Approximation Method for Solution of Rate Equations in Homogeneous Reaction Field

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(Received May 1, 1990)

Analysis of a reaction mechanism by assembling the scheme with elementary reactions requires numerical solution of the reaction rate equations. The numerical procedure is time-consuming because of the stiffness of rate equations particularly when temperature varies with the reaction progress. This investigation proposed an approximation method which can save computational time for solving reaction rate equations in a homogeneous reaction field. The approximation method reduces the rate equations, which are a set of simultaneous differential equations, to independent differential equations for each species by simplifying the original equations according to the reaction characteristics; the resultant differential equations can be solved analytically within small time intervals. The validity of these differential equations was verified by comparing the obtained changes in temperature and the species concentrations in hydrogen combustion with those calculated from the original equations with the Runge-Kutta-Gill method.

The mechanism of a chemical reaction is usually investigated by either of the two ways: (1) an analytical approach where the reaction is decomposed into elementary reactions, and (2) a synthetic approach where it is assembled by using elementary reactions. The former is an experimental way where the reaction paths and their rates are determined in an actual system by measuring the concentration changes in chemical species, particularly active species by spectroscopic methods, for instance. When the rate constants of the elementary reactions possibly occurring in a system are known, on the other hand, the reaction rate equations of the species are expressed as the sums of the elementary reaction rates and both species concentration changes and the individual elementary reaction rates are calculated by integrating the rate equations; the reaction paths are thus determined also by the latter method. The rate equations are generally nonlinear, and in addition, they are a set of simultaneous differential equations. When the exothermicity and endothermicity of the reactions are not negligibly small and consequently temperature of the system is not kept constant like that in combustion reactions, one must calculate simultaneously not only the concentrations but also temperature. The rate equations unavoidably become too complicated to be solved directly by means of analytical methods and, therefore, must be solved numerically by using the Runge-Kutta-Gill or the Gear methods[1,2] for example.

The numerical solution of rate equations is time-consuming because these equations, particularly those of reactions occurring at high temperatures, are stiff. The purpose of this investigation is to propose a semi-analytical solution of rate equations in a homogeneous reaction field; the rate equation set of simultaneous differential equations are transformed into independent differential equations which are then solved analytically for the sequence of small time intervals.

Simulation Model

The following assumptions were taken in making the simulation model:

1. The system is isolated from its surroundings.
2. Temperature and the concentrations of chemical species are homogeneous throughout the system, just like those observed in well-stirred reactors. Since the gradients of temperature and the species concentrations are zero, the transport processes such as convection, diffusion, and conduction are not present.

According to the above assumptions, the basic equations derived under an isobaric condition, for instance, are

change in species concentrations:

$$\frac{\mathrm{d}c_n}{\mathrm{d}t}=\sum_i \nu_{ni}\phi_i \quad n=1,\cdots,N, \tag{1}$$

change in temperature:

$$C_p c\frac{\mathrm{d}T}{\mathrm{d}t}=\sum_i \phi_i h_i, \tag{2}$$

equation of state:

$$c=\frac{p}{RT}, \tag{3}$$

restriction condition:

$$c=\sum_n c_n, \tag{4}$$

where c is the total molar concentration; C_p the molar heat; T the temperature; ϕ_i the rate of the ith reaction; h_i the thermal energy released by the ith reaction; c_n the concentration of the nth species; ν_{ni} the stoichiometric coefficient of the nth species in the ith reaction; N the number of the chemical species participating in the reactions. The last equation gives the total concentration as the sum of the species concentrations.

Approximation Method

Temperature and species concentrations in a system can be predicted at an arbitrary time by solving Eqs. 1—4 when their initial values are given. Numerical procedures are capable of giving smooth solutions for the above equations. However, one strict condition must be satisfied to solve stably the rate equations. In solving Eq. 1 for a certain species by the Runge-Kutta-Gill method, for example, the time interval for the numerical integration is restricted such that the product of the time interval and the sum of the rates of the reactions in which the species participates does not exceed a critical value determined as a certain fraction of the concentration of the species concerned. The minimum value among the time intervals for each chemical species in the system, practically, is equal to the one determined for an active species; such species are present in small amounts but yield large reaction rates. In high-temperature reactions like combustion reactions, the time interval may be as small as 1—100 ns.

In this investigation, an approximation method is proposed for solving reaction rate equations. A set of simultaneous differential equations describing the concentration changes, Eq. 1, can be reduced to independent differential equations of each species contained in the time-derivative term if temperature and the concentrations of the species other than that in question can be expressed as functions of time; the time-dependent changes in temperature and the other species concentrations are here predicted in due consideration of the characteristics of chemical reactions. This method is, hence, composed of the three processes: (1) approximation of the time-dependent changes in temperature and species concentrations to functions of time, (2) transformation of the set of simultaneous differential equations into independent differential equations by use of the above approximate functions, and (3) solution of the resultant differential equations, which can be solved analytically within a short time interval. We will describe the processes (2), (3), and then (1).

Species Concentrations. Since elementary reactions are unimolecular or bimolecular except recombination reactions with third bodies, the reaction rate equation of the nth species is actually expressed with either of the following equations:

$$\frac{\mathrm{d}c_n}{\mathrm{d}t}+f(T,c')c_n=g(T,c'), \tag{5}$$

$$\frac{\mathrm{d}c_n}{\mathrm{d}t}+f_1(T,c')c_n+f_2(T,c')c_n^2=g(T,c'), \tag{6}$$

where the concentrations of the other species are collectively expressed by c'. Equation 5 is a rate equation when the nth species is consumed only by unimolecular reactions, and Eq. 6 is one when it is consumed by both unimolecular and bimolecular reactions.

The rate constant, k, of an elementary reaction is generally expressed as

$$k=A\cdot T^n\cdot\exp\left(-\frac{E}{T}\right). \tag{7}$$

The term of T^n causes difficulties in mathematical treatments but less than 20% of reactions include this term in their rate expressions.[3] Then we eliminated the exponential term by the approximation of Eq. 7 to a simple Arrhenius expression by using a least-square method, which was applied to the logarithmic form of Eq. 7, for a certain temperature range. This approximation brought about errors of only around 2% for the most elementary reactions in the hydrogen and simple hydrocarbon combustion schemes and about 10% at maximum. These errors are small enough, since reaction constants themselves involve errors of about 10%.[3]

The time-dependent change in temperature of the system is assumed to be simply expressed as

$$T=T_0(1+\beta t), \tag{8}$$

within a small time interval, t. In this equation, T_0 is the temperature at t=0 and β is the increment factor for the temperature change during the time interval. When the time interval is chosen so that $\beta t\ll 1$,

$$\begin{aligned}\frac{1}{T}&=\frac{1}{T_0(1+\beta t)}\\&\approx\frac{1}{T_0}(1-\beta t)=\frac{1}{T_0}-\frac{\beta t}{T_0}.\end{aligned} \tag{9}$$

The substitution of Eq. 9 into Eq. 7 reduces the rate

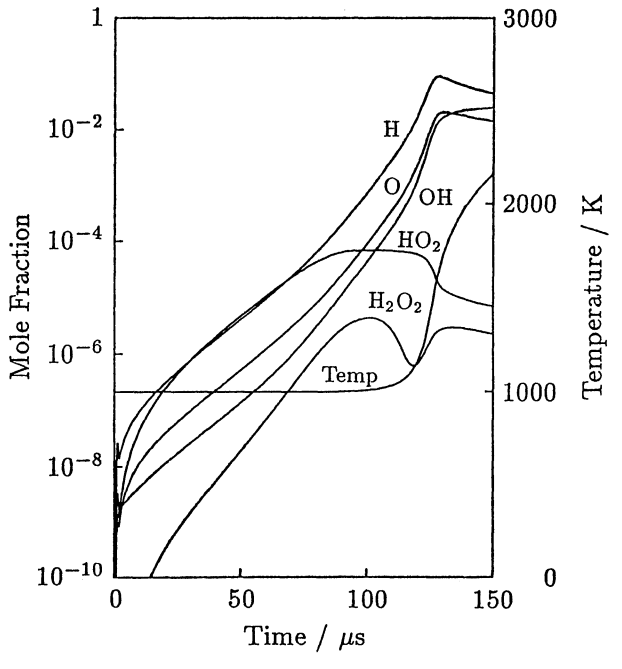

Fig. 1. Tim-dependent changes in temperature and chemical species in a stoichiometric hydrogen-air premixed gas. The initial temperature is 1000 K.

constants of all the reactions to functions of time as

$$\begin{aligned} k &= A\cdot\exp\left(-\frac{E}{T}\right) \\ &\approx A\cdot\exp\left(-\frac{E}{T_0}\right)\cdot\exp\left(\frac{E\beta t}{T_0}\right), \end{aligned} \tag{10}$$

during the time interval; in this equation A and E are not the same as those in Eq. 7 except the case of n=0.

Species concentrations approximately change along exponential curves through a chemical reaction as shown in Fig .1 as a typical example, if temperature does not largely vary during the reaction. The changes in the species concentrations and temperature shown in Fig. 1 were obtained by solving the governing equations, Eqs. 1—4, by means of the Runge-Kutta-Gill method. We accordingly assumed the changes in species concentrations during each time interval as

$$c_n = c_{n0}\cdot\exp(\alpha_n t), \tag{11}$$

where c_{n0} is the concentration of the n th species at t=0 and α_n is the increment factor for its concentration change during the time interval, t.

Equations 8 and 11 transform $f(T,c')$ and $g(T,c')$ of Eq. 5 into

$$f(T,c') = \sum_i k_i^1\cdot\exp(\gamma_i t), \tag{12}$$

$$g(T,c') = \sum_j k_j\cdot\exp(\delta_j t). \tag{13}$$

In these equations, k_i^1 and k_j are the rate constants of the i th and j th reactions, and are given as Eq. 14 by using the initial values of temperature and the species concentrations at t=0; the superscript 1 in k_i^1 indicates that the i th reaction is unimolecular as for the n th species (see also Eqs. 5 and 6).

$$\left.\begin{aligned} k_i^1 &= A_i\cdot\exp\left(-\frac{E_i}{T_0}\right)\cdot c_{10}^{\nu_{1i}}\cdot c_{20}^{\nu_{2i}}\cdots \\ k_j &= A_j\cdot\exp\left(-\frac{E_j}{T_0}\right)\cdot c_{10}^{\nu_{1j}}\cdot c_{20}^{\nu_{2j}}\cdots \end{aligned}\right\} \tag{14}$$

In Eq. 14, $\nu_{1i},\nu_{2i}\cdots$, and $\nu_{1j},\nu_{2j}\cdots$ are the stoichiometric coefficients of the first and the second species and so on, and equal 0, 1, or 2 depending on the number of the molecules participating in the i th and j th reactions, respectively. The constants in the exponentials of Eqs. 12 and 13 are given as

$$\left.\begin{aligned} \gamma_i &= \frac{E_i\beta}{T_0} + (\nu_{1i}\alpha_1 + \nu_{2i}\alpha_2 + \cdots) \\ \delta_j &= \frac{E_j\beta}{T_0} + (\nu_{1j}\alpha_1 + \nu_{2j}\alpha_2 + \cdots). \end{aligned}\right\} \tag{15}$$

According to Eqs. 12 and 13, both $f(T,c')$'s and $g(T,c')$'s of Eq. 5 are transformed into functions of only time interval, t, and thus Eq 5, which were originally a set of simultaneous differential equations of temperature and concentration of each species, are reduced to differential equations, each of which includes only one dependent variable, c_n:

$$\frac{\mathrm{d}c_n}{\mathrm{d}t} + p(t)\cdot c_n = q(t) \qquad n = 1,\cdots,N \tag{16}$$

where $p(t)$ and $q(t)$, emphasizing to be functions of t, correspond to the $f(T,c')$ and $g(T,c')$ of Eqs. 12 and 13, respectively. The ordinary differential equation 16 has a general solution of

$$c_n = \mathrm{e}^{-\int p(t)\mathrm{d}t}\left\{\int \mathrm{e}^{\int p(t)\mathrm{d}t} q(t)\mathrm{d}t + C\right\}, \tag{17}$$

where C is an integral constant.

Substitution of Eqs. 12 and 13 into Eq. 17 yields the analytical solution for each species concentration as follows. The integral contained in the exponential terms of Eq. 17 is

$$\int p(t)\mathrm{d}t = \int \sum_i k_i^1 \mathrm{e}^{\gamma_i t}\,\mathrm{d}t = \sum_i k_i^1\cdot\frac{\mathrm{e}^{\gamma_i t}}{\gamma_i}.$$

Since t is assumed to be small enough,

$$\mathrm{e}^{\gamma_i t} \approx 1 + \gamma_i t, \tag{18}$$

and the integral is then simplified as

$$\int p(t)\mathrm{d}t = \int \sum_i \frac{k_i^1 \mathrm{e}^{\gamma_i t}}{\gamma_i}\,\mathrm{d}t \approx \sum_i k_i^1\left(\frac{1}{\gamma_i} + t\right).$$

Therefore

$$\begin{aligned} \mathrm{e}^{\int p(t)\mathrm{d}t} q(t) &= \mathrm{e}^{\Sigma k_i^1\cdot(1/\gamma_i + t)}\cdot\sum_j k_j \mathrm{e}^{\delta_j t} \\ &= \sum_j k_j \mathrm{e}^{\Sigma k_i^1/\gamma_i}\cdot\mathrm{e}^{(\Sigma k_i^1 + \delta_j)t} \end{aligned}$$

and then

$$\begin{aligned} \int \mathrm{e}^{\int p(t)\mathrm{d}t} q(t)\mathrm{d}t &= \sum_j k_j \mathrm{e}^{\Sigma k_i^1/\gamma_i}\cdot\int \mathrm{e}^{(\Sigma k_i^1 + \delta_j)t}\mathrm{d}t \\ &= \sum_j \frac{k_j \mathrm{e}^{\Sigma k_i^1/\gamma_i}}{\sum k_i^1 + \delta_j}\cdot\mathrm{e}^{(\Sigma k_i^1 + \delta_j)t}. \end{aligned}$$

Equation 17 thus becomes

$$c_n = \sum_j \frac{k_j}{\sum k_i^1 + \delta_j}\cdot\mathrm{e}^{\delta_j t} + C\cdot\mathrm{e}^{-\Sigma k_i^1\cdot(1/\gamma_i + t)}. \tag{19}$$

The integral constant C of Eq. 19 is evaluated from the initial condition, that is, $c_n = c_{n0}$ when t=0, and finally the solution is given as

$$c_n = \sum_j \frac{k_j}{\sum k_i^1 + \delta_j}(\mathrm{e}^{\delta_j t} - \mathrm{e}^{-\Sigma k_i^1 t}) + c_{n0}\cdot\mathrm{e}^{-\Sigma k_i^1 t}. \tag{20}$$

As for the species which are consumed by both unimolecular and bimolecular reactions, the rate equation becomes

$$\frac{\mathrm{d}c_n}{\mathrm{d}t} + p_2(t)\cdot c_n^2 + p_1(t)\cdot c_n = q(t) \tag{21}$$

under the assumptions of Eqs. 8 and 11. This Riccati-type differential equation generally cannot be solved with any integration methods. Therefore, we linearized the c_n^2 term as follows based on the assumption of small time intervals:

$$\begin{aligned} c_n^2 &= (c_{n0} + \Delta c_n)^2 = c_{n0}^2 + 2c_{n0}\Delta c_n + (\Delta c_n)^2 \\ &\approx c_{n0}^2 + 2c_{n0}\Delta c_n = 2c_{n0}c_n - c_{n0}^2 \end{aligned} \tag{22}$$

where Δc_n is the concentration increment of the n th species during the time interval. The substitution of Eq. 22 into Eq. 21 gives the differential equation of the same type as Eq. 16,

$$\frac{\mathrm{d}c_n}{\mathrm{d}t}+\{2c_{n0}p_2(t)+p_1(t)\}\cdot c_n=q(t)+c_{n0}^2p_2(t), \qquad (23)$$

though the terms corresponding to $p(t)$ and $q(t)$ in Eq. 16 are much complicated here. The analytical solution of this equation is obtained by the same procedure as the derivation of Eq. 20 for Eq. 16

$$\begin{aligned}c_n=&\sum_j\frac{k_j}{\sum k_i^1+2c_{n0}\sum k_l^2+\delta_j}(\mathrm{e}^{\delta_j t}-\mathrm{e}^{-\sum k_i^1 t}\cdot\mathrm{e}^{-2c_{n0}\sum k_l^2 t})\\&+c_{n0}^2\sum_l\frac{k_l^2}{\sum k_i^1+2c_{n0}\sum k_l^2+\gamma_l}(\mathrm{e}^{\gamma_l t}-\mathrm{e}^{-\sum k_i^1 t}\cdot\mathrm{e}^{-2c_{n0}\sum k_l^2 t}) \qquad (24)\\&+c_{n0}\cdot\mathrm{e}^{-\sum k_i^1 t}\cdot\mathrm{e}^{-2c_{n0}\sum k_l^2 t}.\end{aligned}$$

where the subscript l and the superscript 2 in k_l^2 indicate that the l th reaction is bimolecular regarding the n th species.

Eventually, the rate equations 5 and 6 are both transformed to independent differential equations, and their analytical solutions are given as Eqs. 20 and 24, respectively, if the parameters, $\alpha_1,\alpha_2,\cdots$ and β are correctly preestimated for the variations in the species concentrations and temperature during the time interval in which the dependent variables are calculated.

Temperature. The time-dependent temperature change is basically given by Eq. 2, which can also be transformed into a differential equation having only one dependent variable, T, by using the assumptions of Eq. 8 and 11 in a similar manner described above. However, we can alternatively use the relation of the conservation of enthalpy per unit mass of gas mixture:

$$\sum_n(\Delta H_n+h_{fn})\cdot\frac{c_n}{\rho}=\text{const.} \qquad (25)$$

In this equation, ΔH_n and h_{fn} are the amount of enthalpy depending on the temperature difference from the standard temperature and the heat of formation of the n th species, respectively, and ρ is the density of the gas mixture. Since only ΔH_n is a function of temperature and the others are constants or given as known values at the time in question, Eq. 25 is considered to be an algebraic equation for temperature, and hence the temperature at that time is obtained by solving this equation. Some thermochemical data such as the JANAF data[4)] are available for the expansion of enthalpies as functions of temperature.

Prediction of the Increment Factors. The increment factors for species concentrations and temperature, α_n and β, respectively, for the coming time interval must be determined before the calculations for that time interval, though they are expected to be almost constant at least for some successive time intervals. There could be two ways in the prediction of the increment factors: (1) one calculates provisionally temperature and species concentrations by use of the increment factors for the previous time interval, reestimates the factors based on these values and calculates again temperature and the concentrations using the recalculated factors; (2) one predicts directly the increment factors for the coming time interval by extrapolating the values which have been calculated for the past time intervals. The method (1) can be described with a simple algorithm and saves computer memory though it may take a long computational time. We will explain the second method.

Equations 11 and 8 can also be written in the form

$$\alpha_n=\frac{1}{t}\ln\frac{c_n}{c_{n0}} \qquad (26)$$

$$\beta=\frac{T-T_0}{T_0 t}. \qquad (27)$$

Under the assumption that α_n's and β are expressed with quadratic functions of time, the coefficients of the equations for the increment factors were determined by the least square method for the latest sequence of ten time intervals, for example (too few time intervals would cause lack of smoothness and too many would cause lack of time resolution for the changes in temperature and species concentrations), and their new values were evaluated by extrapolation of the equations for the next time interval.

The increment factors cannot be obtained at the beginning of the calculation because no data are available for the extrapolation. A usual numerical integration such as the Runge-Kutta-Gill method may be applied or all the increment factors, for convenience, may be set to unity during the first several time intervals until the extrapolations become possible by the least square method.

Verification of the Approximation Method

We applied this approximation method to the calculations of time-dependent changes in the species concentrations and temperature in a stoichiometric hydrogen-air premixed gas under the constant pressure of 1.01325×10^5 Pa and with the initial temperature of 1000 K; the elementary reactions assumed to occur are tabulated in Table 1 together with their rate data; the species present in the system are OH, H, O, HO_2, H_2O_2, H_2O, H_2, O_2, and N_2; nitrogen is inert and works only as a diluent.

The simulation results were compared with those obtained by the Runge-Kutta-Gill method and the Gear method. Figure 2 shows the changes in the stable and active species and that in temperature, and, for instance, those changes calculated by the Runge-Kutta-Gill method. In the approximation method the prediction of the increment factors was done according to the method (2) described above, though the method (1) gave almost the same results.

Table 1. Hydrogen-Oxygen Reaction Scheme
$k=AT^n\exp(-E/T)$[a]

No.	Reaction	A	n	E	Ref.
R1	$H_2+O_2 \rightarrow OH+OH$	2.50E06	0.0	19600.0	3
R2	$H+O_2 \rightarrow OH+O$	2.20E08	0.0	8450.0	3
R3	$O+H_2 \rightarrow OH+H$	1.80E04	1.0	4480.0	3
R4	$OH+OH \rightarrow O+H_2O$	6.30E06	0.0	550.0	3
R5	$OH+H_2 \rightarrow H+H_2O$	2.20E07	0.0	2590.0	3
R6	$H+H+M \rightarrow H_2+M$	2.60E06	−1.0	0.0	3
R7	$O+O+M \rightarrow O_2+M$	1.90E01	0.0	−900.0	3
R8	$H+O+M \rightarrow OH+M$	3.60E06	−1.0	0.0	5
R9	$OH+H+M \rightarrow H_2O+M$	4.06E10	−2.0	0.0	3
R10	$H+O_2+M \rightarrow HO_2+M$	5.00E03	0.0	−500.0	3
R11	$H+HO_2 \rightarrow H_2+O_2$	2.50E07	0.0	350.0	3
R12	$H+HO_2 \rightarrow OH+OH$	2.50E08	0.0	950.0	3
R13	$H+HO_2 \rightarrow O+H_2O$	9.00E05	0.5	2000.0	3
R14	$OH+HO_2 \rightarrow H_2O+O_2$	5.00E07	0.0	500.0	6
R15	$O+HO_2 \rightarrow OH+O_2$	6.30E07	0.0	350.0	7
R16	$HO_2+H_2 \rightarrow H+H_2O_2$	7.30E05	0.0	9400.0	3
R17	$HO_2+HO_2 \rightarrow H_2O_2+O_2$	8.50E06	0.0	500.0	3
R18	$OH+H_2O_2 \rightarrow HO_2+H_2O$	1.00E07	0.0	910.0	3
R19	$H+H_2O_2 \rightarrow OH+H_2O$	2.20E09	0.0	5900.0	3
R20	$O+H_2O_2 \rightarrow OH+HO_2$	2.80E07	0.0	3200.0	3
R21	$H_2O_2+M \rightarrow OH+OH+M$	1.20E11	0.0	22900.0	3

a) The rate constants are expressed in m · mol · s units.

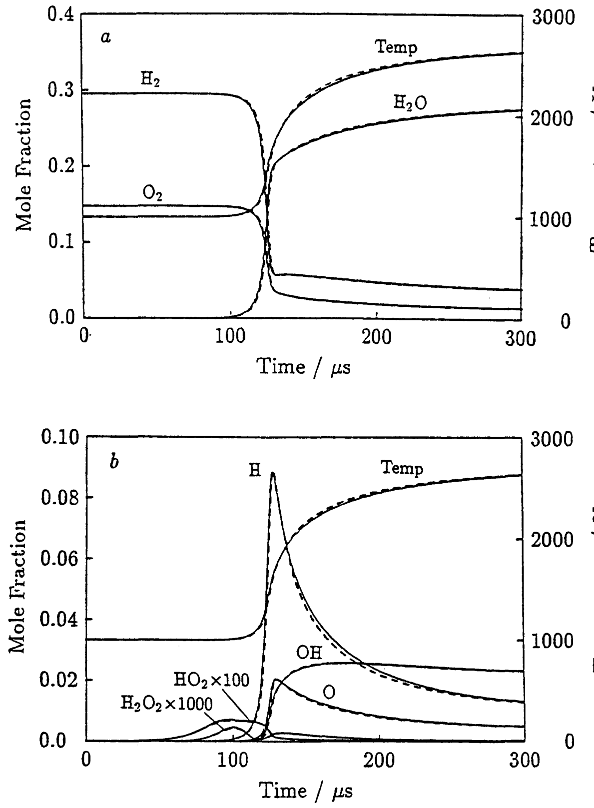

Fig. 2. Comparison of the time-dependent changes in temperature and the concentrations of stable (a) and active (b) species in a stoichiometric hydrogen-air premixed gas. The simulation started from 1000 K by using the approximation method (solid lines) and the Runge-Kutta-Gill method (broken lines).

The changes in the species concentrations and temperature obtained by the two different method are in good agreement. The validity of the proposed method was consequently confirmed. The time interval, t, is prescribed by Eqs. 7, 11, 18, and also 22. These equations are valid when t is reduced so that the maximum value of $\alpha_n t$ and βt does not exceed 1—2%; the time interval was varied from 10 ns to 1 μs in the approximation method, while in the Runge-Kutta-Gill method it was 10 ns. The computational speed of the approximation method is 18—120 times as large as that of the Runge-Kutta-Gill method, and 0.52—2.7 times as large as that of the Gear method.

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