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Note

Inclusion of Temperature Variations in a Numerical Scheme for Partial Equilibrium Flow*

An improved iteration scheme for partial equilibrium flow [1] was recently described [2]. Its function is to enforce, on each time step of a transient calculation, an appropriate temporal difference approximation to the equilibrium constraints on the species concentrations. The simplest such approximation was adopted, in which the equilibrium constants are evaluated at a fixed value of the temperature (e.g., the temperature on the previous time level). This value changes from one time step to the next, but it does not vary within the iteration on a given time step. This approximation is appropriate when the temperature changes resulting from the equilibration are small, which in turn requires that for every equilibrium reaction either the progress increment is small, the heat of reaction is small, or the concentrations of the participating species are small. When none of these conditions is satisfied, however, the approximation in question suffers from a lack of self-consistency between the final converged values of the temperature T and the species concentrations ρ_k/M_k. In extreme cases this has been observed to cause spurious oscillations in T and the ρ_k from one time step to the next, even though the iteration scheme itself continues to behave well and converge normally. This difficulty can be eliminated by adopting a more accurate approximation to the equilibrium constraints, in which the equilibrium constants are allowed to vary in response to the temperature changes brought about by the equilibration. Our purpose here is to propose such an approximation and to describe the simple modifications to the iteration scheme that are required to implement it.

The present discussion should be regarded as a supplement to Ref. [2], which the reader is assumed to have close at hand. Quantities not defined herein will be understood to have the same meanings as in Ref. [2]. Equation (n) of Ref. [2] will be referred to as Eq. (I.n).

The equilibrium constraint conditions that we wish to satisfy are given by Eq. (I.2), in which the species densities ρ_k are related to their starting values $\tilde{\rho}_k$ by Eq. (I.3). The temperature T in Eq. (I.2) was previously held fixed, but now it is allowed to vary along with the ρ_k. The temperature variations will be obtained by linearizing the caloric equation of state about the starting conditions. Thus T is related to its starting value $\tilde{T}$ by

$$T = \tilde{T} + (\rho c_v)^{-1} \sum_s Q_s \omega_s, \tag{1}$$

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where ρ is the total density (i.e., the sum of the ρ_k, which of course is independent of the ω_s), c_v is the mixture specific heat at constant volume evaluated at the values $\tilde{\rho}_k$ and $\tilde{T}$, and Q_s is the negative heat of reaction at constant volume for equilibrium reaction s at temperature $\tilde{T}$. For simplicity, we approximate Q_s by its value at absolute zero instead of $\tilde{T}$. (This is a good approximation if Q_s is large, while if Q_s is small, the temperature variations are negligible in any case.) The approximation to T after iteration ν is

$$T^\nu = \tilde{T} + (\rho c_v)^{-1} \sum_s Q_s \omega_s^\nu. \tag{2}$$

We shall also need to refer to intermediate temperatures defined by

$$T(\nu, s) = \tilde{T} + (\rho c_v)^{-1} \sum_{z=1}^{s-1} Q_z \omega_z^\nu + (\rho c_v)^{-1} \sum_{z=s}^{N} Q_z \omega_z^{\nu-1}. \tag{3}$$

The dependence of $K_c^s(T)$ upon T will be approximated by linearizing $\ln K_c^s(T)$ about the starting temperature; i.e.,

$$\ln K_c^s(T) = \ln K_c^s(\tilde{T}) + D_s(T - \tilde{T}), \tag{4}$$

where $D_s = (\partial \ln K_c^s(T)/\partial T)_{T=\tilde{T}}$. The proposed new approximation to the equilibrium constraints of Eq. (I.2) is therefore

$$\prod_k (\rho_k/M_k)^{b_{ks} - a_{ks}} = K_c^s(\tilde{T}) \exp\{D_s(T - \tilde{T})\}, \tag{5}$$

where ρ_k and T are given in terms of the progress variables ω_s by Eqs. (I.3) and (1), respectively.

The next step is to precondition Eq. (5) by raising both sides to the power $p_s = 1/q_s$, just as in Ref. [2]. The result can again be written as $F_s = 0$ (Eq. (I.9)), but with F_s redefined as

$$F_s = G_s^{-p_s} - \exp\{p_s D_s(T - \tilde{T})\}, \tag{6}$$

where G_s is given by Eq. (I.7) but with T replaced by $\tilde{T}$ therein. The partial derivatives $\partial F_s/\partial \omega_t$ are easily evaluated from Eq. (6), with the result

$$\frac{\partial F_s}{\partial \omega_t} = p_s G_s^{-p_s} A_{st} - (p_s D_s Q_t/\rho c_v) \exp\{p_s D_s(T - \tilde{T})\}. \tag{7}$$

All that remains is to replace the previous F_s and $\partial F_s/\partial \omega_t$ by the new ones (Eqs. (6) and (7)) in the Gauss–Seidel–Newton and Newton–Raphson iteration formulae. The result for the Gauss–Seidel–Newton iteration is

$$\omega_s^{\nu+1} = \omega_s^\nu + \frac{q_s[G_s^{p_s} \exp\{p_s D_s(T - \tilde{T})\} - 1]}{A_{ss} - (D_s Q_s/\rho c_v)\, G_s^{p_s} \exp\{p_s D_s(T - \tilde{T})\}}, \tag{8}$$

where G_s and A_{ss} are evaluated at $\rho(\nu+1, s)$, and T is evaluated as $T(\nu+1, s)$. Equation (8) now replaces Eq. (I.14). Similarly, the Newton–Raphson iteration becomes

$$\sum_t [A_{st} - (D_s Q_t/\rho c_v)\, G_s^{p_s} \exp\{p_s D_s(T^\nu - \tilde{T})\}](\omega_t^{\nu+1} - \omega_t^\nu)$$
$$= q_s[G_s^{p_s} \exp\{p_s D_s(T^\nu - \tilde{T})\} - 1], \qquad (9)$$

where G_s and A_{st} are evaluated at ρ^ν. Equation (9) now replaces Eq. (I.17). Note that the matrix that must be inverted to obtain the $\omega_s^{\nu+1}$ is no longer symmetric.

The benefits of these modifications are most clearly illustrated by means of a test calculation in which a large inconsistency between the temperature and species densities is artificially introduced into the initial conditions. To this end, we consider a closed volume which initially contains a mixture of CO_2 and H_2O, and no other species. The initial temperature and species concentrations are

$$T_0 = 3000^\circ \text{ K},$$
$$[H_2O]_0 = [CO_2]_0 = 2.0 \times 10^{-5} \text{ moles/cm}^3,$$

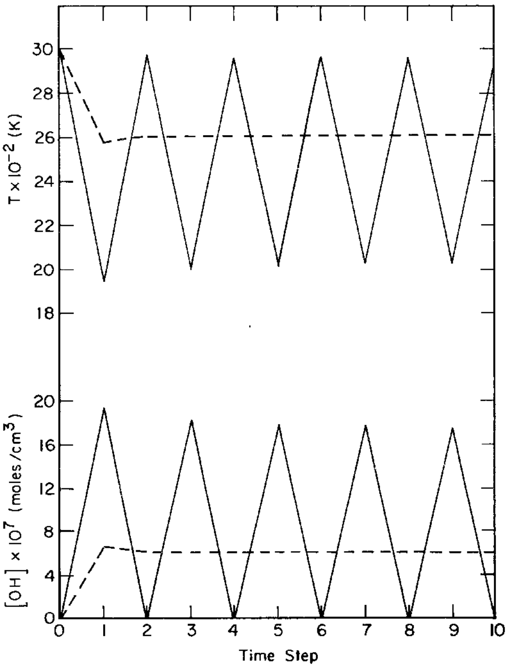

FIG. 1. Temperatures and OH concentrations for the first 10 time steps of test calculations with inconsistent initial conditions using the original scheme of Ref. [2] (solid lines) and the modified scheme described herein (dashed lines).

and the allowed equilibrium reactions are the dissociation reactions

$$2\,CO_2 \rightleftarrows 2\,CO + O_2,$$

$$2\,H_2O + O_2 \rightleftarrows 4\,OH,$$

$$2\,OH \rightleftarrows H_2 + O_2.$$

(Dissociation of H_2 and O_2 are neglected for simplicity.) Figure 1 shows the evolution of temperature and OH concentration over the first ten time steps of a transient calculation with the original scheme of Ref. [2] (solid lines) and with the modified scheme described above (dashed lines). The original scheme produces large oscillations in temperature and species concentrations, which represent periodic overshoots in the amounts of dissociation and recombination. There is too much dissociation on the first time step because the associated temperature drop is not felt until the next time step. Thus the temperature drops too much, there is too much recombination on the second time step, and so on. This vicious cycle is completely eliminated by the modified scheme, which produces self-consistent equilibrium values of temperature and species densities within two time steps. In both calculations the iteration scheme itself is well behaved and converges rapidly on each time step.

The modifications described above are easily incorporated into any computer program based on the method of Ref. [2]. These modifications have been used with good results in a numerical study of entrained flow coal gasification [3].

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