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Letter to the Editor

On the Solution of Differential Equations Arising in Chemical Kinetics

Gelinas [1] has recently published some observations on the numerical integration of systems of stiff differential equations encountered in problems in chemical kinetics. Gear's method of integration which he used has been in use at Bell Laboratories for some time for the solution of this type of problem [2, 4] and we are in agreement with his observations regarding the superiority of this technique for the particular kind of stiff equation prevalent in chemical problems.

Considerable discussion is devoted to the use of steady state approximations, i.e., the explicit algebraic solution of the differential equation for a particular component when its derivative is close to zero. Comparison of a result of a full integration is made with calculations of Westberg and Cohen [5] who solved a photochemical smog model with the a priori assumption that several components satisfied the criteria for use of a steady state approximation during the entire problem history. Gelinas concluded that these results were suspect because this assumption was not justified; indeed there were particularly flagrant violations of these conditions. There are, however, a number of programs [6], [7] in which steady-state assumptions are not invoked until a test shows that they are indeed valid; one of these programs [7] even goes so far as to continue to monitor the validity of the approximation and discard it when it ceases to be true at a later time in the problem. Gelinas leaves the implication that, under these circumstances, steady-state procedures might be admissible, with some possible savings of computer time. Our experience has been that even under these conditions, erroneous results can be obtained with steady-state approximations, although they may appear superficially to be a reasonable solution.

The source of these errors was pointed out some years ago [8, 9] although it apparently has not been generally recognized. Any chemical problem is subject to the constraint of the conservation of matter, and although this condition is not explicitly stated, it is implicit in the differential equations if they are properly formulated. Linear single-or-multi-step integration procedures maintain this condition because the truncation errors are consistent among the several components; our experience with Gear indicates that stoichiometry is maintained to within rounding errors even after several thousand steps. Once steady-state procedures are invoked, chemical balance restrictions are lost; there seems to be no way in which this constraint can be superimposed upon the system. Although the error in overall stoichiometry may be small, the error in a particular component may be significant and this error can propagate through the system because of the way in which the several components are coupled, as Gelinas correctly points out. While a system of chemical kinetic equations has a large amount of negative feedback, this cannot correct for these deviations once they occur. Indeed the errors have the effect of redefining the system being modeled; the calculation continues based on the new composition. For this reason, conservation of matter must be considered a necessary (but not sufficient) condition for validation of the results of a computation.

The steady-state approximation has historically played a useful role in the modeling of chemical systems, in providing analytic solutions, however limited their validity, when there was no other course. With the advent of numerical methods and high speed computers, it provided a way out of the stiffness problem. Now that methods such as Gear are available, it seems that the time has come to relegate it to honorable retirement, although it may yet find some utility as a secondary method of computation. In those cases where its validity can be established against a complete time-dependent calculation, interpolation between established checkpoints or the fast reproduction of numerical results for input to other problems could be usefully performed.

These considerations become important in the modeling of large, open, non-uniform systems, such a planetary atmospheres, where the coupling between many volume elements by transport mechanisms must be considered, and extreme demands are placed on computational resources. Where the time constants for the chemical processes are much smaller than those for transport, the two can be decoupled and a steady-state analytic function should suffice to describe the chemistry. At the other extreme, the chemical steady state is not valid, but the predominant transport effects remove the stiffness from the equations so that less demanding integration techniques can be used. It is in the intermediate range, where some of the equations are stiff, but no general steady-state approximation can be validated, that the most difficulty, and consequently the greatest opportunity for progress, exists.

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