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Integrating Chemical Kinetic Rate Equations by Selective Use of Stiff and Nonstiff Methods

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INTEGRATING CHEMICAL KINETIC RATE EQUATIONS BY SELECTIVE USE OF STIFF AND NONSTIFF METHODS

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Abstract

The effect of switching between nonstiff and stiff methods on the efficiency of algorithms for integrating chemical kinetic rate equations is presented. Different integration methods are tested by application of the packaged code LSODE to four practical combustion kinetics problems. The problems described adiabatic, homogeneous gas-phase combustion reactions. It is shown that selective use of nonstiff and stiff methods in different regimes of a typical batch combustion problem is faster than the use of either method for the entire problem. The implications of this result to the development of fast integration techniques for combustion kinetic rate equations are discussed.

Introduction

The ordinary differential equations (ODE's) describing complex chemical reactions are characterized by widely different time constants. Although the differential equations are stable, standard numerical techniques such as the explicit Runge-Kutta and Adams methods are prohibitively expensive to use because of the severe step-length restriction imposed by the requirements for numerical stability. Such systems of differential equations are commonly referred to as "stiff" systems.

The problem of stiffness has been recognized for some time, e.g., and several techniques have been developed for stiff ODE's. At the present time, the packaged codes EPISODE and LSODE represent the most extensively documented, tested and used routines for stiff ODE's. Among several codes examined in recent detailed studies, LSODE was found to be the fastest for solving chemical kinetic rate equations. However, it is recognized by combustion device modelers that LSODE is not fast enough for economical calculations of multidimensional reacting flow problems.

The numerical solution of combustion kinetic rate equations is complicated by the existence of a narrow region ("heat release" zone) where the species concentrations and temperature change rapidly, as illustrated in Fig. 1 for a typical batch reaction combustion problem. In the heat release regime, especially in the early part, many of the species and the temperature have positive time constants -- an indication that the governing ODE's are unstable. Since small steplengths are required for solving unstable ODE's, the use of methods designed for stiff problems -- designated herein as "stiff methods" -- may be inefficient. During

Early heat release explicit "nonstiff methods" -- i.e., methods suitable for nonstiff problems -- may be adequate. However, implicit methods are more accurate than explicit methods, which are therefore used only as predictors in predictor-corrector algorithms. It is not clear what corrector iteration technique is optimal in the nonstiff regime. Both simple or functional iteration and Jacobian iteration techniques have been used because they avoid the expense associated with forming and inverting Jacobian matrices, which is required by Newton-Raphson iteration. However, much larger steplengths can be used with Newton-Raphson iteration. For unstable ODE's this advantage may not be of much help and it is therefore not apparent which technique is the most efficient.

During late heat release and equilibration the governing ODE's are stable so that Newton-Raphson iteration is the optimal convergence method. In these regimes, especially during equilibration, the different species approach the equilibrium state at different rates and the ODE's are stiff -- i.e., classical numerical techniques will require prohibitive amounts of computer time in these regimes. Here, stiff methods are better suited to solving the problem.

In developing an efficient algorithm to solve combustion kinetic rate equations, it is important to recognize and accommodate the widely different characteristics of the three regimes (induction, heat release and equilibration) encountered in a typical combustion problem. Such a situation where the problem changes character, occurs in other areas and schemes have been proposed for automatic switching between stiff and nonstiff methods.

The objective of the present investigation is to examine the nature of the ODE's arising in combustion chemistry. In particular, we examine the effect of switching between stiff and nonstiff methods on the computational work required to solve combustion kinetic rate equations. We also examine the use of different corrector iteration techniques with nonstiff methods.

Governing Ordinary Differential Equations

The first order ODE's describing the time rate of change of species \(i\) (\(i = 1, NS\)) can be written as

\[
\frac{dn_i}{dt} = f_i(n_k, T) \quad i,k = 1, NS
\]

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

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

where \(n_i\) is the mole number of species \(i\); \(NS\) is the total number of distinct species in the gas mixture; \(T\) is the temperature; and \(f_i\) is the net rate of formation of species \(i\) due to all forward reactions.

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and reverse reactions in which species $i$ participates. A more detailed description of the governing ODE's is given to Refs. 12 and 13.

The initial value problem is to solve the system of Eqs. (1) for the chemical composition and temperature at the end of a prescribed time interval, given the initial conditions and the reaction mechanism. All problems considered in the present study involve only adiabatic, homogeneous, gas phase chemical reactions. The problems are, however, of two types -- constant pressure and constant density. The following conservation equations serve as algebraic constraints on the species rate equations:

**Constant pressure:**

$$\sum_{i=1}^{NS} n_i h_i = H_0 = \text{constant} \quad (2a)$$

**Constant density:**

$$\sum_{i=1}^{NS} n_i (h - RT) = U = \text{constant} \quad (2b)$$

where $h_i$ is the molal-specific enthalpy of species $i$; $R$ is the universal gas constant; $H_0$ and $U$ are the mass-specific enthalpy and internal energy, respectively, of the ideal gas mixture.

Time differentiation of Eqs. (2a) and (2b) provides the following ODE's for the temperature:

**Constant pressure:**

$$\frac{dT}{dt} = -\sum_{i=1}^{NS} f_i h_i \quad (3a)$$

**Constant density:**

$$\frac{dT}{dt} = -\sum_{i=1}^{NS} n_i (c_{p_i} - R) \quad (3b)$$

where $c_{p_i}$ is the constant-pressure molal specific heat of species $i$.

### Methods and Iteration Techniques Examined

The objective of the present investigation was to examine the effect on the computational speed of using stiff and nonstiff methods in different regimes of a typical combustion kinetics problem.

To accomplish this objective the packaged code LSODE was used because it contains both stiff and nonstiff methods and switching between the two methods is relatively straightforward. The methods included in this package are a variable-step, variable-order implicit Adams method, suitable for nonstiff problems, and a variable-step, variable-order backward differentiation formula (BDF), suitable for stiff problems. These methods are among the most efficient currently available for nonstiff and stiff problems, respectively.

Both techniques employ a standard explicit predictor formula -- a Taylor series expansion using the method devised by Nordsieck -- to provide an initial estimate of the solution. To correct this estimate a range of iteration formulas is included in LSODE. The methods and corrector techniques attempted in this study are examined briefly; details are available in Refs. 7, 23 and 24.

The ODE's presented in the previous section can be generalized as follows:

$$\frac{dy}{dt} = f(y, t), \quad i, k = 1, N \quad (4a)$$

or using vector notation

$$\frac{d\mathbf{y}}{dt} = \mathbf{f}(\mathbf{y}) \quad (4b)$$

where

$$\mathbf{y}_i = y_i, \quad i = 1, N_S$$

$$\mathbf{y}_{NS+1} = T$$

$$N = NS + 1$$

and an underscore represents a vector quantity.

The techniques used in this study are step-by-step methods. They compute approximations $\mathbf{y}_n(= y_i, n = 1, N)$ to the exact solution $\mathbf{y}(t)$ at discrete points in time $t_n (n = 1, 2, ...)$ assuming that solutions $\mathbf{y}_{n-1}, \mathbf{y}_{n-2}, ...$ have been obtained at times $t_{n-1}, t_{n-2}, ...$ the methods used in LSODE to advance the solution $\mathbf{y}_n$ involve linear multistep formulas of the type

$$\mathbf{y}_{i,n} = \sum_{j=1}^{K_1} a_j \mathbf{y}_{i,n-j} + h_n \sum_{j=0}^{K_2} b_j \dot{\mathbf{y}}_{i,n-j} \quad i = 1, N \quad (6)$$

where $h_n (= t_n - t_{n-1})$ is the size of the step-length to be attempted; $\mathbf{y}_{i,n}$ is the approximation to the exact derivative $\dot{\mathbf{y}}_{i,n}$; $f_i(y_k, n)$ is the approximation to the exact derivative $\dot{\mathbf{y}}_{i,n}$; $f_i(y_k, n)$; and $K_1, K_2, a_j$, and $b_j$ are associated with the formula selected to solve the problem over this time step. For the implicit Adams method of order $q$, $K_1 = 1, K_2 = q - 1$ and Eq. (6) becomes

$$\mathbf{y}_{i,n} = \mathbf{y}_{i,n-1} + h_n \sum_{j=0}^{q-1} b_j \dot{\mathbf{y}}_{i,n-j} \quad i = 1, N \quad (7)$$

For a BDF of order $q$, $K_1 = q, K_2 = 0$ and Eq. (6) becomes

$$\mathbf{y}_{i,n} = \sum_{j=1}^{q} a_j \mathbf{y}_{i,n-j} + h_n \mathbf{a}_0 \dot{\mathbf{y}}_{i,n} \quad i = 1, N \quad (8)$$

Equations (7) and (8) can be written in the general form

$$\mathbf{y}_{i,n} = \mathbf{y}_{i,n-1} + h_n \mathbf{a}_0 \dot{\mathbf{y}}_{i,n} \quad i = 1, N \quad (9)$$

where $\mathbf{y}_{i,n}$ contains previously computed information. In vector notation, Eq. (9) becomes

$$\mathbf{y}_{i,n} = \mathbf{y}_{i,n-1} + h_n \mathbf{a}_0 \mathbf{f}(\mathbf{y}_k, n) \quad i = 1, N \quad (9)$$
more efficient, which may also be the case when
regt-ir- °requent updating of the Jacobian for suc-
clearly the optimal method. For unstable regimes,
where the Jacobian changes slowly NR iteration is
converge at slower rates. For stable problems
-- better than linear but not quite quadratic.

This technique is as simple as functional iteration
in the sense that no matrix inversion is involved. Also
it converges faster than functional iteration
-- better than linear but not quite quadratic.19

In summary, functional and JN iteration tech-
niques require much less work per step than NR
iteration but have to use smaller steplengths and
converge at slower rates. For stable problems
where the Jacobian changes slowly NR iteration is
clearly the optimal method. For unstable regimes,
however, where rapidly changing solutions may
require frequent updating of the Jacobian for suc-
cessful convergence, simple or JN iteration may be
more efficient, which may also be the case when
very accurate numerical solutions are required.

In LSODE both the basic method and the correc-
tor iteration technique are selected by a method
flag, MF. If NR iteration is employed, either the
user can provide analytical expressions for the
elements of the Jacobian matrix or the code will
estimate these elements by finite-difference
approximations. For JN iteration, however, this
option is not available and the code uses
internally-generated finite-difference approxima-
tions for the diagonal elements of the Jacobian
matrix. For all results obtained with NR iteration
analytical Jacobians were used. The basic methods
and iteration techniques employed in the present
study are summarized in Table I, together with the
relevant values for MF.

Test Problems

Four practical combustion kinetics problems
were used in the present study. All four cases
described adiabatic, homogeneous, gas-phase, tran-
sient, batch combustion reactions. Test problem 1
described the ignition and subsequent combustion
of a mixture of 33 percent carbon monoxide and
67 percent hydrogen with 100 percent theoretical
air at an initial temperature of 1000 K and pres-
sure of 1 atm. It involved 12 reactive species and
31 reactions. Test problem 2, involving 30 reactions
among 15 species, described the ignition and subse-
cquent combustion of a stoichiometric hydrogen-air
mixture at 2 atm and 1500 K initial temperature.
Both test cases 1 and 2 were at constant pressure
and are discussed in more detail in Ref. 12. Test
problem 3, taken from Burcat and Radhakrishnan,12
described the ignition and subsequent combustion
of a stoichiometric propane-oxygen-argon mixture at
an initial temperature and pressure of 1700 K and
4 atm, respectively. This constant density test case
consisted of 113 reactions among 31 species.
The reaction mechanism and rate constants were
taken from Westbrook and Pitz.25 Test case 4,
taken from Bittner and Scullin,27 was a lean
methane-air ignition and combustion problem at
a constant pressure of 1 atm and initial temperature
of 1645 K. This test problem involved 58 reactions
among 24 species.

Figure 1 presents the variation with time of the
chemical species mole fractions and temperature
for test problem 1. The variation of the tempera-
ture with the reaction time for all four test cases
is shown in Fig. 1. All four test problems were
solved over a time period of 1 ms. This reaction
period encompassed all three combustion regimes
(induction, heat release and equilibration) for
test problems 1–3. Test case 4, however, included
the first two regimes (induction and heat release)
but only the beginning of equilibration.
Results

In this section we present the effects on the computational work of using stiff and nonstiff methods in different regimes of a typical combustion kinetics problem. All results were obtained on the NASA Lewis Research Center's ION 370/3033 computer using single-precision accuracy.

As illustrated in Fig. 1 and discussed in the section INTRODUCTION, a typical combustion kinetics problem consists of three distinctly different regimes: induction, heat release and equilibration. During induction and early heat release, when many of the ODE's have positive time constants, small step-sizes must be used to ensure solution accuracy.11,13 In these regimes non-stiff methods may be more efficient.12 During late heat release and equilibration when the ODE's are more stable, much larger step-lengths can be used and NR iteration is the optimal convergence methods.10,12,13 In these later regimes, especially during equilibration, the ODE's are stiff so that stiff methods are appropriate.

To investigate if it is more efficient to use a nonstiff method during induction and early heat release, the variation of the computer time with the reaction time was examined for all values of the method flag, MF = 10, 11, 13, and 21, after - see Table I, That was presented in this study. Pure relative error control is appropriate for the problems employed in this study. However, it could not be used because many of the mole numbers had zero initial values. A mixed relative and absolute error control was therefore used. Sufficiently small values for the local absolute error tolerances for the species were used to make the error control substantially relative for mole fractions greater than 0.1 ppm. For temperature pure relative error control was used. To ensure that a comparison of computational work was made among comparably accurate methods, the same values for the absolute error tolerances were used with all methods and corrector iteration techniques. For clarity in presentation, methods corresponding to method flag MF = 10, 11, 13, and 21 thereafter be designated as methods 10, 11, 13, and 21, respectively.

Figures 1 and 2 present the variation of the computer time (i.e., reaction time) with the reaction time for heat problem 1 using values for the local relative error tolerance (EPS) of 10^-2 and 10^-3, respectively. For method 10 (implicit Adams with functional iteration) and EPS = 10^-3, the CPU time required up to the onset of heat release (reaction time t = 9 us, see Figs. 1 and 2) exceeded that required by method 21 (BDF with NR iteration using an analytical Jacobian) to solve the complete problem (Fig. 3). For EPS = 10^-5, however, the CPU times required during induction and early heat release were about the same for both methods (Fig. 4). For methods 11 (implicit Adams with NR iteration using an analytical Jacobian) and 13 (Implicit Adams with JN iteration using internally generated approximations for the diagonal elements of the Jacobian matrix), the CPU times required during induction and early heat release compared favorably with, or were less than, those required by method 21. Note, however, that the CPU time required by method 21 for the complete problem was less than that required by all the nonstiff methods, indicating that the problem was stiff.

The results given in Figs. 3 and 4 show that JN and NR iteration techniques are more efficient than functional iteration in the nonstiff regime. These results indicate also that the use of a nonstiff method during induction and early heat release and a stiff method for the remainder of the problem would be more efficient than using either method for the complete problem. To examine the effects of such a switch the following procedure was used. The code was run up to reaction time t = tswitch with a nonstiff method. After every step successfully executed by the routine, the value of the time reached by the integrator was checked to ensure that it did not exceed tswitch. If the time exceeded tswitch, the method was switched to 21 and the problem was run to completion with the stiff method. Upon completion of the problem, the CPU time required to solve the problem was calculated. In addition, the following performance parameters which give an indication of the computational work required to solve the problem were noted: total number of steps required to solve the problem (NSTEP), total number of functional (i.e., derivative) evaluations (NF), and total number of Jacobian evaluations (NJ).

Different values for tswitch were attempted and the value resulting in the least CPU time to solve the problem was obtained by a trial-and-error process. Since the objective of the present investigation was only to determine if switching methods resulted in efficiency increases and to identify the optimal iteration technique to be used in the nonstiff regime, no attempt was made to incorporate automatic method selection procedures.

Table II presents the minimal CPU times obtained for test problem 1 using the two-stage solution scheme outlined above and different iteration techniques in the nonstiff regime. In this table tswitch is the reaction time (in us) up to which the program was run with the nonstiff method and the indicated iteration technique. For values of reaction time t > tswitch the solution was obtained with the stiff method 21. Also given in Table II is the computational work required by method 21 to solve the complete problem. For method 10 and EPS = 10^-5 the CPU times required up to the onset of heat release exceeded those required by method 21 to solve the complete problem. Therefore no switching was attempted for these values of EPS and method 10. For EPS = 10^-3, however, the combination of methods 10 and 21 was about 20 percent faster than method 21 for the complete problem (Table II). Note that fewer steps and functional evaluations were required by the stiff method, indicating that the average step-length was smaller for method 10. However, the use of method 10 during induction and early heat release resulted in significantly fewer Jacobian evaluations. This was due to (a) not computing the Jacobian in the initial regime and (b) fewer Jacobian evaluations being required in the second regime because of the use of smaller step-lengths.

The combinations of methods 11 and 21 and of 13 and 21 resulted in decreased CPU times (i.e., relative to method 21 for the complete problem) for most of the error tolerances (Table II). Also, in all cases the combination of nonstiff and stiff methods was faster than using the same method for the complete problem. Note that the time at which methods had to be switched generally increased with decreasing EPS, i.e., increasing
accuracy requirements. This implies that when \( EPS \) is decreased, accuracy requirements control the step size for a longer time. When accuracy requirements, and not numerical solution stability requirements, control the size of the step, the use of either a stiff method or a nonstiff method becomes relevant. However, the time over which it was more efficient to use a nonstiff method increased with decreasing \( EPS \).

The combination of methods 11 and 21 resulted in CPU time decreases ranging from negligibly small to over 40 percent for test problem 1 (Table II). This switching process, i.e., use of a nonstiff method during induction and early heat release and of a stiff method for the remainder of the problem, is not entirely satisfactory in that it does not always result in significant savings over the use of the stiff method 21 for the complete problem. Similar remarks apply to the use of method 13 in the initial regimes. Note that for method 13 \( HNE \) includes two types of Jacobian matrix evaluations -- the first number is the total number of complete (i.e., analytical) Jacobian matrix evaluations required and the second number is the total number of diagonal matrix approximations (Table II). One of the difficulties encountered with the use of method 13 was that it returned inaccurate solutions when relatively large values of \( EPS \) were used. This problem has been reported by others. It is not clear if this was caused by poor approximations for the diagonal elements or by an unreliable convergence test. Another difficulty encountered with this method was serious numerical instability for some test problems and values of \( EPS \). Because of these problems with method 13 it was not attempted with the other three test cases.

For the other three test problems and most of the error tolerances used, the runs with method 10 required more CPU time until the onset of heat release than method 21 for the complete problem, (e.g., Fig. 5). Hence, method 10 was also not attempted in the nonstiff regime for test problems 2 to 4.

Tables III, IV and V present the effects of switching between methods 11 and 21 for test problems 2, 3 and 4, respectively. For purposes of efficiency comparison, the computational work required by method 21 for the complete problem is also given in these tables. The results for test problem 2 (Table III) were very similar to those obtained for test problem 1. The use of the two-region scheme resulted in efficiency increases for most of the error tolerances and, as \( EPS \) was decreased, the switching had to be performed at later times.

For test problem 3, however, no significant efficiency increases could be obtained by using the nonstiff method 11 during induction and early heat release and then switching to the stiff method 21 at a later time (Table IV). Efficient efficiency increases could be obtained by switching before the onset of heat release (Table IV). Note that for \( EPS = 10^{-5} \) switching from method 11 to method 21 at \( t = 0.03 \) \( \mu s \) (for this problem heat release started at about 3 \( \mu s \), Fig. 2) resulted in a CPU time decrease of over 40 percent. For test problem 3, unlike test problems 1 and 2, the temperature dropped by a significant amount (less than 1 K) during induction. This decrease in temperature was diagnosed by the code as an indication of stiffness, especially when low values were used for \( EPS \). Note the sharp increase in CPU time incurred by the nonstiff methods during induction (Fig. 5).

Test problem 4 was also quite different from test problems 1 and 2. Although the temperature drop during induction was not as significant (less than 1 K), this problem was characterized by a fairly long ignition delay period (Fig. 2). In addition, when the temperature started to increase (at \( t = 20 \) \( \mu s \)) it did so gradually and not as rapidly as for the other problems. For example, at \( t = 100 \) \( \mu s \) the temperature had risen by only about 10 K. Unlike the other three test problems, test problem 4 included only the beginning of the equilibration regime. A nonstiff method was therefore expected to be more efficient for most of the problem. However, the results given in Table V show that for increased efficiency switching had to be performed during induction. This indicates that for test problem 4 also it was more efficient to use a stiff method during induction, as it was in Fig. 6 for \( EPS = 10^{-4} \). Note the large increase in CPU time for method 11 between \( t = 1 \) and 20 \( \mu s \). For method 21 the CPU time showed a large increase between approximately 300 and 350 \( \mu s \), corresponding to the rapid increase in the computer time between these times (Fig. 2). In this interval method 11 was more efficient (Fig. 6) because accuracy requirements control the step size. The effect of using a nonstiff method in this interval was examined as follows for \( EPS = 10^{-4} \). The program was run with method 11 up to 2.5 \( \mu s \) and between 300 and 350 \( \mu s \). At all other times method 21 was used. This resulted in a total CPU time requirement of 7.6 \( \mu s \) -- which was significantly faster than both the simple switch performed earlier (i.e., two-stage solution scheme) and method 21 for the complete problem (Table V).

The results discussed above indicate that the induction regime is not necessarily nonstiff so that the use of a nonstiff method in this regime does not guarantee minimal computational work. In this regime the use of either a stiff method or a combination of nonstiff and stiff methods may require the least computational work. To test this hypothesis the following procedure was adopted. The program was run with the stiff method 21 until the onset of heat release and then used to carry out heat release and equilibration. During early heat release, however, a nonstiff method was used.

Table VI presents the minimal CPU time obtained for test problem 1 using the three-region solution scheme discussed above -- all iteration techniques were attempted during early heat release. In this table \( t_{SW} \) and \( t_{SW2} \) are the times at which the methods were switched from nonstiff to stiff and from stiff to nonstiff, respectively. Note that as \( EPS \) was increased \( t_{SW} \) had to be increased because heat release was predicted to start at an earlier time. As discussed previously \( t_{SW2} \) had to be increased with decreasing \( EPS \). A comparison of Tables II and VI shows that for almost all iteration techniques and error tolerances the three-stage solution scheme was faster than both the two-stage solution scheme proposed earlier and the stiff method 21 for the complete problem. Note that the use of this combination of stiff and nonstiff methods has resulted in about a 50 percent reduction in the CPU time for \( EPS = 10^{-5} \) and method 13 during early heat release. Although the use of method 10 also resulted in efficiency
Increases, a very low value of EPS (10−5) was required for significant reductions in the CPU time (Table VI). The use of such low values of EPS is wasteful, especially for multidimensional reacting flow calculations. This indicates that either JN or NR iteration should be used during early heat release. For small values of EPS JN iteration (method 13) is more efficient, but for large values of EPS NR iteration (method 11) is superior (Table VI).

The results presented above indicate that for efficient solution of combustion kinetic rate equations, nonstiff methods should be used during early heat release. However, it is not clear if JN or NR iteration should be used in this regime. For large values of the local error tolerance JN iteration resulted in significant errors. This could be due to the approximations for the Jacobian elements used in LSODE. No such problem was encountered with CREXID-CLA which employs JN iteration but with an analytical Jacobian. This suggests that JN iteration with analytical Jacobian should be attempted during early heat release. During late heat release and equilibration, however, a stiff method should be used. During induction either a stiff method or a combination of nonstiff and stiff methods appears to be the optimal choice.

Conclusions

A major conclusion of the present work is that the combination of a nonstiff method during induction and early heat release and a stiff method during late heat release and equilibration does not always result in the optimal algorithm for solving combustion kinetic rate equations. During induction the use of either a stiff method or the combination of nonstiff and stiff methods is indicated. During early heat release a nonstiff method should be employed. However, it is not evident if Newton-Raphson or Jacobian-Newton iteration is the optimal convergence technique in the nonstiff regime. For large values of the local relative error tolerance Jacobian-Newton iteration technique included in the packaged code LSODE produced large errors and also resulted in unstable solutions. This may be the result of poor approximations for the Jacobian. Further experimentation, especially with an analytical Jacobian, is necessary to resolve the question of which iteration technique to select. During late heat release and equilibration stiff methods are optimal.

References


TABLE I. - SUMMARY OF METHODS AND CORRECTOR ITERATION TECHNIQUES EXAMINED

<table>
<thead>
<tr>
<th>Method</th>
<th>Basic method</th>
<th>Iteration technique</th>
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<tbody>
<tr>
<td>10</td>
<td>Variable-step, variable order</td>
<td>Simple or functional Newton-Raphson with analytical Jacobian</td>
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<tr>
<td></td>
<td>implicit Adams</td>
<td>Jacobian-Newton with finite difference generated Jacobian</td>
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<td>11</td>
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<td>13</td>
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<tr>
<td>21</td>
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<td>backward differentiation formula</td>
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TABLE II. - SUMMARY OF COMPUTATIONAL WORK REQUIRED BY TWO-REGION SOLUTION FOR TEST PROBLEM 1

<table>
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<tr>
<th>Method</th>
<th>EPS</th>
<th>t_switch</th>
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</tr>
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<td>21</td>
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<td>--</td>
<td>115</td>
<td>183</td>
<td>30</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>10^-4</td>
<td>--</td>
<td>207</td>
<td>340</td>
<td>46</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>10^-5</td>
<td>--</td>
<td>308</td>
<td>504</td>
<td>57</td>
<td>1.08</td>
</tr>
</tbody>
</table>

For Method 13 the first number is the total number of complete Jacobian matrix evaluations and the second number is the total number of diagonal matrix approximations.
### TABLE III. - SUMMARY OF COMPUTATIONAL WORK

**REQUIRED BY TWO-REGION SOLUTION FOR TEST PROBLEM 2**

<table>
<thead>
<tr>
<th>Method</th>
<th>EPS</th>
<th>t_{\text{switch}} µs</th>
<th>NSTEP</th>
<th>NFE</th>
<th>NJE</th>
<th>CPU, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>11/21</td>
<td>10^{-2}</td>
<td>3</td>
<td>96</td>
<td>158</td>
<td>29</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>10^{-3}</td>
<td>5</td>
<td>159</td>
<td>255</td>
<td>43</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>10^{-4}</td>
<td>4.5</td>
<td>237</td>
<td>368</td>
<td>43</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td>10^{-5}</td>
<td>20</td>
<td>2646</td>
<td>4686</td>
<td>422</td>
<td>16.5</td>
</tr>
<tr>
<td>21</td>
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<td>---</td>
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<td>163</td>
<td>29</td>
<td>0.71</td>
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<tr>
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<td>---</td>
<td>157</td>
<td>243</td>
<td>36</td>
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</tr>
<tr>
<td></td>
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<td>---</td>
<td>295</td>
<td>471</td>
<td>63</td>
<td>1.07</td>
</tr>
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<td>---</td>
<td>3527</td>
<td>5705</td>
<td>579</td>
<td>20.5</td>
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</table>

### TABLE IV. - SUMMARY OF COMPUTATIONAL WORK

**REQUIRED BY TWO-REGION SOLUTION FOR TEST PROBLEM 3**

<table>
<thead>
<tr>
<th>Method</th>
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<th>NJE</th>
<th>CPU, s</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.5</td>
<td>163</td>
<td>273</td>
<td>46</td>
<td>3.07</td>
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<tr>
<td></td>
<td>10^{-3}</td>
<td>5.0</td>
<td>368</td>
<td>590</td>
<td>94</td>
<td>7.83</td>
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<td>1133</td>
<td>212</td>
<td>15.8</td>
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<tr>
<td></td>
<td>10^{-5}</td>
<td>.03</td>
<td>1148</td>
<td>1794</td>
<td>200</td>
<td>20.9</td>
</tr>
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<td>---</td>
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<td>380</td>
<td>74</td>
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<td>612</td>
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<td>1355</td>
<td>273</td>
<td>19.5</td>
</tr>
<tr>
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<td>2706</td>
<td>449</td>
<td>35.9</td>
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</tbody>
</table>
### TABLE V. SUMMARY OF COMPUTATIONAL WORK REQUIRED BY TWO-REGION SOLUTION FOR TEST PROBLEM 4

<table>
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<th>NFE</th>
<th>NJE</th>
<th>CPU, s</th>
</tr>
</thead>
<tbody>
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<td>1176</td>
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<td>9.76</td>
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<td>1590</td>
<td>2843</td>
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</tr>
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<td>-----</td>
<td>198</td>
<td>326</td>
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</tbody>
</table>

For Method 13 the first number is the total number of complete Jacobian matrix evaluations and the second number is the total number of diagonal matrix approximations.

### TABLE VI. SUMMARY OF COMPUTATIONAL WORK REQUIRED BY THREE-REGION SOLUTION FOR TEST PROBLEM 1

<table>
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<th>t_{\text{Switch}2}</th>
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<th>NFE</th>
<th>NJE</th>
<th>CPU, s</th>
</tr>
</thead>
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<td>349</td>
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<tr>
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<td>406</td>
<td>633</td>
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<tr>
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<td>1726</td>
<td>70</td>
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<td>8.5</td>
<td>15</td>
<td>104</td>
<td>157</td>
<td>30</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
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<td>8.5</td>
<td>22</td>
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<td>263</td>
<td>34</td>
<td>0.52</td>
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<td>435</td>
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<td>1634</td>
<td>132</td>
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<td>136</td>
<td>231</td>
<td>393</td>
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</tr>
<tr>
<td></td>
<td>10^{-3}</td>
<td>8.0</td>
<td>13.5</td>
<td>220</td>
<td>403</td>
<td>324</td>
<td>0.70</td>
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<tr>
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<td>981</td>
<td>1691</td>
<td>951</td>
<td>2.62</td>
</tr>
</tbody>
</table>
Figure 1. - Variation with reaction time of the chemical species mole fractions and temperature for test problem 1 (initial temperature = 1000 K, pressure = 10 atm).

Figure 2. - Variation of the temperature with reaction time for test problems 1-4.
Figure 3. - Variation of the CPU time with reaction time for methods 10, 11, 13, and 21 (test problem 1, local relative error tolerance, EPS = $10^{-2}$).

Figure 4. - Variation of the CPU time with reaction time for methods 10, 11, 13, and 21 (test problem 1, local relative error tolerance, EPS = $10^{-5}$).
Figure 5. - Variation of the CPU time with reaction time for methods 10, 11, 13, and 21 (test problem 3, local relative error tolerance, $\text{EPS} = 10^{-9}$).

Figure 6. - Variation of the CPU time with reaction time for methods 11 and 21 (test problem 4, local relative error tolerance, $\text{EPS} = 10^{-9}$).