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A New Technique for the Numerical Analysis of Nonequilibrium Flows

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A new technique for the computation of inviscid flows with finite rate chemistry is presented. The case of hydrogen-air combustion is studied in full detail, but this technique can be applied to other mixtures. Difficulties because of instability in existing techniques are eliminated. Consequently, the stepsize in the numerical finite-difference procedure can be increased by 2 to 5 orders of magnitude; the stepsize is unlimited in a state of equilibrium or near to equilibrium. Lengthy calculations that make the programming of two-dimensional flows with finite rate chemistry uneconomical are reduced to a few seconds on a high-speed computer. A comparison of results of this technique with those of other techniques is presented.

I. Introduction

IN recent years, several attempts have been made to analyze gaseous flow fields in which the gas is not in chemical equilibrium. Typical problems are nozzle flows,[1–4] wake flows,[5] and stream-tube combustion processes.[6, 7]

In flow problems where the gas may be considered in chemical and thermodynamic equilibrium at every point, two thermodynamic parameters (i.e., the pressure p and the enthalpy h) are sufficient to determine any other thermodynamic quantity, either by assuming that the gas is perfect, or by using a fit for the Mollier chart of the gas.

If the gas is not in chemical equilibrium, a point-by-point evaluation of its composition is necessary. Starting at a point on a streamline where all the parameters are known, the mass-fractions α_i, the temperature T, and the density ρ at the next point are to be determined as functions of p, h, and the flow time Δt, elapsed between the two points, taking into account the chemical reactions that occur in the time Δt. Several species are created and destroyed in the process. The rates of production of all the species at a point may be

determined as functions of the macroscopic thermodynamic parameters and the initial composition.

II. Difficulties of the Numerical Integration

The problem, as stated previously, has no conceptual difficulties. The analysis along a streamline may be performed, in principle, by solving a system of ordinary differential equations with T, ρ, and the mass fractions as unknowns. Different techniques have been used, including sophisticated schemes such as the Runge-Kutta or the predictor-corrector methods.[7, 8]

Unfortunately, the maximum stepsize Δt is severely limited by stability criteria, although the resulting curves of mass fractions vs time are very smooth, when properly computed. Consider, for example, a semilogarithmic plot of the atomic hydrogen mass fraction vs time in a one-dimensional problem of combustion at constant pressure (Fig. 1).[7] In the first phase of the phenomenon ($0 < t < 7 \times 10^{-6}$ sec), the curve is a straight line. The same is true for all the other mass fractions. Moreover, in this range, density, and temperature are constant. Since all the significant parameters are linear functions of time, one could expect correct results from a single-step computation, with a stepsize of the order of 5×10^{-6} sec. However, it has been found[7] that steps slightly larger than 1.7×10^{-8} sec lead to unstable results. The analysis of processes near equilibrium yields the same
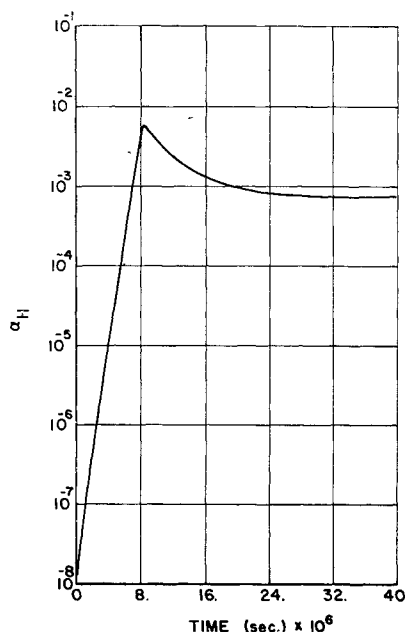
Fig. 1 H mass fraction vs time.

conclusions.[8] Consequently, thousands of steps must be taken to perform the analysis of a process along one streamline (with an average stepsize of 10^{-8} sec, one hundred thousand steps are needed to cover 1 msec, that is, about 10 ft at $M = 8$), and this makes the computation of a two-dimensional flow with several streamlines impractical on economic grounds.

The reason for this handicap is to be found in the "stiffness" of some of the differential equations. An analysis of the problem has been given in Ref. 9 together with a suggestion for overcoming the difficulty. However, in that paper, the method is applied only to a single differential equation of the type $dy/dx = [y - G(x)]/a(x)$. Other difficulties are encountered again when several more complicated equations must be solved simultaneously, as in the present problems.

III. Outline of a New Technique

A different approach is used in this paper. In order to show its principal features, an aerodynamically simple problem will be considered: a one-dimensional flow at constant pressure with chemical reactions. On aerodynamical grounds, constant pressure implies a constant enthalpy h.

Let y_i be the concentration of species i (in moles per cubic centimeter) and W_i be its molecular weight. Then

$$y_i = \rho \alpha_i / W_i \tag{1}$$

At any instant of time, the rate of change of the concentration of species i in reaction j, $\dot{y}_{ij}$, is given by the general formula

$$\dot{y}_{ij} = f_j \Pi y_k^{\nu_k{}'} - b_j \Pi y_k^{\nu_k{}''} \tag{2}$$

where $\nu_k{}'$ and $\nu_k{}''$ are either zero or integers, and the factors

f_j and b_j, "forward and backward reaction rate coefficients," are functions of temperature only. The total rate of change of the concentration of species i caused by all of the chemical reactions is

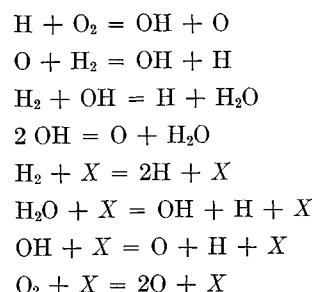$$\dot{y}_i = \sum_j \dot{y}_{ij} = F_i(T;\ y_1, y_2, \ldots, y_N) \tag{3}$$

Suppose a step must be taken in a phase in which variations ρ and T are negligible. If the system of equations (1) could be solved analytically in closed form, an exact set of solutions

$$y_i = y_i(t) \tag{4}$$

would be obtained. This is not the case, because Eqs. (3) are not linear. However, let us investigate the possibility of replacing Eqs. (3) with a system of linear equations by dropping higher-order terms that are negligible along the whole step. This may be done if the linearization is performed as shown in the next section. Consequently, the solution of the linearized system can still be considered as an "exact" solution and, since it is available in closed form, no stability problems arise. The advantage of this technique stems from the fact that the size of a step in which the original and the linearized system of equations are equivalent is several orders of magnitude larger than the maximum stepsize for any other existing technique. The advantage is particularly evident in the first phase of a combustion process and in conditions near equilibrium. In the latter case, all the variables are practically constant. Therefore, a linear system of equations is a very good approximation to the actual one for as large a stepsize as is ordinarily required. In the next sections, a specific combustion problem will be examined in detail.

IV. Combustion of Hydrogen in Air at Constant Pressure

Let air be represented by a mixture of inert, undissociated nitrogen and oxygen, which can dissociate and react with hydrogen. Six variable species are considered: H, O, H_2O, OH, O_2, and H_2, which will be numbered 1, 2, 3, 4, 5, and 6. Eight reactions are assumed to be significant[7]:

$$H + O_2 = OH + O$$
$$O + H_2 = OH + H$$
$$H_2 + OH = H + H_2O$$
$$2\,OH = O + H_2O$$
$$H_2 + X = 2H + X$$
$$H_2O + X = OH + H + X$$
$$OH + X = O + H + X$$
$$O_2 + X = 2O + X$$

where X is a catalyst. Equations (2) now read

$$
\begin{aligned}
&\dot{y}_{21} = f_1 y_1 y_5 - b_1 y_2 y_4 & &\dot{y}_{41} = \dot{y}_{21} & &\dot{y}_{11} = \dot{y}_{51} = -\dot{y}_{21} \\
&\dot{y}_{12} = f_2 y_2 y_4 - b_2 y_1 y_4 & &\dot{y}_{42} = \dot{y}_{12} & &\dot{y}_{22} = \dot{y}_{62} = -\dot{y}_{12} \\
&\dot{y}_{13} = f_3 y_6 y_4 - b_3 y_1 y_3 & &\dot{y}_{33} = \dot{y}_{13} & &\dot{y}_{63} = \dot{y}_{43} = -\dot{y}_{13} \\
&\dot{y}_{24} = f_4 \, y_4{}^2 - b_4 y_2 y_3 & &\dot{y}_{34} = \dot{y}_{24} & &\dot{y}_{44} = -2\dot{y}_{24} \\
&\dot{y}_{15} = f_5 y_6 Y - b_5 y_1{}^2 Y & &\dot{y}_{65} = -\tfrac{1}{2}\dot{y}_{15} & & \\
&\dot{y}_{16} = f_6 y_3 Y - b_6 y_1 y_4 Y & &\dot{y}_{46} = \dot{y}_{16} & &\dot{y}_{36} = -\dot{y}_{16} \\
&\dot{y}_{17} = f_7 y_4 Y - b_7 y_1 y_2 Y & &\dot{y}_{27} = \dot{y}_{17} & &\dot{y}_{47} = -\dot{y}_{17} \\
&\dot{y}_{28} = f_8 y_5 Y - b_8 y_2{}^2 Y & &\dot{y}_{58} = -\tfrac{1}{2}\dot{y}_{28} & &
\end{aligned}
\tag{5}
$$

where Y is the concentration of the catalyst, which is assumed to be approximately the sum of the concentrations of all species including N_2:

$$Y = \Sigma\, y_i \tag{6}$$

The expressions assumed for the f_j and b_j are listed in Appendix A. Equations (3) now read

$$\left.\begin{aligned}
\dot{y}_1 &= \dot{y}_{11} + \dot{y}_{12} + \dot{y}_{13} + \dot{y}_{15} + \dot{y}_{16} + \dot{y}_{17}\\
\dot{y}_2 &= \dot{y}_{21} - \dot{y}_{12} + \dot{y}_{24} + \dot{y}_{17} + \dot{y}_{28}\\
\dot{y}_3 &= \dot{y}_{13} + \dot{y}_{24} - \dot{y}_{16}\\
\dot{y}_4 &= \dot{y}_{21} + \dot{y}_{12} - \dot{y}_{13} - 2\dot{y}_{24} + \dot{y}_{16} - \dot{y}_{17}\\
\dot{y}_5 &= -\dot{y}_{21} - \tfrac{1}{2}\dot{y}_{28}\\
\dot{y}_6 &= -\dot{y}_{12} - \dot{y}_{13} - \tfrac{1}{2}\dot{y}_{15}
\end{aligned}\right\} \quad (7)$$

The following two equations are obtained as linear combinations of Eq. (7)

$$\left.\begin{aligned}
2\dot{y}_6 + \dot{y}_1 + \dot{y}_4 + 2\dot{y}_3 &= 0\\
2\dot{y}_5 + \dot{y}_2 + \dot{y}_4 + \dot{y}_3 &= 0
\end{aligned}\right\} \quad (8)$$

It is known that these two equations express the conservation of the number of atoms of oxygen and hydrogen.[6]

To these equations, the following must be added in order to make the problem determined:

Conservation of Species

$$\rho \frac{D\alpha_i}{Dt} = W_i \dot{y}_i \quad (9)$$

Equation of State

$$p = R\,T\,Y \quad (10)$$

Definition of Enthalpy

$$h = \Sigma\, \alpha_i h_i \quad (11)$$

Here R is the gas constant, D/Dt means substantial differentiation, and h_i is the partial enthalpy of species i (the summation is extended to all species including N_2). These partial enthalpies are defined through the partition functions of the species, which are functions of T. For practical purposes, piecewise parabolic fits can be used

$$h_i = A_i + B_i T + C_i (T - T_{0i})^2 \quad (12)$$

as shown in Appendix B. Consequently, T can be easily obtained as a function of h by solving the second-order equation

$$A T^2 - 2BT + C = 0 \quad (13)$$

where

$$A = \Sigma\, \alpha_i C_i$$
$$B = \Sigma\, \alpha_i (C_i T_{0i} - B_i/2)$$
$$C = \Sigma\, \alpha_i (A_i + C_i T_{0i}{}^2) - h$$

The solution to be used is the one with the positive square root.

To summarize, Eqs. (1, 6, 7, 9, 10, and 13) are twenty-one equations with the twenty-one unknowns T, Y, ρ, α_i, y_i, $\dot{y}_i$ ($i = 1, 2, \ldots, 6$). At this stage, a different treatment is given to the macroscopic quantities T, Y, and ρ, and to the microscopic quantities α_i, y_i, and $\dot{y}_i$.

V.   Linearized Equations for the Concentrations

The mass fractions α_i can be eliminated by computing the substantial derivative of y_i as expressed by (1). If substantial derivatives are denoted by primes,

$$y_i' = \rho' \frac{\alpha_i}{W_i} + \rho \frac{\alpha_i'}{W_i}$$

and, with (9),

$$y_i' = \dot{y}_i + (\rho'/\rho) y_i \quad (14)$$

In every computational step, the following simplifying assumptions will be made:

1) The reaction rate coefficients, f_j and b_j, are constant throughout a step (that is, the change in temperature throughout a step is not so large as to affect the values of the reaction rate coefficients).

2) The logarithm of the density is a linear function of time throughout a step. Consequently, a parameter

$$\delta = \rho'/\rho \quad (15)$$

constant throughout a step, can be introduced. Hence, if ρ° and ρ are the initial and final values of the density in a step, the ratio $\gamma = \rho/\rho^\circ$ is given by

$$\gamma = \rho/\rho^\circ = 1 + \delta\Delta t \quad (16)$$

3) The sum of the concentrations Y is also constant in Eqs. (5) and consequently in Eqs. (7).

Now Eqs. (7) and (5) can be used to eliminate the terms $\dot{y}_i$ in Eqs. (14). The result is a system of ordinary differential equations in the concentrations, with the unknown δ as an additional parameter. An attempt can be made to solve these equations in closed form throughout a step.

First, Eqs. (8) and (14) are used to eliminate two of the concentrations. The slowly variable concentrations of O_2 and H_2 are chosen. The result is

$$\left.\begin{aligned}
y_5 &= -\frac{y_2 + y_3 + y_4}{2} + \gamma \left(y_5 + \frac{y_2 + y_3 + y_4}{2}\right)^\circ\\
y_6 &= -\frac{y_1 + y_4}{2} - y_3 + \gamma \left(y_6 + y_3 + \frac{y_1 + y_4}{2}\right)^\circ
\end{aligned}\right\} \quad (17)$$

where $(\ )^\circ$ means "initial value at the beginning of the step." Letting

$$\left.\begin{aligned}
b &= \gamma \left(y_5 + \frac{y_2 + y_3 + y_4}{2}\right)^\circ\\
c &= \gamma \left(y_6 + y_3 + \frac{y_1 + y_4}{2}\right)^\circ
\end{aligned}\right\} \quad (18)$$

Eqs. (17) can be restated in the form

$$\left.\begin{aligned}
y_5 &= b - \frac{y_2 + y_3 + y_4}{2}\\
y_6 &= c - \frac{y_1 + y_4}{2} - y_3
\end{aligned}\right\} \quad (19)$$

At this stage, the expressions (19) for y_5 and y_6 can be substituted into Eqs. (5) and the resulting formulas can be used in the right-hand sides of the first four rows of Eqs. (7). Therefore, $\dot{y}_1$, $\dot{y}_2$, $\dot{y}_3$, and $\dot{y}_4$ now depend only on the variables y_1, y_2, y_3, y_4, and δ and contain a number of constant coefficients defined by the values of T and of each concentration at the beginning of an integration step. If Eqs. (14) with $i = 1$ to 4 are used, with $\delta = \rho'/\rho$ and the $\dot{y}_i$ as described previously, a system of four ordinary differential equations in the four unknowns y_1, y_2, y_3, and y_4 is obtained, where the time is the independent variable. These equations have the general form

$$y_i' = F_i(y_k;\ \delta) \qquad (i, k = 1, 2, 3, 4) \quad (20)$$

where the $F_i(y_k;\ \delta)$ are linear combinations of constant terms, first-order terms, and second-order terms in the y_k. The parameter δ is to be determined by making use of another equation. However, the problem of finding a formal solution for the system (20) is not complicated by the presence of δ, which has been assumed to be constant throughout a step.

A system such as (20) cannot be solved in closed form, but can be easily reduced to a linear system by writing

$$y_i y_k = -y_i^\circ y_k^\circ + y_i^\circ y_k + y_k^\circ y_i \quad (21)$$

After substitution of all the terms $y_i y_k$ with (21), the system of equations (20) is approximated by the linear, nonhomogeneous system

$$y_i' = \Sigma\, a_{ik} y_k + c_i \qquad (i, k = 1, 2, 3, 4) \quad (22)$$

Appendix C gives the expressions of the constant coefficients a_{ik} and c_i.

The system of equations (22) can now be solved by standard methods. The first step consists of finding the four roots of the characteristic equation

$$||a_{ik} - \delta_{ik}r|| = 0 \qquad (23)$$

where δ_{ik} is Kronecker's delta. If all these four roots r_k are simple, the solution is

$$y_i = \Sigma \lambda_{ik}e^{r_k\Delta t} + A_i \qquad (i, k = 1, 2, 3, 4) \qquad (24)$$

where

$$\Sigma a_{ij}A_j = -c_i \qquad \lambda_{jk} = \mu_{jk}\Lambda_j$$

$$\mu_{1k} = 1 \qquad \Sigma (a_{ij} - r_k\delta_{ij})\mu_{jk} = -(a_{i1} - r_k\delta_{i1})$$

$$\Sigma \mu_{ik}\Lambda_k = y_i{}^\circ - A_i \qquad (i, j, k = 1, 2, 3, 4)$$

Since the roots r_k may be real or complex, the coefficients λ_{ik} are to be considered in general as complex numbers. Special provisions may be taken for the cases of multiple roots (which, however, are highly improbable in a numerical computation).

If an assumed value of δ has been used, the final values of y_1, y_2, y_3, and y_4, consistent with it, are now determined, and the final values of y_5 and y_6 can be computed from Eqs. (19).

VI.   Computation of Density and Temperature

The result of the computation described previously is a set of final values of the concentrations as functions of the unknown parameter δ. Now, the remaining equations [(6, 10, and 13)] must be used to determine Y, ρ, and T.

Since the density is defined as

$$\rho = \Sigma W_iy_i \qquad (25)$$

and since the mass fraction of nitrogen (α_7) does not change, it follows that

$$\rho = [1/(1 - \alpha_7)]\Sigma' W_iy_i \qquad (26)$$

where Σ' means that the sum is extended to all the active species. Then

$$y_7 = \rho\alpha_7/W_7$$

The temperature can be obtained either from (10) or from (13). Obviously, the two results must agree. If they differ by a quantity τ, the error may be attributed to a bad choice
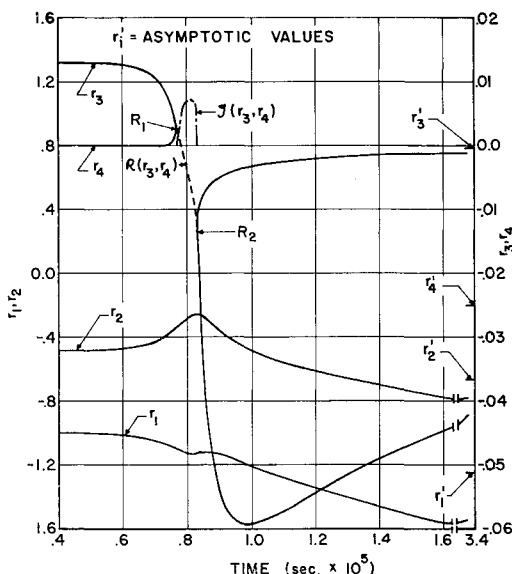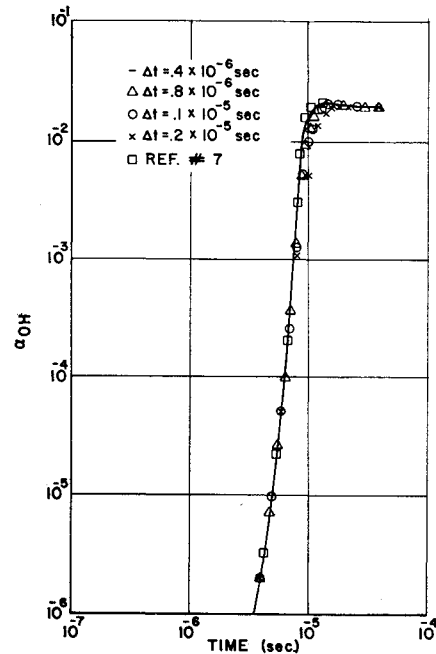
Fig. 2   Roots.

Fig. 3 α_{OH} vs time.

of δ (which provided a wrong value of ρ at the end of the step). A different value of δ leads to a different set of final values of y_i, ρ, and to a different value of τ. A simple iteration scheme can be set up to provide a value of τ less than $\frac{1}{10}{}^\circ$. It has been found that, in general, two iterations only are needed.

VII.   Further Details of the Analysis

A closer analysis of the problem is necessary in order to provide a complete background for a digital computer program. In a combustion process, three phases can be observed: 1) an initial phase, in which density and temperature remain practically constant, whereas the mass fractions of H, O, OH, and H_2O change by several orders of magnitude; 2) an intermediate phase, in which the temperature rises and the density drops very steeply, the rate of change of the mass fractions also diminishes (in particular, the mass fraction of atomic hydrogen reaches a maximum); and 3) a final phase, in which the temperature still increases and the density diminishes, but more and more slowly (these two parameters as well as the mass fractions approach their equilibrium values asymptotically).

Only the first four reactions of the list in Sec. IV are significant in the first phase.[6, 10] If the significant terms are retained in Eqs. (7), these are simplified as follows:

$$\begin{aligned}
\dot{y}_1 &= -\dot{y}_{21} + \dot{y}_{12} + \dot{y}_{13} \\
\dot{y}_2 &= \dot{y}_{21} - \dot{y}_{12} + \dot{y}_{24} \\
\dot{y}_3 &= \dot{y}_{13} + \dot{y}_{24} \\
\dot{y}_4 &= \dot{y}_{21} + \dot{y}_{12} - \dot{y}_{13} - 2\dot{y}_{24} \\
\dot{y}_5 &= -\dot{y}_{21} \\
\dot{y}_6 &= -\dot{y}_{12} - \dot{y}_{13}
\end{aligned} \qquad (27)$$

Therefore, a third equation can be added to Eqs. (8)

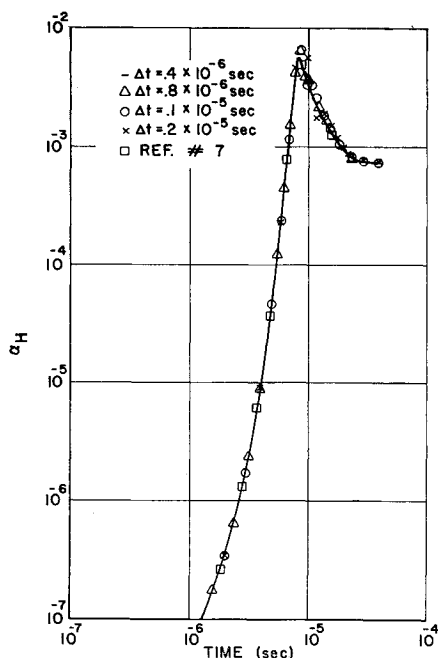$$\dot{y}_1 + \dot{y}_2 - \dot{y}_3 = 0 \qquad (28)$$

and the equation

$$y_1 = a + y_3 - y_2 \qquad (29)$$

with

$$a = \gamma(y_1 + y_2 - y_3)^\circ \qquad (30)$$

Fig. 4 α_H vs time.

can be used, together with Eqs. (19). The system (22) is then reduced to a system of three equations with the three unknowns y_2, y_3, and y_4. Since the density remains constant in the first phase, δ is obviously zero, and no iteration is needed to determine it.

It is clear that, in such first phase, the determinant of the a_{ik} matrix vanishes because of a linear dependence of parallel rows. Consequently, a suitable test must be used in the computer program, in order to switch from the general procedure to another one, based upon Eqs. (27–30), when necessary.

The three phases are easily detected by the analysis of the four characteristic roots. Figure 2 shows such roots plotted vs time in a sample problem. The roots r_1 and r_2 are always negative. The root r_3 is positive; the root r_4 is about zero in the first phase. In this phase, all the roots are practically constant. In the third phase, all the roots are negative. The roots r_1 and r_2 again are practically constant, and r_3 and r_4 vary very slowly. In the second phase the transition is achieved as follows. First, the root r_3 diminishes faster and faster, and r_4 increases until r_3 and r_4 attain a common value R_1. Then r_3 and r_4 take on complex values, the real part moving from R_1 to a negative value R_2, whereas the imaginary part goes from zero to a maximum and then to zero again. At R_2, r_3, and r_4 branch off again with real values.

VIII. Problem of the Optimum Stepsize

The foregoing analysis of the characteristic roots provides the necessary information for the discussion of the stepsize. If the linear system of equations (22) were the exact description of the whole process, the solution would be given by Eqs. (24) with four constant values of the r_k, independent of the value of Δt.

On the contrary, if it were discovered that, upon recomputing the roots at the end of a step, their values were substantially different from the values used along the step, it would mean that the linear system (22) is a very poor approximation to the actual system (20), since the roots would be functions of time themselves.

Consequently, in the first phase of the combustion process, where all four roots are constant, a single step can be used in the numerical computation. As was pointed out before, this result is just the opposite of that reached by the lengthy procedure that stems from a Runge–Kutta or predictor–

corrector integration technique. When the equilibrium conditions are asymptotically approached, a similar conclusion can be drawn. The stepsize, near equilibrium, can be increased beyond any limit.

In the second phase, where r_3 and r_4 change, the optimum stepsize may be defined, in practice, on the basis of the degree of accuracy which is required.

IX. Discussion of Some Numerical Results

The technique outlined in the preceding sections has been programed in Fortran for the IBM 7094 computer. Test runs have been made, using the same expressions for the f_j and b_j, the same pressure, and the same initial values of temperature and mass fractions as in some cases considered in Ref. 7. In order to test the conclusions in Sec. VIII, several runs have been made with a constant stepsize throughout. A brief comparison will disclose the advantages of the present technique.

The combustion of a stoichiometric mixture at $p = 1.51$ atm and an initial temperature $T = 1340\,°K$ was computed,[7] using a Runge–Kutta integration technique, in 4150 steps of variable size, $\Delta t = 0.17 \times 10^{-7}$ and $\Delta t = 0.8 \times 10^{-8}$ being its maximum and its minimum values, respectively. The same problem has been computed with the present technique, using the following constant stepsizes and the corresponding number of steps:

$$\Delta t = 0.4 \times 10^{-7} \qquad N = 1000$$
$$= 0.2 \times 10^{-6} \qquad = 200$$
$$= 0.4 \times 10^{-6} \qquad = 100$$
$$= 0.8 \times 10^{-6} \qquad = 50$$
$$= 0.1 \times 10^{-5} \qquad = 40$$
$$= 0.2 \times 10^{-5} \qquad = 20$$

Figures 3 and 4 are plots of mass-fractions of OH and H in these runs vs time. As anticipated in Sec. VIII, all the curves coincide in the first phase. In the second phase, the greater the stepsize, the poorer is the accuracy. It is significant, however, that the general trend of the curves is maintained, and the order of magnitude of the results is not lost, even when the stepsize is 200 times as large as the one used with the Runge–Kutta technique. It is also significant (and this testifies to the stability of the present method) that the errors are wiped out as the equilibrium conditions are approached.

All these results agree with the remarks in Sec. VIII. The same conclusions can be reached by inspecting the curves of T and ρ, shown in Fig. 5 and 6. The maximum error in ρ, for example, is of the order of 5%.
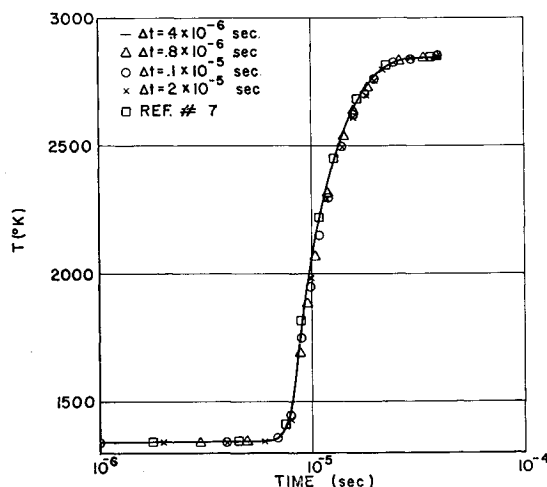

Fig. 5   Temperature vs time.

In similar problems where the initial pressure and temperature are lower and the combustion starts with difficulty, the advantage of the present procedure over the Runge-Kutta integration technique is even more evident, since thousands of steps in the first phase can be evaluated in one single step. Another advantage of the present technique is that it gives the possibility of a quick evaluation of the general features of a combustion process by using a coarse stepsize without loss of accuracy.

X. Fixed Stepsize vs Variable Stepsize

The computational time required for a single case on the IBM 7094 computer is of the order of seconds (about 700 steps are computed in 1 min). Therefore, there is no need for a refinement of the program in order to change the stepsize in the three phases of the combustion process. A single step could be taken in the first phase and another single step in the third phase, but the limits of the second phase should be determined. This would entail a number of logical complications in the program and some increase in computational time, which partially balances the reduction due to the use of a very large stepsize in the first and last phases.

XI. Stream-Tube Flow at Variable Pressure

The technique described previously is easily adapted to compute stream-tube flows (quasi-one-dimensional flows) in which either the cross-sectional area or the pressure is prescribed along the stream tube. Suppose, for example, that the pressure is given as a function of t. At the end of each step, the enthalpy is obtained from the equation

$$Dh/Dt = (1/\rho)(Dp/Dt)$$

Then the computation proceeds along the same lines as in the case of constant pressure.

If the initial conditions correspond to a state of equilibrium, the initial steps are extremely critical in the technique of Ref. 7. This again is not the case with the present technique. For example, assuming a pressure distribution as in Fig. 7, our results, obtained with a stepsize of 0.5×10^{-5} sec, match exactly the results obtained by the technique used in Ref. 7, using stepsizes as small as 10^{-10} sec at the beginning, and increasing to the order of 0.5×10^{-8} sec later on.

XII. Conclusions†

Increases of several orders of magnitude in the stepsize permit one to keep more complicated programs of nonequilibrium flow within reasonable limits of machine time. An application to the problem of supersonic combustion controlled by mixing has been presented at the AIAA meeting in New York, in January 1964.[11]

The author is pleased to acknowledge that, in the process of extending the present method to more complicated combustion processes,[12] his colleague, James DeGroat, applies a different technique in order to solve the system of equations (22). His technique avoids the use of exact solutions in ex-

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† *Note added in proof.* After this paper was submitted for publication, a report by C. E. Treanor on the same subject [Treanor, C. E., "A method for the numerical integration of coupled first order differential equations with greatly different time constants," Cornell Aeronautical Lab. Rept. AG-1729-A-4 (January 1964)] was brought to the attention of the author. Treanor's technique is strictly a successful attempt to improve the Runge-Kutta technique. However, since the latter is used to provide the basic information at each of Treanor's steps, the instability inherent to the Runge-Kutta method is not suppressed. As a consequence, Treanor's technique increases the stepsize 25 times, whereas the increase according to the present method may be of several orders of magnitude.
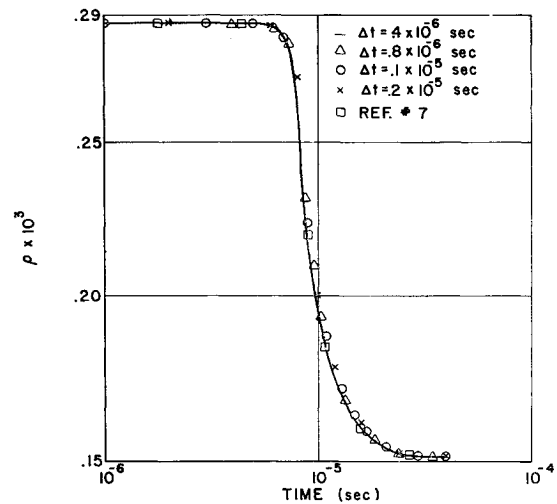

Fig. 6 Density vs time.

ponential form and makes the search for the solutions much simpler from the point of view of computer programing, particularly when the number of differential equations is greater than four. In addition to J. DeGroat, the author's thanks go to Michael Abbett for his valuable help in this project and its extensions.

Appendix A: Forward and Backward Reaction Coefficients as Functions of Temperature

$$
\begin{aligned}
f_1 &= 3 \times 10^{14} e^{-8.81/T} & b_1 &= 2.48 \times 10^{13} e^{-.66/T} \\
f_2 &= 3 \times 10^{14} e^{-4.03/T} & b_2 &= 1.30 \times 10^{14} e^{-2.49/T} \\
f_3 &= 3 \times 10^{14} e^{-3.02/T} & b_3 &= 1.33 \times 10^{15} e^{-10.95/T} \\
f_4 &= 3 \times 10^{14} e^{-3.02/T} & b_4 &= 3.12 \times 10^{15} e^{-12.51/T} \\
f_5 &= 1.85 \times 10^{17} e^{-54/T}/T & b_5 &= 10^{16} \\
f_6 &= 9.66 \times 10^{18} e^{-62.2/T}/T & b_6 &= 10^{17} \\
f_7 &= 8 \times 10^{16} e^{-52.2/T}/T & b_7 &= 10^{16} \\
f_8 &= 5.8 \times 10^{16} e^{-60.6/T}/T & b_8 &= 6 \times 10^{14}
\end{aligned}
$$

(A1)

T is the absolute temperature in °K, divided by 1000. The rate coefficients f_j and b_j are in mole/(cm³-sec), except for b_5, b_6, b_7, and b_8 which are in mole²/(cm⁶-sec). These data have been assumed according to Ref. 6.

Appendix B: Enthalpy Fits

The partial enthalpies (in kilocalories per gram) are fitted by means of the following equations:

$$
h_i = \begin{cases}
A_i + B_i T & T \leqslant T_{0i} \\
A_i + B_i T + C_i(T - T_{0i})^2 & T_{0i} \leqslant T \leqslant T_{1i} \\
D_i + E_i T & T_{1i} \leqslant T < 6
\end{cases}
$$

T is the absolute temperature in °K, divided by 1000. The values of the constants are given in Table 1.

Appendix C: Coefficients Used in Eq. (22)

$$a_{11} = f_1[-b + (y_2 + y_4 + y_3)/2] - (f_2 y_2 + f_3 y_4)/2 -$$
$$[b_2 y_4 + b_3 y_3 + Y f_5/2 + b_6 y_4 + b_7 y_2 Y] - 2 b_5 y_1 Y + \delta$$

$$a_{12} = f_2[c - (y_1 + y_4 + 2y_3)/2] + y_1(f_1/2 - b_7 Y) + b_1 y_4$$

$$a_{13} = f_1 y_1/2 - (f_2 y_2 + f_3 y_4 + b_3 y_1) + (f_6 - f_5)Y$$

$$a_{14} = f_3[c - y_1/2 - (y_3 + y_4)] + (f_1 y_1 - f_2 y_2)/2 +$$
$$[b_1 y_2 - b_2 y_1 + Y(f_7 - f_5/2 - b_6 y_1)]$$

<div align="center">

Table 1   Enthalpy fits coefficients

</div>

		A_i	B_i	C_i	D_i	E_i	T_{0i}	T_{1i}
1	H	50.22	4.93	0.	0.	0.	6.	6.
2	O	3.622	0.3187	0.	0.	0.	6.	6.
3	H_2O	−3.3395	0.4464	0.0681	−3.9456	0.7902	0.5	3.94
4	OH	0.4247	0.4158	0.0201	0.1631	0.5422	0.5	3.64
5	O_2	−0.0648	0.2206	0.0198	−0.2297	0.3168	0.5	2.93
6	H_2	−1.004	3.403	0.1968	−4.286	4.831	0.5	4.096
7	N_2	−0.074	0.2488	0.0190	−0.1859	0.3239	0.5	2.48

$$a_{21} = f_1[b - (y_2 + y_3 + y_4)/2] + (f_2/2 - b_7Y)y_2 + b_2y_4$$

$$a_{22} = -f_2[c - (y_1 + y_4 + 2y_3)/2] - (f_1/2 + b_7Y)y_1 -$$
$$(b_1y_4 + b_4y_3) - (f_8/2 + 2b_8y_2)Y + \delta$$

$$a_{23} = -f_1y_1/2 + (f_2 - b_4)y_2 - f_8Y/2$$

$$a_{24} = (f_2y_2 - f_1y_1)/2 + (b_2y_1 - b_1y_2) + 2f_4y_4 + (f_7 - f_8/2)Y$$

$$a_{31} = (b_6Y - f_3/2)y_4 - b_3y_3$$

$$a_{32} = -b_4y_3$$

$$a_{33} = -(f_3y_4 + b_3y_1 + b_4y_2 + f_6Y) + \delta$$

$$a_{34} = f_3[c - (y_1 + 2y_4 + 2y_3)/2] + 2f_4y_4 + b_6y_1Y$$

$$a_{41} = f_1[b - (y_2 + y_3 + y_4)/2] + (-f_2/2 + b_7Y)y_2 +$$
$$(f_3/2 - b_2 - b_6Y)y_4 + b_3y_3$$

$$a_{42} = f_2[c - (y_1 + y_4 + 2y_3)/2] + (b_7Y - f_1/2)y_1 -$$
$$b_1y_4 + 2b_4y_3$$

$$a_{43} = (b_3 - f_1/2)y_1 + (2b_4 - f_2)y_2 + f_3y_4 + f_6Y$$

$$a_{44} = -f_3[c - y_1/2 - (y_3 + y_4)] - [f_1/2 + b_2 + b_6Y]y_1 -$$
$$(b_1 + f_2/2)y_2 - 4f_4y_4 - f_7Y + \delta$$

$$c_1 = (f_2y_2 + f_3y_4)[(y_1 + y_4)/2 + y_3] + b_2y_1y_4 -$$
$$f_1y_1(y_2 + y_3 + y_4)/2 - b_1y_2y_4 + b_3y_1y_3 +$$
$$(b_6y_4 + b_5y_1 + b_7y_2)y_1Y + f_5Yc$$

$$c_2 = f_1y_1(y_2 + y_3 + y_4)/2 + b_1y_2y_4 -$$
$$f_2y_2[(y_1 + y_4)/2 + y_3] - b_2y_1y_4 - f_4y_4{}^2 +$$
$$b_4y_2y_3 + (b_7y_1 + b_8y_2)y_2Y + f_8Yb$$

$$c_3 = f_3y_4[(y_1 + y_4)/2 + y_3] + b_3y_1y_3 - f_4y_4{}^2 +$$
$$b_4y_2y_3 - b_6y_4y_1Y$$

$$c_4 = f_1y_1(y_2 + y_3 + y_4)/2 + b_1y_2y_4 + (f_2y_2 - f_3y_4) \times$$
$$[(y_1 + y_4)/2 + y_3] + b_2y_1y_4 - b_3y_1y_3 +$$
$$2f_4y_4{}^2 - 2b_4y_2y_3 + (b_6y_4 - b_7y_2)y_1Y$$

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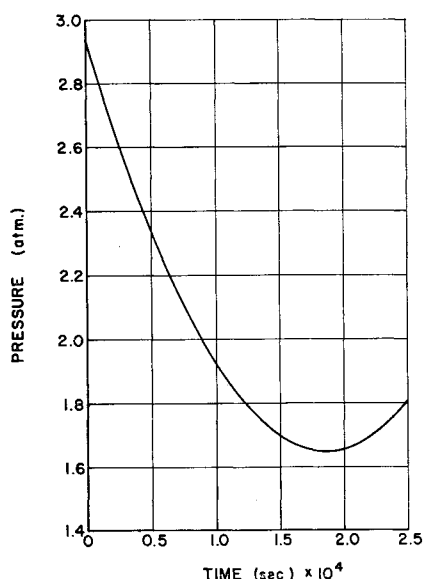[12] DeGroat, J. and Abbett, M., "A computation of one-dimensional combustion of methane," AIAA J. 3, 381–383 (1965).

Fig. 7   Pressure (atm) vs time (sec).