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Computer Simulation in Chemical Kinetics

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Summary. Numerical methods for modeling complex chemical reactions are being used to gain insight into the mechanisms of these systems as well as to provide a capability for predicting their behavior from a knowledge of elementary physical and chemical processes. The state of the art is reviewed, and some projections about likely future developments are made.

Chemical reactions not only are responsible for life on our planet, but have been harnessed to the point where they are indispensable to our present highly developed civilization. Many centuries of experimentation and more recent theoretical study have enabled us to make practical use of these processes as well as to accumulate a wealth of knowledge about them. It may therefore appear incongruous that we still understand some of these complex systems only in gross terms. The reason is not hard to find: the immense number of simultaneously occurring chemical and physical processes in phenomena such as combustion, atmospherics, life cycles, and even chemical manufacturing operations defy a quantitative description of the whole, even though we may know in great detail the behavior of the individual components.

Mathematics is the language in which any quantitative description must be written; yet the capacity of analytic methods to solve such complex problems has been far outstripped. Resort can be made to a numerical treatment instead. As computers have become larger and faster, the feasibility of their use to solve these problems has grown, and computer simulation has invaded many fields in the physical, biological, and social sciences, engineering, and the world of commerce. The terms modeling and simulation have come to encompass a broad spectrum of meanings, ranging from the simple fitting of measurements to a mathematical function (however arbitrary) to a causality-based description combining the underlying fundamentals of the many components of a highly complex system. The latter interpretation will be used in this article. Simulation techniques in chemical kinetics have matured over the past decade. Their scope of application as a correlative and predictive tool has widened, and the realization of their capacity for providing insight into the mechanism of reaction continues to grow. In this article I will broadly summarize the present state of the art and will venture a few predictions about the directions in which future progress is likely to occur.

Mass Action Kinetics; Homogeneous Systems

The formal mathematical theory of chemical kinetics was developed during the 19th century and culminated with the exposition of the law of mass action. Simply stated, this gives the rate (number of occurrences per unit time) of the elementary reaction

$$n_{\mathrm{A}}\mathrm{A} + n_{\mathrm{B}}\mathrm{B} + \cdots \rightarrow n_{\mathrm{X}}\mathrm{X} + n_{\mathrm{Y}}\mathrm{Y} + \cdots \tag{1}$$

as the product

$$\frac{-1}{r}\frac{d[\mathrm{A}]}{dt} = \frac{-1}{n_{\mathrm{B}}}\frac{d[\mathrm{B}]}{dt} = \frac{1}{n_{\mathrm{X}}}\frac{d[\mathrm{X}]}{dt} = \frac{1}{n_{\mathrm{Y}}}\frac{d[\mathrm{Y}]}{dt} = \cdots = k[\mathrm{A}]^{n_{\mathrm{A}}}[\mathrm{B}]^{n_{\mathrm{B}}} \cdots \tag{2}$$

where n_{A} is the number of molecules of species A, square brackets denote concentration, and the rate constant k is considered a fundamental property of the reaction. The time evolution of the reacting system is given by solutions of ordinary differential equations (ODE's) of this type. These successfully explained much of the data on rates of reaction, at the same time spurring an expansion of experimentation in a broad range of chemical systems. Inevitably, cases were found that did not fit these simple rate laws; these situations were gradually clarified as the concept of chemical mechanism emerged, with many reactions occurring concurrently or consecutively. Each component of such a mechanism was considered to follow its own rate law, given by Eq. 2, the behavior of the complex system being a result of the simultaneous operation of all processes. The set of simultaneous differential equations given by the application of the mass action principle could be solved analytically only for a few relatively simple cases. Methods for treating more complicated cases grew up from layer upon layer of reduction, simplification, and approximation. As a consequence, a substantial literature on chemical mechanism developed which appears to be superficially reasonable, but in detail is often more a function of the choice of solvable mathematics than of the true chemistry.

The availability of high-speed computers after World War II led a number of workers to investigate the possibility of their use for the solution of mass action

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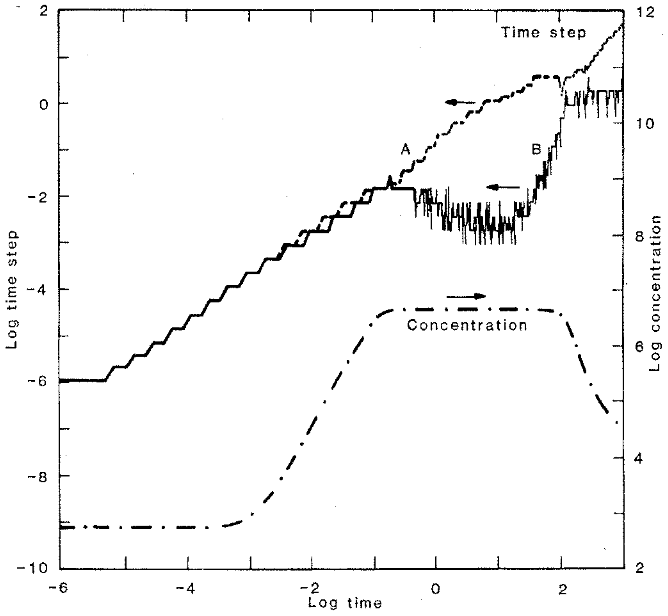


Fig. 1. Comparison of the performance of a stiff (A) and nonstiff (B) ODE solver for a problem exhibiting steady-state behavior (broken line). The time step of the nonstiff program is severely constrained during the steady-state period. The nonstiff program had about 75 times as many steps and took about 50 times as long to solve the problem.

differential equations that could not be achieved by analytic means. These efforts met with varying degrees of success, for although the numerical solution of ODE's was fairly well developed by that time, chemical rate equations presented difficulties which appeared to contradict the experience gained with other problems. Automatic ODE solvers (*1*) advance the problem stepwise in time, adjusting this increment as the rate of change and curvature of the solution varies, to maintain a prescribed accuracy. The expected behavior of the computation for a chemical reaction system was that a relatively short time step would be used at the outset, when concentrations are rapidly changing, and this would gradually increase as the reaction slows down and approaches equilibrium. Experience proved to be just the opposite; the time step became incredibly small at steady-state conditions, when concentration changes are minimal (Fig. 1).

The cause of this seemingly anomalous behavior was first explained by Curtiss and Hirschfelder (*2*) as due to the large negative feedback inherent in a chemical system in a steady state resulting from the balance of opposing reactions. Any slight displacment from this condition will be followed by a rapid return to the steady state. The time step in a numerical integration of the corresponding equations must be constrained to values commensurate with this fast restoring force in order to maintain the solution stable, that is, to prevent the error from propagating and growing from step to step. Differential equation systems exhibiting this propety were termed "stiff" in analogy with the similar behavior of mechanical servomechanisms.

The enormous amount of time required for the solution of kinetic problems exhibiting the stiffness characteristic rendered their treatment on the relatively slow machines of the 1950's and 1960's impractical, and the field languished. There were occasional applications, particularly in chemical engineering, where this difficulty was circumvented by the expedient of a steady-state formulation of those differential equations in the set which were responsible. In many of these it did not matter if the answers obtained were not correct solutions to the original problem, since the objective for engineering purposes was usually to find a way to simulate process data in order to interpolate and extrapolate from experimental measurements. As long as the computational procedure for arriving at the model parameters was the same as that used in the subsequent simulations, it did not matter much that the mathematical solutions were incorrect, nor for that matter was it even important that the model itself be exact. However, when this same approach was tried for fundamental kinetic studies, inconsistencies in rate constant assignments began to develop; unfortunately, many of these were not recognized as being the result of these errors until better numerical solutions were available, sometimes years later (*3*).

Mathematical interest in these stiff differential equations was reinforced during this time as needs grew for the simulation of large atmospheric systems for environmental and other purposes. Largely through the work of Dahlquist (*4*), the stability characteristics of the methods of solution became understood, and it was shown that an implicit method, involving the solution of a set of simultaneous algebraic equations in the partial derivatives (Jacobian matrix) at each time step, was required. Gear (*5*) investigated the trade-offs between accuracy and stability, and published a practical code for performing this calculation in an economical way (Fig. 1). Refinements have since been made in this technique, and other methods have been devised. The field has been reviewed by Warner (*6*), and Byrne (*7*) recently surveyed some of the available codes.

An alternative method of modeling kinetic chemical processes considers the probability of discrete reaction events occurring in each time interval. This "stochastic" approach (*8, 9*) has been shown to be essentially equivalent to the "deterministic" technique of solving the differential equations for a continuous system. The numerical Monte Carlo computations required, although much simpler to implement than the ODE solutions, converge slowly and become expensive for large systems. For this reason, they have been little used in reaction simulation.

One of the earliest applications of simulation to research in chemical kinetics was made by Allara and Edelson (*10*), who introduced a new philosophy in the study of complex mechanisms. The process they studied was the constant-volume, constant-temperature pyrolysis of the lower alkanes. These systems had been studied experimentally for many years and a considerable body of information on reaction rates and product distributions had developed. A typical example of the observed behavior is given in Fig. 2, where the rate of decomposition of propane, as monitored by the appearance of one of the products, methane, is shown as a function of time. A common feature with most of the alkanes is the onset, early in the reaction, of a decrease in the rate of pyrolysis. Many explanations for this self-inhibition effect had been proposed. Although some of these involved mechanisms with as many as 15 or 20 reactions, they had been treated only approximately, and controversy had developed over the true cause of the effect. Paradoxically, a wealth of information had also been accumulated on the rates of the elementary free-radical reactions from which the proper mechanism would have to be constructed. Allara and Edelson proposed that all this information be utilized, and that numerical methods be employed to obtain solutions to the large set of ODE's which resulted. They simulated the process with a mechanism of several hundred chemical reactions. Despite the fact that rate constants for many of these reactions were no more than crude estimates, they obtained good agreement with the experimental values; the line in Fig. 2 is the calculated result. The product distributions were also shown to be correctly modeled.

This approach to the kinetics of complex mechanisms through computer simulation was at first greeted with considerable skepticism. It was considered absurd, for example, to expect the rather simple curve of Fig. 2 to reflect the information contained in hundreds of rate constants. This misinterprets the significance of these results, since the extensive background of independent experimental evidence from which these rate constants were extracted also has to be considered. The proper conclusion is that the mechanism yielding these results is consistent with this total body of information. The authors developed a band in which the behavior of the mechanism would lie, based on error estimates of the individual reaction rates. It was not possible, however, to state that the proposed mechanism was unique. Examination of the calculated concentrations of the radical intermediates and the fluxes of the individual reactions implied that a possible cause of the self-inhibition effect was the growing importance of less reactive unsaturated radicals at late times. This conclusion, although qualitative and somewhat subjective, was one of the earliest indications of the usefulness of the modeling approach for gaining insight into the controlling paths in a complex reaction mechanism.

Despite the initial reluctance of a large segment of the chemical community to accept simulation as a valid approach to the resolution of complex mechanistic problems, the next few years saw a gradually increasing number of areas in which it contributed to the understanding of reaction systems. A symposium held in March 1977 (*11*) reviewed a broad range of these successes in fields as diverse as electrochemistry, combustion, atmospheric chemistry, and biochemistry. A particularly interesting application was to oscillating reactions, where the use of simulation in unraveling the complex Belousov-Zhabotinsky reaction (*12*) complemented the purely mathematical application of bifurcation theory to these oscillations (*13*). It showed that oscillation was possible in a purely chemical system, and furthermore that the transition to the oscillatory state was a consequence of mass action kinetics and did not require the occurrence of fluctuations in a multiple steady-state system.

Inhomogeneous Systems; Partial Differential Equations

The use of simulation as a predictive tool for large-scale systems also expanded from the early defense applications, which were concerned with nuclear weapons effects and missile reentry in the upper atmosphere. The atmospheric environment attracted much attention because of concern over possible changes in the ozone layer and the alteration of climate as the result of emissions from supersonic transports (*14*) or fluorocarbon aerosol sprays (*15*). Motor vehicle emissions and their effect on air quality through the production of nitrogen oxides, ozone, irritants, and smog were a prime target of the modelers as debate raged over suitable control strategies (*16*). Associated with this were combustion studies (*17*), since engines and furnaces are the source of the primary pollutants. A further impetus was provided by the rapidly changing economics of the fuel industry and the need to combine the most efficient energy extraction with the minimal environmental impact. In all these efforts simulation was used to merge the vast pool of fundamental information on the many chemical and physical processes making up the problem into a comprehensive description of a complex system. Their common goal was the prediction of system behavior in circumstances where direct experimentation would have been outrageously expensive, ridiculously impractical, or both (or, as in the case of nuclear effects, ruled out by political considerations).

It will be immediately recognized that these real systems (as opposed to the idealized constant-volume, well-mixed reactor of a laboratory experiment) are of a different order of mathematical complexity, since they involve spatial as well as temporal dependence of the concentrations of chemical species, and physical processes such as heat and mass transport must be included as well as chemical reaction. Frequently, the latter processes are so complex in themselves that the modeler is content to solve them alone with no chemistry at all. Sometimes the chemistry can be decoupled from the system and solved separately, as in atmospheric problems where the transport is driven by external energy inputs such as sunlight and the chemistry is often but a minor perturbation. Perhaps the most complex system is that of combustion, where the chemistry provides the energy that drives the transport, which in turn affects the rate of chemical reaction. To render these problems tractable, the details of the chemistry are often condensed into a minimal set of reactions by "lumping"—that is, by combining reactions of the same type into one—and assigning an average or "global" rate constant to the aggregate species concentrations. In the extreme, all the chemistry can be expressed in one equation:

$$\text{Fuel} + \text{oxidizer} \rightarrow \text{products} + \text{heat} \qquad (3)$$

Obviously, the details of the chemistry are lost. For many problems in combustion, such as the modeling of a steady flame, this approach may be sufficient to describe the temperature and flow characteristics of the system. Other problems in which the desired description involves chemical details, such as ignition or pollution, cannot be handled in this fashion.

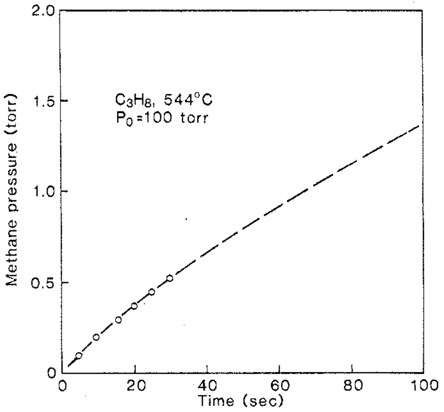


Fig. 2. Time-dependence of the formation of methane during the pyrolysis of propane. Simulation results based on a mechanism of 293 reactions are compared with experimental data (circles). [Reprinted from (*10*) with permission]

Mathematically, these problems comprise a class of partial differential equations (PDE's) in space and time, in contrast to the well-stirred reactor, which is an ordinary differential equation in time only. Computational techniques for solution of these problems are not nearly as far advanced as those for ODE's (*18*). One broad class of methods that is widely applied is known as the method of lines, further subdivided into finite-difference and finite-element techniques. The spatial domain is divided into a grid or "mesh" of smaller regions. In the finite-difference procedure, the spatial dependence is approximated by a constant value in each subinterval, replacing the continuous function by a stepwise representation. A sufficiently fine division of the spatial region is required so that the stepwise representation approximates the solution to the desired accuracy. A set of kinetic differential equations

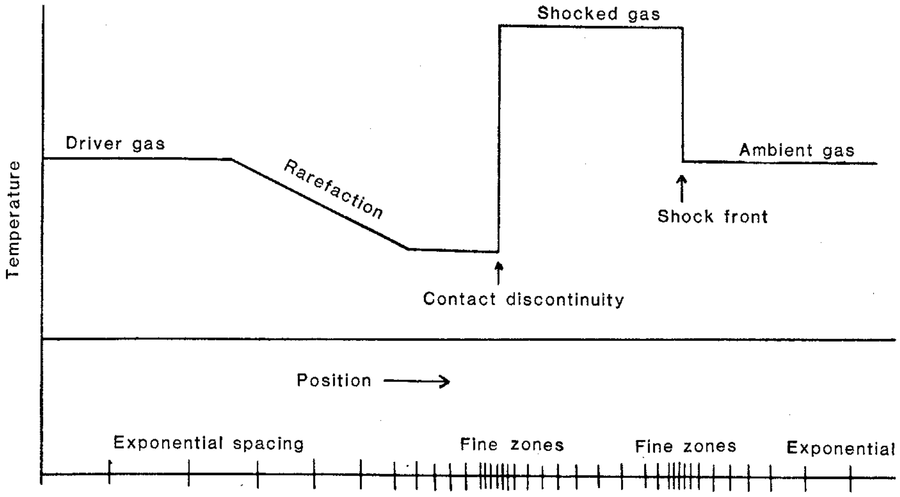
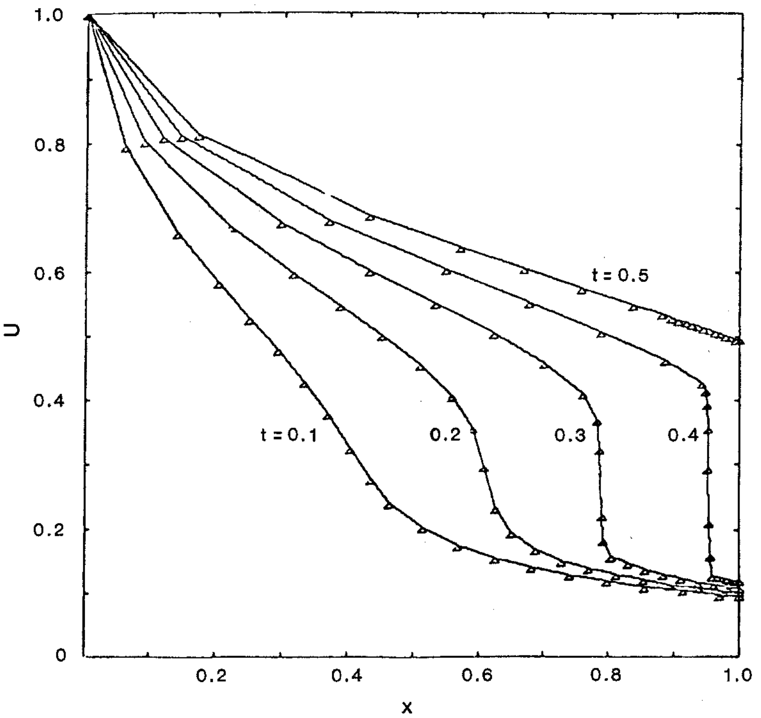


Fig. 3. A variable mesh scheme for a finite-difference method-of-lines PDE solver applied to a traveling shock wave. [Courtesy of E. S. Oran]

is written for each interval, to which are added terms representing the flow of mass (and energy) between neighboring elements. The simulation has thus been converted from a partial differential equation problem to one in ordinary differential equations with a multiplicity of dependent variables equal to the number of mesh elements (*19*). The stiff-ODE technique previously referred to may be used to solve this problem. However, since the computer core storage required goes roughly as the square of the number of variables, and the arithmetic increases between the square and the cube, the expense of performing these computations grows very rapidly.

An alternative procedure, the finite-element technique, represents the solution in each mesh element in terms of a set of basis functions, generally polynomial splines, which are constrained to join continuously through the mesh boundaries. Application of the Rayleigh-Ritz-Galerkin minimization technique for finding the best fit converts the problem into a set of ODE's in the polynomial coefficients (*20*). Fewer mesh elements are required than for the equivalent finite-difference method, but there are more coefficients per variable; the computation expense, for a well-behaved problem with gentle spatial dependence, has been shown to be about the same for both methods (*21*).

As these spatially dependent problems become larger and larger, the problem of maintaining the most economic usage of computer resources becomes more severe. This is especially true for certain classes of problems, such as flames and shocks, in which most of the chemistry takes place in a very narrow region, and as a consequence the simulation exhibits steep gradients in concentration. It is therefore necessary to use a fine mesh for an adequately accurate representation of the solution, but for reasons of economy it is not desirable to continue this fine subdivision outside the region of steep gradient (Fig. 3). If the steep gradient is in motion, one may elect to solve the problem either on a fixed grid in a moving frame of reference, or with a moving grid in a fixed coordinate system (or some combination of the two) (*22*). Finite-element techniques are especially well suited for use with automatically adaptive variable mesh schemes. One method recently developed attempts to minimize the error in the polynomial representation of the solution by adjusting the location of the mesh boundaries



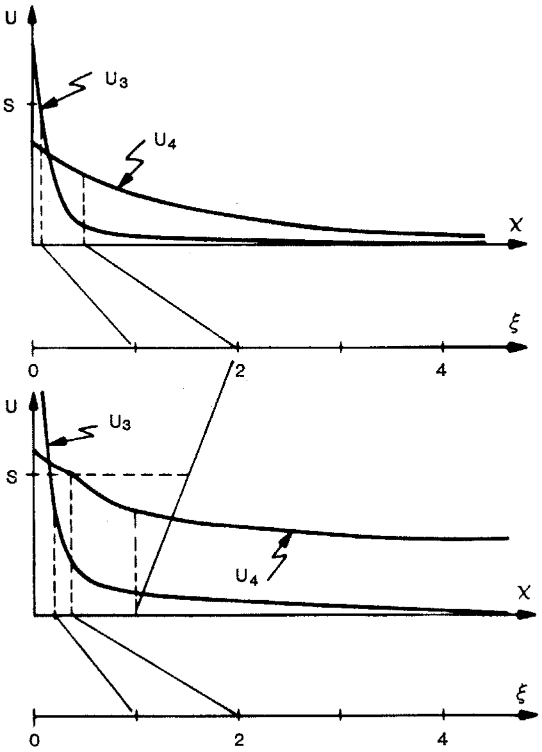


Fig. 4 (left). Solution of a moving gradient problem with a moving-finite-element PDE solver. The points show the location of the mesh nodes as a function of time. [Reprinted from (*23*) with permission]

Fig. 5 (right). Adaptive finite-element PDE solution of a reaction-diffusion problem with a moving phase boundary. The moving mesh boundaries of variables U_3 and U_4 are continuously mapped from the real coordinate x to the coordinate system ξ in which the problem is solved on a constant uniform mesh. When the discontinuity in U_4 develops (lower diagram) a new mapping to coordinate ξ' is automatically created and the solution proceeds without interruption.

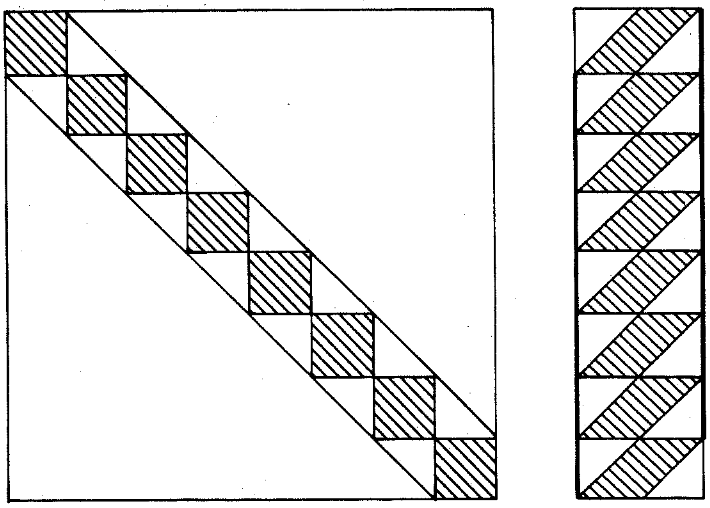


Fig. 6 (left). Left: block-tridiagonal structure of the Jacobian matrix for a one-dimensional finite-difference PDE scheme. The nonzero elements are located in the shaded areas and along the heavy lines. Right: banded matrix representation of the same Jacobian, illustrating the conservation of storage space.

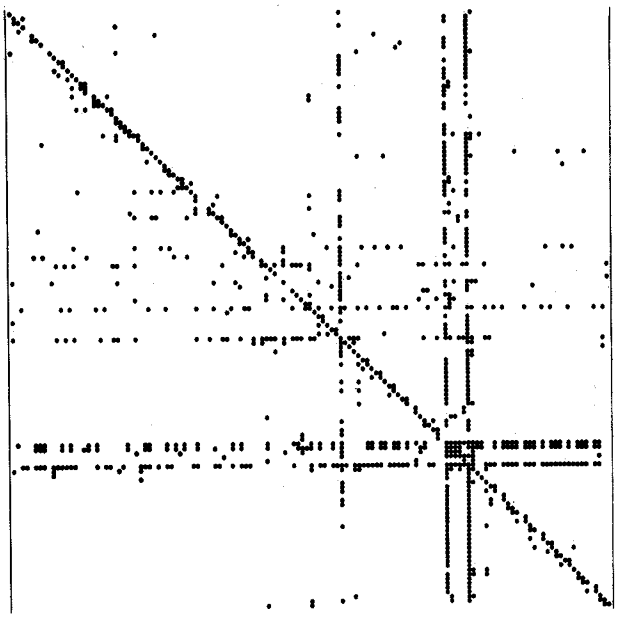


Fig. 7 (right). Location of nonzero terms of the Jacobian matrix for a large environmental chemistry reaction mechanism. The participating species have been arbitrarily ordered. Reordering to take advantage of structural features may be possible, leading to substantial savings in computation by the use of sparse matrix techniques.

(Fig. 4) (*23*). These mesh coordinates then become variables in an auxiliary set of differential equations, which is solved simultaneously with the main problem. Another approach maps a variable mesh of the real problem into a fixed mesh in which the problem is solved, with the transformation constrained to follow expected features of the solution (Fig. 5) (*24*). The latter technique is especially well suited to systems having moving discontinuities, such as phase boundaries, whose locations must be accurately followed and located on a mesh boundary. Active development of other strategies is taking place because of the importance of several problems of this class.

Most of the computer time in simulating these large problems is spent in solving the linear algebraic system required by the implicit differential equation solution technique. The matrices encountered in these systems are often sparse—that is, they have few nonzero terms—and may have certain structure as well. For example, the finite-difference formulation of the one-dimensional flow and chemistry problem has a Jacobian matrix which is block-tridiagonal (Fig. 6). Special procedures are available for handling this "banded" matrix that make it unnecessary to compute with or store the large numbers of zero elements, thus affording substantial savings. The matrices which represent the chemical interactions may be sparse in themselves, although of no particular structure (Fig. 7). Reordering techniques (*25*) may be applied to transform these to matrices having structure that can be used to advantage; otherwise, general sparse matrix methods may serve. Application of these is still in its infancy but can be expected to grow. Problems in two or three spatial dimensions have correspondingly larger matrices to be handled, rapidly increasing the costs of the computations. In these cases, the structures become exceedingly complex, and at the present time there are no special methods for their treatment. Advances in the state of the art of simulating these higher dimensionality problems will be closely linked with the development of efficient ways for solving the matrix equations.

Sensitivity Analysis

The use of mathematics to obtain the behavior of a physical or chemical system from causality model yields a description in which the variables are related to each other by functions that contain parameters characteristic of various components of the model. If this description can be obtained in analytic form, the dependence of the behavior on these parameters is transparent, and it is a simple matter to calculate the effect of changes in them, or to see the relative importance of parts of the model. When these solutions must be obtained by computer, however, this connection between input and output is lost, and the more complex the model becomes the more difficult it is to deduce the parts of the mechanism responsible for certain features of the simulation, or to see how changes would affect this behavior. It is, of course, possible to repeat the calculation with many variations of the parameters. For a purely chemical mechanism of n species involved in r reactions this would require the solution of a set of n ODE's for a variation of each of the rate parameters in turn, that is, $r + 1$ times. For large mechanisms, such as the pyrolysis system of Fig. 2, when n can be of the order of 50 and r may be several hundred, this "brute force" approach can become tedious and very expensive. More formal mathematical treatments of this "sensitivity analysis" problem give results which may be more intellectually satisfying, but most are no less work to obtain. One approach, however, which uses a Green's function transformation (*26*), reduces the main part of the problem to the solution of n (rather than r) sets of n ODE's. Furthermore, the solution of each set gives the sensitivity of one specie with respect to all the rate constants (instead of all species with respect to one rate constant, which is characteristic of other methods). Realizing that very few of the species in a complex mechanism are observable, it is seen that the solution of very few sets of equations will usually suffice to give all the useful sensitivity information. This has brought extensive sensitivity analysis within the range of practical computation.

A great deal more than the formal result of the effect of parameter variation can be gleaned from sensitivity analysis. This has been dramatically shown by an analysis of the extensive pyrolysis mechanism previously mentioned (*27*). A ranking of relative sensitivities of all the reactions, for a wide range of reaction conditions, serves to find the most sensitive components, as well as the rate

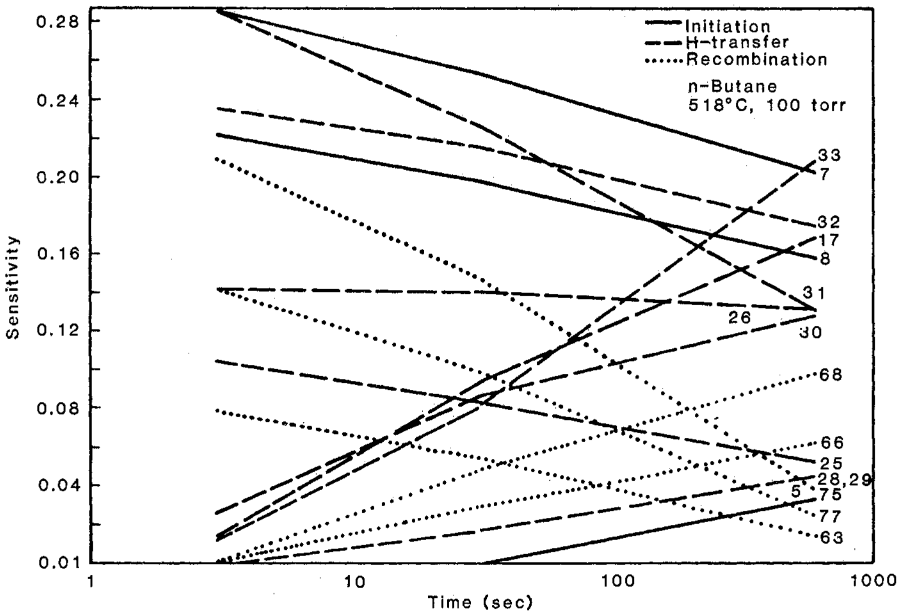


Fig. 8. Sensitivity coefficients for various reactions in the mechanism for the pyrolysis of *n* butane. The increasing and decreasing trends offer proof of the role of unsaturated radicals in the self-inhibition of the reaction system. [Reprinted from (*27*) with permission]

constants that should be subject to further scrutiny. As a corollary, the reactions that are the least important may be weeded out. In a sense, sensitivity is a measure of reaction significance, although the tendency to think of these terms as synonymous must be avoided. Nevertheless, this concept can be applied in cases, such as the pyrolysis study, where many more reactions were included than necessary in order to reduce the possibility of something important being left out. Sensitivity information then offers an objective criterion for selecting a minimal reaction set, which becomes crucial when coupling the chemistry with a transport problem when computer resources are at a premium.

The most important product of sensitivity analysis can be added insight into the workings of the mechanism itself. Figure 8 shows the time dependence of the sensitivities of the most important reactions in the pyrolysis mechanism. Some reaction sensitivities increase in time while others decrease, yet there is no correlation of this behavior with reaction type. A deeper probing, however, showed that those that increase in time all involve unsaturated radicals, and those that decrease do not. This offers an objective proof of the role of unsaturated radicals in the self-inhibition of the pyrolysis process, which had been postulated but could not be quantitatively supported.

Other important conclusions regarding mechanism can be reached. The mechanistic components responsible for features of the system which are complicated functions of the directly simulated species concentrations may be identifiable. For example, the reactions controlling the period of oscillating chemical systems (*28, 29*) have been found by analyzing the repetition of the concentration-time dependence. Parameter-parameter interactions can be assessed which provide answers to the question of how errors in known parameters affect the ability to use the mechanism to determine unknown parameters. Similarly, the effects of errors in concentration measurement on these determinations can be evaluated. The most probing question, that of whether anything important has been left out, can be approached in a limited manner (*30*). The entire technique is undergoing rapid development and will undoubtedly become a most important aspect of reaction simulation.

Looking Ahead

A common factor affecting all these endeavors is computability. In the previous discussion, progress in the art of simulation was linked to the development of appropriate algorithms for solving the differential equations. This stress on software certainly has been the main driving force in these advances, but developments in hardware must not be overlooked. The past decade has seen the preferred implementation for these large compute-bound programs swing from large mainframe machines to dedicated mini- and midicomputers and recently back to large supercomputers with vector processing capability. Numerical mathematics has advanced to the point where, in principle, systems of great complexity can be satisfactorily modeled; the question that remains is how much resources and expense can be committed to a particular problem. The major part of the computational expense is for the solution of the linear equations required by the implicit integration methods. Supercomputers are designed to do this type of calculation exceedingly well, and major changes in the practicality of large calculations, such as sensitivity analysis, have already been seen (*31*). As these new computer architectures become more widespread, and maximum advantage is taken of their capabilities through special development and optimization of software, the next few years promise to see tremendous advances in the application of simulation to reaction systems.

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