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Iteration Scheme for Implicit Calculations of Kinetic and Equilibrium Chemical Reactions in Fluid Dynamics*

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An iteration scheme for the implicit treatment of equilibrium chemical reactions in partial equilibrium flow has previously been described (J. D. Ramshaw and A. A. Amsden, *J. Comput. Phys.* **59**, 484 (1985); **71**, 224 (1987)). Here we generalize this scheme to kinetic reactions as well as equilibrium reactions. This extends the applicability of the scheme to problems with kinetic reactions that are fast in some regions of the flow field but slow in others. The resulting scheme thereby provides a single unified framework for the implicit treatment of an arbitrary number of coupled equilibrium and kinetic reactions in chemically reacting fluid flow. © 1995 Academic Press, Inc.

I. INTRODUCTION AND SUMMARY

Partial equilibrium flow [1, 2] is a useful idealization of multicomponent fluid flow with multiple chemical reactions, some of which are so fast that they may be assumed to be in equilibrium, while the remaining slower reactions are computed kinetically. The equilibrium reactions require an implicit treatment, which produces a system of coupled nonlinear equations that must in general be solved iteratively [3, 4].

Each reaction in a partial equilibrium flow must be classified as "fast" or "slow" globally, i.e., independently of position and time [1, 2]. Thus a reaction must be fast *everywhere* to be considered an equilibrium reaction. This framework is clearly not well suited to problems with reactions that are fast in some regions but slow in others. Such reactions cannot be considered equilibrium reactions globally, so they must be treated kinetically. This is often done using simple explicit or partially implicit methods (e.g., [5, 6]). Unfortunately, such methods require the use of very small time steps for stability and/or accuracy in the fast regions, and this largely negates the benefits of the partial equilibrium description.

The need for small time steps in such problems can be removed by treating all fast and equilibrium reactions together in a fully implicit and fully coupled manner. Our purpose here is to show how this may be done by suitably generalizing a previously described iteration scheme for the equilibrium reactions alone [3, 4]. Reactions that are *slow* everywhere may still be treated by explicit or partially implicit methods in the usual way, or they may be included in the iteration if desired. Thus the present scheme provides a general method for fully implicit treatment of chemical reactions in multicomponent fluid dynamics, which applies as a special case to problems in which some or all of the reactions are in equilibrium.

The present scheme retains the overall structure of the previous equilibrium scheme [3, 4], in which the first several iterations are performed with a simple one-step Gauss–Seidel–Newton method, while subsequent iterations are performed using a full Newton–Raphson method. However, the residual associated with each reaction must now be suitably redefined to include the kinetic terms. The presence of the latter terms is unfortunately incompatible with the nonlinear preconditioning that was previously used, so this too must be modified in defining the residuals. The redefined residuals then imply a corresponding redefinition of their Jacobian matrix with respect to the progress rates. The remainder of the previous scheme [3, 4] is basically unchanged, except that we have considerably simplified the logic for scaling back Newton–Raphson overshoots. Consequently, any computer code based on the original scheme can easily be converted to the new scheme by relatively minor modifications. In particular, the new scheme has been incorporated into the LAVA code for simulating thermal plasma processes [7, 8], and we are hopeful that it will also prove useful to the growing KIVA [5, 6] user community.

II. TIME DIFFERENCING

We consider a multicomponent fluid flow with multiple simultaneous chemical reactions. The reactions to be treated in a fully implicit and fully coupled manner are labeled by the index s and are symbolized by

$$\sum_k a_{ks} X_k \rightleftharpoons \sum_k b_{ks} X_k, \tag{1}$$

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where s ranges from 1 to N, a_{ks} and b_{ks} are dimensionless stoichiometric coefficients, and X_k represents one mole of species k. The progress rate for reaction s is denoted by $\dot{\omega}_s$ and is given by the kinetic rate expression

$$\dot{\omega}_s = k_{fs} R_s - k_{bs} P_s, \tag{2}$$

where k_{fs} and k_{bs} are respectively the forward and backward rate coefficients for reaction s (which are functions of the temperature T), and

$$R_s = \prod_k \left(\frac{\rho_k}{M_k}\right)^{a_{ks}}; \quad P_s = \prod_k \left(\frac{\rho_k}{M_k}\right)^{b_{ks}}, \tag{3}$$

where ρ_k and M_k are respectively the partial mass density and molecular weight of species k. In what follows it will be convenient to eliminate k_{bs} in favor of the (concentration) equilibrium constant $K_s = k_{fs}/k_{bs}$, which is a purely thermodynamic quantity. Equilibrium reactions can then be treated as special cases of kinetic reactions by sending $k_{fs} \longrightarrow \infty$ at constant K_s, while unidirectional kinetic reactions with $k_{bs} = 0$ can be treated by sending $K_s \longrightarrow \infty$ at constant k_{fs}.

The chemical reactions contribute source terms to the evolution equations for ρ_k and for the specific thermal internal energy e, as given by

$$\frac{\partial \rho_k}{\partial t} = \left[\frac{\partial \rho_k}{\partial t}\right]_0 + M_k \sum_s (b_{ks} - a_{ks}) \dot{\omega}_s \tag{4}$$

$$\frac{\partial (\rho e)}{\partial t} = \left[\frac{\partial (\rho e)}{\partial t}\right]_0 + \sum_s Q_s \dot{\omega}_s, \tag{5}$$

where $\rho = \sum_k \rho_k$ is the total mass density, Q_s is the negative heat of reaction for reaction s at $T = 0$ K, and $[\partial \rho_k/\partial t]_0$ and $[\partial(\rho e)/\partial t]_0$ represent the effects of convection, diffusion, source and sink terms, and any chemical reactions not treated implicitly.

We are concerned with time-marching methods in which the evolution equations are solved numerically by using finite differences to approximate time derivatives. Such methods generate the approximate solution at a sequence of discrete times t^n separated by time steps $\Delta t \equiv t^{n+1} - t^n$. As usual, the time level will be displayed as a superscript, so that G^n denotes the difference approximation to the quantity $G(t)$ at $t = t^n$. Superscript $n + 1$ (the "new" time level) will frequently be suppressed for simplicity. We restrict attention to two-level schemes in which the time derivative $\partial G/\partial t$ is simply approximated by $(G^{n+1} - G^n)/\Delta t$. The present method is primarily intended for use in conjunction with time-splitting schemes in which the terms $[\partial \rho_k/\partial t]_0$ and $[\partial(\rho e)/\partial t]_0$ may be evaluated without exact knowledge of the final new-time values ρ_k^{n+1} and e^{n+1}. These terms may therefore be regarded as known for present purposes. The difference approximations to Eqs. (4) and (5) may then be written in the form

$$\rho_k = \rho_k^{n+1} = \tilde{\rho}_k + M_k \sum_s (b_{ks} - a_{ks}) \omega_s \tag{6}$$

$$\rho e = (\rho e)^{n+1} = \widetilde{\rho e} + \sum_s Q_s \omega_s, \tag{7}$$

where $\omega_s = \dot{\omega}_s \Delta t$ is the progress increment for reaction s on the current time step and

$$\tilde{\rho}_k = \rho_k^n + \Delta t \left[\frac{\partial \rho_k}{\partial t}\right]_0 \tag{8}$$

$$\widetilde{\rho e} = (\rho e)^n + \Delta t \left[\frac{\partial (\rho e)}{\partial t}\right]_0. \tag{9}$$

The latter quantities represent partially updated values of ρ_k and ρe which serve as the initial or starting values for the iteration scheme.

The progress increments are determined by a suitable implicit approximation to Eq. (2), namely

$$\frac{\omega_s}{\Delta t k_{fs}} = R_s - \frac{P_s}{K_s}, \tag{10}$$

where R_s and P_s are evaluated using the new-time ρ_k given by Eq. (6), and k_{fs} and K_s are suitable approximations to their values at $T = T^{n+1}$. These approximations are defined by

$$\ln k_{fs} = \ln k_{fs}(T^n) + \left(\frac{\partial \ln k_{fs}}{\partial T}\right)^n (T - T^n) \tag{11}$$

$$\ln K_s = \ln K_s(T^n) + \left(\frac{\partial \ln K_s}{\partial T}\right)^n (T - T^n), \tag{12}$$

where T is an approximation to T^{n+1} given by

$$T = T^n + \frac{(\rho e) - (\rho e)^n}{\rho c_v} = \tilde{T} + \frac{1}{\rho c_v} \sum_s Q_s \omega_s \tag{13}$$

with ρe given by Eq. (7). Here c_v is the specific heat at constant volume, and $\tilde{T}$ is defined by

$$\tilde{T} = T^n + \frac{(\widetilde{\rho e}) - (\rho e)^n}{\rho c_v}. \tag{14}$$

Note that Eqs. (11)–(13) become exact rather than approximate in steady state. Note also that Eq. (10) has been written in a form which remains well behaved in the special cases of equilibrium reactions ($k_{fs} \to \infty$) and unidirectional reactions ($K_s \to \infty$).

III. THE ITERATION SCHEME

The P_s and R_s depend on the ω_s through Eqs. (3) and (6), while k_{fs} and K_s depend on the ω_s through Eqs. (11)–(13). Equation (10) may therefore be regarded as a system of N coupled nonlinear equations in the N unknowns ω_s. This is the system of equations which the iteration scheme must solve.

In the previous scheme for equilibrium reactions [3, 4], it was found that convergence could be substantially accelerated by the use of nonlinear preconditioning to make the equations more nearly linear in the progress increments. In the present context, however, the kinetic term $\omega_s/(\Delta t k_{fs})$ in Eq. (10) is already linear in ω_s, so preconditioning is needed only when this term becomes small, i.e., for reactions close to equilibrium. For such reactions, however, preconditioning is essential to obtain convergence rates comparable to those of the previous scheme.

Unfortunately, the previous preconditioning procedure [3] no longer applies due to the presence of the kinetic term. We must therefore devise an alternative procedure which is similar in spirit and effect. We begin by identifying the species involved in reaction s whose concentration depends most sensitively on ω_s; i.e., the species for which $\rho_k^{-1}|\partial \rho_k/\partial \omega_s| = (M_k/\rho_k)|b_{ks} - a_{ks}|$ is a maximum. This species is referred to as the *reference species* for reaction s and is denoted by species index $k = \kappa(s)$. (This definition of reference species differs slightly from that used in the equilibrium case [3].) To simplify the notation, it is convenient to let $a_s \equiv a_{\kappa(s),s}$ and $b_s \equiv b_{\kappa(s),s}$. Note that $b_s \neq a_s$. It is also convenient to denote the reference species concentration by $c_s \equiv \rho_{\kappa(s)}/M_{\kappa(s)}$. The primary dependence on ω_s in the right member of Eq. (10) is now regarded as being contained in c_s.

The next step is to determine which of the two terms in the right member of Eq. (10) is the more nonlinear in ω_s. For this purpose we shall evaluate rough approximations to the second derivatives of these terms with respect to ω_s, based on the simplifying assumption that they depend on ω_s only through the factors $c_s^{a_s}$ and $c_s^{b_s}$ in R_s and P_s, respectively. Under this assumption, we find that the second derivatives of the terms R_s and P_s/K_s are proportional to the quantities $D_s^R \equiv a_s(a_s - 1)R_s$ and $D_s^P \equiv b_s(b_s - 1)P_s/K_s$, respectively, where the coefficient of proportionality is the same for both terms.

We now consider the primary nonlinear dependence on ω_s in Eq. (10) to be contained in the term P_s/K_s if $D_s^P > D_s^R$, and in the term R_s if $D_s^P < D_s^R$. The nonlinearity can then be isolated by solving Eq. (10) for P_s or R_s, respectively. Since c_s itself is linear in ω_s, the primary dependence on ω_s can then be made to manifest itself linearly by raising both sides of the resulting equation to the power

$$e_s = \begin{cases} 1/b_s & (D_s^P > D_s^R) \\ 1/a_s & (D_s^P < D_s^R). \end{cases} \tag{15}$$

According to the above procedure, Eq. (10) is now replaced by the equivalent system

$$F_s = 0, \tag{16}$$

where the residual F_s is defined by

$$F_s = \begin{cases} P_s^{e_s} - U_s^{e_s} & (D_s^P > D_s^R) \\ R_s^{e_s} - V_s^{e_s} & (D_s^P < D_s^R) \end{cases} \tag{17}$$

in which

$$U_s = K_s\left(R_s - \frac{\omega_s}{\Delta t k_{fs}}\right) \tag{18}$$

$$V_s = \frac{P_s}{K_s} + \frac{\omega_s}{\Delta t k_{fs}}. \tag{19}$$

As discussed above, preconditioning is unnecessary when the kinetic term is sufficiently large that reaction s is no longer close to equilibrium. We consider this to be the case when $|\omega_s|/(\Delta t k_{fs}) > 0.1 P_s/K_s$. This condition is dynamically monitored on every iteration, and whenever it is satisfied we simply turn off the preconditioning by setting $e_s = 1$ for the remainder of the iterations on that particular time step.

Equation (16) is the system that will actually be solved. To do so, we employ the same two-stage procedure used in the equilibrium case [3, 4] in which the first several iterations are performed with a one-step Gauss–Seidel–Newton (GSN) method, while subsequent iterations (if necessary) are performed using a full Newton–Raphson (NR) method. This procedure requires evaluation of the Jacobian matrix of partial derivatives $\partial F_s/\partial \omega_t$, which may be expressed in terms of the simpler and more basic derivatives

$$A_{st} \equiv \frac{\partial \ln R_s}{\partial \omega_t} = \sum_k \frac{M_k}{\rho_k} a_{ks}(b_{kt} - a_{kt}) \tag{20}$$

$$B_{st} \equiv \frac{\partial \ln P_s}{\partial \omega_t} = \sum_k \frac{M_k}{\rho_k} b_{ks}(b_{kt} - a_{kt}) \tag{21}$$

$$\alpha_{st} \equiv \frac{\partial \ln k_{fs}}{\partial \omega_t} = \left(\frac{\partial \ln k_{fs}}{\partial T}\right)^n \frac{Q_t}{\rho c_v} \tag{22}$$

$$\beta_{st} \equiv \frac{\partial \ln K_s}{\partial \omega_t} = \left(\frac{\partial \ln K_s}{\partial T}\right)^n \frac{Q_t}{\rho c_v}, \tag{23}$$

where use has been made of Eqs. (3), (6), and (11)–(13). It is convenient to first evaluate $\partial U_s/\partial \omega_t$ and $\partial V_s/\partial \omega_t$, with the results

$$\frac{\partial U_s}{\partial \omega_t} = K_s\left\{R_s(A_{st} + \beta_{st}) + \frac{1}{\Delta t k_{fs}}[\omega_s(\alpha_{st} - \beta_{st}) - \delta_{st}]\right\} \tag{24}$$

$$\frac{\partial V_s}{\partial \omega_t} = \frac{P_s}{K_s}(B_{st} - \beta_{st}) + \frac{1}{\Delta t k_{fs}}(\delta_{st} - \omega_s \alpha_{st}), \tag{25}$$

where δ_{st} is the Kronecker delta. Differentiating Eq. (17), we finally obtain

$$\frac{\partial F_s}{\partial \omega_t} = e_s \begin{cases} P_s^{e_s} B_{st} - U_s^{e_s - 1}(\partial U_s/\partial \omega_t) & (D_s^P > D_s^R) \\ R_s^{e_s} A_{st} - V_s^{e_s - 1}(\partial V_s/\partial \omega_t) & (D_s^P < D_s^R). \end{cases} \tag{26}$$

We are now in a position to define the one-step GSN and NR methods of which the present scheme is comprised. The iteration index ν will be displayed as a superscript in parentheses, so that $G^{(\nu)}$ denotes the value of G after iteration ν. The one-step GSN method is defined by [3]

$$\begin{aligned} \delta\omega_s &\equiv \omega_s^{(\nu+1)} - \omega_s^{(\nu)} \\ &= \frac{-F_s(\omega_1^{(\nu+1)}, \ldots, \omega_{s-1}^{(\nu+1)}, \omega_s^{(\nu)}, \ldots, \omega_N^{(\nu)})}{\partial F_s(\omega_1^{(\nu+1)}, \ldots, \omega_{s-1}^{(\nu+1)}, \omega_s^{(\nu)}, \ldots, \omega_N^{(\nu)})/\partial \omega_s^{(\nu)}} \end{aligned} \tag{27}$$

subject to the restriction [3]

$$0.9\delta\omega_s^{\min} \le \delta\omega_s \le 0.9\delta\omega_s^{\max}, \tag{28}$$

where $\delta\omega_s^{\min}$ and $\delta\omega_s^{\max}$ are respectively the minimum and maximum values of $\delta\omega_s$ that preserve the nonnegativity of the ρ_k, which are given by

$$\begin{aligned} \delta\omega_s^{\min} &= \left[\min_k \frac{M_k(a_{ks} - b_{ks})}{\rho_k}\right]^{-1}; \\ \delta\omega_s^{\max} &= \left[\max_k \frac{M_k(a_{ks} - b_{ks})}{\rho_k}\right]^{-1}, \end{aligned} \tag{29}$$

in which the ρ_k represent the current intermediate approximation to the species densities, as discussed below. The full NR method is defined by

$$\sum_t (J_{st}/J_{ss})\delta\omega_t = -F_s^{(\nu)}/J_{ss}, \tag{30}$$

where $J_{st} = (\partial F_s/\partial \omega_t)^{(\nu)}$. Since the J_{st} often vary by many orders of magnitude, these equations have been scaled so that the diagonal elements of the associated matrix are all unity. To obtain the $\delta\omega_s$, and thereby the $\omega_s^{(\nu+1)}$, it is necessary to solve the linear system of Eq. (30). This may be done using any of the standard methods; we simply use the LAPACK [9] subroutine DGESVX to solve the system by Gaussian elimination with partial pivoting.

Each iterative approximation to the ω_s produces a corresponding approximation to the ρ_k and ρe via Eqs. (6) and (7), and thereby to the P_s and R_s via Eq. (3) and to k_{fs} and K_s via Eqs. (11)–(14). Once the iteration has converged, the resulting final values of the ω_s then combine with Eqs. (6) and (7) to give the final new-time values of the ρ_k and ρe. Note that the $\delta\omega_s$ are computed sequentially in the GSN method, but simultaneously in the NR method. Consequently, each GSN iteration actually produces N intermediate approximations to the ω_s, whereas each NR iteration produces only one. The corresponding intermediate GSN approximations to the ρ_k and ρe are needed to evaluate F_s and $\partial F_s/\partial \omega_s$ in Eq. (27). If the ρ_k and ρe are continually updated as running sums, these intermediate approximations are simply the "current" values of these sums [3, 4].

The iteration scheme as a whole is structured just as before [3]. The iteration is initialized by setting $\omega_s^{(0)} = 0$, which implies that $\rho_k^{(0)} = \tilde{\rho}_k$ and $(\rho e)^{(0)} = \tilde{\rho}\tilde{e}$. The first N_0 iterations are performed with the one-step GSN method, and if convergence has not already occurred, all subsequent iterations are performed with the Newton–Raphson method. We currently take $N_0 = 10$. The iteration scheme is considered to have converged when

$$\left|\frac{P_s}{K_s} + \frac{\omega_s}{\Delta t k_{fs}} - R_s\right| < \varepsilon \max\left(\frac{P_s}{K_s}, R_s, \left|\frac{\omega_s}{\Delta t k_{fs}}\right|, 10^{-13}\frac{\Delta\omega_s}{\Delta t k_{fs}}\right) \tag{31}$$

for all s, where $\Delta\omega_s \equiv \delta\omega_s^{\max} - \delta\omega_s^{\min}$. Currently ε is taken to be 0.02, but convergence is typically so fast at the end that much smaller values of ε require only a few additional iterations.

In Ref. [3] we noted that the Jacobian matrix becomes ill-conditioned when a single trace species of very small concentration is involved in two or more reactions. When this happens, Eq. (30) may produce overshoots in the $\omega_s^{(\nu+1)}$ large enough to drive the ρ_k and/or e negative. A trial-and-error procedure for successively scaling back $\delta\omega_s$ in such situations was presented in Ref. [3]. Here we replace this previous procedure by a much simpler single-step procedure for scaling the $\delta\omega_s$ back to values that preserve the positivity of the ρ_k and e. We first compute the changes in ρ_k and ρe produced by the unscaled $\delta\omega_s$ given by Eq. (30). According to Eqs. (6) and (7), these changes are

$$\delta\rho_k = M_k \sum_s (b_{ks} - a_{ks})\delta\omega_s \tag{32}$$

$$\delta(\rho e) = \sum_s Q_s \delta\omega_s. \tag{33}$$

The scaling procedure then consists in simply replacing $\delta\omega_s$ by $\mu\delta\omega_s$, where μ is the largest value in the interval $0 < \mu \le 1$ for which $\rho_k^{(\nu)} + \mu\delta\rho_k > \gamma\rho_k^{(\nu)}$ for all k and $(\rho e)^{(\nu)} + \mu\delta(\rho e) > \gamma(\rho e)^{(\nu)}$, where the parameter $\gamma > 0$ specifies the margin of safety. This value of μ is readily found to be

$$\mu = \min\left[1, \frac{\gamma - 1}{\min(\delta\rho_k/\rho_k^{(\nu)}, \delta(\rho e)/(\rho e)^{(\nu)})}\right]. \tag{34}$$

We currently take $\gamma = 0.02$.

In the present context there is also an entirely new source of ill-conditioning that must be considered. This arises due to the fact that chemical reaction mechanisms often contain reactions that are independent in a kinetic sense but which become linearly dependent in the equilibrium limit of large rate coefficients. Consider, for example, the system

$$2H_2 \rightleftharpoons H_2 + 2H$$
$$H_2 + H \rightleftharpoons 3H,$$

representing dissociation of H_2 due to collisions with the third bodies H_2 and H, respectively. For this system, Eq. (10) takes the form

$$\frac{\omega_1}{k_{f1}\Delta t} = [H_2]^2 - \frac{[H_2][H]^2}{K}$$
$$\frac{\omega_2}{k_{f2}\Delta t} = [H_2][H] - \frac{[H]^3}{K},$$

where $[X] = \rho_X/M_X$ is the molar concentration of species X. In the equilibrium limit as $k_{f1}, k_{f2} \to \infty$, these equations become functionally dependent and $\mathbf{J}$ consequently becomes singular. This degeneracy is due to the fact that in this limit, the system depends on the ω_s only through the species concentrations and the energy, which in turn do not depend on each of the ω_s separately but only on a smaller number of linear combinations of them. In the present example, the H_2 and H concentrations and the energy do not depend on ω_1 and ω_2 separately, but only on their sum. The separate values of ω_1 and ω_2 are then underdetermined, but this has no physical consequences; any solution with the correct value of $\omega_1 + \omega_2$ produces the correct ρ_k and ρe. In such situations, it is therefore merely necessary to determine any one of the infinite number of solutions for the ω_s. This may readily be accomplished by switching to a suitable method for solving an underdetermined system whenever the Jacobian matrix becomes nearly singular. In our implementation, whenever DGESVX finds that the reciprocal condition number of $\mathbf{J}$ is less than 100 times the machine precision, we simply switch to the LAPACK [9] routine DGELSS, which uses singular value decomposition to compute the minimal-norm solution to the nearly singular system.

IV. EXAMPLE CALCULATION

The method described above was tested on the following simplified set of hydrogen–oxygen reactions [10]:

$$H + O_2 \rightleftharpoons OH + O$$
$$H_2 + O \rightleftharpoons OH + H$$
$$H_2O + O \rightleftharpoons 2OH$$
$$H_2 + OH \rightleftharpoons H_2O + H$$
$$H + H + H_2O \rightleftharpoons H_2 + H_2O$$
$$H + OH + H_2O \rightleftharpoons H_2O + H_2O$$
$$H + O + H_2O \rightleftharpoons OH + H_2O$$
$$O + O + H_2O \rightleftharpoons O_2 + H_2O.$$

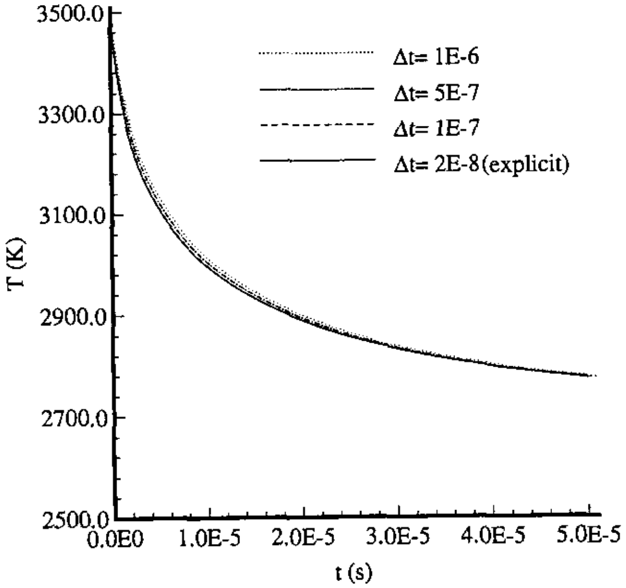

FIG. 1. *Temperature histories for different values of* Δt.

The first four reactions are relatively fast two-body exchange reactions, while the next four are relatively slow three-body dissociation/recombination reactions. Reactions involving third bodies other than H_2O are neglected for simplicity, since H_2O has the highest third-body efficiency and is present in the largest concentrations.

These reactions were allowed to proceed in a closed volume initially filled with pure H_2O at $T = 3500$ K and atmospheric pressure. This problem contains no fluid dynamics, so $[\partial\rho_k/\partial t]_0 = [\partial(\rho e)/\partial t]_0 = 0$. Only four of these reactions are linearly independent in the equilibrium limit, so the calculation was first performed in this limit (by setting the k_{fs} to very large values) in order to test the logic for dealing with an underdetermined system. The correct equilibrium solution was indeed obtained without any numerical difficulties.

The true kinetic problem was then solved, using the correct values of the k_{fs} [10], for $\Delta t = 10^{-7}$, 5×10^{-7}, and 10^{-6} s. For comparison purposes, the problem was also solved using a simple explicit scheme with a very small time step of $\Delta t = 2 \times 10^{-8}$ s, which was empirically found to be about 80% of the explicit stability limit. The calculations were run out to a final time of $t = 5.0 \times 10^{-5}$ s, which is perhaps 25% of the way to steady state. The resulting temperature and OH molar concentration histories are shown in Figs. 1 and 2, respectively. The results for $\Delta t = 10^{-7}$ s are visually indistinguishable from those of the explicit calculation with $\Delta t = 2 \times 10^{-8}$ s, while those for $\Delta t = 5 \times 10^{-7}$ and 10^{-6} s show small errors due to the larger values of Δt. In this problem, therefore, the present

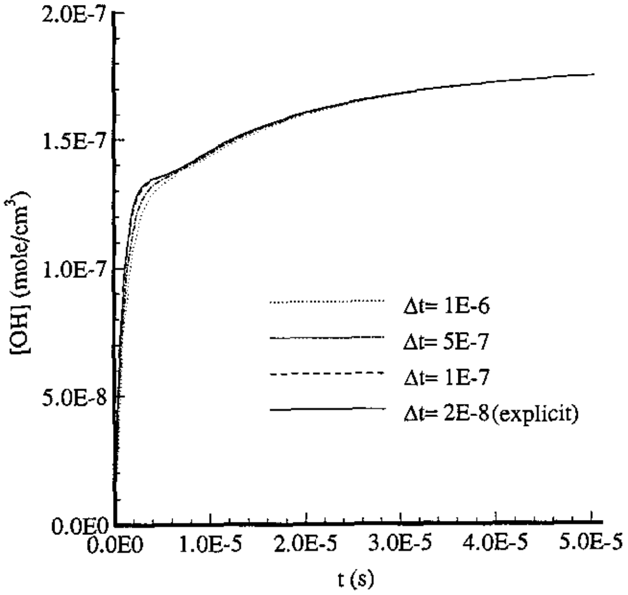

FIG. 2. OH molar concentration histories for different values of Δt.

implicit method produces reasonably time-accurate solutions with time steps some 50 times larger than typical explicit time steps. This factor is of course problem-dependent, as it is determined by the separation between the slow and fast chemical time scales in the problem. Iteration counts per time step in these calculations ranged between three and 12, and showed the expected tendency to be highest for large Δt and early in the transient.

This same problem was also solved with $\Delta t = 10^{-6}$ s using a noniterative linearly implicit scheme often used for kinetic reactions in combustion calculations [5, 6]. The calculation was stable but the resulting solution was highly inaccurate. This illustrates the important point that simple partially implicit schemes may be stable for large Δt, yet still have accuracy restrictions comparable to explicit stability limits. Of course, schemes of this type are not generally intended for use with very large Δt. Fully implicit schemes are much more faithful to the physics in problems where strongly coupled effects come into balance with each other on time scales short compared to those of interest in the calculation.

In the preceding test problem, the benefits of the nonlinear preconditioning are minimal because the reactions are usually first order in the reference species. To obtain a better indication of the benefits of preconditioning, the method was also applied to the following set of equilibrium reactions frequently used in combustion simulations:

$$\begin{gathered} H_2 \rightleftharpoons 2H \\ O_2 \rightleftharpoons 2O \\ N_2 \rightleftharpoons 2N \\ O_2 + H_2 \rightleftharpoons 2OH \\ O_2 + 2H_2O \rightleftharpoons 4OH \\ O_2 + 2CO \rightleftharpoons 2CO_2 \end{gathered}$$

which involve concentrations raised to powers as high as four. The k_{fs} were all set to very large values, and the reactions were allowed to occur in a closed volume initially at atmospheric pressure with molar concentration ratios of

$$\begin{aligned} &[H]:[H_2]:[O]:[O_2]:[N]:[N_2]:[OH]:[H_2O]:[CO]:[CO_2] \\ &\quad = 0.01:0.01:0.01:0.16:0.01:0.58:0.01:0.1:0.01:0.1 \end{aligned}$$

with initial temperatures ranging from 1300 K to 4900 K in 100 K increments. The calculations were performed both with and without preconditioning. The average iteration count was 7.9 with preconditioning, and 15.1 without.

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