambda_2)$. Therefore, the stiffer the system, the smaller will be the contribution from the stiff eigenvalue and the less the accuracy requirement for numerical integration.

The A-stable trapezoidal rule

$$\mathbf{z}(n+1) = \mathbf{z}(n) + (h/2)\,[\mathbf{F}(n+1) + \mathbf{F}(n)]$$

was applied to (7) with $a = 1$, $\lambda_1 = -1$, $\lambda_2 = 1\,000$, $x(0) = 1$, $y(0) = 1$, only a moderately stiff problem. Equation (8) gives the alternative pssa initial condition $y_o(0) =$

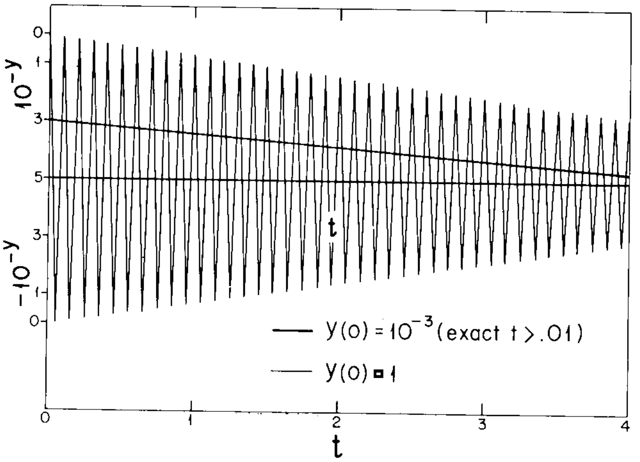

Fig. 2. Problem approximation to nonlinear kinetics example.

10^{-3}. The results of using the original initial conditions and (7) are shown in Figure 1. The original initial condition causes severe accuracy problems for $h = 0.05$, although it eventually converges to the steady state, as the trapezoidal rule must. The use of (8), however, gives better than 0.01% agreement with the exact solution for times greater than the boundary-layer length [approximately $t = 0.01$, as computed by (6*a*) when $Y_o(t)/Y_o(0) = 10^{-3}$] and step sizes of 0.1. In order to eliminate the oscillations with the original initial conditions, step sizes of not larger than 0.001 are required, many orders of magnitude slower than using (8).

The second example is a nonlinear problem in reaction kinetics used first by Liniger and Willoughby (1970):

$$\frac{dx}{dt} = 0.01 - (1 + x^2)(0.01 + x + y), \quad x(0) = 0 \tag{9a}$$

$$\frac{dy}{dt} = 0.01 - [1 + (y + 10^3)(y + 1)]\,(0.01 + x + y), \quad y(0) = 0 \tag{9b}$$

The initial ratio of eigenvalues is 1 : 10^7; later, at $t = 80$, the ratio is about 1 : 10^5, and at $t = 100$ the eigenvalues vary rapidly. Application of the pssa initially to the derivative of the stiff variable (9*b*) gives

$$0 = y_o(0)^3 + [1\,001.01 + x(0)]y_o(0)^2 + (1\,011.01 + 1\,001\,x(0))y_o(0) + 1\,001\,x(0) + 10 \tag{10}$$

Because of the nonlinearities, a choice of the roots for $y_o(0)$ in (10) must be made. However, the only stable root (for which $\partial y/\partial y < 0$) is

$$y_o(0) = -0.009989909 \tag{11}$$

Although this pssa derived initial condition is close to that of the original initial condition, a substantial increase in accuracy results over most of the solution domain with $y(0) = y_o(0)$, as shown in Figure 2. There, solutions for each initial condition are drawn as solved by the trapezoidal rule with the Newton-Raphson method to solve the implicit equation. Use of (11) for steps $h = 1.0$ gives better than 0.01% accuracy with two Newton-Raphson iterations per step. A step of 1.0 jumps over the boundary-layer region [here $t = 10^{-2}$, as computed by (6*a*)] in which the pssa is not valid, so that each step gives the same result as an accurate, stable solution with the original initial conditions; this is generally possible. Use of the original initial condition, however, yields an increasingly inaccurate solution which actually enters the domain of influence of another of the three steady states.

TWO-POINT BOUNDARY-VALUE PROBLEMS

The initial-value approximation for stiff equations is also of use for two-point boundary-value problems (TPBVP). It is possible to provide as many new equations for the missing conditions as there are stiff variables in the problem. Consider for illustration the classical dimensionless equations for the isothermal steady state tubular reactor

$$\frac{1}{Pe}\,\frac{d^2x}{ds^2} = 2\,\frac{dx}{ds} + R(x) \tag{12a}$$

with

$$\frac{dx(0)}{ds} = 2Pe\,[x(0) - 1] \quad \text{and} \quad \frac{dx(1)}{2s} = 0 \tag{12b}$$

where differentiation is with respect to axial distance from entrance to exit ($s = 0$ to 1), x is related to concentration, Pe is the Peclet number, and R is the reaction rate. The solution of Equations (12) for realistic Pe (> 20) requires a prohibitive amount of computation with conventional methods. The iterative nature of most methods for TPBVP magnifies this difficulty. Although some special singular perturbation approaches have been devised (O'Malley, 1970; Ray and Ajinkya, 1973), there exists no general approach. As will be shown, this problem can be particularly simple to solve by the initial-value approximation, with (12) written in the partitioned form of (3); namely

$$\frac{dx}{ds} = y \tag{13a}$$

$$\left(\frac{1}{Pe}\right)\frac{dy}{ds} = 2y + R(x) \tag{13b}$$

$$y(0) = 2Pe\,[x(0) - 1] \quad \text{and} \quad y(1) = 0 \tag{14}$$

Notice that there is only one initial-value relation for this two-variable set. As the local Jacobian of Equations (13) has positive eigenvalues, the equations are usually integrated from the end of the reactor back to the front to take advantage of the higher stability regions of most accurate methods when applied to equations with negative eigenvalues. By defining $t = s - 1$, (13) and (14) become

$$\frac{dx}{dt} = -y \tag{15a}$$

$$\left(\frac{1}{Pe}\right)\frac{dy}{dt} = -2y - R(x) \tag{15b}$$

$$y(1) = 2Pe\,[x(1) - 1] \quad \text{and} \quad y(0) = 0 \tag{16}$$

Equations (15) have the same characteristics as discussed previously for (3); that is, there is a small region near $t = 0$, over which y varies rapidly, causing the severe accuracy and stability limitations. As has been indicated, the initial condition on y can be set to any value within the domain of influence of the desired solution. Because the only initial condition provided (16) is on the stiff variable, however, no additional condition is provided by the pssa. From consideration of (15), the pssa is expected to apply to (15*b*) beyond the boundary layer up to and including the bed entrance. Thus we may use (15), with

$$0 = 2y(0) + R[x(0)] \tag{17}$$

and (14), to determine the initial conditions. These yield a good approximation to the actual initial conditions, since the pssa is valid at this point. Equation (3) may then be solved by any method stable for large eigenvalues and with moderate accuracy. The solution from the reactor entrance need be continued only up to the boundary layer at the end of the reactor [as can be estimated by (6a)], since beyond that point the nonstiff concentration variable is approximately constant.

As an example, (13) was solved with $Pe = 1\,000$, and $R = 10x^2$. Equations (14) and (17) give $x(0) = 0.9975124$ and $y(0) = -4.97520$. The solution obtained with the trapezoidal rule and steps of $h = 0.1$ was about 0.1% accurate over $0 \leqq s \leqq 1$. The computation time for the problem as formulated is very small compared with other TPBVP methods and is significantly easier than applying special singular perturbation methods.

We need to point out that the crux of the present concept lies in breaking an overall system into the form of (3). In other words, it is necessary to be able to identify the stiff and the nonstiff variables. When m is large (> 10 to 15), such a discrimination may not be obvious and may require an a priori analysis of the total set of differential equations. Further, a large system may contain stiff, semi-stiff, and nonstiff variables; current work in progress is directed toward this latter case.

NOTATION

$\mathbf{f}(\mathbf{x}, \mathbf{y})$ = general function of dependent variables $\mathbf{x}$ and $\mathbf{y}$
$F(\mathbf{z})$ = general function of dependent variable $\mathbf{z}$
$\mathbf{g}(\mathbf{x}, \mathbf{y})$ = general function of dependent variables $\mathbf{x}$ and $\mathbf{y}$
h = step size
n = the n^{th} step
m = total number of differential equations
Pe = Peclet number
R = reaction rate
s = axial distance from reactor entrance
t = independent variable
$\mathbf{x}$ = nonstiff dependent variable
$\mathbf{y}$ = stiff dependent variable
$\mathbf{Y}$ = inner stiff dependent variable
$\mathbf{z}$ = general dependent variable
λ_i = i^{th} eigenvalue

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Blending of Polymer Solutions With Different Rheological Properties

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Blending of polymer solutions with different rheological properties is a fairly frequent problem in the polymer industry. Examples include the blending of a polymer solution or melt with a stream of monomer, plasticizer, antistatic, or foaming additives. The process may be carried out either in stirred tanks or in motionless mixers. Although the components are completely miscible, at least in the range of concentrations relevant for the process, the blending takes a considerable time owing to large differences in viscosities and characteristic times of the components. In this note results are reported on the blending of aqueous solutions of two polymers in a vessel stirred by a helical screw impeller operating in a centrally positioned draught tube. An empirical correlation is then proposed for the dimensionless blending time $N\theta_B$ which takes into account the zero-shear viscosities of the initial constituent solutions and their initial orientation.

EXPERIMENTAL PART

The mixer used was comprised of a flat-bottomed vessel and a centrally located draught tube (for dimensions see Table 1) made of transparent acrylic glass. Three impellers of two different radii (see Table 2) were rotated both clockwise and anticlockwise centrally in the draught tube.

Aqueous solutions of sodium carboxymethylcellulose (CMC) made by ICI under the trade name Edifas B and of polyacrylamide (PAA) manufactured by Dow Chemicals under the name Separan AP 273 were used up to 2% concentration, thus allowing the zero-shear viscosities to vary by a factor between 10^2 and 2.10^3 and the characteristic times by a factor of about 10.

The rheological properties of all liquids used were measured by Rheogoniometer R18. In this rheometer, where the liquid sample is placed between a flat plate and a cone with large apex angle, both the torque T and the total axial thrust F between the cone and the plate are measured. The variable viscosity η of the liquid is then given by

$$\eta = 3T/2\,\pi R^3\,\dot{\gamma} \qquad (1)$$

where $\dot{\gamma} = \omega/\alpha$ is the shear rate in the conical gap (α being the complementary apex angle and ω the angular velocity), and R is the radius of the cone-and-plate setup. Two cones were used with the apex angles of 178 and 176 deg., respectively.

The axial thrust F is used to calculate the primary normal stress coefficient of the liquid σ_1 which is the measure of the liquid's elasticity:

$$\sigma_1 = 2F/\pi R^2\,\dot{\gamma}^2 \qquad (2)$$

The rheometric data were obtained in the range of $10^{-1}\ \text{s}^{-1} < \dot{\gamma} < 10^3\ \text{s}^{-1}$.