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New Integration Techniques for Chemical Kinetic Rate Equations II—Accuracy Comparison

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NEW INTEGRATION TECHNIQUES FOR CHEMICAL KINETIC RATE EQUATIONS
II - ACCURACY COMPARISON

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ABSTRACT

A comparison of the accuracy of several techniques recently developed for solving stiff differential equations is presented. The techniques examined include two general-purpose codes EPISODE and LSODE developed for an arbitrary system of ordinary differential equations, and three specialized codes CHEMEQ, CREK1D and GCKP84 developed specifically to solve chemical kinetic rate equations. The accuracy comparisons are made by applying these solution procedures to two practical combustion kinetics problems. Both problems describe adiabatic, homogeneous, gas-phase chemical reactions at constant pressure, and include all three combustion regimes: induction, heat release and equilibration. The comparisons show that LSODE is the most efficient code - in the sense that it requires the least computational work to attain a specified accuracy level - currently available for chemical kinetic rate equations. An important finding is that an iterative solution of the algebraic enthalpy conservation equation for the temperature can be more accurate and efficient than computing the temperature by integrating its time derivative.

NOMENCLATURE

ATOL   absolute error tolerance for species mole numbers

CPU   total computer time required on IBM 370/3033 computer, sec

$c_{p,i}$ constant-pressure molal-specific heat of species i, J/kmol K

E_{rms} mean integrated global root-mean-square error (Eq. (7))

EPS   for all methods, except EPISODE, local relative error tolerance; for EPISODE: local relative error tolerance for species with initially non-zero mole numbers and for the temperature, and local absolute error tolerance for species with initially zero mole numbers.

ERMAX   relative error tolerance for Newton-Raphson iteration for temperature

e_i error in ith species mole fraction, (Eq. (4))

e_{rms} root-mean-square error in species mole fractions and temperature (eq. (6))

e_T error in temperature (Eq. (5))

f_i net rate of formation of species i (Eq. (1)), kmole i/kg mixture sec

H0   initial steplength to be attempted by integrator, sec

h_i molal-specific enthalpy of species i, J/kmol

h_0 mass-specific enthalpy of mixture, J/kg

NS   total number of distinct chemical species in mixture

n_i mole number of species i, kmole i/kg mixture

T   temperature, K

T_{ST} standard solution for temperature, K

t   time, sec

Y_i mole fraction of species i

$Y_{i,ST}$ standard solution for the mole fraction of species i

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INTRODUCTION

Many practical chemical reaction flow problems require the simultaneous solution of systems of coupled first-order ordinary differential equations (ode's). These ode's describe the time rate of change of species concentration and temperature. For species i ($i = 1,NS$) the governing ode can be written as

$$\frac{dn_i}{dt} = f_i(n_k,T); \qquad i,k = 1, NS$$

$$n_i(t=0) = \text{given} \qquad (1)$$

$$T(t=0) = \text{given}$$

where, n_i is the mole number of species i (kmole i/kg mixture); t is the time (s), T is the temperature (K); f_i is the net rate of formation of species i (kmole i/kg mixture/sec) due to all forward and reverse reactions in which species i participates; and NS is the total number of distinct chemical species in the gas mixture.

The initial value problem is to solve the system of Eqs. (1) for the chemical composition (i.e., n_i, $i = 1$, NS) and temperature at the end of a specified time interval, given the initial conditions and the reaction mechanism. Classical methods such as the popular explicit Runge-Kutta method require prohibitive amounts of computer time to solve large sets of chemical kinetic rate equations (1-4). This is due to the extremely small steplengths that classical methods have to use to satisfy stability requirements. Stable differential equations that impose severe step-length limitations on numerical integration routines are classified as stiff differential equations (e.g., 5,6).

Several solution techniques have been proposed and developed for stiff systems of ode's. In Part I of this effort and other recent publications (1-4), the computational work required by several recently developed routines in solving chemical kinetic rate equations has been examined in detail. In the present paper we compare their accuracy. The techniques examined in these studies include the general-purpose packages EPISODE and LSODE (7-9), developed as multi-purpose stiff differential equation solvers, and the specialized methods CHEMEQ (10), CREK1D (11,12) and GCKP84 (13,14), all of which have been developed specifically for chemical kinetics applications. These solution procedures are summarized in Table I and discussed in more detail in Ref. (3).

All of the above numerical methods are step-by-step methods (i.e., they compute approximations to the exact solutions of the ode's at discrete points in time). They limit the estimated local truncation error (i.e., estimates of the error incurred over one time step) to be less than a user-supplied local error tolerance. However, the quantity that is of interest to the user is the global (i.e., actual) error incurred by a technique in solving the problem. In the present paper, which is based on a recent critical analysis of the accuracy of the above techniques (15), we provide an estimate of the mean global error and examine its variation with the user-supplied local error tolerance (EPS) for two practical combustion kinetics problems. We also study the computational cost (expressed as the computer time required) associated with attaining desired accuracy levels.

The motivation for this work is the increasing interest in both multidimensional modeling of chemically reacting flows and in developing detailed reaction mechanisms for the combustion of fuels and pollutant formation and destruction. Computational speed is of primary concern in the former application and moderate accuracy is adequate (10-12). However, for developing and validating reaction mechanisms accuracy is of critical importance.

EVALUATION OF TEMPERATURE

The routines GCKP84 and CREK1D have been developed specifically for nonisothermal combustion rate equations and therefore include calculation procedures for the temperature. For the other techniques, however, the temperature had to be solved for along with the composition. This was done using one of two different methods (A and B) described below.

In the present work, as in Part I, attention is restricted to adiabatic, homogeneous, gas-phase chemical reactions at constant pressure. For such reactions, the following enthalpy conservation equation

$$\sum_{i=1}^{NS} n_i h_i = h_o = \text{constant} \qquad (2)$$

is an algebraic constraint on the species rate equations. In Eq. (2), h_i is the molal-specific enthalpy of species i (J/kmol i) and h_o is the mass-specific enthalpy of the gas mixture (J/kg). In method A the temperature was calculated from the solution for the species mole numbers, n_i ($i = 1$, NS) using the initial mixture mass-specific enthalpy, Eq. (2) and a Newton-Raphson iteration technique with a user-supplied local relative error tolerance, ERMAX. The temperature was therefore not an explicit dependent variable and the integrator tracked only the solution for species mole numbers.

In method B the temperature was evaluated by solving its time-derivative obtained by differentiating Eq. (2) with respect to time, t

$$\frac{dT}{dt} = \frac{\sum\limits_{i=1}^{NS} f_i h_i}{\sum\limits_{i=1}^{NS} n_i c_{p,i}} \qquad (3)$$

where $c_{p,i}$ is the constant-pressure molal specific-heat of species i (J/kmol K). In this method the temperature was an explicit dependent variable and the integrator tracked the solutions for both the species mole numbers and the temperature.

TEST PROBLEMS

The accuracy of the techniques summarized in Table I was examined by application to two practical combustion kinetics problems. Both problems describe adiabatic, homogeneous, constant-pressure, transient, batch chemical reaction and include all three combustion regimes: induction, heat release and equilibration.

Test problem 1 describes the ignition and subsequent combustion of a mixture of 33 percent carbon monoxide and 67 percent hydrogen with 100 percent

theoretical air at 10 atm and 1000 K initial tempera-
ture. It involves 12 reactions among 11 species.
Test problem 2, involving 30 reactions and 15 species,
describes the ignition and subsequent combustion of a
stoichiometric hydrogen-air mixture at 2 atm and
1500 K initial temperature. The reaction mechanisms
and rate constants for the two problems are given in
Ref. (3).

Figures 1 and 2 present the variation of the
species mole fractions and temperature with time for
test problems 1 and 2, respectively. Both problems
were integrated up to time t = 1 ms to obtain near-
equilibration of all chemical species and temperature.

COMPUTATIONAL PROCEDURE

The aim of the present work was to compare the
accuracy of currently available techniques in solving
chemical kinetic rate equations. In the absence of
exact solutions to the test problems, the only way to
assess the accuracy of a technique is by comparing
solutions generated with a particular value for the
local error tolerance (EPS) with those generated with
a reduced EPS, using either the same technique or a
different one. To prevent any bias in favor of one
technique, global errors for each technique were esti-
mated by comparing its solutions with those generated
by itself using a reduced EPS. For each technique and
test problem, the solution used as a basis of compar-
ison was the most accurate generated and is referred
to as its standard solution. For example, for CREK1D
standard solutions were generated with CREK1D and EPS
= 10^{-5}. These standard solutions were compared with
runs using CREK1D and EPS = 10^{-2}, 10^{-3}, and 10^{-4}
to assess the global errors incurred by the latter.

A typical computational run consisted of initial-
izing the time (t, set equal to zero), the species
mole numbers and the temperature. The integrator was
called with values for the necessary input parameters
including the local error tolerance (EPS) and the time
at which the integration was to be terminated (= 1 ms
for both problems). The values used for the other
input parameters, obtained in a previous study (3) by
a trial-and-error procedure, resulted in the least CPU
time for each technique and value of EPS. After each
step successfully executed by the code, values for the
time reached by the integrator and the species mole
fractions and temperature computed at that time were
saved. The values saved for the time served as input
data for the output stations at which the standard
solution was to be generated. The global errors in
the solutions for the species mole fractions and tem-
perature were estimated by comparisons with the stan-
dard solution values for these quantities as follows.

$$e_i(t) = \frac{Y_i(t)}{Y_{i,ST}(t)} - 1 \qquad (4)$$

$$e_T(t) = \frac{T(t)}{T_{ST}(t)} - 1 \qquad (5)$$

In Eqs. (4) and (5) $e_i(t)$ and $e_T(t)$ are, re-
spectively, the global errors at time t, in the mole
fraction, $Y_i(t)$, of species i and the temperature,
$T(t)$, $Y_{i,ST}(t)$ and $T_{ST}(t)$ are, respectively, the
standard solution values for the mole fraction of spe-
cies i and the temperature at time, t. The global
errors in species mole fractions and temperature and
the corresponding times were saved for later analysis.
In this way time histories of the errors in species

mole fractions and temperature were generated. De-
tailed plots of $e_i(t)$ and $e_T(t)$ are presented
in Ref. (15).

Standard Solutions. For consistency, standard
solutions were generated with the same value of EPS
(=10^{-5}) for all methods, except EPISODE. In con-
trast to the other routines for which EPS is the local
relative error tolerance, it is a mixed error toler-
ance for EPISODE - relative for species with initially
nonzero mole numbers (i.e., reactants) and for the
temperature; and absolute for species with initially
zero mole numbers (i.e., all intermediate species and
products) (15). EPISODE is therefore inferior to the
other codes - i.e., for a given value of EPS, it pro-
duces less accurate solutions (3,15). With EPISODE,
we have therefore used the smallest value of EPS
(=10^{-6}) that the single-precision version allowed.

All the techniques examined here required the
specification of several input parameters, in addition
to the local error tolerance, EPS. In generating
standard solutions for each technique, the values used
for the input parameters were those that resulted in
the most accurate solution - see Ref. (15) for de-
tails. For GCKP84, however, since details of the in-
tegration technique are not yet known, default values
were used for all parameters except the initial step-
length (HO) to be attempted by the ode solver. In our
previous work (1-3) with GCKP84, a default value of
HO = 10^{-6} s had been used. However, Bittker and
Scullin (14) have since then set the default value for
HO at 5×10^{-8} sec. We have, nevertheless, used HO
= 10^{-6} sec because it produced more accurate results.

RESULTS AND DISCUSSION

The procedure outlined in the section Computa-
tional Procedure was used to examine the global errors
incurred by all techniques in solving the two problems
described in the section Test Problems. All results
presented herein were obtained on the NASA Lewis
Research Center's IBM 370/3033 computer using single-
precision accuracy, except GCKP84 which was in
double-precision.

With LSODE, EPISODE and CHEMEQ, both temperature
methods A and B were attempted. The following naming
convention was used. Techniques using temperature
method A were given the suffix A (LSODE-A, EPISODE-A
and CHEMEQ-A) and those using temperature method B
were given the suffix B (LSODE-B, EPISODEB and
CHEMEQ-B). For consistency between the two methods,
ERMAX (the maximum local relative error allowed in the
temperature in method A) was set equal to EPS which is
approximately the maximum local relative error allowed
in the temperature in method B.

To facilitate accuracy comparisons, at each value
of the time where global errors had been evaluated
(and saved), the root-mean-square (rms) error, $e_{rms}(t)$
was computed using

$$e_{rms}(t) = \sqrt{\frac{\sum_{i=1}^{NS} e_i^2(t) + e_T^2(t)}{NS + 1}} \qquad (6)$$

To prevent the possibility of requiring accuracy
from species with immeasurably small concentrations,
the summation in Eq. (6) does not include species
whose standard solution mole fractions were less than

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0.1 ppm – for such species, $e_i(t)$ was set equal to zero.

The maximum percent root mean square error incurred by all techniques are given in Tables II and III, respectively, for test problems 1 and 2. Also given in these tables are the values used for the input parameters required by each method. These values, taken from Radhakrishnan (3), resulted in the least CPU time (CPU in Tables II and III) to solve the problem with the given value of EPS. In these tables, HO is the user-supplied value for the initial steplength to be attempted by the integrator, and ATOL is the absolute error tolerance for all species mole numbers – a value of zero was used for the absolute error tolerance for the temperature (required by LSODE-B).

For test problem 1, the run with GCKP84 and EPS $= 10^{-2}$ displayed serious instability and so was terminated. For values of EPS $\geq 5 \times 10^{-6}$, EPISODE-A and -B predicted little or no change from the initial composition or temperature after an elapsed time of 1 ms. Similar remarks apply to test problem 2 and the runs with EPISODE-A and EPS $\geq 5 \times 10^{-4}$ and those with EPISODE-B and EPS $\geq 5 \times 10^{-3}$. Although the runs with EPISODE-B and EPS $= 10^{-3}$ and 5×10^{-4} were successfully completed in that correct solutions were returned at t = 1 ms, they were significantly inaccurate during heat release. For example, the run with EPS $= 5 \times 10^{-4}$ predicted little or no change from the initial conditions until t $\approx$ 40 μs when heat release was predicted to start. In contrast, for the standard solution heat release is almost over by this time (Fig. 2).

Tables II and III show large variations in the maximum root mean square error incurred by the different techniques. GCKP84 and EPISODE experienced the greatest difficulty in tracking their standard solutions and maximum root mean square errors of over 100 percent were obtained with these codes. In contrast, the maximum errors incurred by CHEMEQ, CREK1D and LSODE were significantly smaller. Comparisons of the runs with the largest values of EPS show that LSODE was the most accurate code for test problem 1, and CREK1D for test problem 2.

The accuracy obtained with LSODE was strongly influenced by the value selected for ATOL (the absolute error tolerance for the species mole numbers). For problem 2 LSODE-A showed little sensitivity to changes in EPS, because all runs used the same ATOL (Table III). In contrast, the runs with LSODE-B showed decreased errors with reductions in EPS because of the use of smaller values of ATOL. Note the significant reduction in the maximum root mean square error obtained by decreasing ATOL from 10^{-8} to 10^{-12} for LSODE-B and EPS $= 10^{-4}$ (Table III). This decrease in the maximum error with a reduction in ATOL is further illustrated for problem 2 by the results presented in Table IV for LSODE-B and EPS $= 10^{-5}$. These results show that great care must be exercised in specifying values for ATOL. A poor guess for ATOL can result in significantly inaccurate solutions. The CPU time required by LSODE was also affected by ATOL. In general, a trial-and-error procedure was necessary to obtain the optimum value for ATOL – defined as that value which results in the least CPU time while satisfying prescribed accuracy requirements. This trial-and-error search – which can be time consuming, especially for large systems of ode's – for the optimum value for ATOL is the main difficulty associated with using LSODE for solving chemical kinetic rate equations. The use of extremely low values for ATOL

to ensure accuracy can result in excessively large CPU times. For example, for test problem 2 the run using LSODE-B with EPS $= 10^{-5}$ and ATOL $= 10^{-11}$ required about 3.4 sec CPU time; in contrast, the run with ATOL $= 10^{-15}$ required almost 20 sec although the solution was not significantly different. In addition, as discussed in Part I (4), the solution can be adversely affected by a poor choice for the output stations at which the solution is desired.

Tables II and III show also that the use of temperature method A does not result in significantly larger errors than those incurred by temperature method B. On the contrary, method A can be more accurate than method B – this difference in accuracy is most marked for CHEMEQ.

To provide a more comprehensive measure of the accuracy than the maximum root mean square error, we have adopted the following procedure. For each run a mean integrated root mean square error, E_{rms}, was calculated as follows:

$$E_{rms} = \frac{1}{t_{end}} \int_0^{t_{end}} e_{rms}(t) \, dt \qquad (7)$$

where t_{end} is the end of the prescribed time interval.

Equation (7) provides a single quantity that is a measure of the average error incurred in solving the complete problem. The integral was evaluated numerically using Simpson's rule modified for unequal step sizes.

Figures 3 and 4 present the variation of E_{rms} with the user-supplied local error tolerance, EPS. In addition, Table IV gives values of E_{rms} incurred by the different runs with LSODE-B and EPS $= 10^{-5}$ for test problem 2. These results illustrate the increasing accuracy obtained with reductions in ATOL and the significant errors that can be incurred by a poor guess for ATOL. Figures 3 and 4 show that all methods used in the present study are tolerance-effective (i.e., decreasing EPS results in reduced error). For both problems temperature method A is as accurate as method B – in many cases, it is significantly more accurate. For problem 2 and EPS $= 10^{-4}$, LSODE-B is more accurate than LSODE-A because of the smaller ATOL used.

Figures 3 and 4 illustrate the significant discrepancies between the values specified for EPS and the errors actually obtained. For example, for problem 1 a value of EPS $= 10^{-2}$ (1 percent) has resulted in an average error of almost 50 percent error for CHEMEQ-B. These plots show that for a given value of EPS, LSODE is the most accurate code currently available for solving chemical kinetic rate equations. However, GCKP84, CREK1D and CHEMEQ-A compare very favorably with LSODE for small values of EPS. EPISODE is significantly less accurate than the other codes because the error control used in it is inappropriate for chemical kinetics applications (3).

Figures 5 and 6 present the variation of the computational work (expressed as the CPU time in seconds required on the NASA Lewis Research Center's IBM 370/3033 computer) with the mean integrated error for test problems 1 and 2, respectively. For both problems the CPU times required by temperature method A are less than, or compare favorably with, those required by method B to attain the same accuracy levels. This

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difference is most pronounced for CHEMEQ and EPISODE. Note that for EPISODE-B the computational work increases with increasing error.

Figures 5 and 6 illustrate the large differences in the computational work required by the different techniques to attain comparable accuracy levels. For problem 1 and a one-half percent mean global error, the CPU time varies from about 0.37 sec for LSODE-A to over 40 sec for CHEMEQ-A. For problem 2 this difference is even greater. For both test problems LSODE is the most efficient code in the sense that it requires the least CPU time to attain a specified accuracy level.

For test problem 2 EPISODE-A compares very favorably with LSODE (Fig. 6). However, the solution generated by EPISODE was found to strongly depend on the value selected by the user for the initial steplength (HO) to be attempted by the integrator. A poor guess for HO can result in inaccurate and unstable solutions (1-4). It can also result in excessive CPU times. For example, the run using EPISODE-A with EPS = 10^{-4} and HO = 10^{-8} sec required almost 129 sec for problem 2; in contrast, the run with HO = 10^{-7} sec required only about 0.6 sec.

To attain the same accuracy level, CREK1D requires more CPU time than LSODE for both test problems. CREK1D is, however, attractive for the following reason. It is intended primarily for performing multidimensional calculations of chemically reacting flows by coupling it with a hydrodynamic equation solver. Currently available hydrodynamic codes are at best accurate to within a few percent, so generation of highly accurate chemical kinetic solutions is wasteful (10). For problem 1 CREK1D requires approximately 0.3 sec to produce a solution with a mean global error of about 5 percent, which is sufficiently accurate for multipoint calculations of reacting flows. This CPU time compares favorably with the 0.37 sec required by LSODE-A.

CONCLUSIONS

A comparison of the accuracy of several recently developed numerical techniques (GCKP84, CREK1D, LSODE, EPISODE, and CHEMEQ) in solving chemical kinetic rate equations has been made. This study has shown that LSODE is the most efficient code - in the sense that it requires the least CPU time to attain a specific accuracy level - currently available for solving chemical kinetic rate equations. The major difficulty associated with its use is the trial-and-error procedure necessary to obtain optimum values for the absolute error tolerances for the variables. A poor guess for the absolute error tolerance can result in excessive CPU times or in seriously inaccurate solutions. When accuracy is not of primary concern, as in multidimensional chemically reacting flow calculations, CREK1D is an attractive alternative to LSODE.

An important conclusion is that the use of an algebraic enthalpy conservation equation for calculating the temperature can be more accurate and efficient than evaluating the temperature by integrating its time-derivative.

REFERENCES

1. Radhakrishnan, K., "A Comparison of the Efficiency of Numerical Methods for Integrating Chemical Kinetic Rate Equations," NASA TM-83590, 1984.

2. Radhakrishnan, K., "Fast Algorithms for Combustion Kinetics Calculations: A Comparison," Combustion Fundamentals Research, NASA CP-2309, 1984, pp. 257-267.

3. Radhakrishnan, K., "Comparison of Numerical Techniques for Integration of Stiff Ordinary Differential Equations Arising in Combustion Chemistry," NASA TP-2372, 1984.

4. Radhakrishnan, K., "New Integration Techniques for Chemical Kinetic Rate Equations. I. Efficiency Comparison," (submitted for publication in Combustion Science and Technology).

5. Gelinas, R.J., "Stiff Systems of Kinetic Equations-A Practitioner's View," Journal of Computational Physics, Vol. 9, No. 4, Apr. 1972, pp. 222-236.

6. Pratt, D.T., and Radhakrishnan, K., "Physical and Numerical Sources of Computational Inefficiency in the Integration of Chemical Kinetic Rate Equations: Etiology, Treatment and Prognosis," (submitted for publication in Combustion and Flame).

7. Hindmarsh, A.C. and Byrne, G.D. "EPISODE: An Effective Package for the Integration of Systems of Ordinary Differential Equations," UCID-30112-Rev. 1, Lawrence Livermore Laboratory, 1977.

8. Hindmarsh, A.C., "LSODE and LSODI, Two New Initial Value Ordinary Differential Equation Solvers," SIGNUM Newsletter, Vol. 15, No. 4, Dec. 1980, pp. 10-11.

9. Hindmarsh, A.C., "ODEPACK, A Systematized Collection of ODE Solvers," UCRL-88007, Lawrence Livermore Laboratory, 1982.

10. Young, T.R., and Boris, J.P., "A Numerical Technique for Solving Stiff Ordinary Differential Equations Associated with the Chemical Kinetics of Reactive-Flow Problems," Journal of Physical Chemistry, Vol. 81, No. 25, Dec. 15, 1977, pp. 2424-2427.

11. Pratt, D.T., "CREK-1D: A Computer Code for Transient, Gas-Phase Combustion Kinetics," Proceedings, Spring Meeting of the Western States Section of the Combustion Institute, Paper WSCI 83-21, Apr. 1983.

12. Pratt, D.T., and Radhakrishnan, K., "CREK1D: A Computer Code for Transient, Gas-Phase Combustion Kinetics," NASA TM-83806, 1984.

13. Zeleznik, F.J., and McBride, B.J., "Modelling the Internal Combustion Engine," NASA RP-1094, 1984.

14. Bittker, D.A., and Scullin, V.J., "GCKP84 - General Chemical Kinetics Code for Gas-Phase Flow and Batch Processes Including Heat Transfer," NASA TP-2320, 1984.

15. Radhakrishnan, K., "A Critical Analysis of the Accuracy of Several Numerical Techniques for Chemical Kinetic Rate Equations," NASA TP, 1984.

TABLE I — SUMMARY OF SOLUTION PROCEDURES EXAMINED

Method	Description
GCKP84	Details not yet available
CREK1D	Variable-step, predictor-corrector method based on an exponentially fitted trapezoidal rule, includes filtering of ill-posed initial conditions and automatic selection of functional iteration or Newton iteration
LSODE EPISODE	Variable-step, variable-order backward differentiation method with a generalized Newton iteration[a]
CHEMEQ	Variable-step, second-order predictor-corrector method with an asymptotic integration formula for stiff equations

[a]Other options are included in these packages but this option was found to be the fastest for both problems, and is the only one considered in this work.

TABLE II — MAXIMUM PERCENT RMS ERRORS AND MINIMUM
CPU TIMES REQUIRED FOR TEST PROBLEM 1

Method	EPS	ATOL	HO, sec	Max rms error, percent	CPU, sec
GCKP84	[a]10^{-2}	-----	[b]10^{-6}	467 9	(a)
	5×10^{-3}	-----	[b]10^{-6}	467 9	86
	10^{-3}	-----	[b]10^{-6}	258 6	.98
	10^{-4}	-----	[b]10^{-6}	115 0	1.13
CREK1D	10^{-2}	-----	-----	30 79	27
	10^{-3}	-----	-----	7.218	.33
	10^{-4}	-----	-----	2 311	67
LSODE-A	10^{-2}	10^{-12}	-----	10.52	.37
	10^{-3}	10^{-11}	-----	8 596	.46
	10^{-4}	10^{-11}	-----	4.786	.63
LSODE-B	10^{-2}	10^{-12}	-----	10.57	40
	10^{-3}	10^{-11}	-----	8 167	.44
	10^{-4}	10^{-11}	-----	6 366	59
EPISODE-A	5×10^{-6}	-----	10^{-7}	825.7	.034
EPISODE-B	5×10^{-6}	-----	10^{-7}	825.9	.035
CHEMEQ-A	10^{-2}	-----	-----	34.47	15.1
	10^{-3}	-----	-----	6.580	28.4
	10^{-4}	-----	-----	.868	39 8
CHEMEQ-B	10^{-2}	-----	-----	57.61	15.5
	10^{-3}	-----	-----	19.48	22 7
	10^{-4}	-----	-----	2.219	36 5

[a]Terminated at t $\approx$ 3 7x10^{-5} sec because of problems
   with serious instability.
[b]Default value

TABLE III. – MAXIMUM PERCENT RMS ERRORS AND MINIMUM
CPU TIMES REQUIRED FOR TEST PROBLEM 2

Method	EPS	ATOL	HO, sec	Max rms error, percent	CPU, sec
GCKP84	10^{-2}	-----	$a10^{-6}$	227.2	1.85
	10^{-3}	-----	$a10^{-6}$	98.65	1.91
	10^{-4}	-----	$a10^{-6}$	21.76	2.44
CREK1D	10^{-2}	-----	-----	3.959	1 18
	10^{-3}	-----	-----	2.148	1.07
	10^{-4}	-----	-----	0.612	2.32
LSODE-A	10^{-2}	10^{-8}	-----	29.38	.54
	10^{-3}	10^{-8}	-----	27.37	.78
	10^{-4}	10^{-8}	-----	29.44	.94
LSODE-B	10^{-2}	10^{-8}	-----	30 53	.52
	10^{-3}	10^{-9}	-----	3.484	.94
	10^{-4}	10^{-8}	-----	$1 528 \times 10^{3}$	1.49
	10^{-4}	10^{-12}	-----	8.641	1.46
EPISODE-A	5×10^{-4}	-----	10^{-7}	290 4	065
	10^{-4}	-----	10^{-7}	121 8	.59
	10^{-5}	-----	10^{-6}	54 08	.78
EPISODE-B	5×10^{-4}	-----	10^{-10}	280.1	2.38
	10^{-4}	-----	10^{-11}	131 6	91
	10^{-5}	-----	10^{-9} `	78.31	.88
CHEMEQ-A	10^{-2}	-----	-----	26.97	37 7
	10^{-3}	-----	-----	2.133	47.3
	10^{-4}	-----	-----	.207	76.1
CHEMEQ-B	10^{-2}	-----	-----	23 80	36.3
	10^{-3}	-----	-----	4.631	43.0
	10^{-4}	-----	-----	2.341	87.6

aDefault value

TABLE IV. – EFFECTS OF ABSOLUTE ERROR
TOLERANCE FOR SPECIES MOLE NUM-
BERS (ATOL) ON MAXIMUM PERCENT
ROOT MEAN SQUARE ERROR,
MEAN INTEGRATED ROOT
MEAN SQUARE (E_{rms})
AND CPU TIME
[All results obtained with LSODE-B
and EPS=10^{-5} for problem 2.]

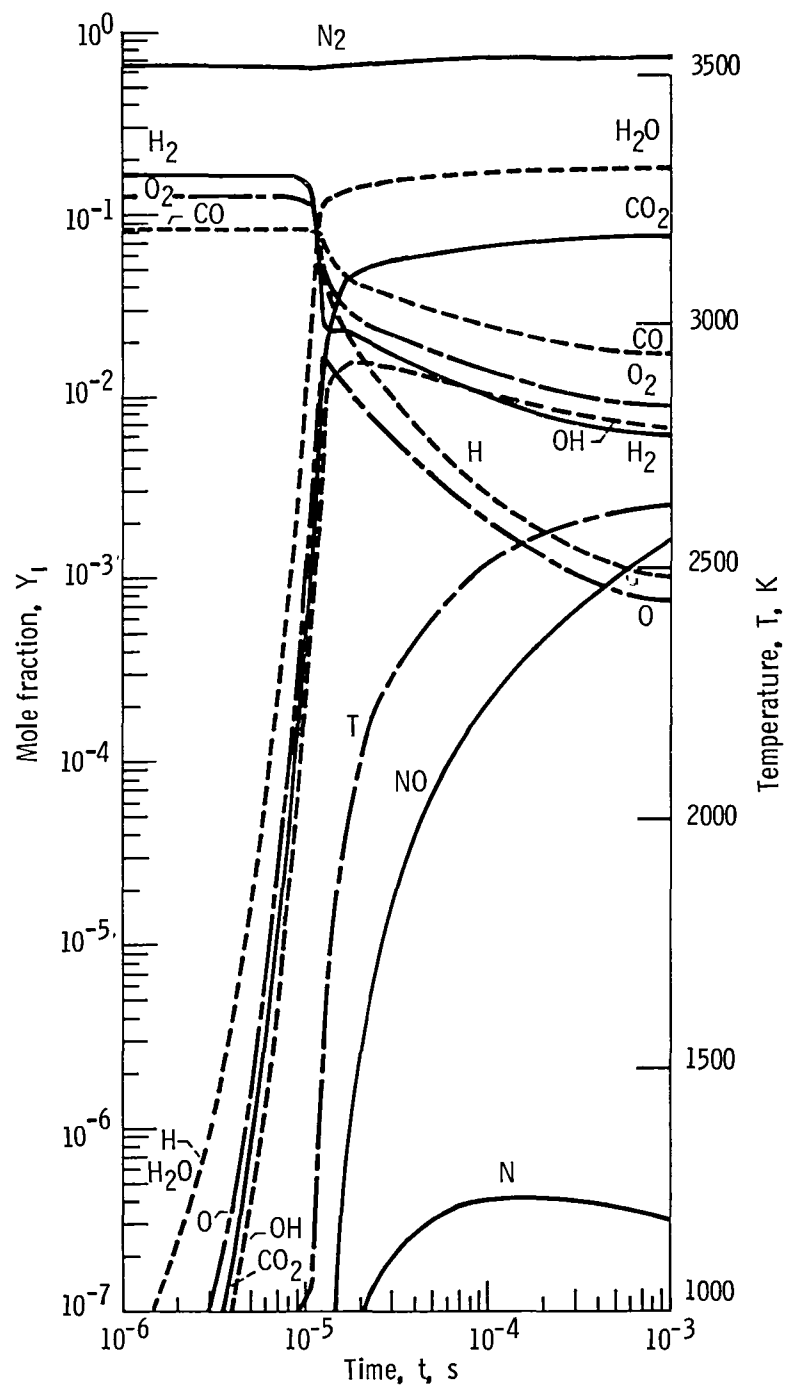| ATOL	Max rms error, (percent)	E_{rms}	CPU, (sec)
10^{-8}	$1 112 \times 10^{4}$	2.792×10^{-1}	4 17
10^{-9}	$2 022 \times 10^{3}$	4.011×10^{-2}	3 24
10^{-10}	20.25	9.421×10^{-4}	2.52

Figure 1. – Variation of temperature and species
mole fractions with time for test problem 1.
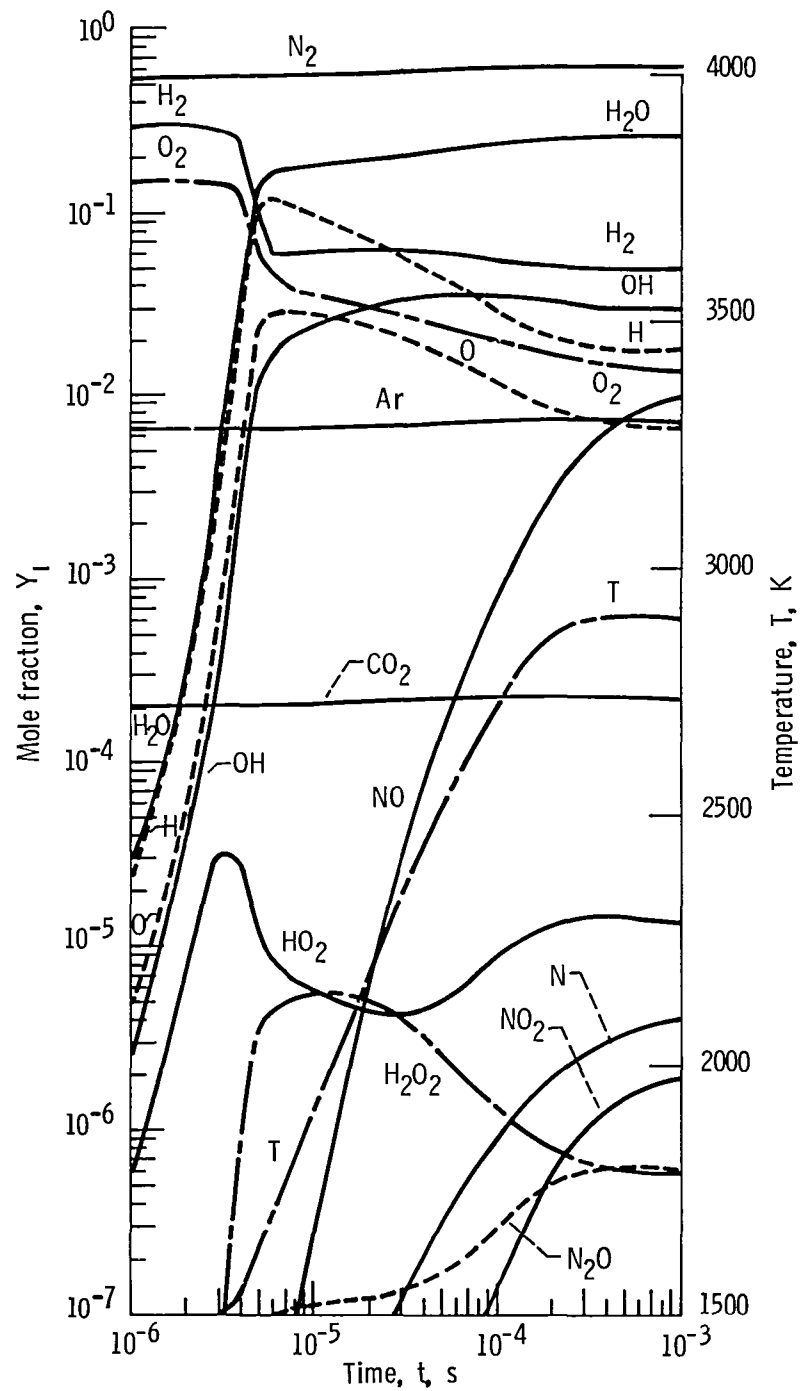Solution generated using LSODE-B with EPS =
10^{-5}.

Figure 2. - Variation of temperature and species mole fractions with time for test problem 2. Solution generated using LSODE-B with EPS = 10^{-5}.
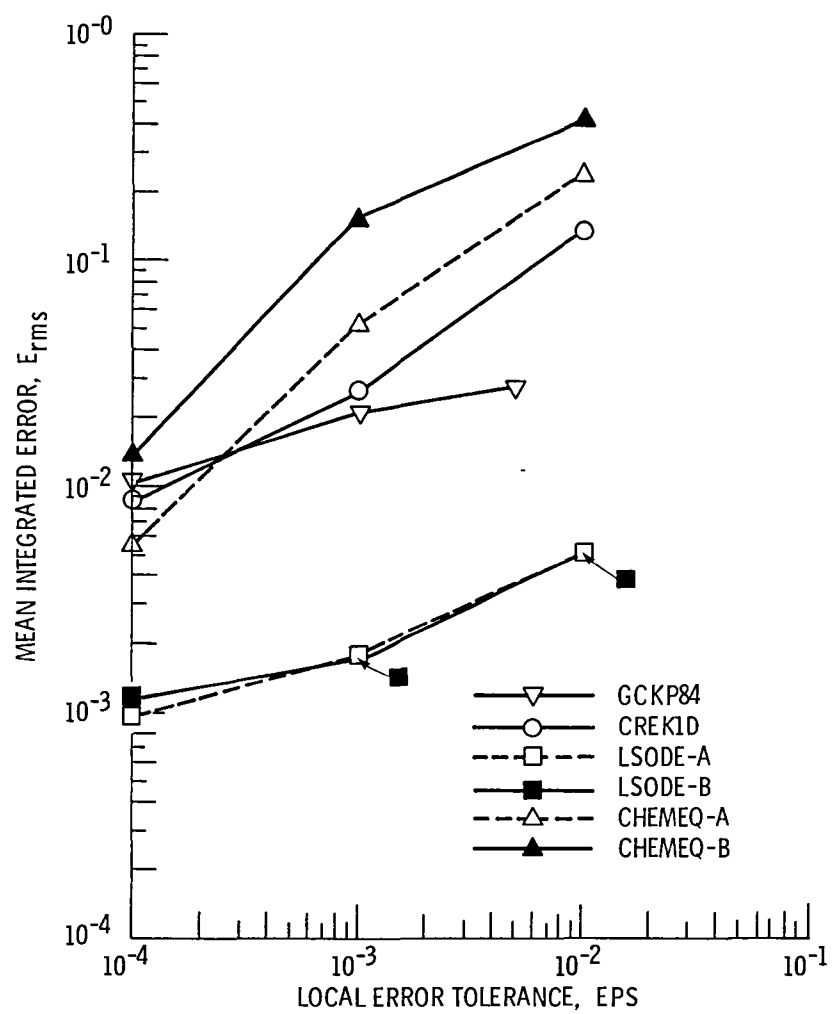
Figure 3. – Variation of the mean integrated global error (E_{rms}) with the local error tolerance (EPS) for test problem 1.
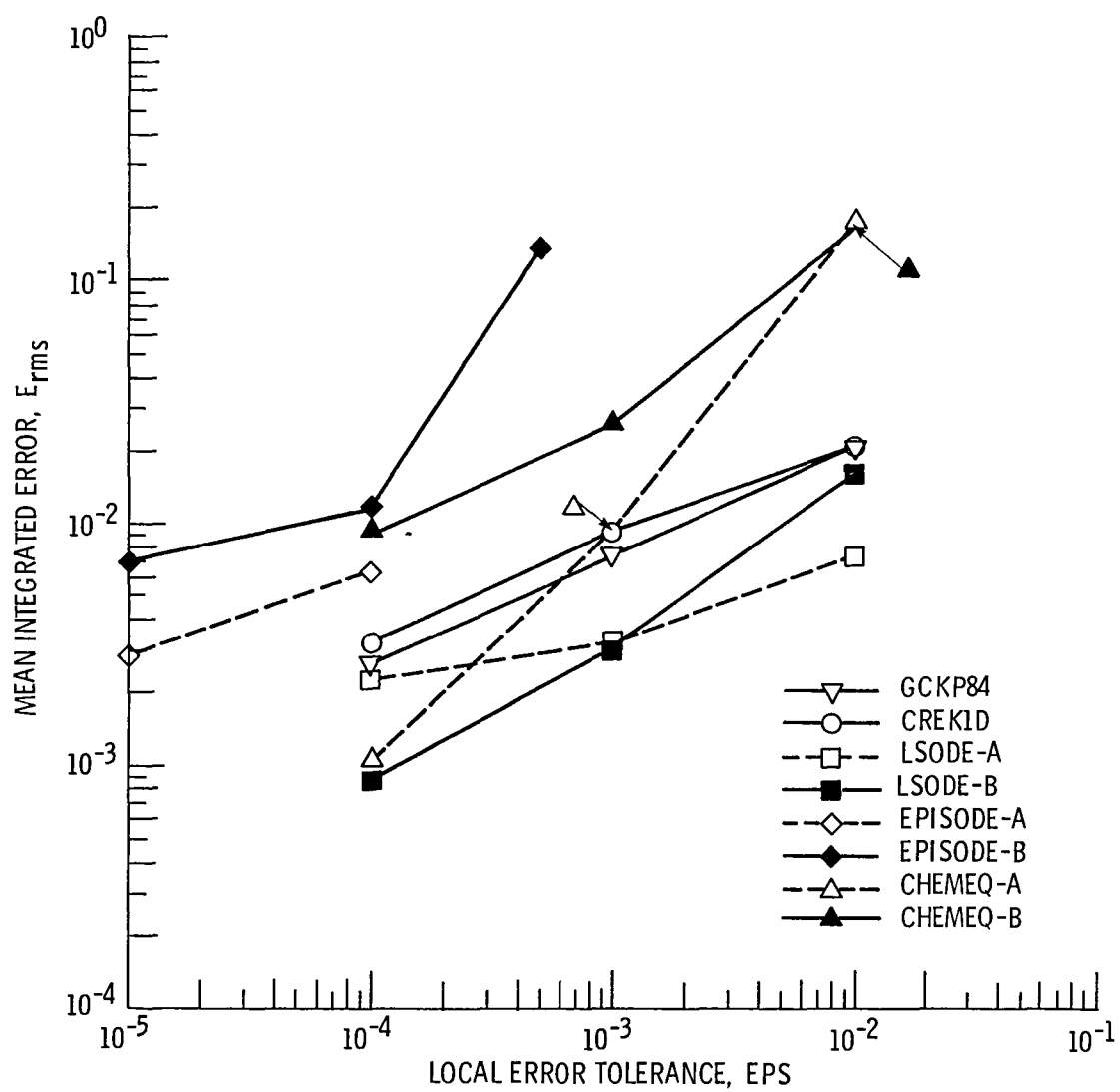
Figure 4 – Variation of the mean integrated global error (E_{rms}) with the local error tolerance (EPS) for test problem 2.
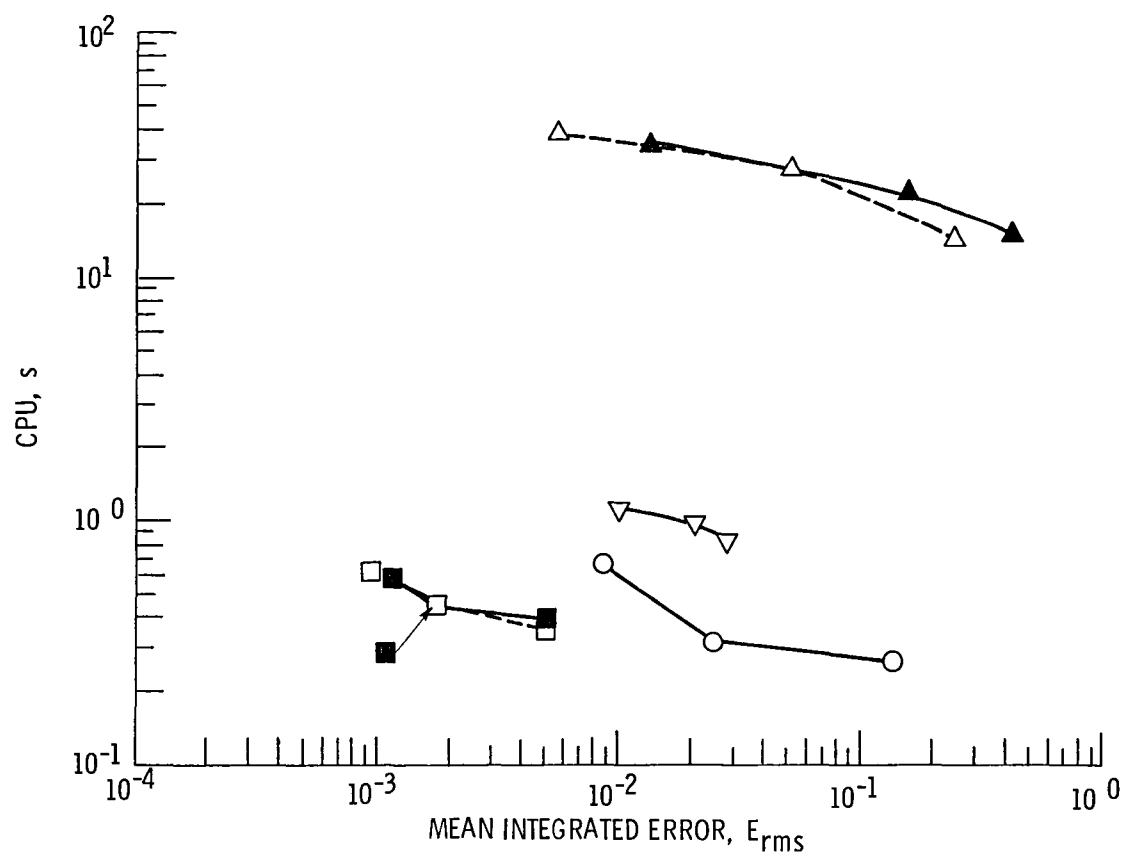
Figure 5. -Variation of the CPU time (s) with the mean integrated global error (E_{rms}) for test problem 1. All runs on the IBM 370/3033 computer. For symbol key, see figure 3.
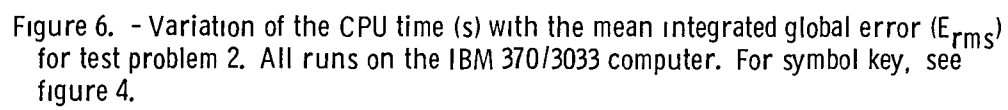
Figure 6. – Variation of the CPU time (s) with the mean integrated global error (E_{rms}) for test problem 2. All runs on the IBM 370/3033 computer. For symbol key, see figure 4.

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16 Abstract

A comparison of the accuracy of several techniques recently developed for solving stiff differential equations is presented. The techniques examined include two general-purpose codes EPISODE and LSODE developed for an arbitrary system of ordinary differential equations, and three specialized codes CHEMEQ, CREK1D, and GCKP84 developed specifically to solve chemical kinetic rate equations. The accuracy comparisons are made by applying these solution procedures to two practical combustion kinetics problems. Both problems describe adiabatic, homogeneous, gas-phase chemical reactions at constant pressure, and include all three combustion regimes: induction, heat release, and equilibration. The comparisons show that LSODE is the most efficient code - in the sense that it requires the least computational work to attain a specified accuracy level - currently available for chemical kinetic rate equations. An important finding is that an iterative solution of the algebraic enthalpy conservation equation for the temperature by integrating its time derivative.

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