will represent it satisfactorily in the case of a first-order kinetic. Not to speak about the case of a very rapid first-order or pseudo first-order reaction, where $k_L' = \sqrt{k_2 C_{BL} D_A}$, and k_L has no influence on the mass transfer rate.

In the case of a second-order reaction, however, the influence may be much more important, and careful experiments have been performed by Merchuk et al. (1970) in order to determine the distribution function.

The consideration of the distribution of the local value of k_L (Merchuk et al., 1970) allows us to predict small positive deviations of ϕ in the case of a first-order reaction, and negative deviations for higher reaction orders. Indeed, that is the tendency which can be seen in the data by Jhaveri and Sharma (1970) (Figure 1).

Even if the influence of the distribution of the local mass transfer coefficients is not too important from a practical point of view, since the errors that result from not considering such distribution are not too big (about 15% in the only reported data, Merchuk et al., 1970), the understanding of the phenomenon is important from a more basic point of view and explains why the Danckwerts and Gillham's method is better than a simple correlation between mass transfer coefficients of a model and those of industrial equipment.

NOTATION

a = interfacial area per unit volume, cm^{-1}
CA_i = concentration of dissolved gas at interface in equilibrium with gas at interface, mol/cc
C_{BL} = concentration of reactant B in the bulk of the liquid, mol/cc
D_A = diffusivity of dissolved gas, cm^2/s
D_B = diffusivity of reactant B, cm^2/s
k_L = liquid film mass transfer coefficient cm/s
k_L' = liquid film mass transfer coefficient, with chemical reaction, cm/s
k_2 = second-order rate constant for reaction of A, cc/mol s
z = number of moles of reactant B reacting with each mole of solute A

Greek Letters

γ = Damköelher number, given by Equation (4), dimensionless
ϕ = enhancement factor for an instantaneous second-order reaction, dimensionless

Subscripts

c = packed column, industrial apparatus
m = laboratory model

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Pseudo Steady State Approximation for the Numerical Integration of Stiff Kinetic Systems

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Recently Aiken and Lapidus (1974) have derived a solution approximation for stiff systems of the partitioned form

$$\dot{\mathbf{x}} = \frac{d\mathbf{x}(t)}{dt} = \mathbf{f}(\mathbf{x}, \mathbf{y}), \ \mathbf{x}(0) \tag{1}$$

$$\dot{\mathbf{y}} = \frac{d\mathbf{y}(t)}{dt} = \mathbf{w}(\mathbf{x}, \mathbf{y}), \ \mathbf{y}(0) \tag{2}$$

where y denotes the stiff variable vector and x the nonstiff variable vector. The solution was given in terms of zeroth-order inner (X_0, Y_0) and outer (x_0, y_0) and first-order inner and outer (X_1, Y_1, x_1, y_1) terms

$$\begin{aligned} \mathbf{x} &\simeq \mathbf{X}_1 + \epsilon\mathbf{X}_1 + \mathbf{x}_0 + \epsilon\mathbf{x}_1 \\ \mathbf{y} &\simeq \mathbf{Y}_0 + \epsilon\mathbf{Y}_1 + \mathbf{y}_0 + \epsilon\mathbf{y}_1 \end{aligned} \tag{3}$$

where ϵ is an artificial bookkeeping indication of the degree of stiffness in (2), defined by

$$\epsilon\dot{\mathbf{y}} = \mathbf{g}(\mathbf{x}, \mathbf{y}, \epsilon) \tag{4}$$

where $\mathbf{g} \equiv \epsilon\mathbf{w}$. This parameter need not actually exist or be identified for the solution (3). The outer terms are of more interest than the inner terms, which are important only within a relatively small boundary layer region of the transient. For systems stiff enough to require special integration techniques, the zeroth-order outer approximation often is sufficiently accurate

$$\dot{\mathbf{x}}_0 = \mathbf{f}(\mathbf{x}_0, \mathbf{y}_0), \quad \mathbf{x}_0(0) = \mathbf{x}(0) \tag{5a}$$

$$0 = \mathbf{g}(\mathbf{x}_0, \mathbf{y}_0) = \mathbf{w}(\mathbf{x}_0, \mathbf{y}_0) \tag{5b}$$

The last equality in (5b) is made since ϵ is not zero. This is properly what has been referred to as the pseudo steady state approximation (pssa). The conditions for the validity of (5), or for regular degeneracy to the low-order solution, briefly, require that the initial conditions $\mathbf{x}(0) = \boldsymbol{\zeta}$, $\mathbf{y}(0) = \boldsymbol{\eta}$ be within the region of asymptotic stability of

$$\frac{d\mathbf{y}}{d\tau} = \mathbf{g}(\boldsymbol{\alpha}, \mathbf{y}) \tag{6}$$

where $\tau \equiv t/\epsilon$, and $\mathbf{x}$ is replaced by some constant vector $\boldsymbol{\alpha}$ at each instant (Tikhonov, 1952).

PREVIOUS USE

The pssa has been used for some time to permit an analytical solution or to aid data gathering and parameter fitting of ordinary differential equations, as Bodenstein (1924) first demonstrated for chemical kinetic schemes. The pssa has been used extensively in more recent years to aid numerical computation of stiff equations although the theoretical basis for this was heretofore unclarified. For example, Luss and Amundson (1968) examined a simplified model for the dynamics of a catalytic fluidized bed in which the concentration and temperature of the interstitial fluid is assumed in equilibrium with the particle; this was stated necessary because it "might be the only feasible way to carry out the transient computations." Gelinas (1972) applied the pssa to a large set modeling photochemical smog; Herriott et al. (1972) to a large set for the pyrolysis of propane. In nuclear reactor kinetics, the pssa is called the *zero power approximation* (Birkhoff, 1966), obtained by setting to zero the small perturbing prompt neutron lifetime.

In spite of all the applications of the pssa, there is some confusion as to its interpretation and validity. The zeroth-order outer expansion is derived without the assumption of the perturbing parameter's value. As such, it is not true that the pssa is defined as the original model with ϵ equal to zero. For systems in the singular perturbed form (1) and (4), with ϵ identified, the pssa may be mechanically obtained by setting ϵ to zero. For systems not obviously in singular perturbed form, the pssa may be obtained mechanically by setting the time derivations of the stiff variables to zero; this is recommended even for systems obviously in singular perturbed form as otherwise regularly perturbed terms are also lost, unnecessarily decreasing accuracy and changing the equilibrium point (Ray, 1969). Note, however, that this does not imply that the stiff variables are necessarily invariant over any domain, as is often believed to be required for the pssa to be valid. Thus, Edelson and Allara (1973), examining the pssa applied to a stiff model of propane pyrolysis, report agreement with an accepted solution as surprisingly good since the stiff variables do not settle to a steady state during most of the transient.

ACCURACY AND REGION OF APPLICABILITY ESTIMATION

There are two main difficulties in the use of a valid pssa to the partitioned stiff system: a priori knowledge of the applicable region of the domain and the accuracy within this region. Hirschfelder (1957) suggested that the length of the boundary layer alone be used as a qualitative gauge of the stiffness and so the accuracy of the pssa although he gives no practical method of arriving at the boundary layer length. Johnson (1966) uses chemical rate constants related to the stiffness of certain kinetic schemes to guide application of the pssa. Snow (1966) has written a computer package which compares results from integration of the full equations with that from a pssa, then uses only the pssa when the agreement is close; Keneshea (1967) continues to periodically examine this agreement. Ponzo and Wax (1972) derived a criterion for the accuracy and region of applicability of the pssa for the particular form of the Liénard equation. Their criterion, however, is not practical to use. Heinecken et al. (1967) explain that the Monod kinetics can be expected more likely valid for very low initial enzyme concentrations. This can be shown to diminish the magnitude of the stiff variables within the boundary layer and thus require less accuracy for simulation of the large negative eigenvalue.

Consideration of the pssa as the zeroth-order outer approximation (5) reveals that the region of applicability corresponds to the region where the outer variables are much more dominant than the inner ones. The inner variables are then important only within a narrow initial boundary layer and thus can be used to define this region. The zeroth-order inner term for the stiff variable is by far the most dominant (Aiken and Lapidus, 1974):

$$\mathbf{Y}_0(t) = \mathbf{Y}_0(0) \exp[\partial\mathbf{w}/\partial\mathbf{y}(\mathbf{x}_0, \mathbf{y}_0)t] \tag{10}$$

where $\mathbf{Y}_0(0) = \mathbf{y}(0) - \mathbf{y}_0(0)$. Experience by the authors has indicated that (10) is capable of providing an a priori estimate of the boundary layer for linear and nonlinear applications. In this way the boundary layer is defined as a fractional decay of the zeroth-order stiff inner variable, the effective boundary layer length given by t_I:

$$t_I = \frac{|\ln[Y_0(t)/Y_0(0)]|}{\left\|\frac{\partial\mathbf{w}}{\partial\mathbf{y}}(\mathbf{x}_0(0), \mathbf{y}_0(0))\right\|} \tag{11}$$

where $||\cdot||$ is a suitable matrix norm. Since for any matrix $\mathbf{A}$,

$$||\mathbf{A}|| > \rho(\mathbf{A})$$

where $\rho(\mathbf{A})$ is the spectral radius of $\mathbf{A}$,

$$\rho(\mathbf{A}) \equiv \max_{\cancel{\forall i}} |\lambda_i|$$

a conservative estimate of the boundary layer is thus provided by the use of the spectral radius for the matrix norm, that is, if the first step can be taken greater than this boundary layer estimate, the pssa is applicable.

The accuracy of using only the zeroth-order approximation is indicated by the magnitude of the first-order outer terms (Aiken and Lapidus, 1974)

$$\epsilon x_1(t) = (\epsilon x_1(0) + b/a)\exp(at) - b/a \qquad (12)$$

$$\epsilon y_1(t) = b/f_y - w_x \epsilon x_1(t)/w_y \quad f_y = \partial f/\partial y, \text{ etc.}$$

where

$$a = f_x - w_x f_y / w_y$$

$$b = -w_x f f_y / w_y^2$$

$$\epsilon x_1(0) = \frac{Y_0(0)}{2w(x(0), y(0))}\,[f(x(0), y(0)) - f(x(0), y_0(0))] \qquad (13)$$

all derivatives are evaluated at (x_0, y_0), and dimensional notation has been suspended. Note that w_y may not be singular. The initial condition $\epsilon x_1(0)$ may be derived in a more direct manner than (13) used in our earlier paper: Since

$$\epsilon x_1(0) + \epsilon X_1(0) = 0$$

and

$$\lim_{t \to \infty} X_1(t) = 0$$

Then

$$\epsilon x_1(0) = \epsilon \int_0^\infty \frac{dX_1}{d\tau}\,d\tau$$

$$= \epsilon \int_0^\infty [f(x(0), y_0(0) + Y_0(\tau)) - f(x(0), y_0(0))]d\tau$$

$$= \epsilon f_y(x(0), y_0(0)) \int_0^\infty Y_0(\tau)\,d\tau$$

If $Y_0(\tau)$ is assumed linear over τ, with slope defined by $\dot{Y}_0(0) = \epsilon w(x(0), y(0))$,

$$\epsilon x_1(0) = f_y(x(0), y_0(0))\, Y_0^2(0)/2w(x(0), y(0)) \qquad (14)$$

This is seen to be a lower-order approximation to our previous condition, now derived in a less ad hoc fashion. Experience has shown (14) and (13) agree almost exactly. Since (12) may easily be evaluated periodically at any time during the solution, a convenient upper bound on the error of using the pssa for many common systems is $\epsilon x_1(t)/x_0(t)$ or $\epsilon y_1(t)/y_0(t)$. If these ratios are less than say 0.001, the accuracy of the pssa is indicated to be better than 0.1%.

NUMERICAL EXPERIMENTS

As a simple illustration of the effectiveness of the boundary layer and accuracy estimates, consider the linear system $(\lambda_2 << \lambda_1 < 0)$

$$\dot{x} = \lambda_1 x, x(0)$$
$$\dot{y} = \alpha x + \lambda_2 y, y(0)$$

with the solution

$$x(t) = x(0)\exp(\lambda_1 t)$$
$$y(t) = {}^{1}(t) + y^0(t)$$
$$y^1(t) = [y(0) - \alpha x(0)/(\lambda_1 - \lambda_2)]\exp(\lambda_2 t)$$
$$y^0(t) = [1/(\lambda_1 - \lambda_2)]\,\alpha x(0)\exp(\lambda_1 t)$$

where y^1 and y^0 represent contributions important in the inner and outer regions, respectively. Using the boundary layer estimate (11),

$$Y_0(t) = [y(0) + \alpha x(0)/\lambda_2]\exp(\lambda_2 t)$$

Comparison of Y_0 with $y(t)$ shows exact agreement of decay rates and quite good agreement of magnitudes, the agreement being better the stiffer the system.

The pssa gives

$$y_0(t) = [\alpha x(0)/-\lambda_2]\exp(\lambda_1 t)$$

From (12)

$$\epsilon y_1(t) = [-\alpha\lambda_1 x(0)/\lambda_2^2]\exp(\lambda_1 t)$$

Thus the second-order approximation is

$$y_0 + \epsilon y_1 = -[(1 + \lambda_1/\lambda_2)/\lambda_2]\,\alpha x(0)\exp(\lambda_1 t)$$

It can be shown that the accuracy of inclusion of the first-order term is given by

$$\frac{y - (y_0 + \epsilon y_1)}{y} = \left(\frac{\lambda_1}{\lambda_2}\right)^2$$

while the accuracy of the pssa is

$$\frac{y - y_0}{y} = \left(\frac{\lambda_1}{\lambda_2}\right)$$

and the contribution of the first-order term in comparison to the zeroth-order term, the indication of accuracy recommended earlier, is

$$\epsilon y_1/y_0 = \lambda_1/\lambda_2$$

which agrees exactly with the real accuracy in this simple linear example.

Hence the solution $y_0 + \epsilon y_1$ is always more accurate than just y_0, the difference being greater the stiffer the system (that is, the smaller λ_1/λ_2). This first-order contribution can thus become large enough to require inclusion in the solution for sufficient accuracy; the system is then not stiff enough for the pssa.

REMARKS

The preceding analysis is useful only for systems which have $w_y < 0$, an initial monotonically decreasing boundary layer. Fortunately this seems to be true for the great majority of applications in stiff chemical kinetics. It also appears that within this practical context, the dependent variables divide into the stiff and nonstiff groups, and these are often identifiable from a priori considerations. If not, a few small integration steps within the boundary layer will reveal those variables with comparatively rapid transients.

A special characteristic of kinetic systems is that rarely does the model represent the chemical phenomena closely enough to require better than moderate accuracy in the numerical integration. This suggests the permissibility of a model approximation like the pssa. Thus for systems too stiff to be integrated by conventional means, the pssa is likely to yield quite adequate solution accuracy.

The pssa may prove invaluable for the integration of large systems, as explicit routines may be used to eliminate the need to invert a large Jacobian, necessary in all implicit methods. When w is linear in y, often the case in kinetics, a decomposition may be effected to decrease the dimensionality.

The pssa with region of applicability and accuracy estimates as presented in this paper is amenable for inclusion into a general use package. The main difficulty would be obtaining a criterion for finding the stiff variables. For the boundary layer estimate to give a solution accurate to about 0.1%, a value for $Y_0(t)/Y_0(0)$ of 10^{-3} is recommended.

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NOTATION

$f(x, y)$ = general function of dependent variables x and y
$g(x, y, \epsilon)$ = general function of dependent variables x, y and of parameter ϵ
t = independent variable
t_l = boundary layer length
$w(x, y)$ = general function of dependent variables x and y
x = nonstiff dependent variable
x_0, x_1 = nonstiff outer variables
X_0, X_1 = nonstiff inner variables
y = stiff dependent variable
y_0, y_1 = stiff outer variables
Y_0, Y_1 = stiff inner variables

Greek Letters

ϵ = bookkeeping indication of degree of stiffness
ζ = initial condition on nonstiff variable
η = initial condition on stiff variable
α = dimensionless constant
λ_i = ith eigenvalue
ρ = spectral radius
τ = expanded inner t scale, t/ϵ

Subscripts

x = partial derivative with respect to x
y = partial derivative with respect to y
0 = zeroth-order expansion in ϵ
1 = first-order expansion in ϵ

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Prediction of "Tortuosity Factors" from Pore Structure Data

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In a recent paper the author has proposed a new network permeability model of porous media (Dullien, 1975) consisting of a set of cubic networks of arbitrary orientation with respect to the macroscopic flow direction. This model has resulted in the following formula to predict permeabilities:

$$k_m = \frac{\epsilon}{96\, \Sigma_i \Sigma_j V_{ij}} \sum_i \frac{(\Sigma_j V_{ij}/D_j^2)^2}{\Sigma_j V_{ij}/D_j^6} \tag{1}$$

where ϵ is the porosity corresponding to the pores considered in the calculations and V_{ij} is the volume of the pores of diameter D_j, the entry to which is controlled by pore necks of diameter D_i. The bivariate pore size distribution V_{ij} can be estimated from the mercury intrusion porosimetry and the photomicrographic pore size distribution curves of the sample. In the same paper the author has shown that a cubic network of capillary tubes has isotropic permeability which is independent of the orientation of the network. The calculations have shown that the network behaves in every orientation as if 1/3 of the tubes were conducting, resulting in the factor 3×32 in the denominator of Equation (1). In other treatments (Haring and Greenkorn, 1970; Johnson and Stewart, 1965; Wiggs, 1958), it has been shown that for pores of random orientation also a factor of 1/3 results as compared with the factor 1 for the case when all the pores are lined up parallel to the macroscopic flow direction. Often it has been the custom to call the reciprocal of this factor tortuosity T.

Equation (1) has been applied successfully to highly compacted materials of very different permeabilities (Dullien, 1975).

In the case of pore diffusion and of electric conductivity measurements in porous media, a different kind of tortuosity X has been defined by the equation (Wyllie and Rose, 1950; Cornell and Katz, 1953)

$$F = \frac{X}{\epsilon} \tag{2}$$