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Visualization methods in analysis of detailed chemical kinetics modelling

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Abstract

Sensitivity analysis, principal component analysis of the sensitivity matrix, and rate-of-production analysis are useful tools in interpreting detailed chemical kinetics calculations. This paper deals with the practical use and communication of the sensitivity analysis and the related methods are discussed. Some limitations of sensitivity analysis, originating from the mathematical concept (e.g. first-order or brute force methods) or from the software-specific implementation of the method, are discussed. As supplementary tools to the current methods, three novel visual tools for analysis of detailed chemical kinetics mechanisms are introduced: (a) scaled sensitivity analysis which is especially suited for studying initiation reactions where the span of reaction rates is high; (b) automated generation of reaction pathway plots which provides an immediate graphical illustration of the chemical processes occurring; (c) explorative (or chemometric) analysis of accumulated rate of progress matrices which assist in the identification of reaction subsets. The application of these tools are demonstrated by analysing NO_x enhanced oxidation of methane at 700–1200 K. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Sensitivity analysis; Detailed chemical kinetics; CHEMKIN; SENKIN; Scaled sensitivity analysis; Rate-of-production analysis; Reaction pathway plots; Chemometrics

1. Introduction

Detailed chemical reaction mechanisms are often used in the analysis of gaseous chemical reactions such as combustion processes, processes in the upper atmosphere and chemical vapour deposition processes. During the development and use of a detailed chemical kinetic model, it is important to understand the role of specific reactions. One method for this is sensitivity analysis, a field which has been studied extensively. Several publications on sensitivity analysis are available, including the reviews by Rabitz et al. (1983), Turányi (1990a), Radhakrishnan (1991) and Tomlin et al. (1997); however, apart from an article by Yetter et al. (1985), most reported work focus on the mathematical foundations of sensitivity analysis, while the practical application, limitations of available software and interpretation and communication of the results are seldom discussed.

In the present paper some potential limitations of sensitivity analysis are discussed and methods for graphical post-processing of sensitivity analysis and rate-of-production results are presented. The basis for the discussion and calculations is the SENKIN code by Lutz et al. (1988), which employs a first-order sensitivity analysis method, but the concepts are considered of general interest.

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2. First-order local sensitivity analysis

The most common software for analysis of and simulation with a detailed chemical kinetic mechanism is the CHEMKIN-II package developed by Kee et al. (1989). The package includes application codes for a number of reactor types including perfectly-stirred reactors, plug-flow reactors and laminar premixed flames. In the present work we focus on batch reactor/plug-flow reactor simulations, using SENKIN (Lutz et al., 1988). A detailed chemical kinetic model of the processes occurring in a homogeneous, isothermal and isobaric batch or plug-flow reactor is defined by the differential Eq. (1), where the mathematical link between reactor types is the transformation of length to residence time downstream in the plug-flow reactor.

$$\frac{\mathrm{d}c_j}{\mathrm{d}t} = v\frac{\mathrm{d}c_j}{\mathrm{d}x} = f_j(\underline{c}, \underline{k}) = \sum_{i=1}^{m} \nu_{ji} R_i(k_i);$$

$$R_i = k_i \prod_{j=1}^{n} \{c_j^{\nu_{ji}} | \nu_{ji} > 0\}; \qquad (1)$$

$$k_i = A_i T^{\beta_i} e^{-\frac{E_{a,i}}{R_u \cdot T}} \qquad (2)$$

The solution (i.e. the dependent parameters) of this model is a vector of outlet concentrations. The independent parameters are the problem conditions, i.e. the inlet concentrations, pressure, temperature and residence time as well as the parameters describing the rates of the reactions, as defined by the Arrhenius expression Eq. (2). Dependent on the physical system studied, Eq. (1) may be expanded, but the general concepts will remain the same. For simplicity, the present discussion will be based on Eq. (1).

In the formulation of a kinetic model, it is useful to know the impact of modifications of parameters. This knowledge is often obtained through sensitivity analysis, i.e. by perturbation of the parameter vector by $\Delta\boldsymbol{k}$ and by observing the change in the vector of predicted concentrations. One method for sensitivity analysis is 'brute force' sensitivity analysis which is simply based on modification of one or several parameters. As discussed below brute force sensitivity analysis has some benefits. However, for analysis of complex systems brute force methods become computationally demanding. For this reason a low order Taylor expansion Eq. (3) of the perturbation of the parameter vector is often used.

$$c_i(t,\boldsymbol{k} + \Delta\boldsymbol{k}) = c_i(t,\boldsymbol{k}) + \sum_{j=1}^{m} \frac{\delta c_i}{\delta k_j}\Delta k_j + \frac{1}{2}\sum_{l=1}^{m}\sum_{j=1}^{m} \frac{\delta^2 c_i}{\delta k_l \delta k_j}\Delta k_l \Delta k_j + \cdots \qquad (3)$$

Usually, only the first term of the Taylor expansion is included. This first term is often called the (local first-order) sensitivity coefficient. The integrated local first-order sensitivity coefficients may be obtained from the differential Eq. (4) and solved efficiently together with Eq. (1) (Dunker, 1981).

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\delta \underline{c}}{\delta k_j} = \underline{\underline{\mathrm{J}}}(t)\frac{\delta \underline{c}}{\delta k_j} + \frac{\delta \underline{f}(t)}{\delta k_j} \qquad (4)$$

The sensitivity coefficients obtained by solution of Eq. (4) are not suited for analysis since Eq. (4) provides an un-scaled value which depends on the choice of units. Therefore it has become common practice to consider the normalized sensitivity values, the sensitivity matrix, $\underline{\underline{\mathrm{S}}}$, as defined by Eq. (5).

$$S_{ij} = \left(\frac{k_j}{c_i}\frac{\delta c_i}{\delta k_j}\right) = \left(\frac{\delta \ln c_i}{\delta \ln k_j}\right) \qquad (5)$$

The sensitivity coefficient S_{ij} corresponds to the effect of changing k_j upon c_i. A positive value of S_{ij} indicates that an increase in the parameter k_j results in a higher predicted value of c_i. The type of analysis based on Eqs. (4) and (5) is called local sensitivity analysis because the parameter perturbation studied is quite small, whereas a global method would include a perturbation corresponding to the parameter uncertainty (Rabitz et al., 1983; Turányi, 1990a). The local first-order sensitivity coefficients are also the coefficients calculated during SENKIN sensitivity analysis, except for the fact that the perturbed parameter is the pre-exponential factor A from the Arrhenius expression Eq. (2).

3. Potential limitations of sensitivity analysis

Limitations of sensitivity analysis may originate from the mathematical concept, e.g. first-order local sensitivity analysis, or from the specific implementation of the method in the software used. The impact of the limitations will depend on the objective of sensitivity analysis.

'First-order local sensitivity analysis' is a one-dimensional technique and for this reason inter-dependent reactions may not correctly be identified as important. Examples are consecutive reactions with different rates (Frenklach, 1984) or reactions that are inter-dependent through shared intermediates. Higher order sensitivity analysis will be more suitable at identifying such couplings. 'Brute force sensitivity analysis' overcomes this limitation, but this method is quite demanding computationally if all reactions of a large reaction set are analysed. Analysing only a part of the reaction set makes the method more feasible, but this requires a priori knowledge of the important reactions. Proper use of the brute force method requires that parameters are varied within the correct range. An important assumption is that no couplings exist between the perturbed parameters. For this reason it may be desirable to employ a proper statistical design (see e.g. Box et al.,

1978) in conjunction with brute force sensitivity analysis.

Independent of the choice of method, sensitivity analysis coefficients are mostly obtained through perturbation of the pre-exponential factor A in the Arrhenius equation. For pressure dependent reactions care must be taken to perturb the effective reaction rate k. In SENKIN, the perturbed parameter is the pre-exponential factor in the high pressure limit, A^{∞}. For a pressure dependent reaction close to the low pressure limit, the sensitivity coefficient calculated this way will be in error since the perturbation of A^{∞} does not influence k^0 or k. For this reason care must be taken when analysing reaction sets with 6- or 9-parameter expressions for pressure-dependent reactions. One way is to derive and use 3-parameter rate constants, valid over the T/P regime of interest, for the pressure dependent reactions.

A potential problem with sensitivity analysis is the interpretation of sensitivity coefficients for reversible reactions. Intuitively, the sign and magnitude of the sensitivity coefficient S_{ij} refers to the forward reaction j. However, for reversible reactions, where the rate of the reverse reaction is calculated from the forward rate and the equilibrium constant for the reaction (based on thermodynamic data), the forward and reverse rates are proportional and the sensitivity coefficient refers to the rate of the net reaction. Even though it is trivial that the sensitivity coefficient may refer to the reverse reaction rather than the forward, this is sometimes overlooked. In Fig. 1 this problem is illustrated by the S_{CO2} for the reaction $O + OH \rightleftharpoons O_2 + H$. The reason for the high value of this coefficient is that the reverse reaction is the key chain branching step and strongly promotes methane oxidation. To avoid this ambiguity sensitivity analysis is sometimes carried out on sets of irreversible reactions.

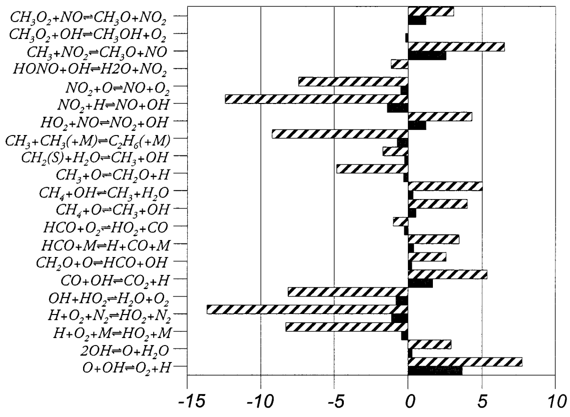

Fig. 1. A CO_2 sensitivity bar plot for NO sensitized methane oxidation. Solid bar are calculated using brute force sensitivity analysis, and hashed bars using SENKIN method. Conditions are written in the text.

4. Practical analysis of detailed chemical kinetics calculations

For many applications a large detailed chemical kinetic mechanism is required to describe the chemistry of interest. One example is the NO_x sensitised oxidation of methane, described in the proceeding case study section. For this reaction system a mechanism with 77 species and 484 reactions has been proposed (Bendtsen et al., 2000). For such a mechanism, the sensitivity matrix will contain more than 37 000 elements for each time step and care must be taken to use an appropriate graphical representation, even if only a single species is of interest. In addition to sensitivity analysis, principal component analysis of the sensitivity matrix and/or rate-of-production analysis may be useful in interpreting calculations. The practical use and communication of the sensitivity analysis and the related methods are discussed below. Some of these tools are implemented in the CHEMKIN software package, others such as principal component analysis can be found only in specialised software such as the KINALC package (Turányi, 1995; Tomlin et al., 1997).

4.1. Graphical representation of the sensitivity matrix

A common way of illustrating a single time step of a sensitivity analysis is the 'bar-plot' (e.g. Warnatz, 1984). This plot depicts the sensitivities of the concentration of a single species at a single simulation time for a given mixture and temperature. The plot presents the reactions with the highest sensitivity coefficients at a single time for the selected set of conditions and the species selected.

Another graphical representation of the sensitivity matrix is the 'sensitivity line plot' (Caracotsios and Stewart, 1985; Yetter et al., 1985), which is commonly used. The sensitivity line plot depicts sensitivities versus time for a limited number of important reactions in the sensitivity analysis of a selected species. The benefit of the time plot is that the development of a reaction over time is revealed. Unfortunately, the early stage of a reaction will often be controlled by the slow initiation reactions, causing minute changes in reactant concentrations. For the reactants this will result in very low sensitivity coefficients, compared to those found at a later stage. However, the resulting low sensitivity coefficients do not necessarily indicate unimportant reactions; the reactions may have derived effects due to for instance production of radicals and initiation of a branching reaction.

4.2. Principal component analysis of detailed chemical kinetics

Principal component analysis (PCA) (Pearson, 1901; Wold et al., 1987) has been used for identification of correlations and exploration of latent structures in analytical chemistry and in process analysis. It was introduced in kinetic research by Vajda et al. (1985).

In phenomenological terms PCA extracts the dominant factors of variation in a data-set. The first factor is the primary source of variation, the second factor the secondary source of variation, etc. For a large data-set it is often found that the pre-dominant variation may be described by relatively few factors. In mathematical terms PCA decomposes for instance a sensitivity matrix into a sum of orthogonal rank-one matrices (factors), which each may be written as a product of two vectors: A column vector weighting the reactions (the loading vector) and a row vector weighting the species (the scores vector). Each factor may then be interpreted as an underlying phenomenon, but it is important to keep in mind that the extracted phenomena are found only on a statistical basis, and that the results may be distorted, for instance by two correlated physical phenomena being merged into a single PCA factor. However, experience has shown that the PCA technique is very useful in identifying correlations which may be used in the subsequent analysis of the physical phenomena.

Vajda et al. (1985) and Turányi (1990b) pioneered the use of PCA in relation to chemical kinetics by analysis of both the sensitivity matrix $\underline{\underline{S}}$ defined in Eq. (5) and the rate-of-production matrix $\underline{\underline{F}}$ (defined by $F_{ij} = v_{ij}R_i$). Their work as well as subsequent work (Brown et al., 1997) have produced interesting results, applicable a.o. for the reduction of reaction mechanisms.

4.3. Pathway plots

From an analysis of the rate-of-production of selected species, a plot of reaction pathways may be constructed. Such a plot shows the flow of species from reactants to products. In some cases a reaction pathway plot may also include a graphical representation of the importance of the paths. The manual generation of a pathway plot is not an easy task, however. NIST (1996) offers the XSENKPLOT program for semi-automatic generation of pathway plots. This code provides a graphical presentation of the reactions paths, after the user has specified the important species. In spite of the benefits provided by the automatic plotting of pathways, the user still has the challenge of identifying which species are important and this may not be a simple task.

5. Novel tools for analysis of detailed chemical kinetics models

To overcome some of the limitations of conventional sensitivity analysis, we have developed a set of tools for the analysis of detailed reaction mechanisms. These tools, which are described in the following, will be compared to the conventional methods for sensitivity analysis in a case study.

5.1. Scaled sensitivity plots

As mentioned above, it may be difficult to use the sensitivity matrix directly for analysis of certain chemical problems. The wide range of sensitivities as a function of time may cause problems since it will be impossible, on the same plot, to encompass positive and negative sensitivities which vary by several orders of magnitude. One approach to deal with this limitation is presented by Amano and Dryer (1998) who rank the sensitivities for two sets of conditions and compare the rankings.

For the purpose of illustrating trends in the data there is no problem in scaling the sensitivity coefficients. An approach, which immediately springs to the mind, is to select a method of scaling so that the span of sensitivity is unity. Unfortunately, this may introduce some artefact peaks on the sensitivity plots solely due to the scaling. A method of scaling, which we have found appropriate, is for each time step of the integration to divide the vector of sensitivity coefficients of a selected species with the standard deviation of this vector as shown in Eq. (6). To further augment the visualization of initiation reactions, the use of a logarithmic time scale may be appropriate.

$$\underline{\tilde{S}_{i\cdot}}(t) = \frac{\underline{S_{i\cdot}}(t)}{\sigma(\underline{S_{i\cdot}}(t))} \tag{6}$$

5.2. Automatic pathway plots

The major difficulty in the manual construction of a pathway plot is book-keeping of species and production rates at different times. The mere concentration levels of intermediates are not sufficient for judging whether an intermediate is sufficiently important to be included in the pathway plot. For this reason an automatic selection of key species is desirable. The selection procedure developed is based on a 'reaction matrix', which is an n by n matrix (for n species). The element P_{ij} in the matrix corresponds to production of species j from reactions with species i as reactant (Eq. (7)). The elements of $\underline{\underline{P}}$ may be a sum of contributions from more than one reaction.

$$P_{ij} = \sum_{k=1}^{m} \{v_{ik}R_k | v_{jk} \neq 0\} \tag{7}$$

If a species contributes more than a certain percentage of the overall removal or production of an important product or reactant, this species is selected as important for the overall reaction of the system. The threshold value chosen in the present work is 10%. The selection procedure may then be re-applied, this time including the species added in the first iteration. After few iterations the 'pool' of key species will remain constant, the results may be plotted, and the process can be repeated at the next time step. With the Pathway Plot program, a manual and a flow chart showing the detailed principles are included.

After automatic or manual positioning of the species, they are connected by arrows. The width (and the colour tone) of the line is proportional to the logarithm of the absolute rate of conversion. However, to simplify the graphical display, arrows are only drawn if the corresponding reactions contribute with more than 10% of the removal or production of a species.

5.3. Explorative analysis of rate-of-production

During analysis of chemical reaction sets it is typically found that subsets of reactions are responsible for individual phenomena, such as initiation, propagation, etc. To identify these subsets, reactions must be studied at varying residence times and conditions. Still, it is not straightforward to identify these subsets, especially since the same reaction may be active in different subsets. Principal component analysis (PCA) discussed above is a common method for identification of correlated phenomena in matrix data. If the analysis is based on the $\underline{\underline{F}}$ matrix for a specific time (Vajda et al., 1985; Turányi, 1990b), the possibility of simultaneously analysing different time steps or different conditions is lost. This may be overcome by 'stacking' $\underline{\underline{F}}$ matrices corresponding to different time steps and/or conditions. The resulting tensor can then be analysed using multi-way methods (e.g. Bro, 1997, 1998). However, one possible decomposition $\underline{\underline{F}}$ matrix is already defined by the stoichiometric coefficients and the reaction rates.

We therefore suggest that the matrix to be analysed is not the $\underline{\underline{F}}$ matrix, but instead an $\underline{\underline{R}}$ matrix, as defined in Eq. (8), built of $\underline{R'}$ row vectors: With a fixed reaction set, for each time and set of conditions, a reaction vector $\underline{R}$ may be defined. Element i in this vector corresponds to the rate of reaction i. In this way for each time a 'reaction spectrum' may be obtained which will characterise the reactions occurring. In order to analyse reactions at various reaction times and conditions, the $\underline{R}$ vectors from different times and simulations may be stacked. This will produce a matrix in which each column corresponds to a reaction and each row to a simulation point. In this way a consistent combination of several simulations may be made. Since the absolute values of rates will differ by orders of magnitude with varying conditions and times, the results benefit from scaling each row to a uniform variance. This will have the effect of emphasizing the slow but often important initiation reactions, ensuring that their contribution to the overall picture of the processes is not ignored by the PCA.

$$\underline{\underline{R}} = \begin{bmatrix} \underline{R'}(\underline{c_1},t_1) \\ \underline{R'}(\underline{c_1},t_2) \\ \cdots \\ \underline{R'}(\underline{c_2},t_1) \\ \underline{R'}(\underline{c_2},t_2) \\ \cdots \end{bmatrix} \qquad \tilde{\underline{\underline{R}}} = \begin{bmatrix} \underline{R'_1}\sigma(\underline{R_1}) \\ \underline{R'_2}\sigma(\underline{R_2}) \\ \cdots \\ \cdots \\ \cdots \\ \cdots \\ \underline{R'_p}\sigma(\underline{R_p}) \end{bmatrix} \tag{8}$$

If the reaction mechanism analysed is based on irreversible reactions it may be of benefit to use the alternating least squares (ALS) method suggested by Karjalainen (1989) in the implementation of Andersson and Hansen (1998). ALS is a variant of PCA, imposing a non-negativity constraint on the analysis which makes it possible to define that the loadings must be positive values.

6. Analysis of NO_x sensitized methane oxidation

As an example of the use of the methods and techniques described above, we have analysed the low temperature oxidation of methane in the presence of nitrogen oxides. In the presence of nitric oxide and nitrogen dioxide the oxidation of methane may take place at lower temperatures, compared to similar conditions with no presence of nitrogen oxides. Bendtsen et al. (2000) recently proposed a reaction set for this chemistry. The mechanism was in part deduced with the aid of the methods described above. To assist the reader unfamiliar with NO_x enhanced methane oxidation, the important features of the reaction is summarized in the following. Reactions are numbered in accordance with the listing of Bendtsen et al. (2000).

The key reactions in NO_x enhanced methane oxidation is the oxidation of CH_3 to CH_2O which may follow three paths, a direct path A, a two step path B, or a three step path C. The direct path, A, consists of reaction (R56):

$$CH_3 + O_2 \leftrightharpoons CH_3O + O \qquad \text{(R56)}$$

Path B (NO_2 sensitized oxidation) involves the steps (R409) and (−R112) with regeneration of NO_2 in (R241).

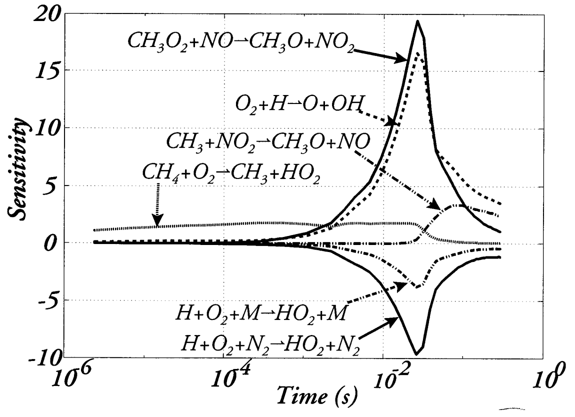

Fig. 2. A CO_2 sensitivity versus time plot of NO enhanced oxidation. See the text for conditions.

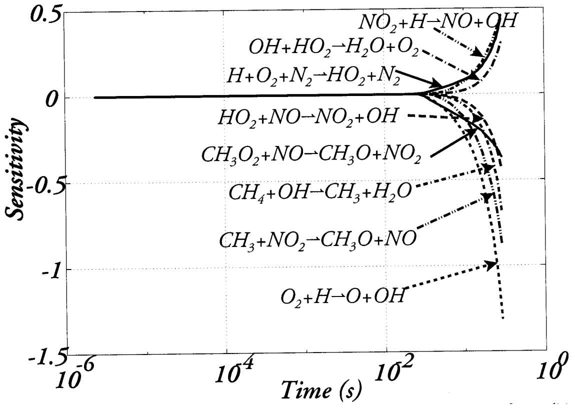

Fig. 3. A CH_4 sensitivity versus time plot of NO enhanced methane oxidation. See the text for conditions.

$$CH_3 + NO_2 \rightleftharpoons CH_3O + NO \qquad (R409)$$

$$CH_3O(+M) \rightleftharpoons CH_2O + H(+M) \qquad (-R112)$$

$$NO + HO_2 \rightleftharpoons NO_2 + OH \qquad (R241)$$

Path C (NO sensitized oxidation) consists of (R445), (R464) and (−R112).

$$CH_3 + O_2(+M) \rightleftharpoons CH_3O_2(+M) \qquad (R445)$$

$$CH_3O_2 + NO \rightleftharpoons CH_3O + NO_2 \qquad (R464)$$

$$CH_3O(+M) \rightleftharpoons CH_2O + H(+M) \qquad (-R112)$$

In addition to these steps, reactions producing or removing radicals are also important. In the early stage of combustion hydrogen abstraction reactions of CH_4 are important and in the late stages further oxidation of CH_2O to HCO, CO and CO_2.

The case study involves the oxidation of 1500 ppm CH_4 in the presence of 200 ppm NO, 6% H_2O, 3% O_2 in N_2 at 948 K. A comparison of conventional tools and the three novel tools described above is made. The sensitivity bar plot is based on a reaction set involving reversible reactions with temperature and pressure dependence. In the presentation of the sensitivity versus time plot and the three novel tools a representation based on irreversible reactions is chosen, with rates obtained at a fixed temperature and pressure. The effect of various third-bodies in the pressure dependent reactions was approximated through the use of a fixed composition, corresponding to an average composition.

6.1. Sensitivity bar plot

In Fig. 1 the sensitivity of CO_2 concentrations towards the most important reaction rates is shown for a reaction time of 0.28 s, corresponding to complete oxidation. This bar-plot shows that the dominant reaction is $O + OH \rightleftharpoons O_2 + H$. However, as discussed previously, the high positive sensitivity towards the $O + OH$ reaction is an artefact; actually the reverse step $H + O_2$ is the important reaction. From this plot it is also revealed that CH_3O_2, CH_3O, NO_2 and NO play an active role in the decomposition of CH_4.

To avoid the ambiguity introduced by the use of reversible reactions, the remaining analysis will be based on irreversible reactions, as calculated with the MECHMOD code which may be obtained together with KINALC (Turányi, 1995).

6.2. Sensitivity versus time plot

In Fig. 2 the sensitivity of CO_2 concentrations towards the most important reactions is shown as a function of time. The final values of the sensitivity coefficients correspond to the bar-plot in Fig. 1. The results confirm that the dominant reaction is $H + O_2 \rightharpoonup O + OH$, but initiation takes place through the reaction $CH_4 + O_2 \rightharpoonup CH_3 + HO_2$. In addition it is interesting to note that the maximum importance of the reactions $CH_3O_2 + NO \rightharpoonup CH_3O + NO_2$ and $CH_3 + NO_2 \rightharpoonup CH_3O + NO$ does not coincide in time. The first reaction is responsible for formation of NO_2 which subsequently is active in the second (faster) reaction.

6.3. Scaled sensitivity versus time plot

The information from Fig. 2 is quite accessible. However, the similar plot for CH_4 (Fig. 3) is less informative in terms of the temporal development of the combustion process and it tells nothing about the initiation reactions; in fact, it would not be of more use than a sensitivity bar plot. Yet, when scaling the sensitivities by using Eq. (6) as shown in Fig. 4 a clear picture unfolds: The species responsible for attacking CH_4 during initiation (O_2) and burn-out (OH) are identified, as well as the other reactions of importance found above.

6.4. Brute force sensitivity analysis

In Fig. 1 the results of brute force sensitivity analysis are presented together with the results of SENKIN sensitivity analysis. It is seen that the qualitative results are similar, even though the absolute values of sensitivities differ. From a brute force sensitivity analysis plots similar to those presented in Fig. 2 and Fig. 3 may also be calculated, but an additional simulation must be run for each reaction. Fig. 5 compares a brute force sensitivity calculation with a SENKIN sensitivity analysis, looking at the sensitivity of CH_4 and CO_2 towards the reaction $CH_3O_2 + NO \rightleftharpoons CH_3O + NO_2$. Both methods correctly identifies this reaction as being a key step. It is seen that the modification of the reaction by a factor of 10 has a higher implication at long reaction times than predicted by the local first-order sensitivity analysis (SENKIN). The reason for this is that even though the $CH_3O_2 + NO$ reaction is less active at later times, it produces NO_2 which becomes active through the reaction $CH_3 + NO_2 \rightleftharpoons CH_3O + NO$.

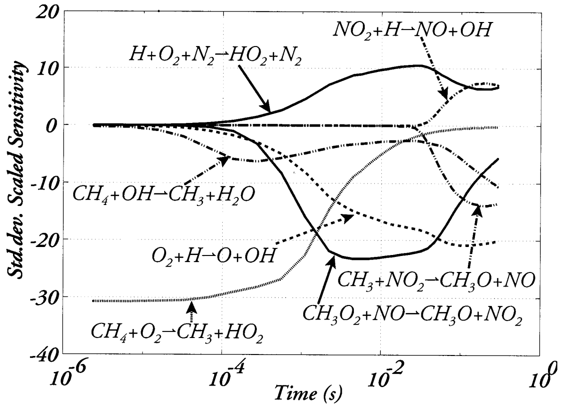

Fig. 4. A scaled CH_4 sensitivity versus time plot of NO enhanced methane oxidation. Scaling was based on standard deviation (see Eq. (6)). See the text for conditions.

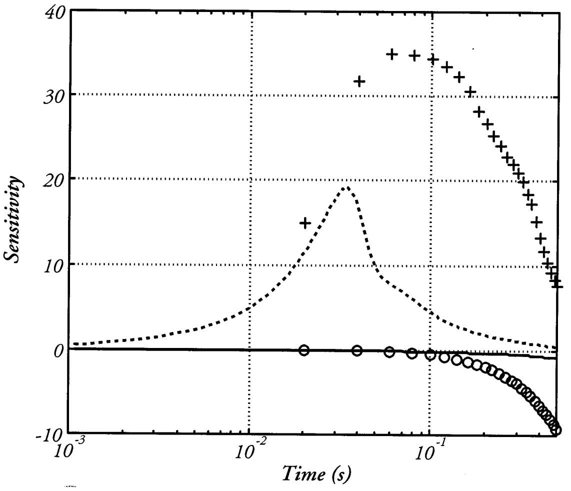

Fig. 5. Sensitivty versus time plot, based on perturbation of the reaction $CH_3O_2 + NO \rightleftharpoons CH_3O + NO_2$ by a factor of 10. Symbols correspond to brute force analysis and lines to SENKIN sensitivity analysis (+ and dashed lines are CO_2 sensitivity and ○ and solid lines are CH_4 sensitivity). See the text for a discussion of the results.

6.5. Automated pathway plots

As shown above, sensitivity analysis correctly identify the species CH_3O_2, CH_3O, NO_2 and NO as being important during methane oxidation in the presence of nitric oxide at low temperatures. The activity of these species is also revealed by the pathway plot shown in Fig. 6. This plot, which was constructed with the pathway plot program, illustrates the progress of oxidation. Initially CH_3 and O_2 recombines to CH_3O_2 which reacts with NO to form CH_3O and NO_2. The methoxy radical, CH_3O, decomposes to form CH_2O while contributing an H-atom to the radical pool. As the concentration of NO_2 builds up, CH_3 reacts with NO_2 to form NO and CH_3O. This path is the more rapid and will take over when sufficient NO_2 is formed.

On a computer monitor the lines between species will be shown in colours, facilitating an understanding of the most active paths in the reaction set at different reaction times.

6.6. Explorative analysis of rate-of-production

This example extends the case study by combining analysis of three simulation series with similar conditions. The inlet composition was 1500 ppm CH_4, 3% O_2, and 6% H_2O with (a) no nitrogen oxides; (b) 200 ppm NO_2, or (c) 200 ppm NO (the base case), all with N_2 as balance. Each simulation series consisted of 20 different isothermal simulations (with temperatures from 773 to 1248 K), making up a set of 60 time series. To save space and calculation time, simulation of each time series was logged in logarithmic steps, i.e. at approximately 10, 100 μs and 1, 10 and 100 ms, instead of at all simulation points. The PCA analysis of the resulting *R* matrix revealed the loadings shown in Fig. 7 and the scores for selected simulations in Fig. 8.

The first loading (Fig. 7) is dominated by the partial $CH_3 + O_2$ equilibrium, the second by an initiation reaction involving NO_2, the third by the initiation reactions $CH_4 + O_2 \rightharpoonup CH_3 + HO_2$ and $CH_4 + M \rightharpoonup CH_3 + H + M$, the fourth and fifth by radical interactions (especially with OH), the sixth by the carbon reaction chain propagation reactions from CH_4 via CH_3 and CH_3O to CH_2O. When looking at the scores from the simulation at 1198 K (Fig. 8) the pattern for absence of NO_x and presence of NO alone is similar: Initiation

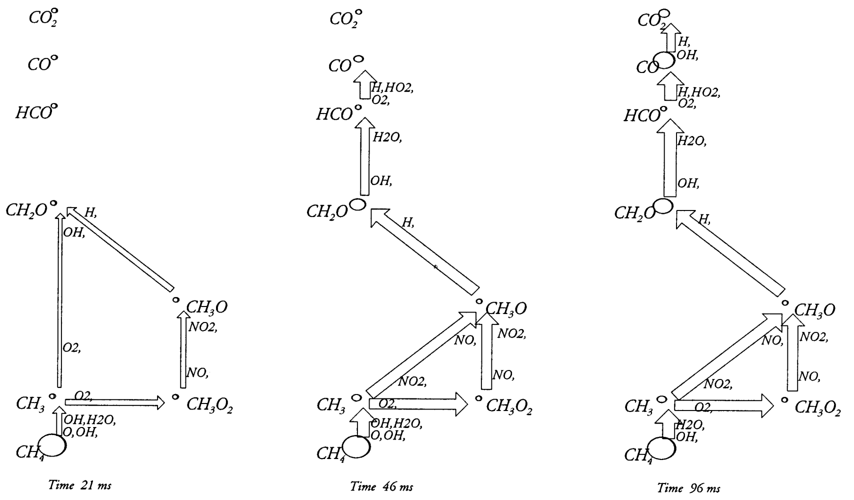

Fig. 6. Pathway plots for different time steps, as generated by the Pathway Plot program described in the text.

(factor 3) followed by the $CH_3 + O_2$ equilibrium (factor 1) and finally radical reactions (factor 4). In the presence of NO_2 at 1198 K the pattern is different: Initiation through NO_2 reactions (factor 2), then propagation through CH_3O (factors 1 and 6), and finally radical reactions (factors 4 and 5). At 948 K in the absence of NO_x the only active factor is the $CH_3 + O_2$ equilibrium. In the presence of NO alone this is also an important factor, and later factor 6 (propagation through CH_3O) becomes active. The pattern for NO_2 is similar to that of a higher temperature, but burn-out occurs without significant contribution from factor 4 and 5 (radical interactions). In calculations, which are not presented here, we found that when using ALS a slightly poorer description of the simulation data was obtained, but the results were more comprehensible, due to the absence of negative loadings.

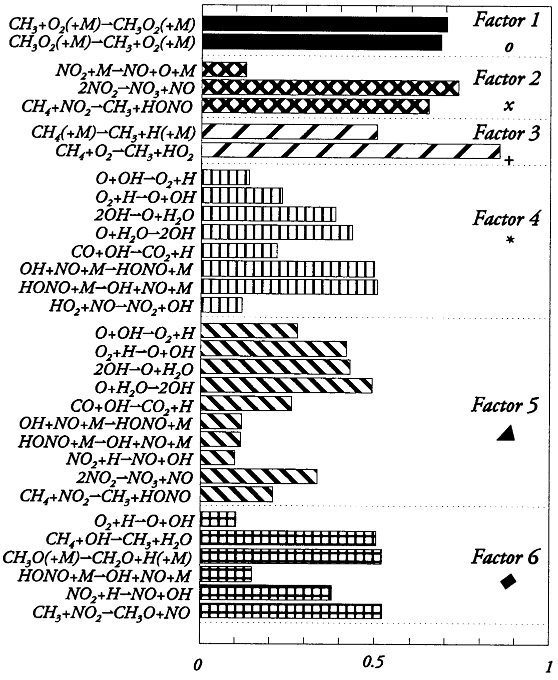

Fig. 7. Loadings of the six dominant factors in the ALS analysis. Symbols to the right correspond to the line graph of scores in Fig. 8. Only the dominant reactions are listed. The remainder of reactions do have input in the loadings, but it is less than 0.1.

7. Conclusion

We have demonstrated the use and some limitations of the current methods for analysis of chemical reaction

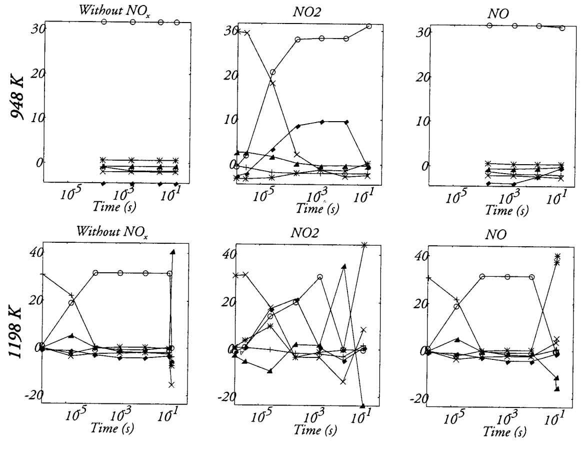

Fig. 8. Score versus time plot for three different chemical conditions and two temperatures. The figure is discussed in detail in the text. Each line corresponds to a score. Symbols by factors: 1, ○; 2, ×; 3, +; 4, *; 5, ▲; 6, ◆.

sets, especially the various aspects of sensitivity analysis. Three novel visual tools have been introduced: Scaled sensitivity analysis, automated pathway plots and principal component analysis of accumulated rate-of-progress matrices.

Scaled sensitivity analysis was demonstrated to be powerful, especially in the analysis of initiation reactions, since it provided a way of inspecting slow initial reaction on the same plot as the more rapid propagation reactions.

Automated pathway plots provide an immediate and rapid overview of a simulation, by graphically showing the path of the key species. This graphical representation of the important reactions is helpful in understanding the processes occurring.

Explorative analysis of the rate-of-production was especially interesting for obtaining an understanding of the relations between sub-processes. This tool improved the understanding of several steps in NO_x enhanced low temperature oxidation of methane.

8. Availability of software

The automatic generation of pathway plots is made by a Salford Fortran 77 program, 'PATHWAY PLOT'. Scaled sensitivity line plots and explorative analysis of rate-of-production was made in MATLAB 4.2.

The source code, as well as a compiled version of 'PATHWAY PLOT' is available from the authors. The software is provided free of charge, provided registration is made with the authors and that use of the software is acknowledged through a reference to the present paper.

9. Nomenclature

Single underline $(\underline{Y})$ is used to indicate vectors and double underline $(\underline{\underline{X}})$ to indicate matrices. A subscript for a vector (Y_i) or a matrix (X_{ij}) indicates a single element. For a matrix the first subscript is the row and the second is the column. A row vector of a matrix is written $(\underline{X}_{i\cdot})$. When a third dimension, time, is used it is indicated in a parenthesis $X(t)$.

A	pre-exponential Arrhenius parameter
$\underline{c}$	concentration of species (size n)
E_a	activation energy (Arrhenius equation parameter)
$\underline{\underline{F}}$	the rate-of-production matrix (size m by n) $(F_{ij} = v_{ij}R_i)$
$\underline{\underline{J}}$	the Jacobian matrix $(\frac{\partial \underline{f}}{\partial \underline{c}})$ (size m by n)
$\underline{k}(T,P)$	the vector of reaction rate constants (size m)
m	the number of reactions
n	the number of species
R_u	universal gas constant
$\underline{R}$	the reaction rate of progress vector as defined in Eq. (1) (size m)
$\underline{\underline{R}}$	the reaction rate matrix defined in Eq. (8) (size p by m, where p depends on the problem)
$\underline{\underline{S}}$	the normalized sensitivity matrix defined in Eq. (5) (size m by n)
$\underline{\underline{\tilde{S}}}$	the standardized sensitivity matrix defined in Eq. (6) (size m by n)
t	time
T	temperature
v	linear flow rate
x	linear distance downstream in the reactor
β	temperature exponent (Arrhenius equation parameter)
$\underline{\underline{v}}$	the matrix of stoichiometric coefficients. v_{ij} is the coefficient of species i in reaction j (size n by m)
σ	function returning the standard deviation of the argument vector

Superscripts

∞	high pressure limit
0	low pressure limit

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