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DISCUSSION

of the Bates-Watts paper, Multiresponse Estimation With Special Applications to First Order Kinetics.

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The authors presented an interesting approach to parameter estimation for first order kinetic systems. The method is user oriented and particularly suited for computer implementation as a "canned" program. Indeed, present chemical kinetic codes input reaction mechanism in a natural chemical language, that is, specifying reactions (usually in unformatted READ routines) as they are conventionally written on the paper. This information is automatically converted to a so-called reaction matrix and, based on it, to differential equations describing the kinetics of reaction species. The reaction matrix, which contains all the stoichiometry of the system, can conveniently provide the required input information.

Another important feature, from the user's point of view, is that the presented method is applicable to multiresponse data. It should be realized that modern problems of interest to chemical kinetics get tougher, as for example, formation of pollutants in hydrocarbon combustion. The experimental answer to the growing complexity of the systems is the employment of multiple diagnostics for simultaneous monitoring of various process variables. However, interpretation of the experimental results cannot be fully realized without reliable and convenient multiresponse methods.

The following are some of my thoughts on the needs in this area:

1) Often, kineticists exhibit a philosophical resistance to a multiparameter approach to experimation for automatic coding of the method of Bates and Watts.

[1] Michael Frenklach's contribution to the subject stems from work performed in the Department of Chemical Engineering, Louisiana State University.

mentation. A classical way is to "isolate" a given reaciton of interest; under such conditions the rate coefficient parameters can be determined by a simple well-established straight-line treatment. Determination of more than one rate coefficient in a single set of experiments is considered "not clean experimentation." In principal, however, the isolation is not possible: there are always other reactions occurring simultaneously with the one of interest. The researchers usually engage in an elaborate line of reasoning to assume, sometimes unjustifiably, single-reaction conditions. These kineticists must realize that multiparameter analysis using rigorous multiresponse techniques can provide more accurate and informative answers. Neglecting, for instance, a chemical reaction with the rate contribution of, let us say, 10%, can lead to a much larger than 10% distortion in the estimation of the main parameter. Statisticians, on the other hand, should demonstrate the techniques they develop on examples of current interest and difficulty.

2) Although first order kinetic models constitute an important class, higher order kinetics are of more general interest and there is a great need for development of statistical methods for these nonlinear systems.

3) Most estimation methods, including the one presented by Bates and Watts, concentrate on determining the solution which minimizes the objective function and only approximate confidence limits. What is of interest to many applications is the joint confidence region. It should be noted that in the problems of chemical kinetics these regions are usually not ellipsoidal, for which second order approximation methods are sufficient, but crescent shaped.

4) While estimating parameters, it is most important to check the model adequacy. This point was excellently demonstrated by Box and Draper (1965). These authors warn that "the investigator should not resort immediately to the joint analysis of responses. Rather he should... consider the consistency of the information from various responses." To my knowledge, however, a formal multivariate lack-of-fit test for a general nonlinear case has not been developed.

5) A question on the number of degrees of freedom was brought up by Bates and Watts. Using fast digital sampling electronics, the number of observations per response can be very large (in our laboratory this number was approximately 1000). Does this number determine the degrees of freedom? If so, then one can easily increase this number by orders of magnitude by using faster electronics. This point should be clarified.

Finally, I would like to point out that in an attempt to resolve some of the issues brought up above, a method for multiresponse parameter estimation applicable to a dynamic model of general order was developed in our laboratory (Miller and Frenklach, 1983; Frenklach, 1984; Frenklach and Miller, 1985). The method is based on approximating the solution of the differential equations describing the kinetics of reactive system instead of the equations themselves. The approximation is developed following the methods of empirical model building (Box et al. 1978) and the concept of computer experiment of Box and Coutie (1956). Once the approximations to all responses are obtained, the parameter estimation, determination of joint confidence region, and lack-of-fit test are easily performed following the approach of Box and Draper (1965).

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