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Numerical Method for Partial Equilibrium Flow*

JOHN D. RAMSHAW AND LAWRENCE D. CLOUTMAN

Theoretical Division, Group T-3, Los Alamos National Laboratory,
Los Alamos, New Mexico 87545

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A numerical method is presented for chemically reactive fluid flow in which equilibrium and nonequilibrium reactions occur simultaneously. The equilibrium constraints on the species concentrations are established by a quadratic iterative procedure. If the equilibrium reactions are uncoupled and of second or lower order, the procedure converges in a single step. In general, convergence is most rapid when the reactions are weakly coupled. This can frequently be achieved by a judicious choice of the independent equilibrium reactions. In typical transient calculations, satisfactory accuracy has been achieved with about five iterations per time step.

I. INTRODUCTION

There is a great deal of current interest in reactive fluid dynamics, and in numerical techniques for solving the equations that govern it. One of the main obstacles to be overcome is the frequent occurrence in practical problems of chemical time scales that are very short in comparison to typical fluid dynamical characteristic times. The chemical rate equations then become "stiff" in character, and require special techniques for their solution [1, 2]. A further difficulty is that reaction mechanisms, rate laws, and rate coefficients for fast reactions of practical interest are often not reliably known. Both of these difficulties may be circumvented by assuming that the fast reactions are always in equilibrium, while those reactions having time scales which are comparable to or longer than characteristic fluid dynamical times are treated kinetically. This situation may be referred to as partial equilibrium flow [3].

The concept of partial equilibrium flow is most useful in situations where each reaction may be classified as "fast" or "slow" independently of position and time. Whether or not this is possible will depend on the reaction rates and on the temperature and pressure extremes in the flow field. When such a simple classification is not possible, it will be necessary to supplement the partial equilibrium description with criteria for determining whether or not a given reaction

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is essentially in equilibrium. Such criteria will necessarily be kinetic in nature, and will involve both the forward and reverse reaction rates. We shall not discuss the formulation or implementation of such criteria here; we simply assume that a decision has somehow been reached in advance as to which reactions are in equilibrium and which need to be treated kinetically. We caution the reader that if this decision is incorrectly made then the results of the calculation will be physically incorrect, even though the calculation may still be well behaved and produce results that look reasonable.

It should also be emphasized that even when the partial equilibrium description is otherwise appropriate, it will always be incorrect during a short initial transient during which the partial equilibrium is established kinetically. Clearly, the partial equilibrium description is useful only in problems where the features of interest are insensitive to the details of this initial transient. If these details are of crucial importance then the partial equilibrium description is not appropriate and a completely kinetic description must be used instead, at least during the initial transient interval.

Alternative formulations of the governing equations for partial equilibrium flow have been presented elsewhere [3]. In this paper we present a numerical method for solving the so-called primitive governing equations [3], in which the progress rates for the equilibrium reactions are not given explicitly but are determined implicitly by the equilibrium constraint conditions. Our discussion will be restricted to ideal gas mixtures. The use of the method is illustrated by showing some results from a numerical simulation of the compression and power strokes of a single-cylinder in an internal combustion engine.

Our method establishes the equilibrium constraints by a quadratic iterative procedure. This procedure has been designed so that convergence is immediate if the equilibrium reactions are uncoupled and of second or lower order. In the general case, convergence is most rapid if the equilibrium reactions are selected so that the coupling between them is as weak as possible. No attempt is made to formulate general selection criteria, but the practical process of selecting nearly uncoupled reactions is illustrated within the context of the sample problem.

The iteration is considered to have converged when all the equilibrium constraints are satisfied to within some specified tolerance. In transient calculations, we have found that 2% accuracy usually requires an average of about five iterations per time step on each cell of the finite-difference mesh. The rapid convergence is due in large part to the fact that (except perhaps at the beginning of the calculation) the starting conditions are relatively close to equilibrium, since they differ from the equilibrium state of the previous time step only by contributions of order Δt.

The remainder of the paper is organized as follows. Section II summarizes the relevant primitive equations for partial equilibrium flow, specialized to the case of an ideal gas mixture. The numerical method for treating the equilibrium reactions is presented in Section III. In Section IV we present some results from a test calculation performed using the method in conjunction with the CONCHAS computer code [4]. It should be relatively easy to implement the method in other reactive fluid dynamics codes, since most of the necessary coding can be localized in a modular subroutine.

II. DIFFERENTIAL EQUATIONS

The primitive governing equations for partial equilibrium flow have been summarized elsewhere [3]. Here we are concerned only with those equations that involve the chemical reactions directly. Attention is restricted to ideal gas mixtures.

The continuity equation for species k is

$$\partial \rho_k/\partial t + \nabla \cdot (\rho_k \mathbf{u}) = -\nabla \cdot \mathbf{J}_k + \dot{\rho}_k^C, \tag{1}$$

where ρ_k is the mass of species k per unit volume, $\mathbf{u}$ is the fluid velocity vector, $\mathbf{J}_k$ is the diffusional mass flux of species k, and $\dot{\rho}_k^C$ is the rate of change of ρ_k due to chemical reactions.

The chemical reactions occurring in the system are of two types: kinetic reactions, labeled by the index r, and equilibrium reactions, labeled by the index s. The kinetic reactions are collectively symbolized by

$$\sum_k a_{kr} X_k \rightleftarrows \sum_k b_{kr} X_k, \tag{2}$$

where a_{kr} and b_{kr} are dimensionless stoichiometric coefficients, and X_k represents one mole of species k. Similarly, the equilibrium reactions are collectively symbolized by

$$\sum_k a_{ks} X_k \rightleftarrows \sum_k b_{ks} X_k. \tag{3}$$

The chemical mass exchange terms $\dot{\rho}_k^C$ are given by

$$\dot{\rho}_k^C = M_k \sum_r (b_{kr} - a_{kr})\, \dot{\omega}_r + M_k \sum_s (b_{ks} - a_{ks})\, \dot{\omega}_s, \tag{4}$$

where M_k is the molecular weight of species k, $\dot{\omega}_r$ is the rate of progress of kinetic reaction r, and $\dot{\omega}_s$ is the rate of progress of equilibrium reaction s. The kinetic progress rates are determined by rate expressions of the form

$$\dot{\omega}_r = k_{fr} \prod_k (\rho_k/M_k)^{d_{kr}} - k_{br} \prod_k (\rho_k/M_k)^{e_{kr}}, \tag{5}$$

where k_{fr} and k_{br} are the forward and backward rate coefficients, and the exponents d_{kr} and e_{kr} specify the order of the reaction. For elementary reactions $d_{kr} = a_{kr}$ and $e_{kr} = b_{kr}$. The equilibrium progress rates are determined implicitly by the equilibrium constraint conditions

$$K_c^s(T) = \mathscr{P}_s/\mathscr{R}_s, \tag{6}$$

$$\mathscr{P}_s = \prod_k (\rho_k/M_k)^{b_{ks}}, \tag{7}$$

$$\mathscr{R}_s = \prod_k (\rho_k/M_k)^{a_{ks}}, \tag{8}$$

where $K_c^s(T)$ is the concentration equilibrium constant for equilibrium reaction s, which depends only on the temperature T.

The central problem to which this paper is addressed is how to determine the $\dot{\omega}_s$ so that the constraint conditions of Eq. (6) are satisfied within the framework of a time-marching numerical calculation. Since Eq. (6) is a system of coupled nonlinear equations, it is evident that some sort of iterative procedure will be required. One such procedure is developed in the next section.

III. NUMERICAL METHOD

We begin by combining Eqs. (1) and (4) to obtain

$$\partial \rho_k/\partial t = (\partial \rho_k/\partial t)_0 + M_k \sum_s (b_{ks} - a_{ks})\, \dot{\omega}_s, \tag{9}$$

where

$$(\partial \rho_k/\partial t)_0 = -\nabla \cdot (\rho_k \mathbf{u}) - \nabla \cdot \mathbf{J}_k + M_k \sum_r (b_{kr} - a_{kr})\, \dot{\omega}_r \tag{10}$$

is the value that $\partial \rho_k/\partial t$ would have in the absence of the equilibrium reactions. In a time-marching numerical calculation, temporal derivatives are approximated by finite differences performed with reference to a sequence of discrete times t^n ($n = 0, 1, 2, \ldots$). The superscript n is the time level, and the increment $\Delta t^n \equiv t^{n+1} - t^n$ is the time step. When Δt appears without a superscript, Δt^n is understood. The numerical representation of spatial derivatives will not be specified, as it is immaterial for present purposes. Such derivatives might be approximated by standard finite-difference techniques, finite element techniques, Galerkin methods, or in other ways.

Perhaps the simplest temporal difference scheme that might be used to approximate Eqs. (9) and (6) is the following:

$$\frac{\rho_k^{n+1} - \rho_k^n}{\Delta t} = \left(\frac{\partial \rho_k}{\partial t}\right)_0^n + M_k \sum_s (b_{ks} - a_{ks})\, \dot{\omega}_s^{n+1}, \tag{11}$$

$$K_c^s(T^n) = \mathcal{P}_s^{n+1}/\mathcal{R}_s^{n+1}. \tag{12}$$

The rationale for this scheme is as follows. All of the terms contained in $(\partial \rho_k/\partial t)_0$ are explicitly known in terms of the dependent variables, and therefore may be evaluated at the previous time level n. The quantities $\dot{\omega}_s$, on the other hand, are not explicitly known in terms of the other variables. They must therefore be evaluated at time level $n+1$; otherwise the scheme would not contain $\dot{\omega}_s^{n+1}$ and could not be advanced in time. (The pressure must be evaluated at time level $n+1$ in numerical calculations of incompressible flow for the same reason.) But now, in addition to the original N_s unknowns ρ_k (where N_s is the number of chemical species), the scheme involves the N_{eq} additional unknowns $\dot{\omega}_s^{n+1}$ (where N_{eq} is the number of equilibrium reactions).

Since Eq. (11) represents only N_s equations, it is necessary to evaluate at least the right member of Eq. (6) at time level $n+1$ to obtain the additional N_{eq} equations needed to close the system. Equations (11) and (12) then constitute $N_s + N_{eq}$ equations in the $N_s + N_{eq}$ unknowns ρ_k^{n+1} and $\dot{\omega}_s^{n+1}$.

It is convenient to define intermediate species densities $\tilde{\rho}_k$ given by

$$\tilde{\rho}_k = \rho_k^n + \Delta t(\partial \rho_k/\partial t)_0^n. \tag{13}$$

The $\tilde{\rho}_k$ can be calculated explicitly and may therefore be regarded as known. Combining Eqs. (11) and (13), we obtain

$$\rho_k^{n+1} = \tilde{\rho}_k + M_k \sum_s (b_{ks} - a_{ks}) \Delta\omega_s, \tag{14}$$

where $\Delta\omega_s \equiv \dot{\omega}_s^{n+1} \Delta t$. Equation (14) now replaces Eq. (11).

If desired, the ρ_k^{n+1} could now be eliminated from $\mathscr{P}_s^{n+1}$ and $\mathscr{R}_s^{n+1}$ by means of Eq. (14). Then $\mathscr{P}_s^{n+1}$ and $\mathscr{R}_s^{n+1}$ would become functions of the quantities $\Delta\omega_s$ alone, and Eq. (12) would represent a system of only N_{eq} equations in the N_{eq} unknowns $\Delta\omega_s$. For our purposes, however, it will be more convenient to retain both Eqs. (12) and (14).

Since Eqs. (12) and (14) constitute a coupled nonlinear equation system, it is evident that an iterative procedure will be required for their solution. Let the iteration index be ν, which will be displayed as a superscipt in parentheses. The value of $\Delta\omega_s$ on iteration ν is then $\Delta\omega_s^{(\nu)}$. According to Eq. (14), the corresponding value of ρ_k is

$$\rho_k^{(\nu)} = \tilde{\rho}_k + M_k \sum_s (b_{ks} - a_{ks}) \Delta\omega_s^{(\nu)}. \tag{15}$$

The initial values for the iteration procedure are

$$\Delta\omega_s^{(0)} = 0, \qquad \rho_k^{(0)} = \tilde{\rho}_k. \tag{16}$$

It is convenient to formulate the iteration scheme in terms of the changes in the quantities $\Delta\omega_s$ and ρ_k from one iteration to the next. These changes are given by

$$\delta\omega_s^{(\nu)} \equiv \Delta\omega_s^{(\nu)} - \Delta\omega_s^{(\nu-1)}, \tag{17}$$

$$\delta\rho_k^{(\nu)} \equiv \rho_k^{(\nu)} - \rho_k^{(\nu-1)} = M_k \sum_s (b_{ks} - a_{ks}) \, \delta\omega_s^{(\nu)}, \tag{18}$$

where Eq. (15) has been used. The iteration scheme is determined by specifying how $\delta\omega_s^{(\nu)}$ is to be calculated.

The most obvious choice of an iteration scheme would be the Newton–Raphson method. Unfortunately, this method requires the inversion of a square matrix of order N_{eq} on every iteration. In addition, the Newton–Raphson method is susceptible to large overshoots in the vicinity of the extrema of $K_c^s \mathscr{R}_s - \mathscr{P}_s$. For these reasons, we have developed a new quadratic iteration scheme.

The quadratic iteration scheme utilizes intermediate species densities that have been updated due to all the equilibrium reactions on previous iterations and all reactions preceding reaction s on the current iteration. These intermediate species densities are given by

$$\rho_k(\nu, s) = \rho_k^{(\nu-1)} + M_k \sum_{z=1}^{s-1} (b_{kz} - a_{kz})\, \delta\omega_z^{(\nu)}, \tag{19}$$

where z is a dummy s index. (It is not necessary to explicitly code Eq. (19) into a computer program, however, since if ρ_k is evaluated as a running sum then $\rho_k(\nu, s)$ is simply the "current" value of ρ_k just prior to the calculation of $\delta\omega_s^{(\nu)}$.) The corresponding current values of $\mathscr{P}_s$ and $\mathscr{R}_s$ are given by

$$\hat{\mathscr{P}}_s = \prod_k [\rho_k(\nu, s)/M_k]^{b_{ks}}, \tag{20}$$

$$\hat{\mathscr{R}}_s = \prod_k [\rho_k(\nu, s)/M_k]^{a_{ks}}, \tag{21}$$

and the corresponding deviation of reaction s from equilibrium is

$$D_s = K_c^s(T^n)\, \hat{\mathscr{R}}_s - \hat{\mathscr{P}}_s. \tag{22}$$

The iteration scheme is based on the intuitive idea that $\delta\omega_s^{(\nu)}$ should attempt to unilaterally reduce the deviation from equilibrium of reaction s from its current value of D_s to zero. The coupling between the equilibrium reactions (i.e., the fact that the other reactions may disturb the equilibrium of reaction s) is ignored in computing each $\delta\omega_s^{(\nu)}$. However, this coupling is implicitly taken into account by the iteration procedure as a whole, and the final converged solution is therefore fully coupled.

The species densities resulting from $\delta\omega_s^{(\nu)}$ are simply

$$\rho_k(\nu, s+1) = \rho_k(\nu, s) + M_k(b_{ks} - a_{ks})\, \delta\omega_s^{(\nu)}. \tag{23}$$

The corresponding values of $\mathscr{P}_s$ and $\mathscr{R}_s$ are obtained by replacing ρ_k with $\rho_k(\nu, s+1)$ in Eqs. (7) and (8), and are functions of $\delta\omega_s^{(\nu)}$ according to Eq. (23). These functional relations will be indicated by the notation $\mathscr{P}_s(\delta\omega_s^{(\nu)})$ and $\mathscr{R}_s(\delta\omega_s^{(\nu)})$. We want to determine $\delta\omega_s^{(\nu)}$ so that

$$K_c^s(T^n)\, \mathscr{R}_s(\delta\omega_s^{(\nu)}) = \mathscr{P}_s(\delta\omega_s^{(\nu)}). \tag{24}$$

However, in the general case, $\mathscr{P}_s$ and $\mathscr{R}_s$ are polynomials of arbitrary orders in $\delta\omega_s^{(\nu)}$, and the exact solution of Eq. (24) is not an appealing prospect. We shall therefore approximate $\mathscr{P}_s$ and $\mathscr{R}_s$ by quadratic functions of $\delta\omega_s^{(\nu)}$; Eq. (24) then becomes a quadratic equation in $\delta\omega_s^{(\nu)}$, and can be solved explicitly. Thus we write

$$\mathscr{P}_s(x) \cong \hat{\mathscr{P}}_s(1 + \alpha_s x + A_s x^2), \tag{25}$$

$$\mathscr{R}_s(x) \cong \hat{\mathscr{R}}_s(1 + \beta_s x + B_s x^2), \tag{26}$$

where x is a dummy argument representing $\delta\omega_s^{(\nu)}$, and we have made use of the fact that $\mathscr{P}_s$ and $\mathscr{R}_s$ reduce to $\hat{\mathscr{P}}_s$ and $\hat{\mathscr{R}}_s$, respectively, when $\delta\omega_s^{(\nu)} = 0$. Of course, if reaction s is of second or lower order then Eqs. (25) and (26) will be exact rather than approximate.

The coefficients α_s and β_s will be determined by requiring the derivatives $\partial\mathscr{P}_s(x)/\partial x$ and $\partial\mathscr{R}_s(x)/\partial x$ to be correct at $x = 0$. Therefore

$$\alpha_s = \frac{1}{\hat{\mathscr{P}}_s} \frac{\partial \mathscr{P}_s(x)}{\partial x}\bigg|_{x=0} = \frac{\partial \ln \mathscr{P}_s(x)}{\partial x}\bigg|_{x=0}, \tag{27}$$

$$\beta_s = \frac{1}{\hat{\mathscr{R}}_s} \frac{\partial \mathscr{R}_s(x)}{\partial x}\bigg|_{x=0} = \frac{\partial \ln \mathscr{R}_s(x)}{\partial x}\bigg|_{x=0}. \tag{28}$$

Evaluating the indicated derivatives in a straightforward fashion, we find that

$$\alpha_s = \sum_k M_k(b_{ks} - a_{ks})\, b_{ks}/\rho_k(\nu, s), \tag{29}$$

$$\beta_s = \sum_k M_k(b_{ks} - a_{ks})\, a_{ks}/\rho_k(\nu, s). \tag{30}$$

The coefficients A_s and B_s could be evaluated in a similar way by matching the second derivatives at $x = 0$, but we prefer an alternative prescription that brings in information from a wider range of x. The information that we want to utilize is that if $\delta\omega_s^{(\nu)}$ is too large or too small at least one of the species densities will be driven negative. There is thus a critical upper value of $\delta\omega_s^{(\nu)}$, call it $\delta\omega_s^{\max}$, at which $\mathscr{R}_s$ goes to zero. Similarly, there is a critical lower value $\delta\omega_s^{\min}$ at which $\mathscr{P}_s$ goes to zero. These values are readily found to be

$$\delta\omega_s^{\max} = \min_{\{k \mid a_{ks} > b_{ks}\}} \left(\frac{\rho_k(\nu, s)/M_k}{a_{ks} - b_{ks}} \right), \tag{31}$$

$$\delta\omega_s^{\min} = \max_{\{k \mid a_{ks} < b_{ks}\}} \left(\frac{\rho_k(\nu, s)/M_k}{a_{ks} - b_{ks}} \right). \tag{32}$$

We now determine A_s by requiring the approximate $\mathscr{P}_s(x)$ given by Eq. (25) to vanish at $x = \delta\omega_s^{\min}$. This yields

$$A_s = -(1 + \alpha_s\, \delta\omega_s^{\min})/(\delta\omega_s^{\min})^2. \tag{33}$$

Similarly, the requirement that the approximate $\mathscr{R}_s(x)$ given by Eq. (26) vanish at $x = \delta\omega_s^{\max}$ yields

$$B_s = -(1 + \beta_s\, \delta\omega_s^{\max})/(\delta\omega_s^{\max})^2. \tag{34}$$

Substitution of Eqs. (25) and (26) into Eq. (24) yields

$$D_s + E_s x + F_s x^2 = 0, \tag{35}$$

where D_s is given by Eq. (22) and

$$E_s = K_c^s(T^n)\, \hat{\mathscr{R}}_s \beta_s - \hat{\mathscr{P}}_s \alpha_s, \tag{36}$$

$$F_s = K_c^s(T^n)\, \hat{\mathscr{R}}_s B_s - \hat{\mathscr{P}}_s A_s. \tag{37}$$

The solutions of Eq. (35) are

$$x = \delta\omega_s^{(\nu)} = [-E_s \pm (E_s^2 - 4D_sF_s)^{1/2}]/2F_s. \tag{38}$$

The sign ambiguity may be resolved by requiring $\delta\omega_s$ to remain finite as $F_s \to 0$. For this to occur, the sign chosen must be the same as the sign of E_s. One readily verifies that $E_s < 0$; therefore the negative sign must be taken, and we obtain

$$\delta\omega_s^{(\nu)} = -[E_s + (E_s^2 - 4D_sF_s)^{1/2}]/2F_s. \tag{39}$$

Equation (39) is our basic formula for $\delta\omega_s^{(\nu)}$. However, it must be supplemented with prescriptions for handling certain special cases that may arise. First of all, we cannot allow $\delta\omega_s^{(\nu)}$ to be greater than $\delta\omega_s^{\max}$ or smaller than $\delta\omega_s^{\min}$. Actually we insert a safety factor of 0.9 for good measure, so if Eq. (39) yields a value of $\delta\omega_s^{(\nu)}$ that exceeds $0.9\,\delta\omega_s^{\max}$ we set $\delta\omega_s^{(\nu)} = 0.9\,\delta\omega_s^{\max}$. Similarly, if Eq. (39) gives a $\delta\omega_s^{(\nu)}$ less than $0.9\,\delta\omega_s^{\min}$, we set $\delta\omega_s^{(\nu)} = 0.9\,\delta\omega_s^{\min}$.

It is clear physically that $\delta\omega_s^{(\nu)}$ must have the same sign as D_s for the reaction to be driven toward equilibrium. Therefore, if Eq. (39) yields a $\delta\omega_s^{(\nu)}$ that differs in sign from D_s, $\delta\omega_s^{(\nu)}$ is set equal to zero.

Equation (39) breaks down if $F_s = 0$ or if $4D_sF_s > E_s^2$. If either of these conditions occurs, we revert to the linear relaxation formula obtained by taking the limit $F_s \to 0$, namely

$$\delta\omega_s^{(\nu)} = -D_s/E_s, \tag{40}$$

which incidentally is the formula corresponding to Newtonian iteration on the isolated reaction s. Since $E_s < 0$, $\delta\omega_s^{(\nu)}$ has the correct sign.

This completes the specification of our iteration scheme. Since it ignores the coupling between equilibrium reactions in computing $\delta\omega_s^{(\nu)}$, it converges most rapidly when the equilibrium reactions are chosen to be as nearly uncoupled as possible. This can frequently be achieved by replacing strongly coupled reactions with appropriate linear combinations of reactions, as illustrated in the next section. Depending on the way in which the equilibrium reactions are coupled, the rate of convergence may also depend on the sequential ordering of the reactions, since on a given iteration the ρ_k are updated due to each reaction before proceeding to the next reaction. The reactions may be coupled in an almost infinite variety of ways, and we have therefore made no attempt to formulate general rules for the optimal ordering of the reactions. In particular cases, however, it may be possible to identify the best ordering by inspection.

IV. Sample Calculation

In this section we present some results obtained from the present method in a numerical simulation of the compression and power strokes in an internal combustion engine cylinder. The calculation was performed with the CONCHAS computer code [4], in which the present method has been incorporated as a modular subroutine. CONCHAS is an arbitrary Lagrangian–Eulerian (ALE) finite-difference code [5], in which the mesh cells are arbitrary quadrilaterals and the mesh points may move in an arbitrarily specified manner. The latter capability allows a straightforward representation of the moving piston.

The geometry of the engine cylinder is shown in Fig. 1. The cylinder is axisymmetric and the piston is cupped. The calculation is two-dimensional; the plane of calculation is a typical plane containing the symmetry axis. The fluid velocity includes a swirling component about the axis as well as the two components in the plane of calculation. The condition of axial symmetry implies that all dependent variables, including the swirl velocity, are independent of a rotation about the axis. The symmetry axis is a free slip boundary, while no-slip conditions are imposed at all other boundaries. All the boundaries are adiabatic.

Thermodynamic quantities (such as equilibrium constants and species internal energies as functions of temperature) were obtained from the JANAF tables [6]. The calculation includes 12 chemical species, among which occur three kinetic reactions

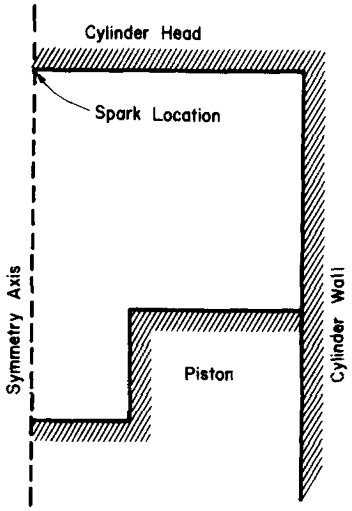

FIG. 1. Schematic of engine cylinder geometry.

and six equilibrium reactions. The chemical species are C_8H_{18}, O_2, O, N_2, N, H_2, H, CO_2, CO, H_2O, OH, and NO. The kinetic reactions are

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O, \tag{a}$$

$$N + O_2 \rightleftarrows NO + O, \tag{b}$$

$$O + N_2 \rightleftarrows NO + N. \tag{c}$$

Reaction (a) is a single-step (global) octane oxidation reaction, and reactions (b) and (c) represent the simplified Zel'dovich mechanism for NO production.

The six equilibrium reactions basically represent the dissociation of O_2, N_2, H_2, CO_2, H_2O, and OH. It is conventional to write such equilibrium reactions in such a way that they represent the formation of chemical compounds from elements in their standard states. According to this convention, our six equilibrium reactions would be taken to be

$$O_2 \rightleftarrows 2O, \tag{d}$$

$$N_2 \rightleftarrows 2N, \tag{e}$$

$$H_2 \rightleftarrows 2H, \tag{f}$$

$$2CO_2 \rightleftarrows 2CO + O_2, \tag{g}$$

$$2H_2O \rightleftarrows 2H_2 + O_2, \tag{h}$$

$$2OH \rightleftarrows H_2 + O_2. \tag{i}$$

Here CO is considered an "elementary" constituent of CO_2, since it is very stable under conditions of present interest.

Reactions (d)–(i) are a perfectly legitimate set of equilibrium reactions for the problem under consideration. However, they suffer from the disadvantage that reactions (h) and (i) are very strongly coupled, which retards convergence of the iteration procedure described in Section III. The strong coupling results from the fact that, at moderate temperatures and in the presence of reasonable amounts of O_2, the equilibrium of reaction (i) lies far to the left; that is, the amount of H_2 present is much less than the amount of OH. This means that almost all of the H_2 produced by reaction (h) will subsequently have to be converted into OH by reaction (i). It is clear that it would be much better to let H_2O dissociate directly into OH and O_2, thereby eliminating the middleman, so to speak. Accordingly, we replace reaction (h) by the appropriate linear combination of reactions (h) and (i), namely, reaction (h) minus twice reaction (i):

$$2H_2O + O_2 \rightleftarrows 4OH. \tag{h'}$$

With reaction (h) replaced by reaction (h′), the system of equilibrium reactions becomes weakly coupled and the iteration procedure of Section III converges rapidly.

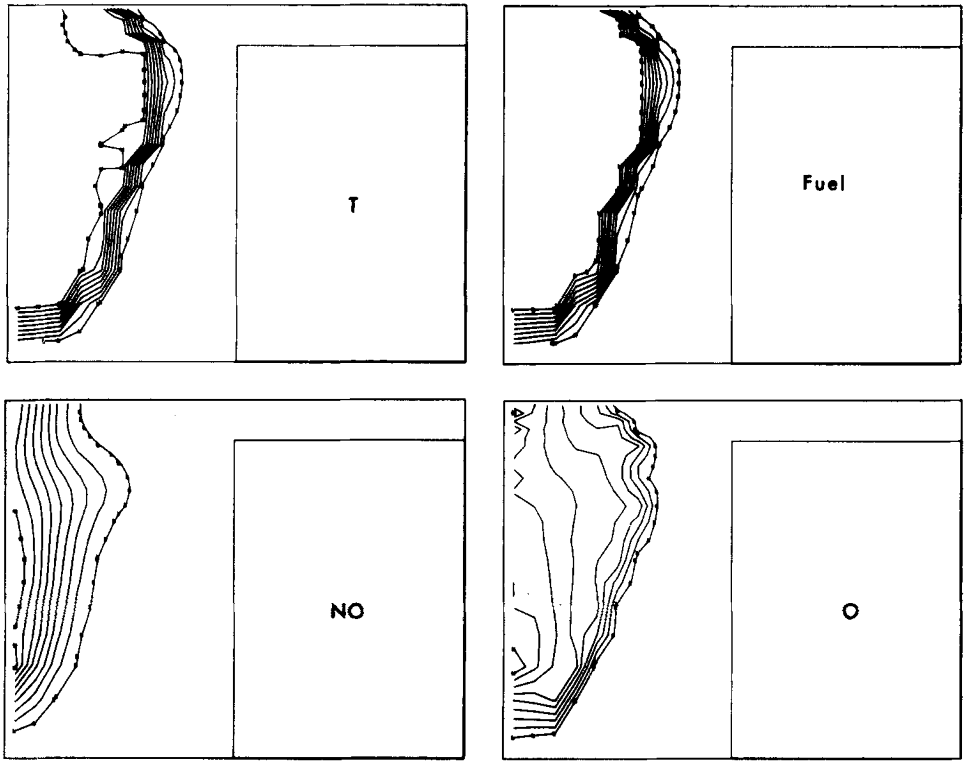

FIG. 2. Contour plots of temperature (T) and mass fractions of fuel (C_8H_{18}), NO, and O at 6° after top dead center.

In any particular application of the present method, it will be advantageous and possibly essential to select the equilibrium reactions to be as weakly coupled as possible. This involves taking appropriate linear combinations of the basic formation reactions as illustrated above. Notice that the best choice of reactions does *not* necessarily correspond to the physical reaction mechanism; it is rather a function of which species are present in the largest amounts in the temperature and concentration ranges of interest.

The initial charge in the engine cylinder is homogeneous with an equivalence ratio (fuel–air ratio relative to stoichiometric) of 0.95. The charge is initially swirling about the axis at 8000 RPM. The engine speed is 1600 RPM. The calculation begins at bottom dead center, just prior to the compression stroke. Ignition occurs at 17° before top dead center.

Figure 2 shows contour plots of temperature and the mass fractions of fuel (C_8H_{18}), NO, and O at 6° after top dead center, which is about 3 msec after ignition. The piston is beginning to move downward again, causing gas to be pulled back into the "squish" region between the top of the piston and the cylinder head. This gas flow is responsible for the bump in the contours just below the lip of the piston cup. The flame front is located where the temperature contours are closely spaced, and delineates the burned region. This region is elongated along the axis because of the centrifugal buoyancy effect. Note that the fuel contours are nearly identical to the isotherms, because the spent fuel is responsible for the temperature rise at each point. The dissociation reactions (d)–(i) have the effect of reducing the temperature of the burned material behind the flame. These reactions are negligible in the unburned material ahead of the flame. Consequently, the steepest gradients in atomic concentrations will also occur in the vicinity of the flame front, as is observed in the *O* contours in Fig. 2. *NO* is produced kinetically by the simplified Zel'dovich mechanism, which proceeds slowly compared to the other reactions in the system. Therefore the greatest *NO* concentrations tend to be found in the regions that have been hottest for the longest time, as is qualitatively apparent from a comparison of the isotherms and *NO* contours.

Figure 3 shows the total mass of *NO* in the cylinder as a function of time. The curve labeled "swirl" is from the present calculation, while the curve labeled "no swirl" is from a similar calculation in which the initial charge was quiescent rather than swirling. Prior to 20 msec a small amount of *NO* in the cylinder is left from the previous cycle. The rapid rise corresponds to the rapid phase of octane combustion. The curve levels off after 24 msec. All the fuel is consumed and expansion of the gas by withdrawl of the piston cools the fluid, stopping the *NO* reactions. As the figure shows, *NO* production was significantly reduced in the absence of swirl. Because *NO* produced by automotive engines is a significant component of air pollution, this kind of numerical simulation has definite potential for helping engineers design cleaner engines.

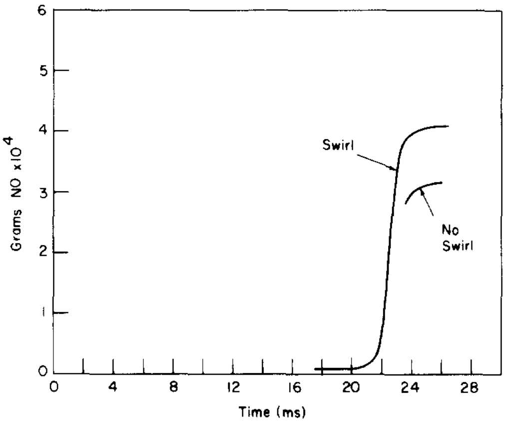

FIG. 3. Total NO mass in the cylinder versus time.

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