

Applications of sensitivity analysis to combustion chemistry

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Combustion chemical models usually contain several hundred or thousand kinetic rate parameters. Most simulation packages calculate local concentration sensitivities, but it is frequently not easy to extract meaningful information from large sensitivity matrices. Principal component analysis is a simple post-processing technique that summarizes sensitivity information and also reveals the effect of simultaneously changing parameters.

A new program package, called KINALC, has been created for the analysis of gas-phase reaction systems. This program is an extension to CHEMKIN based simulation programs. KINALC processes the concentration sensitivity information in four different ways and allows a comparison of the sensitivity information to other methods, based on the study of reaction rates and stoichiometry, for the analysis of complex mechanisms. KINALC is available through the World Wide Web.

The various methods are illustrated by the analysis of a detailed chemical model for hydrogen combustion. Local sensitivity analysis of models of homogeneous hydrogen explosion and of premixed laminar hydrogen-air flame has been carried out and the sensitivity results reveal that the chemical processes are very similar in these physically different systems at the corresponding temperatures. © 1997 Elsevier Science Limited.

1 INTRODUCTION

Combustion is a very complex phenomenon, characterized by interaction and competition of various physical and chemical processes. The correct description of chemical changes requires the application of reaction mechanisms consisting of several hundred or thousand reactions. This means that the chemistry of combustion processes is described by a huge number of parameters and hence the application of sensitivity analysis techniques is very useful for its understanding.

Combustion of hydrogen is one of the simplest combustion processes. The spectacular flame at the launch of a space shuttle is produced by hydrogen burning. A typical hydrogen combustion mechanism consists of about 40 reactions of 8 reactive species. Combustion of natural gas (mixture of mainly methane and ethane) is an industrially very important process and a detailed mechanism contains about 30 species and 200 to 300 reactions. Detailed chemical mechanisms have not been suggested for the combustion of petrol, but a detailed mechanism for

the combustion of n-heptane, a single component of petrol, contains several thousand reactions.

Most rate parameters in combustion are known with rather large error. Rates of very few reactions are known as precisely as 10%. Typical uncertainty of rate constants of high temperature gas phase reactions is 2 to 3, which is defined as the ratio of the best estimation and the possible extreme values. These uncertainties are listed in collections of evaluated reactions (see, e.g., [1]).

Applications of sensitivity analysis in combustion chemistry are usually related to either the huge size and complexity of combustion models or the high uncertainty of their parameters. Sensitivity analysis can be applied for the *analysis of combustion chemical models*. Such an analysis reveals which are the main control parameters in the model, which are the indirect effects of parameter changes and provides information about the structure of the model. Detailed chemical models are too big for many practical combustion simulations. Sensitivity analysis can be used for *mechanism reduction*, that is, finding a smaller model that produces similar predictions for

some of the variables (i.e., species concentrations and temperature). Also, sensitivity analysis can be applied for *uncertainty analysis*, that is characterizing the uncertainty of model output as a result of improperly known parameters.

Applications of sensitivity methods in chemical kinetics have been reviewed several times. Rabitz *et al.* [2] concentrated mainly on the interpretation of sensitivity coefficients in reaction–diffusion systems. Turányi [3] considered sensitivity methods as tools for studying reaction kinetics problems. This review contains an almost complete list of publications on the application of sensitivity analysis in reaction kinetics up to 1989. Recently, Radhakrishnan has published several articles (see, e.g., [4,5]) on the numerical comparison of methods for the calculation of local sensitivities. Tomlin *et al.* [6] have discussed sensitivity analysis as one of the mathematical tools applied in combustion chemistry.

The objective of this article is to give a limited review on the applications of sensitivity methods to the investigation of combustion models. Some of the important aspects are briefly described in Sections 2–5 and references are given to more detailed descriptions and further topics. In Section 6, a new computer code is presented that allows the comfortable application of most of the described methods. In the last section, typical sensitivity analysis results are listed and interpreted for the combustion of hydrogen.

2 NUMERICAL SIMULATION OF COMBUSTION PHENOMENA

Simulation of spatially homogeneous combustion systems is equivalent to the solution of the following initial value problem:

$$\frac{d\mathbf{c}}{dt} = \mathbf{f}(\mathbf{c}, \mathbf{k}), \quad \mathbf{c}(t_0) = \mathbf{c}^0 \quad (1)$$

where \mathbf{c} is the n -vector of concentrations, \mathbf{k} is the m -vector of rate coefficients and \mathbf{c}^0 are the initial concentrations. Equation (1) is a stiff and non-linear system of ODEs. The right hand side of ODE eqn (1) can be calculated from the rates of reaction steps:

$$f_i(\mathbf{c}, \mathbf{k}) = \sum_j \nu_{ij} R_j \quad (2)$$

where f_i is the rate-of-production of species i , R_j is the rate of reaction j and ν_{ij} is the stoichiometric coefficient of the i -th species in the j -th reaction.

For non-isothermal reactions we have to include also the energy balance:

$$\frac{dT}{dt} = \frac{1}{C_p} \left(\sum_j q_j R_j + \frac{\chi S}{V} (T - T_a) \right) \quad (3)$$

assuming a Newtonian cooling through the walls. Here, C_p is the heat capacity, q_j is the exothermicity of the j -th reaction step, χ is the heat transfer coefficient, T_a is the ambient temperature, and T , S and V are the temperature, surface and the volume of the reactor, respectively.

Many practical applications require the study of spatially inhomogeneous combustion systems. The corresponding mathematical equations are stiff non-linear systems of partial differential equations, which consist of the conservation equations for mass, momentum, energy, and species masses (Navier-Stokes equations). In these equations the right hand side of eqn (1) is the chemical source term. Simulation of one-dimensional laminar flames is common in the combustion simulation practice. However, analysis and reduction of chemical mechanisms are usually carried out at the conditions of homogeneous combustion.

3 LOCAL SENSITIVITIES IN CHEMICAL KINETICS

The *sensitivity analysis* methods investigate the output of models as a function of parameters. In *local sensitivity analysis* this relation is given as the partial derivative of the output of the model with respect to the parameters. These partial derivatives can be simply introduced via a Taylor series expansion:

$$c_i(t, \mathbf{k} + \Delta\mathbf{k}) = c_i(t, \mathbf{k}) + \sum_{j=1}^m \frac{\partial c_i}{\partial k_j} \Delta k_j + \dots \quad (4)$$

where the partial derivatives $\partial c_i / \partial k_j$ are called the *first-order local concentration sensitivity coefficients*. Calculation of these local sensitivities can be considered as if the parameters were perturbed at time t_1 , and the change in concentrations was studied at a later time t_2 . In uncertainty analysis the problem is assessing the consequences of a different parameter set and, therefore, t_1 is always set to be equal to the starting time of simulation. In mechanism analysis and reduction, however, t_1 can be selected arbitrarily ($t_1 < t_2$), and selection t_1 is a degree-of-freedom of the method. Features of mechanisms depend on the concentrations and change continuously during a simulation. By moving observation window (t_1, t_2) , the changing features of a mechanism can be monitored.

The simplest method for the calculation of local sensitivities is by changing each parameter by a small amount, re-running the model, and approximating the sensitivities by differences. This brute force method is only appropriate if better methods are not available, since it is relatively slow and inaccurate. If the original

system of kinetic differential eqn (1) is differentiated with respect to k_j , the following set of sensitivity differential equations is obtained:

$$\frac{d}{dt} \frac{\partial \mathbf{c}}{\partial k_j} = \mathbf{J}(t) \frac{\partial \mathbf{c}}{\partial k_j} + \frac{\partial \mathbf{f}(t)}{\partial k_j}, \quad j = 1, \dots, m \quad (5)$$

where $\mathbf{J}(t) = \partial \mathbf{f} / \partial \mathbf{c}$ and the initial condition for $\partial \mathbf{c} / \partial k_j$ is a zero vector. Equation (1) and eqn (5) are coupled through matrices $\partial \mathbf{f} / \partial \mathbf{c}$ and $\partial \mathbf{f} / \partial \mathbf{k}$, that is, eqn (5) can only be solved if the concentration values, to be calculated by eqn (1), are available at times where the above matrices are calculated during the numerical solution of the sensitivity eqn (5). The most efficient and now generally used algorithm for the solution of the sensitivity differential equations is called the *decoupled direct method* (DDM), which was first applied in chemical kinetics by Dunker [7, 8].

The sensitivity coefficient $\partial c_i / \partial k_j$ is of limited applicability in its original form. The parameters and the various output quantities of a model may have different units. For example, rate coefficients belonging to reactions of different orders have different units. In such cases, the elements of the sensitivity matrix are incomparable. The usual solution to this problem is the introduction of normalized sensitivity coefficients. These coefficients form the *normalized sensitivity matrix*:

$$\tilde{\mathbf{S}} = \left(\frac{k_j}{c_i} \frac{\partial c_i}{\partial k_j} \right) = \left(\frac{\partial \ln c_i}{\partial \ln k_j} \right). \quad (6)$$

The normalized sensitivity coefficients represent the fractional change in concentration c_i caused by a fractional change of parameter k_j .

In flames, the ratio of concentration sensitivity *vs* space variable (distance) functions, where the sensitivities are calculated with respect to any two parameters, are found to be the same for all the concentrations and the temperature of the model. This phenomenon is called the *self-similarity of sensitivity functions* [9]. In flames the temperature is the dominant variable and any perturbation in the system affects the concentration–distance functions mainly through the changes induced in the temperature [10].

The solution of combustion models can not only represent concentration *vs* time or concentration *vs* distance functions, but also some features of the model. Such features could include the time to ignition or the flame velocity of freely propagating premixed flames. The sensitivity of these features can also be investigated. *Flame velocity sensitivities* are frequently calculated and used for investigation of reaction mechanisms (see, e.g., the review of Warnatz [11]).

Several program packages are available for the simulation of various 0D (spatially homogeneous) and 1D combustion phenomena. The best known simula-

tion packages, like CHEMKIN [12] or RUN1DL [13], all calculate local sensitivities as well.

4 PRINCIPAL COMPONENT ANALYSIS

The sensitivity matrix itself accounts for the change of a single variable as a result of the change of individual parameters. In many cases one is interested in the effect of a parameter change on the concentrations of several species. This effect can be interpreted as the sensitivity of the value of an objective function, where the objective function is defined as the sum of squares of normalized differences in the original and perturbed concentrations. This sensitivity value, called the *overall sensitivity* [14], can easily be calculated from the normalized local sensitivities:

$$B_j = \sum_i \left(\frac{\partial \ln c_i}{\partial \ln k_j} \right)^2 \quad (7)$$

where the summation runs over the indices of species present in the group investigated. The overall sensitivities show the effect of individual parameter changes on the calculated concentrations.

In most applications the parameters may change simultaneously. Principal component analysis is a mathematical method that assesses the effect of simultaneously changing parameters on several outputs of a model [14]. The objective function of the principal component analysis is the square of the normalized deviation of concentrations, summed over all concentrations, and for all time points:

$$\alpha = \sum_{h=1}^l \sum_{i=1}^n \left(\frac{\Delta c_i(t_h)}{c_i(t_h)} \right)^2 \quad (8)$$

where $\Delta c_i(t_h)$ is the deviation of concentration at time t_h as a result of parameter change $\Delta \alpha$, where $\Delta \alpha = \alpha - \alpha^0$, $\alpha_j = \ln k_j$. This function can be approximated using the sensitivity matrix:

$$\alpha \approx \Delta \alpha^T \tilde{\mathbf{S}}^T \tilde{\mathbf{S}} \Delta \alpha \quad (9)$$

where $\tilde{\mathbf{S}} = \{\tilde{\mathbf{S}}_1, \tilde{\mathbf{S}}_2, \dots, \tilde{\mathbf{S}}_h, \dots, \tilde{\mathbf{S}}_l\}^T$ and $\tilde{\mathbf{S}}_h$ is the normalized sensitivity matrix for time t_h . Let \mathbf{U} denote the matrix of normalized eigenvectors \mathbf{U}_j of $\tilde{\mathbf{S}}^T \tilde{\mathbf{S}}$ such that $\mathbf{U}^T \mathbf{U} = \mathbf{I}$. The new set of parameters $\Psi = \mathbf{U}^T \alpha$ are called *principal components*. The objective function can also be expressed in terms of the principal components:

$$\alpha \approx \sum_{j=1}^m \lambda_j \Delta \psi_j^2 \quad (10)$$

where $\Delta \psi = \mathbf{U}^T \Delta \alpha$ and λ_j are the eigenvalues of $\tilde{\mathbf{S}}^T \tilde{\mathbf{S}}$.

It is apparent from the last equation that the eigenvectors of matrix $\tilde{\mathbf{S}}^T \tilde{\mathbf{S}}$ reveal the related

parameters and the corresponding eigenvalues express the weight of these parameter groups. Principal component analysis (PCA) provides a way of summarising the information contained in the sensitivity matrix, and at the same time reveals connections between parameters which would not be apparent when studying the raw sensitivity matrix.

5 APPLICATIONS OF LOCAL CONCENTRATION SENSITIVITIES

Local sensitivity information has numerous applications in uncertainty analysis, parameter estimation, experimental design, mechanism investigation, and mechanism reduction. Uncertainty analysis is a quantitative study of the effect of parameter uncertainties on the solution of models. Although applications of real uncertainty analysis have been rare (if any) in combustion chemistry, sensitivity analysis has frequently been applied for a qualitative assessment which parameters have to be known more precisely to reproduce better the experimental results. Warnatz [15] has produced combined sensitivity–uncertainty indices from the local sensitivities and the tabulated uncertainties of evaluated reactions. This is a semi-quantitative approach to uncertainty analysis. Note that global methods have not been used in combustion chemistry.

Sensitivity analysis can be a useful ingredient of any parameter estimation procedure [3]. Since parameter estimations are often based on the method of least-squares, principal component analysis is easily applicable in conjunction with these techniques and can be used to avoid ill-conditioned problems [14]. Also, design of experiments is closely related to the optimization of parameter estimation [3].

Sensitivity analysis can also be applied in the reduction of mechanisms. A reaction is redundant if its sensitivity is small with respect to each species of the reaction system at all times in the interval considered [16]. Principal component analysis has also been applied several times to mechanism reduction [3].

Reactions with high sensitivities have been considered to be identical to the rate limiting steps [17]. Based on the definition of rate-limiting steps, the significance of these high sensitivities can be understood, and a more formal method can be elaborated. According to a proposed definition [18], a reaction step is rate-limiting if an increase in its rate coefficient causes a significant change in the overall reaction rate. This overall reaction rate is usually considered to be equal to the production (or consumption) rate of an important species. In many systems a single overall reaction rate is not interpretable, and several rate-limiting steps, corres-

ponding to several important species, can be found. Such a system is, for example, the combustion of fuel mixtures. The sensitivity of production rates to the rate coefficients is given by the following equation:

$$\left(\frac{\partial \mathbf{c}}{\partial k_j}\right) \frac{d\mathbf{c}}{dt} = \mathbf{J}(t) \frac{\partial \mathbf{c}}{\partial k_j} + \frac{\partial \mathbf{f}}{\partial k_j}, \quad j = 1, \dots, m. \quad (11)$$

This equation is identical to eqn (5) which has been applied to the calculation of local sensitivities, but it can also be used for finding rate limiting steps. The rate limiting step of the i th species can be identified (if it exists) by searching for a very large element in the i th row of the normalized form of matrix

$$\frac{\left(\frac{\partial \mathbf{c}}{\partial \mathbf{k}}\right)}{dt} = \frac{d}{dt} \frac{\partial \mathbf{c}}{\partial \mathbf{k}}.$$

Interactions among parameters, as revealed by the principal component analysis, always have kinetic reasons. Such interacting parameter groups stem from fast equilibrium conditions or from the existence of quasi-steady-state species. Thus, sensitivity and principal component analyses can be used for the detection of such kinetic features. Note, that similar information can be derived from reaction rates and stoichiometry.

6 KINALC: A PROGRAM FOR THE KINETIC ANALYSIS OF GAS-PHASE REACTION MECHANISMS

A program has been written for the *kinetic analysis* of combustion mechanisms. This program, called KINALC, is a postprocessor to the simulation programs of the CHEMKIN package [12] (SENKIN, PREMIX, PSR, SHOCK, and EQLIB) and also to the RUN1DL package [13]. KINALC carries out three types of analysis: processing concentration sensitivity analysis results, extracting information from reaction rates and stoichiometry, and providing kinetic information about the species.

KINALC processes the concentration sensitivity information in four ways:

1. KINALC can extract the important pieces of information from the sensitivity matrices dumped by the simulation programs. KINALC normalizes the sensitivity matrices (see eqn (6)) and produces ordered lists of sensitivities of some selected species (and temperature) at selected reaction times (or distances).
2. KINALC can calculate the sensitivity of objective functions (see eqn (7)). The user has to name which species are present in the objective

function and the program provides ordered overall sensitivities at any time or distance.

3. KINALC can carry out principal component analysis of the concentration sensitivity matrix. The input is the list of species, present in the objective function, and the time (distance) interval investigated. The result of eigenvalue–eigenvector analysis shows which are the effective parameters and provides hints at the effect of simultaneously changing parameters. The program suggests a reduced mechanism.
4. KINALC determines rate limiting steps on the basis of eqn (11). The user must define the rate of which species is considered to be characteristic for the reaction system.

The further options of KINALC utilize other investigation methods. Principal component analysis of the algebraic rate sensitivity matrix provides an effective method for mechanism reduction. The program also offers traditional ways for mechanism investigation and reduction, such as rate-of-production analysis and calculation of the fluxes of elements from species to species and the contribution of each reaction to these fluxes. The analysis of the Jacobian allows a reduction in the number of species and the estimation of the instantaneous error of QSSA species. KINALC can be used to getting overlapping mechanistic information in several different ways, based on concentration sensitivities, partial derivatives of reaction rates or traditional methods of reaction kinetics. This allows an easy comparison of the old and new, more or less formal methods.

KINALC has been designed to be very user friendly. It accepts simple keywords and may provide a detailed explanation of the results. The program has a modular structure and can be easily extended by other methods for the analysis of reaction mechanisms and can be interfaced easily to other simulation programs. KINALC is available from the World Wide Web at address <http://chem.leeds.ac.uk/Combustion/Combustion.html>

7 SENSITIVITY ANALYSIS OF A HYDROGEN COMBUSTION MECHANISM

Making a detailed mechanism for hydrogen combustion was a by-product of the generation of a new methane oxidation mechanism [19] at the University of Leeds. Both mechanisms are available through the Internet from the above address.

The hydrogen oxidation mechanism contains 8 reactive species (H_2 , O_2 , H_2O , H , O , OH , HO_2 , and H_2O_2), two inert species (N_2 and Ar) and 46 reactions. The mechanism has been tested against experimental data.

The homogeneous combustion of a stoichiometric hydrogen–air mixture was simulated by program SENKIN, assuming 1200 K initial temperature, 1 atm constant pressure and adiabatic conditions. At these circumstances the mixture explodes after 4.5×10^{-5} s delay time. The concentration–time and temperature–time curves are seen in Fig. 1. The combustion of the same mixture was simulated by program PREMIX in an adiabatic, atmospheric 1D premixed laminar flame, assuming that the temperature of the inlet gas was 300 K. The concentration–distance and temperature–distance functions are given in Fig. 2. Both simulation programs calculated local concentration sensitivities and recorded them as binary files.

KINALC can be used to fetch the sensitivities belonging to any variable at any given time, distance, or temperature, and to derive various quantities from the raw sensitivities. Inspecting the sensitivity results of the homogeneous simulation at a series of temperatures, it was apparent that the results change sharply at about 1700 K. The sensitivity results, characteristic for the unburnt conditions, were studied at 1300 K. Table 1 shows the sensitivity of H_2O concentration with respect to the rate coefficients. Qualitatively very similar results were obtained for the sensitivities of all the other concentrations and of the temperature. The overall sensitivities of the concentrations of the major species (H_2 , O_2 , H_2O) also show the same order of high sensitivity reactions (see Table 2). The same reactions appear also in the list of rate limiting steps (Table 3).

The reason for the significance of these reactions is clear. Reaction 9 ($\text{O}_2 + \text{H} = \text{OH} + \text{O}$) is the most important chain branching step in every combustion process where H atoms are present. Reactions 9 and 1 together convert O_2 and H_2 to two OH radicals and therefore increase the concentration of radicals and accelerate combustion. Reaction 5 ($\text{O}_2 + \text{H} + \text{M} = \text{HO}_2 + \text{M}$) has a negative sensitivity coefficient and really this reaction consumes the reactive H radical and slows down the oxidation. Reaction 3 ($\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$) is the main reaction for the conversion of H_2 to H_2O .

In the induction part of the reaction the most important event is the accumulation of radicals. As a result, the concentration of all species are sensitive to the rate of reactions that are important for the radical budget, with positive sensitivity for radical producing and negative sensitivity to radical consuming reactions.

The principal component analysis of the sensitivity functions in the range 1300 K to 1700 K was carried out considering H_2 , O_2 , and H_2O in the objective function. Only two eigenvectors were greater than 0.1. The first reaction group, characterized with a very high eigenvalue, contained the most important radical consuming and producing reactions. The second group

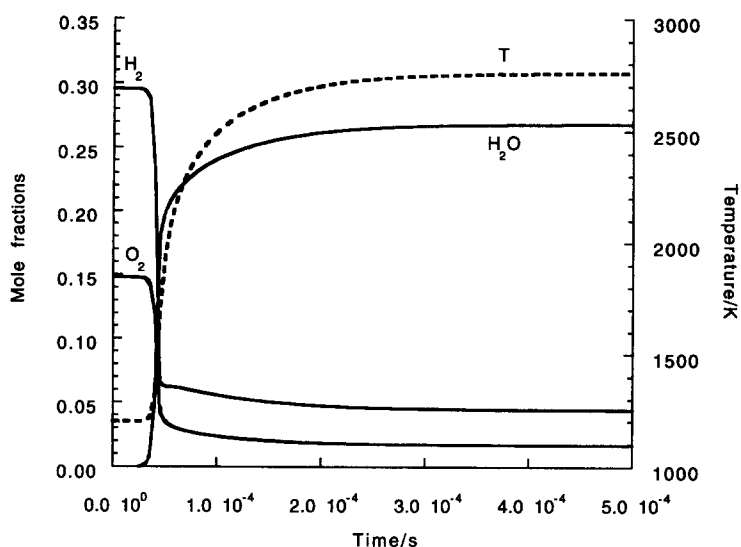


Fig. 1. Concentration–time and temperature–time curves during a homogeneous hydrogen explosion.

contained the less important, but still significant reactions (See Table 4).

It is interesting to compare the sensitivity results with the rate-of-production listings. The latter shows that the main producer of H atoms are reaction 3 (64.6%) and reaction 1 (30.7%), the main consumer is reaction 9 (67.8%). Water is produced mainly (95.6%) in reaction 3. The main (47.1%) producers of OH are reactions 9 and 1 (47.1% and 38.0%, respectively), while the main (84.7%) consumer of it is reaction 3. These figures indicate the same reactions to be important, but say nothing about the interaction of reactions.

In the burnt state, exemplified by the results at temperature 2200 K, other reactions are important.

Considering the sensitivity of water concentration (Table 5), reactions with high positive sensitivity contribute to the production of water from H_2 and O_2 , while reactions with high negative sensitivity convert water back to H_2 and O_2 . This indicates that the reaction is now close to the equilibrium. Similar results (with opposite signs) were obtained for the H_2 and O_2 sensitivities. The list of rate limiting steps of water production, given in Table 6, also include the other combination reactions 27 and 25.

Investigation of the hydrogen flame sensitivity results can provide further information on the hydrogen combustion. Figure 3 shows the highest flame velocity sensitivities. The velocity of a flame also depends on the rate of radical production and

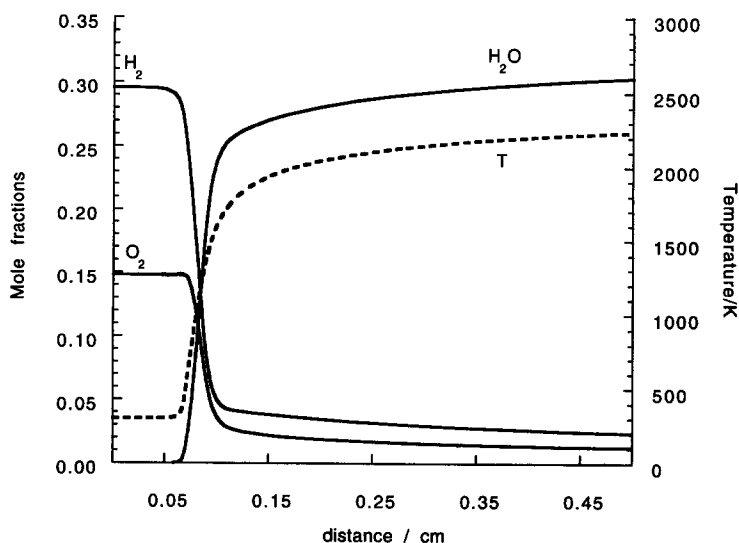


Fig. 2. Concentration–distance and temperature–distance functions in a freely propagating 1D premixed laminar hydrogen–air flame.

Table 1. Sensitivity of the concentration of H₂O with respect to the rate coefficients

No	Sensitivity	#	Reaction
1	1.31560E + 01	9	O ₂ + H =>OH + O
2	2.55376E + 00	1	H ₂ + O =>OH + H
3	-1.58702E + 00	5	O ₂ + H + M =>HO ₂ + M
4	1.10723E + 00	3	H ₂ + OH =>H ₂ O + H
5	1.09612E + 00	30	H ₂ + O ₂ =>H + HO ₂

Table 2. Overall sensitivities considering species H₂, O₂, and H₂O

No	Overall sens.	#	Reaction
1	1.93369E + 02	9	O ₂ + H =>OH + O
2	7.28151E + 00	1	H ₂ + O =>OH + H
3	2.82252E + 00	5	O ₂ + H + M =>HO ₂ + M
4	1.36238E + 00	3	H ₂ + OH =>H ₂ O + H
5	1.34097E + 00	30	H ₂ + O ₂ =>H + HO ₂

therefore many of the reactions that have high sensitivity at homogeneous conditions have also high flame velocity sensitivity.

The sensitivity of concentrations in the flame was also investigated at 1300 K and 2200 K. At the lower temperature, the same reactions proved to be of high

Table 3. Rate limiting steps of the production rate of species H₂O

1	1.14638E + 01	9	O ₂ + H =>OH + O
2	2.31090E + 00	1	H ₂ + O =>OH + H
3	-1.28020E + 00	5	O ₂ + H + M =>HO ₂ + M
4	1.09480E + 00	3	H ₂ + OH =>H ₂ O + H
5	8.99051E - 01	30	H ₂ + O ₂ =>H + HO ₂

Table 4. Principal component analysis of the concentration sensitivity matrix. Concentrations of H₂, O₂, and H₂O were considered in the objective function

No 1 Eigenvalue: 1.10561E + 03 eigenvector:			
1	0.966	9	O ₂ + H =>OH + O
2	0.199	1	H ₂ + O =>OH + H
3	-0.104	5	O ₂ + H + M =>HO ₂ + M
4	0.099	3	H ₂ + OH =>H ₂ O + H
5	0.077	30	H ₂ + O ₂ =>H + HO ₂
No 2 Eigenvalue: 8.05363E - 01 eigenvector:			
1	-0.618	3	H ₂ + OH =>H ₂ O + H
2	0.422	10	OH + O =>O ₂ + H
3	0.360	4	H ₂ O + H =>H ₂ + OH
4	-0.354	1	H ₂ + O =>OH + H
5	0.308	2	OH + H =>H ₂ + O
6	-0.258	5	O ₂ + H + M =>HO ₂ + M
7	0.114	9	O ₂ + H =>OH + O

Table 5. Sensitivity of the concentration of H₂O at 2200 K in the homogeneous explosion model

No	Sensitivity	#	Reaction
1	1.71283E - 01	9	O ₂ + H =>OH + O
2	9.31257E - 02	3	H ₂ + OH =>H ₂ O + H
3	-8.07469E - 02	4	H ₂ O + H =>H ₂ + OH
4	6.36368E - 02	1	H ₂ + O =>OH + H
5	-5.06797E - 02	10	OH + O =>O ₂ + H
6	-3.95848E - 02	2	OH + H =>H ₂ + O

Table 6. Rate limiting steps of the production rate of H₂O at 2200 K in the homogeneous explosion model

1	1.44923E + 02	9	O ₂ + H =>OH + O
2	4.20900E + 01	1	H ₂ + O =>OH + H
3	2.49128E + 01	27	H + OH + M =>H ₂ O + M
4	2.40452E + 01	3	H ₂ + OH =>H ₂ O + H
5	1.63269E + 01	25	H + O + M =>OH + M
6	-1.55485E + 01	2	OH + H =>H ₂ + O
7	-1.49071E + 01	10	OH + O =>O ₂ + H

sensitivity than in the homogeneous case, that is reactions 9, 3, 5, and 1. The only exception is the high negative sensitivity of reaction 10 (OH + O =>O₂ + H). Due to diffusion processes, at this temperature the OH and O concentrations in the flame are higher than at homogeneous conditions and it increases the significance of this reaction. At 2200 K, reactions 4, 3, 27, 10, 9, 2, 1 have high sensitivity, similarly to the homogeneous case. This indicates that the main chemical processes in a homogeneous hydrogen explosion and in a hydrogen flame are similar, although the physical processes and the way of the initiation are quite different.

8 CONCLUSION

Local concentration sensitivities are now routinely calculated by the widely available combustion simulation programs, but the utilization of these sensitivities requires further work and it discourages their widespread application. KINALC is a post-processor to CHEMKIN based programs, which contains several advanced handling of the raw sensitivities, including calculation of sensitivities of objective functions, of reaction rates and also principal component analysis of the concentration sensitivity matrix. These measures can be used for the understanding of complex kinetic reactions, as it has been demonstrated on investigation of a detailed chemical mechanism of hydrogen combustion at homogeneous explosion and premixed laminar flame conditions.

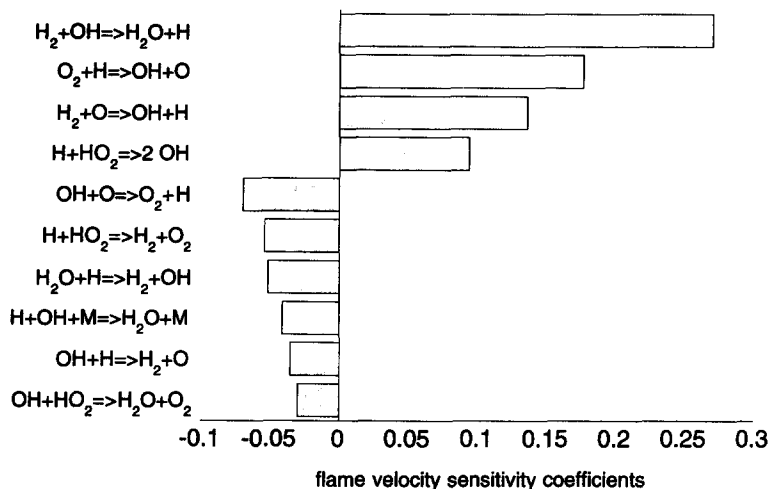


Fig. 3. Normalized sensitivities of the velocity of atmospheric, stoichiometric hydrogen-air flame with respect to the rates of chemical reactions.

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