NASA Technical Memorandum 83806

CREK1D: A Computer Code for Transient, Gas-Phase Combustion Kinetics

David T. Pratt
University of Washington
Seattle, Washington

and

Krishnan Radhakrishnan
Lewis Research Center
Cleveland, Ohio

October 1984

NASA

CREK1D: A COMPUTER CODE FOR TRANSIENT, GAS-PHASE COMBUSTION KINETICS

David T. Pratt
University of Washington
Department of Mechanical Engineering
Seattle, Washington 98195

and

Krishnan Radhakrishnan*
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

E-2176

SUMMARY

This report describes a new algorithm for fast, automatic integration of chemical kinetic rate equations describing homogeneous, gas-phase combustion at constant pressure. Particular attention is paid to the distinguishing physical and computational characteristics of the induction, heat-release and equilibration regimes. The two-part predictor-corrector algorithm, based on an "exponentially-fitted trapezoidal rule", includes filtering of ill-posed initial conditions, automatic stepsize selection, and automatic selection of Newton-Jacobi or Newton iteration for convergence to achieve maximum computational efficiency while observing a prescribed error tolerance. The new algorithm was found to compare favorably with LSODE on two representative test problems drawn from combustion kinetics.

INTRODUCTION

The problem of economical integration of the coupled, nonlinear ordinary differential equations describing exothermic, homogeneous gas phase combustion reaction kinetics has not yet been optimally solved. Multistep methods, based on traditional explicit numerical integration schemes such as the fourth-order Runge-Kutta method, dominated the thinking of early workers performing single-point calculations modeling one-dimensional combustion processes in shock tubes and rocket nozzles. In the 1960's, considerable progress was made with respect to reliability and efficiency of single-point calculations, due to the introduction of implicit methods by Tyson (ref. 1), and Treanor's introduction of locally exact solutions (exponential functions) to extend the convergence radius of explicit Runge-Kutta methods (ref. 2). Lomax and Bailey (ref. 3) explored the combined use of explicit and implicit methods based on low-order polynomial approximations as an alternative to Treanor's method.

In the 1970's, Treanor's algorithm was utilized by Dimitrov to model hydrogen-air combustion (ref. 4), and Tyson's and Lomax and Bailey's ideas were incorporated into production codes (refs. 5,6). The first implementation

---

*NRC-NASA Research Associate, on leave from The University of Michigan, Department of Mechanical Engineering and Applied Mechanics, Ann Arbor, Michigan 48109.

N85-10068#
N-155,012

of Gear's variable-order, variable-step, backward-difference formulas (refs. 7,8) was produced by Lawrence Livermore Laboratory (ref. 9).

At the same time, increasing attention was focused on multipoint calculations, required for modeling of multidimensional reactive flows (refs. 10-12). This increasing interest in modeling of furnaces and combustors resulted in a major reassessment of available algorithms. It was recognized that all proposed techniques for modeling of complex chemically reacting flow--whether Eulerian space discretization with operator splitting for treating coupled phenomena, or Lagrangian mass or vorticity discretization with coupled phenomena treated by the method of fractional steps--all require a very stable but only moderately accurate homogeneous batch chemistry integrator (refs. 10-12). The same requirements exist for the single-point, stochastic simulation of turbulent mixing-influenced, inhomogeneous gas-phase continuous combustion systems (refs. 13-16).

At the present time, the latest of a series of Lawrence Livermore Laboratory's implementations of the Gear algorithms, LSODE (refs. 17,18) is considered to be the best available, state-of-the-art code for solving stiff systems of ODE's. However, it is recognized by combustion device modelers that LSODE is not fast enough for economical calculations of multidimensional reacting flowfields.

While LSODE is regarded as the best available "packaged" code for solving an arbitrary system of ODE's, it may be possible to construct a superior method for solving a uniquely specified system of ODE's. A clue to a better method for the present problem than the variable order-variable stepsize algorithm utilized by LSODE is given by Lambert (ref. 9, p. 18):

> "For stiff equations, for which a typical solution is a rapidly decaying exponential, the error in interpolating such functions by a polynomial of high degree is very large, and correspondingly we find that linear multistep methods of high stepnumber cannot be used successfully for such problems."

The present paper describes the development of an algorithm, denoted CREK1D (for Combustion Reaction Kinetics-One-Dimensional), which has been specifically designed to integrate chemical kinetic rate equations, and which compares favorably with LSODE.

GOVERNING ALGEBRAIC AND DIFFERENTIAL EQUATIONS

The equations for adiabatic, homogenous gas-phase chemical reaction kinetics at constant pressure are given by:

$$\frac{d\sigma_i}{dt} = f_i(\sigma_k, T), \quad i,k = 1,N \tag{1}$$

where

$$f_i = -\rho^{-1} \sum_{j=1}^{J} (\alpha'_{ij} - \alpha''_{ij})(R_j - R_{-j}) \tag{2}$$

where

$$R_j = A_j T^{B_j} \exp(-E_j/RT) \prod_{k=1}^{N} (\rho\sigma_k)^{\alpha'_{kj}} \tag{3a}$$

and

$$R_{-j} = A_{-j} T^{B_{-j}} \exp(-E_{-j}/RT) \prod_{k=1}^{N} (\rho\sigma_k)^{\alpha''_{kj}} \tag{3b}$$

In equations (1) to (3), σ_i is the mole number of the ith species ($i = 1,N$); T is the temperature; ρ is the mass density; α'_{ij} and α''_{ij} are the stoichiometric coefficients of species i ($i = 1,N$) in reaction $j(j = 1,J)$ as a reactant and as a product species, respectively; A_j, A_{-j}, B_j, B_{-j}, E_j, and E_{-j} are constants in the modified Arrhenius rate expressions for R_j and R_{-j}, which in turn are the forward and reverse rates of the jth reaction ($j = 1,J$) as a reactant and as a product species, respectively. N and J are, respectively, the total number of distinct chemical species in the gas mixture and the total number of distinct elementary reactions in the reaction mechanism.

For adiabatic constant-pressure chemical reaction, the following enthalpy conservation equation constitutes an algebraic constraint on equations (1) to (3):

$$\sum_{i=1}^{N} \tilde{h}_i \sigma_i = H_0 = \text{const.} \tag{4}$$

where $\tilde{h}_i$ is the molal-specific enthalpy of species i, and H_0 is the mass-specific enthalpy of the mixture.

The mass density ρ in equations (2) and (3) is determined by the equation of state for an ideal gas,

$$\rho = P/(RT\sigma_m) \tag{5}$$

where P is the absolute pressure, R the universal gas constant, and

$$\sigma_m = \sum_{i=1}^{N} \sigma_i \tag{6}$$

is the reciprocal mean molar mass of the mixture.

PHYSICAL AND COMPUTATIONAL SCENARIOS

A typical constant pressure batch combustion problem consists of three distinctly different chemical-physical regimes: induction, heat release and equilibration (see fig. 1). To accommodate the widely different characteristics of these regimes, a two-part algorithm was developed as follows.

During induction and early heat-release, the species equations are dominated by positive time constants, and the temperature also exhibits a positive time constant. Since very small steps are required for integrating unstable equations, a simple predictor-corrector scheme with functional iteration assures the least computational work possible. However, during late heat release and equilibration, when the temperature and species equations exhibit negative time constants, large stepsizes can be used, so Newton-Raphson iteration with calculation of the full Jacobian matrix is the optimal convergence method.

Although the governing ordinary differential equations (ODE's) are stable during late heat release and equilibration, they are characterized by widely differing time constants. This behavior--termed "stiff" by Curtiss and Hirschfelder (ref. 20)--causes classical integration techniques (such as the popular explicit Runge-Kutta method) to use very small steplengths, thereby resulting in excessive computational work (refs. 19, 21-23).

The equilibration process does not have a clearly defined termination, due to the asymptotic nature of the approach to the chemical equilibrium state. Since equilibrium values of temperature and species concentration can be determined a priori by a Gibbs function minimization scheme (refs. 11,24), the end of the equilibration period can be defined as the time at which all of the mole numbers and the temperature are within (say) one percent of their chemical equilibrium values.

CANDIDATE ALGORITHMS

A number of single-step algorithms were considered, including:

1. Implicit Euler rule (refs. 1, 3, 19, 25, and 26)
2. Implicit midpoint rule (refs. 27, and 28)
3. Trapezoidal rule (ref. 19)
4. Exponential-fitted trapezoidal rule: "Liniger-Willoughby No. 1" (refs. 12, 25, 26, and 29-31)
5. Trapezoidal rule with end correction: cubic spline, or "Obreschkoff (2,2)" (refs. 25, 28, and 29)
6. Exponential-fitted trapezoidal rule with end correction: "Liniger-Willoughby No. 3" (refs. 25, 26, and 29)
7. Locally-exact or exponential solutions (refs. 19, 25, and 26).

Variations and combinations of the seven basic algorithms were explored; for example, Young and Boris' SAIM (Selected Asymptotic Integration Method), which utilizes a combination of locally-exact ("asymptotic") solutions and an explicit Euler-trapezoidal rule predictor-corrector method (refs. 10, 32, 33).

Of the seven algorithms and their variants tested, it was found that the most useful algorithms were variations of "Liniger-Willoughby No. 1," the exponential-fitted trapezoidal rule.

METHOD FORMULATION: THE EXPONENTIAL-FITTED TRAPEZOIDAL RULE

Consider an approximate solution to equation (1) based on a variation of the trapezoidal rule, the "tuneable trapezoid" (refs. 12, 25, and 26) or "theta-method" (ref. 28), as follows:

$$\sigma_{i,n+1} = \sigma_{i,n} + h[U_i f_{i,n+1} + (1 - U_i)f_{i,n}], \; i = 1,N \qquad (7)$$

where, $\sigma_{i,n}$ is the approximation to the exact solution to equation (1) at the current time, t_n, h is the time steplength ($= t_{n+1} - t_n$), $f_{i,n} = f_i(\sigma_{k,n},T_n)$, and T_n, the temperature at t_n, is obtained from equation (4)--see appendix A for details. Also, U_i is a degree-of-implicitness or "tuning" factor such that $U_i = 0$ recovers the explicit Euler approximation, $U_i = 1$ recovers the implicit Euler approximation, and $U_i = 1/2$ recovers the trapezoidal rule (or modified Euler method).

Following the ideas of Liniger and Willoughby (ref. 29) and of Brandon (refs. 30 and 31), we introduce the concept of "exponential-fitting" the parameter U_i to a locally-exact solution of equation (1). Assume a locally-linearized form of the rate equations, equation (1):

$$f_i = (f_{i,n} - \theta_i\sigma_{i,n}) + \theta_i\sigma_i \qquad (8a)$$

or

$$\frac{d\sigma_i}{dt} = (f_{i,n} - \theta_i\sigma_{i,n}) + \theta_i\sigma_i \qquad (8b)$$

where the choice of θ_i, a suitable linearization constant, is discussed in detail in the next section. Integration of equation (8b) gives the following result

$$\sigma_{i,n+1} = \sigma_{i,n} + hf_{i,n}\left[\frac{\exp(\theta_i h)-1}{\theta_i h}\right], \; i = 1,N \qquad (9)$$

which Miranker (ref. 26) calls the "filtered Euler" approximation.

Application of equation (8a) to the entire step of length h gives

$$f_{i,n+1} = (f_{i,n} - \theta_i\sigma_{i,n}) + \theta_i\sigma_{i,n+1} \qquad (10)$$

Substituting equation (10) for the term $f_{i,n+1}$ in equation (7), eliminating $\sigma_{i,n+1}$ between equations (7) and (9), and solving explicitly for U_i

$$U_i = \frac{1}{\theta_i h} + \frac{1}{1-\exp(\theta_i h)} \qquad (11)$$

which relates the tuning factor U_i in equation (7) to the linearization constant θ_i in equation (8). Equation (11) is graphed in figure 2.

However, in order to maintain the absolute A-stability of equation (7) (i.e., $\sigma_{i,n+1}$ remains bounded as h is increased indefinitely), it is necessary to restrict U_i to the interval (0.5, 1.0) (refs. 19, 25, 26, and 28-31). Thus, equation (7) is made to default to the second-order-accurate trapezoidal rule whenever θ_i is greater than zero. However, whenever θ_i is negative, equations (7) and (11) together are equivalent to the locally-exact or exponential solution, equation (9). Brandon (refs. 30 and 31) has shown that the equivalent polynomial accuracy of equation (9) is typically of order six to eight.

Thus, equations (7) and (11), with the restriction ($0.5 < U_i < 1$), constitute an exponential-fitted trapezoidal rule, a method which is A-stable, and has a polynomial-order accuracy of at least two, and as great as six-to-eight. It is interesting to note that, using Liniger and Willoughby's terminology, Treanor's method (ref. 2) would be called an "exponential-fitted, fourth-order Runge-Kutta" method.

LINEARIZATION OF THE RATE EQUATIONS

There are at least two distinct ways of interest to determine the linearization constants θ_i in equations (8) to (11). First, the traditional "chemist's" approach, which may be termed a formal linearization, is reviewed.

Formal Linearization of the Rate Equations: "L-Formulation"

Equation (2) may be expressed as a difference between two positive-definite terms as follows (refs. 10, 32, 33)

$$f_i = Q_i - D_i \tag{12}$$

where

$$Q_i \equiv \rho^{-1} \sum_{j=1}^{J} (\alpha'_{ij}R_{-j} + \alpha''_{ij}R_j) \tag{13}$$

$$D_i \equiv \rho^{-1} \sum_{j=1}^{J} (\alpha'_{ij}R_j + \alpha''_{ij}R_{-j}) \tag{14}$$

The terms Q_i and D_i represent the gross rates of production and consumption of species-i, respectively, due to the contributions of all J forward and reverse reactions. The objective of this decomposition is to enable factorization of the mole number from the destruction term:

$$D_i = L_i\sigma_i \tag{15}$$

where L_i, obtained simply by dividing D_i by σ_i, is given by

$$L_i \equiv (\rho\sigma_i)^{-1} \sum_{j=1}^{J} (\alpha'_{ij}R_j + \alpha''_{ij}R_{-j}) \tag{16}$$

With the notation of equations (12) to (16), equation (1) may be rewritten as:

$$\frac{d\sigma_i}{dt} = Q_i - L_i\sigma_i \tag{17}$$

Equation (17) is now formally linear in σ_i, and it can be seen by inspection that $(-L_i)$ is the appropriate linearization constant θ_i. With θ_i replaced by $(-L_i)$, and f_i replaced by $(Q_i - L_i\sigma_i)$, equation (8a) may be rewritten in the form

$$\sigma_{i,n+1} = [Q_{i,n}/L_{i,n}] + [\sigma_{i,n} - Q_{i,n}/L_{i,n}] \exp(-L_{i,n}h) \tag{18}$$

Since the loss coefficients (L_i, $i = 1,N$) are all positive-definite, the first terms in brackets in equation (18) may be regarded as the local asymptotic solution (refs. 10, 32), which represents the large-timestep value of the locally exact solution, equation (18).

Inspection of equation (18) reveals that the coefficients (L_i, $i = 1,N$) represent inverse characteristic time constants for the L-formulated rate equations; that is, an accurate approximate solution according to equation (18) would have to be resolved on a steplength of order $1/(L_i)_{max}$.

Functional Linearization of the Rate Equations: "Z-Formulation"

Integration of equation (17) to yield equation (18) required that Q_i and L_i in equation (17) be constant over the timestep h. It very often happens that this condition does not exist. Therefore, a more careful examination of the actual coupling between variables in equation (1) requires a functional linearization of the rate equations.

Equation (10) can be solved explicitly for θ_i to give

$$\theta_i = \frac{f_{i,n+1} - f_{i,n}}{\sigma_{i,n+1} - \sigma_{i,n}} \equiv Z_i \tag{19}$$

The parameter Z_i is termed by Brandon the "diagonal transition matrix" or the "state variable differential" (ref. 30). Also, Z_i may be recognized as the average value over the interval h of the ratio of second-to first-time derivatives of the mole number σ_i:

$$\frac{d^2\sigma_i/dt^2}{d\sigma_i/dt} = \frac{df_i/dt}{f_i} \tag{20}$$

Therefore, Z_i is a measure of the local curvature of the trace of σ_i with time, as for example in figure 1. The parameter Z_i is also equivalent to Treanor's parameter P_{ii} (ref. 2).

An important relationship which follows from the locally exact solution is obtained by substituting equation (9) into equation (10) (with $\theta_i = Z_{i,n}$) to give

$$f_{i,n+1} = f_{i,n} \exp (Z_{i,n}h) \qquad (21)$$

Equation 21 emphasizes the role of the state variable differential Z_i as a "diagonal transition matrix" (refs. 30, 31). Thus Z_i may be thought of as a finite-difference analog of the eigenvalues of the Jacobian matrix of equations (1) and (2).

Comparison of Land Z-Formulations

Because the loss coefficients L_i, equation (16), are all positive-definite, the integrated rate equations, equations (7) to (11), are always stable when $\theta_i = -L_i$. However, they are not always accurate, because strong coupling between variables often results in observed positive time constants Z_i for traces of σ_i versus time--see figure 1.

In contrast to the formally-linearized equations ($\theta_i = -L_i$), the functionally-linearized equations ($\theta_i = Z_i$) are always accurate, but are stable only when Z_i is negative; when any species exhibits a positive Z_i, both the physical equation and the corresponding approximate solution, equations 7 to 11 with $\theta_i = Z_i$, are unstable. As a consequence, when the rate equations are dominated by positive Z_i's, as occurs during induction and early heat release, it is necessary to take small steplengths of the order $1/|Z_i|_{max}$.

The use of the Z-formulated equations may result in extremely small steplengths (of size $1/|Z_i|_{max}$) being taken if the initial values for $\sigma_i(i = 1,N)$ are ill-posed. These non-physical initial conditions may arise, for example in multidimensional modeling because of the averaging of mole numbers over adjacent grid nodes. In this case, use of $\theta_i = -L_i$ with a time steplength of order $1/|L_i|_{max}$ is desirable. On the first call to CREK1D, the L-formulated equations are solved over one timestep of length $1/|L_i|_{max}$ to filter the initial conditions--that is, to remove spurious transients of time scale $1/|Z_i|_{max}$ and to provide physically meaningful initial values.

Another difficulty with the use of the Z-formulated equations arises whenever any species is in "quasi-steady state"; that is, when the time trace of σ_i closely approaches an asymptote or passes through an extremum. In either case, Z_i becomes singular due to division by zero or a small number (see eq. 19). When this condition occurs--that is, when $f_i \sim 0$ and/or $(\sigma_{i,n+1} - \sigma_{i,n}) \sim 0$--$Q_i$ and L_i (eq. 17) are locally only slowly varying with time, so that use of the L-formulated equations (i.e., $\theta_i = -L_i$), which are now both stable and accurate, is appropriate.

SOLVING THE INTEGRATED RATE EQUATIONS

A fundamental question which must be addressed is whether or not to use Newton-Raphson iteration to converge the implicit equations, equations (7) to (11), together with the enthalpy conservation constraint, equation (4). The tradeoffs which must be considered involve accuracy, convergence radius and rate, and computational work.

Newton-Raphson (NR) iteration is attractive because it converges quadratically and has an infinite convergence radius. However, NR iteration requires frequent evaluation of the Jacobian matrix and its inverse, usually done by either Gaussian elimination or (equivalently) LU-decomposition and back-substitution (ref. 34).

On the other hand, functional iteration techniques such as nonlinear Gauss-Seidel, Jacobi, or Jacobi-Newton (JN) iteration (ref. 35) do not require evaluation of the Jacobian matrix or its inverse, but have severely restricted convergence radii. In addition, for these methods, the convergence rate is only linear, or at best, super linear--better than linear but not quite quadratic--in the case of JN iteration.

For reasons presented in the section Physical and Computational Scenarios, JN iteration is used during induction and early heat release; however, during late heat release and equilibration, NR iteration is used. Details of both JN and NR iteration methods are given in appendix A.

Approximations for State Variable Differentials

The "tuning factors" U_i in equation (7) are given by equation (11) with θ_i representing the corresponding state variable differentials $Z_{i,n}$. To minimize computational work, the $Z_{i,n}$'s are evaluated only once per step--at the beginning of the time step, using equation (19). However, since $\sigma_{i,n+1}$ and $f_{i,n+1}$ are not known at the start of the step, an approximation has to be developed for $Z_{i,n}$. This is done simply by using values from the previous step, so

$$Z_{i,n} \cong \frac{f_{i,n} - f_{i,n-1}}{\sigma_{i,n} - \sigma_{i,n-1}} \tag{22}$$

Selecting the Iteration Technique

CREK1D automatically selects the iteration scheme (JN or NR) to be used for solving equation (7). During induction and heat release, when small steplengths are required for solution stability (refs. 21, 23), JN iteration is used to minimize computational work. During late heat release and equilibration when the differential equations are more stable and larger steplengths can be used (refs. 21, 23), NR iteration is preferred since it has a much larger radius of convergence than JN iteration. The regime identification test exploits the fact that during extrema or equilibration ("quasi-steady state": QSS) many reactions achieve a condition in which the forward and reverse reactions are large but with vanishingly small differences (refs. 36, 37). The actual test employed at the beginning of the time step is

$$|f_i| \leqq 10^{-3}(Q_i + D_i) \tag{23}$$

where, Q_i and D_i are the production and destruction rates, respectively, of species i (see eqs. 12 to 14). If any two are in QSS--that is, satisfies equation (23)--NR iteration is used for the step. If fewer than two species satisfy equation (23) JN iteration is used for the step.

Non-Physical Initial Conditions

As discussed in the section Comparison of L and Z-formulations, nonphysical initial conditions may result in extremely small steplengths being taken. To filter the initial conditions--that is, to provide physically meaningful initial mole numbers and net species production rates--the L-formulated equations are solved over one timestep. On the first call to CREK1D, it uses this formulation over a timestep of length h_1 given by

$$h_1 = \frac{1}{\max\limits_i \ L_i} \tag{24}$$

The predictor-corrector algorithm uses equation (18) as the predictor

$$\sigma_{i,1}^{(0)} = \sigma_i(0) + h_1 f_i(0) \left[\frac{1 - \exp(-L_i(0)h_1)}{L_i(0)h_1} \right] \tag{25}$$

An implicit Euler corrector equation is then iterated to convergence

$$\sigma_{i,1}^{(m+1)} = \sigma_i(0) + h_1 f_{i,1}^{(m+1)} \tag{26}$$

In these equations $\sigma_i(0)$ are the initial values, $f_i(0) = f_i(\sigma_k(0), T(0))$, $T(0)$ is the initial temperature, and the subscript 1 is used to indicate that this is the first step. Using equations (17) and (A12)

together with the approximations $Q_{i,1}^{(m+1)} = Q_{i,1}^{(m)}$ and $L_{i,1}^{(m+1)} = L_{i,1}^{(m)}$, equation (26) can be rewritten to provide the following expression for the log-variable corrections $\Delta\log\sigma_{i,1}^{(m)}$

$$\Delta\log\sigma_{i,1}^{(m)} = \frac{\sigma_i(0) - \sigma_{i,1}^{(m)} + h_1 f_{i,1}^{(m)}}{\sigma_{i,1}^{(m)} + h_1 D_{i,1}^{(m)}}; \quad i = 1,N \tag{27}$$

Equation (27) is iterated until converged (see appendix A). If convergence is not achieved after 10 iterations, the steplength is halved and the step retried. If convergence is obtained after M ($M \leq 10$) iterations, the step is accepted as successful, and the solution for σ_i is updated

$$\sigma_{i,1} = \sigma_{i,1}^{(M)}; \quad i = 1,N \tag{28}$$

and the temperature T_1 is obtained by a single Newton-Raphson iteration

$$T_1 = T(0) + \frac{H_0 - \sum\limits_{i=1}^{N} \sigma_{i,1}\tilde{h}_i(T(0))}{\sum\limits_{i=1}^{N} \sigma_{i,1}\tilde{c}_{pi}(T(0))} \tag{29}$$

where $\tilde{c}_{pi}$ is the constant-pressure molal specific-heat of species i.

Species in Quasi-Steady State

Whenever the reaction rate for any species i satisfies equation (23), that species is considered to be in "quasi-steady state" (QSS). For reasons presented in the section Solving the Integrated Rate Equations, the L-formulated equations ($\theta_i = -L_i$) are employed for all species in quasi-steady state.

ACCURACY, STABILITY, CONVERGENCE AND STEPLENGTH CONTROL

It is particularly useful to define two timescales needed for steplength control: "h_{accy}," the estimated maximum stepsize to stay within a prescribed local truncation error tolerance ϵ, and "h_{iter}," the maximum stepsize which will admit efficient convergence (refs. 38, 39).

Local Truncation Error (lte)

In the nonstiff regime where JN iteration is used, many species equations have positive time constants. Such species, which we term unstable, have values of $Z_i > 0$. In the present version of the code, whenever $Z_i > 0$, the "tuning factor" U_i (eq. 7) is set equal to 0.5, so that with the following relations deduced from equation (11) (with $\theta_i = Z_i$),

$$\frac{\exp(Z_i h) - 1}{Z_i h} = \frac{1}{1 - U_i Z_i h} = \frac{1}{1 - \frac{1}{2} Z_i h} \tag{30}$$

the predictor equation (A21) for unstable species becomes

$$\sigma_{i,n+1}^{(0)} = \sigma_{i,n} + \frac{hf_{i,n}}{1 - \frac{1}{2} Z_{i,n} h} \tag{31}$$

where $Z_{i,n}$ is determined by equation (22). The corrector equation for unstable species is equation (7) with $U_i = 0.5$--that is, the trapezoidal rule

$$\sigma_{i,n+1}^{(m+1)} = \sigma_{i,n} + \frac{h}{2}\left[f_{i,n} + f_{i,n+1}^{(m)}\right] \tag{32}$$

It can be shown that equation (31) has approximately the same lte as a second-order Adams-Bashforth predictor, so the lte for unstable species can be conservatively estimated as

$$(\text{lte})_i \sim \frac{1}{6}\left|\sigma_{i,n+1} - \sigma_{i,n+1}^{(0)}\right| \tag{33}$$

where $\sigma_{i,n+1}$ is the converged solution.

Species equations that are stable are not limited to $U_i = 0.5$, so equation (33) does not apply for such species. In fact, no such estimate as equation (33) can be made for the present method because it is not a polynomial method (refs. 30 and 31). Nevertheless, equation (33) is used even though it seriously overestimates the lte for stable species.

For all species, stable and unstable, an average weighted lte estimate is made by

$$\mathrm{lte} = \frac{1}{6}\sqrt{\frac{1}{N}\sum_{i=1}^{N}\left\{\frac{\sigma_{i,n+1} - \sigma_{i,n+1}^{(0)}}{\max(\sigma_{i,n}, \sigma_{i,n+1})}\right\}^{2}} \tag{34}$$

and the projected next steplength which would satisfy the user-specified local error tolerance ε is calculated from

$$h_{accy} = h(\varepsilon/\mathrm{lte})^{1/3} \tag{35}$$

In the computationally stiff regime where more of the species are stable, and where use of the NR iteration permits much larger steplengths, equations (33) to (35) are far too conservative. In fact, in this regime, the local truncation error for stable species may decrease with an increase in the steplength. Therefore, a different estimate of the lte is used in the stiff regime. The estimate is based on the norm of the difference between the converged solution and that obtained after the first Newton iteration. This estimate is actually a measure of the local linearization error due to the use of NR iteration, and not that of the local truncation error. The relations used in the stiff regime in place of equations (34) and (35) are

$$\mathrm{lte} = \frac{1}{3}\sqrt{\frac{1}{N}\sum_{i=1}^{N}\left\{\frac{\sigma_{i,n+1} - \sigma_{i,n+1}^{(1)}}{\max(\sigma_{i,n}, \sigma_{i,n+1})}\right\}^{2}} \tag{36}$$

and

$$h_{accy} = h(\varepsilon/\mathrm{lte})^{1/3} \tag{37}$$

In equations (36) and (37), the factor (1/3) must be regarded as strictly empirical.

Convergence Control

During JN and NR iteration the rate of convergence is monitored, both to detect divergence and to optimize the rate of iterative convergence. Following Shampine (refs. 38, 39) and Pratt (ref. 40), the convergence rate R_{conv} is defined by

$$R_{conv} = \frac{\sqrt{\sum_{i=1}^{N} (\Delta \log \sigma_{i,n+1}^{(m)})^2/N}}{\sqrt{\sum_{i=1}^{N} (\Delta \log \sigma_{i,n+1}^{(m-1)})^2/N}} \tag{38}$$

where (m-1) and (m) denote the iteration numbers. Note that at least two iterations are required to define R_{conv}; if convergence is obtained after the first iteration, a default value of $R_{conv} = 0.1$ for JN iteration and 0.05 for NR iteration is used. As with the convergence test, the summations in equation 38 include only species with mole numbers greater than 10^{-20}.

If R_{conv} is greater than one, the solution is diverging and the step must be attempted with a decreased steplength. In CREK1D, a more conservative test $R_{conv} \geq 0.8$ is used to detect divergence. If convergence is not obtained or if divergence is detected, the steplength is decreased as discussed in the next section.

Steplength Control

During both JN and NR iteration the convergence rate, R_{conv}, is used to control the steplength. If corrector convergence is not obtained after ITMAX iterations, where ITMAX is the user-supplied maximum number of corrector iterations to be attempted, or if divergence is detected (i.e., $R_{conv} \geq 0.8$), the steplength is decreased. The new steplength, h', is calculated as follows

$$h' = h \min \left\{ 0.5, \max(0.1,\ 0.5/R_{conv}) \right\} \tag{39}$$

and the step retried with the decreased steplength.

After corrector convergence, the steplength is adjusted up or down as necessary to keep R_{conv} in the range (0.4, 0.5). An estimate, h_{iter}, is made of the steplength that would result in the desired convergence rate:

$$h_{iter} = \begin{cases} h(0.4/R_{conv})^{1/2}; & R_{conv} < 0.4 \\ h & ;\ 0.4 \leq R_{conv} \leq 0.5 \\ h(0.5/R_{conv})^{1/2}; & R_{conv} > 0.5 \end{cases} \tag{40}$$

In addition, the maximum permissible steplength, h_{accy} (given by eq. 35 or 37) that would result in a local truncation error equal to the user-specified value for the local relative error, ϵ, allowed per step, is calculated.

The steplength, h', to be attempted for the next step is then taken to be the minimum of h_{iter} and h_{accy}; however, the ratio h'/h is restricted to be no larger than 10. Hence, h' is given by

$$h' = \min\,(h_{iter},\ h_{accy},\ 10h) \tag{41}$$

To inhibit oscillations of the steplength, h (due to repeated failures of the convergence test after increases in h), an increase in h is allowed only if convergence was obtained in the previous step without a reduction in h. Following any step for which corrector convergence could not be obtained or divergence was detected (and so h was reduced), the new steplength h' is calculated from

$$h' = \min\,(h,\ h' \text{ given by eq. 41}) \tag{42}$$

COMPUTATIONAL STRATEGY

The objective of the calculation is to efficiently and reliably solve the following initial value problem: given a set of initial conditions (σ_i; i = 1,N), T and P (constant), find the values of σ_i (i = 1,N) and T at the end of a prescribed time interval Δt. The overall steps taken to accomplish this are:

a. Filter the initial conditions: evaluate the f_i's; choose a timestep $h_1 = 1/(L_i)_{max}$; use the "filtered Euler" predictor, equation (9) with $\theta_i = -L_i$ (i = 1,N), and converge equations (A19) and (A20) by JN iteration, with all U_i's set to unity (implicit Euler corrector).

b. Adjust the timestep according to the observed R_{conv} from step a. Use an explicit Euler predictor (eq. 9) with $\theta_i = 0$ (i = 1,N); use JN iteration, equations (A19) and (A20), with all U_i's set equal to one-half (trapezoidal rule).

c. Calculate R_{conv}, h_{accy} and h_{iter}; choose JN or NR iteration, according to whether or not two or more species are in QSS. Adjust the timestep as described in the section Steplength Control.

d. Evaluate Z_i's from equation (22), U_i's from equation (11) and iterate equation (17) until converged.

e. Repeat step d to the end of the prescribed interval Δt; return solution.

The strategy outlined above, in conjunction with the robust integration algorithm, leads to minimum computational time with acceptable accuracy.

COMPUTATIONAL TACTICS

The computational work of evaluating logarithms and exponentials may be avoided by judicious use of approximating functions. For example, the term $(e^x - 1)/x$ in equation (9) is evaluated in the code by means of a (2,2) diagonal Pade' (rational function) approximation for e^x,

$$e^x_{(2,2)} \cong \frac{1 + \frac{x}{2} + \frac{x^2}{12}}{1 - \frac{x}{2} + \frac{x^2}{12}} \tag{43}$$

which results in

$$\frac{e^{x} - 1}{x}(2,2) \cong \frac{1}{1 - x(1/2 - x/12)}, \quad x < 0 \qquad (44)$$

Similarly, the "tuning factor" U_i of equation (11) can be evaluated with sufficient accuracy by means of an approximation which has no singularity

$$\frac{1}{x} + \frac{1}{1-e^{x}} \simeq 1 - \frac{1}{2} e^{\left(\frac{x-|x|}{12}\right)} \qquad (45)$$

The right-hand side of equation (44) requires only five operations to evaluate, and does not exhibit the singularity at $x = 0$ of the exact left-hand side. Equation (44) is used only for the predictor equation (9). Equation (45) is graphed in figure 2; note that equation (45) defaults to $U_i = 0.5$ (the trapezoidal rule) for $x > 0$.

Another significant reduction in computational work was achieved by locally linearizing the fifth-order polynomial approximations used in evaluating the species-i enthalpy $\tilde{h}_i$ and specific heat capacities $\tilde{c}_{pi}$, which appear in equations (A11) and (A20).

Finally, it should be noted that, while log-variable corrections are used in the algorithm, (appendix A), evaluation of logarithms of the variables themselves is avoided by use of the approximate equations (A12). The only evaluation of exponentials in the code are those necessarily required for the Arrhenius rate expressions in equation (3) and those required for the tuning factor, equation (45).

PERFORMANCE OF CREK1D--COMPARISON WITH LSODE

A preliminary version of CREK1D (ref. 40) has been tested by Radhakrishnan (refs. 21 to 23) against LSODE (refs. 17,18) on two test problems drawn from combustion kinetics. Both problems described adiabatic, constant pressure, transient batch chemical reaction and included all three regimes of combustion--induction, heat release and equilibration.

Test problem 1, illustrated in figure 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 a pressure of ten atmospheres and 1000 K initial temperature. It consisted of 12 reactions involving 11 species. Test problem 2 described the ignition and subsequent combustion of a stoichiometric mixture of hydrogen and air at a pressure of two atmospheres and 1500 K initial temperature. It involved 30 reactions among 15 species. Both test problems were solved over a time period of 1 ms in order to obtain near-equilibration of all species and the temperature.

In applying LSODE to the problem of solving chemical kinetic rate equations, two different methods (A and B) for calculating the temperature were attempted. In method A (LSODE-A), the temperature was calculated from the mole numbers and the initial mixture enthalpy using the algebraic enthalpy conservation equation (4) and a Newton-Raphson iteration technique. In method B (LSODE-B) the temperature was evaluated by integrating its time-derivative, obtained by differentiating equation 4 with respect to time

$$\frac{dT}{dt} = \frac{-\sum_{i=1}^{N} \tilde{h}_i f_i}{\sum_{i=1}^{N} \sigma_i \tilde{c}_{p_i}} \tag{46}$$

In applying the present version of CREK1D to the two test problems discussed above, we have adopted the procedure described by Radhakrishnan (ref. 23) and summarized here. A typical computational run consisted of initializing the species mole numbers, temperature and CPU time. The integrator was then called with values for the necessary input parameters, including the local error tolerance, ε, required of the numerical solution and the elapsed time (= 1 ms for both problems) at which the integration was to be terminated. On return from the integrator, the total computer time (CPU) required to solve the problem was calculated.

Figures 3 and 4 present the computational work (expressed as the CPU time in seconds required on the NASA Lewis Research Center's IBM 370/3033 computer) required by the single-precision codes CREK1D and LSODE, plotted against the local relative error tolerance, ε.

Figures 3 and 4 show that CREK1D compares favorably with LSODE for large values of the relative error tolerance, ε. But for small values of ε CREK1D is slower than LSODE. However, use of low values of ε is wasteful because of uncertainties in reaction rate coefficients (ref. 10). In addition, the proposed purpose of CREK1D is to perform multipoint calculations of chemically reacting flows by coupling it with a hydrodynamic equation solver. These solvers are at best accurate to within a few percent, so generation of highly accurate chemical kinetic solutions is wasteful (ref. 10).

The solution of the coupled hydrodynamic-reaction rate equations requires the solution of the reaction rate equations at several thousand grid points for relatively short periods of time (ref. 10). Hydrodynamic codes also have large storage requirements. Hence, reaction rate integrators with both a small storage requirement and a low initialization (start-up) time are needed. The storage and start-up time requirements of CREK1D have been shown to be significantly less than those required by LSODE (ref. 24). These factors make CREK1D more attractive than LSODE for multipoint calculations.

To further explore the differences in computational work required by CREK1D and LSODE, we present in figures 5 and 6 plots of the steplength successfully used by these codes through the course of each problem. For test problem 1 (fig. 5) and for test problem 2 at long times (fig. 6), the steplengths selected by CREK1D are comparable to those selected by LSODE. However, at early times ($t \lesssim 5$ µs) for problem 2, CREK1D uses much smaller steplengths than LSODE and is hence slower.

The present version of CREK1D will be available for testing from COSMIC, University of Georgia, Athens, Georgia 30602. Details of the subprograms included in CREK1D are given in appendix B. In appendix C, we present a sample input data set and the resulting output. These were generated on the NASA Lewis Research Center's IBM 370/3033 using single-precision accuracy.

CONCLUSIONS

A major conclusion of the present work is that the L-formulated equations, widely used at present for modeling both atmospheric chemistry (refs. 32 and 33) and combustion processes (ref. 10), should be employed in the initial induction period, when some mole numbers may be very small, and whenever any species is in quasi steady-state. At all other times, use of the Z-formulated equations completely obviates the need to use asymptotic or quasi-steady-state assumptions to resolve the near-equilibrium stiffness problem uniquely associated with the L-formulated equations (refs. 10, 27, 32, and 33). For atmospheric chemistry problems in particular, the present algorithm without the enthalpy constraint should constitute a very fast and robust method for calculation of isothermal, batch homogeneous gas-phase kinetics.

The success of the present algorithm stems from recognition of the fact that the approximating equations describing the induction processes are stability-limited, whereas the corresponding post-induction equations are accuracy-limited. In the former case, low-accuracy methods with the least possible computational work per iteration are indicated due to the necessarily restricted stepsize, as pointed out by Young and Boris (ref. 10). However, in the post-induction processes, where inherent stability is not a problem, stepsizes may be as large as the accuracy and convergence radius of the approximating equations permit. The use of exponentials as approximating functions satisfies the accuracy requirement, and Newton-Raphson iteration gives an infinite convergence radius. The added computational work of Jacobian evaluation and matrix inversion required for Newton-Raphson iteration is offset by very large stepsizes and quadratic convergence (refs. 19, 25, and 26).

NOMENCLATURE

A_j, A_{-j}	preexponential constants in forward and reverse rate equations for reaction j (eq. 3), units depend on reaction type
B_j, B_{-j}	temperature exponent in forward and reverse rate constants for reaction j (eq. 3)
CPU	total CPU time required on IBM 370/3033, s
$\tilde{c}_{pi}$	constant-pressure molal-specific heat of species i, J/kmole K
D_i	rate of destruction of species i (eq. 12), kmole i/kg mixture s
E_j, E_{-j}	activation energy in forward and reverse rate equations for reaction j (eq. 3), cal/mole
f_i	net rate of formation of species i (eq. 2), kmole i/kg mixture s
H_0	initial mixture mass-specific enthalpy, J/kg

h	steplength used by integrator, s
h_{accy}	estimated steplength that would result in solution with desired accuracy (eqs. 35 and 37), s
h_{iter}	estimated steplength that would result in a convergence rate in the range (0.4, 0.5) (eq. 40), s
$\tilde{h}_i$	molal-specific enthalpy of species i, J/kmole
ITMAX	maximum number of corrector iterations to be attempted by the integrator
J	total number of distinct elementary reactions in reaction mechanism
L_i	loss coefficient for species i, inverse of characteristic time constant for species i (eq. 15), 1/s
lte_i	local truncation error for species i
N	total number of distinct chemical species in the gas mixture
P	absolute pressure, N/m^2
Q_i	production rate of species i (eq. 12), kmole i/kg mixture s
R	universal gas constant, 8314.3 J/mole K (1.9872 cal/mole K)
R_{conv}	iteration convergence rate (eq. 38)
R_j, R_{-j}	molar forward and reverse rates per unit volume for reaction j (eq. 3), kmole/m^3s
T	temperature, K
t	time, s
U_i	degree of implicitness or tuning factor for species i (eq. 7)
Z_i	state variable differential for species i (eq. 19)
α'_{ij}, α''_{ij}	stoichiometric coefficients for species i in forward and reverse reaction j (eq. 3), number of kmoles i in elementary reaction j as a reactant and as a product, respectively
ε	local relative error tolerance
θ_i	suitable linearization constant for species i (eq. 8)
ρ	mixture mass density, kg/m^3
σ_i	mole number of species i, kmole i/kg mixture
σ_m	reciprocal of mixture mean molar mass (eq. 6), kmole/kg

APPENDIX A

OUTLINE OF NR AND JN ITERATION TECHNIQUES

Newton-Raphson Iteration

A Newton-Raphson functional $F_{i,n+1}^{(m)}$ is defined from equation (7) by

$$F_{i,n+1}^{(m)} \equiv \frac{\sigma_{i,n+1}^{(m)} - \sigma_{i,n}}{U_i h} - \left[\frac{1-U_i}{U_i}\right] f_{i,n} - f_{i,n+1}^{(m)} \tag{A1}$$

where m is the iteration number, $f_{i,n+1}^{(m)} = f_i(\sigma_{k,n+1}^{(m)}, T_{n+1}^{(m)})$, and $\sigma_{k,n+1}^{(m)}$ $(k = 1,N)$ and $T_{n+1}^{(m)}$ are the mth approximations to the exact values $\sigma_k(t_{n+1})$ and $T(t_{n+1})$, respectively.

The Newton-Raphson functional for temperature is determined from equation (4),

$$F_{T,n+1}^{(m)} = \sum_{i=1}^{N} \sigma_{i,n+1}^{(m)} \tilde{h}_i(T_{n+1}^{(m)}) - H_0 \tag{A2}$$

where $\tilde{h}_i\ (T_{n+1}^{(m)})$ is the molal-specific enthalpy of species i at temperature $T_{n+1}^{(m)}$ and H_0 is the initial mixture mass-specific enthalpy.

Newton-Raphson corrector equations with log variable corrections (for self-scaling of the widely-varying mole numbers) are given by

$$\sum_{k=1}^{N} \frac{\partial F_{i,n+1}^{(m)}}{\partial \log \sigma_{k,n+1}^{(m)}} \Delta \log \sigma_{k,n+1}^{(m)} + \frac{\partial F_{i,n+1}^{(m)}}{\partial \log T_{n+1}^{(m)}} \Delta \log T_{n+1}^{(m)} = -F_{i,n+1}^{(m)};\ i = 1 - N \tag{A3}$$

$$\sum_{k=1}^{N} \frac{\partial F_{T,n+1}^{(m)}}{\partial \log \sigma_{k,n+1}^{(m)}} \Delta \log \sigma_{k,n+1}^{(m)} + \frac{\partial F_{T,n+1}^{(m)}}{\partial \log T_{n+1}^{(m)}} \Delta \log T_{n+1}^{(m)} = -F_{T,n+1}^{(m)} \tag{A4}$$

The partial derivatives in equation (A3) are given by

$$\frac{\partial F_{i,n+1}^{(m)}}{\partial \log \sigma_{k,n+1}^{(m)}} = \frac{\delta_{ik}\sigma_{i,n+1}^{(m)}}{U_i h} + \rho^{-1} \sum_{j=1}^{J} (\alpha'_{ij} - \alpha''_{ij})(R_j \alpha'_{kj} - R_{-j}\alpha''_{kj}),\ i = 1,N \tag{A5}$$

and

$$\frac{\partial F^{(m)}_{i,n+1}}{\partial \log T^{(m)}_{n+1}} = -\rho^{-1}\sum_{j=1}^{J}\left(\alpha'_{ij}-\alpha''_{ij}\right)\Big[R_j(B_j + E_j/RT^{(m)}_{n+1} - n'_j + 1)$$

$$- R_{-j}(B_{-j} + E_{-j}/RT^{(m)}_{n+1} - n''_j + 1\Big] \qquad (A6)$$

In the above equations, δ_{ik} is the Kronecker symbol

$$\delta_{ik}\begin{cases} = 0\ ;\ i \neq k \\ = 1\ ;\ i = k \end{cases} \qquad (A7)$$

and n'_j and n''_j are the molecularities of the forward and reverse reactions j respectively,

$$n'_j = \sum_{i=1}^{N} \alpha'_{ij}$$

$$n''_j = \sum_{i=1}^{N} \alpha''_{ij} \qquad (A8)$$

In equations (A3, A5 and A6), the partial derivatives with respect to the reciprocal of the mean molar mass, σ_m, are assumed to be negligible in comparison with the other terms.

The partial derivatives in equation (A4) can be derived from equation (A2) and are given by

$$\frac{\partial F^{(m)}_{T,n+1}}{\partial \log \sigma^{(m)}_{k,n+1}} = \sigma^{(m)}_{k,n+1}\ \tilde{h}_k\ T^{(m)}_{n+1} \qquad (A9)$$

$$\frac{\partial F^{(m)}_{T,n+1}}{\partial \log T^{(m)}_{n+1}} = T^{(m)}_{n+1}\sum_{i=1}^{N} \sigma^{(m)}_{i,n+1}\ \tilde{c}_{pi}\ T^{(m)}_{n+1} \qquad (A10)$$

where $\tilde{c}_{pi}(T^{(m)}_{n+1})$ is the constant-pressure molal-specific heat of species i at temperature $T^{(m)}_{n+1}$. Substitution of equations (A9) and (A10) into equation (A6) results in the following log-variable correction equation for the temperature

$$\sum_{k=1}^{N} \sigma^{(m)}_{k,n+1}\tilde{h}_k(T^{(m)}_{n+1})\Delta\log \sigma^{(m)}_{k,n+1} + T^{(m)}_{n+1}\sum_{i=1}^{N} \sigma^{(m)}_{i,n+1}\ \tilde{c}_{pi}(T^{(m)}_{n+1})\Delta\log T^{(m)}_{n+1} = -F^{(m)}_{T,n+1} \qquad (A11)$$

Equations (A3) and (A11) are solved simultaneously by LU-decomposition and back-substitution, and the resulting log variable corrections are used to update the current iterate values of $\sigma_{i,n+1}$ and T_{n+1} by the approximate equations

$$\sigma_{i,n+1}^{(m+1)} = \sigma_{i,n+1}^{(m)} \left[1 + \Delta \log \sigma_{i,n+1}^{(m)} \right]; \; i = 1,N \tag{A12a}$$

and

$$T_{n+1}^{(m+1)} = T_{n+1}^{(m)} \left[1 + \Delta \log T_{n+1}^{(m)} \right] \tag{A12b}$$

To start this iteration process, the predicted values denoted by $\sigma_{i,n+1}^{(0)}$ ($i = 1,N$) and $T_{n+1}^{(0)}$ are obtained quite simply by setting them equal to the values at the current time step

$$\sigma_{i,n+1}^{(0)} = \sigma_{i,n}; \; i = 1,N \tag{A13a}$$

$$T_{n+1}^{(0)} = T_n \tag{A13b}$$

Jacobi-Newton Iteration

The form of equations (A1), (A3), (A5) and (A6) was chosen to ensure diagonal dominance of the Jacobian matrix. If it is further assumed that the off-diagonal elements can be neglected with respect to the diagonal elements, equations (A3) and (A11) can be rewritten as

$$\frac{\partial F_{i,n+1}^{(m)}}{\partial \log \sigma_{i,n+1}^{(m)}} \Delta \log \sigma_{i,n+1}^{(m)} = -F_{i,n+1}^{(m)}; \; i = 1,N \tag{A14}$$

and

$$T_{n+1}^{(m)} \sum_{i=1}^{N} \sigma_{i,n+1}^{(m)} \, \tilde{c}_{pi}(T_{n+1}^{(m)}) \Delta \log T_{n+1}^{(m)} = -F_{T,n+1}^{(m)} \tag{A15}$$

In equation (A14), the partial derivatives are given by

$$\frac{\partial F_{i,n+1}^{(m)}}{\partial \log \sigma_{i,n+1}^{(m)}} = \frac{\sigma_{i,n+1}^{(m)}}{U_i h} + \rho^{-1} \sum_{j=1}^{J} (\alpha'_{ij} - \alpha''_{ij})(R_j \alpha'_{ij} - R_{-j} \alpha''_{ij}); \; i = 1,N \tag{A16}$$

which is approximated by

$$\frac{\partial F_{i,n+1}^{(m)}}{\partial \log \sigma_{i,n+1}^{(m)}} = \frac{\sigma_{i,n+1}^{(m)}}{U_i h} + \rho^{-1} \sum_{j=1}^{J} (\alpha'_{ij} R_j + \alpha''_{ij} R_{-j}) \tag{A17}$$

which when combined with equation (14) gives

$$\frac{\partial F_{i,n+1}^{(m)}}{\partial \log \sigma_{i,n+1}^{(m)}} = \frac{\sigma_{i,n+1}^{(m)}}{U_i h} + D_{i,n+1}^{(m)} \tag{A18}$$

where $D_{i,n+1}^{(m)}$, the destruction rate of species i, can be evaluated along with $f_{i,n+1}^{(m)}$, without calculating the entire Jacobian matrix. With this simplification, equation (A14) can be solved explicitly for the iterative corrections

$$\Delta \log \sigma_{i,n+1}^{(m)} = -F_{i,n+1}^{(m)} \Bigg/ \left(\frac{\sigma_{i,n+1}^{(m)}}{U_i h} + D_{i,n+1}^{(m)} \right) ; i = 1,N \tag{A19}$$

The temperature corrector equation (A15) can be solved for the log-temperature correction

$$\Delta \log T_{n+1}^{(m)} = -F_{T,n+1}^{(m)} \Bigg/ \left[T_{n+1}^{(m)} \sum_{i=1}^{N} \sigma_{i,n+1}^{(m)} \tilde{c}_{pi} \left(T_{n+1}^{(m)} \right) \right] \tag{A20}$$

As with NR iteration, the iterate values of $\sigma_{i,n+1}$ and T_{n+1} are updated using the approximate equations (A12)

$$\sigma_{i,n+1}^{(m+1)} = \sigma_{i,n+1}^{(m)} \left[1 + \Delta \log \sigma_{i,n+1}^{(m)} \right] ; \; i = 1,N \tag{A12a}$$

and

$$T_{n+1}^{(m+1)} = T_{n+1}^{(m)} \left[1 + \Delta \log T_{n+1}^{(m)} \right] \tag{A12b}$$

To start the iteration process, the predicted values $\sigma_{i,n+1}^{(0)}$ are obtained from equation (9). (with $\Theta_i = Z_i$)

$$\sigma_{i,n+1}^{(0)} = \sigma_{i,n} + hf_{i,n} \left[\frac{\exp(Z_{i,n} h) - 1}{Z_{i,n} h} \right] ; \; i = 1,N \tag{A21}$$

The predicted temperature is obtained by a single Newton-Raphson iteration.

$$T_{n+1}^{(0)} = T_n + \frac{H_0 - \sum_{i=1}^{N} \sigma_{i,n+1}^{(0)} \tilde{h}_i(T_n)}{\sum_{i=1}^{N} \sigma_{i,n+1}^{(0)} \tilde{c}_{pi}(T_n)} \tag{A22}$$

Convergence Test

For both NR and JN iteration, the test for convergence of the iterates $\sigma_{i,n+1}^{(m+1)}$ is based on the values $\Delta \log \sigma_{i,n+1}^{(m)}$ and is given by

$$\sqrt{\frac{\sum_{i=1}^{N} \left(\Delta \log \sigma_{i,n+1}^{(m)}\right)^2}{N}} \leq \varepsilon \tag{A23}$$

where, ε is a user-supplied local relative error tolerance. The above test is used only for species whose mole numbers are greater than 10^{-20}; i.e., the summation does not include species with mole numbers less than or equal to 10^{-20}. In addition, mole numbers less than 10^{-20} are set equal to 10^{-20}. If convergence is not obtained after ITMAX iterations, where ITMAX is the user-supplied maximum number of corrector iterations to be attempted, the steplength is reduced as discussed in the section Steplength Control and the step retried. If convergence is achieved in M iterations ($M \leq$ ITMAX), the step is accepted as successful and the solution is updated.

$$\sigma_{i,n+1} = \sigma_{i,n+1}^{(M)}; \quad i = 1 - N$$

$$T_{n+1} = T_{n+1}^{(M)} \tag{A24}$$

APPENDIX B

DESCRIPTION OF SUBPROGRAMS

ALGOR1 - Filters initial conditions. Computes initial stepsize, iterates L-formulated implicit Euler approximations to convergence.

ALGOR2 - Nonstiff regime solver. Employs JN iteration to solve equations.

ALGOR3 - Stiff regime solver. Employs NR iteration.

BSOLV - Standard routine for forward and back substitution of a previously LU-decomposed matrix.

CONVG - Manages control and monitoring of both NR and JN iteration; indicates when convergence criteria have been satisfied.

CREKEQ - Manages calls to subroutine EQUIL.

CREKO - Initializing routine for elemental and thermochemical data. Reads and catalogs data in NASA format from data file.

CREK1D - Main routine. Sets initial timestep, manages control of solution until end of prescribed timestep, and returns solution to calling program.

DCOMP - Performs standard LU-decomposition of a square matrix.

DERIVS - Evaluates kinetic expressions, and on demand, elements of Jacobian matrix.

EQUIL - Calculates adiabatic flame temperature and equilibrium species distribution for a mixture of gases at prescribed pressure and enthalpy.

ERATIO - Calculates fuel-air equivalence ratio of a mixture of gases.

GLOBL - Calculates kinetic rates and contributions to Jacobian for specially -prescribed global kinetic rate expressions.

HCPG - Evaluates enthalpy, constant-pressure specific heat capacity and one-atmosphere specific molar Gibbs function of a mixture of gases.

MECHN - Initializing routine for reading and cataloging kinetic rate data and establishing reaction stoichiometry vectors.

NAMLST - Initializing routine for reading and cataloging problem control parameters, debugging options, etc.

TEMPRK - Performs a single Newton iteration to determine the temperature of a given mixture of gases.

APPENDIX C

SAMPLE INPUT AND OUTPUT

Sample input

```
ELEMENTS
C         12.01115  4.0
H         1.00797   1.
O         15.9994   -2.0
N         14.0067   0.0

THERMO
CO                  J 9/65C  1.0  1.00 0.00 0.G   300.000  5000.000
 0.29840689E 01 0.14891387E-02-0.57899678E-06 0.10364576E-09-0.69353499E-14
-0.14245227E 05 0.63479147E 01 0.37100916E 01-0.16190964E-02 0.36923584E-05
-0.20319673E-08 0.23953344E-12-0.14356309E 05 0.29555340E 01
CO2                 J 9/65C  1.0  2.00 0.00 0.G   300.000  5000.000
 0.44608040E 01 0.30981717E-02-0.12392566E-05 0.22741323E-09-0.15525948E-13
-0.48961438E 05-0.98635978E 00 0.24007788E 01 0.87350905E-02-0.66070861E-05
 0.20021860E-08 0.63274039E-15-0.48377520E 05 0.96951447E 01
H                   J 9/65H  1.00 0.00 0.00 0.G   300.000  5000.000
 0.25000000E 01 0.0            0.0            0.0            0.0
 0.25471625E 05-0.46011758E 00 0.25000000E 01 0.0            0.0
 0.0            0.0            0.25471625E 05-0.46011758E 00
H2                  J 3/61H  2.0  0.0  0.0  0.G   300.000  5000.000
 0.31001883E 01 0.51119458E-03 0.52644204E-07-0.34909964E-10 0.36945341E-14
-0.87738013E 03-0.19629412E 01 0.30574446E 01 0.26765198E-02-0.58099149E-05
 0.55210343E-08-0.18122726E-11-0.98890430E 03-0.22997046E 01
H2O                 J 3/61H  2.0  1.00 0.00 0.G   300.000  5000.000
 0.27167616E 01 0.29451370E-02-0.80224368E-06 0.10226681E-09-0.48472104E-14
-0.29905820E 05 0.66305666E 01 0.40701275E 01-0.11084499E-02 0.41521180E-05
-0.29637404E-08 0.80702101E-12-0.30279719E 05-0.32270038E 00
N                   J 3/61N  1.00 0.00 0.00 0.G   300.000  5000.000
 0.24502678E 01 0.10661458E-03-0.74653315E-07 0.18796520E-10-0.10259837E-14
 0.56116035E 05 0.44487572E 01 0.25030699E 01-0.21800181E-04 0.54205284E-07
-0.56475602E-10 0.20999038E-13 0.56098898E 05 0.41675749E 01
NO                  J 6/63N  1.0  1.00 0.00 0.G   300.000  5000.000
 0.31889992E 01 0.13382279E-02-0.52899316E-06 0.95919314E-10-0.64847928E-14
 0.98283242E 04 0.67458115E 01 0.40459509E 01-0.34181783E-02 0.79819174E-05
-0.61139254E-08 0.15919072E-11 0.97453867E 04 0.29974976E 01
N2                  J 9/65N  2.0  0.0  0.0  0.G   300.000  5000.000
 0.28963194E 01 0.15154863E-02-0.57235275E-06 0.99807385E-10-0.65223536E-14
-0.90586182E 03 0.61615143E 01 0.36748257E 01-0.12081496E-02 0.23240100E-05
-0.63217520E-09-0.22577253E-12-0.10611587E 04 0.23580418E 01
O                   J 6/62O  1.00 0.00 0.00 0.G   300.000  5000.000
 0.25420580E 01-0.27550603E-04-0.31028029E-08 0.45510670E-11-0.43680494E-15
 0.29230801E 05 0.49203072E 01 0.29464283E 01-0.16381664E-02 0.24210303E-05
-0.16028432E-08 0.38906964E-12 0.29147641E 05 0.29639931E 01
OH                  J 3/66O  1.H  1.00 0.00 0.G   300.000  5000.000
 0.29106417E 01 0.95931627E-03-0.19441700E-06 0.13756646E-10 0.14224542E-15
 0.39353811E 04 0.54423428E 01 0.38375931E 01-0.10778855E-02 0.96830354E-06
 0.18713971E-09-0.22571089E-12 0.36412820E 04 0.49370009E 00
O2                  J 9/65O  2.0  0.0  0.0  0.G   300.000  5000.000
 0.36219521E 01 0.73618256E-03-0.19652219E-06 0.36201556E-10-0.28945623E-14
-0.12019822E 04 0.36150942E 01 0.36255980E 01-0.18782183E-02 0.70554543E-05
-0.67635071E-08 0.21555977E-11-0.10475225E 04 0.43052769E 01

MECHANISM
CO      OH                CO2      H                    11.49   0.0      0.596   CGS     1
```

```
H       02              O       OH              14.34   0.0     16.492  CGS      2
H2      O               H       OH              13.48   0.0     9.339   CGS      3
H2O     O               OH      OH              13.92   0.0     18.121  CGS      4
H       H2O             H2      OH              14.0    0.0     19.870  CGS      5
N       02              NO      O               9.81    1.0     6.250   CGS      6
N2      O               N       NO              13.85   0.0     75.506  CGS      7
NO      M               N       O       M       20.60   -1.5    149.025 CGS      8
H       H       M       H2              M       18.0    -1.0    0.0     CGS      9
O       O       M       02              M       18.14   -1.0    0.340   CGS     10
H       OH      M       H2O             M       23.88   -2.6    0.0     CGS     11
H2      02              OH      OH              13.0    0.0     43.0    CGS     12

 &INPUT EPS=1.0E-02,ITMAX=10,TKIN=1000.0,PATM=10.0,LDEBUG=.F.,
   NDEBUG=1,DELT=2.0,SECS=1.E-3, STOP=1.E-03  &END
REACTANTS
C 1.     O 1.                           CO        1.0       M      G         STOICH,
H 2.                                    H2        2.0       M      G         PYRLIZED
N 2.                                    N2        7.52      M      G         CH4-AIR
O 2.                                    O2        1.5       M      G         MIXTURE.
```

```
     ELEMENTS
C           12.011149       4.000000

H            1.007970        1.000000

O           15.999399       -2.000000

N           14.006700        0.000000

     THERMO
        CO                J 9/65  C    1.0    1.00   0.00   0.  G     300.000  5000.000             0
         0.29840689E 01 0.14891387E-02-0.57899678E-06 0.10364576E-09-0.69353465E-14    0
        -0.14245227E 05 0.63479147E 01 0.37100916E 01-0.16190964E-02 0.36923575E-05    0
        -0.20319673E-08 0.23953344E-12-0.14356309E 05 0.29555340E 01                   0

        CO2               J 9/65  C    1.0    2.00   0.00   0.  G     300.000  5000.000             0
         0.44608040E 01 0.30981717E-02-0.12392566E-05 0.22741323E-09-0.15525948E-13    0
        -0.48961438E 05-0.98635978E 00 0.24007788E 01 0.87350905E-02-0.66070852E-05    0
         0.20021860E-08 0.63274039E-15-0.48377520E 05 0.96951447E 01                   0

        H                 J 9/65  H    1.00   0.00   0.00   0.  G     300.000  5000.000             0
         0.25000000E 01     0.00000000     0.00000000     0.00000000     0.00000000    0
         0.25471625E 05-0.46011758E 00 0.25000000E 01     0.00000000     0.00000000    0
             0.00000000     0.00000000 0.25471625E 05-0.46011758E 00                   0

        H2                J 3/61  H    2.0    0.0    0.0    0.  G     300.000  5000.000             0
         0.31001883E 01 0.51119458E-03 0.52644204E-07-0.34909964E-10 0.36945341E-14    0
        -0.87738013E 03-0.19629412E 01 0.30574446E 01 0.26765198E-02-0.58099140E-05    0
         0.55210343E-08-0.18122726E-11-0.98890430E 03-0.22997046E 01                   0

        H2O               J 3/61  H    2.0    1.00   0.00   0.  G     300.000  5000.000             0
         0.27167616E 01 0.29451370E-02-0.80224368E-06 0.10226681E-09-0.48472070E-14    0
        -0.29905816E 05 0.66305666E 01 0.40701275E 01-0.11084499E-02 0.41521180E-05    0
        -0.29637404E-08 0.80702101E-12-0.30279719E 05-0.32270032E 00                   0

        N                 J 3/61  N    1.00   0.00   0.00   0.  G     300.000  5000.000             0
         0.24502678E 01 0.10661458E-03-0.74653315E-07 0.18796520E-10-0.10259837E-14    0
         0.56116031E 05 0.44487572E 01 0.25030699E 01-0.21800181E-04 0.54205284E-07    0
        -0.56475602E-10 0.20999038E-13 0.56098895E 05 0.41675749E 01                   0

        NO                J 6/63  N    1.0    1.00   0.00   0.  G     300.000  5000.000             0
         0.31889992E 01 0.13382279E-02-0.52899316E-06 0.95919300E-10-0.64847928E-14    0
         0.98283203E 04 0.67458115E 01 0.40459509E 01-0.34181783E-02 0.79819165E-05    0
        -0.61139254E-08 0.15919072E-11 0.97453828E 04 0.29974976E 01                   0

        N2                J 9/65  N    2.0    0.0    0.0    0.  G     300.000  5000.000             0
         0.28963194E 01 0.15154863E-02-0.57235275E-06 0.99807385E-10-0.65223536E-14    0
        -0.90586182E 03 0.61615143E 01 0.36748257E 01-0.12081496E-02 0.23240100E-05    0
        -0.63217498E-09-0.22577253E-12-0.10611587E 04 0.23580418E 01                   0

        O                 J 6/62  O    1.00   0.00   0.00   0.  G     300.000  5000.000             0
         0.25420580E 01-0.27550603E-04-0.31028027E-08 0.45510670E-11-0.43680494E-15    0
         0.29230801E 05 0.49203072E 01 0.29464283E 01-0.16381664E-02 0.24210294E-05    0
        -0.16028432E-08 0.38906964E-12 0.29147641E 05 0.29639931E 01                   0

        OH                J 3/66  O    1.H    1.00   0.00   0.  G     300.000  5000.000             0
```

```
    0.29106417E 01 0.95931627E-03-0.19441700E-06 0.13756646E-10 0.14224542E-15    0
    0.39353809E 04 0.54423428E 01 0.38375931E 01-0.10778853E-02 0.96830354E-06    0
    0.18713971E-09-0.22571089E-12 0.36412820E 04 0.49370009E 00                   0

   02                J 9/65  0    2.0    0.0    0.0    0.  G     300.000  5000.000            0
    0.36219521E 01 0.73618256E-03-0.19652214E-06 0.36201556E-10-0.28945621E-14    0
   -0.12019822E 04 0.36150942E 01 0.36255980E 01-0.18782183E-02 0.70554543E-05    0
   -0.67635071E-08 0.21555969E-11-0.10475225E 04 0.43052769E 01                   0

MECHANISM

    1.  CO      OH                CO2     H                       11.490         0.000         0.596     CGS    1
  CALCULATED REVERSE RATE DATA, STD DEV AND CORR COEF  =          13.545         0.000        22.716     6.513E-02 9.996E-01

    2.  H       O2                O       OH                      14.340         0.000        16.492     CGS    2
  CALCULATED REVERSE RATE DATA, STD DEV AND CORR COEF  =          13.235         0.000         0.476     2.083E-02 9.262E-01

    3.  H2      O                 H       OH                      13.480         0.000         9.339     CGS    3
  CALCULATED REVERSE RATE DATA, STD DEV AND CORR COEF  =          13.123         0.000         7.308     2.608E-03 1.000E 00

    4.  H2O     O                 OH      OH                      13.920         0.000        18.121     CGS    4
  CALCULATED REVERSE RATE DATA, STD DEV AND CORR COEF  =          12.923         0.000         1.025     1.380E-02 9.922E-01

    5.  H       H2O               H2      OH                      14.000         0.000        19.870     CGS    5
  CALCULATED REVERSE RATE DATA, STD DEV AND CORR COEF  =          13.359         0.000         4.803     1.634E-02 9.995E-01

    6.  N       O2                NO      O                        9.810         1.000         6.250     CGS    6
  CALCULATED REVERSE RATE DATA, STD DEV AND CORR COEF  =          12.800         0.000        41.408     5.705E-02 9.999E-01

    7.  N2      O                 N       NO                      13.850         0.000        75.506     CGS    7
  CALCULATED REVERSE RATE DATA, STD DEV AND CORR COEF  =          13.196         0.000         0.281     4.718E-03 9.881E-01

    8.  NO      M                 N       O       M               20.600        -1.500       149.025     CGS    8
  CALCULATED REVERSE RATE DATA, STD DEV AND CORR COEF  =          11.420         0.000        -6.109     5.933E-02 9.959E-01

    9.  H       H       M         H2              M               18.000        -1.000         0.000     CGS    9
  CALCULATED REVERSE RATE DATA, STD DEV AND CORR COEF  =          17.949         0.000       101.227     5.105E-02 1.000E 00

   10.  O       O       M         O2              M               18.140        -1.000         0.340     CGS   10
  CALCULATED REVERSE RATE DATA, STD DEV AND CORR COEF  =          18.837         0.000       115.552     7.434E-02 1.000E 00

   11.  H       OH      M         H2O             M               23.880        -2.600         0.000     CGS   11
  CALCULATED REVERSE RATE DATA, STD DEV AND CORR COEF  =          18.611         0.000       111.213     1.489E-01 9.999E-01

   12.  H2      O2                OH      OH                      13.000         0.000        43.000     CGS   12
  CALCULATED REVERSE RATE DATA, STD DEV AND CORR COEF  =          11.538         0.000        24.955     1.825E-02 1.000E 00
   1.      CO      OH              ----=    CO2     H

   2.      H       O2              ----=    O       OH

   3.      H2      O               ----=    H       OH

   4.      H2O     O               ----=    OH      OH

   5.      H       H2O             ----=    H2      OH

   6.      N       O2              ----=    NO      O

   7.      N2      O               ----=    N       NO
```

```
     8.    NO             M        ----=    N      O        M

     9.    H       H      M        ----=    H2              M

    10.    O       O      M        ----=    O2              M

    11.    H       OH     M        ----=    H2O             M

    12.    H2      O2              ----=    OH     OH


                               KINETIC RATE DATA IN SI UNITS
     J       MODR          ID                     BX        TEN        TACT            BX2       TEN2        TACT2

    1.        1      1   10    2    3          8.490      0.000      299.949         10.545     0.000    11432.273
    2.        1      3   11    9   10         11.340      0.000     8299.945         10.235     0.000      239.505
    3.        1      4    9    3   10         10.480      0.000     4700.047         10.123     0.000     3677.744
    4.        1      5    9   10   10         10.920      0.000     9119.770          9.923     0.000      515.668
    5.        1      3    5    4   10         11.000      0.000     9999.996         10.359     0.000     2417.458
    6.        1      6   11    7    9          6.810      1.000     3145.446          9.800     0.000    20839.703
    7.        1      8    9    6    7         10.850      0.000    37999.977         10.196     0.000      141.567
    8.        2      7    0    6    9         17.600     -1.500    74999.938          5.420     0.000    -3074.641
    9.        3      3    3    4    0         12.000     -1.000        0.000         14.949     0.000    50944.621
   10.        3      9    9   11    0         12.140     -1.000      171.112         15.837     0.000    58153.891
   11.        3      3   10    5    0         17.880     -2.600        0.000         15.611     0.000    55970.461
   12.        1      4   11   10   10         10.000      0.000    21640.668          8.538     0.000    12558.973
&INPUT
DELT= 2.0
EPS= 0.9999998E-02
ITMAX= 10
TKIN= 1000.0
PATM= 10.0
TINY= 0.10E-19
SECS= 0.9999999E-03, 29*0.10E10
STOP= 0.9999999E-03
LDEBUG= F
NDEBUG= 1
&END

     REACTANTS
  C   1.00000  O   1.00000       0.00000       0.00000  CO           1.00000  M  G       1
  H   2.00000      0.00000       0.00000       0.00000  H2           2.00000  M  G       1
  N   2.00000      0.00000       0.00000       0.00000  N2           7.52000  M  G       1
  O   2.00000      0.00000       0.00000       0.00000  O2           1.50000  M  G       1

*** REACTANT STREAM  1 ***

     I     SPECIES               MOLECULAR WEIGHT    MOLE NUMBERS         MASS FRACTIONS
                                 (KGMOLE I)/(KG I)   (KGMOLE I)/(KG X)    (KG I)/(KG X)

     1.     CO                      2.801E 01          3.440E-03           9.636E-02
     2.     CO2                     4.401E 01              0.000               0.000
     3.     H                       1.008E 00              0.000               0.000
     4.     H2                      2.016E 00          6.880E-03           1.387E-02
     5.     H2O                     1.802E 01              0.000               0.000
     6.     N                       1.401E 01              0.000               0.000
```

```
      7.    NO                  3.001E 01          0.000           0.000
      8.    N2                  2.801E 01      2.587E-02       7.247E-01
      9.    O                   1.600E 01          0.000           0.000
     10.    OH                  1.701E 01          0.000           0.000
     11.    O2                  3.200E 01      5.160E-03       1.651E-01

            TEMPERATURE =    1.000E 03   DEG K
            ENTHALPY =       5.090E 05   JOULES/KG
            PRESSURE =       1.013E 06   N/M**2
            DENSITY =        2.947E 00   KG/M**3
            MEAN MOL WT =    2.418E 01   KG/KGMOLE

HSUBO, ER, PA, SM, RHOP, TK, TAU, TIME, NSTEP =
  5.090E 05 1.000E 00 1.013E 06 3.674E-02 1.266E 00 2.6192E 03     0.000 9.990E 09    0
        SPECIES NAMES

  CO          CO2         H           H2          H2O         N           NO          N2          O           OH
  O2
        SPECIES MOLE NUMBERS, S2(I)

  6.6051E-04   2.7794E-03   3.8895E-05   2.4178E-04   6.4945E-03   8.1164E-09   1.9647E-04   2.5770E-02   2.5897E-05   2.4847E-04
  2.8757E-04

         SPECIES MOLE FRACTIONS

  1.7976E-02   7.5645E-02   1.0586E-03   6.5802E-03   1.7675E-01   2.2090E-07   5.3472E-03   7.0136E-01   7.0481E-04   6.7624E-03
  7.8265E-03
HSUBO, ER, PA, SM, RHOP, TK, TAU, TIME, NSTEP =
  5.090E 05 1.000E 00 1.013E 06 3.666E-02 1.269E 00 2.6186E 03 7.064E-05 1.000E-03   99
        SPECIES NAMES

  CO          CO2         H           H2          H2O         N           NO          N2          O           OH
  O2
        SPECIES MOLE NUMBERS, S2(I)

  6.1412E-04   2.8292E-03   3.9434E-05   2.1601E-04   6.3588E-03   1.1887E-08   5.7265E-05   2.5840E-02   3.2643E-05   2.7593E-04
  3.9741E-04

         SPECIES MOLE FRACTIONS

  1.6752E-02   7.7173E-02   1.0756E-03   5.8921E-03   1.7345E-01   3.2425E-07   1.5620E-03   7.0484E-01   8.9041E-04   7.5267E-03
  1.0840E-02
```

REFERENCES

1. Tyson, T. J.: An Implicit Integration Method for Chemical Kinetics. TRW-9840-6002-RU-000, TRW Space Technology Laboratory Report, 1964.

2. Treanor, Charles E.: A Method for the Numerical Integration of Coupled First-Order Differential Equations with Greatly Different Time Constants. Mathematics of Computation, vol. 20, 1966, pp. 39-45.

3. Lomax, Harvard; and Bailey, Harry E.: A Critical Analysis of Various Numerical Integration Methods for Computing the Flow of a Gas in Chemical Non-equilibrium. NASA TN D-4109, 1967.

4. Dimitrov, V. I.: Some Mathematical Modeling Problems in Chemical Kinetics of High-Speed Processes. Arch. Termodyn. Spalania, vol. 6, no. 1, 1975, pp. 117-133.

5. Bittker, David A.; and Scullin, Vincent J.: General Chemical Kinetics Computer Program for Static and Flow Reactions, with Application to Combustion and Shock-Tube Kinetics. NASA TN D-6586, 1972.

6. Nickerson, G. R.; Frey, H. M.; and Coats, D. E.: Generalized Kinetic Analysis Program. Dynamic Science, Inc., 1971.

7. Gear, C. W.: Numerical Initial Value Problems in Ordinary Differential Equations. Prentice-Hall, 1971.

8. Gear, C. W.: The Automatic Integration of Ordinary Differential Equations. Commun. ACM, vol. 14, no. 3, Mar. 1971, p. 176.

9. Dickinson, Robert P.; and Gelinas, Robert J.: GENKIN-I: A General Kinetics Code-Atmospheric Applications. UCID-16577, Lawrence Livermore Laboratories, 1974.

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. J. Phys. Chem., vol. 81, no. 25, Dec. 15, 1977, pp. 2424-2427.

11. Pratt, D. T.: Calculation of Chemically Reacting Flows With Complex Chemistry. Studies in Convection, Vol. II, B. F. Launder, ed., Academic Press, 1976, pp. 191-220.

12. Pratt, David T.: New Computational Algorithms for Chemical Kinetics. National Bureau of Standards Special Publication 561-2, 1979, pp. 1265-1279.

13. Pratt, David T.: Coalescence/Dispersion Modeling of High-Intensity Combustion. J. Energy vol. 3, no. 3, May-June 1979, pp. 177-180.

14. Radhakrishnan, Krishnan; Heywood, John B.; and Tabaczynski, Rodney J.: Premixing Quality and Flame Stability: A Theoretical and Experimental Study. NASA CR-3216, 1979.

15. Radhakrishnan, Krishnan; and Heywood, John B.: Effects of Combustor Inlet Conditions on Flame Stability. Combustion Science and Technology, vol. 24, no. 5-6, 1981, pp. 165-178.

16. Radhakrishnan, K.; and Pratt, D. T.: A Coalescence/Dispersion Model for Turbulent Flame Stability. AIAA Journal, vol. 22, no. 3, Mar. 1984, pp. 388-393.

17. Hindmarsh, A. C.: LSODE and LSODI, Two New Initial Value Ordinary Differential Equation Solvers. ACM-Signum Newsletter, vol. 15, no. 4, Dec. 1980, pp. 10-11.

18. Hindmarsh, Alan C.: ODEPACK, A Systematized Collection of ODE Solvers. UCRL-88007, Lawrence Livermore Laboratory, 1982.

19. Lambert, J. D.: Computational Methods in Ordinary Differential Equations, John Wiley and Sons, 1973.

20. Curtiss, C. F.; and Hirschfelder, J. O.: Integration of Stiff Equations. Proc. Natl. Acad. Sci., vol. 38, 1952, pp. 235-243.

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

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

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

24. Gordon, Sandford; and McBride, Bonnie J.: Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations. NASA SP-273, 1971.

25. Lapidus, Leon; and Seinfeld, John H.: Numerical Solution of Ordinary Differential Equations. Academic Press, 1971.

26. Miranker, Willard L.: Numerical Methods for Stiff Equations and Singular Perturbation Problems. D. Reidel Publishing Co., 1981.

27. Edsberg, L.: Integration Package for Chemical Kinetics. Stiff Differential Systems, Ralph A. Willoughby, ed., Plenum Press, 1974, pp. 81-94.

28. Wanner G.: On the Integration of Stiff Differential Equations. Numerical Analysis, J. Descloux and J. Marti, eds., International Series in Numerical Mathematics, Vol. 37, Birkhauser (Switzerland) 1977, pp. 209-226.

29. Liniger, Werner; and Willoughby, Ralph A.: Efficient Integration Methods for Stiff Systems of Ordinary Differential Equations. SIAM Journal of Numerical Analysis, vol. 7, no. 1, Mar. 1970, pp. 47-66.

30. Brandon, Daniel M. Jr.: A New Single-Step Implicit Integration Algorithm with A-Stability and Improved Accuracy. Simulation, vol. 23, no. 1, July 1974, pp. 17-29.

31. Babcock, Paul D.; Stutzman, Leroy F.; and Brandon, Daniel M. Jr.: Improvements in a Single-Step Integration Algorithm. Simulation, vol. 28, no. 1, July 1979, pp. 1-10.

32. Moore, W. M.; and Eccles, T. K.: Developmental Studies of the Hydrogen-Nitrogen-Oxygen Systems. AFCRL-TR-73-0749, Utah State University, 1974. (AD-775752.)

33. McRae, J.; Goodin, W. R.; and Seinfeld, J. H.: Numerical Solution of the Atmospheric Diffusion Equation for Chemically Reacting Flows. J. Comput. Phys.,vol. 45, no. 1, Jan. 1982, pp. 1-42.

34. Atkinson, Kendall E.: An Introduction to Numerical Analysis. John Wiley and Sons, 1978.

35. Ortega, James; and Rheinbolt, W.: Iterative Solution of Nonlinear Equations in Several Variables. Academic Press, 1970.

36. Pratt, David T.; and Radhakrishnan, Krishnan: Fast Algorithms for Combustion Kinetics Calculations. Presented at the Fall Technical Meeting of the Western States Section of the Combustion Institute, Oct. 1981.

37. Pratt, D. T.: Fast Algorithms for Combustion Kinetics Calculations. Presented at the International Conference on Stiff Computation, (Park City, UT), Apr. 12-14, 1982.

38. Shampine, L. F.: Type-Insensitive ODE Codes Based on Implicit A-Stable Formulas. Mathematics of Computation, vol. 36, no. 154, Apr. 1981, pp. 499-510.

39. Shampine, L. F.: Type-Insensitive ODE Codes Based on A(α)-Stable Formulas. Mathematics of Computation, vol. 39, no. 159, July 1982, pp. 109-123.

40. Pratt, David T.: CREK-1D: A Computer Code for Transient, Gas-Phase Combustion Kinetics. Presented at the Spring Technical Meeting of the Western States Section of the Combustion Institute, Apr. 1983.

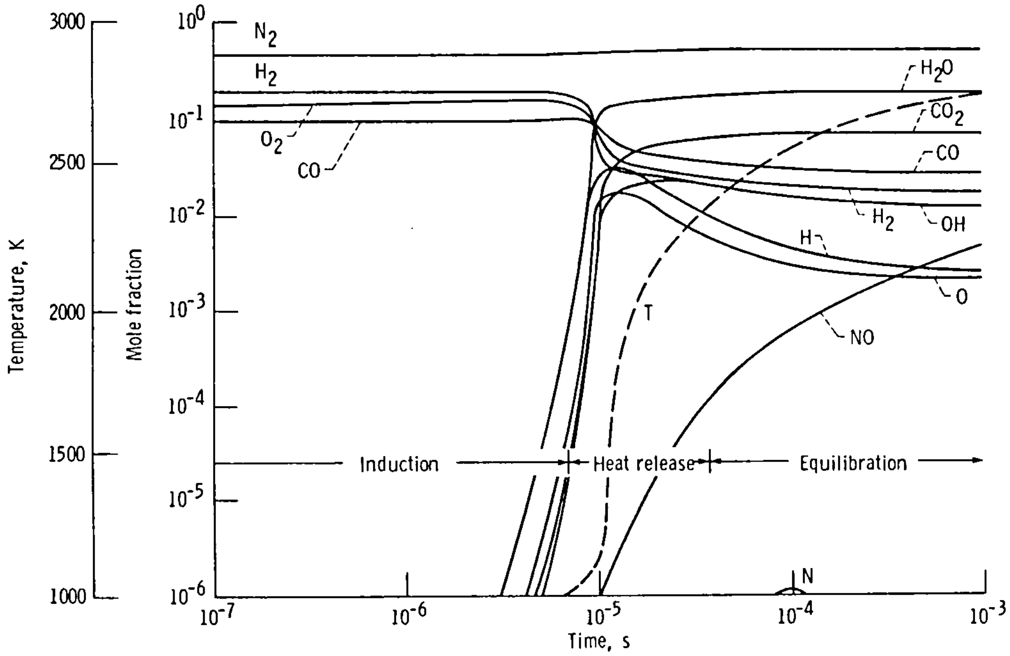

Figure 1. - Variation with time of chemical species mole fraction and temperature in adiabatic batch reaction. (Pryolized methane-air, stoichiometric, initial temperature = 1000 K, pressure = 10 atm).

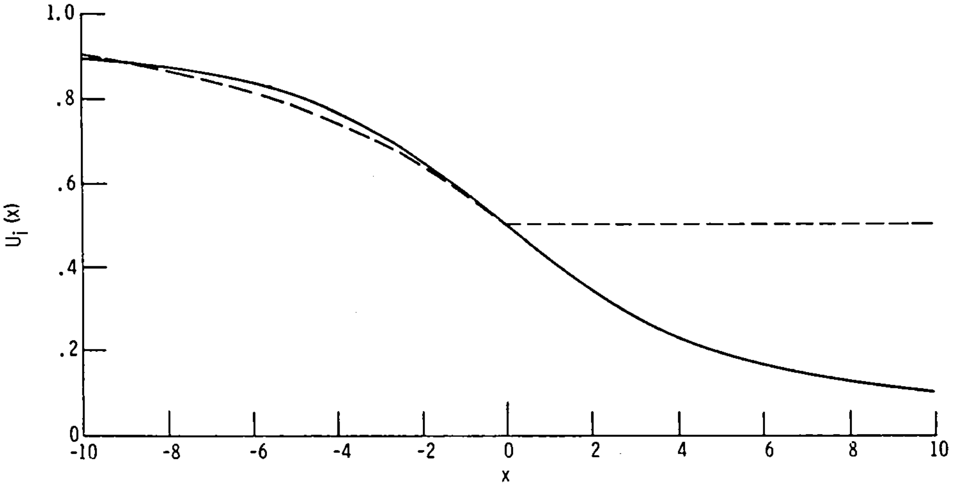

Figure 2. - Degree-of-implicitness or "tuning" factor U_i in equation (7). Solid curve is the exact equation (11), dashed curve is the approximate equation (45).

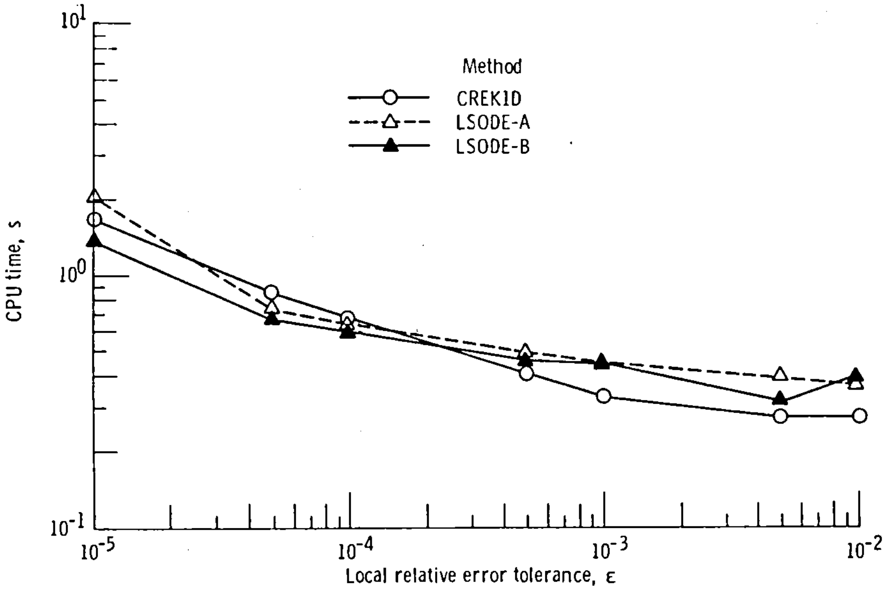

Figure 3. - Variation of CPU time with local relative error tolerance for test problem 1.

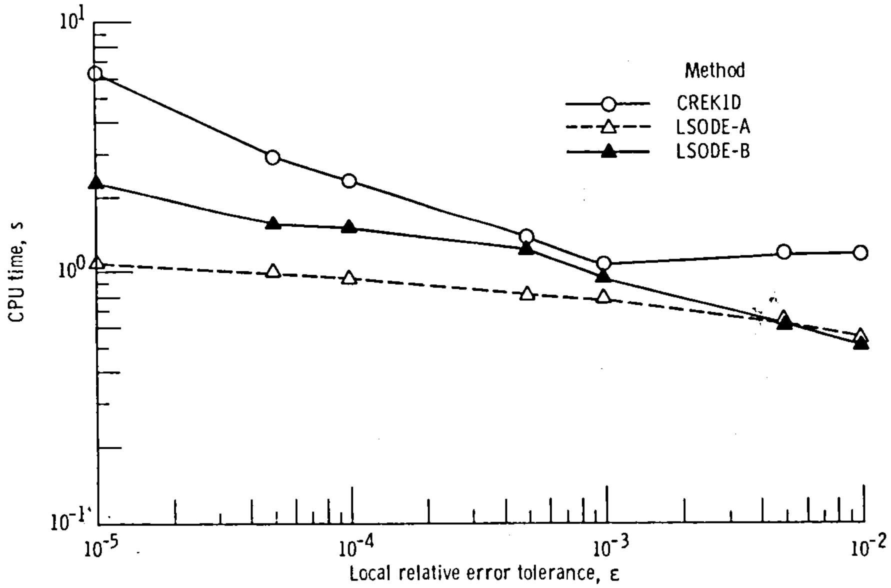

Figure 4. - Variation of CPU time with local relative error tolerance for test problem 2.

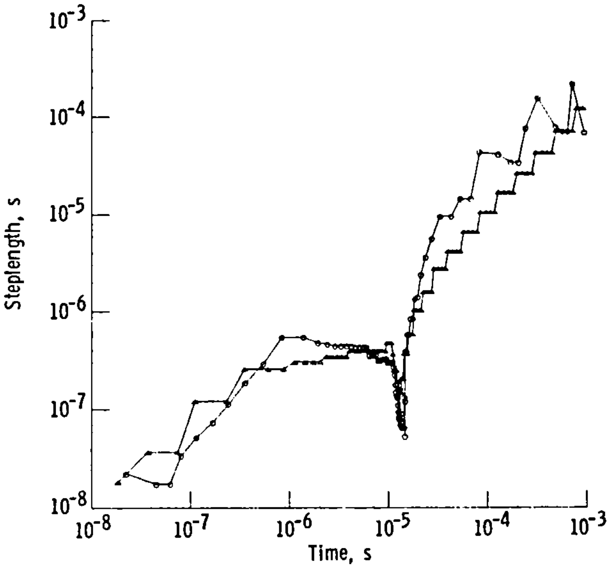

Figure 5. - Variation with time of steplength successfully used by CREK1D (o) and LSODE (△) for test problem 1.

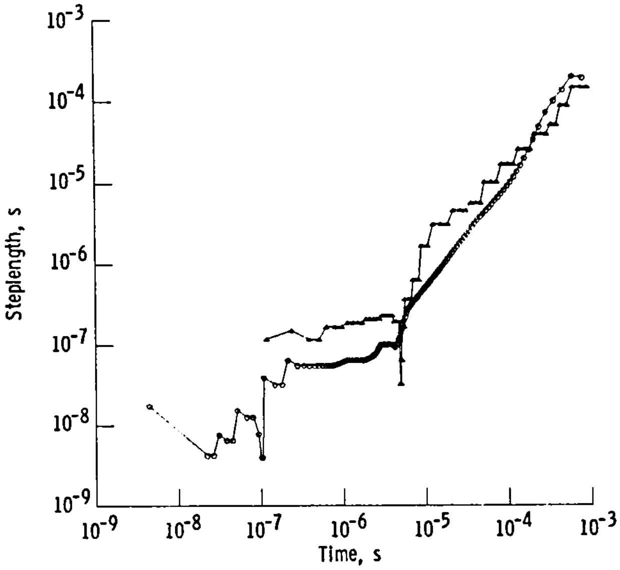

Figure 6. - Variation with time of steplength successfully used by CREK1D (o) and LSODE (△) for test problem 2.

1. Report No. NASA TM-83806	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle

CREK1D: A Computer Code for Transient, Gas-Phase Combustion Kinetics

5. Report Date

October 1984

6. Performing Organization Code

505-31-42

7. Author(s)

David T. Pratt and Krishnan Radhakrishnan

8. Performing Organization Report No.

E-2176

10. Work Unit No.

9. Performing Organization Name and Address

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

11. Contract or Grant No.

13. Type of Report and Period Covered

Technical Memorandum

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Washington, D.C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes

David T. Pratt, University of Washington, Dept. of Mechanical Engineering, Seattle, Washington 98195 (work performed under NASA Grant NAG 3-147); Krishnan Radhakrishnan; NRC-NASA Research Associate, on leave from the University of Michigan, Dept. of Mechanical Engineering and Applied Mechanics, Ann Arbor, Michigan 48109.

16. Abstract

This report describes a new algorithm for fast, automatic integration of chemical kinetic rate equations describing homogeneous, gas-phase combustion at constant pressure. Particular attention is paid to the distinguishing physical and computational characteristics of the induction, heat-release and equilibration regimes. The two-part predictor-corrector algorithm, based on an "exponentially-fitted trapezoidal rule," includes filtering of ill-posed initial conditions, automatic selection of Newton-Jacobi or Newton iteration for convergence to achieve maximum computational efficiency while observing a prescribed error tolerance. The new algorithm was found to compare favorably with LSODE on two representative test problems drawn from combustion kinetics.

17. Key Words (Suggested by Author(s)) Chemical kinetics; Stiff ODE; Numerical methods; Exponential fitting; Tunable trapezoidal rule	18. Distribution Statement Unclassified - unlimited STAR Category 07

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of pages	22. Price*

*For sale by the National Technical Information Service, Springfield, Virginia 22161

National Aeronautics and
Space Administration

Washington, D.C.
20546

Official Business
Penalty for Private Use, $300

SPECIAL FOURTH CLASS MAIL
BOOK

Postage and Fees Paid
National Aeronautics and
Space Administration
NASA-451

DO NOT REMOVE SLIP FROM MATERIAL

Delete your name from this slip when returning material to the library.

NAME	DATE	MS
Ali S. Kheireddin	12/3/92	238

NASA Langley (Rev. Dec. 1991) RIAD N-75

NASA

ER: If Undeliverable (Section 158
Postal Manual) Do Not Return