JOURNAL OF COMPUTATIONAL PHYSICS 34, 111–123 (1980)

Note

More Efficient Numerical Solution of Diurnal Kinetics Problems

Variable-step, variable-order algorithms are the most powerful general methods presently available for the solution of systems of ordinary differential equations. Only few of these have achieved some success in obtaining highly accurate solutions of stiff diurnal kinetics problems with rapidly varying (periodic) reaction rates that occur in the field of stratospheric chemistry. A method is proposed here to be used in conjunction with these algorithms to provide greater computational efficiency in solving problems of this type.

1. INTRODUCTION

Theoretical investigations of the chemical composition of the stratosphere often lead to kinetics problems that are not amenable to numerical solution even by the most advanced techniques. Diurnally varying photodissociation rate coefficients exhibit rapid changes in short time intervals near the beginning and end of daylight hours causing chemical concentrations to behave nearly like step functions. Moreover, the differential equations governing these concentrations may be characterized by the quality of stiffness which refers to the presence of very small time constants whose occurrence allows the use of only special classes of solution techniques. The intractable nature of the equations has hindered the development of dynamic–kinetic models of the stratosphere [1]. In an effort to avoid the numerical difficulties, some modelers have assumed very short-lived species to be in photochemical equilibrium. Others have resorted to the use of constant (mean-value) photodissociation coefficients to provide more easily calculable approximate solutions. Gelinas [2], Whitten and Turco [3], and Martin [4], however, have shown that such methods can lead to significant error in some cases.

Numerical problems of the type described have led to the development of algorithms designed with the aim of achieving reasonable efficiency in calculating highly accurate solutions that reproduce realistic diurnal variation of species concentrations. The only schemes that have achieved some degree of success appear to be those which automatically vary both the step size and the order of the finite-difference approximation in such a way as to maximize the step size under the constraint that local truncation error remain within a user-specified tolerance. One such scheme has been used by Wuebbles and Chang [5] to show the great importance of using diurnally varying parameters in calculating trace constituent distributions over multiyear periods. For some stiff diurnal chemistry problems, step-size selection algorithms arrive at time increments that vary over many orders of magnitude in the course of a one-day

0021-9991/80/010111-13$02.00/0

simulation. For other problems, no allowable step size can be found in the course of the solution procedure, and the integration fails [1].

For hard-to-solve diurnal chemistry problems, it would seem advantageous to "help" the step-size selection algorithms by transformation of the independent variable t (time) to a new variable t' for which the optimum step size is nearly constant. This approach has been used successfully in satellite-motion calculations where a change in the independent variable which eliminates most of the step-size variation results in a much more efficient numerical solution process [6]. Diurnal chemistry problems, which also lead to approximately periodic variation in the step size, are well suited to this technique. Integration over one representative cycle (day) without change in variable serves to reveal the behavior of the step size for the algorithm under consideration. From this information, a suitable transformation can be found to limit the variation in step size over all succeeding cycles.

2. APPROACH

We are concerned with the solution of systems of nonlinear kinetic equations of the form

$$\frac{dc_i}{dt} = f_i(c_1,..., c_I, t), \qquad i = 1,..., I, \tag{1}$$

with specified initial values, where c_i denotes chemical species concentration and f_i is a function that accounts for all chemical and radiative production and loss terms to be considered. For some diurnal problems occurring in stratospheric chemistry, c_i may be small during the nighttime hours, suddenly increase orders of magnitude at the coming of daylight, vary slowly during the day achieving a maximum at noon, and then sharply drop orders of magnitude near sunset. Accurate integration requires the use of very small time increments near sunup and sundown when species concentrations are varying rapidly. Automatic step changing algorithms will attempt to accommodate this need and to allow, for the sake of computational efficiency, considerable expansion of the time increment to a maximum value occurring around noontime. Accordingly, the step size will undergo frequent updates which can consume significant computer time and which occasionally will result in the failure of the algorithm to determine an allowable sequence of step sizes.

We seek to determine a new independent variable t' that will provide greater efficiency and perhaps greater chance of success in carrying out the numerical integration of (1). The variable t' is defined through the relation

$$\frac{dt}{dt'} = \phi(t) \tag{2}$$

so that (1) becomes

$$\frac{dc_i}{dt'} = \phi[t(t')] f_i[c_1,..., c_I, t(t')], \qquad i = 1,..., I. \tag{3}$$

To find a suitable function ϕ, the following approach can be taken. First, the integration is carried out over one diurnal cycle (unless the integration is aborted) with time as the independent variable using a variable-step, variable-order algorithm. An approximate analytic representation of t as a function of the time step n is determined. The variable t' then is selected so that $t'[t(n)]$ is approximately linear in n; i.e., so that the step size in t' is nearly constant. Having used this representative diurnal cycle to determine the appropriate transformation, the new independent variable is used on succeeding integration cycles.

Our main concern is with the daylight hours (which we take to be $2m \leqslant t/T \leqslant 2m + 1$, $m = 0, 1, 2, \ldots$, where $T = 43{,}200$ sec) since these are the hours during which the numerical difficulties occur. Relatively uniform, large time steps carry the integration efficiently through the nighttime hours. The differential-equation solver used in our experiments is that developed by Byrne and Hindmarsh [7], whose algorithm bears some similarities to the methods of Brayton *et al.* [8] and Gear [9]. The Byrne–Hindmarsh algorithm, encoded in a widely used program called EPISODE (Effective Package for Integration of Systems of Ordinary Differential Equations), is stable under somewhat less restrictive conditions than are some of the earlier methods. The EPISODE program was selected for this work since it is well tested, well documented, and seems to have been designed with diurnal photochemical problems in mind. (The EPISODE program and user manual are available from the National Energy Software Center.)

Numerical solutions of two prototype diurnal kinetics problems have been computed for five diurnal cycles. In each case, it has been found that for the daylight hours, the EPISODE step-size selection algorithm leads to a function $t(n)$ that can be well approximated by an S-shaped curve centered about n_m, the time step corresponding to the noontime value of t. For the initial daytime period $0 \leqslant t/T \leqslant 1$, for example, we can take as an approximating function

$$t(n) \approx T \left\{ 0.5 + \beta^{-1} \tanh \left[\alpha \left(\frac{n - n_m}{n_m - 1} \right) \right] \right\}, \qquad n = 1, \ldots, n_M \tag{4}$$

which for $\alpha \gg 1$ and $\beta \approx 2$ will be of the required form. Here n_M is the last time step used before t reaches the value 43,200 sec. If we define the new independent variable as

$$t' = \operatorname{arctanh}\{\beta[(t/T) - 0.5]\}, \qquad 0 \leqslant t/T \leqslant 1, \tag{5}$$

it follows from (4) that t' is a linear function of n. The form of ϕ, which in this case is

$$\phi[t(t')] = T(1 - \tanh^2 t')/\beta, \tag{6}$$

has computational significance since the solution of (3) requires evaluation of this factor at each step. This added computation is a drawback of the approach but nevertheless can be countered by substantial reduction in the number of steps that results when the integration is performed on (3) rather than (1). On more complex problems, suitable transformation could involve functions more expensive to evaluate. However, as the number of equations is increased, calculation of ϕ becomes a smaller portion of the total computation, ϕ being a common factor in each equation.

The shape of the approximating function is adjusted by selection of the parameters α and β which can be determined through simultaneous solution of equations for t and dt/dn at any point on the curve $t(n)$. The parameter β alone then can be used to relate t and t'. If we arbitrarily perform the curve fit at $n = 1$, thereby opting for a close approximation in the tail of the curve, an appropriate initial time increment τ must be determined. We choose τ to be the largest step size allowed by the algorithm; i.e., the largest step capable of providing the specified accuracy. Then,

$$\tau = t(1) = T(0.5 - \beta^{-1} \tanh \alpha) \tag{7}$$

and

$$\tau = \frac{dt}{dn}(1) = T\alpha\beta^{-1}(n_m - 1)^{-1} \operatorname{sech}^2 \alpha. \tag{8}$$

Equation (7) yields the relation

$$\beta = \frac{\tanh \alpha}{0.5 - \tau/T}, \tag{9}$$

while elimination of β from (8) gives

$$\frac{\sinh 2\alpha}{2\alpha} = \frac{(0.5T/\tau) - 1}{n_m - 1}. \tag{10}$$

An iterative procedure can be used to solve (10) for α; this value is then substituted in (9) for the direct calculation of β. In practice, β can take on a value slightly less than 2, and it is convenient to write

$$\beta = 2 - \delta. \tag{11}$$

In the numerical experiments carried out so far, optimum values of δ have been found to range from 0.4×10^{-3} to 0.5.

The original variable t serves well to efficiently carry the integration through the night. To maintain this property but avoid restarting the integration procedure at sunset, the function $t'(t)$ can be extended by defining

$$t' = P + Q(t/T), \qquad 1 \leqslant t/T \leqslant 2, \tag{12}$$

for the nighttime hours. The constants P and Q are chosen to satisfy the relations

$$Q = \frac{\beta}{1 - (\beta/2)^2} \tag{13}$$

and

$$P = \operatorname{arctanh}(\beta/2) - Q, \tag{14}$$

in order to provide continuity of t' and dt'/dt at $t/T = 1$. These conditions imply the continuity of c_i and dc_i/dt', the leading elements of the history array used in EPISODE; the higher-order derivatives of c_i fail to be continuous by terms of order δ. A restart is suggested, however, at sunup of each new day [1]. Definitions (5) and (12) can be suitably extended for succeeding days.

Before proceeding further, a fundamental difficulty of the transformation approach should be pointed out. For an approximating function such as $t(n)$ in (4), $t'(t)$ is defined so that the differential dt' $(= dt/\phi) =$ const $\times$ dn in the hope that an analogous finite-difference relation will result; i.e., so that the constant (integral) increment in n will produce a constant increment in the new variable t'. Thus if h and h' are the step sizes in t and t', respectively, we would expect that $h' \approx h/\phi =$ const based on consideration of the differential formula alone. Due to the error control mechanism in EPISODE, however, a more complicated relationship exists between h' and h even for the case in which the order of accuracy is held fixed. The step size h' may or may not be close to h/ϕ in value depending on the particular functional forms of ϕ and f.

3. NUMERICAL EXPERIMENTS

To evaluate the effectiveness of the approach described, two diurnal chemical kinetics test problems were considered. Numerical solutions were carried out on the CDC-7600 using single precision. The first problem [7] is a mockup of a photochemical reaction which takes the form

$$\dot{c} = \dot{H} - B(c - H), \qquad 0 \leqslant t \leqslant 10T, \tag{15}$$

and

$$c(0) = H(0), \tag{16}$$

where

$$H(t) = [D + AE(t)]/B,$$

$$A = 10^{-18}, \qquad B = 10^{8}, \qquad D = 10^{-19},$$

$$E(t) = \begin{cases} \exp(-\gamma\omega/\sin \omega t), & \sin \omega t > 0 \\ 0, & \sin \omega t \leqslant 0, \end{cases}$$

$$\gamma = 4, \qquad \omega = \pi/T,$$

and the constants A, B, and D are in appropriate units. The solution to (15) and (16) is $c(t) = H(t)$, nearly a square wave. The eigenvalue $(-B)$ gives rise to a small time constant of 10^{-8} sec, and the problem must be solved by methods designed for stiff systems. By use of the appropriate algorithm contained in EPISODE, (15) with (16) was first integrated over the interval $0 \leqslant t/T \leqslant 1$ for a prescribed local error tolerance. Semirelative error control was used in this run whereby the error at time $t(n)$ was controlled relative to $\max_{0 \leqslant i \leqslant n} | c[t(i)]|$. The only modification made to the EPISODE package was the incorporation of a print statement to provide output at every step of the integration process in order to follow the variation of the step size. The behavior of t/T as a function of the time step n is shown by the solid line in Fig. 1. The quantity τ/T, the largest acceptable initial step size, was determined to be 0.5×10^{-5}. With $n_m = 276$, relations (9) through (11) yield the parametric values

$$\alpha = 4.3797, \qquad \beta = 1.99939, \qquad \delta = 0.00061. \tag{17}$$

The resulting approximating function $t(n)$ given by (4) is indicated by the dashed line in Fig. 1.

In spite of the expectation of nearly uniform step size in t', all runs in the transformed variable were carried out using the full EPISODE algorithm for error control and step-size selection. Any gain in efficiency is thus due to reduction in the number of steps required and not a result of deleting the error control mechanisms. The step-

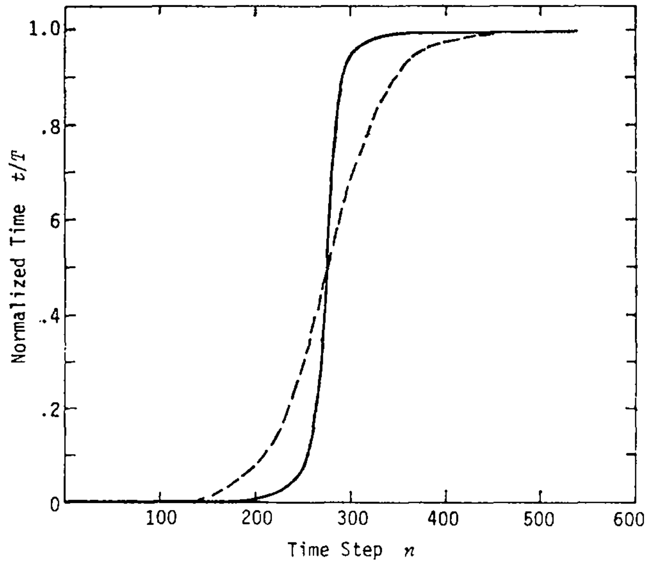

FIG. 1. Normalized time t/T versus the time step n over one-half diurnal cycle $0 \leqslant t/T \leqslant 1$ (daylight) determined by application of the automatic step-changing algorithm (solid line) and by evaluation of an approximating function (dashed line) for the mockup photochemical reaction (15).

changing process remains crucial, for despite our efforts, t' (as determined by EPISODE) falls far short of being a linear function of n.

Numerical integration of the transformed system determined by (17) produces the variation of t' with (normalized) time step indicated in Fig. 2 (solid line); the dashed line indicates the theoretical (linear) variation of t' with time step. For the initial step size, an arbitrarily chosen small value was selected to allow EPISODE to automatically increase the step size to an appropriate value within a few steps. The transformation reduces the number of steps required from 538 to 415 with a 17 % saving in running time (n_m is reduced from 276 to 269).

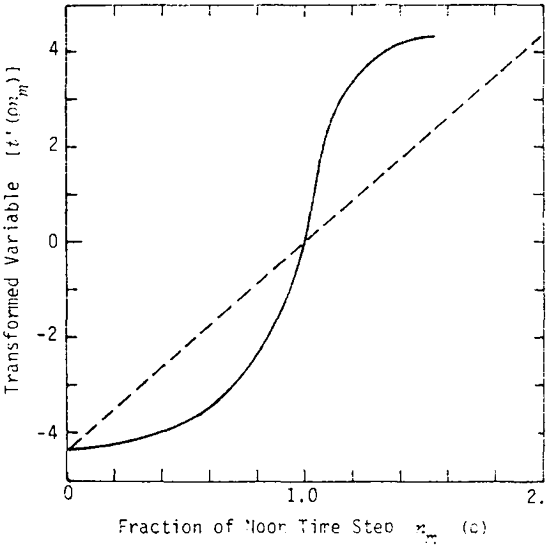

FIG. 2. Transformed variable t' versus the time step (as a multiple of n_m, the step number at noon) determined by the automatic step-changing algorithm (solid line) and the theoretical linear variation of t' (dashed line) with time step for the mockup photochemical reaction (15).

Some further numerical experimentation, however, shows the optimum of δ to be somewhat smaller than the derived value. Table I contains the relevant data for comparing the numerical integration of the untransformed equation (15) (base run) with the numerical integration of the transformed equation using the independent variable t' defined in (5) for several values of δ (or alternatively, β). This table includes the computer processing (CP) seconds required for executing each run on the CDC-7600, the number of steps required, the number of function evaluations (NFE) of the right-hand side of (15), and the number of Jacobian evaluations (NJE). The results indicate an optimum value of $\delta = 0.4 \times 10^{-3}$ in which case the integration required about 27 % less processing time than that required for the base run. With the corresponding value of α (4.58) determined from (7), the approximating function for optimal δ differs little in graphical form from that shown by the dashed line in Fig. 1. While

TABLE I

Computer Processing Statistics for Comparing Direct Integration of (15) with Integration of Transformed Equation for $0 \leqslant t/T \leqslant 1$, Using Several Values of δ

$\delta \times 10^3$	0.300	0.350	0.375	0.400	0.425	0.450	0.500	Base run
CPs	Integration aborted	0.258	0.276	0.219	0.258	0.234	Integration aborted	0.298
Steps		432	466	365	426	394		538
NFE		901	930	751	845	826		1085
NJE		133	172	113	159	104		114

some values of δ led to aborted integrations, all full-term integrations using t' as the independent variable ran faster than did the base run.

A five-day integration was carried out using the original equation and the transformed equation with the optimum δ. The run data are presented in Table II. While the percent saving achieved for the first 24 hr period is not maintained over the full five-day period, an overall 17.5 % reduction in the number of steps is realized along with a 16.9 % reduction in processing time. By adjustment of the arbitrarily chosen initial step size, further runs produced yet greater reduction in steps with up to 20.8 % reduction in run time (CPs = 1.288).

TABLE II

Computer Processing Statistics for Comparing Direct Integration of (15) With Integration of Transformed Equation Over a Five-Day Period

	$\delta = 0.4 \times 10^{-3}$			Base run		
Day	NSTEPS	NFE	NJE	NSTEPS	NFE	NJE
1	432	843	171	591	1154	160
2	526	1031	206	595	1146	143
3	511	949	241	633	1200	211
4	497	982	206	607	1167	153
5	517	1012	203	582	1136	173
Total	2483	4817	1027	3008	5803	840
CPs		1.352			1.627	

While the actual variation of t' with n can in no way be considered linear in the above experiment, the transformation does supply considerable uniformity by cutting the range of step size from six (decimal) orders of magnitude in the t formulation to but three or four orders of magnitude in the t' formulation.

From Fig. 1 it is seen that the fitted curve is in poor agreement with the actual data in the region near $n = n_m$ (noontime) where the curve rises sharply, suggesting that α should take on a larger value to increase the slope of the approximating function. Accordingly, the parameters were rederived by fitting the function (4) at $n = 1$ and $n = \tilde{n}$ where $t(\tilde{n})/T = 0.25$, $\tilde{n}$ ($= 267$) lying close to n_m. This fit gives much better agreement near noontime, but results in a small negative value of δ for which $t'(0)$ is not defined. Nevertheless, starting at $t = \tau$, integration of the transformed system was carried out using the recomputed value of δ with the result that little efficiency was gained (total CPs = 0.281 for the initial 12-hr period). The result suggests that it is more advantageous to determine the approximation parameters in such a way as to arrive at a close fit in the periods near sunrise and sunset where the step size is smallest.

From Table II it is seen that for each day, solution of the transformed system entails more Jacobian evaluations than does the base run. The Jacobian matrix, as part of the Newton iteration matrix, is updated if the product of step size and the leading coefficient of the multistep method is changed significantly; an update also occurs if the Jacobian varies so much that reevaluation is needed to achieve convergence of the iterative solution procedure. For the idealized problem at hand, the Jacobian matrix is constant in the original t-formulation, so that updates occur only as a result of step size and order changes. In the t'-formulation, however, the Jacobian varies in proportion to $\phi[t(t')]$. A possible explanation for the increased number of NJE's is that the greater variation in the Jacobian more than offsets the reduced variation in step size in determining the number of updates required to solve the transformed equation.

In the unsuccessful runs indicated in Table I, the specified accuracy could not be maintained. Both aborted runs terminated just before sunset with the integrator attempting to use the scheme of highest order (viz., fifth order). Full-term integrations were achieved by increasing the error tolerance from 0.1×10^{-6} to 0.1×10^{-4} for $\delta = 0.5 \times 10^{-3}$ and to 0.1×10^{-2} for $\delta = 0.3 \times 10^{-3}$.

The occurrence of the aborted runs suggests the possibility that transformations may be found to provide successful integration in a new variable t' for cases in which the initial run in t is aborted. As long as the initial run terminates at a value of $t \geqslant$ noontime, all parameters required by the above transformation technique are available to determine a more uniformly varying independent variable. As in the above experiments, the parameters may be varied but here with the primary aim of achieving a full-term integration.

The second test problem [10] involves the Chapman mechanism for ozone kinetics: the governing equations are of the form

$$\dot{c}^1(t) = -k_1 c^1(t)\, c^3 - k_2 c^1(t)\, c^2(t) + 2k_3(t)\, c^3 + k_4(t)\, c^2(t), \tag{18}$$

$$\dot{c}^2(t) = k_1 c^1(t)\, c^3 - k_2 c^1(t)\, c^2(t) - k_4(t)\, c^2(t), \qquad 0 \leqslant t \leqslant 10T \tag{19}$$

with initial conditions

$$c^1(0) = 10^6, \qquad c^2(0) = 10^{12}, \tag{20}$$

where

$$k_1 = 1.63 \times 10^{-16}, \qquad k_2 = 4.66 \times 10^{-16},$$

$$k_i = \begin{cases} \exp(-\gamma_i/\sin \omega t), & \sin \omega t > 0 \\ 0, & \sin \omega t \leqslant 0 \end{cases} \qquad i = 3, 4$$

and

$$\gamma_3 = 22.62, \qquad \gamma_4 = 7.601, \qquad c^3 = 3.7 \times 10^{16}, \qquad \omega = \pi/T.$$

Here c^1 denotes the concentration of the oxygen atom (O), c^2 the concentration of ozone (O_3), and c^3 (assumed constant) the concentration of oxygen (O_2). Once again the diurnal functions, used to represent photochemical reactions, are nearly square waves that increase rapidly at dawn, vary little during the daytime ($\sin \omega t > 0$) with a flat maximum at noon, and drop sharply to zero at sunset.

The linearization of (18) and (19) gives rise to two eigenvalues and hence two time constants, the smaller of which is about $\frac{1}{6}$ sec; the system is considered stiff and hence was solved with the same stiff-system integrator that was used in the preceding example. For this example, however, the error in c^i ($i = 1, 2$) at time $t(n)$ was controlled relative to $\max\{| c^i |, 10^{-20}\}$ using the latest computed values of c^1, c^2. The floor value of 10^{-20} was included to allow meaningful error control during those time periods when the concentration of O drops to extremely small values. While this test problem is more physically realistic than the first with regard to the interaction among the various species, the first problem with its extremely small time constant is perhaps more (numerically) representative of many diurnal kinetic processes.

Integration of (18) and (19) over five days reveals an unexpected pitfall; viz., due to the initial conditions used, the first cycle is atypical of the remaining days. (After the first day, the concentration of O is $\leqslant 1$ at sunup.) Accordingly, the second day was taken as the representative period from which to estimate the transformation parameters. The variation of t/T with time step for $2 \leqslant t/T \leqslant 3$ is shown by the solid line in Fig. 3. The curve is similar to its counterpart in Fig. 1 except for the sudden rises near sunup and sunset. These jumps occur at times when c^1 falls below the floor value of 10^{-20}. The exceptional behavior near sunup complicates the parameter estimation procedure used in the preceding example since we do not wish to base our approximation upon an anomalous part of the curve. Accordingly, the parametric values were roughly estimated by considering that part of the curve for which $15 \leqslant n \leqslant 558$, where the function $t(n)$ exhibits regular behavior. With suitable modification of the approximating function (4) to account for the shortened intervals in t and n, the parametric values

$$\alpha = 1.85, \qquad \beta = 1.90, \qquad \delta = 0.1 \tag{21}$$

were obtained using the EPISODE-generated step size of $0.38 \times 10^{-3} T$ sec at $n = 15$ with $n_m = 256$. Substitution of the derived values in (4) results in the approximating function shown by the dashed line in Fig. 3.

Numerical integration of the transformed system over a two-day period reveals that exactly the same number of steps are required to carry the integration over the

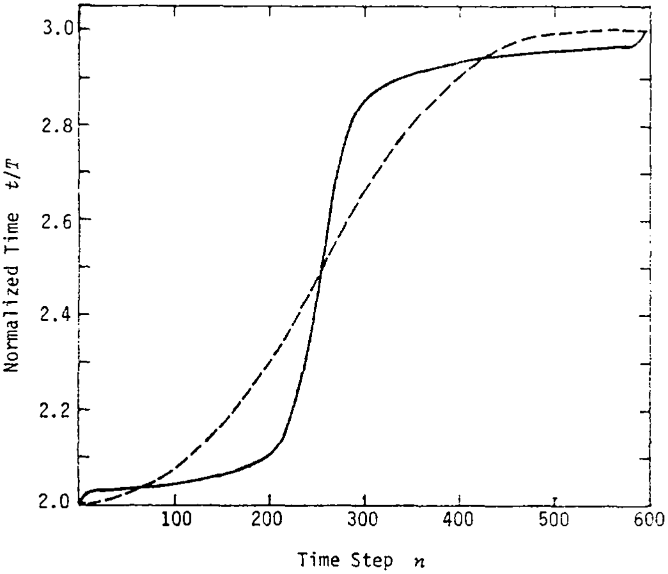

FIG. 3. Same as legend of Fig. 1 but with $2 \leqslant t/T \leqslant 3$ for the Chapman mechanism (18) and (19).

interval $2 \leqslant t/T \leqslant 3$ as are required in the base run for the same interval. The variation of t' with n is similar in character to the variation of t with n. A brief search using nearby values of δ, however, shows that some efficiency can be gained. Table III contains the run statistics for the second daylight period obtained by integrating the transformed system over the interval corresponding to $2 \leqslant t/T \leqslant 3$ using δ-values in the range 0.1 to 0.7. The base-run data are included for comparison. The results indicate an optimum δ of 0.5. Table IV contains the day-by-day run data for a five-day integration of both the transformed ($\delta = 0.5$) and original system. The transformation provides an overall 9 % saving in steps with a corresponding 6 % saving in processing time. The results suggest that the variable transformation technique should be more effective when applied to systems having numerical properties more akin to those of the first test problem.

TABLE III

Computer Processing Statistics for Comparing Direct Integration of (18) and (19) with Integration of Transformed System for $2 \leqslant t/T \leqslant 3$ Using Several Values of δ

δ	0.1	0.2	0.3	0.4	0.5	0.6	0.7	Base run
Steps	596	552	591	558	506	507	548	596
NFE	1088	972	1085	1000	909	929	973	1070
NJE	101	112	122	94	80	79	95	118

TABLE IV

Day-by-Day Computer Processing Statistics for Comparing Direct Integration of (18) and (19) with Integration of Transformed System for $0 \leqslant t/T \leqslant 10$ Using Optimum δ

	$\delta = 0.5$			Base run		
Day	NSTEPS	NFE	NJE	NSTEPS	NFE	NJE
1	893	1369	143	985	1556	176
2	520	927	94	608	1084	130
3	548	971	117	601	1073	116
4	542	945	102	599	1077	137
5	569	1017	140	584	1047	112
Total	3072	5229	596	3377	5837	671
CPs		1.945			2.073	

4. CONCLUSIONS

Some diurnal chemical kinetics problems such as those arising in stratospheric chemistry defy solution by standard numerical techniques due to the presence of short time constants and step-function-like reaction rates. Highly accurate and reasonably efficient solution to such problems can be achieved only by recently developed automatic step-changing, order-changing algorithms. Even the most advanced of these methods can require considerable computer time and can totally fail in some cases. Because of the periodic nature of the problem, the variation in the step size selected by the algorithm is approximately periodic. We propose to take advantage of this feature by determining an appropriate transformation of the independent variable based upon the behavior of the step size through one representative integration cycle and then solving the transformed system on all succeeding integration cycles. The transformation is chosen in such a way as to eliminate much of the variation in step size that occurs in the course of the integration since the use of a nearly uniform step size can significantly reduce computer time.

Only two test problems have been considered thus far but in each example a crude procedure for transforming the variable reduced computer time, in one case by about 21 %. Such reductions could be of importance when integrating large systems of coupled kinetics equations over long periods of time or when running three-dimensional dynamic–kinetic models of the stratosphere. The technique described here would be of particular value for verification of free-radical photochemistry by comparing model results with observations.

No doubt there are more effective transformations and better ways to determine the free parameters such as by least-squares approximations or by direct reference to the reaction rates that play such a large role in limiting the step size. The latter approach would be especially useful for the many photochemistry problems in which the rate constants are not accurately known. In these cases, the modeler often finds it necessary to perform a series of simulation runs in which the rate constants are varied over some range of values.

The present method is not intended to replace simpler approximation procedures that may offer satisfactory accuracy for a particular problem. This method, however, can be used to more efficiently evaluate such approximation procedures (e.g., equilibrium assumptions) by solving the particular system under consideration with and without the simplifying assumptions included. In cases where such simplifications prove acceptable and diurnal variation remains essential, the present method can be applied to the reduced system in succeeding experiments. While the reduction of computer time is worthwhile, the transformation technique would gain great importance if the method could be used to achieve successful integration when integration of the untransformed system leads to failure.

The purpose of this work is to point up the potential of the transformation technique for the type of problems discussed; the full power of the method is yet to be determined.

ACKNOWLEDGMENTS

This research was supported by the Atmospheric Sciences Section of the National Science Foundation under Grant ATM74-09959-A02. The author is especially grateful to referees Alan Hindmarsh and Brian Martin for their valuable suggestions that led to substantial improvement of the original paper. Thanks are also extended to Margaret G. Atticks for preparing the manuscript.

REFERENCES

1. R. J. GELINAS, Diurnal Kinetic Modeling, *in* "Proceedings of the International Conference on Structure, Composition and General Circulation of the Upper and Lower Atmospheres and Possible Antropogenic Perturbations," Vol. II, pp. 849–868, The International Association of Meteorology and Atmospheric Physics, Toronto, 1974.
2. R. J. GELINAS, *J. Computational Phys.* **9** (1972), 222–236.
3. R. C. WHITTEN AND R. P. TURCO, *J. Geophys. Res.* **79** (1974), 1302–1304.
4. B. MARTIN, *J. Atmospheric Sci.* **33** (1976), 131–134.
5. D. J. WUEBBLES AND J. S. CHANG, *J. Geophys. Res.* **80** (1975), 2637–2642.
6. F. T. KROGH, *SIAM J. Numer. Anal.* **10** (1973), 949–965.
7. G. D. BYRNE AND A. C. HINDMARSH, *ACM Trans. Math. Software* **1** (1975), 72–96.
8. R. K. BRAYTON, F. G. GUSTAVSON, AND G. D. HACHTEL, *Proc. IEEE* **60** (1972), 98–108.
9. C. W. GEAR, "Numerical Initial Value Problems in Ordinary Differential Equations," Prentice-Hall, Englewood Cliffs, N.J., 1971.
10. A. C. HINDMARSH AND G. D. BYRNE, Applications of EPISODE: An experimental package for the integration of systems of ordinary differential equations, *in* "Numerical Methods for Differential Systems, Recent Developments in Algorithms, Software and Applications" (L. Lapidus and W. E. Schiesser, Eds.), Academic Press, New York, 1976.

RECEIVED: June 19, 1978

PHILIP S. BROWN, JR.

The Center for the Environment and Man, Inc.,
275 Windsor Street, Hartford, Connecticut 06120