NASA Contractor Report 4196

A Generalized Chemistry Version of SPARK

Mark H. Carpenter

CONTRACT NAS1-18599
DECEMBER 1988

NASA

NASA Contractor Report 4196

A Generalized Chemistry Version of SPARK

Mark H. Carpenter
Analytical Services and Materials, Inc.
Hampton, Virginia

Prepared for
Langley Research Center
under Contract NAS1-18599

National Aeronautics
and Space Administration

Scientific and Technical
Information Division

1988

A GENERALIZED CHEMISTRY VERSION OF SPARK

Mark H. Carpenter*
Analytical Services and Material, Inc.
107 Research Drive, Hampton, VA 23665

ABSTRACT

An extension of the reacting H_2-air computer code SPARK is presented, which enables the code to be used on any reacting flow problem. Routines are developed that calculate in a general fashion, the reaction rates, and chemical Jacobians of any reacting system. In addition, an equilibrium routine is added so that the code will have frozen, finite rate, and equilibrium capabilities. The reaction rates for the species are determined from the law of mass action using Arrhenius expressions for the rate constants. The Jacobian routines are determined by numerically or analytically differentiating the law of mass action for each species. The equilibrium routine is based on a Gibbs free energy minimization routine. The routines are written in Fortran 77, with special consideration given to vectorization. Run times for the generalized routines are generally 20% slower than reaction specific routines. The numerical efficiency of the generalized analytical Jacobian, however, is nearly 300% better than the reaction specific numerical Jacobian used in SPARK.

NOMENCLATURE

A_j : reaction rate constant for jth reaction
b_j : body force of species i
C_i : concentration of species i
$\dot{C}_j$: time rate of change of C_j
C_p : specific heat at constant pressure
E : total internal energy; activation energy

---

*Presently, Research Scientist working under contract for NASA Langley Research Center

f_i : mass fraction of species i
g_j : Gibbs free energy of species i
G_R : Gibbs energy of reaction
h_i : enthalpy of species i
h_j^o : base enthalpy of species i
K_f : forward rate constant
K_b : backward rate constant
K_{eq} : equilibrium constant
M_i : molecular weight of species i
n_i : moles of species i
nl : number of species constraint equations
ns : number of chemical species
nr : number of chemical reactions
p : pressure
$\dot{q}$: heat flux
R^o : universal gas constant
S : entropy
T : temperature
T_R : reference temperature = $298^o K$
t : time
u : streamwise velocity
v : transverse velocity
$\tilde{u}_i$: streamwise diffusion velocity of species i
$\tilde{v}_i$: transverse diffusion velocity of species i
$\tilde{V}_i$: diffusion velocity vector of species i
x : streamwise coordinate
y : transverse coordinate
X_i : mole fraction of species i
λ : second viscosity coefficient; Lagrangian Multiplier
γ : stoichiometric coefficient; specific heat ratio
ρ : density
σ : normal stress
τ : shear stress
$\dot{\omega}_i$: species production rate of species i
μ_i : chemical potential of species i
μ : laminar viscosity
ξ : computational streamwise coordinate
η : computational transverse coordinate

INTRODUCTION

The SPARK [1] code is a two-dimensional Navier-Stokes and chemistry code which has gained wide acceptance as a means of resolving flows involving reacting hydrogen and air. In addition to solving the conservation equations of mass, momentum and energy, it tracks nine chemical species, eighteen reaction paths, and uses finite rate chemical kinetics to simulate the chemical reactions. Numerically, it is an explicit, time accurate, spatially elliptic finite difference code, which uses MacCormack's technique[2] to integrate the equations spatially and temporally. The codes' architecture incorporates vectorization whenever possible for the numerous spatial arrays in the formulation, making it highly efficient. One disadvantage with the present formulation of the SPARK code is that it is written specifically for the H_2-air reaction. It would be advantageous if the reaction specific chemistry could easily be modified so that any chemically reacting flow could be modeled without substantially rewritting the code.

For certain flows, it is informative to compare finite rate results with those obtained assuming frozen and equilibrium chemical approximations. The frozen and equilibrium limits represent the lower and upper bounds achievable from chemical interactions and bracket the finite rate results between them. For H_2-air systems, seldom is the equilibrium approximation strictly valid, owing to the rapid hydrodynamic timescales in the problems. It is, however, useful to perform bracket analyses on reacting flows, to see how nearly frozen or equilibrated each flow is. Nozzles have traditionally been calculated assuming the frozen and equilibrated chemistry approximations, thus relying heavily on the equilibrated flow capabilities.

For flows where the chemistry timescale is orders of magnitude faster than the hydrodynamic timescales, the equilibrium approximation becomes a realistic means of accounting for the chemical relaxation processes, at considerable savings over full finite rate calculations. In particular, high temperature air chemistry fits into this category, and could be reasonably approximated with an equilibrium chemical assumption.

The most efficient means of calculating a particular flow depends in the ratios between the chemical and hydrodynamic timescales. For fast (slow) chemistry, the equilibrium (frozen) approximation can be used effectively. If the timescales are of the same order, a finite rate calculation must be used. Which chemical species and reaction paths are needed to resolve the physics, or whether a frozen or equilibrated flow is applicable, is generally not known before starting the calculation, and must be iterated on to find the most efficient method for each problem. This iterative process makes a generalized SPARK code very desirable.

The principle motivation for this work is the need for a modified version of the existing SPARK [1] code, capable of accommodating any reaction system. It must be easy and systematic to modify, thus reducing programming time and errors. The SPARK code is presently capable of tracking the governing fluid mechanical equations, as well as any number of chemical species. Since the chemistry portion of the SPARK code is modular in structure, the underlying framework need not be changed to accommodate different chemical species, reactions or reaction rates. Only the subroutines in which these features are calculated must be modified.

Specifically, the SPARK code is modified in the following way. A generalized properties routine is added to the code, in which the thermodynamic and kinematic properties of the reacting species are introduced. Where or how these properties are obtained from the literature is left up to the user. The existing reaction rate routine is replaced by a generalized routine, capable of determining the reaction rate of any reacting system. The chemical Jacobian routine which calculates the numerical Jacobian of the H_2-air reacting system is replaced by a generalized numerical Jacobian routine. In addition, a generalized analytical chemical Jacobian is developed to promote numerical accuracy and efficiency. Finally, a routine which calculates the equilibrium species concentrations given a particular temperature and pressure is added. All subroutines which are developed are built around the existing SPARK code structure in which the unknowns (for instance the species reaction rates) are calculated simultaneously at all grid points in the domain. As in SPARK, a judicious attempt is made to utilize vectorization whenever possible.

The usefulness and need for a generalized reaction scheme as well as a generalized Jacobian for the SPARK code is clearly evident from the above discussion. This code could be used during an optimization study to vary reacting species and paths systematically, or to model any chemically reacting system. Thus, given sufficient knowledge of the relevant reaction species, the appropriate reaction routes, and accurate reaction rates, any chemically reaction flow can be resolved in a spatially and temporally developing manner. Although the code was designed specifically for the SPARK code, it is hoped that the basic ideas can be extended to other chemistry codes which need similar modifications.

ANALYSIS

Governing Equations

Since extensive detail of the SPARK code exists in Reference [1], particularly the governing equations and numerical techniques needed to solve these equation, only a brief summary of the equations will be presented here. The chemistry equations will be addressed with more rigor since they are the emphasis of this work.

The equations governing the conservation of mass, momentum in two dimensions, and energy, and the species conservation equations can be written as [1]

$$\rho_t + (\rho u)_x + (\rho v)_y = 0 \tag{1}$$

$$(\rho u)_t + (\rho uu - \sigma_x)_x + (\rho uv - \tau_{xy})_y = \rho \sum_{i=1}^{ns} f_i b_{ix} \tag{2}$$

$$(\rho v)_t + (\rho uv - \tau_{yx})_x + (\rho vv - \sigma_y)_y = \rho \sum_{i=1}^{ns} f_i b_{iy} \tag{3}$$

$$(\rho E)_t + [(\rho E - \sigma_x)u - \tau_{xy} v + q_x]_x + [(\rho E - \sigma_y)v - \tau_{yx} u + q_y]_y = \rho \sum_{i=1}^{ns} f_i \vec{b}_i \cdot (\vec{V} + \tilde{\vec{V}}) \tag{4}$$

$$(\rho f_i)_t + [\rho(u + \tilde{u})f_i]_x + [\rho(v + \tilde{v})f_i]_y = \dot{\omega} \tag{5}$$

$$\sigma_x = -p + \lambda(u_x + v_y) + 2\mu u_x \tag{6}$$

$$\sigma_y = -p + \lambda(u_x + v_y) + 2\mu v_y \tag{7}$$

$$\tau_{xy} = \tau_{yx} = \mu(u_y + v_x) \tag{8}$$

$$q_x = -kT_x + \rho \sum_{i=1}^{ns} h_i f_i \tilde{u}_i + R^o T \sum_{i=1}^{ns} \sum_{j=1}^{ns} \frac{X_j D_{Ti}}{M_i D_{ij}} (\tilde{u}_i - \tilde{u}_j) \tag{9}$$

$$q_y = -kT_y + \rho \sum_{i=1}^{ns} h_i f_i \tilde{v}_i + R^o T \sum_{i=1}^{ns} \sum_{j=1}^{ns} \frac{X_j D_{Ti}}{M_i D_{ij}} (\tilde{v}_i - \tilde{v}_j) \tag{10}$$

$$E = \sum_{i=1}^{ns} h_i f_i - \frac{p}{\rho} + \frac{u^2 + v^2}{2} \tag{11}$$

$$h_i = h_i^o + \int_{T_r}^{T} C_{p_i} dT \tag{12}$$

$$\frac{C_{p_i}}{R} = A_i + B_i T + C_i T^2 + D_i T^3 + E_i T^4 \tag{13}$$

$$p = \rho R^o T \sum_{i=1}^{ns} \frac{f_i}{M_i} \tag{14}$$

Equations 1-4 represent the continuity, u- and v- momentum, and energy equations. Equation 5 is the individual species mass conservation equation. Equations 6-13 describe how particular terms in equations 1-5 are modeled. Note that the enthalpy of the mixture is the summation of the partial enthalpies of the chemical species, and that C_p is modeled with a 4th order polynomial [3].

Generalized Chemistry

Chemical reaction rate expressions are usually determined by summing the contributions from each relevant reaction route (or path), to obtain the total rate of change of each species. Each path is governed by a law of mass action expression in which the rate constants can be determined from a temperature dependent Arrhenius expression. The reaction rate terms $\dot{\omega}$ present in equation 5, written in this form can be expressed as follows:

$$\sum_{i=1}^{ns} \gamma'_{ji} C_i \overset{K_{f_j}}{\rightleftharpoons} \sum_{i=1}^{ns} \gamma''_{ji} C_i \qquad j = 1, nr \tag{15}$$

$$\dot{\omega}_i = M_i \dot{C}_i = M_i \sum_{j=1}^{nr} (\gamma''_{ji} - \gamma'_{ji}) [K_{f_j} \prod_{m=1}^{ns} C_m^{\gamma'_{jm}} - K_{b_j} \prod_{m=1}^{ns} C_m^{\gamma''_{jm}}] \qquad i = 1, ns \tag{16}$$

where equation 15 describes the relevant chemical reaction paths for the system of species present in equation 5, and equation 16 is the reaction rates for each species i, as determined by the law of mass action.

The reaction constants K_{f_j} and K_{b_j} are determined as follows:

$$K_{f_j} = A_j T^{N_j} \exp(\frac{-E_j}{R^o T}) \tag{17}$$

$$K_{b_j} = \frac{K_{f_j}}{K_{eq_j}} \tag{18}$$

$$K_{eq_j} = (\frac{1}{R^o T})^{\Delta n} \exp(\frac{-\Delta G_{R_j}}{R^o T}) \tag{19}$$

$$\Delta G_{R_j} = \sum_{i=1}^{ns} \gamma''_{ji} g_i - \sum_{i=1}^{ns} \gamma'_{ji} g_i \qquad j = 1, nr \tag{20}$$

$$\frac{g_i}{R} = A_i (T - T \ln T) + \frac{B_i}{2} T^2 + \frac{C_i}{6} T^3 + \frac{D_i}{12} T^4 + \frac{E_i}{20} T^5 + F_i - G_i T \tag{21}$$

The forward reaction rate for each reaction path is determined from equation 17 from an Arrhenius law expression. The reverse reaction rate is back-calculated in equation 18 from the equilibrium constant defined in equation 19. Equations 20 and 21 describe how the change in Gibbs free energy for each reaction is calculated.

Generalized Jacobian

For some reacting flows, the chemical Jacobians of the chemical system must be evaluated. Certain chemical systems are numerically unstable when integrated with a time step comparable with the CFL condition. One remedy for this instability is treating implicitly the destabilizing chemical source terms $\dot{\omega}_i$ [10]. This technique requires the Newton linearization of the chemical source terms about the previous time step and results in the need for a chemical Jacobian relating the rate of change of each source term with respect to each species. This Jacobian can be calculate either numerically or analytically, and presents no real problem once a relevant system of reactions and species has been introduced.

Analytically, the chemical Jacobian is obtained by differentiating equation 16, and is defined by:

$$\frac{\partial \dot{C}_i}{\partial C_m} = \sum_{j=1}^{nr} (\gamma''_{ji} - \gamma'_{ji}) [\frac{K_{f_j} \gamma'_{jm}}{C_m} \prod_{l=1}^{ns} C_l^{\gamma'_{jl}} - \frac{K_{b_j} \gamma''_{jm}}{C_m} \prod_{l=1}^{ns} C_l^{\gamma''_{jl}}] \quad i = 1, ns \tag{22}$$

The numerical Jacobian is calculated by approximating the limit formula for the derivative as:

$$\frac{\partial \dot{C}_i}{\partial C_m} = \lim_{\Delta C_m \to 0} \frac{\dot{C}_i(P, T, C_1, ..C_{m-1}, C_m + \Delta C_m, C_{m+1}, ..C_{ns})}{\Delta C_m} \tag{23}$$

Each species concentration is individually perturbed while holding all others constant. The change in reaction rate is then assessed. Note that, in both Jacobian routines, the third body concentrations relevant in some of the chemical reactions are assumed constant to simplify the procedures. This is a valid assumption since the perturbation concentration is negligible compared with the combined concentrations of all species present. Also note that the third body collision efficiency is assumed equal to one for all species. This has been shown to be an invalid approximation [9] under certain flow situations, but is used here for simplicity.

Equilibrium Equations

Calculations which assume the flow to be in thermodynamic equilibrium, require an additional equation and do not rely on equation 5 for the local species mass fractions. The equilibrium state is characterized by the fact that the total Gibbs free energy of the mixture is at a minimum at this point, subject to the constraints of conservation of atomic species [5]:

$$G = \sum_{j=1}^{ns} \mu_i n_i \tag{24}$$

$$\sum_{j=1}^{ns} a_{lj} n_j - b_l^o = 0 \qquad l = 1, nl \tag{25}$$

Equation 24 defines the Gibbs free energy of the system, defined as the summation of the individual components free energy. Equation 25 relates the species constraint equations dictating the conservation of atomic mass of each elemental species. These equations are most easily solved using the method of Lagrangian multipliers. With this technique equations 24-25 become:

$$\begin{gathered} \mu_j + \sum_{i=1}^{ns} \lambda_i a_{ij} = 0 \\ \sum_{j=1}^{ns} a_{lj} n_j - b_l^o = 0 \qquad l = 1, nl \end{gathered} \tag{26}$$

where the λ_i are the Lagrangian multipliers, and nl is the number of constraints. Note that equation 26 is not solved when finite rate chemistry is being used. It is introduced only for the purpose of enabling SPARK to be run in the equilibrium mode.

GENERALIZED REACTION PROGRAM

The generalized chemistry routine consists of five subroutines: 1) PROPS, 2) GENRATE, 3) GENJACA, 4) GENJAC, and 5) EQUIL. Subroutine PROPS specifies the constants for the chemical species begin studied, so that its exact form depends on the chemical system being modeled. The other four subroutines have been written in a general form which applies for any chemical system obeying equations 1 - 21.

In subroutine PROPS, all of the constants used to define the chemical species' thermodynamic and kinematic properties, as well as the appropriate reaction rate constants are specified. The exact structure of PROPS is strongly dependent on the chemical system being simulated, on how the thermodynamic and kinematic features are modeled, and what form of chemical kinetics is used to calculate reaction rates. Implicit, however, is the assumption that all chemical systems behave according to the law of mass action through equations 15-23.

For SPARK, nine chemical species are used to represent the H_2 - air chemical reaction system. The thermodynamic properties (enthalpies, entropies, Gibbs free energies, and specific heats) are specified in PROPS from fourth order polynomial fits obtained from McBride [3]. The species' kinematic properties are specified from analytic expressions obtained from Williams [4] and White [11]. Specifically, the molecular viscosities and conductivities are modeled using Sutherlands law [3,11,13], and the binary diffusivities are obtained from Williams, and White [4,11]. Arrhenius type expressions are used for the reaction rates (equations 15 - 21), and appropriate reactions and coefficients are obtained from Jachimowski, and Dixon-Lewis [14,15]. The exact form of the properties routine will certainly change with different chemical reactions and is only presented here as an example.

GENRATE

Subroutine GENRATE calculates the reaction rates $\dot{\omega}$ for each of the chemical species as a function of space and time. The control elements of the routine are two (nr x ns+1) bit vectors describing γ'_{ij} and γ''_{ij}, the stoichiometric coefficients i for each reaction j. If γ'_{ij} is zero, then species i does not occur in reaction j. If γ'_{ij} is greater than one, then species i occurs γ'_{ij} times in reaction j. Note that there are ns+1 apparent species in the vector. The last species is the third body species, defined as the summation of all individual species concentrations present in the mixture. The third body becomes important in some reaction paths where three body collisions are required to stabilize the reaction.

The routine is essentially composed of two parts. In the first part, all the forward and backward reaction rates are calculated from equations 17-19, as well as all the species concentrations. The second portion of the routine calculates the species reactions rates directly from equation 16. This is done by summing the individual contributions to the species creation and depletion rates over all the reaction paths. Because the GENRATE routine is completely general it only depends on properties provided to it from the PROPS routine.

GENJACA

Subroutine GENJACA calculates the Jacobian matrix $J = \frac{\partial \omega_i}{\partial (\rho f_i)}$ analytically. Like the GENRATE routine, its control elements are the two bit vectors γ'_{ij} and γ''_{ij} describing which species i are involved in reaction j. The structure of the code is nearly identical to the GENRATE routine except that equation 22 is used instead of equation 16. The first part of the code calculates all the forward and backward reaction rates from equations 17 - 19 and the species concentrations. The second portion of the routine uses equation 22 to calculate each component of the (ns-1 x ns-1) Jacobian matrix describing the rate of change of reaction rate i with respect to species m. Again, as in the GENRATE code, each element of the Jacobian is the summation over all the reactions of the forward and backward contribution to the derivative. Also note that no where does division by species "C_m" occur in the program; rather the exponent γ'_{ij} is decreased by one to account for this effect. The GENJAC program is completely general, and depends only on the property information given to it by subroutine PROPS.

GENJAC

Subroutine GENJAC calculates the Jacobian matrix $J = \frac{\partial \omega_i}{\partial (\rho f_i)}$ numerically. It approximates each element of the matrix according to equation 23 by perturbing each species independently, and accessing the change in the reaction rate. Care must be take to ensure that the perturbation is of the proper order. If the perturbation concentration is too small, its effect may be indistinguishable from machine roundoff error. If it is too large, the approximation to the derivative may be poor. To avoid these problems, a median perturbation is used in which the perturbed value of the concentration is approximately equal to the change experienced by that concentration over the previous time step, or 10^{-6}, which ever is larger.

The routine is again composed of two parts. In the first, all the reaction rates are determined from equations 17 - 19 as well as the unperturbed species concentrations. Then a perturbation concentration is proposed and the reaction rates for each species are determined in a manner identical to that used in GENRATE: i.e. the cumulative addition to each species forward and backward reaction rate from each reaction route. Finally, the simple calculation of $[\dot{\omega}_i(C_m+\Delta C_m)-\dot{\omega}_i(C_m)]/\Delta C_m$ yields the explicit values for J. Again the routine is completely general and only depends on the properties given to it by the PROPS routine.

EQUIL

The EQUIL routine calculates the species concentration profiles at each spatial location, assuming the species to be in chemical equilibrium. The routine is based on a scalar version of an equilibrium routine developed by Gordon and McBride [5,6]. Since details about the theory and implementation of the Gordon and McBride codes can be found in the literature, only a brief review of the theory will be presented here.

The EQUIL routine solves equation 24 at each gridpoint. Since the equation is a nonlinear algebraic system, a Newton iteration is used to seek the root. The iteration is relaxed initially to ensure more robust convergence properties. The relaxation is determined by monitoring the rate of change in iteration space of the species concentrations. As the solution approaches the root, the relaxation is eliminated, thus resulting in quadratic convergence to the root. Generally, between 5 and 20 iterations are required to drive the residual down 10 orders of magnitude (far more than is actually needed), depending on the accuracy of the initial guess.

The routine minimizes the total Gibbs free energy of the mixture using the method of Lagrangian multipliers. The species Gibbs free energy is calculated from the thermodynamic data available in the PROPS routine using equations 21. The constraints on the atomic mass b_i^o are imposed by summing the initial levels of atomic species present at the spatial location. No provision is made for spatially varying constraint equations, since the computational efficiency of this technique was found to be uncompetitive with simple finite rate calculations. The minimization assumes that the pressure and the enthalpy of the mixture remain constant during the minimization. Thus, new species concentrations and a new temperature are the resultant of the minimization.

The coupling between the SPARK code and the EQUIL routine is very arbitrary. For most time steps, the SPARK code is run in frozen mode, and the frozen species values are updated periodically. This eliminates the need to explicitly account for the species continuity equations, and makes the procedure only slightly less efficient than a frozen flow calculation. However, the entire calculation is no longer time accurate due to the lagging in the chemistry. The species concentrations are assumed frozen between each call. The call updates the local species concentrations and temperature subject to the constraints of mass conservation, and constant pressure and mixture enthalpy. This was found by Davy [8] to be the most efficient method of coupling the hydrodynamic and species equations.

For each problem the most efficient method of updating can be found by trial and error. In general, the EQUIL routine should be called as infrequently as possible because of the amount of CPU time required by the Newton iteration. The problem, geometry, initial conditions, and various other parameters dictate this coupling. In general, the EQUIL routine is called about every 25-50 iterations.

The EQUIL routine vectorizes in the spatial direction, thus promoting computational efficiency. In addition, the EQUIL routine is written to accommodate the need (the SPARK code is presently not formulated with this feature) for spatially varying constraint equations, such as would be the case in diffusionally driven reacting flows. For these problems, the situation exists where certain portions of the flow will converge more rapidly than others. In this case, the converged elements of the vector are eliminated and the vector is repacked to again ensure vector efficiency.

RESULTS

The generalized reaction routines have been run in conjunction with the SPARK code to access their validity, accuracy and efficiency. The code exhibits striking simplicity in changing from one chemical reaction system to another. If the thermodynamic and kinematic information is readily available for the reacting species, testing various reaction paths is a matter of forming the control bit vectors γ'_{ij} and γ''_{ij}, and increasing the accompanying vector lengths. An obvious advantage in the formulation is that the chances for human error are greatly reduced. For example, changing the code from a Carbon based reacting flow to a H_2-air reacting system can be done in a matter of minutes if the properties of all the relevant species are presently known.

The scheme exhibits two minor disadvantages; 1) increased program complexity, and 2) decreased computational efficiency. A direct comparison between the existing SPARK reaction specific rate routine and the generalized scheme, each involving nine species and 18 reactions, shows the generalized scheme to require 20% more CPU time. A 30% increase in CPU time is required when using the generalized numerical Jacobian to replace the reaction specific Jacobian in SPARK. Because only a portion of the total computer time used by a code is used in these subroutines, the total increase in run time for SPARK is a somewhat smaller percentage. For example, for typical fully explicit runs, the 20% increase in the generalized reaction routine translates to about a 10% increase in total run time (50% of total time is spent in the reaction routine for a time accurate calculation). For implicit calculations where both the generalized reaction and Jacobian routines are used, total computer time increases greater than 20% are found since nearly 65% of all the time is spent in calculating the numerical Jacobians at each time step.

In comparing the run times of the generalized analytic and numerical Jacobians (a reaction specific analytical Jacobian does not exist at present in the spark code), the numerical Jacobian is about 285% more costly. Comparing the generalized analytic Jacobian with the reaction specific numerical Jacobian finds the reaction specific Jacobian over 200% more costly. Thus, the use of the generalized analytic Jacobian in SPARK decreases run-times by 25% for fully implicit runs! A reaction specific analytical Jacobian could be expected to increase the efficiency of fully implicit SPARK by approximately 30% based on these findings.

The use of the EQUIL routine increases the run-time of the SPARK code about 10% over the frozen run-time. It should be noted that the frozen and the equilibrium chemistry modes for the SPARK code are at least an order of magnitude more efficient than finite rate results using full chemistry.

Figure 1 shows the final calculations performed during the testing of the equilibrium routine. In each figure the frozen and equilibrium limits were found for a chemically reacting system. Then the reacting rates were increased and decreased from their actual values to see if in the limits the frozen and equilibrium values were approached. This was achieved by multiplying the pre-exponential factors for all the reaction paths by an arbitrary constant. By varying this constant, the chemistry time could be varied from "infinitely fast" to "infinitely slow". Figure 1 shows this test on the H_2-air system. The thrust levels from the nozzle are plotted against the log of the arbitrary multiplicative constant. The figure shows that asymptotic convergence is achieved at both the fast and slow extremes.

Figures 2-11 are presented to exhibit the capabilities of the generalized version of the SPARK code. They are not meant to display intricate details of specific reacting flows, but rather show a situation where a generalized version of the SPARK code is very convenient. The figures show the flow through a supersonic nozzle as calculated assuming two different chemical reaction systems. The question being addressed here is the overall importance of reacting nitrogen in nozzles of similar design and inlet conditions. This flow is complicated by the stiff nature of the reaction terms near the inlet [7] making the use of a chemical Jacobian essential. The nozzle inlet conditions are representative of combustor exit conditions in which H_2 and air were combusted at stoichiometric conditions, and are very nearly in chemical equilibrium. The two reacting systems, being compared here are, 1) 9 species and 18 reactions assuming nitrogen to be inert, and 2) 15 species and 35 reactions accounting for nitrogen chemistry.

Figures 2-5 show the velocity vectors, the pressure contours, the temperature contours, and the water mass fraction contours, respectively, for a two-dimensional supersonic nozzle. The lower surface represents the lower wall of the nozzle, and the upper surface is the centerline, or line of symmetry of the nozzle. The nozzle is calculated on a 30 by 20 grid, which by no means fully resolves the boundary layer along the wall. Figures 6-11 show a comparison of temperature profiles as calculated assuming various chemistry models. All of the figures show the axial variation of the temperature along the wall, J=1, midpoint, J=11, and the centerline, J=20. Figures 6-8 show a frozen, a finite rate chemistry, and an equilibrium calculation, calculated assuming nitrogen to be inert, with the nine species reaction scheme. Figures 9-11 show the flows calculated in the same manner with full account of any nitrogen reactions which may be present. Comparisons of the differences resulting from each chemistry model are easily made using the generalized code. Thus, an appropriate determination of the best chemistry model to be used for this flow can be made.

Presently, work is continuing to optimize the generalized routines' numerics and to make the properties more applicable to non-SPARK type CFD codes.

CONCLUDING REMARKS

A generalized reaction code has been developed as an add-on feature for the presently existing SPARK code. It has been written so as to eliminate the tedious steps necessary in converting the SPARK code from one particular reacting system to another. Its usefulness has been demonstrated in modeling a variety of H_2-air chemical reaction systems. The generalized routines have a slight decrease in efficiency associated with them, so that if numerous runs are to be made with one reaction system it is advantageous to develop a reaction specific code. The study also dictates that the use of an analytic Jacobian should be made whenever possible.

References

[1] Drummond, J.P, Rogers, R.C. and Hussainni, M.Y., "A Detailed Numerical Model of a Supersonic Reacting Mixing Layer," AIAA/ASME/SAE/ASEE 22nd Joint Propulsion Conference, Huntsville, Al., June 16-18, 1986.

[2] MacCormack, R.W., "The Effect of Viscosity in Hypervelocity Impact Cratering," AIAA Paper No. 69-354, April, 1969.

[3] McBride, B.J., Heimel, S., Ehlers, J.G., and Gordon, S., "Thermodynamic Properties to 6000$^o k$ for 210 Substances Involving the First 18 Elements," NASA SP-3001, 1963.

[4] Williams, F.A., Combustion Theory. Addison-Wesley Publishing Company, Inc., Reading, MA, 1965.

[5] Gordon, S. McBride, B.J., "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations," NASA SP-273, 1971.

[6] Svebla R.A., McBride, B.J., "Fortran IV Computer Program for Calculation of Thermodynamic and Transport Properties of Complex Chemical Systems," NASA TN D-7056, 1973.

[7] Emanuel, G., "Problems Underlying the Numerical Integration of the Chemical and Vibrational Rate Equations in a Near-Equilibrium Flow," AEDC-TDR-63-82, U.S. Air Force, March, 1963.

[8] Davy, W.C., Lombard, C.K., Green, M.J., "Forebody and Base Region Real-Gas Fow in Severe Planetary Entry by a Factored Implicit Numerical Method - Part II: Equilibrium Reactive Gas,", AIAA 19th Aerospace Sciences Meeting, St. Louis, Missouri, Jan 12-15, 1981.

[9] Rogers, R.C., and Schexnayder, C.J. Jr., "Chemical Kinetics Analysis of Hydrogen Air Ignition and Reaction Times," NASA TP-1856, July, 1981.

[10] Bussing,T.R.A.; and Murman, E.M., "A Finite Vvolume Method for Calculation of Compressed Chemically Reacting Flows," AIAA Paper No. 85-0331, Jan, 1985.

[11] White, F.M., Viscous Fluid Flow. McGraw-Hill, Inc., New York, 1974, pp 28-36.

[12] Suehla, R.A., "Estimated Viscosities and Thermal Conductivities of Gases at High Temperatures," NASA TR R-132, 1962.

[13] Wilke, C.R., "A Viscosity Equation for Gas Mixtures," Journal of Chem. Phy., V 18, No. 4, 1950, pp 517-519.

[14] Jachimowski, C.S., and Houghton, W.M., "Shock-Tube Study of the Initiation Process in the Hydrogen-Oxygen Reaction," Comb and Flame, no. 17, pp 25-30.

[15] Dixon-Lewis, G., and Williams, D.S., "Comprehensive Chemical Kinetics," C.H. Bamford and C.F.H. Tipper, Eds., Elsevier Press, Amsterdam, Vol. 17, 1977.

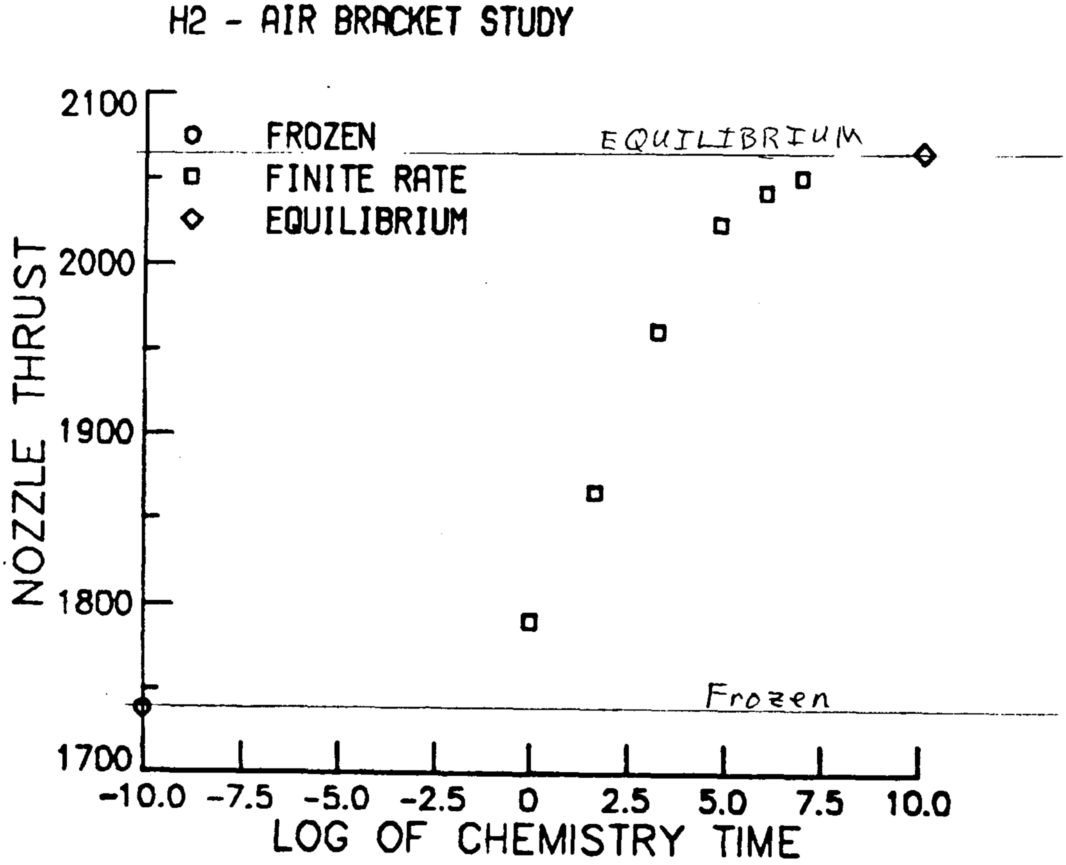

Figure 1: H_2- air asymptotic finite rate chemistry study. Chemistry approaches the frozen and equilibrium limits as the rate constants are adjusted.

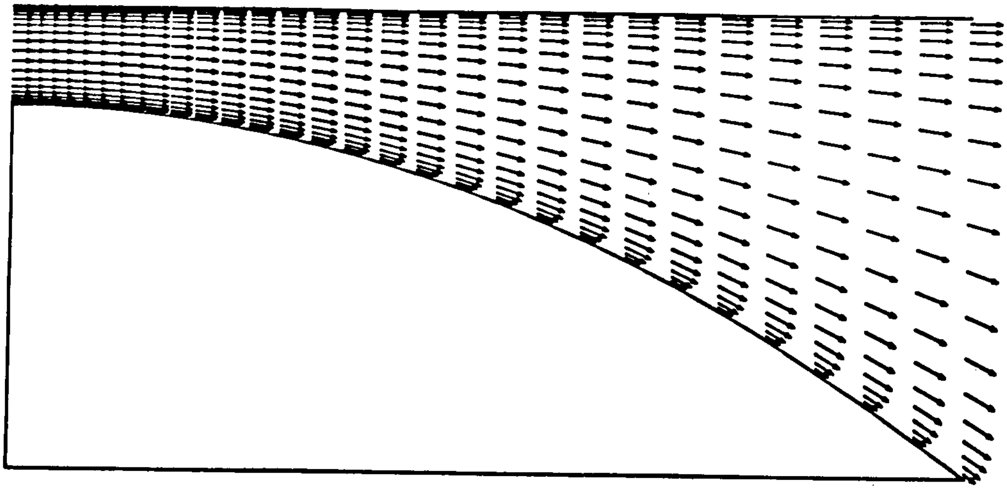

Figure 2: Velocity vectors for viscous flow through nozzle.

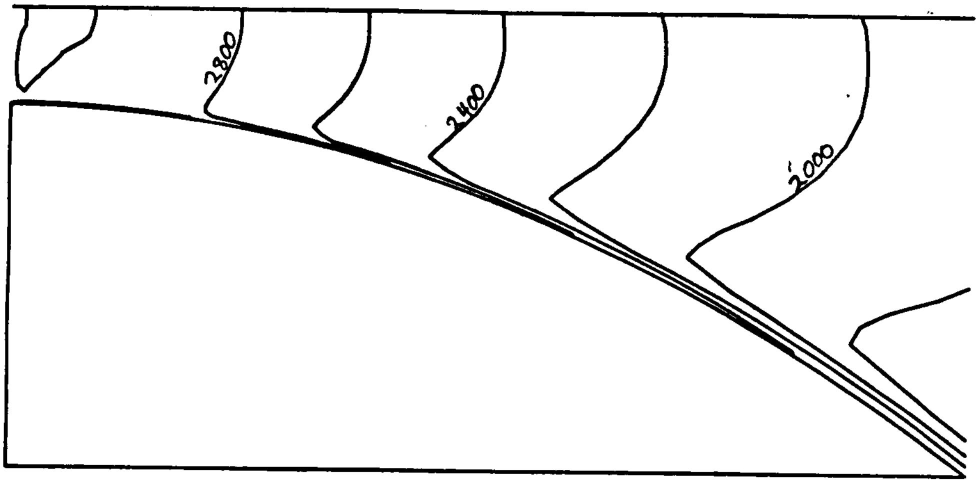

Figure 3: Temperature contours for viscous flow through nozzle.

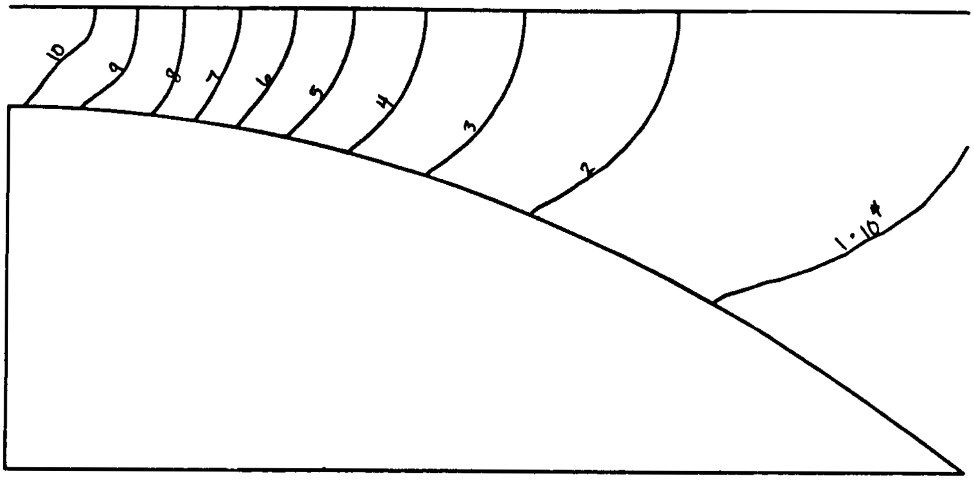

Figure 4: Pressure contours for viscous flow through nozzle.

Figure 5: Water mass fraction contours for viscous flow through nozzle.

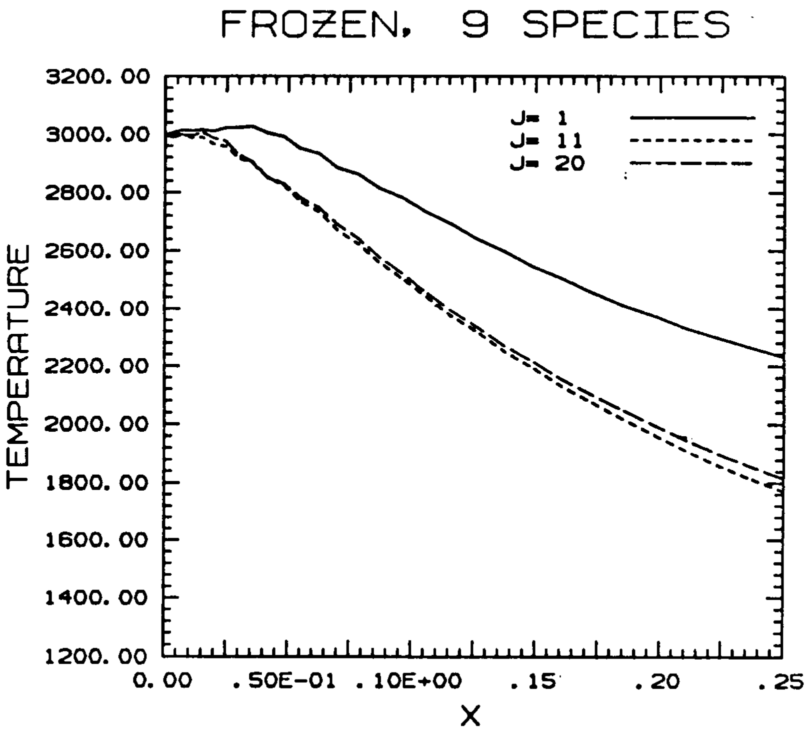

Figure 6: Frozen temperatures along the wall, midpoint and centerline.

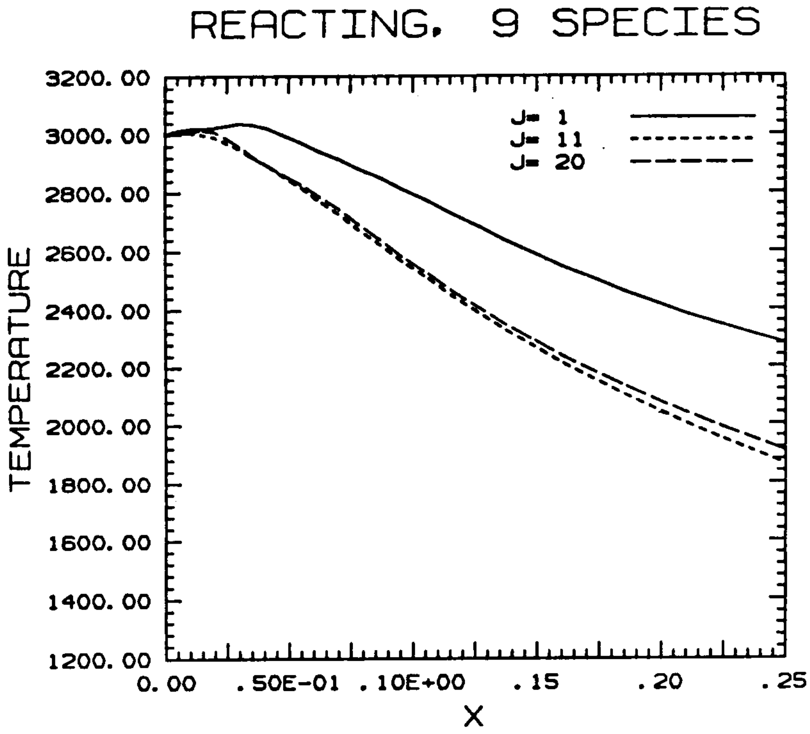

Figure 7: Reacting temperatures along the wall, midpoint and centerline.

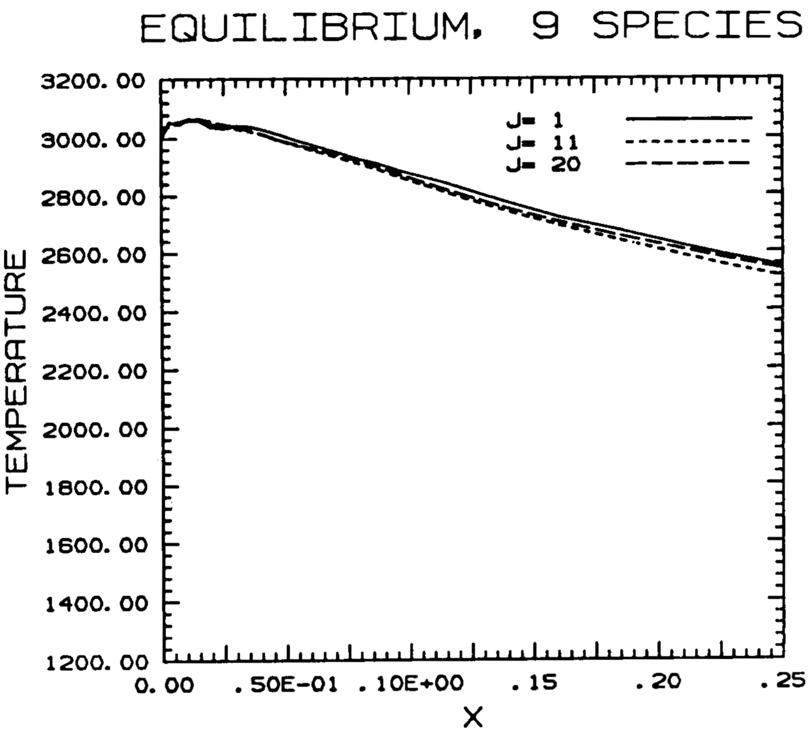

Figure 8: Equilibrium temperatures along the wall, midpoint and centerline.

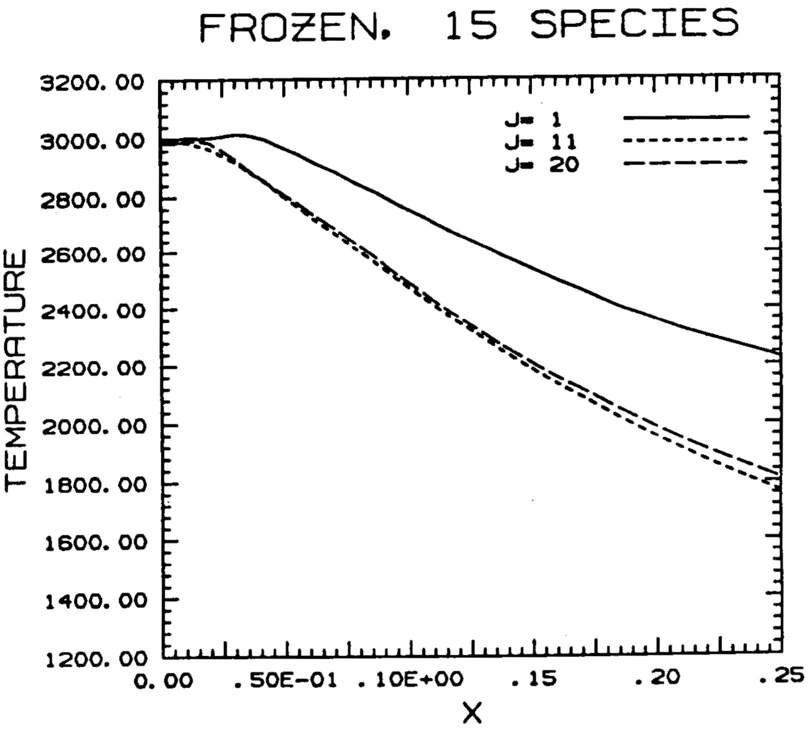

Figure 9: NO_x Frozen temperatures along the wall, midpoint and centerline.

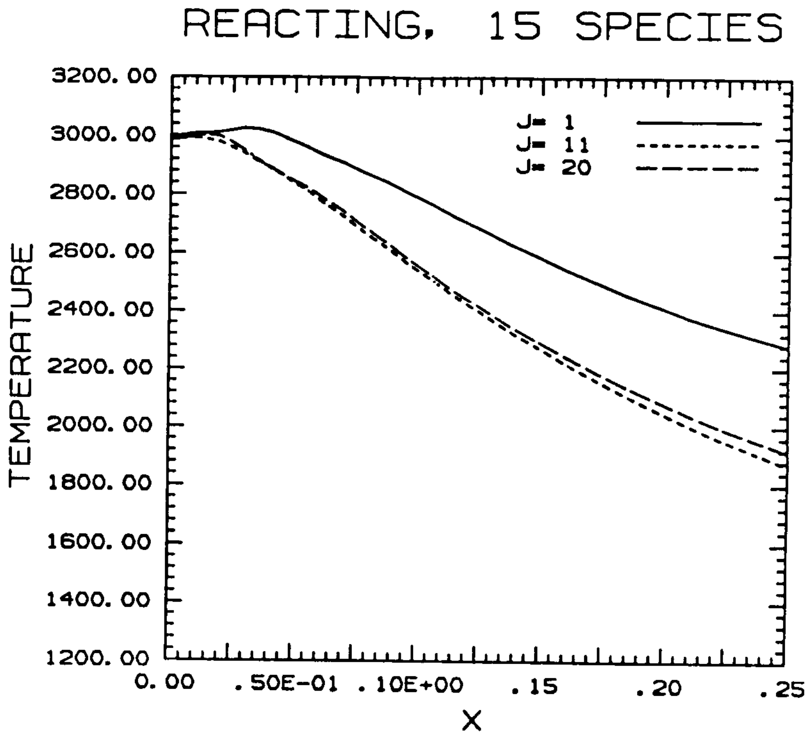

Figure 10: NO_x Reacting temperatures along the wall, midpoint and centerline.

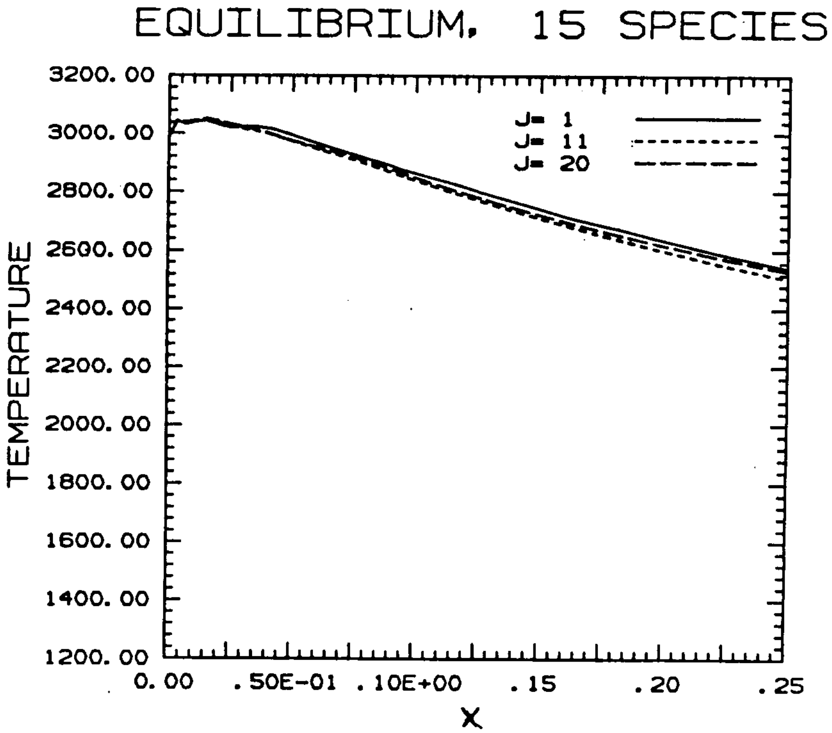

Figure 11: NO_x Equilibrium temperatures along the wall, midpoint and centerline.

National Aeronautics and Space Administration

Report Documentation Page

1. Report No. NASA CR-4196	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle

A Generalized Chemistry Version of SPARK

5. Report Date

December 1988

6. Performing Organization Code

7. Author(s)

Mark H. Carpenter

8. Performing Organization Report No.

10. Work Unit No.

505-60-01-02

9. Performing Organization Name and Address

Analytical Services and Materials, Inc.
Hampton, Virginia 23666

11. Contract or Grant No.

NAS1-18599

13. Type of Report and Period Covered

Contractor Report

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Langley Research Center
Hampton, VA 23665-5225

14. Sponsoring Agency Code

15. Supplementary Notes

Langley Technical Monitor: Ajay Kumar

16. Abstract

An extension of the reacting H_2-air computer code SPARK is presented, which enables the code to be used on any reacting flow problem. Routines are developed that calculate in a general fashion, the reaction rates, and chemical Jacobians of any reacting system. In addition, an equilibrium routine is added so that the code will have frozen, finite rate, and equilibrium capabilities. The reaction rates for the species are determined from the law of mass action using Arrhenius expressions for the rate constants. The Jacobian routines are determined by numerically or analytically differentiating the law of mass action for each species. The equilibrium routine is based on a Gibbs free energy minimization routine. The routines are written in Fortran 77, with special consideration given to vectorization. Run times for the generalized routines are generally 20% slower than reaction specific routines. The numerical efficiency of the generalized analytical Jacobian, however, is nearly 300% better than the reaction specific numerical Jacobian used in SPARK.

17. Key Words (Suggested by Author(s))

SPARK
finite-rate chemistry
chemical equilibrium
chemical Jacobian

18. Distribution Statement

Unclassified - Unlimited

Subject Category 02

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of pages	22. Price
Unclassified	Unclassified	24	A02

NASA FORM 1626 OCT 86

NASA-Langley, 1988

For sale by the National Technical Information Service, Springfield, Virginia 22161-2171