

determined without reference to the chemical kinetics. Mixing of equilibrium and nonequilibrium equations is valid if the chemical system is treated as two subsystems, one of which is assumed to be in local chemical equilibrium and the other rate-controlled. The systems are coupled through the requirements of element conservation, and the rate-controlled subsystem can be thought of as a source or sink of chemical species which forms a set of boundary conditions for the equilibrium subsystem. If the equilibrium subsystem is assumed to include species 1, . . . , M , the conditions $DG_i/Dt = 0$ yield M equations:

$$\frac{\partial G_k}{\partial \rho} \left(\rho \frac{D\rho}{Dt} \right) + \frac{\partial G_k}{\partial T} \left(\rho \frac{DT}{Dt} \right) = - \sum_{i=1}^N \left(\frac{\partial G_k}{\partial Y_i} \right) \left(\rho \frac{DY_i}{Dt} \right) \quad k = 1, \dots, M \quad (2)$$

as shown by Libby. The right-hand side of each equation will involve only $Y_k, Y_{N-L+1}, \dots, Y_N$. There will be $N-L-M$ equations of the form of Eq. (1) remaining:

$$\rho(DY_i/Dt) = w_i \quad i = M+1, \dots, N-L \quad (3)$$

Since none of the $\sigma_j, j = 1, \dots, M$ appear in these equations, the right-hand sides will be determinate. Together with the element conservation equations, these form a set of algebraic equations that may be solved for the unknown species derivatives at any point in the flow.

The reason that the mixing of equilibrium and nonequilibrium assumptions must be approached with such care is that the equilibrium limit of the nonequilibrium problem is a singularity. For true chemical equilibrium to exist, as required by the condition $G_j = 0$, there must be no net production or consumption of any chemical species. This is impossible in any system in which finite gradients are present, as in a reacting flow. In computer solutions of reacting flow problems, difficulties are encountered when the forward and reverse reaction rates both are very large and their difference is too small to compute accurately. In such cases the equilibrium assumption that both forward and reverse rates are infinitely large and equal may furnish a good approximation. However, the gradient in species concentration computed from Eq. (2) is not dependent on the known finite rates of any reactions involving species k . Rather it is the rate at which the species concentration must change in order to maintain equilibrium (zero net production) when the density and temperature are changing. Hence the analogy between equilibrium and nonequilibrium is not complete.

Author's Reply to Comment by R. E. Mates

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THE present author assumed in the note under discussion¹ that the problem was "well-posed," that is, that the equilibrium conditions corresponding to the "fast" reactions, $G_j \approx 0$, were indeed all independent; if they are not, the problem is "ill-posed" by definition. Thus the observations in the second paragraph do not appear appropriate.

In addition, the present author does not understand the first two sentences of the third paragraph of the foregoing comment. It is precisely in order "to compute contributions

to gradients in species concentrations due to individual reactions," namely, from the "fast" reactions, and because the concentration of a species "involved in local chemical equilibrium with some other species" cannot "be determined without reference to the chemical kinetics" of the "slow" reactions that there exists a problem in applying the concept of partial equilibrium in flowing systems, a problem posed and solved by one of perhaps several methods by the present author.

The system described in connection with Eq. (2) of the preceding comment appears to be highly artificial in that the M fast reactions are postulated to involve only M species; in this case, the commentor is correct that no indeterminacies arise and that no problem exists.

With respect to the final paragraph, it is understood generally by fluid mechanicians that the concept of equilibrium chemical behavior in a flowing system involves whatever "net production or consumption of any chemical species" required to maintain at each point in the flow an equilibrium state. The forward and reverse rates corresponding to a single reaction step at equilibrium are relatively large *but not equal*. The difficulties connected with obtaining equilibrium flows from computer programs applicable to finite rate chemistry are well known and, of course, are associated with the size of the reaction rates.

In view of the doubts raised by Mates¹ concerning the present author's treatment of partial equilibrium, it may be appropriate to point out that the procedure in question has been employed to study the heat release phase of the hydrogen-air reaction carried out at constant pressure;² there was no difficulty encountered in applying the treatment under discussion.

References

- 1 Mates, R. E., "Comments on 'Treatment of partial equilibrium in chemically reacting flows,'" *AIAA J.* **1**, 723-724 (1963).
- 2 Ferri, A., Libby, P. A., and Zakkay, V., "Theoretical and experimental investigation of supersonic combustion," *Polytech. Inst. of Brooklyn, Aerodynamics Lab., PIBAL Rept. 713, ARL 62-467, AD 291712* (September 1962); also *Proceedings of the Third International Council of Aeronautical Sciences Congress* (to be published).

Errata: "The Status of Unsteady Aerodynamic Influence Coefficients"

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THE derivation of aerodynamic influence coefficients (AICs) from slender-body theory given in Ref. 1, pp. 60-72, has been found to be incorrect. Since the standard NASA stability-axis system is used (with the relative wind in the *negative x* direction), the substantial derivative operator in Eq. (179) et seq. should read $-V(\partial/\partial x) + (\partial/\partial t)$, and, hence, the sign of the velocity should be reversed throughout the derivation. The net result is that the signs of the imaginary parts of all the AIC elements (i.e., the damping terms) are reversed; the signs of the real parts are not affected. The mistake was discovered while programming the equations for digital computation, and the corrected derivation as well as the FORTRAN computer program are reported in Ref. 2.

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