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On the similarity of the sensitivity functions of methane combustion models

I. GY. ZSÉLY*, J. ZÁDOR and T. TURÁNYI

Department of Physical Chemistry, Eötvös University (ELTE), P.O. Box 32,
H-1518 Budapest, Hungary

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It is widely known that detailed kinetic mechanisms with identical reaction steps but with very different rate parameters may provide similar simulation results in combustion calculations. This phenomenon is related to the similarity of sensitivity functions, which arises if low-dimensional manifolds in the space of variables, and autocatalytic processes are present. We demonstrated the similarity of sensitivity functions for adiabatic explosions and burner-stabilized laminar flames of stoichiometric methane–air mixtures. The cause of similarities was investigated by calculating the dimension of the corresponding manifolds, and the pseudo-homogeneous property of the sensitivity ordinary differential equation (ODE). The methane explosion model showed global similarity, which means that different parameter sets could provide the same simulation results. This was demonstrated by numerical experiments, in which two significantly different parameter sets resulted in identical concentration profiles for all species. This phenomenon is important from a practical point of view in the fields of 'validation' of complex reaction mechanisms and parameter estimation of chemical kinetic systems.

Keywords: Methane combustion; Sensitivity analysis; Manifold; Global similarity

1. Introduction

To describe the combustion of a number of fuels, detailed reaction mechanisms have been employed. To model the burning of the most important fuels, such as methane, several (up to 7−10) independently and concurrently elaborated reaction mechanisms are available in the literature. These mechanisms were usually developed knowing the same experimental results for the elementary reactions; therefore, one might expect that the accomplished mechanisms are very similar. Surprisingly, this is not the case. In a recent article by Hughes *et al.* [1], the Leeds methane oxidation mechanism [1, 2], the GRI mechanism (see [3]), and the mechanisms of Konnov [4] and Chevalier [5] were compared. The latter was the 1993-year version methane oxidation mechanism of Warnatz and coworkers. These mechanisms had been tested on similar experimental data, and the agreement between the experimental and simulation results were of similar level. In Hughes *et al.* [1], sensitivity analysis was used to identify reaction steps, for which a small deviation in the rate coefficient significantly changed the simulation results at any of the tested conditions. There were 44 such reactions out of the 350 irreversible reactions of the Leeds methane oxidation mechanism. Almost all of these reactions were also present in

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*Corresponding author. E-mail: zsigy@vuk.chem.elte.hu

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the other three mechanisms, but usually with different Arrhenius parameters. For 14 reaction steps out of the 46, the rate coefficient was more than three-fold different in the 1000–2000 K temperature range in at least one of the mechanisms. How could combustion models based on these mechanisms produce very similar results if several of the critical rate coefficients were fundamentally different?

In a similar study of Hughes *et al.* [6] four recent NO_x mechanisms were compared; these were the Leeds NO_x mechanism [1, 2], the GRI-Mech (Version 3.0) [3], the NO_x mechanism of Glarborg, Milles and coworkers [7], and the mechanism of Dean and Bozelli [8]. Again, the simulations based on these mechanisms reproduced experimental data with similar accuracy. The Leeds NO_x mechanism contained 678 irreversible reactions, and 67 of them had high sensitivity at any of the test conditions. Only a single reaction step from these reactions had identical Arrhenius parameters in all of the mechanisms, and for 34 reactions the difference in the rate coefficients was greater than a factor of 3 in the temperature range 1000–2000 K in at least one of the mechanisms.

Several experimental methods for the determination of rate coefficients are based on the application of small mechanisms by fitting unknown reaction parameters to measured data using literature rate parameters for the rest of the reaction steps. These types of experiments include the determination of rate coefficients by fitting them to concentrations of end products, concentration profiles in flames, and shock tube measurement data. In several cases, there had been a good agreement between the measured and the simulated data, but subsequent direct measurements indicated that the determined rate coefficients were substantially wrong. The same measurement data could be equally well described by another model, based on the same reaction steps, but with very different rate parameters.

In all of the above cases, the models contained identical reaction steps with very different rate coefficients, but produced similar results. This phenomenon is related to the similarity of the sensitivity functions of combustion models [9]. In the recent articles of Zsély *et al.* (see [9–11]), the similarity of sensitivity functions of hydrogen–air combustion models was studied at different equivalence ratios. The investigated systems were homogeneous explosions, freely propagating and burner-stabilized flames, both at adiabatic conditions and assuming a fixed temperature profile. Zsély *et al.* [9] briefly demonstrated that local and global similarities were also present in methane–air explosion models, but there was no systematic investigation for that case. In this paper, similarities of the sensitivity functions of methane–air explosion and flame models are investigated.

In section 2, the main features of the similarities of the sensitivity functions are summarized along with a brief literature review. In section 3, a new proof is given that local similarity and pseudo-homogeneity are necessary conditions of global similarity. In the next section, existence of local similarity, scaling relation and global similarity of sensitivity functions of models of methane–air explosions and flames is demonstrated. In section 5, conditions for the origin of the similarities of sensitivities are investigated. In section 6, two consequences of the similarities of sensitivity functions are illustrated by numerical examples: the rank of the local sensitivity matrix is low, and models with very different parameter sets can produce almost identical results.

2. Similarity of the sensitivity functions

Sensitivity analysis is a widely used tool for the study of chemical kinetic and combustion models [12]. The majority of the combustion simulation programs calculate local sensitivity coefficients $s_{ik} = \partial Y_i / \partial p_k$, which show the change of model result Y_i if parameter p_k has been slightly altered. The sensitivity coefficients constitute the first order local sensitivity matrix $\mathbf{S} = \{s_{ik}\}$. Let $\mathbf{s}_i = \partial Y_i/\partial \mathbf{p}$ denote the vector of the ith row of the sensitivity matrix. Sensitivity function is defined as the change of the local sensitivity coefficient as a function of the independent variable, which is time (in time-dependent spatially homogeneous systems) or the spatial coordinate (in stationary flat flames).

In the case of a general mathematical model, no relation is expected among the rows and/or the columns of the sensitivity matrix. However, in several chemical kinetic systems the following relations have been observed (see [9, 13]):

(i) Local similarity: Value

$$\lambda_{ij}(z) = \frac{s_{ik}(z)}{s_{jk}(z)} \tag{1}$$

depends on the independent variable z (time or distance) and the model results Y_i and Y_j selected, but is independent of parameter p_k perturbed. In some systems, equation (1) holds only for some parameters. If it is valid for each parameter, then the local similarity for all sensitivity coefficients implies relation

$$\mathbf{s}_i(z) = \lambda_{ij}(z)\,\mathbf{s}_j(z) \tag{2}$$

for all rows of the sensitivity matrix. In this case, the rank of the sensitivity matrix is one.

(ii) Scaling relation: Equation

$$\frac{(\mathrm{d}Y_i/\mathrm{d}z)}{(\mathrm{d}Y_j/\mathrm{d}z)} = \frac{s_{ik}(z)}{s_{jk}(z)} \tag{3}$$

is valid for any parameter p_k. Existence of scaling relation presumes the presence of local similarity.

(iii) Global similarity: Value

$$\mu_{ikm} = \frac{s_{ik}(z)}{s_{im}(z)} \tag{4}$$

does not change with z within interval (z_1, z_2). It has been shown (see [9]), that the simultaneous presence of local and global similarities implies that μ_{ikm} is identical for all model output Y_i, denoted from now as μ_{km}. This also means that vectors $\partial\mathbf{Y}/\partial p_k$ belonging to $z_a, z_b \subset (z_1, z_2)$ are interrelated by the equation

$$\frac{\partial \mathbf{Y}}{\partial p_k}(z_a) = \mu_{km}\frac{\partial \mathbf{Y}}{\partial p_m}(z_b) \tag{5}$$

Global similarity and scaling relation of sensitivity functions were detected in a simple flame model by Reuven *et al.* [14]. Similarity of sensitivity functions were found in adiabatic premixed hydrogen–air [13, 15, 16], and CO/H_2/O_2 flames [17]. In the recent articles of Zsély *et al.* (see [9–11], the similarities of sensitivity functions of hydrogen–air combustion models were systematically studied at various conditions. Perfect local similarity, scaling relation and global similarity were found only in the cases of adiabatic explosions. Fixed temperature-profile explosions expressed local similarity for some parameters. Even for these parameters, scaling relation was not valid. Adiabatic burner-stabilized flames showed all the three types of similarity, but only for some parameters. Similarity was not found for freely propagating flames and for fixed temperature profile burner-stabilized flames.

The level of local similarity can be characterized by the difference of the directions of two sensitivity vectors in the space of parameters [11], which can be obtained by the calculation of the following scalar product of the normalized sensitivity vectors:

$$\hat{\mathbf{s}}_i\hat{\mathbf{s}}_j = \cos\theta_{ij} \tag{6}$$

Here $\hat{\mathbf{s}}_i = \mathbf{s}_i/\|\mathbf{s}_i\|$ and $\hat{\mathbf{s}}_j = \mathbf{s}_j/\|\mathbf{s}_j\|$ are the unit length sensitivity vectors, and θ_{ij} is their angle in the parameter space. $\cos\theta_{ij} = \pm 1$ means that the sensitivity vectors are locally similar, and are positively or negatively correlated. If $\cos\theta_{ij}$ is not close to ± 1 then the sensitivity vectors are poorly correlated and are not locally similar.

Zsély *et al.* [9] have shown that the similarity of sensitivity functions is related to the existence of low-dimensional manifolds in chemical kinetic systems. The *scaling relation* can be explained on the basis of two assumptions: (i) the dynamical behaviour of the system is controlled by a one-dimensional slow manifold in the space of the variables; (ii) infinitesimal change of a parameter changes the velocity of the movement on the manifold, but negligibly dislocates the manifold. The second assumption is related to the parametric sensitivity analysis of manifolds. This topic was discussed in the paper of Skodje and Davis [18], where among others, sensitivity analysis of attracting low-dimensional manifolds (ALDMs) was examined. Sensitivities parallel to the manifold were reported to be about four magnitudes larger than the perpendicular ones, which dislocate the manifold. König and Maas [19] introduced a new method for the calculation of the sensitivity of the instrinsic low-dimensional manifolds (ILDMs). In a model of $CO/H_2/O_2/N_2$ flame they found that far from the equilibrium, the sensitivity of the ILDM with respect to parameter perturbation was large, and near the equilibrium point, it became smaller having components only parallel to the ILDM.

3. Relation of the similarity of sensitivities to the pseudo-homogeneity of the sensitivity ODE

In the cases of dynamical systems that can be defined by a system of ordinary differential equations

$$\dot{\mathbf{Y}} = \mathbf{f}(\mathbf{Y}, \mathbf{p}) \tag{7}$$

the sensitivity matrix can be calculated by solving equation

$$\dot{\mathbf{S}} = \mathbf{JS} + \mathbf{F} \tag{8}$$

assuming initial value $\mathbf{S}(t = 0) = \mathbf{0}$, where $\mathbf{J} = \partial\mathbf{f}/\partial\mathbf{Y}$ is the Jacobian and $\mathbf{F} = \partial\mathbf{f}/\partial\mathbf{p}$. These equations are widely used in conjunction with the chemical kinetics of spatially homogeneous reaction systems [12, 20]. Equation (8) would be homogeneous, if matrix **F** were a zero matrix. In some systems, $\|\mathbf{F}\| \ll \|\mathbf{JS}\|$ was found, and in this case equation (8) was called pseudo-homogeneous [21]. Pseudo-homogeneity of this equation means that parameter perturbations have little direct effect on the calculated sensitivity functions when the change of sensitivities becomes significant due to the **JS** term; this feature is related to the autocatalytic changes in chemical kinetic systems [9].

Vajda and Rabitz [21] suggested that a necessary condition of global similarity is the pseudo-homogeneity of the sensitivity differential equation (8). Their derivation was based on the analysis of a two-variable system. This reasoning was modified, extended and developed further by Zsély *et al.* [9], arriving at the conclusion that the pseudo-homogeneous property of the sensitivity differential equation (8) and the presence of local similarity together imply global similarity. This proof was based on an analysis of Green's function. Here, an alternative reasoning is presented.

Global similarity means that

$$s_{ik}(t) = \mu_{ikm}\, s_{im}(t) \tag{9}$$

This implies that:

$$\dot{s}_{ik}(t) = \mu_{ikm}\,\dot{s}_{im}(t) \tag{10}$$

For variable i and parameter k, equation (8) has the form

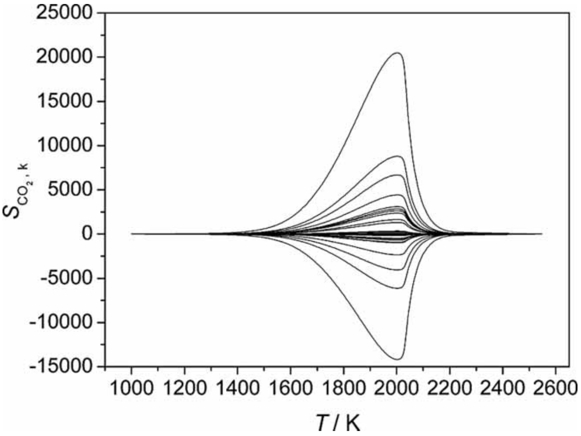
$$\dot{s}_{ik} = \sum_j J_{ij}s_{jk} + F_{ik} \tag{11}$$

Substituting the corresponding forms to equation (10) yields

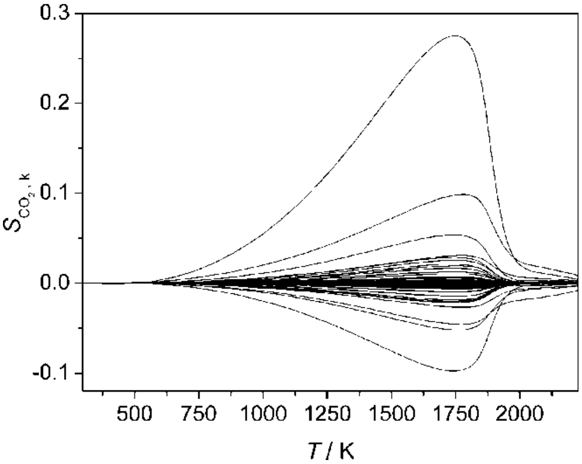
$$\sum_j J_{ij}s_{jk} + F_{ik} = \mu_{ikm}\left(\sum_j J_{ij}s_{jm} + F_{im}\right) \tag{12}$$

Substituting equation (9) for variable j, $s_{jk}(t) = \mu_{jkm}s_{jm}(t)$, in equation (12) gives

$$\sum_j J_{ij}s_{jk} + F_{ik} = \mu_{ikm}\left(\sum_j J_{ij}\frac{s_{jk}}{\mu_{jkm}} + F_{im}\right) \tag{13}$$



(a)



(b)

Figure 1. Semi-normalized $\partial w_i/\partial \ln A_k$ sensitivity coefficient–temperature functions for the mass fraction of CO_2 of: (a) adiabatic explosion and (b) burner-stabilized flame.

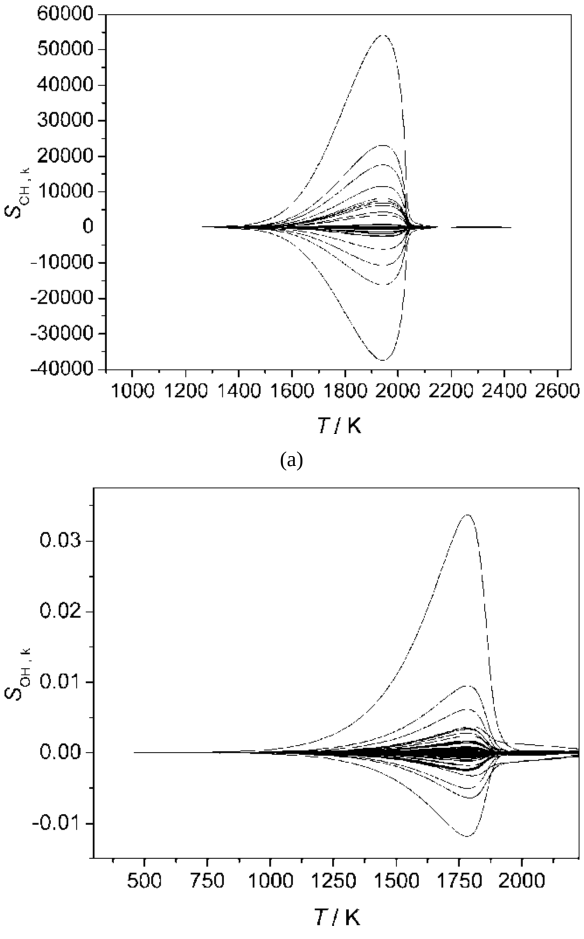
If local similarity holds, then $\mu_{ikm} = \mu_{jkm} = \mu_{km}$ for all pairs of i and j and therefore

$$\sum_j J_{ij} s_{jk} + F_{ik} = \sum_j J_{ij} s_{jk} + \mu_{km} F_{im} \tag{14}$$

Since F_{ik} is in general not equal to $\mu_{km} F_{im}$ for any i, k and m, these quantities should be negligibly small to fulfil equation (14), which then becomes an identity. Elements of **F** being negligible small mean that the sensitivity differential equation (8) is pseudo-homogeneous. Thus, global similarity is true if local similarity and pseudo-homogeneity are both present.

4. Similarity of the sensitivity vectors of methane–air combustion models

In all numerical examples of this paper, the combustion of stoichiometric methane–air mixtures was investigated. Concentration–time and sensitivity–time curves of adiabatic explosions were calculated by the program SENKIN [22]. Initial conditions were $p = 1$ atm, $T_0 = 1000$ K. Burner-stabilized adiabatic premixed laminar flames were simulated by the program PREMIX [23]. The cold boundary conditions were $p = 1$ atm and $T_c = 298.15$ K. The simulations were based on the Leeds methane oxidation mechanism v1.5 [1, 2], except when noted otherwise.



(a)

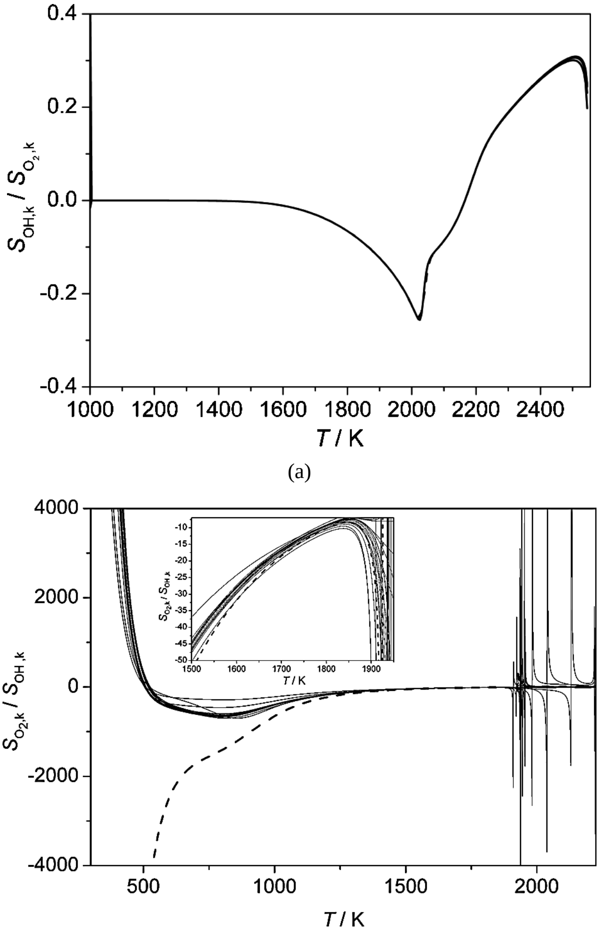
(b)

Figure 2. Semi-normalized $\partial w_i / \partial \ln A_k$ sensitivity coefficient–temperature functions for the mass fraction of OH of: (a) adiabatic explosion and (b) burner-stabilized flame.

In the figures, the results were usually plotted as a function of temperature, instead of time (explosions) or distance (1D stationary flames). This is an equivalent representation of the data, because temperature continuously increases with time and distance in these adiabatic homogeneous explosions and 1D stationary flames, respectively. The sensitivities of the calculated concentrations and temperature with respect to only the pre-exponential factors *A* of the reactions were investigated. Results of the explosion and burner-stabilized flame calculations are presented in parallel, to facilitate comparison.

Figures 1 and 2 show the sensitivity–temperature functions of the calculated CO_2 and OH mass fractions, respectively, in the cases of adiabatic explosion and burner-stabilized flame. These sensitivity curves are surprisingly well ordered, except for the flame above about 1800 K. The sensitivity curves of all other species show this highly ordered structure.

Existence of local similarity and scaling relation was explored by calculating appropriate ratios of sensitivity functions and production rates or spatial gradients. Several parameters of the model were not effective, i.e. the corresponding sensitivity functions were close to zero, and their values were calculated with large relative numerical error. This is emphasized when the ratios of such numbers are calculated. In figure 3, the ratios of the sensitivity functions of



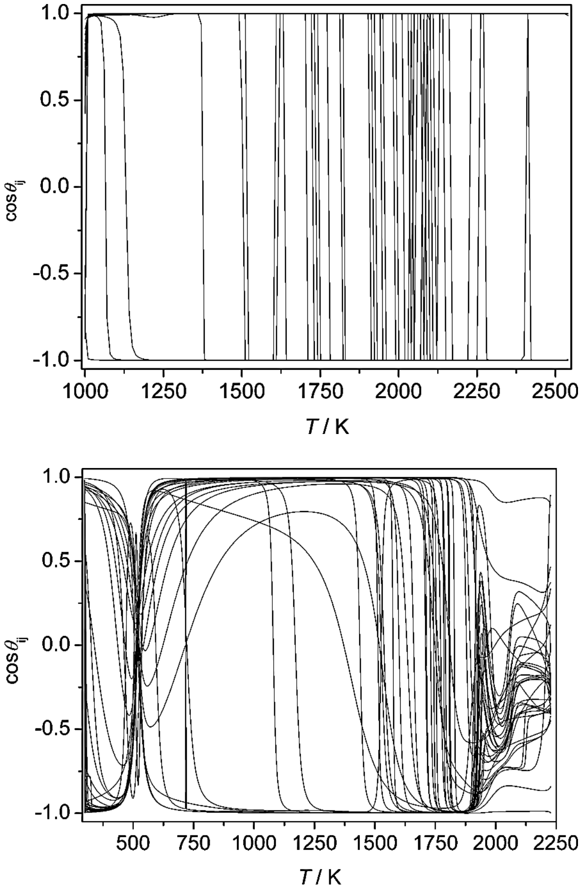
(a)

(b)

Figure 3. The solid lines show the ratio of the sensitivity functions of OH and O_2 for the 22 most sensitive pre-exponential factors for: (a) adiabatic explosion and (b) burner-stabilized flame. The dashed line indicates the ratio of the corresponding production rates (a) and spatial gradients (b).

the 22 most effective parameters and the ratio of the production rates (for the explosion) or the spatial gradients (for the flame) of OH and O_2 are plotted. Figure 3a shows that the ratios of the sensitivity functions of OH and O_2 agree very well and the ratio of the production rates of OH and O_2 coincides exactly with the ratio of the sensitivities in the whole temperature range. Figure 3b shows that the ratios of the sensitivity functions of O_2 and OH agree well below 1900 K; also, these coincide with the ratio of the gradients above 1700 K. The coincidences of the ratios of the sensitivity functions vanish above 1900 K and sharp peaks appear, in accordance with the loss of similarity in figures 1b and 2b in this region. Similar figures were obtained for all other pairs of species.

Local similarity of sensitivity vectors can be investigated further by calculating the correlation of the vectors according to equation (6). Figure 4a shows that the sensitivity vector of a CO_2 mass fraction is always well correlated (positively or negatively) with the sensitivity vectors of the mass fractions of all other species in the case of adiabatic explosion. This means that local similarity is valid for the sensitivity vectors of all species. If scaling relation is also valid, the changes of the correlation coincide with the concentration extremes of the corresponding species [11]. Accordingly, in the present case, the correlation changes are also at the location of the minimum or maximum of the related concentration profiles. Figure 4b shows



(b)

Figure 4. Correlation of all other sensitivity vectors with the sensitivity vector of CO_2 as a function of temperature for: (a) adiabatic explosion and (b) burner-stabilized flame.

the correlation of the sensitivity vector of CO_2 mass fraction with the sensitivity vectors of all other species as a function of temperature for the burner-stabilized flame. The sensitivity vectors of most species are well correlated with that of the CO_2 below 1900 K. The correlation is poor above 1900 K, in accordance with figure 3b. Figure 4b is also in accordance with the observations of Zsély *et al.* [9] that diffusion decreases the level of local similarity.

In the case of the adiabatic explosion, the calculated CO_2 concentration is most sensitive to the pre-exponential factor of reaction $O_2 + CH_3 \rightarrow CH_2O + OH$. Ratios of the sensitivity coefficients of all other reactions and that of this reaction were calculated according to equation (4) and are plotted in figure 5a. The ratios are constant above 1400 K, indicating that global similarity is valid in this region for the sensitivity functions of adiabatic methane–air explosions. Similar horizontal lines were obtained when the sensitivity ratios belonging to other species were plotted. In the case of the burner-stabilized flame, the most sensitive reaction was $O_2 + H \rightarrow OH + O$, therefore, this was chosen as the reference reaction and the ratios obtained are presented in figure 5b. Global similarity is valid in a wide temperature interval, about from 900 to 1800 K. Loss of global similarity at 1800 K is in coincidence with the disappearance of local similarity.

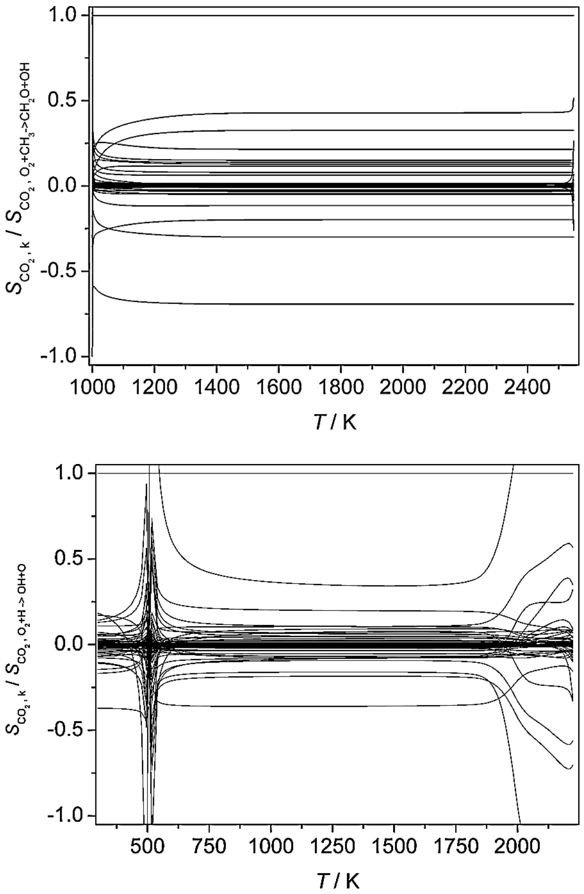


Figure 5. The ratio of the sensitivities of the calculated CO_2 mass fraction with respect to the pre-exponential factors of each reaction and that of most sensitive reaction (adiabatic explosion: $O_2 + CH_3 \rightarrow CH_2O + OH$, burner-stabilized flame: $O_2 + H \rightarrow OH + O$).

Sensitivity curves for the adiabatic explosions of atmospheric, stoichiometric methane–air mixtures were also calculated using the GRI mechanism [3], and the mechanism of Konnov [4]; results are presented in figures 6 and 7, respectively. Unlike in the other cases, the initial temperature was 1100 K in the case of the GRI mechanism, because no ignition was predicted at 1000 K using this mechanism. The sensitivity–time curves obtained also show a very high level of similarity for these two mechanisms, which illustrates that the similarity features of the sensitivity functions of mechanisms alike do not depend on the mechanistic details, although the actual shape of the sensitivity functions are different.

5. Cause of the similarity of the sensitivity functions

Local similarity and scaling relation of the sensitivity functions were related [9] to the existence of low-dimensional manifolds. We have shown in the previous section (see figure 3) that for methane–air explosions and flames, the ratios of the sensitivity functions are identical that is local similarity is present. The scaling relation was valid in the whole temperature range for the explosion, and it is valid in a temperature range for the flame. Figures 3b and 4b show that local similarity is not valid in the flame above approximately 1900 K.

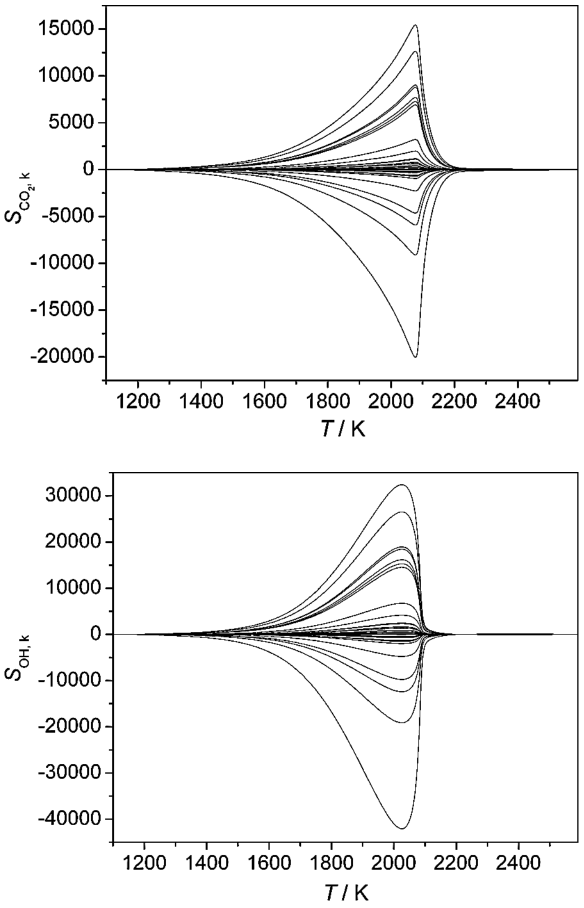


Figure 6. Semi-normalized CO_2 and OH sensitivity–temperature curves for the adiabatic explosion of methane–air mixture using the GRI 3.0 mechanism.

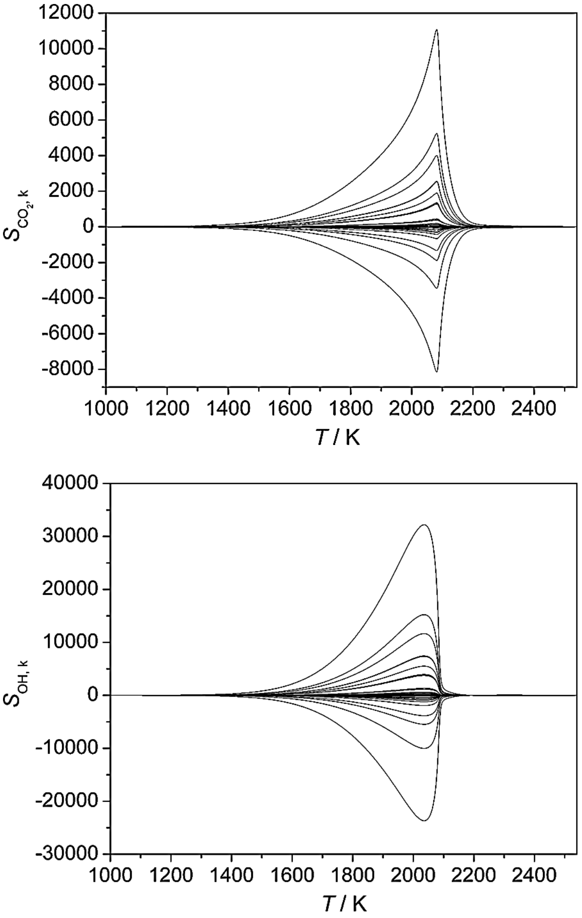
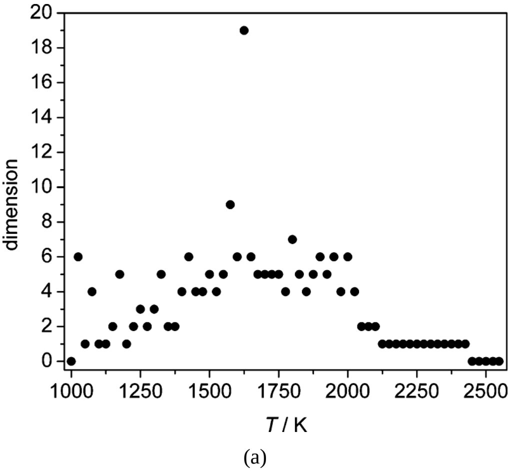


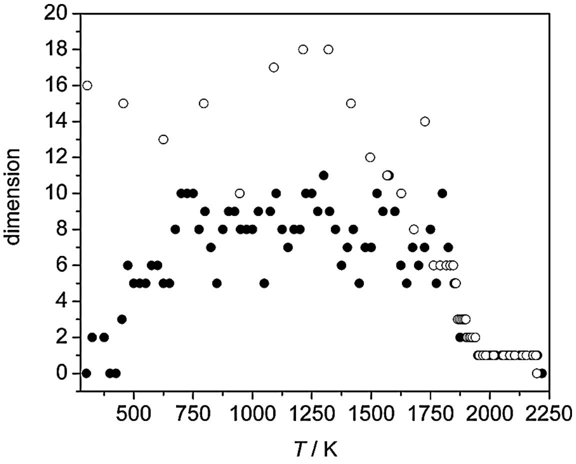
Figure 7. Semi-normalized CO_2 and OH sensitivity–temperature curves for the adiabatic explosion of methane–air mixture using the Konnov mechanism.

In this section, the dimension of the manifold was estimated for both methane–air explosions and flames. The method used was published by Tomlin *et al.* [24] and Büki *et al.* [25], and had been encoded in program KINALC [26]. According to this method, the dimension of the manifold is equal to the number of variables minus the sum of the number of conservation relations (indicated by the number of zero eigenvalues of the Jacobian) and the number of relaxed modes, which was calculated on the basis of the eigenvalue–eigenvector decomposition of the Jacobian. This estimation is based on local linearization, and is affected by numerical inaccuracies. However, the results have been found to be in accordance with the expectations, and the results of other methods.

Figure 8 shows that the calculated dimension of the manifold for both the explosion and the burner-stabilized flame increases with the temperature, reaches a plateau, and after a given temperature starts to decrease, reaching one (2125 K) and finally becomes zero close to the equilibrium. Schmidt *et al.* [27] also calculated the dimension of the ILDM in premixed stoichiometric methane–air flame using very similar conditions to ours ($p = 1$ bar, $T_c = 298$ K). The calculated dimension of Schmidt *et al.* [27] is also presented in figure 8b as a function of temperature. In the original publication the relaxed modes vs. mass fraction of CO_2 was presented. We converted these quantities to the dimension of the manifold vs. temperature, using the CO_2 mass fraction–temperature profile from our calculations (their CO_2 mass



(a)



(b)

Figure 8. Dimension of the manifold as a function of temperature calculated for the (a) adiabatic explosion and (b) burner-stabilized flame. Figure (b) contains the calculated dimension from Schmidt *et al.* [27] with empty circles.

fraction–temperature profile was not published). The basic features of the two dimensions vs. temperature plots are similar and there is a quantitative agreement above 1850 K.

It is interesting to compare the dimension vs. temperature plots to the results of sensitivity calculations. For the adiabatic explosion, the sensitivity ratios run together with each other and the ratios of the production rates from the beginning of the calculation, but the dimension becomes one only from about 2100 K, indicating that the presence of one-dimensional manifold is a sufficient but not necessary condition of local similarity and scaling relation. For the burner-stabilized flame, the local similarity and the scaling relation becomes approximately valid from 1250 K, while the estimated dimension of the manifold becomes one at and above 1925 K. It shows that the presence of the low-dimensional manifold is a sufficient condition of local similarity; in the systems investigated the sensitivities became similar at lower temperature, when the calculated dimension was still about five to eight. Since the system has 37 variables, dimension of five to eight already enforces an ordering of the sensitivity functions.

Presence of local similarity and the pseudo-homogeneity of the sensitivity differential equations were shown to be a sufficient condition of global similarity. To check the latter condition in the case of the adiabatic explosion, the ratios of the norms of the inhomogeneous $\mathbf{F}_j$ and the

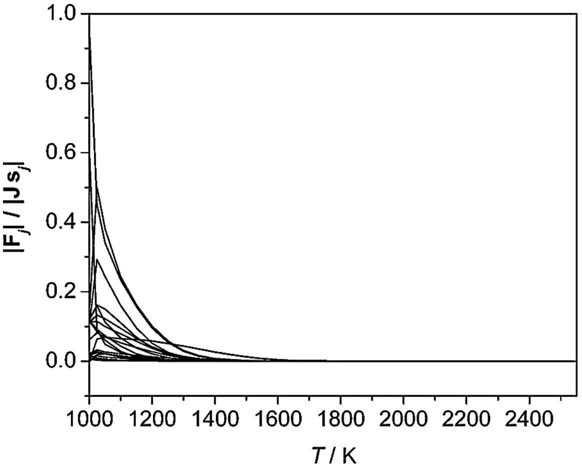
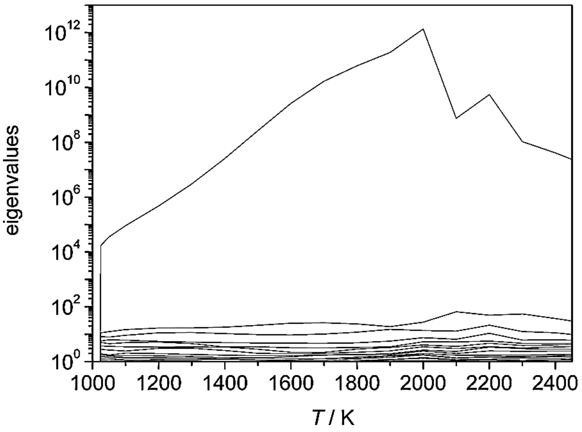
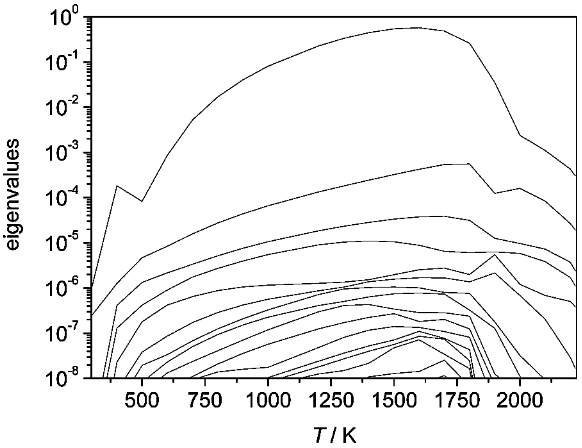


Figure 9. Ratio of the norms of the inhomogeneous $\mathbf{F}_j$ and homogeneous $\mathbf{Js}_j$ terms for each parameter j of sensitivity differential equation (8) in the case of the adiabatic explosion.



(a)



(b)

Figure 10. Eigenvalues of the $\mathbf{S}^T\mathbf{S}$ matrix as a function of temperature calculated for (a) explosion and (b) burner-stabilized flame.

homogeneous $\mathbf{Js}_j$ terms for each parameter j of the sensitivity differential equation (8) were calculated. Figure 9 demonstrates that the ratios are almost zero above temperature 1400 K for each parameter, showing the pseudo-homogeneity of the sensitivity ODE. It is in perfect agreement that global similarity becomes valid at 1400 K.

6. The consequences of the similarity of the sensitivity functions

The rank of the local sensitivity matrix was claimed by Zsély *et al.* [9] to be less than or equal to the dimension of the manifold. The rank of matrix $\mathbf{S}$ is equal to the rank of the $\mathbf{S}^T\mathbf{S}$ matrix. In the case of the adiabatic hydrogen–air explosion, Zsély *et al.* [9] demonstrated that one eigenvalue of the $\mathbf{S}^T\mathbf{S}$ matrix is much greater than the others, and therefore the approximate rank is one. Here, the approximate rank of the $\mathbf{S}^T\mathbf{S}$ matrix is calculated in a similar way for the stoichiometric methane–air adiabatic explosion and burner-stabilized flame. Figure 10 shows that for the adiabatic explosion the first eigenvalue is 10^5 to 10^{10} times larger than the second one. In the case of the flame, the first eigenvalue is 10^2 to 10^3 times larger than the second one and it is 10^3 to 10^5 times larger that the fifth one. This means that the rank of sensitivity matrix of explosion can be considered one and the approximate rank is also small for the sensitivity matrix of the flame. This is in good agreement with figure 4, which shows the correlations of sensitivity vectors.

Presence of both local and global similarities means that if several parameters are changed in a model, its overall effect can be fully compensated by changing a single effective parameter, because the ratio of the sensitivity functions is identical everywhere in the region of similarity. This way, the values of *all* variables can be restored to the original value in a *wide range* of time or distance. If only local similarity is present, the values of *all* variables can be restored simultaneously, but only at a single point of the independent variable.

This feature was demonstrated for H_2/O_2 explosions [9]. Figures 11 and 12 report the results of numerical experiments for methane explosion. Concentration–time curves for species CO_2, OH, CH_3 and CH had been calculated for the adiabatic methane–air explosion using the original mechanism; the results were plotted with solid lines. Sensitivity analysis identified that changing the pre-exponential factors of reactions $2CH_3(+M) \rightarrow C_2H_6(+M)$, $CH_3 + HO_2 \rightarrow CH_3O + OH$, $CH_4 + H \rightarrow CH_3 + H_2$ and $CH_2O + OH \rightarrow HCO + H_2O$ have high influence on the calculated concentrations. These pre-exponential factors were increased by 50%; the calculated concentration curves are given in figure 11 by dashed lines. According to the sensitivity analysis, changing the pre-exponential factor of reaction $O_2 + CH_3 \rightarrow CH_2O + OH$ has the highest influence; in the next step, it was increased to shift the OH peak back to the original time. The required modification found by iteration was 9.875%, and then the calculated results *for all species at all times* became very similar to the original ones (see dotted lines). This means that although in the final mechanism the values of five of the most effective parameters were very different from the original ones, the model results were almost identical for all concentration curves at all times. Similar results could be obtained, if the modification of the parameters were much larger. In another numerical experiment the pre-exponential factors of the same reactions were increased by 400% and this change could be compensated by increasing the pre-exponential factor of the reaction $O_2 + CH_3 \rightarrow CH_2O + OH$ by 56.82%. As figure 12 shows, the agreement of the concentration curves of the original and the 5-reaction-modified mechanism is still good, but worse than in the previous case. Note that global similarity is based on local sensitivity vectors, which are supposed to be informative for small parameter changes only. Our results indicate that the behaviour predicted by global similarity is also valid for large parameter changes, but inaccuracy increases, increasing the change of the parameters.

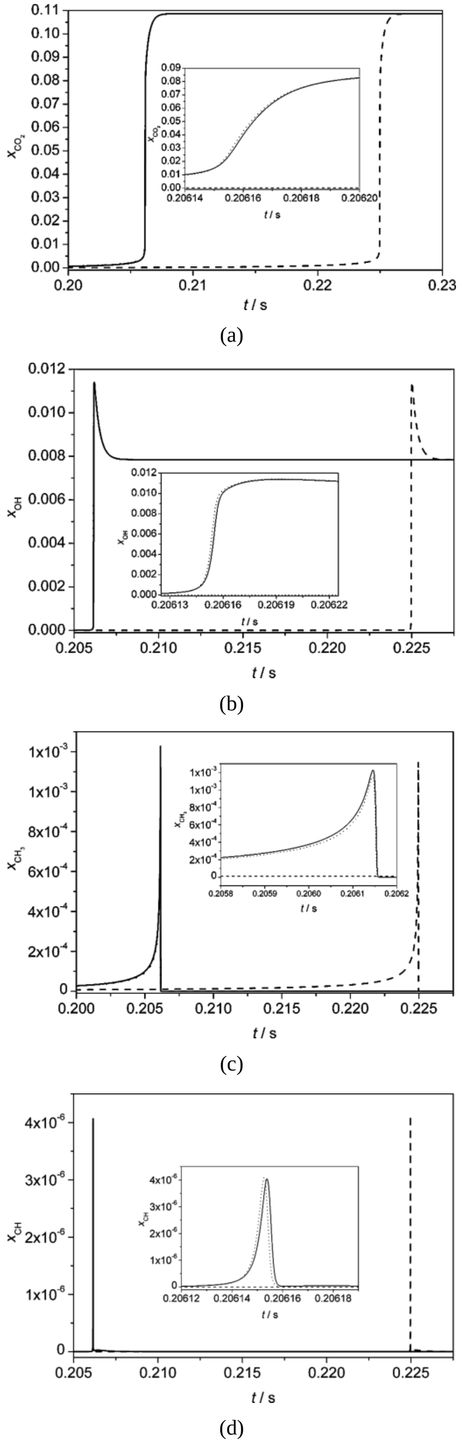


Figure 11. Concentration–time curves for species (a) CO_2, (b) OH, (c) CH_3, and (d) CH, calculated for the adiabatic methane–air explosion using the original mechanism (solid line); a modified mechanism, obtained by increasing four of the most sensitive rate parameters by 50% (dashed line); and a third mechanism, obtained by an appropriate modification of an additional fifth parameter (increased by 9.875%, dotted line). The solid and the dotted lines can be distinguished only in the blown-ups.

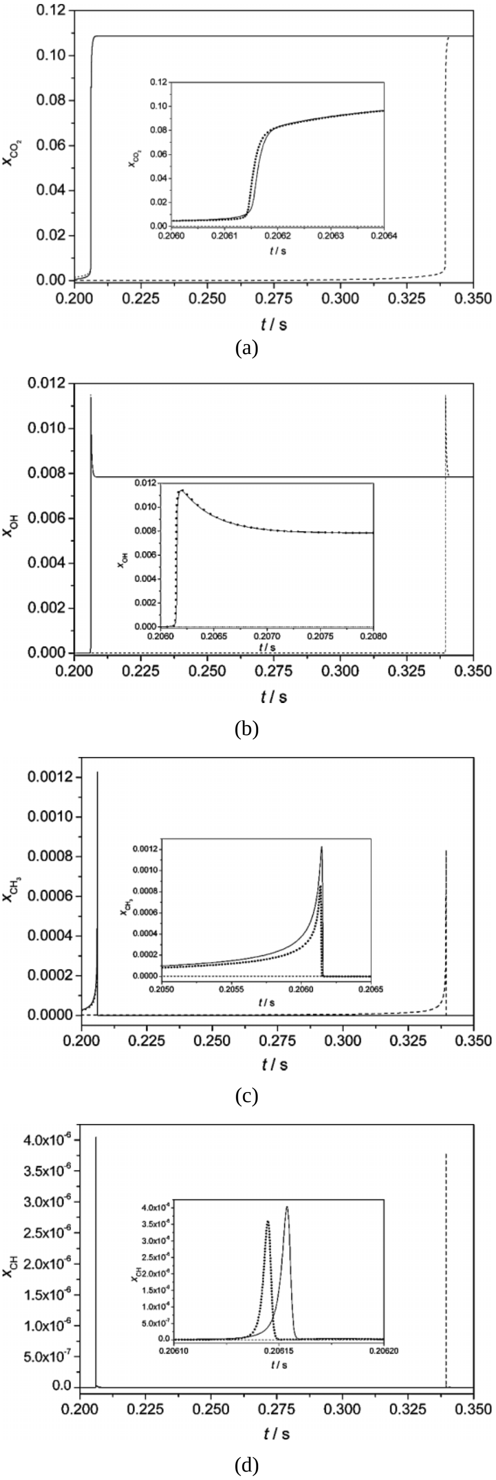


Figure 12. Concentration–time curves for species (a) CO_2, (b) OH, (c) CH_3, and (d) CH, calculated for the adiabatic methane–air explosion using the original mechanism (solid line); a modified mechanism, obtained by increasing four of the most sensitive rate parameters by 400% (dashed line); and a third mechanism, obtained by an appropriate modification of an additional fifth parameter (increased by 56,82%, dotted line). The solid and the dotted lines almost coincide and are well separated only in the blown-ups.

7. Conclusion

In the cases of all mechanistic combustion models that describe high temperature chemical reactions, there is a large separation in the time scales of the model. The presence of low-dimensional manifolds induces local similarity of the sensitivity functions. A general feature of most high temperature combustion models is that a rapid transition occurs from the unburnt state to the burnt state, and this transition has an autocatalytic nature. In the autocatalytic transition period, a parameter perturbation has negligible direct effect on the calculated results, but the interaction of the variables is significant. This feature is equivalent to the pseudo-homogeneity of the sensitivity differential equations. A novel proof is presented in this paper that local similarity and pseudo-homogeneity together is a sufficient condition of global similarity. Since presence of low-dimensional manifolds and fast autocatalytic transition from unburnt to burnt states are general features of high-temperature combustion models, global similarity of the sensitivity functions also seem to be a general feature of such models.

Existence of local similarity, scaling relation and global similarity of sensitivity functions of models of adiabatic, stoichiometric methane–air explosions and burner-stabilized flames was investigated using the Leeds methane oxidation mechanism. In the cases of explosions, a high level of local and global similarity and scaling relation were found for almost the whole temperature range. In the cases of burner-stabilized flames, local and global similarity, and scaling relation were found in the temperature range of 900–1800 K. We verified that the results are not characteristic for the Leeds methane oxidation mechanism only, since the sensitivity curves for the GRI mechanism, and the mechanism of Konnov also showed very good similarity.

Local similarity of the sensitivity functions was related to the existence of low-dimensional manifolds. The typical dimension was small for both the explosion and the flame, about five to eight, decreasing to one, and finally to zero, as the trajectory approached the burnt state. Good agreement was found between the region of pseudo-homogeneity and that of global similarity, as predicted by the theory. One of the consequences of the local similarity of the sensitivities is that the rank of the sensitivity matrix is less than or equal to the dimension of the manifold. The calculated rank of the sensitivity matrix during the explosion was one. If local and global similarities are both present, very different parameter sets can produce identical results. The model of the adiabatic explosion of methane showed perfect local and global similarity. In accordance, changing the most influential parameters by 50%, the concentration–time curves could be reproduced for all species at all time points by tuning a single, arbitrarily chosen other influential parameter.

In physical models, all parameters are believed to have a ‘true’ value, which can be unambiguously determined in independent experiments. If a physical parameter is determined in a system of global similarity by fitting experimental data, errors in the fixed parameter values cause the obtained parameter to become erroneous. However, the fitted model perfectly reproduces all experimental data, even if the values of several variables are measured at several time points or distances.

We consider that the similarity of sensitivity functions is a very important property of combustion models. Models of global similarity are not recommended to be utilized for the determination of rate parameters, and are also not well applicable for the validation of reaction mechanisms.

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References

[1] Hughes, K.J., Turányi, T., Clague, A.R. and Pilling, M.J., 2001, Development and testing of a comprehensive chemical mechanism for the oxidation of methane. *International Journal of Chemical Kinetics,* **33**, 513–538.

[2] Hughes, K.J., Tomlin, A.S., Pilling, M.J. and Turányi, T., 2001, Combustion simulations at Leeds University and at the ELTE. Available online at: http://www.chem.leeds.ac.uk/Combustion/Combustion.html, http://garfield.chem.elte.hu/Combustion/Combustion.html, accessed 25 April 2005.

[3] Smith, G.P., Golden, D.M., Frenklach, M., Moriary, N.W., Eiteneer, B., Goldenberg, M., Bowman, C.T., Hanson, R.K., Song, S., Gardiner, W.C. *et al*., 1999, GRI-Mech 3.0. Available online at: http://www.me.berkeley.edu/gri_mech/, accessed 25 April 2005.

[4] Konnov, A.A., 2000, Detailed reaction mechanism for small hydrocarbons combustion. Release 0.5. Available online at: http://homepages.vub.ac.be/∼akonnov/, accessed 25 April 2005.

[5] Chevalier, C., 1993, *Entwicklung eines detaillierten Reaktionsmechanismus zur Modellierung der Verbrennungsprozesse von Kohlenwasserstoften bei Hoch- und Niedertemperaturbedingungen*, Dissertation, Universität Stuttgart.

[6] Hughes, K.J., Tomlin, A.S., Hampartsoumian, E., Nimmo, W., Zsély, I. Gy., Ujvári, M., Turányi, T., Clague, A.R. and Pilling, M.J., 2001, An investigation of important gas-phase reactions of nitrogenous species from the simulation of experimental measurements in combustion systems. *Combustion and Flame*, **124**, 573–589.

[7] Glarborg, P., Alzueta, M.U., Dam-Johansen, K. and Miller, J.A., 1998, Kinetic modeling of hydrocarbon nitric oxide interactions in a flow reactor. *Combustion and Flame*, **115**, 1–27.

[8] Dean, A.M. and Bozzeli, J.W., 2000, Combustion chemistry of nitrogen. In: W.C.J. Gardiner (Ed.), *Gas-phase Combustion Chemistry*, 2nd edition (New York: Springer).

[9] Zsély, I. Gy., Zádor, J. and Turányi, T., 2003, Similarity of sensitivity functions of reaction kinetic models. *Journal of Physical Chemistry A*, **107**, 2216–2238.

[10] Zsély, I. Gy. and Turányi, T., 2003, The influence of thermal coupling and diffusion on the importance of reactions: The case study of hydrogen–air combustion. *Physical Chemistry Chemical Physics*, **5**, 3622–3631.

[11] Zádor, J., Zsély, I. Gy. and Turányi, T., 2004, Investigation of the correlation of sensitivity vectors of hydrogen combustion models. *International Journal of Chemical Kinetics*, **36**, 238–252.

[12] Tomlin, A.S., Turányi, T. and Pilling, M.J., 1997, Mathematical tools for the construction, investigation and reduction of combustion mechanisms. In: M.J. Pilling and G. Hancock (Eds), *Low-Temperature Combustion and Autoignition*, pp. 293–437 (Amsterdam: Elsevier).

[13] Rabitz, H. and Smooke, M.D., 1988, Scaling relations and self-similarity conditions in strongly coupled dynamical systems. *Journal of Physical Chemistry*, **92**, 1110–1119.

[14] Reuven, Y., Smooke, M.D. and Rabitz, H., 1986, Sensitivity analysis of boundary value problems: Application to nonlinear reaction-diffusion systems. *Journal of Computation Physics*, **64**, 27–55.

[15] Smooke, M.D., Rabitz, H., Reuven, Y. and Dryer, F.L., 1988, Application of sensitivity analysis to premixed hydrogen-air flames. *Combustion Science and Technology*, **59**, 295–319.

[16] Vajda, S., Rabitz, H., and Yetter, R.A., 1990. Effects of thermal coupling and diffusion on the mechanism of H_2 oxidation in steady premixed laminar flames. *Combustion and Flame*, **82**, 270–297.

[17] Mishra, M.K., Yetter, R.A., Reuven, Y. and Rabitz, H., 1994, On the role of transport in the combustion kinetics of a steady-state premixed laminar $CO+H_2+O_2$ flame. *International Journal of Chemical Kinetics*, **26**, 437–453.

[18] Skodje, R.T. and Davis, M.J., 2001, Geometrical simplification of complex kinetic systems. *Journal of Physical Chemistry A*, **105**, 10356–10365.

[19] König, K. and Maas, U., 2005, Sensitivity of intrinsic low-dimensional manifolds with respect to kinetic data. *Proceedings of the Combustion Institute*, **30**, 1317–1323.

[20] Turányi, T., 1990, Sensitivity analysis of complex kinetic systems. *Tools and Applications. Journal of Mathematical Chemistry*, **5**, 203–248.

[21] Vajda, S. and Rabitz, H., 1992, Parametric sensitivity and self-similarity in thermal explosion theory. *Chemical Engineering Science*, **47**, 1063–1078.

[22] Lutz, A.E., Kee, R.J. and Miller, J.A., 1988, SENKIN: A Fortran program for predicting homogeneous gas phase chemical kinetics with sensitivity analysis. Sandia National Laboratories. Report No. SAND 87-8248.

[23] Kee, R.J., Grcar, J.F., Smooke, M.D. and Miller, J.A., 1985, PREMIX: A Fortran program for modeling steady laminar one-dimensional premixed flames. Sandia National Laboratories. Report No. SAND 85-8240.

[24] Tomlin, A.S., Whitehouse, L., Lowe, R. and Pilling, M.J., 2001, Low-dimensional manifolds in tropospheric chemical systems. *Faraday Discussions*, **120**, 125–146.

[25] Büki, A., Perger, T., Turányi, T. and Maas, U., 2002, Repro-modelling based generation of intrinsic low-dimensional manifolds. *Journal of Mathematical Chemistry*, **31**, 345–362.

[26] Turányi, T., 2003, KINALC: a CHEMKIN based program for kinetic analysis. Available online at: http://www.chem.leeds.ac.uk/Combustion/Combustion.html or http://garfield.chem.elte.hu/Combustion/Combustion.html, accessed 25 April 2005.

[27] Schmidt, D., Blasenbrey, T. and Maas, U., 1998, Instrictic low-dimensional manifolds of strained un unstrained flames. *Combustion Theory and Modelling*, **2**, 135–152.