MATHEMATICAL DESCRIPTION OF COMPLEX CHEMICAL KINETICS AND APPLICATION TO CFD MODELING CODES

D. A. BITTKER

National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH 44135, U.S.A.

Abstract—A major effort in combustion research at the present time is devoted to the theoretical modeling of practical combustion systems. These include turbojet and ramjet air-breathing engines as well as ground-based gas-turbine power generating systems. The ability to use computational modeling extensively in designing these products not only saves time and money, but also helps designers meet the quite rigorous environmental standards that have been imposed on all combustion devices. The goal is to combine the very complex solution of the Navier–Stokes flow equations with realistic turbulence and heat-release models into a single computer code. Such a computational fluid-dynamic (CFD) code simulates the coupling of fluid mechanics with the chemistry of combustion to describe the practical devices. This paper will focus on the task of developing a simplified chemical model which can predict realistic heat-release rates as well as species composition profiles, and is also computationally rapid. We first discuss the mathematical techniques used to describe a complex, multistep fuel oxidation chemical reaction and develop a detailed mechanism for the process. We then show how this mechanism may be reduced and simplified to give an approximate model which adequately predicts heat release rates and a limited number of species composition profiles, but is computationally much faster than the original one. Only such a model can be incorporated into a CFD code without adding significantly to long computation times. Finally, we present some of the recent advances in the development of these simplified chemical mechanisms.

INTRODUCTION

One of the significant research thrusts in the field of combustion research today is the theoretical modeling of practical combustion systems. These include turbojet and ramjet air-breathing engines as well as ground-based gas-turbine power generating systems. The ability to use computational modeling extensively in designing these devices not only saves time and money, but also helps us meet the quite rigorous environmental and safety standards which have been imposed on all combustion devices. With the development of high-speed parallel-processor computers significant advances have been made in the field of mathematical modeling of multidimensional turbulent, reactive flow processes. This modeling, of course, involves the numerical solution of the Navier–Stokes flow equations along with models for turbulence generation and heat-release in the flow.[1-4] These computational fluid-dynamic (CFD) codes generally require large amounts of computer time for a complete solution, even with today's advanced machines.

In practical combustion systems the process of heat-release is coupled with the flow phenomena, making a complicated modeling problem much more difficult. For many years combustion effects on the flow process were considered by using very simplified and unrealistic chemical reaction approximations in CFD codes. The combustion process itself is very complicated and requires a large size numerical-analysis computer code to be modeled accurately.[5,6]

Even with today's computer technology, the linking of a fluid-dynamic code with a full combustion kinetics analysis code is not feasible because of the excessively long computational times which would result. Therefore, research in recent years has been directed towards developing simplified, computationally rapid, but still realistic models for chemical reaction and heat-release.[7-9] Only this type of model can be incorporated into existing flow analysis codes without adding significantly to long computational times.

In this paper we first discuss the equations which describe a complex, multireaction fuel oxidation process and the mathematical techniques used to solve them. We then describe a computer code, LSENS, which implements the most efficient solution method, and show its use in developing a detailed molecular reaction mechanism for the oxidation of a particular hydrocarbon fuel.

The remainder of this paper focuses on methods of transforming a detailed mechanism into a form which adequately describes heat-release rates and a limited number of composition profiles, but is computationally faster than the original mechanism. There are several approaches to this simplification task. Among them are (1) use of pseudo steady-state approximations, (2) use of partial equilibrium and rate-controlled constrained equilibrium techniques, and (3) development of a quasi-global chemical mechanism in which most or all of the molecular reactions are replaced by a smaller number of overall or global steps, whose rates are determined empirically by

fitting computed results to a fairly limited range of experimental laboratory measurements. A relatively new approach to simplifying chemical kinetic computations is "solution mapping", which attempts to replace the numerical solution of a set of differential equations by a group of algebraic equations. We will discuss these various approaches to the problem of computational simplification and present the current status of recent work in this field.

The present paper is not meant to be a comprehensive discussion of all chemical mechanism reduction techniques, but only those which are applicable to the objective of predicting system responses in practical problems such as CFD modeling. We do not, therefore, consider the matter of simplification by mathematical or chemical "lumping" of reactions. These methods are described by Frenklach[8] and are applicable to exploratory problems such as determining the mechanism of soot formation in combustion systems.

EQUATIONS FOR CHEMICAL REACTION OF A HOMOGENEOUS GAS MIXTURE

Chemical reactions and rate equations

We consider the reaction of a homogeneous gas mixture of NS species which participate in NR simultaneous molecular reactions which can be written symbolically in the general form[10]

$$\sum_{i=1}^{NS} v'_{ij} S_i \underset{k_{-j}}{\overset{k_j}{\rightleftharpoons}} \sum_{i=1}^{NS} v''_{ij} S_i, \quad j = 1, 2, \ldots, NR. \quad (1)$$
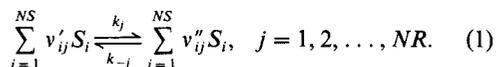
Here v'_{ij} is the number of moles (i.e. stoichiometric coefficient) of reactant species i in the jth reaction, v''_{ij} is the number of moles of product species i in the jth reaction and S_i represents the chemical formula of species i. If a species does not participate in a reaction, both v'_{ij} and v''_{ij} are equal to zero. The arrows indicate that the reaction may be reversible and k_j and k_{-j} are the corresponding forward and reverse direction rate coefficients for the reaction. Each k_j is a function of temperature only and is usually given by the so-called modified Arrhenius expression[11]

$$k_j = A_j T^{n_j} \exp\left(-\frac{E_j}{RT}\right). \quad (2)$$

Here A_j, n_j and E_j are constants, T is the Kelvin temperature and R is the universal gas constant. Each reaction may be either irreversible (i.e. proceed in the forward direction only) or reversible. In the latter case, the reverse rate coefficient, k_{-j}, is related to k_j by the principle of microscopic reversibility[12]

$$k_{-j} = \frac{k_j}{K_{cj}}, \quad (3)$$

where K_{cj} is the concentration equilibrium constant for the jth reaction. For ideal gases this latter quantity is a function of temperature only and is computed from fundamental thermodynamic relationships.

Reaction rates and species formation rates

For our constant volume closed (fixed mass) reacting system the mole number of mole per unit mass of species i present will be called σ_i. The molar rate of change of species i per unit mass is written as by Bittker[6]

$$\frac{d\sigma_i}{dt} = \frac{W_i}{\rho} \quad i = 1, 2, 3, \ldots, NRS,$$

$$\sigma_i(t = t_0) = \sigma_{i0} \quad (4)$$

where NRS is the number of reacting species (which may be less than NS if some species are inert), ρ is the gas mixture density and W_i is the molar formation rate of species i per unit volume given by

$$W_i = \sum_{j=1}^{NR} \omega_{ij}. \quad (5)$$

Here, ω_{ij} is the net rate of formation of species i per unit volume due to reaction j, and is computed from the forward and reverse rates and stoichiometry of the reaction. For molecular reactions these rates obey the law of mass action.[12] This law says that a reaction rate is proportional to the product of the concentrations of all reactants, each raised to a power equal to its stoichiometric coefficient in the reaction.

For constant-density and either constant or assigned temperature problems this set of ODEs completely specifies the time evolution of the chemical system. The pressure, p, is computed from the ideal gas law[6]

$$p = \frac{\rho RT}{M_w}. \quad (6)$$

Here, M_w is the mean molecular weight of the mixture which is related to the $\{\sigma_i\}$ by

$$M_w = \frac{1}{\sum_{i=1}^{NS} \sigma_i}. \quad (7)$$

If temperature is not assigned or density changes in a chemical reaction, differential equations are needed for these variables. Also, if reaction is in a flowing system, a differential equation for the rate of change of velocity would have to be obtained from the momentum conservation law. In this discussion we considered only a constant-volume static reaction in order to simplify the presentation of the theory. Therefore, only an additional temperature equation may be needed.

Temperature differential equation

The variation of temperature, if it is not assigned, is obtained from the energy conservation law for a closed system[6]

$$\mathrm{d}u + p\,\mathrm{d}v = -\mathrm{d}Q, \qquad (8)$$

where u is the mixture internal energy per unit mass, Q is the heat-transfer rate per unit mass of mixture from the reacting gas, and v is the specific volume of the gas. We use the relation[6]

$$h = u + pv \qquad (9)$$

and replace v by the reciprocal of density. Then, differentiation with respect to time gives[6]

$$\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{1}{\rho}\frac{\mathrm{d}p}{\mathrm{d}t} - \frac{\mathrm{d}Q}{\mathrm{d}t}. \qquad (10)$$

In these equations h is the enthalpy per unit mass of mixture. For an ideal gas h is given by

$$h = \sum_{i=1}^{NS} \sigma_i H_i, \qquad (11)$$

where H_i is the molar enthalpy of species i and is a function of temperature only. Differentiation of Eq. (11) gives

$$\frac{\mathrm{d}h}{\mathrm{d}t} = c_p\frac{\mathrm{d}T}{\mathrm{d}t} + \sum_{i=1}^{NRS} H_i\frac{\mathrm{d}\sigma_i}{\mathrm{d}t}, \qquad (12)$$

where

$$c_p = \sum_{i=1}^{NS} \sigma_i (C_p)_i \qquad (13)$$

is the specific heat of the mixture and $(C_p)_i = \mathrm{d}H_i/\mathrm{d}t$ is the molar heat capacity of species i, also a function of temperature only. Equation (12) can now be used, along with the perfect gas law, Eq. (6), to eliminate $\mathrm{d}h/\mathrm{d}t$ from Eq. (10). The result of these substitutions, after simplification and rearrangement, is the following ODE for temperature[10]

$$\frac{\mathrm{d}T}{\mathrm{d}t} = T\left\{\frac{\displaystyle\sum_{i=1}^{NRS}\frac{\mathrm{d}\sigma_i}{\mathrm{d}t} - \sum_{i=1}^{NRS}\frac{H_i}{RT}\frac{\mathrm{d}\sigma_i}{\mathrm{d}t} - \frac{1}{RT}\frac{\mathrm{d}Q}{\mathrm{d}t}}{\dfrac{c_p}{R} - \dfrac{1}{M_w}}\right\}$$

$$T(t = t_0) = T_0. \qquad (14)$$

This equation is solved with the NRS equations of Eq. (4) for the $NRS + 1$ unknowns $\sigma_1, \sigma_2, \ldots, \sigma_{NRS}$, and T. In order to evaluate the $\mathrm{d}\sigma_i/\mathrm{d}t$ terms a chemical reaction mechanism must be formulated and expressions for the forward rate coefficients [Eq. (2)] must be known. Equally as important as the rate coefficient values is a data base of thermodynamic data which are used to compute the reverse rate coefficients [Eq. (3)].

Differential equations for sensitivity analysis

When performing chemical kinetic computations an important question which must be answered is how changing the input parameters affects the computed results. This is especially true for the rate coefficients because their values are often not precisely known. Research in the field of sensitivity analysis has developed methods of answering this question.[13 19] These methods are of two types: (1) local methods and (2) global methods. Local sensitivity analysis methods give the effect of relatively small changes of a parameter above and below its original value. We discuss in this paper only these methods, which have been highly developed. Global methods provide information about the effect of large-magnitude changes in any input parameter, but are more difficult to implement for practical use. We now give a brief description of the theory of local sensitivity analysis.

The purpose of sensitivity analysis is to compute coefficients which tell the percentage change in any dependent variable caused by a given per cent change in an input parameter. We limit this discussion to changes in the three constants A_j, n_j and E_j in the rate coefficient expression [Eq. (2)] for any reaction. First, the previously derived ODEs for a reacting system are rewritten in a more general form. Equations (4) and (14) can be expressed as the set

$$\frac{\mathrm{d}y_i}{\mathrm{d}t} = f_i(\{y_i\}, \{A_j\}, \{n_j\}, \{E_j\}). \qquad (15)$$

In this set of equations index i ranges from 1 to N, the number of dependent variables, and j goes from 1 to NR, the number of chemical reactions. The first order sensitivity coefficient S_{ij} is defined by[10]

$$S_{ij} = \left.\frac{\partial y_i}{\partial \eta_j}\right|_{\eta_k \, k \neq j}, \qquad (16)$$

where η_j represents any of the A_j, n_j and E_j values. This coefficient is the rate of change of any computed y_i when any rate parameter η_j is changed. Since we are considering only a small change $\Delta\eta_j$ in the parameter, the corresponding change in y_i can be approximated by multiplying the latter quantity by the sensitivity coefficient, S_{ij}.

A set of ODEs for these sensitivity coefficients can be obtained by first differentiating Eq. (15) with respect to η_j to get

$$\frac{\partial}{\partial \eta_j}\left(\frac{\mathrm{d}y_i}{\mathrm{d}t}\right) = \sum_{l=1}^{N} \frac{\partial f_i}{\partial y_l}\left.\frac{\partial y_l}{\partial \eta_j}\right|_{\eta_k \, k \neq j} + \left.\frac{\partial f_i}{\partial \eta_j}\right|_{\text{all}}. \qquad (17)$$

The order of differentiation with respect to t and η_j may be interchanged and the definition of Eq. (16) used to obtain

$$\frac{dS_{ij}}{dt} = \sum_{l=1}^{N} \frac{\partial f_i}{\partial y_l} S_{lj} + \frac{\partial f_i}{\partial \eta_j}\bigg|_{\substack{\text{all} \\ y_i}}. \qquad (18)$$

The initial conditions are $S_{ij}(t = t_0) = 0.0$, $i = 1, 2, \ldots, N$. Although the equation set [Eq. (15)] is quite nonlinear, the above equations for the $\{S_{ij}\}$ are linear ODEs. They are, therefore, easier to solve. This solution can, in fact, be accomplished at the same time that the chemical modeling equations [Eq. (15)] are solved.

Sensitivity coefficients are generally presented in normalized form so that meaningful comparisons can be made for widely different values of η_j. For any nonzero η_j this normalizing is easily done by using the relation

$$\langle s_{ij} \rangle = \frac{\eta_j}{y_i} \frac{\partial y_i}{\partial \eta_j} = \frac{\partial \ln y_i}{\partial \ln \eta_j}, \qquad (19)$$

where $\langle S_{ij} \rangle$ is the normalized sensitivity coefficient, or the per cent change in y_i caused be a 1% change in η_j only. This normalization is satisfactory for $\eta_j = A_j$, since this rate coefficient parameter is always nonzero. However, Eq. (19) cannot be used for the n_j and E_j rate parameters, because these may be zero. Other normalization procedures have been developed[10] and in all cases $\langle S_{ij} \rangle$ represents the approximate change in y_i caused by a 1% change in the actual rate coefficient k_j, which is not always a 1% change in the rate parameter of interest.

SOLUTION OF KINETICS AND SENSITIVITY ANALYSIS EQUATIONS

Numerical solution of chemical kinetics ODEs

The first attempts to solve numerically the ODEs modeling complex combustion reactions showed that classical methods such as the explicit Runge–Kutta and Adams methods were highly inefficient. The very small stepsizes these methods require are due to the well known property of "stiffness" shown by these and many other systems of nonlinear differential equations.[5,20,21] Many implicit numerical integration methods for solving such stiff equation systems have been presented over the last 40 years. The first to be applied to the solution of chemical rate equations was the backward differentiation method of Curtis and Hirschfelder.[22] Many other techniques have been described.[6,23–31] The efficiency and accuracy of several of these methods, as applied to combustion problems, have been examined by Radhakrishnan.[32–34] This work showed that the code LSODE[30,31] is the most accurate and efficient algorithm now available for solving these stiff differential equation systems. LSODE is a package of numerical solvers for stiff and nonstiff ODE systems. For stiff problems the implicit backwards differentiation formula (BDF) method is used because of its property of stability for these problems. Thus, the step size is limited only by accuracy requirements and not by stability considerations. LSODE continuously varies the order of the BDF formula (up to a maximum of five) and the step size to obtain good computational efficiency. The code also allows a choice of several corrector methods in the predictor–corrector iteration procedure.

We mention here two computer codes in common use for solving general chemical kinetics problems for any chemical system. The CHEMKIN code[35] allows the user to set up a chemical mechanism and then select from a library of subroutines which define the differential equation system to be solved. This code can be used with any numerical integrator, but LSODE is recommended and used by the authors. The NASA Lewis Research Center general kinetics code LSENS[10,36] also permits the use of any chemical system. However, it has the differential and algebraic equations for many different reaction models and the LSODE integrator built into it. The user does not select FORTRAN routines at execution time. The input data file allows many different problems and options to be selected quite simply. This code will be described in more detail in the following sections.

Numerical solution of sensitivity analysis ODEs

The most direct method of determining the effect of variations in rate coefficients on solution results is to change any rate parameter from its original value and repeat the calculation with the modeling code. This "brute force" approach is not only time consuming but also becomes very computationally expensive when the number of rate parameters is large. For this reason several methods have been developed for solving the system of equations, Eq. (18) for the $\{S_{ij}\}$ rather than computing them from the brute-force variations. The solution is obtained at the same time that the chemical kinetics equations are solved. Some of the methods that have been used are the direct method (DM),[37] the Green's function method (GFM)[38] and its modifications[39,40] and the decoupled direct method (DDM).[41,42]

The DM solves the system of 2N simultaneous differential equations given by the system of equations, Eqs (15) and (18) in one operation for all the dependent variables and their sensitivity coefficients. This technique was found to be rather inefficient and unstable and could not solve some stiff problems.[5] A variation of the direct method is the uncoupling of the model equations from the sensitivity coefficient ODEs. Equation (15) is solved first and the complete solution is stored for use in solving Eq. (18) separately. Although this technique should, in theory, be more efficient, it has shown no efficiency gains over the coupled direct method, and is also unstable for some stiff problems.[5]

The several versions of the GFM compute the Green's function for the sensitivity equations and then obtain the $\{S_{ij}\}$ by integration over the Green's

function. They also do the model solution first and then use the results to integrate the Green's function. Both the accuracy and efficiency of the GFM techniques are sensitive to the selection of error control parameters and the choice of printout stations for the answers.[41]

The DDM also solves the model equations separately from the sensitivity coefficient equations. But the two solutions are done sequentially, i.e. step by step. The results of the model solution on any step are used to solve the sensitivity equations for that same step, so there is no need to store a large amount of information about the model solution. For solving the stiff problems of combustion chemistry the DDM has been shown by Dunker[41] to be more efficient, more stable and equally as accurate as the other methods. The DDM has been combined with the LSODE integrator by Dunker[43] into a very efficient code, CHEMDDM, which solves both the chemical modeling and sensitivity-analysis ODEs for constant temperature problems only. Radharkrishnan[44] has developed a nonisothermal version of the DDM which uses sensitivity analysis subroutines adapted from CHEMDDM. These are combined with a modified version of the LSODE code in the LSENS code mentioned previously.

The LSENS code

Description of the code. The LSENS code has been designed to model a variety of chemical kinetics problems. These include (1) static reacting system, (2) steady, one-dimensional reacting flow, (3) shock initiated chemical reaction, and (4) the perfectly stirred reactor. In addition equilibrium chemical computations can be performed for four different assigned states. Any reaction problem may be adiabatic or have a prescribed heat-transfer rate profile. In addition, for static or flow reactions, a temperature profile may be assigned. In the case of static problems either density is held constant or pressure is assigned as a function of time. For a flow problem either pressure or area may be assigned as a function of time or distance. The code is efficient, accurate, and user friendly, with several convenience features.

During a static reaction sensitivity coefficients can be computed for all dependent variables and their time derivatives with respect to rate coefficient parameters as well as the initial values of the dependent variables. When sensitivity-analysis computations are asked for, the code uses the DDM to solve the kinetics ODEs, Eq. (15), and the sensitivity coefficient ODEs, Eq. (18), sequentially, as mentioned above. It should be noted that the coefficients $\partial f_i/\partial y_l$ in Eq. (18) are exactly the Jacobian elements computed for the solution of Eq. (15) by the predictor–corrector technique of LSODE. After the kinetics solution is advanced from t_{n-1} to t_n, these results are used with the current Jacobian elements to easily solve the sensitivity coefficient equations from t_{n-1} to t_n. The latter solution requires no predictor–corrector procedure.

Both the kinetics and sensitivity coefficient solutions of LSENS have been tested by reproducing published results from other available codes.[10] Sensitivity coefficients computed by LSENS were checked for several cases by also using the brute-force method to calculate the $\{S_{ij}\}$. In all comparisons the results from LSENS agreed well with the published data and with the brute-force results. The computational work for LSENS was less than or equal to that needed by the other codes for all tests against literature data.

Application to mechanism development. Research has been ongoing for many years to elucidate the oxidation mechanism of fuels like hydrogen (H_2) and simple straight-chain and cyclic hydrocarbons (C_xH_y). That this task is very difficult is evidenced by the fact that the oxidation mechanism for the simplest hydrocarbon, methane (CH_4) contains over 125 individual steps. Moreover, the rate coefficient expressions for many of the proposed reactions may not be known accurately. The approach in this work is to propose a set of reactions with either theoretically estimated or (often conflicting) literature values for the rate parameters, and then attempt to compute results obtained in a series of experiments. One needs, therefore, not only a chemical kinetics but also a sensitivity analysis computational capability to efficiently determine the effect of rate-parameter uncertainty. Although much information is now known about the oxidation of many straight-chain hydrocarbons,[45] the simple aromatic fuels benzene (C_6H_6) and toluene (C_7H_8) have not been as well studied until recently. These ring structure fuels react differently from the straight-chain compounds and now constitute a relatively high percentage of today's practical fuels. It is, therefore, important to understand the oxidation mechanism of these aromatic compounds. Recent papers by Bittker[46] and Emdee *et al.*[47] have presented detailed mechanisms for the oxidation of these fuels. We will give a brief summary of the work of Bittker on the fuel benzene. First, however, it should be pointed out that one does not use a completely new mechanism for each fuel studied. Because the larger-molecule fuels react to form smaller hydrocarbon molecules, the oxidation mechanism of the former is built up from the oxidation reactions of the smaller molecules. This is demonstrated in Fig. 1, which shows how toluene reacts to form benzene, which then forms many other smaller hydrocarbons. The oxidation of all hydrocarbons forms molecular hydrogen, so its oxidation is important in the reaction of any fuel.

The benzene mechanism of Bittker employs 29 reactions of benzene and its fragments and 91 oxidation reactions of the fuels methane, ethylene (C_2H_4), acetylene (C_2H_2) and hydrogen to compute two different types of experimental data for benzene oxidation reported in the literature. The LSENS code was used for these kinetics computations and to compute sensitivity coefficients for all dependent variables with respect to all rate coefficients. This

"optimal" mechanism was developed by using the results of the sensitivity analysis computations to find a small number of reactions whose rate coefficients not only had a significant effect on most of the experimental results, but also were not accurately known. These rate coefficients were then adjusted, using sensitivity coefficients as a guide, to give the best possible agreement. The signs and magnitudes of the sensitivity coefficients showed when further changing of these important rate coefficients would not improve the overall agreement. The variation of rate parameters stops when any change that improves agreement for one variable would degrade already good agreement for one or more other variables.

Comparisons of experimental with computed results using the optimal mechanism are shown in Figs 2–4. In Fig. 2 we present concentration versus time profiles for benzene and carbon monoxide (CO) which were measured by Lovell et al.[48] in a constant pressure, well-mixed flow reactor. Benzene was injected into a flowing dilute mixture of oxygen in nitrogen carrier gas and rapidly formed a homogeneous mixture at a temperature of about 1100 K. Velocity profile measurements were used to convert any reactor distance from injection point into a reaction time, so that the reaction could be modeled computationally as a constant-pressure static process. Results are shown for two fuel equivalence ratios (ϕ), i.e. the ratio of the the actual molar benzene–oxygen ratio to the stoichiometric value. The agreement between computation and experiment is generally good, but is better at the lean ϕ value of 0.74 [Fig. 2(a)] than the rich value of 1.36 [Fig. 2(b)]. Also the relative positions of the computed and experimen-
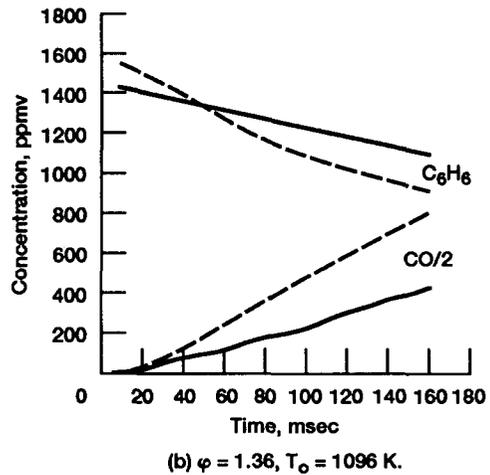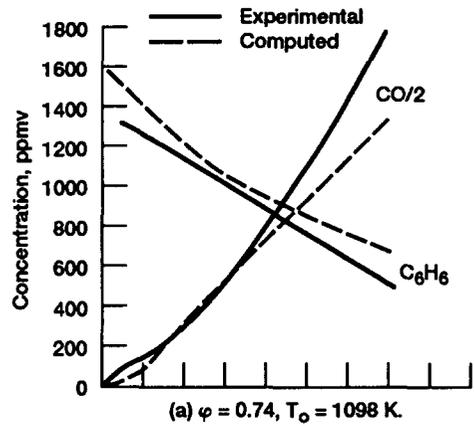

(a) $\varphi = 0.74$, $T_o = 1098$ K.

(b) $\varphi = 1.36$, $T_o = 1096$ K.

Fig. 2. Benzene and CO concentration versus time in a flow reactor.

tal curves change for the two mixtures. Figures 3 and 4 show ignition delay times versus reciprocal Kelvin temperature for two benzene–oxygen–argon mixtures
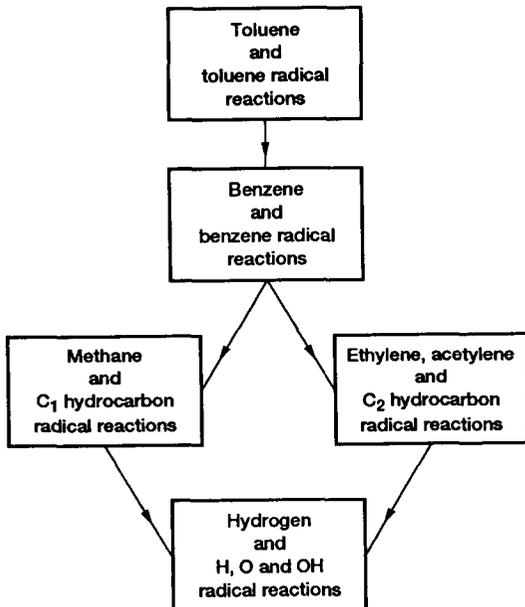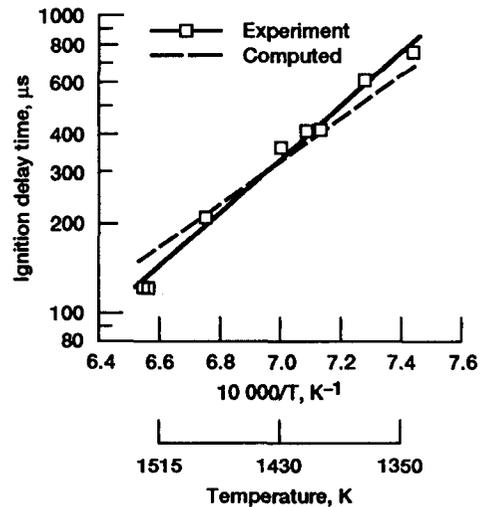

Fig. 1. Interrelation of hydrocarbon oxidation mechanisms.

Fig. 3. Benzene–oxygen–argon ignition delay time versus reciprocal of temperature, $\varphi = 1.0$, dilute mixture 95.6% Ar.
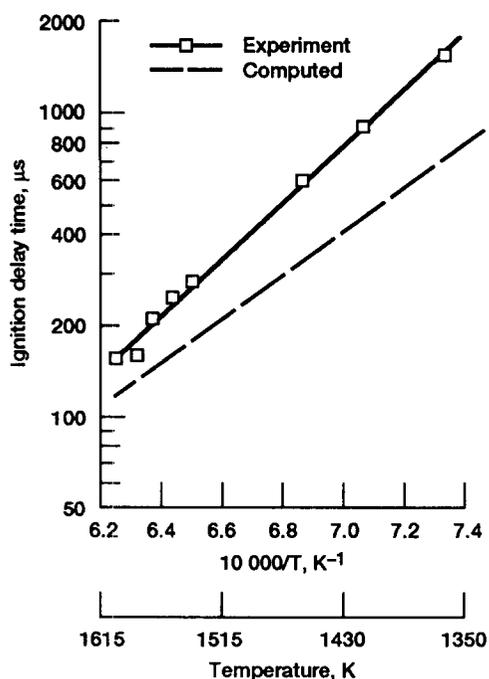
Fig. 4. Benzene–oxygen–argon ignition delay time versus reciprocal of temperature, $\varphi = 2.0$.

ignited behind a reflected shock wave. The experiments were reported by Burcat et al.[49] and the delay times were based on pressure versus time measurements. The reaction behind the shock was modeled, to a good approximation, as a constant-volume static process, and the computed ignition delay times were obtained from calculated pressure versus time plots. We see that agreement between experiment and computation is much better for the stoichiometric ($\phi = 1.0$) mixture (Fig. 3) than for the rich ($\phi = 2.0$) mixture (Fig. 4).

It is apparent from these comparisons that our mechanism is still incomplete. Additional experimental data are needed so that more comparisons between theory and experiment can be done to find as yet undiscovered important reactions and obtain good agreement with all experimental data. This example illustrates the fact that one cannot be completely sure that a chemical mechanism is correct and complete even if it successfully predicts a wide range of experimental data. In fact the mechanism may not be unique. The work of Emdee et al.[47] presents a benzene submechanism, as part of its toluene oxidation mechanism, which differs in several respects from that of Bittker. However, their mechanism predicts the flow reactor profiles of Lovell et al.[48] equally as well as Bittker's does. It has not been tested as to its ability to reproduce the ignition delay time data of Burcat.[49] In summary, obtaining knowledge about the mechanism of the oxidation of hydrocarbon fuels, or any complex chemical process, is a continuous task. As the data base of experimental information about the reaction increases, the mechanism may have to be modified to be consistent with all the available data.'

SIMPLIFICATION OF CHEMICAL KINETICS SOLUTIONS

There are two basically different approaches to the problem of obtaining realistic, but computationally rapid, combustion kinetics solutions which can be used in CFD modeling codes. The first is to reduce the size of the reaction mechanism, while keeping intact its important features. The speed of a chemical kinetics numerical integration increases rapidly as the number of reactions and species is decreased. The second is a relatively new idea called solution mapping, which optimizes the solution with respect to a small number of input variables and then replaces the differential equation solutions by a set of algebraic equations which express the dependent variables as functions of certain input variables of the problem. We conclude this paper with an overview of each of these techniques and their current status.

Reduction of chemical mechanisms

Algebraic simplification. For many years research has been directed towards separating the reactions and species in a mechanism into groups determined by different species reactivities. The solution can be simplified by obtaining algebraic relationships involving the concentrations of certain subgroups of very reactive species and rate coefficients of their reactions. This removes some species as unknowns from the differential equation set [Eq. (4)] and allows their concentrations to be computed algebraically. The numerical solution of the reduced set of species ODEs is then much easier and much more rapid. The three methods that have been used to accomplish this type of simplification are (1) the pseudo steady-state approximation, (2) the partial equilibrium approximation, and (3) the rate-controlled constrained equilibrium method.

The pseudo steady-state approximation (PSSA) is based on the assumption that the rates of formation of certain very reactive atoms and intermediate species called free radicals are very much smaller than those of the other species present. This is often true because their absolute concentrations are extremely small. The net rates of formation of these trace species can then be set equal to zero. They are assumed to achieve this psuedo steady state in a time interval which is short compared to the total reaction time. A simple example will illustrate this technique. We consider the reacting system (which may be part of a larger mechanism)

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \underset{k_4}{\overset{k_3}{\rightleftharpoons}} D$$
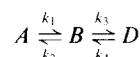
where the concentration of B is much smaller than that of the other two species. The law of mass action gives the following species ODEs:

$$\frac{dc_A}{dt} = k_2 c_B - k_1 c_A \tag{20}$$

$$\frac{dc_B}{dt} = k_1 c_A + k_4 c_D - (k_2 + k_3)c_B \tag{21}$$

$$\frac{dc_D}{dt} = k_3 c_B - k_4 c_D. \tag{22}$$

We now assume $dc_B/dt \cong 0$ and solve Eq. (21) for c_B. When the resulting expression is substituted for c_B in Eqs (20) and (22), the following set of two differential equations in the variables c_A and c_D is obtained:

$$\frac{dc_A}{dt} = (k_2 K_1 - k_1)c_A + k_2 K_2 c_D \tag{23}$$

$$\frac{dc_D}{dt} = k_3 K_1 c_A + (k_3 K_2 - k_4)c_D. \tag{24}$$

Here K_1 and K_2 are functions of the rate coefficients k_1, k_2, k_3 and k_4. In a complex reaction there can be several species which satisfy the conditions for a pseudo steady state, and the original ODE set can be greatly reduced. The major problem with this technique is developing a generalized and efficient method of finding the steady-state species and performing the reduction for any complex system. Significant progress has been made in this task, as shown in the work of Benson,[50] Bowen et al.,[51] and Dixon-Lewis et al.[52]

The partial-equilibrium approximation (PEA) approach also looks for groups of species and reactions which can be used in a partial algebraic solution. However, this technique searches for fast reactions, which are replaced by algebraic relations involving the equilibrium constants rather than rate coefficients. In general these fast reactions are easy to identify without having detailed physical insight into the reaction mechanism. For example, under combustion conditions the following three hydrogen–oxygen reactions are fast enough to be considered in equilibrium:

$$H + O_2 \rightleftharpoons OH + O$$

$$O + H_2 \rightleftharpoons OH + H$$

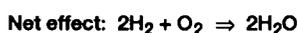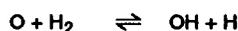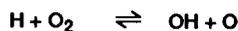$$H_2 + OH \rightleftharpoons H_2O + H.$$
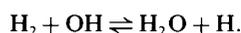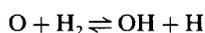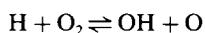
Equilibrium theory then gives algebraic relationships among these species concentrations under the assumption that the atoms H and O and OH (hydroxyl) radical all maintain their equilibrium concentrations. As with the PSSA method, systematic methods are needed for finding the partial equilibrium groupings in any problem. The work of Dixon-Lewis et al.[52] uses

both the PSSA and the PEA approaches in their method of "composite fluxes." Recent papers by Goddard[53] and Rein[54] report two different general methods of separating any reacting system into equilibrium and nonequilibrium groupings. The Goddard formulation implicitly includes the method of composite fluxes. The method of Rein uses the atom and mass conservation conditions that must be satisfied in any chemical system to separate the species and reactions into linearly independent and dependent groupings, and then applies the partial equilibrium approach.

Another approach for simplifying a complex reaction mechanism is the rate-controlled constrained-equilibrium (RCCE) method of Keck and Gillespie.[55] In this method only the slower rate-controlling reactions are treated by finite-rate methods. The method is described in detail by Keck[56] and is applied to the ignition of hydrogen–oxygen mixtures by Law et al.[57] The first step in this method is to assume that all finite-rate reactions are frozen, derive constraints using this assumption and compute the equilibrium state that satisfies these conditions. Next, the constraints are recalculated using the rate equations of the slow reactions. However, the rate-controlling reactions have to be determined by trial and error, so this method will not necessarily be computationally faster than other methods.

Quasi-global mechanisms. Another way to reduce the number of individual molecular reaction steps in a complex mechanism is to combine a group of molecular reactions into one overall or global reaction. The global reaction attempts to summarize the effect of several reactions which form and destroy atoms and reactive radicals, while changing reactant species into stable products. It is chosen to accurately predict the formulation or destruction rate of a stable species without considering the individual molecular steps in the process. An example of this reduction technique is given in Fig. 5. We show part of a detailed mechanism for the oxidation of hydrogen and, below it, a single global reaction that represents

Molecular mechanism (partial)

$$H + O_2 \rightleftharpoons OH + O$$

$$O + H_2 \rightleftharpoons OH + H$$

$$H_2 + OH \rightleftharpoons H_2O + H$$

$$H + OH + M \rightleftharpoons H_2O + M \quad \text{(M = collision partner)}$$

Net effect: $2H_2 + O_2 \Rightarrow 2H_2O$

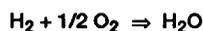**Global reaction**

$$H_2 + 1/2\, O_2 \Rightarrow H_2O$$

Fig. 5. Molecular mechanism and global reaction for oxidation of hydrogen.

the overall process, which is the conversion of 1 mole of H_2 and 0.5 mole of O_2 to 1 mole of water. It is interesting to notice that, if we ignore the fact that the four molecular reactions are allowed to be reversible, the net effect of adding these reactions is the conversion of 2 moles of H_2 and 1 mole of O_2 to 2 moles of water. The global reaction (which will always be irreversible) will be an adequate representation of the kinetics of the combustion if the major interest is the rate of fuel consumption or formation of water. However, the rate of this reaction is not determined by the law of mass action, but by using available experimental data to fit the empirical expression

$$-\frac{dc_{H_2}}{dt} = k(T) \prod_{i=1}^{NS} c_i^{a_i}. \qquad (25)$$

Here, c_i is the concentration of any species in the mixture (not only reactants), and $k(T)$ is a temperature-dependent rate coefficient in the form of Eq. (2). The constants $\{a_i\}$ and the three rate parameters are determined by computer trials and fitting of experimental data. The work of Varma et al.[9] uses the global reaction in Fig. 5 to study premixed hydrogen–air laminar flames.

The rate of a global reaction can depend on the concentrations of species which do not participate in it, because the reaction lumps together the effects of several species, even if they all do not participate explicitly in the reaction. The obvious drawback of the global-reaction approach is that a rate expression determined for one set of experimental conditions may not be valid for a different set of experimental conditions. Also, for a complex system it is often a tedious process to determine how to group the molecular reactions and replace some or all of them by a small number of global reactions. Nevertheless, this technique has been used for many years with some success. For example, Peters and Kee[58] and Peters and Williams[59] have developed simplified three- and four-step mechanisms for the oxidation of methane, which have been applied to both premixed and laminar diffusion flames. The work of Lam and Goussis[60] uses the Computational Singular Perturbation Technique to systematically divide a complex mechanism into reaction groups, each with a single characteristic time scale. These groups are used to develop a reduced and simplified set of global reactions. Different mechanisms can be obtained, depending on which variables are of interest in a given problem. In other work global mechanisms have been developed for the combustion of methane[7] and propane[61] over a range of mixture equivalence ratio. Hautman et al.[62] propose a general hydrocarbon oxidation global mechanism which was verified over a wide range of experimental conditions. In the recent work of Kundu and Deur[63] a quasi-global mechanism which models nitrogen oxide formation in hydrogen–air combustion was developed. Their reduced mechanism, containing both global and molecular
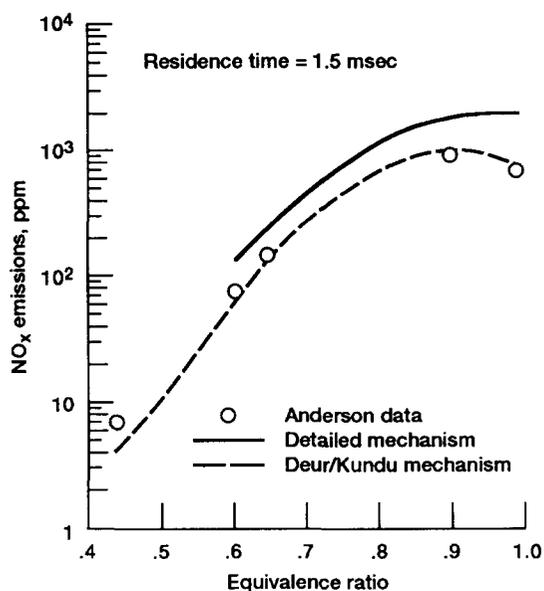

Fig. 6. NO_x emissions comparison as a function of equivalence ratio.

reactions, successfully computes the results of experimental nitric oxide emissions measurements of Anderson[64] in a laboratory combustor over a wide range of fuel equivalence ratio. For these limited experimental conditions the quasi-global mechanism was more successful in modeling the production of nitric oxide than was a much larger detailed molecular chemical mechanism. These comparisons are shown in Fig. 6, which is taken from Kundu and Deur.

Summary. Many partially successful reduced mechanisms, employing all of the simplification techniques that have been discussed here, have been developed. However, none as yet combines good predictive capability with significantly increased computational speed for a very wide range of experimental conditions, and research continues in this field. For a very good recent review of combustion modeling and the use of simplified reaction mechanisms, the paper by Dryer[65] is recommended.

Solution mapping

An entirely different approach to the rapid computation of the kinetics of a complex reaction is the idea of solution mapping, first suggested by Frenklach.[8,66] In chemical modeling, the differential equations describing the system generate solutions (concentrations, temperature) which are model responses to the input parameters of the problem (initial conditions, rate coefficients), which are called the model variables. The idea of solution mapping is to first obtain solutions of the ODEs (responses) for a range of variation of the input variables. These solutions are called computer experiments, and their number does not have to be large if the proper combinations of model variables are selected. The relationship between the model responses and the model variables

is then analysed systematically by assuming the responses are primarily dependent on a limited number of model variables, which are called active parameters. The latter can be found by using the method of local sensitivity analysis described earlier in this paper. The model responses are expressed as algebraic functions (often polynomials) of the active parameters. These functions are called response surfaces, and they are a reduced model of the kinetic process, giving essential dependencies between the variables of the problem. It should be pointed out that a model response can be a quantity derived from the temperature and concentration versus time solutions of Eqs (4) and (14). An example of this is experimental ignition delay time, which can be defined by several different criteria. These include a fixed pressure rise,[49] or temperature rise, or the time needed for a radical species concentration (e.g. hydroxyl, OH), to reach a prescribed value.

A detailed description of the solution mapping technique is given by Frenklach et al.[67] who also describe its application to the kinetics of the combustion of methane. In this work, response surfaces were computed for several ignition delay times and one radical concentration. Although their detailed methane oxidation mechanism contains over 140 reactions, a systematic sensitivity analysis identified only 13 active parameters (i.e. reaction rate coefficients) which controlled the computed results. The resulting polynomials were used to optimize the chemical mechanism by minimizing a weighted least-squares function of the differences between computed and experimental results. The authors point out the significant savings in computer time achieved by substituting evaluations of polynomials for repeated solutions of sets of differential equations when minimizing the least-squares function.

This procedure has also been applied to the simplification of photochemical air pollution models, which require the solution of large systems of stiff ODEs (Marsden et al.[68]). Algebraic models for ozone formation were obtained which computed ozone concentration profiles in excellent agreement with the results of complete ODE model solutions. The approach used in this work could be applied to a combustion flow problem by generating polynomial functions for temperature and a limited number of species concentrations (e.g. fuel, carbon monoxide, nitric oxide) and building these functions into a subroutine of a CFD code. Repeated calling of this subroutine would clearly be less costly than repeated calling of an ODE solver subprogram.

CONCLUDING REMARKS

In this paper we have discussed the need for incorporating realistic heat release and species formation rate computations into CFD reacting flow codes which model practical combustion systems. The general methods by which we theoretically predict the effects of complex chemical reaction in the oxidation and combustion of fuels were described. Because the detailed solutions of large chemical systems are computationally expensive, they must be simplified in order to be used as part of a large reactive-flow modeling code. Several methods of simplification were described. They include (1) using pseudo steady-state or partial equilibrium approximations to reduce the number of differential equations to be solved and substitute algebraic relations, (2) forming a global or quasi-global reduced mechanism which preserves the important features of the detailed mechanism, and (3) using the technique of solution mapping to transform the results of a series of detailed computations into algebraic equations for dependent variables of interest. These equations are functions of several important input "active parameters," which are found by a careful sensitivity analysis of the detailed solutions. Each of these simplification approaches has shown good results when applied to certain selected systems. However, further research is needed on all these techniques to develop an efficient and very general method for chemical kinetic computations in CFD reactive flow codes.

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