Kinetic Mechanism Reduction Based on an Integer Programming Approach

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An approach toward kinetic mechanism reduction, both in terms of reactions and species, is discussed. The driving force of the approach is to derive reduced kinetic models while maintaining the structural integrity of the detailed mechanisms. The mechanism reduction problem is defined as an integer optimization problem with binary variables denoting the existence/nonexistence of reactions or species. A Branch & Bound framework is implemented for the solution of the resulting mathematical programming problem. Several examples, utilizing a variety of kinetic networks, are presented and the results are analyzed.

Introduction

Detailed modeling of chemically reacting systems is an important factor in the analysis of chemical reactors. Byproduct distribution, pollutant formation, and process operation/optimization are greatly influenced by the details of the chemistry. Accurate models that correctly predict the chemical pathways are often extremely complex and involve a large number of reacting species and reaction steps. Keeping track of species evolution in such large systems is a highly demanding computational task. It is therefore imperative to identify alternative representations of detailed kinetic mechanisms to reduce the computational workload. Three types of approaches are commonly used to develop simplified kinetic representations:

Reduction of the Number of Reacting Species and Reactions. In this case the problem is defined as follows: Let the detailed network be composed of N_s species participating in N_r reactions. Let the set of reactions be

$$\mathcal{S}_{N_r} = \{ R_1, R_2, \ldots, R_{N_r} \}$$

$$\mathcal{S}_{N_s} = \{ \sigma_1, \sigma_2, \ldots, \sigma_{N_s} \}$$

A reduced network that maintains the structural integrity of the original is one composed of N_R' reactions belonging to a subset of the original set

$$\mathcal{S}_{N_r}' \subset \mathcal{S}_{N_r}$$

$$\mathcal{S}_{N_s}' \subset \mathcal{S}_{N_s}$$

The reaction pathways remain unaltered, although some branches are removed. Local sensitivity analysis is primarily used to derive such reduced mechanism (Turányi et al., 1989).

Reduced Mechanisms Using Quasisteady-State and Partial Equilibrium Assumptions. By replacing the production rate of species which are quasi-equilibrium with their corresponding equilibrium expressions, new combined steps are determined which no longer correspond to elementary ones. Such reductions have been shown to be extremely effective within the regime at which the reduction assumptions are valid. However, the integrity and physical intuition of the model are often lost. Peters and Williams (1987), for example, reduced systematically through steady-state and partial-equilibrium assumptions a 31-step mechanism of CH_4 combustion to a three-step mechanism

$$CH_4 + O_2 \rightarrow CO + H_2 + H_2O$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

$$O_2 + 2H_2 \rightarrow 2H_2O$$
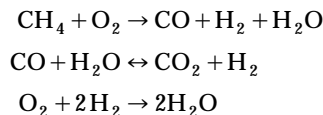
The resulting reaction steps are clearly a combination of elementary ones and do not necessarily reflect the way the reactions are actually taking place.

Mathematical Representations Based on the Time-Scale Separation. Important advances in the theory and practice of mechanism reduction are the result of methods that take into account local dynamics. These methods mathematically construct a lower-dimension subspace over which the dynamics are confined. They follow primarily the work of Maas and Pope (1992) and Lam and Goussis (1994).

A comprehensive review of mechanism reduction techniques can be found in Tomlin et al. (1997). This article presents an alternative approach towards mechanism reduction while maintaining the structural integrity of the detailed ki-

netic networks. It has been motivated by the recent work of Petzold and Zu (1997). Along similar lines is the recent work of Edwards et al. (1999), although a fundamentally different modeling approach and solution methodology is adopted here.

Reducing the Number of Reactions

Problem definition

The problem to be addressed is defined as follows:

Given a detailed reaction network composed of N_R reactions determine the smallest network, subset of the detailed one, having $N_R' \leq N_R$ reactions, that replicates the dynamics of the detailed network with a given accuracy.

The search for this reduced reaction network is mathematically defined as the following optimization problem

$$\min_{\lambda \in \mathfrak{I}^{N_R}} \sum_{r=1}^{N_R} \lambda_r$$

subject to

$$\mathfrak{L} = \left(\sum_{k \in \mathfrak{K}} \omega_K \int_0^Z \left(\frac{y_k^{\text{reduced}}(z) - y_k^{\text{detailed}}(z)}{y_k^{\text{detailed}}(z)} \right)^2 dz \right.$$

$$+ \omega_T \int_0^Z \left(\frac{T^{\text{reduced}}(z) - T^{\text{detailed}}(z)}{T^{\text{detailed}}(z)} \right)^2 dz$$

$$\left. + \omega_\tau \int_0^Z \left(\frac{\tau^{\text{reduced}}(z) - \tau^{\text{detailed}}(z)}{\tau^{\text{detailed}}(z)} \right)^2 dz \right)^{1/2} \leq \delta$$

$$\frac{dy_s^p(z)}{dz} = \sum_{r=1}^{N_R} \lambda_r \alpha_{rs} R_r, \quad s = 1, \ldots, N_s, \quad p = \{\text{reduced}\} \quad (1)$$

$$\frac{dT^p(z)}{dz} = \sum_{s=1}^{N_S} H_s^g \frac{dy_s^p(z)}{dz}, \quad p = \{\text{reduced}\}$$

$$\frac{d\tau^p(z)}{dz} = \frac{\rho}{c_0}, \quad p = \{\text{reduced}\}$$

$$R_r = \mathfrak{K}_F^r \prod_{s=1}^{N_S} [X_s]^{\alpha'_{rs}} - \mathfrak{K}_R^r \prod_{s=1}^{N_S} [X_s]^{\alpha''_{rs}}, \quad r = 1, \ldots, N_R$$

$$\mathfrak{K}_F^r = k_F^r e^{-E_F^r/RT}$$

$$\mathfrak{K}_R^r = k_R^r e^{-E_R^r/RT}$$

$$\lambda \in \mathfrak{I}^{N_R} = \{0,1\}^{N_R}$$

In order for the formulation to be consistent with the way we perform our calculations, y_s denotes mass fractions, while X_s denotes molar concentrations used in the calculation of the reaction rates. ρ stands for the mixture density, which is a function of composition and temperature, and c_0 is the initial mass flux, which is a function of the initial conditions. λ_r is a binary variable used to denote the existence $\lambda_r = 1$ or nonexistence $\lambda_r = 0$ of particular reaction. In the above formulation *detailed* is the network for which all λ_rs are equal to 1. $\mathfrak{K}$ is a user-defined subset of the set of all reacting species (molecular as well as free radicals). The integral error mea-

sure $\mathfrak{L}$ defines the approximation error of the trajectories of the key observable quantities for the interval of interest. The temperature of the system T is also a target. We also allow for an additional observable τ which corresponds to a characteristic time of the system, such as the induction time in combustion systems. The factors ω are appropriately selected weighting factors that represent the biases of the decision-maker in the way different observables are to be considered in the objective. The form of the weight can greatly affect the outcome of the reduction scheme. In all the results presented the value of those parameters are set to 1. One example case will be presented that formulates the problem such that $\omega_k = 0$, $k \in \mathfrak{K}$, $\omega_\tau = 0$, and $\omega_T = 1$ to show the effect of altering the objective. Furthermore, the domain over which the error measure is defined is important, as will be discussed. A plug-flow reactor is used in the actual simulations. A nominal reactor length Z is defined simply to perform the integration. All results are presented in terms of residence times which is an objective measure of the progress of the reaction. For given initial conditions (reactant mole fractions and inlet temperature and pressure), base-case profiles are obtained by simulating the species and temperature evolution with the detailed mechanism for an adiabatic reactor of length Z. It is clear that the form of the reactor does not, and should not affect, the principles used for performing the reduction.

Alternative formulations can also be analyzed in which the error in each different observable is treated as a separate constraint. The presented formulation is adopted because: (i) it is the most simple, (ii) it is numerically less demanding since all gradients are computed numerically and, therefore, the Jacobian of the constraint is essentially a row vector and not a matrix. More advanced schemes could also be used by exploiting the sensitivity equations, for example, but these would only improve the computational efficiency and would not affect the qualitative results related to the reduction as well as computational requirements for solving the integer problem in terms of the Branch & Bound nodes as will be discussed subsequently. There exists a large number of different formulations one could explore and the results would all point to the fact that multi-objective approaches strongly depend on the targets the decision-maker has set for the problem. We will solve a few characteristic instances so as to illustrate the key points of the approach. Formulation 1 aims at identifying the minimum number of reactions $\sum_{r=1}^{N_R} \lambda_r \leq N_R$ that would achieve an adequate representation of the original network, as expressed by the error norm $\mathfrak{L}$. The optimal decision is described by the solution vector $\lambda = \{\lambda_1, \ldots, \lambda_{N_R}\}$, such that, if $\lambda_I = 0$, the particular reaction is not considered. The mathematical representation of (1) defined an integer nonlinear problem for which no standard solution procedures exist. We developed a Branch & Bound framework so as to address this problem. Various results were obtained, and some typical ones will be discussed.

The solution of the resulting integer optimization problem is greatly enhanced if a subset of important reactions is *a priori* determined thus reducing the actual number of binary variables. One way of addressing such an issue is through a pre-processing step in which the relative importance of the various reactive steps is determined in a sequential manner. That can be simply done by running successive simulations in

which one removes reactions one a time. The following is a heuristic used to determine a critical set of reactions that can not be removed from the mechanism: If dropping reaction i from the detailed network, that is, $\lambda_i = 0$, while all other reactions remain active, that is, $\lambda_j = 1$, $j = 1, \ldots, N_R$, $j \neq i$, produces a reduced network with $N_R' = N_R - 1$ reactions that approximates the complete network with an error $\delta' > \delta$ reaction i that must remain active and not be treated as a variable. Thus, one determines a critical reaction set whose presence is required

$$R^{\min}(\delta) \equiv \{ i\text{: for which when } \lambda_i = 0 \text{ and}$$
$$\lambda_j = 1, \ j \neq i \text{ then } \delta' > \delta \} \subset \{1, \ldots, N_R\} \quad (2)$$

The optimization is now constrained on the remaining $N_R - N_{R^{\min}(\delta)}$ reactions from which we need to identify the minimum number required. It should be pointed out that, by using only the reactions defined in $R^{\min}(\delta)$, we do not obtain an approximation within δ of the complete network. However, compensating errors could be present, whereby removing reaction A or reaction B could result in error, but removing reactions A and B might actually cancel out individual errors. Such compensating effects cannot be identified by the heuristic. If this is the case, solving the problem using the heuristic would provide an upper bound on the size of the reduced mechanism. If the reduction is not considered significant, one could simply solve the original problem without invoking the heuristic to, possibly, obtain a better solution. It must be emphasized that the integer optimization approach does not depend on the implementation of the heuristic. Simply, the computational efficiency is improved as the number of binary variables is reduced.

Instead of imposing a bound on the approximation error in the form of a nonlinear constraint, while minimizing the number of required reactions, one could postulate the inverse problem, whereby we minimize the error while postulating the number of reactions

$$\min_{\lambda \in \mathfrak{I}^{N_R}} \mathfrak{L} = \left(\sum_{k \in \mathfrak{K}} \omega_K \int_0^Z \left(\frac{y_k^{\text{reduced}}(z) - y_k^{\text{detailed}}(z)}{y_k^{\text{detailed}}(z)} \right)^2 dz \right.$$
$$+ \omega_T \int_0^Z \left(\frac{T^{\text{reduced}}(z) - T^{\text{detailed}}(z)}{T^{\text{detailed}}(z)} \right)^2 dz$$
$$\left. + \omega_\tau \int_0^Z \left(\frac{\tau^{\text{reduced}}(z) - \tau^{\text{detailed}}(z)}{\tau^{\text{detailed}}(z)} \right)^2 dz \right)^{1/2}$$

subject to

$$\sum_{r=1}^{N_R} \lambda_r = M$$

$$\frac{dy_s^p(z)}{dz} = \sum_{r=1}^{N_R} \lambda_r \alpha_{rs} R_r, \quad s = 1, \ldots, N_s, \quad p = \{\text{reduced}\} \quad (3)$$

$$\frac{dT^p(z)}{dz} = \sum_{s=1}^{N_S} H_s^g \frac{dy_s^p(z)}{dz}, \quad p = \{\text{reduced}\}$$

$$\frac{d\tau^p(z)}{dz} = \frac{\rho}{c_0}, \quad p = \{\text{reduced}\}$$

$$R_r = \mathfrak{K}_F^r \prod_{s=1}^{N_S} [X_s]^{\alpha'_{rs}} - \mathfrak{K}_R^r \prod_{s=1}^{N_S} [X_s]^{\alpha''_{rs}}, \quad r = 1, \ldots, N_R$$

$$\mathfrak{K}_F^r = k_F^r e^{-E_F^r/RT}$$

$$\mathfrak{K}_R^r = k_R^r e^{-E_R^r/RT}$$

$$\lambda \in \mathfrak{I}^{N_R} = \{0, 1\}^{N_R}$$

Equations 1 and 3 are equivalent, however, the computational results presented are obtained via Eq. 1. As will be shown, a very important characteristic of this problem is the fact that the error δ is not a continuous function of the number of reactions.

Branch & Bound algorithms for integer optimization problems with differential equations

The problem at hand is complicated by the fact that the state of the system, that is, objective and constraints, is defined as the time evolution of a dynamic system, and integer decisions have to be made. A Branch & Bound algorithm was developed so as to address these problems.

Branch & Bound algorithms define families of solution algorithms that operate within a search tree. The main objective in a general Branch & Bound algorithm is to perform an enumeration of the alternatives without examining all $0-1$ combinations of the binary variables. A key element in such an enumeration is the representation of alternatives via a binary tree. The basic ideas in a Branch & Bound algorithm are the following. First, a reasonable effort is made to solve the original problem by considering, for instance, the continuous relaxation of it. If the relaxation does not result in an integer-feasible solution, that is, one in which the binary variables achieve $0-1$ at the optimal point, then the root node is separated into two candidate subproblems which are subsequently solved. The separation aims at creating simpler instances of the original problem. Until the problem is successfully solved, this process of generating candidate subproblems is repeated. Branch & Bound algorithms are also known as divide and conquer for that very reason. A basic principle common to all Branch & Bound algorithms is that the solution of the subproblems aims at generating valid lower bounds on the original integer programming problem through its relaxation to a continuous problem. The relaxation results in a nonlinear programming problem (NLP) which, in the general case, is nonconvex and needs to be solved to global optimality so as to provide a valid lower bound. If the NLP relaxation renders an integer solution, then this solution is referred to as valid upper bound. The generation of the sequence of valid upper and lower bounds is called bounding step. The way subproblems are created is by forcing some of the binary variables to take on a value of 0 or 1. This is known as the branching step. Nodes in the tree are pruned when the corresponding valid lower bound exceeds the valid upper bound; this stage is known as the fathoming step. The selection of the branching node, the branching variable, and the generation of the lower bound are very crucial steps whose importance becomes even more pronounced when addressing nonconvex problems.

Two basic strategies exist regarding the selection of the branching node, depending on whether one designs a Branch & Bound based on a depth-first or a breadth-first approach. In the former, the last node created is selected for branching, and in the latter the node that generated the best lower bound is selected. Another alternative is to select nodes based on the deviation of the solution from integrality. It is not clear which strategy is the best and it is often the one that minimizes the computational requirement that is selected (Gupta and Ravindran, 1985). The most common strategy for selecting a branching variable is to select the variable whose value at the solution of some relaxed problem is the farthest from the integer, that is, the most fractional variable (Ostrovsky and Mikhailov, 1990). Finally, one of the most important computational steps is the generation of the lower bound. The effectiveness of a Branch & Bound depends on the quality of the lower bound that is generated. At every node of the Branch & Bound tree, a nonlinear/nonconvex NLP is solved. Two issues are important: the lower bound must be valid, that is, the relaxation at a particular node must underestimate the solution of the original problem for this node, and the lower bound must be tight so as to enhance the fathoming step. The key complexity when dealing with nonconvex MINLPs is that the relaxation solved at each node is, of course, a nonconvex NLP that has to be solved to global optimality. In such cases global optimization algorithms have to be employed for the generation of valid lower bounds. The elements of Branch & Bound can be found in greater detail in Floudas (1995), and in a recent summary of the work on global optimization of problems involving integer variables in Androulakis (2000). Optimization of dynamic models involving binary $(0, 1)$ variables is a further complicated task. In this work, the sequential solution-optimization strategy is adopted and is embedded within the Branch & Bound framework. Alternative approaches based on decomposition schemes are discussed in Allgor (1997).

In the developed Branch & Bound the continuous relaxation of the integer problem is solved using a Successive Quadratic Programming method as implemented in the **NAG** Fortran Library. The integration of the differential equations describing the species and temperature evolution is performed using **DDASSL** (Brenan et al., 1996), while the calculation of the rate expressions and all necessary thermophysical properties is done using **Chemkin-II** (Kee et al., 1990). The basic elements of the developed Branch & Bound framework are shown in Figure 1.

Computational Results

The method is first tested on a fairly simple example problem to identify various characteristics of the approach. Emphasis is given on combustion problems since these define an important class of systems that often lead to large kinetic networks.

H_2 combustion– Model 1

This example is taken from Petzold and Zu (1997). The reaction network is shown in Appendix 1. Equation 1 was used where the set $\mathcal{K}$ contains all the major reacting molecular species, that is, H_2, O_2, H_2O. The profile to be replicated is one that corresponds to the following initial conditions: H_2
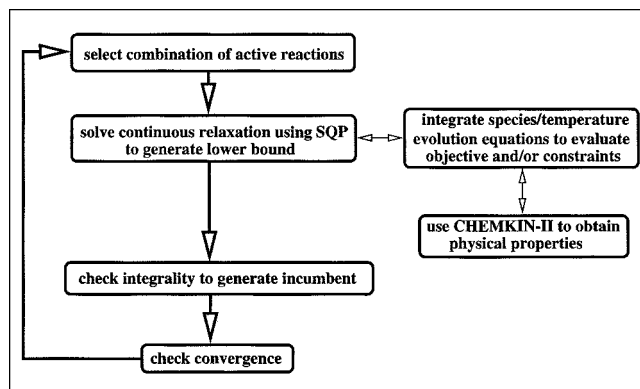

Figure 1. Developed branch and bound framework.

mol frac. $= 0.12$, O_2 mol frac. $= 0.88$, $T_0 = 1{,}000$ K. The error measure was defined as the L_2 norm of the profiles of H_2, O_2, H_2O, temperature, and residence time. For the latter, one additional differential equation is defined which determines the time at which the reaction front reaches a specific location along the length of the reactor. In all cases to be analyzed in this and other examples, we utilize a plug-flow adiabatic reactor. The detailed reaction network is composed of 20 reversible reactions and the reduced mechanism for achieving an error $\delta = 10^{-3}$ contains 9 reactions, which are $\{1, 2, 3, 4, 5, 6, 7, 9, 16\}$ and achieves an error of $6.66 \ 10^{-4}$. The critical set was found to be $R^{\min}(\delta) = \{2, 3, 4, 5\}$. Omitting any of the reactions belonging to the critical set has a profound effect on the approximation and results in error values in the range of $2.80-3.04$, that is, an increase by 4 orders of magnitude. The Branch & Bound tree solves 11 nodes before terminating. Given the minimal set, the effective number of binary variables is reduced to 16. Typical profiles comparing the detailed and reduced mechanism are shown in Figures 2 and 3.

Selection of Appropriate Objective Measures. Reduction techniques that generate global mechanisms and rely on minimizing a user-defined objective are highly sensitive to the form of the objective. By altering it, one clearly affects the
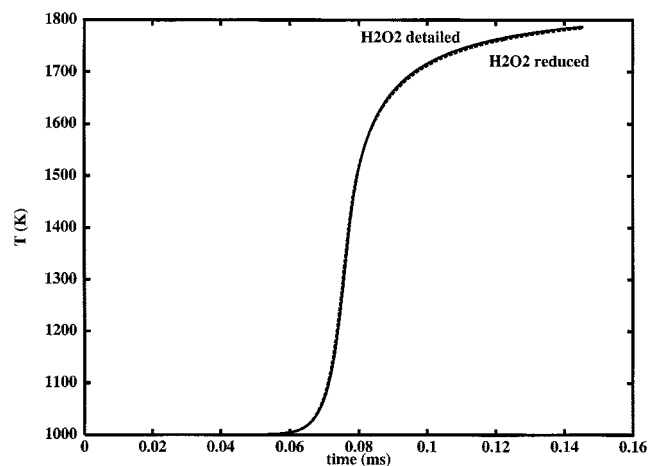

Figure 2. Detailed vs. reduced model.

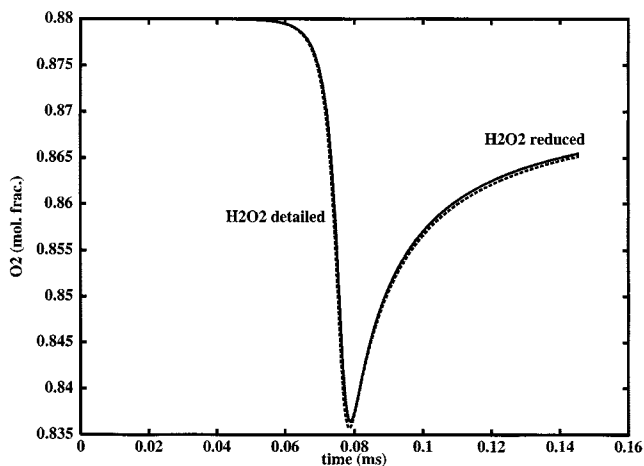Temperature profile for H_2 combustion.

Figure 3. Complete vs. reduced model.

O_2 profile for H_2 combustion.

required degree of detail. More important, predicting conditions not described by the objective becomes unreliable. As an example, the H_2 combustion problem was resolved while trying to match the outlet of the reacting mixture as opposed to the trajectory that leads to the final point. Shown in Figure 4 are the results of a reduced mechanism for the H_2 combustion problem when the objective is to match the outlet condition (compositions and temperature). The network is reduced by three more reactions {7, 9, 16}. It predicts with great accuracy the outlet conditions, but misses important aspects of the dynamic trajectory that lead to these conditions. Not only the minimum in O_2 concentration is missed, but also the ignition time shows a substantial delay.

The weighting factors will also affect the obtained solution. As an example, the same problem was solved with the error function defined in a way that included only the error approximation of the temperature profile. By setting the maximum error $\delta = 10^{-3}$, the reduced network contained reactions {1, 2, 3, 4, 5, 7, 16}, that is, two reactions less than when
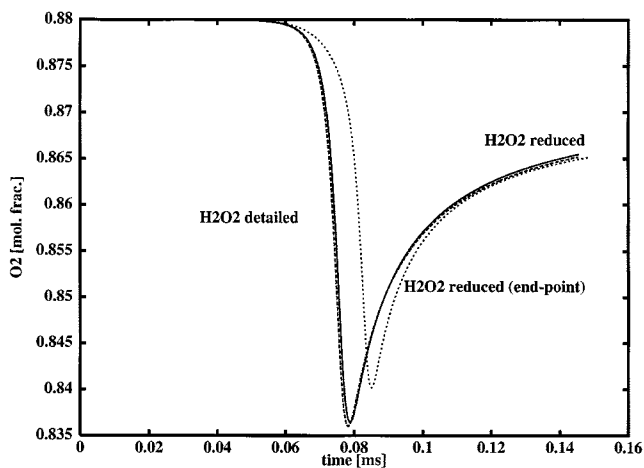
Figure 4. O_2 composition profiles based on an integral objective [H_2O_2 reduced] and an end-point objective [H_2O_2 reduced (end-point)] for H_2 combustion.
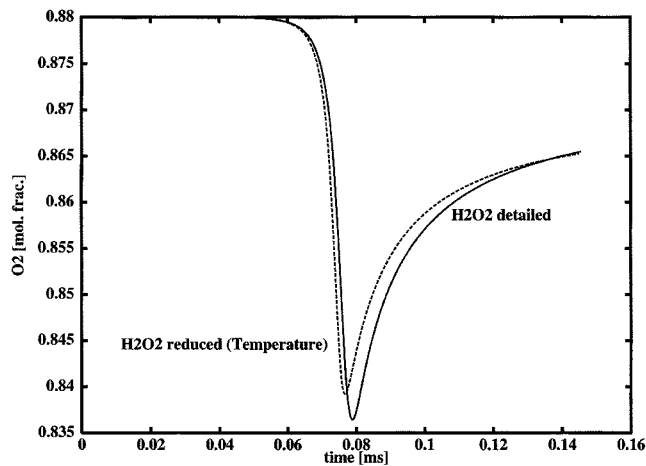
Figure 5. O_2 composition profiles based on an error measure that only accounts for temperature profile.

all the major species are included. This network, although it yields a very good prediction of the temperature profile, fails to correctly predict the evolution of gaseous O_2 as shown in Figure 5.

Multiobjective Nature of the Problem. Although the problem was cast in the form of Eq. 1 with a single objective, in more general terms, it must be posed as a multilevel problem in which one wishes to identify the minimum number of reactions that produce the least approximation error. One way to approach this question is to solve the original problem for different values of the error measure δ. This way, we implicitly construct the set of noninferior solutions that shows the evolution of the approximation error as a function of the size of the reduced network depicted in Figure 6.

A very interesting observation must be made given these results: with up to six reactions one achieves an almost linear (in log-scale) improvement in the error as the size of the reduced network is increasing. An irreducible set of six reactions (reactions {1, 2, 3, 4, 5, 7}) exists that is necessary for a fairly good description of the detailed mechanism. Any fur-
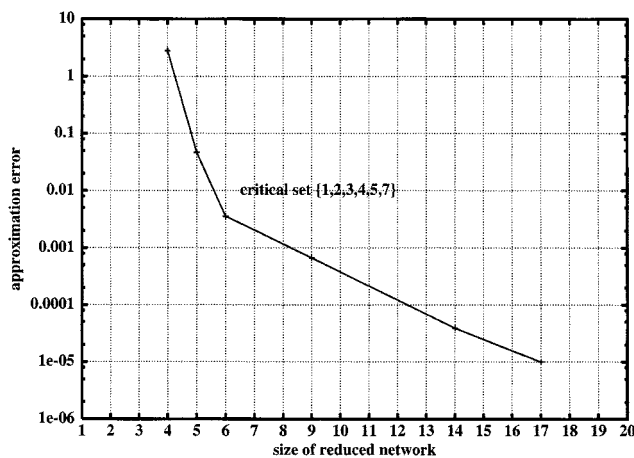
Figure 6. Approximation error δ as a function of the size of the reduced network.

ther reduction below this critical set will substantially deteriorate the quality of the reduced mechanism. This is clearly seen by the fact that the slope of the error changes drastically as we further try to reduce the size of the network. A multiobjective framework allows one to determine such a critical set. The existence of it imposes a practical lower bound on the reduction.

When building the efficient frontier, one must be aware of the fact that because the constraint defining the approximation error is never active at an integer solution, the possibility exists of a multiplicity of solutions. When solving for $\delta = 10^{-3}$, for example, one determines two reduced mechanisms: {1, 2, 3, 4, 5, 6, 7, 9, 16} with an error of $6.66 \times 10^{-4} < \delta$, and {1, 2, 3, 4, 5, 7, 8, 9, 16} with an error $8.22 \times 10^{-4} < \delta$. Both solutions correspond to the same objective; however, both are feasible with the constraint active at the optimal point.

Nonconvex Nature of the Problem. Either formulation of the problem leads clearly to a nonlinear/nonconvex problem in the terms of the NLP continuous relaxation that has to be solved at each Branch & Bound node. Therefore, a Branch & Bound algorithm cannot guarantee the globally optimum solution, assuming that the nonconvex nature of the problem leads to multiple local minima and the NLP relaxation is solved via local optimization techniques.

The problem of global optimization is clearly a very difficult one, and, in our case, is further complicated by the presence of the differential equations and the fact that it is embedded within our Branch & Bound framework. The combination of the results of Adjiman et al. (1997) and Esposito and Floudas (1997) would provide a definite answer. An alternative approach could also be to use stochastic optimization techniques as was done in Edwards et al. (1998). Three alternative strategies were implemented within our framework. One initializes the solution of each NLP continuous relaxation by setting all variables to their upper bounds, the second initializes the NLP relaxation at the solution of the parent node, and, finally, the starting point at each NLP continuous relaxation is set randomly. All approaches provided the same final reduced mechanism. This, of course, does not address the theoretical issues involved but provides some confidence in terms of the results obtained.

Confidence Interval at Reduced Mechanisms. The target of the reduction is to determine a smaller size mechanism that reproduces a representative response of the system. For simplicity, we assumed that the target was a single trajectory. Clearly, multiple trajectories could be defined so as to determine a more comprehensive target. However, for practical purposes only, a finite number of trajectories can be considered. Therefore, the question remains as to how the reduced mechanism would predict conditions other than the ones that were used for the reduction. In Ierapetritou and Androulakis (1999), flexibility analysis within the integer optimization approach was used to determine the feasible region for all the examples studied in this work. It is shown that, although few nominal conditions are used, the actual domain of applicability of the derived reduced mechanism is substantial.

H_2 combustion— Model II

This H_2 combustion mechanism is larger than previous and contains 10 species and 46 irreversible chemical reactions. It
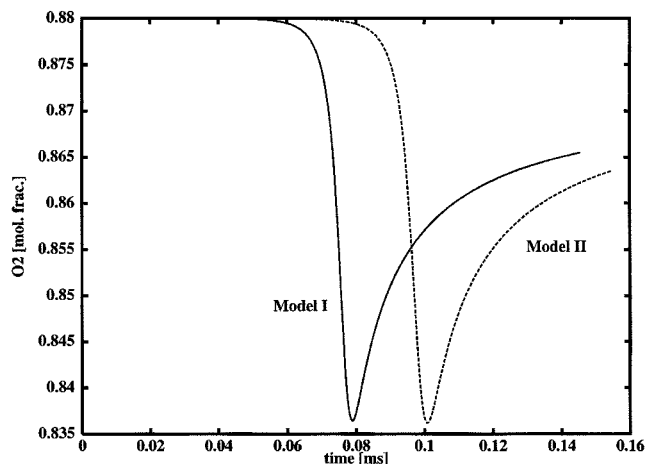
Figure 7. O_2 profiles obtained with two different H_2 combustion networks.

Model I with 20 reactions; model II with 46 reactions.

is a simplification of the Methane Oxidation mechanism developed at the University of Leeds (Pilling et al., 1998). The mechanism is described in Appendix 2. The profile to be replicated is one that corresponds to the following initial conditions: H_2 mol frac. = 0.12, O_2 mol frac. = 0.88, $T_0 = 1,000$ K. For a required accuracy of $\delta = 10^{-3}$, the reduced set is {1, 2, 3, 4, 5, 7, 9, 10, 17, 19, 20, 27, 30, 31, 39, 40, 41}. The indices refer to the order of the reactions as they can be found in the original reference. The approximation error $\epsilon = 9.82 \times 10^{-4}$.

Plotting the O_2 mol fractions, we notice in Figure 7 an important difference between the two models. Although the qualitative behavior of both networks is the same, they differ substantially in terms of the ignition time that they predict. The differences in the minimum and final values for the mol fractions are within 1%, but the difference in the ignition time is about 20%. These kinds of discrepancies do not, of course, affect the reduction process, but they point to the fact that different networks have been developed for different reasons and therefore one should be aware of the peculiarities of each kinetic network. It is important to realize that a reduced network will only be as good as the detailed network.

$CO/H_2/Air$ combustion

This test case considers the model presented in Li and Rabitz (1997). It contains 47 reversible reactions and 13 species, and it models the combustion of a syngas mixture in air. The complete kinetic network is shown in Appendix 3. The profile to be replicated corresponds to the following initial conditions: H_2 mol frac. = 0.05, O_2 mol frac. = 0.189, CO mol frac. = 0.095, N_2 mol frac. = 0.711, $T_0 = 1,600$. The target includes the species profiles of CO, O_2, H_2, CO_2, H_2O, temperature, and residence time. The reduced network for achieving the desired error $\delta = 1.0^{-3}$ consists of a total of 16 reactions out of the 47. In order to obtain the solution, 22 Branch & Bound nodes were explored and the reduced mechanism was composed of reactions {1, 3, 4, 6, 10, 12, 13, 14, 15, 17, 22, 24, 25, 32, 34, 38}. The actual approximation
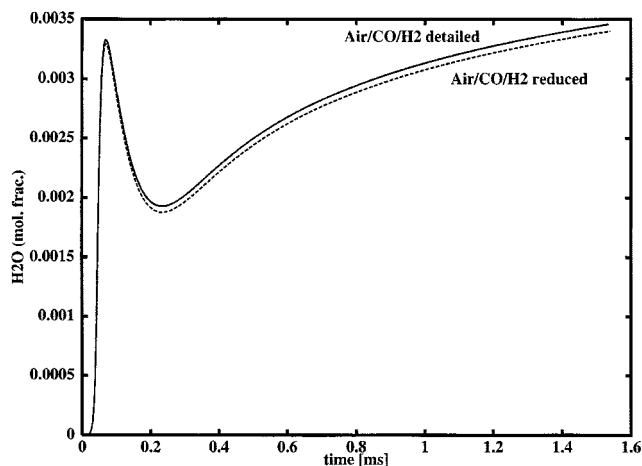
Figure 8. Complete vs. reduced model.

H_2O profile for CO/H_2/Air combustion.

error was $\epsilon = 9.83 \times 10^{-4}$. The indices refer to the order of the reactions as they can be found in Appendix 3. Typical profiles comparing the detailed and the reduced networks are depicted in Figure 8.

Reducing the Number of Species

Mechanism reduction also implies the reduction of the reacting species present in the network. The problem can be formulated in a form similar to the reaction reduction problem. The objective is now to determine the least number of species which are required so as to reproduce accurately some specified targets. Reducing the number of species is of primary importance, since this way we reduce also the number of ordinary differential equations (equivalently partial differential equations) required to model a reactive flow.

Species reduction is the byproduct of the reduction of the number of reactions. A specie is removed from the network if it participates only in reactions that are to be removed. Therefore, reducing the number of reactions implies the reduction of the number of species. In fact, the problem of reducing the number of reactions is a superset of the problem of reducing the number of species. The interest, however, in the species reduction problem is based on the fact that the number of species is expected to be much smaller than the number of reactions. Therefore, the associated optimization problem will be, in principle, easier to solved.

Unlike methods based on quasi steady-state (QSS) or partial equilibrium (PE) assumptions, once a specie is determined to be redundant, it is removed from the list of species of the mechanism and no equations (equilibrium or other) are associated with it.

The mathematical formulation of the species reduction problem is as follows:

$$\min_{\lambda \in \mathcal{G}^{N_S}} \sum_{s=1}^{N_S} \lambda_s$$

subject to

$$\mathcal{L} = \left(\sum_{k \in \mathcal{K}} \omega_K \int_0^Z \left(\frac{y_k^{\text{reduced}}(z) - y_k^{\text{detailed}}(z)}{y_k^{\text{detailed}}(z)} \right)^2 dz \right.$$

$$+ \omega_T \int_0^Z \left(\frac{T^{\text{reduced}}(z) - T^{\text{detailed}}(z)}{T^{\text{detailed}}(z)} \right)^2 dz$$

$$\left. + \omega^\tau \int_0^Z \left(\frac{\tau^{\text{reduced}}(z) - \tau^{\text{detailed}}(z)}{\tau^{\text{detailed}}(z)} \right)^2 dz \right)^{1/2} \leq \delta$$

$$\frac{dy_s^p(z)}{dz} = \sum_{r=1}^{N_R} \alpha_{rs} R_r, \quad s = 1, \ldots, N_s, \quad p = \{\text{reduced}\} \quad (4)$$

$$\frac{dT^p(z)}{dz} = \sum_{s=1}^{N_S} H_s^g \frac{dy_s^p(z)}{dz}, \quad p = \{\text{reduced}\}$$

$$\frac{d\tau^p(z)}{dz} = \frac{\rho}{c_0}, \quad p = \{\text{reduced}\}$$

$$R_r = \left(\prod_{s=1}^{N_s} \langle \lambda_s \rangle_r \right) \left(\mathcal{K}_F^r \prod_{s=1}^{N_S} [X_s]^{\alpha'_{rs}} - \mathcal{K}_R^r \prod_{s=1}^{N_S} [X_s]^{\alpha''_{rs}} \right),$$

$$r = 1, \ldots, N_R$$

$$\mathcal{K}_F^r = k_F^r e^{-E_F^r/RT}$$

$$\mathcal{K}_R^r = k_R^r e^{-E_R^r/RT}$$

$$\langle \lambda_s \rangle_r = \begin{cases} \lambda_s & \text{if specie } s \text{ participates in reaction } r \\ 0 & \text{otherwise} \end{cases}$$

$$\lambda \in \mathcal{G}^{N_S} = \{0, 1\}^{N_S}$$

The introductions of the binary variable λ_s determines whether specie s is present in the reduced network. If the specie is to be neglected, then $\lambda_s = 0$ and all reaction rates which involve that specie will be set to 0.

As was mentioned above, the problem of reducing the number of reactions is a superset of the problem of reducing the number of species. If we analyze the results of the H_2 combustion networks as well as the CO/H_2 combustion problem that were presented earlier, we observe the following:

H_2 Combustion: Model I. Analyzing the achieved reduction for $\delta = 10^{-3}$, one observes that the reactions removed involve H_2O_2, and that H_2O_2 only participated in these reactions. Therefore, one can argue that, as a byproduct of the reaction reduction, the species are also reduced by one. When the problem defined in Eq. 4 is solved for the same value of δ, a solution is recovered which identifies that specie H_2O_2 can be dropped. Obviously, the number of reactions is only reduced by 4, that is, the number of reactions that involve the redundant specie.

H_2 Combustion: Model II. This is an interesting problem, because when we try to reduce the number of reactions, no species are determined to be unimportant. That can be explained by the fact that the detailed Model II and Model I differ substantially in the way that the ignition period is described and, as a result, the more accurate description of Model II requires all species to be present. Of course, when the same model for H_2 combustion is analyzed via the species minimization approach, it is revealed that indeed no species

can be removed from the list, once again deriving similar conclusions as the reactions minimization approach.

CO/H₂/Air Combustion. Once again, the species minimization approach reveals that species H_2O_2, HCO, CH_2O are redundant ones. The same conclusion would have been reached if one were to analyze the reaction reduction results obtained.

Two-State Reduction

The key computational advantage of addressing the species reduction problem, as opposed to the reaction reduction problem, is that the number of species is by far smaller than the number of reactions. A combination of the two would be necessary, because the redundant species participate in a large number of reactions that would be removed. Therefore, a two level approach will offer substantial advantages. The approach was tested on the GRI mechanism (Bowman et al., 1995) without the NO chemistry. The detailed mechanism contains 31 reacting species and 177 reactions. A two-stage approach was used to analyze the derivation of a reduced mechanism for a stoichiometric mixture of CH_4 and air at 1,000 K. The target error was $\delta = 10^{-2}$. In the first stage, the species reduction problem determined the species C, CH, CH_2, CH_2S, C_2H, C_2H_2, C., *C*O, C*C*O and HC#COH to be redundant. Therefore, the number of species is reduced to 21 and the number of reactions is reduced to 100. The reaction reduction problem was subsequently solved in which a total of 67 reactions were determined to be important. For a typical plug-flow calculation, a reduction in computation time of 50% is achieved when the 21 species, 67 reactions mechanism is used. The resulting reduced mechanism predicts with great accuracy the detailed one, as shown in Figure 9.

Amplifying Reaction Effects

In the formalism thus far presented, we assumed that a binary variable was defined so as to determine the existence/nonexistence of specific reactions. An extension to the basic model is now presented that allows to further simplify the reduced mechanism by allowing the amplification of

Figure 9. Complete vs. reduced model.

T profile for stoichiometric CH_4/Air combustion.

selected reactions. In such an expanded model, each reaction is assigned two variables: a binary one λ determining whether that reaction should participate in the model, and a continuous one μ which represents an amplification of the contribution of this reaction. The suggested formulation is presented in Eq. 5

$$\min_{\lambda \in \mathcal{I}^{N_R}, \mu \in \mathfrak{M}} \sum_{r=1}^{N_R} \lambda_r$$

subject to

$$\mathcal{L} = \left(\sum_{k \in \mathcal{K}} \omega_K \int_0^Z \left(\frac{y_k^{\text{reduced}}(z) - y_k^{\text{detailed}}(z)}{y_k^{\text{detailed}}(z)} \right)^2 dz \right.$$

$$+ \omega_T \int_0^Z \left(\frac{T^{\text{reduced}}(z) - T^{\text{detailed}}(z)}{T^{\text{detailed}}(z)} \right)^2 dz$$

$$\left. + \omega_\tau \int_0^Z \left(\frac{\tau^{\text{reduced}}(z) - \tau^{\text{detailed}}(z)}{\tau^{\text{detailed}}(z)} \right)^2 dz \right)^{1/2} \leq \delta$$

$$\frac{dy_s^p(z)}{dz} = \sum_{r=1}^{N_R} \mu_r \lambda_r \alpha_{rs} R_r, \quad s = 1, \dots, N_s, \quad p = \{\text{reduced}\} \quad (5)$$

$$\frac{dT^p(z)}{dz} = \sum_{s=1}^{N_S} H_s^g \frac{dy_s^p(z)}{dz}, \quad p = \{\text{reduced}\}$$

$$\frac{d\tau^p(z)}{dz} = \frac{\rho}{c_0}, \quad p = \{\text{reduced}\}$$

$$R_r = \mathcal{K}_F^r \prod_{s=1}^{N_S} [X_s]^{\alpha'_{rs}} - \mathcal{K}_R^r \prod_{s=1}^{N_S} [X_s]^{\alpha''_{rs}}, \quad r = 1, \dots, N_R$$

$$\mathcal{K}_F^r = k_F^r e^{-E_F^r/RT}$$

$$\mathcal{K}_R^r = k_R^r e^{-E_R^r/RT}$$

$$\mu_j \leq P\lambda_j, \quad j = 1, \dots, N_r$$

$$\lambda \in \mathcal{I}^{N_R} = \{0,1\}^{N_R}, \quad \mu \in \mathfrak{M} \subset \mathfrak{R}_+^{N_R}$$

Table 1 summarizes the comparison between the two models, that is, with and without reaction amplification. The numbers in parentheses denote the amplification factors. The results indicate that additional reductions can be achieved. The overhead, of course, is reflected in the number of variables which increases since now an additional set of continuous variables has to be added.

Concluding Remarks

This article discusses aspects of the problem of reaction mechanism reduction. The focus was on developing reduced mechanisms that maintain the structural integrity of the detailed network over a range of conditions. The problem was cast as an integer programming problem in which the binary decisions are associated with the existence/nonexistence of a given reaction or specie. A performance measure that quantifies the ability of a reduced network to capture important
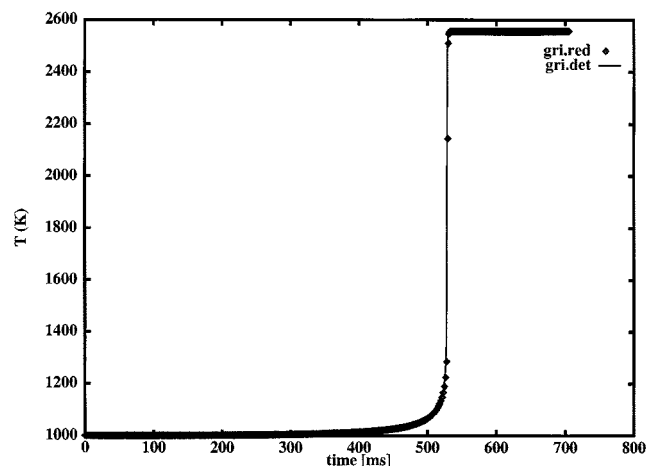
Table 1. Reduced Networks with and without Reaction Amplification

H_2 Model I, $N_R = 20$		H_2 Model II, $N_R = 47$		$CO/H_2/Air$ $N_R = 46$	
Min N_R	Min N_R + Ampl.	Min N_R	Min N_R + Ampl.	Min N_R	Min N_R + Ampl.
1, 2, 3	**1** (**1.026**), 2, 3	1, **2**, 3	1, **2** (**0.733**), 3	1, **3**, 4, **6**	**3** (**1.498**), **6** (**2.481**)
4, 5, 6	4, 5, **6** (**5.524**)	4, 5, 7	5, 9, **10** (**1.620**)	**10**, 12, 13	**10** (**1.006**), **17** (**0.648**)
7, 9, 16	**7** (**0.847**), 9	9, **10**, 17	30, **31** (**0.714**)	14, 15, **17**	32 (**0.937**), **34** (**0.724**)
		19, 20, 27	**40** (**0.179**)	22, 24, 25	**38** (**0.849**)
		29, 30, **31**	**41** (**1.640**)	**32**, **34**, **38**	
		39, **40**, **41**			
$N_R = 9$	$N_R = 8$	$N_R = 18$	$N_R = 10$	$N_R = 16$	$N_R = 7$

features of the detailed one is defined. The measure is defined over a set of important observables such as key reactants and/or products, temperature, and residence time. Based on the obtained results, some important points have to be made:

(1) The performance measure strongly reflects the bias of the decision-maker.

(2) The reduced mechanism strongly depends on the initial conditions used during the reduction process. However, the framework which was presented has been expanded to incorporate flexibility issues so as to determine an extended region of initial conditions over which the reduction is valid (Ierapetritou and Androulakis, 1999).

The results point to a reduction approach that does unravel important dependencies and key reaction pathways. The computational requirement increases as the size of the problem increases pointing towards the direction of developing specialized decomposition schemes for the efficient solution of large-scale nonlinear integer optimization problems. Finally, the solution to global optimality of integer programming problems with models described by differential equations has to be further explored so as to provide a definite answer to the issue of determining global as opposed to local solutions, if the latter exist.

Overall, a systematic approach was presented for mechanism reduction. The approach allows the user to define explicitly a set of targets, and these will subsequently guide the reduction. Both the reaction and species reduction problem were formulated in a similar way and are both solved efficiently using a Branch & Bound algorithm. The extension of the basic model utilizing the amplification parameters allowed further reduction by enhancing the importance of various reaction steps. Finally, the approach naturally provides a framework for addressing the very important question of *a priori* determining the range of validity of the reduced mechanism via flexibility analysis.

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Appendix 1: H_2 Combustion Network I

Reactions Considered	$k = AT**b\exp(-E/RT)$			Reactions Considered	$k = AT**b\exp(-E/RT)$		
	A	b	E		A	b	E
1. $H_2 + O_2 \leftrightarrow 2\,OH$	1.70×10^{13}	0.00	47,780	11. $H + H + H_2 \leftrightarrow H_2 + H_2$	9.20×10^{16}	-0.60	0
2. $OH + H_2 \leftrightarrow H_2O + H$	1.17×10^9	1.30	3,626	12. $H + H + H_2O \leftrightarrow H_2 + H_2O$	6.00×10^{19}	-1.20	0
3. $O + OH \leftrightarrow O_2 + H$	4.00×10^{14}	-0.50	0	13. $H + OH + M \leftrightarrow H_2O + M$	1.60×10^{22}	-2.00	0
4. $O + H_2 \leftrightarrow OH + H$	5.06×10^4	2.70	6,290	H_2O Enhanced by 5.000			
5. $H + O_2 + M \leftrightarrow HO_2 + M$	3.61×10^{17}	-0.70	0	14. $H + O + M \leftrightarrow OH + M$	6.20×10^{16}	-0.60	0
H_2O Enhanced by 1.860×10^1				H_2O Enhanced by 5.000			
H_2 Enhanced by 2.860				15. $O + O + M \leftrightarrow O_2 + M$	1.89×10^{13}	0.00	$-1,788$
N_2 Enhanced by 1.260				16. $H + HO_2 \leftrightarrow H_2 + O_2$	1.25×10^{13}	0.00	0
6. $OH + HO_2 \leftrightarrow H_2O + O_2$	7.50×10^{12}	0.00	0	17. $HO_2 + HO_2 \leftrightarrow H_2O_2 + O_2$	2.00×10^{12}	0.00	0
7. $H + HO_2 \leftrightarrow 2\,OH$	1.40×10^{14}	0.00	1,073	18. $H_2O_2 + M \leftrightarrow OH + OH + M$	1.30×10^{17}	0.00	45,500
8. $O + HO_2 \leftrightarrow O_2 + OH$	1.40×10^{13}	0.00	1,073	19. $H_2O_2 + H \leftrightarrow HO_2 + H_2$	1.60×10^{12}	0.00	3,800
9. $2\,OH \leftrightarrow O + H_2O$	6.00×10^8	1.30	0	20. $H_2O_2 + OH \leftrightarrow H_2O + HO_2$	1.00×10^{13}	0.00	1,800
10. $H + H + M \leftrightarrow H_2 + M$	1.00×10^{18}	-1.00	0				
H_2O Enhanced by 0.000							
H_2 Enhanced by 0.000							

Appendix 2: H_2 Combustion Network II

Reactions Considered	$k = AT**b\exp(-E/RT)$			Reactions Considered	$k = AT**b\exp(-E/RT)$		
	A	b	E		A	b	E
1. $H_2 + O \rightarrow OH + H$	5.12×10^4	2.67	26	21. $2H + M \rightarrow H_2 + M$	1.87×10^{18}	-1.00	0
2. $OH + H \rightarrow H_2 + O$	3.53×10^4	2.62	19	N_2 Enhanced by 4.000×10^{-1}			
3. $H_2 + OH \rightarrow H_2O + H$	1.02×10^8	1.60	14	O_2 Enhanced by 4.000×10^{-1}			
4. $H_2O + H \rightarrow H_2 + OH$	4.52×10^4	1.60	77	H_2O Enhanced by 6.500			
5. $O_2 + H + M \rightarrow HO_2 + M$	2.10×10^{18}	-0.80	0	H_2 Enhanced by 0.000			
N_2 Enhanced by 6.700×10^{-1}				AR Enhanced by 3.500×10^{-1}			
O_2 Enhanced by 4.000×10^{-1}				22. $H_2 + M \rightarrow 2H + M$	6.27×10^{18}	-0.98	437
H_2O Enhanced by 0.000				N_2 Enhanced by 4.000×10^{-1}			
AR Enhanced by 2.800×10^{-1}				O_2 Enhanced by 4.000×10^{-1}			
6. $HO_2 + M \rightarrow O_2 + H + M$	1.16×10^{20}	-1.26	211	H_2O Enhanced by 6.500			
N_2 Enhanced by 6.700×10^{-1}				H_2 Enhanced by 0.000			
O_2 Enhanced by 4.000×10^{-1}				AR Enhanced by 3.500×10^{-1}			
H_2O Enhanced by 0.000				23. $2H + H_2 \rightarrow 2H_2$	9.79×10^{16}	-0.60	0
AR Enhanced by 2.800×10^{-1}				24. $2H_2 \rightarrow 2H + H_2$	3.28×10^{17}	-0.58	437
7. $O_2 + H + H_2O \rightarrow HO_2 + H_2O$	6.89×10^{15}	0.00	-9	25. $H + O + M \rightarrow OH + M$	1.18×10^{19}	-1.00	0
8. $HO_2 + H_2O \rightarrow O_2 + H + H_2O$	3.80×10^{17}	-0.46	203	N_2 Enhanced by 4.000×10^{-1}			
9. $O_2 + H \rightarrow OH + O$	9.76×10^{13}	0.00	62	O_2 Enhanced by 4.000×10^{-1}			
10. $OH + O \rightarrow O_2 + H$	1.45×10^{13}	0.00	3	H_2O Enhanced by 6.500			
11. $H_2O_2 + H \rightarrow HO_2 + H_2$	1.69×10^{12}	0.00	16	AR Enhanced by 3.500×10^{-1}			
12. $HO_2 + H_2 \rightarrow H_2O_2 + H$	1.51×10^9	0.78	84	26. $OH + M \rightarrow H + O + M$	2.73×10^{19}	-1.03	429
13. $H_2O_2 + H \rightarrow OH + H_2O$	1.02×10^{13}	0.00	15	N_2 Enhanced by 4.000×10^{-1}			
14. $OH + H_2O \rightarrow H_2O_2 + H$	6.72×10^7	1.28	296	O_2 Enhanced by 4.000×10^{-1}			
15. $H_2O_2 + O \rightarrow OH + HO_2$	6.62×10^{11}	0.00	17	H_2O Enhanced by 6.500			
16. $OH + HO_2 \rightarrow H_2O_2 + O$	4.07×10^8	0.72	78	AR Enhanced by 3.500×10^{-1}			
17. $H_2O_2 + OH \rightarrow H_2O + HO_2$	7.83×10^{12}	0.00	6	27. $H + OH + M \rightarrow H_2O + M$	5.53×10^{22}	-2.00	0
18. $H_2O + HO_2 \rightarrow H_2O_2 + OH$	4.74×10^{11}	0.45	141	N_2 Enhanced by 4.000×10^{-1}			
19. $H_2O_2(+M) \rightarrow 2\,OH(+M)$	3.00×10^{14}	0.00	203	O_2 Enhanced by 4.000×10^{-1}			
N_2 Enhanced by 4.00×10^{-1}				H_2O Enhanced by 2.540			
O_2 Enhanced by 4.000×10^{-1}				AR Enhanced by 1.500×10^{-1}			
H_2O Enhanced by 6.500				28. $H_2O + M \rightarrow H + OH + M$	1.26×10^{25}	-2.30	503
AR Enhanced by 3.500×10^{-1}				N_2 Enhanced by 4.000×10^{-1}			
Low pressure limit:				O_2 Enhanced by 4.000×10^{-1}			
0.30000×10^{18} 0.00000 0.19040×10^3				H_2O Enhanced by 2.540			
TROE centering:				AR Enhanced by 1.500×10^{-1}			
0.10000×10^1 0.10000×10^1 0.10000×10^1 0.10400×10^4				29. $H + HO_2 \rightarrow H_2 + O_2$	4.28×10^{13}	0.00	6
20. $2\,OH(+M) \rightarrow H_2O_2(+M)$	7.23×10^{13}	-0.37	0	30. $H_2 + O_2 \rightarrow H + HO_2$	2.60×10^{12}	0.48	231
N_2 Enhanced by 4.000×10^{-1}				31. $H + HO_2 \rightarrow 2\,OH$	1.69×10^{14}	0.00	4
O_2 Enhanced by 4.000×10^{-1}				32. $2\,OH \rightarrow H + HO_2$	1.84×10^{10}	0.83	150
H_2O Enhanced by 6.500				33. $H + HO_2 \rightarrow H_2O + O$	3.01×10^{13}	0.00	7
AR Enhanced by 3.500×10^{-1}				34. $H_2O + O \rightarrow H + HO_2$	3.23×10^{11}	0.56	227
Low pressure limit:				35. $2O + M \rightarrow O_2 + M$	5.40×10^{13}	0.00	-7
0.55300×10^{20} -0.76000 0.00000				N_2 Enhanced by 4.000×10^{-1}			
TROE centering:				O_2 Enhanced by 4.000×10^{-1}			
0.10000×10^1 0.10000×10^1 0.10000×10^1 0.10400×10^4				H_2O Enhanced by 6.500			
				AR Enhanced by 3.500×10^{-1}			

Appendix 2 continued

Appendix 2: H₂ Combustion Network II (Continued)

Reactions Considered	$k = AT^{**b}\exp(-E/RT)$ A	b	E	Reactions Considered	$k = AT^{**b}\exp(-E/RT)$ A	b	E
36. $O_2 + M \rightarrow 2O + M$	4.82×10^{16}	-0.43	494	40. $O + H_2O \rightarrow 2OH$	1.49×10^{11}	0.87	75
$\quad N_2$ Enhanced by 4.000×10^{-1}				41. $OH + HO_2 \rightarrow H_2O + O_2$	2.89×10^{13}	0.00	-2
$\quad O_2$ Enhanced by 4.000×10^{-1}				42. $H_2O + O_2 \rightarrow OH + HO_2$	1.19×10^{14}	0.16	290
$\quad H_2O$ Enhanced by 6.500				43. $2HO_2 \rightarrow H_2O_2 + O_2$	4.22×10^{14}	0.00	50
$\quad AR$ Enhanced by 3.500×10^{-1}				44. $H_2O_2 + O_2 \rightarrow 2HO_2$	2.88×10^{16}	-0.29	207
37. $O + HO_2 \rightarrow O_2 + OH$	3.19×10^{13}	0.00	0	45. $2HO_2 \rightarrow H_2O_2 + O_2$	1.32×10^{11}	0.00	-7
38. $O_2 + OH \rightarrow O + HO_2$	1.34×10^{12}	0.43	218	46. $H_2O_2 + O_2 \rightarrow 2HO_2$	9.00×10^{12}	-0.29	150
39. $2OH \rightarrow O + H_2O$	1.51×10^{9}	1.14	0				

Appendix 3: CO/H₂/Air Combustion Network

$k = AT^{**b}\exp(-E/RT)$

Left column

1. $2O + M \leftrightarrow O_2 + M$ — $A = 1.20 \times 10^{17}$, $b = -1.00$, $E = 0$
   - H_2 Enhanced by 2.400
   - H_2O Enhanced by 1.540×10^{1}
   - CO Enhanced by 1.750
   - CO_2 Enhanced by 3.600
   - AR Enhanced by 8.300×10^{-1}
   - CO_2 Enhanced by 3.600
   - AR Enhanced by 8.300×10^{-1}
2. $O + H + M \leftrightarrow OH + M$ — $A = 5.00 \times 10^{17}$, $b = -1.00$, $E = 0$
   - H_2 Enhanced by 2.000
   - H_2O Enhanced by 6.000
   - CO Enhanced by 1.500
   - CO_2 Enhanced by 2.000
   - AR Enhanced by 7.000×10^{-1}
3. $O + H_2 \leftrightarrow H + OH$ — $A = 5.00 \times 10^{4}$, $b = 2.67$, $E = 6{,}290$
4. $O + HO_2 \leftrightarrow OH + O_2$ — $A = 2.00 \times 10^{13}$, $b = 0.00$, $E = 0$
5. $O + H_2O_2 \leftrightarrow OH + HO_2$ — $A = 9.63 \times 10^{6}$, $b = 2.00$, $E = 4{,}000$
6. $O + CO + M \leftrightarrow CO_2 + M$ — $A = 6.02 \times 10^{14}$, $b = 0.00$, $E = 3{,}000$
   - H_2 Enhanced by 2.000
   - O_2 Enhanced by 6.000
   - H_2O Enhanced by 6.000
   - CO Enhanced by 1.500
   - CO_2 Enhanced by 3.500
   - AR Enhanced by 5.000×10^{-1}
7. $O + HCO \leftrightarrow OH + CO$ — $A = 3.00 \times 10^{13}$, $b = 0.00$, $E = 0$
8. $O + HCO \leftrightarrow H + CO_2$ — $A = 3.00 \times 10^{13}$, $b = 0.00$, $E = 0$
9. $O + CH_2O \leftrightarrow OH + HCO$ — $A = 3.90 \times 10^{13}$, $b = 0.00$, $E = 3{,}540$
10. $O_2 + CO \leftrightarrow O + CO_2$ — $A = 2.50 \times 10^{12}$, $b = 0.00$, $E = 47{,}800$
11. $O_2 + CH_2O \leftrightarrow HO_2 + HCO$ — $A = 1.00 \times 10^{14}$, $b = 0.00$, $E = 40{,}000$
12. $H + O_2 + M \leftrightarrow HO_2 + M$ — $A = 2.80 \times 10^{18}$, $b = -0.86$, $E = 0$
    - O_2 Enhanced by 0.000
    - H_2O Enhanced by 0.000
    - CO Enhanced by 7.500×10^{-1}
    - CO_2 Enhanced by 1.500
    - N_2 Enhanced by 0.000
    - AR Enhanced by 0.000
13. $H + 2O_2 \leftrightarrow HO_2 + O_2$ — $A = 3.00 \times 10^{20}$, $b = -1.72$, $E = 0$
14. $H + O_2 + H_2O \leftrightarrow HO_2 + H_2O$ — $A = 9.38 \times 10^{18}$, $b = -0.76$, $E = 0$
15. $H + O_2 + N_2 \leftrightarrow HO_2 + N_2$ — $A = 3.75 \times 10^{20}$, $b = -1.72$, $E = 0$
16. $H + O_2 + AR \leftrightarrow HO_2 + AR$ — $A = 7.00 \times 10^{17}$, $b = -0.80$, $E = 0$
17. $H + O_2 \leftrightarrow O + OH$ — $A = 8.30 \times 10^{13}$, $b = 0.00$, $E = 14{,}413$
18. $2H + M \leftrightarrow H_2 + M$ — $A = 1.00 \times 10^{18}$, $b = -1.00$, $E = 0$
    - H_2 Enhanced by 0.000
    - H_2O Enhanced by 0.000
    - CO_2 Enhanced by 0.000
    - AR Enhanced by 6.300×10^{-1}
19. $2H + H_2 \leftrightarrow 2H_2$ — $A = 9.00 \times 10^{16}$, $b = -0.60$, $E = 0$
20. $2H + H_2O \leftrightarrow H_2 + H_2O$ — $A = 6.00 \times 10^{19}$, $b = -1.25$, $E = 0$
21. $2H + CO_2 \leftrightarrow H_2 + CO_2$ — $A = 5.50 \times 10^{20}$, $b = -2.00$, $E = 0$
22. $H + OH + M \leftrightarrow H_2O + M$ — $A = 2.20 \times 10^{22}$, $b = -2.00$, $E = 0$
    - H_2 Enhanced by 7.300×10^{-1}
    - H_2O Enhanced by 3.650
    - AR Enhanced by 3.800×10^{-1}
23. $H + HO_2 \leftrightarrow O + H_2O$ — $A = 3.97 \times 10^{12}$, $b = 0.00$, $E = 671$
24. $H + HO_2 \leftrightarrow O_2 + H_2$ — $A = 2.80 \times 10^{13}$, $b = 0.00$, $E = 1{,}068$

Right column

25. $H + HO_2 \leftrightarrow 2OH$ — $A = 1.34 \times 10^{14}$, $b = 0.00$, $E = 635$
26. $H + H_2O_2 \leftrightarrow HO_2 + H_2$ — $A = 1.21 \times 10^{7}$, $b = 2.00$, $E = 5{,}200$
27. $H + H_2O_2 \leftrightarrow OH + H_2O$ — $A = 1.00 \times 10^{13}$, $b = 0.00$, $E = 3{,}600$
28. $H + HCO(+M) \leftrightarrow CH_2O(+M)$ — $A = 1.09 \times 10^{12}$, $b = 0.48$, $E = -260$
    - Low pressure limit: 0.13500×10^{25} -0.25700×10^{11} 0.14250×10^{4}
    - TROE centering: 0.78240 0.27100×10^{3} 0.27550×10^{4} 0.65700×10^{4}
    - H_2 Enhanced by 2.000
    - H_2O Enhanced by 6.000
    - CO Enhanced by 1.500
    - CO_2 Enhanced by 2.000
    - AR Enhanced by 7.000×10^{-11}
29. $H + HCO \leftrightarrow H_2 + CO$ — $A = 7.34 \times 10^{13}$, $b = 0.00$, $E = 0$
30. $H + CH_2O \leftrightarrow HCO + H_2$ — $A = 2.30 \times 10^{10}$, $b = 1.05$, $E = 3{,}275$
31. $H_2 + CO(+M) \leftrightarrow CH_2O(+M)$ — $A = 4.30 \times 10^{7}$, $b = 1.50$, $E = 79{,}600$
    - Low pressure limit: 0.50700×10^{28} -0.34200×10^{1} 0.84350×10^{5}
    - TROE centering: 0.93200 0.19700×10^{3} 0.15400×10^{4} 0.10300×10^{5}
    - H_2 Enhanced by 2.000
    - H_2O Enhanced by 6.000
    - CO Enhanced by 1.500
    - CO_2 Enhanced by 2.000
    - AR Enhanced by 7.000×10^{-1}
32. $OH + H_2 \leftrightarrow H + H_2O$ — $A = 2.16 \times 10^{8}$, $b = 1.51$, $E = 3{,}430$
33. $2OH(+M) \leftrightarrow H_2O_2(+M)$ — $A = 7.40 \times 10^{13}$, $b = -0.37$, $E = 0$
    - Low pressure limit: 0.23000×10^{19} -0.90000 -0.17000×10^{4}
    - TROE centering: 0.73460 0.94000×10^{2} 0.17560×10^{4} 0.51820×10^{4}
    - H_2 Enhanced by 2.000
    - H_2O Enhanced by 6.000
    - CO Enhanced by 1.500
    - CO_2 Enhanced by 2.000
    - AR Enhanced by 7.000×10^{-1}
34. $2OH \leftrightarrow O + H_2O$ — $A = 3.57 \times 10^{4}$, $b = 2.40$, $E = -2{,}110$
35. $OH + HO_2 \leftrightarrow O_2 + H_2O$ — $A = 2.90 \times 10^{13}$, $b = 0.00$, $E = -500$
36. $OH + H_2O_2 \leftrightarrow HO_2 + H_2O$ — $A = 1.75 \times 10^{12}$, $b = 0.00$, $E = 320$
37. $OH + H_2O_2 \leftrightarrow HO_2 + H_2O$ — $A = 5.80 \times 10^{14}$, $b = 0.00$, $E = 9{,}560$
38. $OH + CO \leftrightarrow H_2 + CO_2$ — $A = 4.76 \times 10^{7}$, $b = 1.23$, $E = 70$
39. $OH + HCO \leftrightarrow H_2O + CO$ — $A = 5.00 \times 10^{13}$, $b = 0.00$, $E = 0$
40. $OH + CH_2O \leftrightarrow HCO + H_2O$ — $A = 3.43 \times 10^{9}$, $b = 1.18$, $E = -447$
41. $2HO_2 \leftrightarrow O_2 + H_2O_2$ — $A = 1.30 \times 10^{11}$, $b = 0.00$, $E = -1{,}630$
42. $2HO_2 \leftrightarrow O_2 + H_2O_2$ — $A = 4.20 \times 10^{14}$, $b = 0.00$, $E = 12{,}000$
43. $HO_2 + CO \leftrightarrow OH + CO_2$ — $A = 1.50 \times 10^{14}$, $b = 0.00$, $E = 23{,}600$
44. $HO_2 + CH_2O \leftrightarrow HCO + H_2O_2$ — $A = 1.00 \times 10^{12}$, $b = 0.00$, $E = 8{,}000$
45. $HCO + H_2O \leftrightarrow H + CO + H_2O$ — $A = 2.24 \times 10^{18}$, $b = -1.00$, $E = 17{,}000$
46. $HCO + M \leftrightarrow H + CO + M$ — $A = 1.87 \times 10^{17}$, $b = -1.00$, $E = 17{,}000$
    - H_2 Enhanced by 2.000
    - H_2O Enhanced by 0.000
    - CO Enhanced by 1.500
    - CO_2 Enhanced by 2.000
47. $HCO + O_2 \leftrightarrow HO_2 + CO$ — $A = 7.60 \times 10^{12}$, $b = 0.00$, $E = 400$