

## Mechanism Reduction for the Oscillatory Oxidation of Hydrogen: Sensitivity and Quasi-Steady-State Analyses

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A strategy for reducing complex chemical reaction mechanisms is developed and illustrated with reference to the oscillatory  $H_2 + O_2$  system in a CSTR in the region of the second explosion limit. The approach involves the identification of redundant species via rate sensitivity analysis and of redundant reactions by the principal component analysis of the rate sensitivity matrix. Temperature sensitivity analysis is also employed and the application of the quasi-steady-state approximation is discussed briefly and used in the final stages of the reduction. The above procedures are shown to assist the understanding of the underlying mechanisms of the reaction for the chosen conditions and the competition between branching steps during oscillatory ignitions is discussed. The reduced mechanism is compared with models discussed elsewhere.

### NOMENCLATURE

$k_i$	$m$ th order rate constant, (molecule $cm^{-3}$ ) $^{1-m}$ $s^{-1}$
$A$	preexponential factor, (molecule $cm^{-3}$ ) $^{1-m}$ $s^{-1}$
$E$	activation energy, $J mol^{-1}$
$R$	gas constant, $J K^{-1} mol$
$T$	gas temperature, $K$
$T_a$	ambient temperature, $K$
$C_p$	specific heat capacity at constant pressure, $J K^{-1} kg^{-1}$
$C_i$	species concentration, molecule $cm^{-3}$
$t_{res}$	residence time of reactor, $s$
$\rho$	molar flow rate, $mol^{-1}$
$p$	pressure, torr
$\nu_{ij}$	stoichiometric number,
$R_j$	rate of reaction $j$ , molecule $cm^{-3} s^{-1}$
$\sigma$	density, $kg cm^{-3}$
$V$	volume, $cm^3$
$t$	time, $s$
$\Delta H$	enthalpy of reaction, $J molecule^{-1}$
$\chi$	heat transfer coefficient, $W cm^{-2} K^{-1}$
$S$	surface area, $cm^2$

### INTRODUCTION

Combustion reactions are among the most complex chemical processes, containing combinations of initiation, propagation, chain branching, and termination steps. So far much attention has been directed to understanding such reaction mechanisms in their fullest form. Reliable rate coefficient data for component elementary reactions is increasingly available [1] and, at least for the high-temperature combustion of simple fuels, realistic, comprehensive mechanisms can now be formulated that give good agreement with experimental results [2]. However, an understanding of the key interactions in combustion processes is not always easily discerned in such large comprehensive schemes. It is often more instructive to reduce a mechanism to its minimum in order to see how species interact and how coupling can occur between reactions. Such reduced mechanisms also have the advantage that they require less computing time, which is often an important criterion in cases such as computational fluid dynamic calculations of turbulent combustion. In addition, recent advances in techniques, such as path following and stability analysis for steady-state and periodic solutions, can greatly reduce the time taken to explore

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the global behavior of a system, but can be applied only to systems of low dimensionality [3, 4].

Over recent years many methods have become available for the reduction of large mechanisms and have been used successfully in many areas. Such methods include redundant species identification, sensitivity analysis (for concentrations, reaction rates, or temperature) [5-7, 8], quasi-steady-state approximations (QSSA) [9, 10], singular perturbation analysis [11, 12] and species lumping [13, 14]. The present work is part of a program whose aim is to develop a systematic approach to mechanism reduction. Rate sensitivity analysis and the application of the QSSA have been chosen and this article describes the systematic application of these methods to a hydrogen oxidation system in a continuously stirred tank reactor or CSTR via the following steps:

1. Formulation of a full model and decision about important species and reaction features.
2. Identification of redundant species.
3. Identification of redundant reactions via principal component analysis of the rate sensitivity matrix.
4. Investigation of temperature sensitivities.
5. Application of the quasi-steady-state approximation.
6. Comparison of the reduced model with the full model and investigation of its limitations.

Although the  $H_2 + O_2$  system is one of the simplest combustion schemes it shows interesting oscillatory behavior in a CSTR at midrange temperatures and pressures of around 700 K and 30 torr, respectively (i.e., in the region of the second explosion limit) where there is a wealth of experimental results [3, 15, 16]. Oscillating reactions constitute a particularly stringent test of mechanism reduction procedures and so provide an ideal vehicle for the development of a systematic approach.

Previous work on the systematic reduction of the hydrogen oxygen scheme has focused mainly on single ignition phenomena and on flame calculations [9, 11, 17, 18] and has used mainly concentration sensitivity methods. All reduced models for oscillatory systems have

been formulated in an heuristic way on the basis of "experience" of the reaction. Here it is demonstrated that a systematic approach can not only reduce a mechanism but can lead to an improved understanding of the relationships between the elementary reactions involved. Comparisons are made with previous reduced models for both oscillatory [3, 19] and ignition systems [17]. A set of core reactions is identified that is an essential part of the model over a wide range of conditions. We do not seek to analyse the full range of possible pressures and mixtures for the reaction but have concentrated on the three main qualitative regions near the second limit for stoichiometric mixtures. We have used these conditions to illustrate the reduction technique, to highlight its problems and to demonstrate its uses.

## FULL MODEL AND REACTION FEATURES

The full reaction mechanism used in the present analysis consists of 47 steps involving 9 species, as is shown in Table 1 [20]. The third body  $M$  is assumed to be made up from the molecular species  $H_2$ ,  $O_2$ , and  $H_2O$  with relative efficiencies of 1:0.4:6, respectively, for all reactions [21]. Although the chemistry is derived from the original Dougherty and Rabitz scheme, the rate data have been updated and have, where possible, been obtained from the latest EEC evaluation tables [1]. The sources for other reaction rate data are shown in Table 1. The wall termination rate constants,  $k_7 - k_{10}$ , were taken from a previous analysis of  $H_2/O_2$  oscillations in a CSTR [19]. Their equivalence is somewhat unrealistic in view of the differences in the diffusion coefficients and surface reactivities of the radicals involved. The treatment of surface termination possibly represents a weakness in the full model and may lead to some deviations from experimental behaviour. The aim of the present work is, however, to develop reduction methods and the primary concern is the comparison between full and reduced models.

The rate constant for each reaction is in the form  $k_i = AT^n \exp(-E/RT)$  with units  $(\text{mole cm}^{-3})^{1-m} \text{s}^{-1}$  for an  $m$ th order reaction. The temperature dependencies and thermochemical data are described by polynomial fits

TABLE I  
Full Reaction Mechanism, Rate Data, and Sources

Reaction no	Reaction	$3A/(\text{cm}^3 \text{ molecule}^{-1})^{1-m} \text{ s}^{-1}$	$n$	$(E/R)/K$	Reference
1	$\text{O} + \text{HO}_2 \rightarrow \text{O}_2 + \text{OH}$	$2.90 \times 10^{-11}$	0	-200	[30]
2	$\text{H}_2 + \text{O}_2 \rightarrow \text{H} + \text{HO}_2$	$2.40 \times 10^{-10}$	0	28500	[30]
3	$\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}$	$1.70 \times 10^{-16}$	1.60	1660	[1]
4	$\text{O}_2 + \text{H} \rightarrow \text{OH} + \text{O}$	$3.30 \times 10^{-10}$	0	8460	[1]
5	$\text{H}_2 + \text{O} \rightarrow \text{H} + \text{OH}$	$8.50 \times 10^{-20}$	2.67	3160	[1]
6	$\text{O}_2 + \text{H} + \text{M} \rightarrow \text{M} + \text{HO}_2$	$1.37 \times 10^{-32}$	0	-500	[31]
7	$\text{H} \rightarrow \text{WALL}$	75	0	0	[19]
8	$\text{O} \rightarrow \text{WALL}$	75	0	0	[19]
9	$\text{OH} \rightarrow \text{WALL}$	75	0	0	[19]
10	$\text{HO}_2 \rightarrow \text{WALL}$	75	0	0	[19]
11	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$3.10 \times 10^{-12}$		755	[1]
12	$\text{O}_2 + \text{OH} \rightarrow \text{O} + \text{HO}_2$	$3.70 \times 10^{-11}$	0	26500	[30]
13	$\text{H} + \text{HO}_2 \rightarrow 2\text{OH}$	$2.80 \times 10^{-10}$	0	440	[1]
14	$\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}$	$5.00 \times 10^{-11}$	0	866	[1]
15	$\text{HO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}_2 + \text{H}$	$5.00 \times 10^{-11}$	0	13100	[30]
16	$\text{HO}_2 + \text{H} \rightarrow \text{H}_2 + \text{O}_2$	$7.10 \times 10^{-11}$	0	710	[30]
17	$\text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{OH} + \text{M}$	$8.00 \times 10^{-07}$	0	22900	[31]
18	$\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{H}_2 + \text{HO}_2$	$2.80 \times 10^{-12}$	0	1890	[30]
19	$\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{H}_2\text{O} + \text{OH}$	$1.70 \times 10^{-11}$	0	1800	[30]
20	$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$1.30 \times 10^{-11}$	0	670	[1]
21	$\text{H}_2\text{O}_2 + \text{O} \rightarrow \text{OH} + \text{HO}_2$	$1.10 \times 10^{-12}$	0	2000	[1]
22	$\text{H}_2\text{O} + \text{O} \rightarrow 2\text{OH}$	$7.60 \times 10^{-15}$	1.30	8605	[30]
23	$\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2$	$7.50 \times 10^{-16}$	1.6	9270	[1]
24	$\text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2$	$7.50 \times 10^{-10}$	-0.5	30	[1]
25	$\text{OH} + \text{H} \rightarrow \text{O} + \text{H}_2$	$8.10 \times 10^{-21}$	2.8	1950	[30]
26	$2\text{OH} \rightarrow \text{O} + \text{H}_2\text{O}$	$2.50 \times 10^{-15}$	1.14	50	[1]
27	$\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$	$3.90 \times 10^{-25}$	-2.0	0	[31]
28	$\text{H} + \text{O} + \text{M} \rightarrow \text{OH} + \text{M}$	$1.30 \times 10^{-32}$	0	0	[30]
29	$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	$8.30 \times 10^{-33}$	0	0	[31]
30	$\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$	$1.60 \times 10^{-23}$	-3.0	0	[30]
31	$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	$2.20 \times 10^{-28}$	-1.5	0	[30]
32	$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	$4.80 \times 10^{-11}$	0	-250	[1]
33	$\text{H}_2\text{O} + \text{M} \rightarrow \text{H} + \text{OH} + \text{M}$	$3.70 \times 10^{-08}$	0	52900	[31]
34	$\text{H}_2 + \text{M} \rightarrow \text{H} + \text{H} + \text{M}$	$1.46 \times 10^{-09}$	0	48300	[31]
35	$\text{O}_2 + \text{M} \rightarrow \text{O} + \text{O} + \text{M}$	$3.01 \times 10^{-06}$	-1.0	60643	[30]
36	$\text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M}$	$2.15 \times 10^{-34}$	0	345	[32]
37	$\text{O}_3 + \text{M} \rightarrow \text{O}_2 + \text{O} + \text{M}$	$5.80 \times 10^{-16}$	0	0	[33]
38	$\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$	$8.00 \times 10^{-12}$	0	2060	[34]
39	$\text{O}_3 + \text{H} \rightarrow \text{O}_2 + \text{OH}$	$2.15 \times 10^{-34}$	0	345	[35]
40	$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$	$1.60 \times 10^{-12}$	0	940	[34]
41	$\text{O}_3 + \text{HO}_2 \rightarrow 2\text{O}_2 + \text{OH}$	$1.10 \times 10^{-14}$	0	500	[34]
42	$\text{HO}_2 + \text{M} \rightarrow \text{O} + \text{OH} + \text{M}$	$5.30 \times 10^{-11}$	0	0	[31]
43	$\text{H}_2\text{O} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{OH}$	$4.70 \times 10^{-11}$	0	16500	[31]
44	$\text{HO}_2 + \text{M} \rightarrow \text{O}_2 + \text{H} + \text{M}$	$2.00 \times 10^{-05}$	-1.18	24363	[30]
45	$2\text{OH} \rightarrow \text{HO}_2 + \text{H}$	$2.00 \times 10^{-11}$	0	20200	[31]
46	$\text{OH} + \text{M} \rightarrow \text{O} + \text{H} + \text{M}$	$4.00 \times 10^{-09}$	0	50000	[30]
47	$\text{H}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{HO}_2$	$9.00 \times 10^{-11}$	0	20000	[30]

developed by the NASA thermodynamics group [22].

In order to compare our results with reduced models used in previous modeling work covering the oscillatory region we have retained as far as possible the same conditions

[19]. The system modeled is the homogeneous reaction of  $\text{H}_2$  with  $\text{O}_2$  in a continuously stirred tank reactor (CSTR) within the region of the second explosion limit. The equations that describe such a homogeneous mixture at a constant volume are the following set of ordinary

differential equations (ODE):

mass balance:

$$\frac{dC_i}{dt} = f_i(C_i, k_j) = \frac{(C_i^0 - C_i)}{t_{res}} - \sum_j \nu_{ij} R_j, \quad (1)$$

energy balance:

$$\sigma C_p \frac{dT}{dt} = \sum_j R_j (-\Delta H_j) - \left( \frac{\sigma C_p}{t_{res}} + \chi S \right) \frac{(T - T_a)}{V}, \quad (2)$$

where  $C_i$  is the concentration of species  $i$  and  $C_i^0$  is the inflow concentration or the steady-state concentration existing in the vessel when no reaction takes place.  $k_j$  is the rate constant for reaction  $j$ ,  $\nu_{ij}$  the stoichiometry of species  $i$  in reaction  $j$  and  $R_j$  the rate of reaction  $j$ , where  $j$  signifies the reaction number as shown in Table 1. The residence time  $t_{res}$  of the reactor is calculated from the formula  $t_{res} = pV/\rho RT_a$ .  $T_a$  is the ambient temperature,  $p$  the pressure,  $V$  the volume, and  $\rho$  the molar flow rate.

The total heat loss term describes both the loss via the flow of gases leaving the reactor and via Newtonian cooling through the walls. A constant value for  $\chi S/V$  was chosen of  $0.8 \times 10^{-3} \text{ Wcm}^{-3} \text{ K}^{-1}$  to be consistent with previous modeling work [15, 21]. The equations were solved numerically using the package SPRINT [23], which has been specially designed for stiff systems such as the  $\text{H}_2 + \text{O}_2$  reaction. The kinetic analysis of the mechanism was performed by the program package KINAL [24].

Experimental studies of the  $\text{H}_2 + \text{O}_2$  system in a CSTR have revealed three main qualitative regions [15, 21, 25]. At low temperatures there is a negligible conversion of  $\text{H}_2$  to water. At high temperatures "strong" ignition takes place accompanied by a sharp rise in temperature. Between these two regions lies an area of repeated ignitions, that is, an oscillatory region. A  $P$ - $T_a$  diagram for a 2:1 mixture of hydrogen to oxygen is shown in Fig. 1a [25].

Typically the thermokinetic oscillations found in this region have a simple periodic waveform and the representative thermocouple trace shown in Fig. 1b reveals a sharp temperature peak with a fast decay followed by a long period of slow change. All of the following calculations refer to a stoichiometric  $\text{H}_2/\text{O}_2$  system in a CSTR at a total pressure of 20 torr and with a residence time of 8 s for consistency with previous experimental and modeling work. We investigated temperatures within the three reaction regions (between 500 and 2000 K) but concentrated mainly on the oscillatory behavior. Although experimentally the reaction is not detectable at low temperatures, it is still worth studying theoretically in order to assess how the important reactions change as the temperature rises. The reaction has been simulated under isothermal and nonisothermal conditions, primarily to investigate the relationship between reduced schemes for the two situations.

Qualitatively the agreement between the full model and experiment is good and Fig. 2 shows a typical simulated temperature profile. The main aim of the present work, however, is to develop methods for generating a reduced model that reproduces the full model behavior. Close agreement with experiment is, therefore, not an important criterion. In assessing the reduced model the period of oscillation is a demanding test and has been chosen as the main feature for comparison between reduced and full models. We also require that the reduced model should match the concentrations of important species as determined by the full model.

## BACKGROUND TO SENSITIVITY METHODS

### Identification of Redundant Species

In the first stage of the reduction process, the modeler selects the *important* species and features of the reaction. In general the important species will include the initial reactants and main products of the reaction. For nonisothermal reactions, temperature may also be an important feature. The reduced model must generate values for the important species and

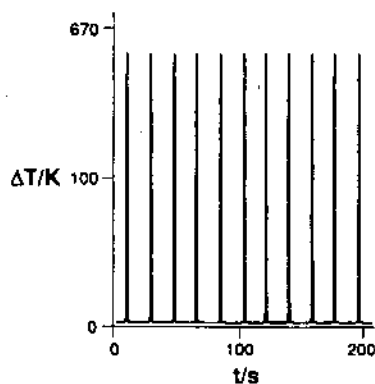
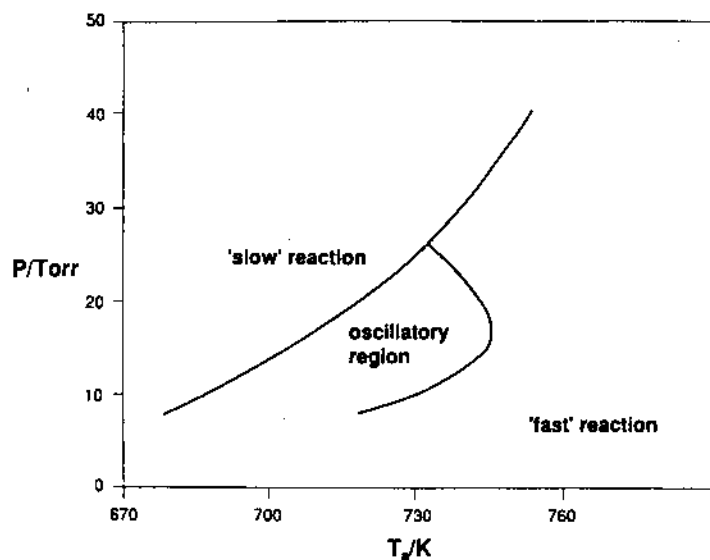


Fig. 1. (a) A typical  $p/T_a$  diagram for a 2:1 mixture of  $H_2:O_2$  in the region of the second explosion limit showing the boundaries between slow reaction, oscillatory ignition, and fast reaction. (b) A thermocouple trace for a total pressure of 17 torr and an ambient temperature  $T_a = 715$  K.

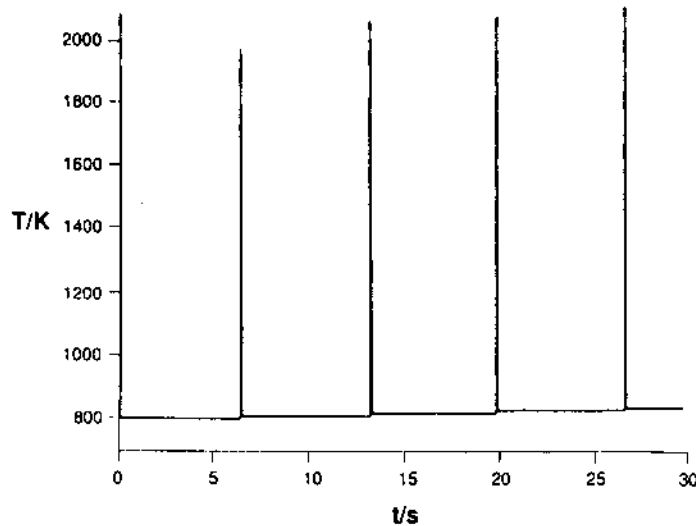


Fig. 2. An example temperature trace from the full 47-step scheme showing a maximum temperature rise of around 1400 K. Pressure = 20 torr,  $T_a = 790$  K.

features, which are in agreement, to a specified accuracy, with those generated by the full model.

The next stage is the identification of *redundant* species, which may be excluded from the model, and *necessary* species, which must be included in order to produce accurate results for the important species. The necessary species will be coupled to the important ones through significant reactions [6]. Redundant species will be those that are not coupled in any significant way to the set of important and necessary species and so can be excluded from the model with only negligible effects on the important concentrations, both directly or indirectly.

The most robust way to find redundant species is simply to remove those reactions whose rates depend directly on a chosen species (i.e., its consuming reactions) and compare the results from a simulation of the resulting model with those from the full model [6]. In this way the effects on both species concentration and reaction features can be assessed. Although this is a very safe method, it is time consuming since it has to be applied to each nonimportant species. A reduced model has to be prepared for each of these species and an integration has to be carried out.

A second method is by the investigation of the Jacobian [6]. A species may be considered redundant if a change in its concentration does not greatly affect  $f_n$ , the rate of production of important and necessary species given. An element of the normalized Jacobian is a measure of this effect. It represents the fractional change in the rate of production of a species  $i$  caused by a fractional change in concentration  $C_j$ . For an  $N$ -membered group of important and necessary species we take the sum of squares of the normalized Jacobian elements:

$$B_i = \sum_{n=1}^N \left( \frac{\partial \ln f_n}{\partial \ln C_i} \right)^2 \quad (3)$$

On the first iteration the higher the value of  $B_i$  the greater the direct effect of a nonimportant species on the set of important ones. At this stage a threshold must be defined. This threshold will be different for each model studied but in most cases a natural limit will exist where

there are several orders of magnitude between the  $B_i$  values for one species and the next; species with  $B_i$  above this limit now become necessary species. Since important species may be coupled through reactions involving several necessary species the identified necessary species have to be admitted to the  $N$ -membered group. The procedure must therefore be iterative in order to account for such indirect effects; on each iteration new necessary species are included in the sum. Usually convergence is achieved after not more than four or five iterations and species still remaining below the threshold are considered redundant.

#### Identification of Redundant Reactions

The second stage of the reduction is the identification of redundant reactions giving the mechanism comprising only important and necessary species. A recent review on sensitivity analysis [7] has shown that one technique employs local concentration sensitivity analysis. An alternative method for investigating sensitivities is via reaction rates, and previous results have shown that rate sensitivity analysis is as effective as concentration sensitivity analysis for mechanism reduction; the results in test cases have been equivalent [8, 26]. Rate sensitivity analysis measures the effect of a perturbation in rate parameter  $k_j$  on the rate of change of species  $i$ . This method has an advantage over concentration sensitivity methods in that the log-normalized rate sensitivity matrix depends algebraically on reaction rates and is easily computed:

$$\bar{F}_{ij} = \frac{\partial \ln f_i}{\partial \ln k_j} = \frac{v_{ij} R_j}{f_i} \quad (4)$$

where  $v_{ij}$  is the stoichiometric number of species  $i$  in reaction  $j$ ,  $R_j$  is the rate of reaction  $j$ , and  $f_i$  is the rate of production of species  $i$ . The computing time required to calculate this matrix is therefore far less than for the concentration sensitivity matrix, and for large mechanisms this can greatly increase the speed of the reduction process.

In the present study there are 9 species and 47 rate parameters and so a large amount of information is contained in the rate sensitivity

matrix which has to be interpreted. An important advance in sensitivity analysis methods has therefore been the application of principal component analysis to sensitivity matrices, which quantifies the importance of reaction groups for the set of important and necessary species [6, 8, 27]. This method has made the interpretation of sensitivity information much simpler and more automatic. A principal component analysis of matrix  $\bar{F}$  is based on the eigenvalue-eigenvector decomposition of the cross-product matrix  $\bar{F}^T \bar{F}$ . The eigenvalues measure the significance of their eigenvectors in the overall mechanism. The eigenvectors represent sets of coupled reactions whose relative contributions are recognized by the relative size of the eigenvector elements.

The eigenvector elements also provide information about the connections between reactions. Defining two thresholds, for the significant eigenvalue and eigenvector elements, therefore provides an automatic way of deciding which parameter groups can be eliminated. The thresholds which have been typically used in the present study have been  $1.00 \times 10^{-4}$  for the eigenvalues and 0.1–0.2 for the eigenvector components, although a more natural threshold may exist in specific cases and should be investigated.

The overall rate sensitivity coefficients [8]

$$V_j = \sum_{i=1}^n \left[ \frac{v_{ij} R_j}{f_i} \right]^2 \quad (5)$$

provide a way of ordering the overall importance of the reactions selected by the principal component analysis at different reaction times.

### Temperature Sensitivity Analysis

Often in combustion modeling the important feature is not species concentration but can be the time to ignition, the maximum temperature rise, or simply the critical ignition temperature. Frequently temperature is a measured quantity in an experiment since measuring species concentrations is more difficult, especially for radicals. The sensitivity of the rate of change of temperature to a change in the rate parameters is therefore of importance. If the reduced model is required only to produce accurate

temperature profiles, then the temperature sensitivities become useful. It is of interest therefore, to compare temperature rate sensitivities with the overall rate sensitivities calculated using the methods referred to in the previous section.

The normalized temperature rate sensitivity is given by

$$\frac{\partial \ln \left( \frac{dT}{dt} \right)}{\partial \ln k_j} = \frac{-\Delta H R_j}{C_p \sigma \frac{dT}{dt}} \quad (6)$$

In the present study it is calculated separately from the usual rate sensitivities and is a simple one-dimensional array. A second approach would be to treat temperature as though it were a concentration and to include it in the eigenvector/eigenvalue analysis.

## RESULTS FROM SENSITIVITY ANALYSIS

The aims of this section are to illustrate the application of the techniques discussed above to the stoichiometric  $H_2 + O_2$  reaction at a pressure of 20 torr and a residence time of 8 s.

### Redundant Species

The important species in this model were chosen as the primary reactions  $H_2$  and  $O_2$ , and the product  $H_2O$ . Table 2 shows examples of redundant species calculations from the full nonisothermal scheme at differing parts of the oscillatory trace and at two different temperatures. They show the effect, on a logarithmic scale, of each species on the rate of production of important and necessary species for the final iteration (i.e., when convergence has been achieved) based on Eq. 3.  $H_2O_2$  and  $O_3$  have by far the lowest  $B_i$  values at all conditions tested and so become the redundant species. Their consuming reactions have the smallest effect on the rates of production of  $H_2$ ,  $O_2$ , and  $H_2O$  both directly and via the necessary species  $H$ ,  $O$ ,  $HO_2$ , and  $OH$  at these conditions. It is also worth noting that  $HO_2$  has a  $B_i$  value below the other remaining radicals at all conditions tested.

TABLE 2

Estimated Effect of Species for the Rate of Change of Necessary Species:  $T = 2311$  K,  $T = 818$  K<sup>a</sup>

2311 K				818 K			
	Species		log $B_i$	Species		log $B_i$	
1	H	+	9.46	OH	+	4.43	
2	H <sub>2</sub>	+	9.45	H <sub>2</sub>	+	4.25	
3	H <sub>2</sub> O	+	9.32	H	+	4.21	
4	OH	+	9.25	H <sub>2</sub> O	+	3.69	
5	O	+	8.50	O	+	3.36	
6	O <sub>2</sub>	+	6.64	O <sub>2</sub>	+	3.27	
7	HO <sub>2</sub>	+	3.16	HO <sub>2</sub>	+	2.89	
8	O <sub>3</sub>	—	-3.66	O <sub>3</sub>	—	-3.87	
9	H <sub>2</sub> O <sub>2</sub>	—	-4.65	H <sub>2</sub> O <sub>2</sub>	—	-4.34	—

<sup>a</sup> — indicates species below the chosen threshold that are therefore redundant.

### Isothermal Conditions

#### Rate Sensitivities and Principal Component Analysis

In principle it may be possible to produce a reduced scheme that models nonisothermal behavior from analysis carried out on an isothermal model. An isothermal system is easier to model since thermodynamic and heat transfer properties can be excluded from the calculations. It is important, however, to make sure that a simulation of the full nonisothermal scheme is first carried out in order to establish the temperature extremes under which the isothermal scheme must be studied. From Figure 2 we see that the extremes of temperature during an oscillation are approximately 700 and 2000 K and we have therefore studied a series of temperatures within this range in order to establish the significant reactions at each temperature. We have also included the study of a low-temperature model at 500 K. The importance of identifying redundant species as a first step has been highlighted above. In order to illustrate this point we have carried out a principal component analysis first including all species in the objective function and second including only the importance and necessary ones.

*Low temperatures.* At low temperatures the reaction is slow and the steady-state concentration of water remains very small. Including only the seven important and necessary species in the objective function shows that at short

times ( $t = 1.0 \times 10^{-6}$  s) only the initiation step 2 and reactions 3 and 4 are significant. As the reaction proceeds a second branching step (reaction 5) becomes important as well as the third body termination step 6 and wall termination steps 7, 8, and 10 at longer reaction times. If all species are included in the objective function, then reactions 11, 36, and 37 are also selected by the principal component analysis even though their removal from the scheme has little effect on the concentrations of the important species.

The same results are obtained from an examination of the overall rate sensitivities considering all species as shown in Table 3 for  $t = 1.0$  s at  $T = 500$  K. Reactions 36 and 37

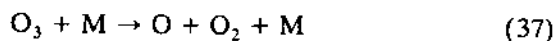
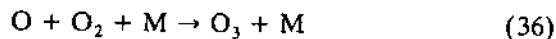


TABLE 3

Ordering of Overall Rate Sensitivities for Isothermal Scheme at  $t = 1.0$  s and 500 K

Order	Reaction Number	Overall Sensitivity
1	4	$2.49 \times 10^9$
2	5	$1.77 \times 10^9$
3	10	$9.25 \times 10^8$
4	2	$6.28 \times 10^8$
5	6	$3.47 \times 10^8$
6	8	$6.02 \times 10^7$
7	3	$2.84 \times 10^7$
8	31	$1.75 \times 10^7$
9	36	$1.22 \times 10^7$
10	7	$4.47 \times 10^6$



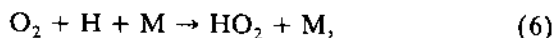
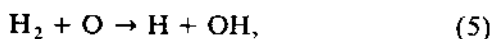
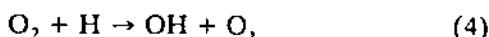
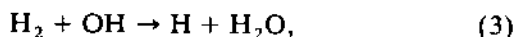
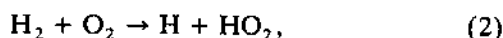
appear in the top ten reactions with sensitivities comparable to that for reaction 3:



Reaction 37 is the reverse of reaction 36 and is rapid under all conditions studied, so that the concentration of  $\text{O}_3$  is kept small and kinetically insignificant. Removing reaction 37 leads to a buildup of  $\text{O}_3$  and therefore produces an effect on the necessary species through other reactions. Removing both reactions however leaves the behavior of the system unchanged. Sensitivity analysis examines the effect of changes in rate coefficients of reactions and quantifies this effect. Although the principal component analysis may contain information about reversible reactions it does not select redundant reactions on this basis. The overemphasis of fast reversible reactions can therefore occur in rate sensitivity analysis. The present analysis demonstrates that, in some cases, such coupled reaction sets can be automatically removed from the model via the identification of redundant species.

Using the results of the principal component analysis, a suitable low-temperature mechanism can be formulated that, for stoichiometric mixtures, includes a core of reactions shown below:

#### Scheme I



This set of reactions is in good agreement with the conclusions of other modeling studies [17, 19, 21].

At low temperatures and low conversions the only other reactions that play a part are the wall reactions of O and  $\text{HO}_2$ . It is interesting to note not only that radical termination at the wall is important but that the major wall termination step switches from the removal of H to the removal of O and  $\text{HO}_2$  as the reac-

tion proceeds. Termination reactions involving OH were not significant at low temperatures.

*High temperatures.* At 1000 K further reactions become significant. Considering the overall sensitivities at  $t = 10^{-2}$  s in Table 4 shows that reaction 13,  $\text{H} + \text{HO}_2 \rightarrow 2\text{OH}$  becomes of major significance at high temperatures and has a higher sensitivity than both reactions 4 and 5. Since  $\text{HO}_2$  is a more stable radical than OH reaction 13 can be effectively considered as a branching step. The product of this reaction, OH, now becomes more significant as is illustrated by the inclusion of reactions 9 and 22-27 in the high temperature mechanism, all of which involve OH. We shall return to a further consideration of this point when we discuss species lifetimes.

Although the third body reaction  $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$  remains the main termination route other termination reactions become important at high temperatures. The system becomes highly sensitive to reaction 16, for example, and to other radical-radical reactions, such as  $\text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2$ , which leads to a reduction in the concentration of the radical pool. These reactions become important only as the reaction proceeds and the radical concentrations buildup. The set of selected reactions at 1000 K therefore consists of the core set of reactions (scheme I) together with the set of reactions shown below:

#### Scheme II

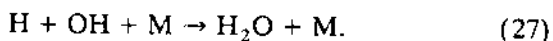
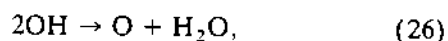
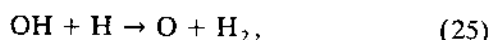
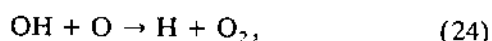
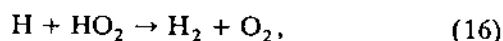
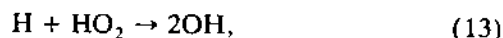
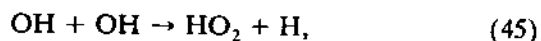
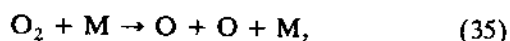
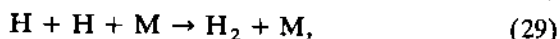
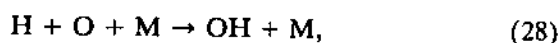
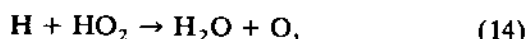


TABLE 4  
Ordering of Overall Rate Sensitivities for Isothermal Scheme at  $t = 1.0 \times 10^{-2}$  s and 1000, 2000 K.

Order	1000 K		2000 K	
	Reaction Number	Overall Sensitivity	Reaction Number	Overall Sensitivity
1	6	$1.37 \times 10^8$	23	$1.13 \times 10^8$
2	13	$7.73 \times 10^7$	3	$1.08 \times 10^8$
3	39	$2.31 \times 10^7$	26	$8.74 \times 10^6$
4	16	$2.90 \times 10^6$	22	$7.72 \times 10^6$
5	14	$1.05 \times 10^6$	6	$3.14 \times 10^6$
6	42	$2.56 \times 10^4$	13	$2.21 \times 10^6$
7	19	$2.14 \times 10^4$	5	$7.64 \times 10^5$
8	11	$1.48 \times 10^4$	25	$4.14 \times 10^5$
9	3	$1.26 \times 10^4$	24	$1.85 \times 10^5$
10	1	$1.14 \times 10^4$	4	$1.85 \times 10^5$
11	23	$9.25 \times 10^3$	16	$1.08 \times 10^5$
12	24	$6.86 \times 10^3$	45	$8.68 \times 10^4$
13	4	$6.16 \times 10^3$	14	$4.60 \times 10^4$
14	6	$5.51 \times 10^3$	2	$1.49 \times 10^4$
15	43	$5.08 \times 10^3$	42	$5.38 \times 10^3$

At 2000 K the following reactions are also selected by the principal component analysis:

#### Scheme III



producing a high-temperature mechanism containing 22 reactions in all. The order of overall sensitivities calculated from Eq. 5 at 2000 K and  $t = 1.0 \times 10^{-2}$  s is given in Table 4.

*Oscillatory region.* Although it has not been possible to isolate isothermal oscillations experimentally for the  $\text{H}_2 + \text{O}_2$  system, it has been shown in previous modeling studies that oscillations have a kinetic origin and so can be generated by an isothermal model. We now examine the oscillatory region at  $T = 790$  K and show how the main reactions switch as the concentrations change in a periodic way. Figure 4a shows the molecular hydrogen concentration. An expanded section of the ignition is shown in Fig. 4b and serves to identify the time points  $t_2$  to  $t_6$  at which the rate sensitivity and principal component analyses were performed.

Table 5 lists the reactions identified as significant using the procedures given in the section on identification of redundant reactions. At  $t_1 = 10.0$  s as hydrogen is replenished in the flow reactor and the radical concentrations are low, the principal components in Table 5 show that only six reactions are of importance (reactions 3–7 and reaction 10). This is equivalent to the "weak" ignition region. In the "strong" ignition stage at time  $t_2$ , reactions 13, 14, 16, and 24 become significant and as the radical concentrations increase and the concentration of  $\text{H}_2$  falls to a minimum at  $t_4$ , reaction 23 becomes an important propagation step. A comparison of the rates of reaction 13 with the combined rates of reactions 4 and 5 in Fig. 3 shows clearly the switch between the two sets of branching reactions as the system moves in and out of ignition.

From the principal component analysis of the rate sensitivity matrix we select 14 reactions in order to reproduce accurately the isothermal oscillations of hydrogen, oxygen, and water found in the full scheme, that is, the core set of reactions (scheme I) along with the following reactions:

#### Scheme IV

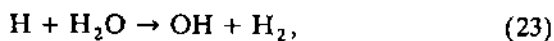
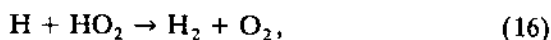
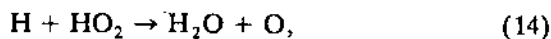


TABLE 5

Comparison of Principal Component Analysis Results in the Oscillatory Region at 790 K.

	$t_1 = 10.00$ s	$t_2 = 14.40$ s	$t_3 = 14.45$ s	$t_4 = 14.50$ s	$t_5 = 14.55$ s	$t_6 = 14.60$ s
3	+	+	+	+	+	+
4	+	+	+	+	+	+
5	+	+	+	+	+	+
6	+	+	+	+	+	+
7	+	+	+	+	+	+
8	-	-	+	-	-	-
9	-	-	+	-	-	-
10	+	+	+	+	+	+
13	-	+	+	+	+	-
14	-	+	+	+	-	-
16	-	+	+	+	-	-
23	-	-	-	-	+	+
24	-	+	-	-	-	-

<sup>a</sup> + indicates the selection of a reaction with thresholds of  $1.00 \times 10^{-4}$  and 0.1 for the eigenvalues and eigenvectors, respectively.



gate the relationship between the isothermal and nonisothermal reduction methods.

**Comparison of Results with the Full Model for Isothermal Reaction**

Figures 4a and 4c compare some results from the 47-step full model and the 14- and 17-step reduced models for  $T = 790$  and  $1000$  K, respectively. In the reduced models the minimum scheme has been chosen at each temperature corresponding to those reactions selected by the principal component analysis, as shown in the previous section. At  $T = 790$  K the reduced model consists of schemes I and IV; at

The next stage of the reduction is to compare the results from the reduced scheme with those from the full model and also to investi-

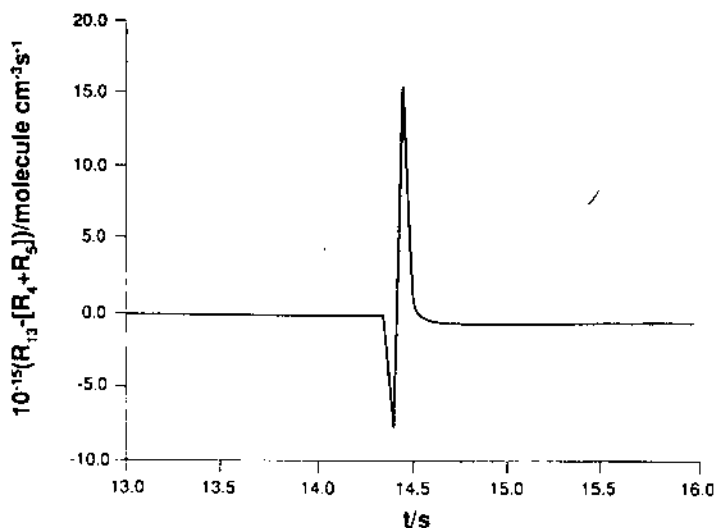


Fig. 3. Comparison of fluxes for reactions 4, 5, and 13 in the reduced isothermal scheme showing how the main branching reaction switches during the ignition.

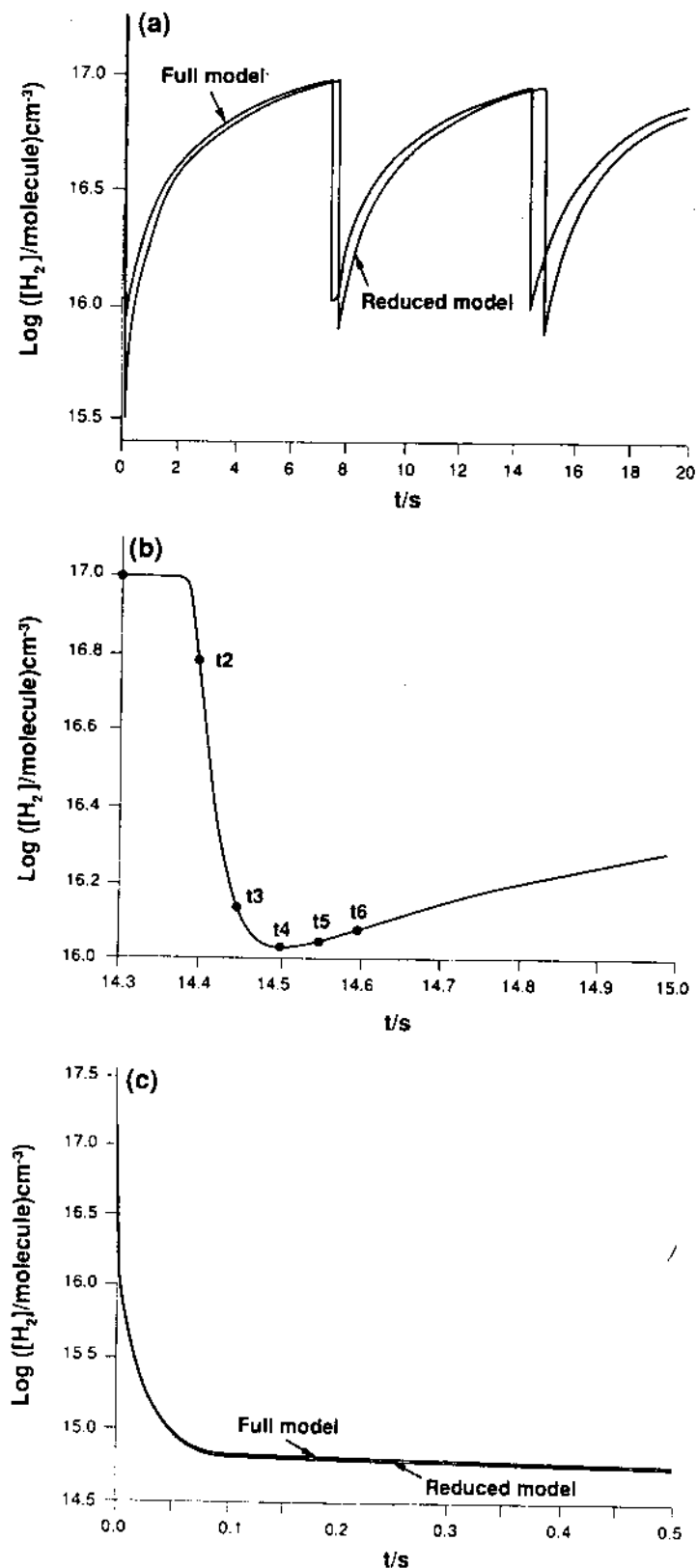


Fig. 4. Comparison of log hydrogen concentrations for full and reduced isothermal schemes (I + IV) and (I + II), respectively. (a)  $T = 790 \text{ K}$ . (b) Closeup of hydrogen peak showing the points at which the sensitivity calculations were carried out. (c)  $T = 1000 \text{ K}$ .

1000 K it consists of schemes I and II. The low-temperature simulation is not included in Fig. 4 since the results are so close as to be indistinguishable.

Results produced by a simulation of the reduced schemes are within 1% of the full model for both times to ignition and steady-state concentrations in both the high- and low-temperature schemes. However, for the oscillatory scheme the percentage deviation at each time point is much greater. This divergence arises because the period of oscillation for the reduced scheme is slightly different from that for the full scheme. The period differs by only a few percent, however, and the qualitative nature of the peaks is satisfactorily reproduced by the reduced scheme.

Reaction 3 is fast and at low temperatures dominates the reactions involving OH. Sensitivity analysis demonstrates, however, that reactions 9 and 24 become significant as the ignition spike develops. Their enhanced contribution arises because of the increase in the lifetime of OH, due to a decrease in  $R_3$  as  $[H_2]$  falls.  $R_{24}$  also increases because of the general increase in radical concentrations in the ignition spike. Figure 5 shows the effect on  $[H_2]$  of removing reactions 9 and 24. They serve to limit the increase in  $[OH]$  during an ignition and hence to reduce the consumption of  $H_2$ , with the result that the recovery of the system is faster with these reactions included and the oscillatory ignition period shorter. The removal of OH radicals is therefore an important factor in determining the period of oscillation. The general importance of wall termination is particularly significant and represents a major limitation in comparing experimental and modelling results since the rate constants for such reactions can vary with the type of vessel used and the coating applied to its walls. In order to match modelling to experiment with any accuracy it seems that the wall constant has to be measured carefully, a consideration that is often either very difficult or is neglected.

### Nonisothermal Modeling

Thus far, reduced models have been applied at different constant temperatures. A nonisother-

mal oscillatory system covers a wide range of temperatures and in this section we develop a reduced model for such a system. A question of interest is whether the sum of the reduced isothermal models, covering the same temperature range, is equivalent to the non-isothermal model.

### Rate Sensitivities and Principal Component Analysis

Nonisothermal analysis has been carried out in the oscillatory region, which covers a wide range of gas temperatures. Again we have used a principal component analysis of the rate sensitivity matrix and we have chosen various times during the ignition and oscillatory region including the maxima and minima as shown in Fig. 6. The objective function again contains the species  $H_2$ ,  $O_2$ ,  $H_2O$ ,  $OH$ ,  $O$ ,  $H$ , and  $HO_2$ . Table 6 lists the reactions selected by the principal component analysis at an ambient temperature of 790 K. The original analysis was carried out at 20 different time points, but certain regions of the oscillation required the same reactions and so for clarity we have included only selected time points in the table of results.

As in the isothermal case we see clearly how certain reactions, in particular radical termination reactions and the reactions of water, become important at high temperatures and high conversions. The highest number of reactions is selected at the peak maximum where the temperature rises above 2000 K. All reactions required by the nonisothermal analysis; reactions 2-10, 13, 14, 16, 22-29, 35, 45 (schemes I + II + III) were featured in one of the isothermal mechanisms. It is therefore possible to produce a reduced scheme for a non-isothermal simulation from an isothermal analysis. Figure 7 compares the full model with schemes (I + II + III) illustrating the excellent agreement.

### Further Reduction and Comparison with Temperature Rate Sensitivity Coefficients

The automatic mechanism reduction methods have led to the reduction of the 47 reaction scheme to schemes involving 6, 14, and 17 reactions at 500, 790, and 1000 K, respectively, and to a 23-step model for nonisothermal oscil-

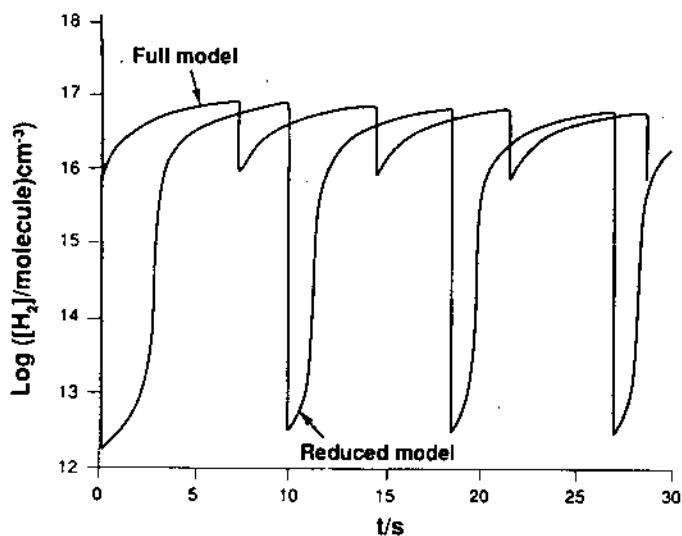


Fig. 5. Comparison of full model with reduced scheme where OH reactions 9 and 24 have been removed, to illustrate the effect of OH concentration on the consumption of hydrogen.  $T = 790$  K.

lations at  $T_a = 790$  K. Having obtained a good reduced scheme by principal component analysis we now wish to eliminate more reactions to obtain a less accurate but smaller reduced model. Overall sensitivities can be used for this task. From Table 6 it can be seen that certain reactions in the reduced scheme are important only during small time periods and if such reactions also have a small overall sensitivity it may be possible to eliminate them. Table 7 shows an example of the top 20 reactions from the overall sensitivities at time  $t_5 = 26.92$  s. Results at other times show that reactions 35 and 14 appear very low in the overall sensitivity order, and reactions 27 and 29 do not appear in the top 20 reactions, even at those

times for which they have been selected by the principal component analysis. It is possible therefore that they can be excluded from the scheme without affecting the important species significantly. Reactions 45 and 37 are also removed since they are important during only small regions of reaction time.

Figure 7 compares the results from this second reduction, under nonisothermal conditions, with both the full and the first reduced scheme (I + II + III). The first reduced scheme is almost identical to the full scheme showing the same period and only a small difference in temperature rise. The second reduction has caused a slight shift in the period of the peaks and also a reduction in the maxi-

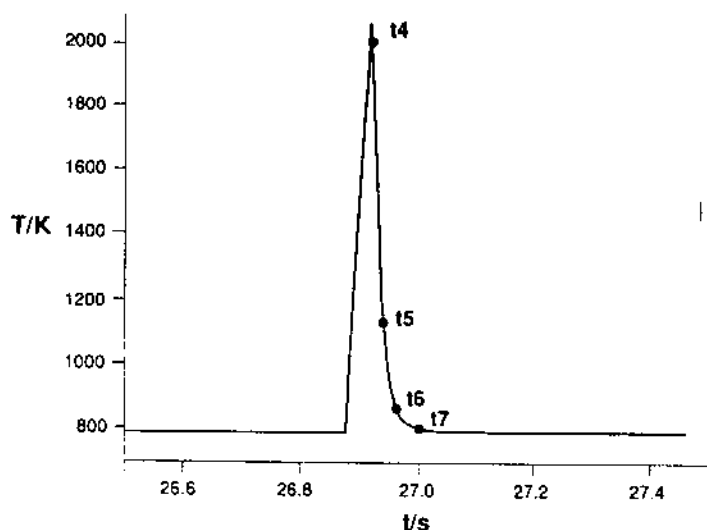


Fig. 6. Closeup of the time points chosen in the ignition region for sensitivity analysis of the nonisothermal scheme:  $T_a = 790$  K.

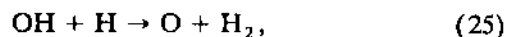
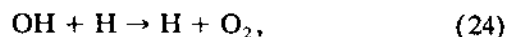
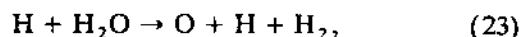
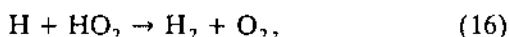
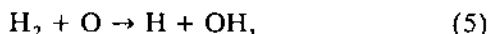
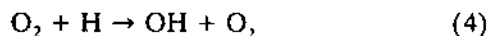
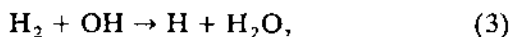
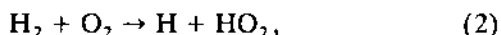
TABLE 6

Reactions Selected by the Principal Component Analysis for Selected Times During the Oscillatory Ignition of the Nonisothermal Scheme at  $T_0 = 790$  K.

	$t_1 = 1.0 \times 10^{-4}$ s $T = 790$ K	$t_2 = 3.5 \times 10^{-2}$ s $T = 2311$ K	$t_3 = 0.1$ s $T = 821$ K	$t_4 = 26.90$ s $T = 817.9$ K	$t_5 = 26.92$ s $T = 2111$ K	$t_6 = 26.96$ s $T = 931$ K	$t_7 = 27.03$ s $T = 791$ K
2	+	+	-	-	+	+	+
3	+	+	+	+	+	+	+
4	+	+	+	+	+	+	+
5	+	+	+	+	+	+	+
6	+	+	+	+	+	+	+
7	+	+	+	+	+	+	+
8	-	+	-	-	+	-	-
9	-	+	-	-	+	-	-
10	-	-	+	-	-	-	+
13	-	+	+	+	+	+	-
14	-	+	-	-	-	-	-
16	-	+	-	+	+	+	-
22	-	+	-	-	+	+	-
23	-	+	+	-	+	+	+
24	-	+	-	-	+	-	-
25	-	+	-	-	+	-	-
26	-	+	-	-	+	-	-
27	-	+	-	-	+	-	-
29	-	+	-	-	-	-	-
35	-	+	-	-	+	-	-
37	-	-	-	-	-	-	+
45	-	+	-	-	+	-	-

imum temperature rise. For modeling features like time to ignition, however, such a scheme would still be useful since the deviations are quite small. This final reduced model (scheme V) achieved by sensitivity analysis contains only 16 reactions and 7 species, approximately a third of the original reaction set:

#### Scheme V



The temperature sensitivities calculated from Eq. 6 are presented for  $t_2$  in Table 7 alongside the overall rate sensitivities. The results as expected are not identical to the rate sensitivities. However, the reactions selected by the principal component analysis remain at the top of the temperature sensitivity order. There are exceptions of course, such as the wall reactions that as formulated have no direct effect on the temperature, and so such an analysis cannot be useful in assessing their significance. By choosing a suitable threshold and taking the sum of all reactions which have a temperature sensitivity higher than this threshold at the chosen time points we should arrive at a scheme close to that obtained from the principal component analysis. In practice however the threshold value is not easily chosen since no natural cut appears in the temperature sensitivity order. Temperature rate sensitivities are therefore

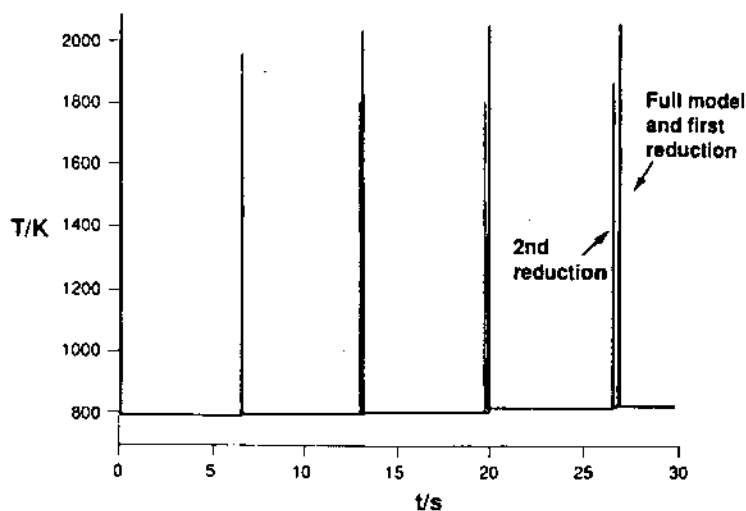


Fig. 7. Comparison of temperature traces from two reduced models (schemes I + II + III) and V) with the full nonisothermal model at  $T_a = 790$  K. The removal of reactions 14, 27, 29, 35, 37, and 45 causes only a small decrease in the oscillatory period.

more useful in assessing the general importance of reactions for temperature changes rather than providing a systematic reduction method and are recommended as a useful tool but not as a single method of model reduction.

## THE QUASI-STEADY-STATE APPROXIMATION (QSSA)

### General Comments

The above methods have enabled the removal of all redundant species and reactions from the original mechanism. Any further reduction will require the possible lumping of reactions and species in order to reduce the number of ODEs required to model the system. One method of combining reactions and species is via the quasi-steady state approximation (QSSA). The concentrations of QSSA species  $C_{qs}$  can be expressed algebraically in terms of other species since it is assumed that their rates of change can be decoupled from the set of ODEs and the right-hand sides set to zero, that is,  $dC_{qs}/dt = 0$ . The number of differential equations is therefore reduced since some have been replaced by algebraic expressions. It may then be possible to substitute for  $C_{qs}$  in the remaining ODEs by analytic solution of the algebraic equations and the solution of this smaller set should require less computing time. The solution of such coupled sets of algebraic equations is made difficult by the nonlinearities present and so numerical solution of the

coupled sets of algebraic-differential equations is often necessary.

An important aspect of applying the QSSA is the choice of QSSA species. The ultimate criterion must be the accuracy of the resulting model, but retaining this accuracy is aided by employing objective procedures for identifying QSSA species. Frank-Kamenetskii [10] suggested that the choice should be based on the species lifetime,  $\tau_i$ , and we discuss the basis of this criterion in greater detail elsewhere [28]. For the present, we shall simply demonstrate its application to the  $H_2 + O_2$  system. The lifetime can be defined as

$$\tau_i = -J_{ii}^{-1}, \quad (7)$$

where  $J_{ii}$  are the diagonal elements of the Jacobian matrix. The lifetime is easily calculated during each simulation since the Jacobian is evaluated at each integration step. It is commonly and wrongly assumed that the application of the QSSA depends on small rates of change of species concentration. An oscillatory system such as hydrogen oxidation, in which radical concentrations change rapidly during an ignition, therefore provides an interesting and testing case for the application of the technique.

### Application

Figure 8 shows some examples of species lifetime for the isothermal system in the oscilla-



TABLE 7

Comparison of Overall Rate Sensitivity and Temperature Sensitivity Order for  $t = 3.5 \times 10^{-2}$  s,  $T = 2311$  K.

Order	Reaction Number	Overall Sensitivity	Reaction Number	Temperature Sensitivity
1	3	$6.94 \times 10^7$	6	0.43
2	5	$1.28 \times 10^7$	3	0.41
3	4	$4.71 \times 10^6$	13	0.22
4	23	$1.72 \times 10^6$	23	0.11
5	22	$2.02 \times 10^5$	16	$0.61 \times 10^{-1}$
6	37	$9.66 \times 10^4$	4	$0.48 \times 10^{-1}$
7	6	$9.81 \times 10^3$	14	$0.34 \times 10^{-1}$
8	10	$7.75 \times 10^3$	22	$0.16 \times 10^{-1}$
9	9	$1.52 \times 10^3$	5	$0.42 \times 10^{-2}$
10	7	$1.09 \times 10^3$	42	$0.41 \times 10^{-2}$
11	8	$9.30 \times 10^2$	1	$0.29 \times 10^{-2}$
12	17	$5.22 \times 10^2$	24	$0.90 \times 10^{-3}$
13	2	1.18	27	$0.58 \times 10^{-3}$
14	35	$2.64 \times 10^{-1}$	32	$0.40 \times 10^{-3}$
15	43	$1.15 \times 10^{-1}$	39	$0.34 \times 10^{-3}$
16	39	$2.64 \times 10^{-2}$	26	$0.19 \times 10^{-3}$
17	19	$2.34 \times 10^{-2}$	29	$0.15 \times 10^{-3}$
18	36	$2.80 \times 10^{-4}$	11	$0.52 \times 10^{-4}$
19	20	$3.48 \times 10^{-5}$	19	$0.21 \times 10^{-4}$
20	14	$1.02 \times 10^{-6}$	28	$0.94 \times 10^{-5}$

tory region at  $T = 790$  K. As expected the lifetime varies periodically with time in the same way as the species concentrations. However, for some species, the lifetime always remains low. OH and O for example have a lifetime that remains below  $10^{-3}$  s throughout the oscillation. The application of the QSSA should therefore be possible for these species. Previously it has been thought by several authors that the QSSA can be applied to all radical species in a model partly because of their low concentrations. H and  $\text{HO}_2$  are therefore also possible candidates.

The model chosen to test the application of the QSSA is scheme (I + IV) under isothermal conditions. Results show that the QSSA is applicable to species O, OH, and  $\text{HO}_2$  with no significant change in the behavior of the system. Figure 9a compares the concentrations of  $\text{H}_2$  and one of the QSSA species OH, with and without the application of the QSSA to OH, O, and  $\text{HO}_2$ . Figure 9b shows the temperature traces from a simulation of the equivalent non-isothermal schemes. Note that the periodically changing OH can still be described by an algebraic function of the non-QSSA species.

The QSSA does not apply to all radicals, however, since its application to H leads to

negative concentrations in H and to concentrations of  $\text{H}_2$  and  $\text{O}_2$  that exceed their initial concentrations. A mathematically real solution of the QSSA equation for H exists but its solutions are not physically realistic. It is perhaps surprising that  $\text{HO}_2$  is a successful QSSA species and H is not, given that H has a lower average lifetime. It has been noted previously that the QSSA cannot successfully be applied to H [9, 18, 29] in the  $\text{H}_2 + \text{O}_2$  system. The probable reason for this is that the errors inherent in the application of quasi-steady states spread quickly to the non-QSSA species causing drastic changes in the dynamics of the system. One measure of the spread of such errors is concentration sensitivity, that is, the effect on species concentration  $C_i$  at a time  $t_2$  of a change in species concentration  $C_j$  at a time  $t_1$  [7]:

$$\frac{\partial C_i(t_2)}{\partial C_j(t_1)} \quad (8)$$

Figure 10 shows examples of such concentration sensitivities for the radical species H, OH, and  $\text{HO}_2$  during the ignition period of the reaction. The effect can be positive or negative (a perturbation can result in an increase or

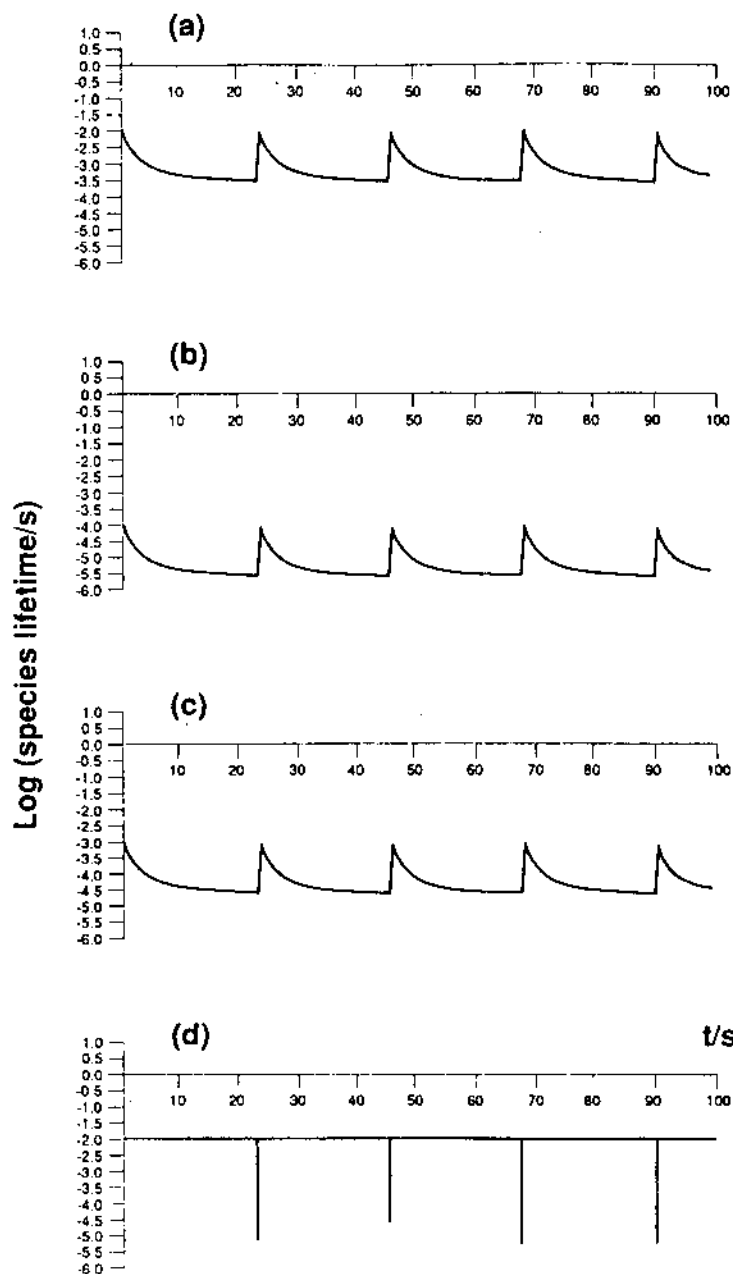


Fig. 8. Log species lifetime for radicals showing OH to be the most likely QSSA species. (a) H (b) OH (c) O (d)  $\text{HO}_2$ .

decrease of the concentration) but for clarity the log of the absolute sensitivities is used. The sensitivity to both H and OH is orders of magnitude higher than to  $\text{HO}_2$  showing that any spread of errors will be much faster for these species. Because OH has a shorter lifetime the QSSA errors propagated are much smaller than in the case of H.  $\text{HO}_2$  has a lifetime comparable to that of H but has a low sensitivity which limits the propagation of er-

rors. We therefore have some indication as to why H is the only unsuccessful radical QSSA species. The question of error estimation and a more rigorous criterion for the application of the QSSA is discussed in detail in a separate article by the authors [28]. The set of ODEs resulting from the application of quasi-steady states to the  $\text{H}_2 + \text{O}_2$  system involves only four species (less than half of the original number).

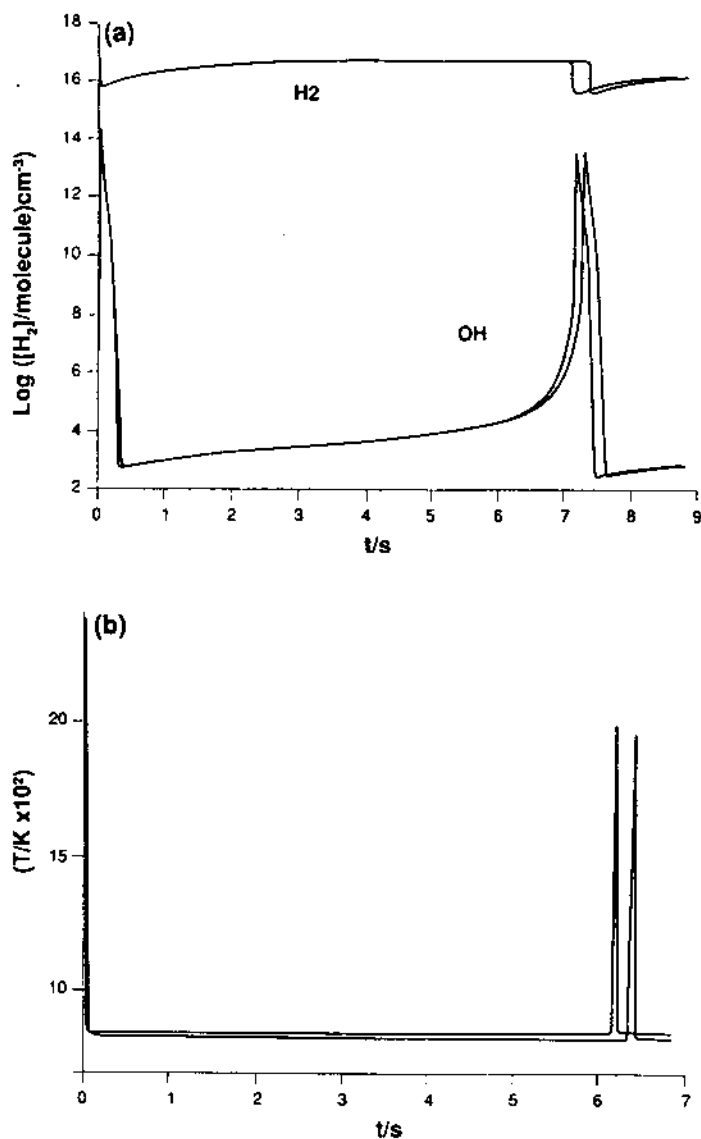


Fig. 9. Example oscillatory traces for skeleton reduced scheme (I + IV) with non-QSSA variables versus schemes where the QSSA has been applied to OH, O, HO<sub>2</sub>. (a) Log OH and H<sub>2</sub> concentration for isothermal scheme. (b) Temperature trace in non-isothermal scheme.

In addition to its use in identifying potential QSSA species, the analysis of the lifetimes of a radical species via the diagonal Jacobian elements can aid the interpretation of the mechanism of a reaction. For example, we referred above to the, at first sight, surprising observation that the wall removal of OH becomes significant as the peak of the ignition is approached. Figure 8 demonstrates clearly the increase in lifetimes of H, OH, and O as the ignition progresses. These increases arise from the reduction in the concentrations of the reactants H<sub>2</sub> and O<sub>2</sub> during the ignition and to the predominance of radical-molecule reac-

tions 3-6 in determining the lifetimes of H, OH, and O at least in the earlier stages of ignition. In contrast, HO<sub>2</sub> shows a decrease in lifetime at the peak of the ignition reflecting the importance of radical-radical reactions in removing HO<sub>2</sub> in this region.

#### The minimum oscillator

In this section we examine how far the scheme can be further reduced while still retaining oscillatory behavior under the conditions discussed above. We do not seek to reproduce the period of the oscillations or even the time to

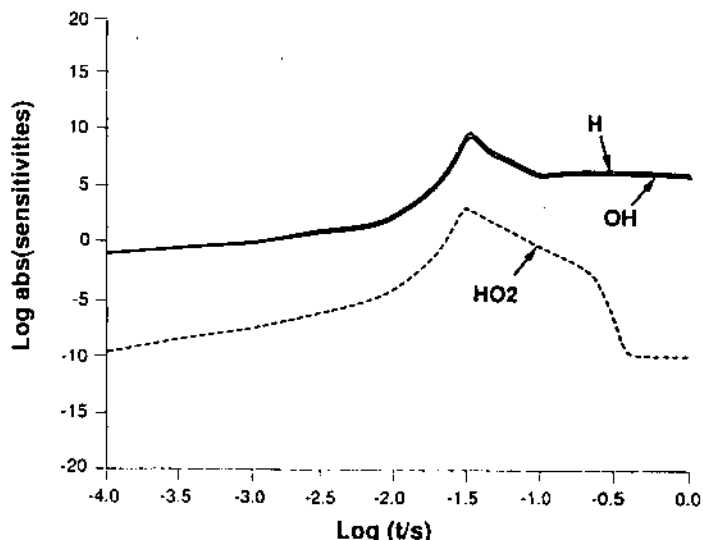
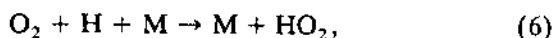
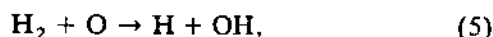
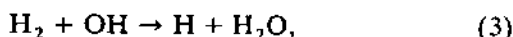
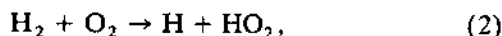


Fig. 10. Concentration sensitivities  $\partial C_i(t_2)/\partial C_i(t_1)$  for radicals H, OH, and HO<sub>2</sub> during the first ignition stages of the reaction showing that the system is far more sensitive to initial errors in H concentration than to errors in the concentration of HO<sub>2</sub>.

ignition but simply to simulate oscillatory behavior. The resulting oscillatory scheme requires the competition of a set of overall branching reactions 3–5 with termination reactions 6 and 7 as follows:



and is identical to the low-temperature scheme I. Note that the wall termination reaction has to be present in order to produce oscillatory behavior for the chosen conditions.

The application of the QSSA to the above scheme leads to a simple set of differential and algebraic equations describing the system and to an algebraic relationship between the QSSA and the non-QSSA species. As above, we choose O and OH as the QSSA species (HO<sub>2</sub> is no longer in the scheme; it is considered a stable product) and set  $d[\text{O}]/dt = d[\text{OH}]/dt = 0$ . This results in the following algebraic equations:

$$[\text{O}]_{\text{qs}} = \frac{k_4[\text{O}_2][\text{H}]}{k_5[\text{H}_2] + \frac{1}{t_{\text{res}}}}, \quad (9)$$

$$[\text{OH}]_{\text{qs}} = \frac{k_4[\text{O}_2][\text{H}] + \frac{k_5 k_4 [\text{H}_2][\text{O}_2][\text{H}]}{k_5[\text{H}_2] + \frac{1}{t_{\text{res}}}}}{k_3[\text{H}_2] + \frac{1}{t_{\text{res}}}}. \quad (10)$$

Substituting for the QSSA species in the original ODEs, the governing set of differential equations for this system becomes

$$\begin{aligned} \frac{d[\text{H}_2]}{dt} &= \frac{[\text{H}_2]_0 - [\text{H}_2]}{t_{\text{res}}} - k_2[\text{H}_2][\text{O}_2] \\ &\quad - k_4[\text{O}_2][\text{H}] - \frac{2k_4 k_5 [\text{H}_2][\text{O}_2][\text{H}]}{k_5[\text{H}_2] + \frac{1}{t_{\text{res}}}}, \end{aligned} \quad (11)$$

$$\begin{aligned} \frac{d[\text{O}_2]}{dt} &= \frac{[\text{O}_2]_0 - [\text{O}_2]}{t_{\text{res}}} - k_2[\text{H}_2][\text{O}_2] \\ &\quad - k_4[\text{O}_2][\text{H}] - k_6[\text{H}][\text{O}_2][\text{M}], \end{aligned} \quad (12)$$

$$\begin{aligned} \frac{d[\text{H}_2\text{O}]}{dt} &= -\frac{[\text{H}_2\text{O}]}{t_{\text{res}}} + k_4[\text{O}_2][\text{H}] \\ &\quad + \frac{k_4 k_5 [\text{H}_2][\text{O}_2][\text{H}]}{k_5[\text{H}_2] + \frac{1}{t_{\text{res}}}}, \end{aligned} \quad (13)$$

$$\begin{aligned} \frac{d[H]}{dt} = & -\frac{[H]}{t_{res}} + k_2[H_2][O_2] \\ & + \frac{2k_4k_5[H_2][O_2][H]}{k_5[H_2] + \frac{1}{t_{res}}} \\ & - k_6[H][O_2][M] \\ & - k_7[H] \end{aligned} \quad (14)$$

Since  $k_3$  is large it is assumed that  $k_3[H_2] \gg 1/t_{res}$  and so we neglect the  $t_{res}$  term in the case of  $[OH]_{qss}$ .  $k_5$  is smaller and a similar assumption cannot be made for  $[O]_{qss}$ .

Figure 11 shows a comparison of the temperature profile obtained from the solution of the above system along with the energy balance equation 2, with that from the original 47-step scheme. The period from the minimum scheme is less than half that for the full scheme and the maximum temperature rise is much less. This scheme could not therefore be used as an accurate representation of experimental results but is of interest because it provides the minimal oscillator that we are able to generate for the present conditions.

In closed systems or even in systems with large residence times it is possible to make further simplifications to the scheme above. In

such cases it can be assumed that  $k_3[H_2] \gg 1/t_{res}$  and the steady-state concentrations for O and OH reduce to

$$[O]_{qss} = \frac{k_4[O_2][H]}{k_5[H_2]}, \quad (15)$$

$$[OH]_{qss} = \frac{2k_4[O_2][H]}{k_3[H_2]}, \quad (16)$$

and the set of ODEs becomes

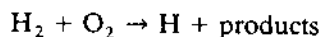
$$\begin{aligned} \frac{d[H_2]}{dt} = & \frac{[H_2]_0 - [H_2]}{t_{res}} \\ & - k_2[H_2][O_2] - 3k_4[O_2][H], \end{aligned} \quad (17)$$

$$\begin{aligned} \frac{d[O_2]}{dt} = & \frac{[O_2]_0 - [O_2]}{t_{res}} \\ & - k_2[H_2][O_2] - k_4[O_2][H] \\ & - k_6[H][O_2][M], \end{aligned} \quad (18)$$

$$\frac{d[H_2O]}{dt} = -\frac{[H_2O]}{t_{res}} + 2k_4[O_2][H], \quad (19)$$

$$\begin{aligned} \frac{d[H]}{dt} = & -\frac{[H]}{t_{res}} + k_2[H_2][O_2] \\ & + 2k_4[O_2][H] - k_6[H][O_2][M] \\ & - k_7[H]. \end{aligned} \quad (20)$$

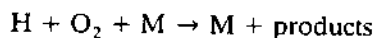
From this set of equations the following set of four global reactions can be derived:



$$\text{rate} = k_2[H_2][O_2],$$



$$\text{rate} = k_4[O_2][H],$$



$$\text{rate} = k_6[H][O_2][M],$$



which describe the overall stoichiometry for slow flow or for a closed system. Mass balance could provide a further reduction of Eq. 17-20 to only three variables. This scheme provides a good estimate for times to ignition in both closed and flow systems since for high  $H_2$

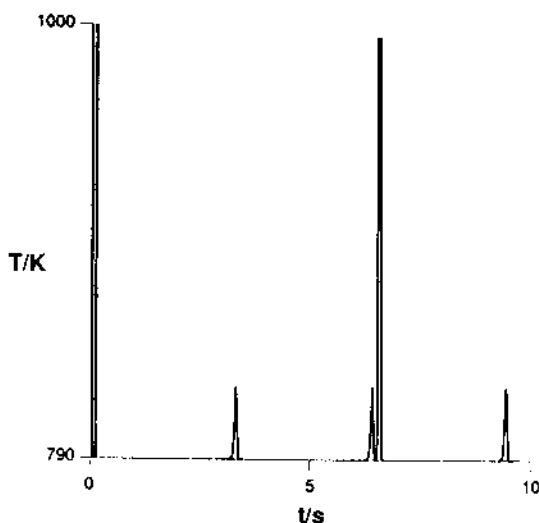


Fig. 11. Temperature profiles for full scheme and minimum four-variable scheme for  $T_0 = 790$  K. The maximum temperature rise for the minimum scheme is only about 30 K.

concentrations the flow is insignificant and the rate of reaction  $3\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{H}$  is a good approximation. At low  $\text{H}_2$  concentrations the rate  $k_4[\text{O}_2][\text{H}]$  is an overapproximation for a flow system and the faster production of  $\text{H}_2\text{O}$  helps to switch off the ignition more quickly. The scheme cannot reproduce sustained oscillatory behavior and Fig. 12 shows how the oscillations found in the scheme are damped and decay to a reacted steady-state. In order to reproduce oscillations successfully we cannot neglect the outflow of QSSA species.

### CONCLUSIONS AND COMPARISONS WITH PREVIOUS WORK

The major aim of the present work was to develop a general algorithm for mechanism reduction and we have demonstrated its application to a 47-step scheme describing the oxidation of hydrogen in a flow reactor. Previous work on reducing the hydrogen-oxygen system has been extended by the present study, which concentrates mainly on oscillatory ignition. The importance of identifying redundant species prior to attempting any reaction elimination has been emphasized. In the present context the removal of fast reversible reactions such as those of  $\text{O}_3$  from the scheme has therefore become possible via the selection of a reduced set of observed species in the principal component analysis of the rate sensitivity matrix. Although the  $\text{H}_2 + \text{O}_2$  system itself is of only

secondary importance in this study, it is of interest to review the conclusions reached.

A core set of six reactions is necessary at all conditions studied which consists of initiation, chain branching and third body termination steps, and the reaction of H with the wall. This set exhibits oscillatory behavior but best describes the reaction at low temperatures such as 500 K. The oscillations shown by this scheme are very different in period to those shown by the full scheme and a further eight reactions are required, in addition to this core set, to reproduce more accurately the oscillations found in an isothermal simulation of the full model. In particular the reactions of  $\text{HO}_2$  with H become significant, providing secondary branching routes. Only small errors in the concentrations and period are found for the resulting 14-step scheme (I + IV).

The main branching reactions in the oscillatory region were identified as reactions 4, 5, and 13 and a switching is found to occur between these reactions during the ignition period. Over a small time period where the radical concentrations are high, reaction 13 becomes faster than 4 and 5. The third body reaction  $\text{H} + \text{O}_2 + \text{M}$  is always the main termination step but during the ignition phase, radical-radical termination steps such as  $\text{O} + \text{OH}$  also become important. The removal of such reactions, and consequent build-up in the simulated OH radical concentration, leads to changes in the period of oscillation since the

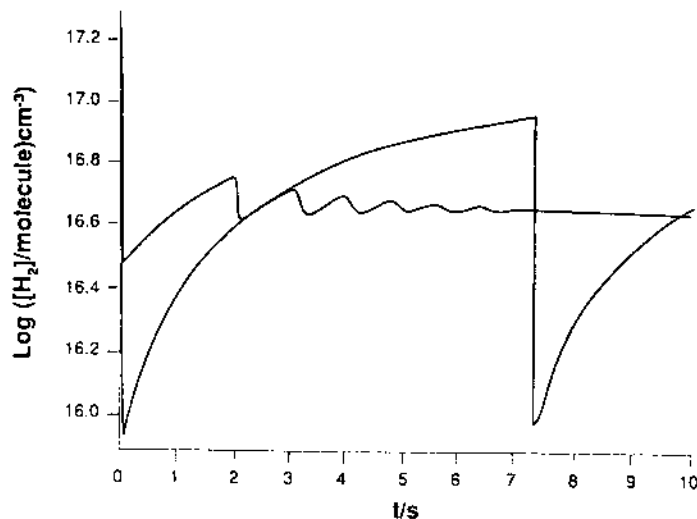


Fig. 12. Comparison of  $\text{H}_2$  concentration profiles for the four-step and the full mechanism for an isothermal simulation in a flow vessel.

extent of conversion of  $H_2$  during a peak is affected.

At high temperatures further radical-radical termination steps are significant, especially the reactions of OH, along with another branching step,  $H + H_2O \rightarrow OH + H_2$ . It is these reactions that have to be added to the 14-step scheme (I + IV) in order to reproduce qualitatively oscillations found in nonisothermal simulations. In all, after the final reduction, 16 reactions were necessary to model thermokinetic oscillations close to those produced by the full scheme.

Interesting comparisons can be made between the results from the present work and other reduced models that have been produced via different sensitivity methods. The results from the present method compare well to previous results and not surprisingly the same set of core reactions are important for many parameter conditions.

Yetter et al. [17] calculated the sensitivity of the largest eigenvalue of the initial concentration sensitivity matrix. This technique is particularly useful for the study of ignition of explosive mixtures. As Yetter et al. investigated  $H_2 + O_2$  mixtures highly diluted by  $N_2$  in a batch reactor at different temperatures and pressures and their mechanism did not contain wall reactions, their results are not directly comparable to ours. However, the reactions of scheme I (except for the wall termination of H) are the most important reactions for their strong ignition conditions.

At weak ignition conditions, 5 of the 11 reactions listed as important are not present in any of our reduced models. These five reactions include the reactions of  $H_2O_2$ , which has been eliminated from our model as a redundant species. A similar point has also been noted by Johnson et al. [3], who found that different reduced schemes were applicable depending on the rate constants for the original scheme in the region of the second explosion limit. Their scheme using the most recent data did not include any reactions of  $H_2O_2$  while the scheme using the data from the Chinnick paper had to include this species in order to retain the essential features of the full mechanism. The differences in rate data for the original schemes may be one reason for the extra reactions included in the low conversion

scheme of Yetter et al. A second reason may be the omission of redundant species selection in their calculations.

The core set of reactions 2-6 in both Yetter's work and the above schemes is in strong agreement with work by Chinnick et al. [19], although the present work highlights the reactions  $O + OH \rightarrow H + O_2$  and  $OH \rightarrow$  WALL as being important in determining the period of oscillation and not just the competition between the main chain branching and third body termination steps. It is clear that, although the competition between branching and termination is responsible for the destabilizing of the steady-state and therefore the existence of periodic behavior, the period of oscillation cannot be calculated accurately from just the core reaction scheme.

The results presented above also provide quantitative evidence for the minimum complex oscillator produced by Johnson et al. [3]. Their reduced schemes were achieved using experience of the full reaction scheme and by simply removing the reactions which seemed to be least important using chemical intuition and recomputing the results. Such an approach may be possible for small schemes such as hydrogen oxidation, but for large combustion schemes of 200-300 reactions an automatic approach employed by programs like KINAL becomes of great advantage. These methods also pinpoint the important reactions at different reaction times, something that is not possible with the sensitivity approach used by Johnson et al. The final 17-step scheme produced by Johnson et al. contains all the reactions in the 14-step scheme outlined above except for reaction 23,  $H + H_2O \rightarrow O + H + H_2$ , which was not present in their original mechanism and some wall reactions which are retained here in order that the boundaries of the oscillatory region remain the same and hence quantitative comparisons with the full scheme can be made. The scheme of Johnson et al. is mainly concerned with reproducing qualitative trends [3].

Although different reduced schemes are required to reproduce the oscillatory behavior found in the full isothermal and nonisothermal schemes it has been shown that a suitable nonisothermal scheme can be found using an isothermal analysis as long as a representative range of ambient temperatures is chosen.

Temperature rate sensitivity analysis of the nonisothermal scheme could be useful, however, particularly in situations where only the temperature profile and not species concentration is of interest.

The QSSA has proved to be a valuable tool even for a scheme with so few radical species. Using the QSSA a minimal scheme involving only four species has been achieved which shows thermokinetic oscillations. This scheme has limitations in that it cannot accurately reproduce oscillatory periods or maximum temperatures, but it has significance as a simple oscillatory combustion scheme. Apart from initial reactants and the product, water, it has been necessary to retain one intermediate (H) in the scheme. This is not surprising since a phase difference between one intermediate and the reactants is usually required to produce oscillatory behavior. For large residence times a further reduction has been achieved leading to the lumping of the branching reactions into the global reaction  $3\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{H}$  with rate  $= k_4[\text{O}_2][\text{H}]$ . This reaction has also been identified by Vajda et al. [18] as one of two global reactions that describe a premixed steady hydrogen flame. They have also found reaction 4 to be the rate determining step. This scheme however, produces only transient oscillations and it is clear that to produce sustained oscillatory behavior it is necessary to retain information about the outflow of the QSSA species.

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