

REDUCTION OF LARGE REACTION MECHANISMS

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ABSTRACT. — Systematic methods for mechanism reduction published so far consider each species equally important and therefore these methods do not eliminate species from a mechanism even if they are insignificant. Two methods are given here for the identification of species, which are necessary for the description of the concentration changes of important species. A reduced mechanism is obtained if the important reactions of important and necessary species are identified by the principal component analysis of the normed algebraic rate sensitivity matrix.

As an example, the well-known low-temperature alkane pyrolysis model of Edelson and Allara, consisting of 98 reactions and 36 species, is reduced to a mechanism for propane pyrolysis which includes 38 reactions of 13 species. The deviations between the two models are in the order of half percent, while the computer time requirement for the solution of the reduced model is about one tenth compared to that of the full model.

Introduction

Rapid growth of kinetic knowledge in the last decades made possible the development of huge reaction mechanisms for the description of the behaviour of complex chemical systems. Such reaction mechanisms may consist of several hundreds of reactions of several dozen species. Kinetics of spatially homogeneous reaction systems are usually described by a system of ordinary differential equations:

$$dc/dt = f(c,k), \quad c(0) = c_0$$

where c denotes the concentration of species, k stands for the parameters (rate coefficients), and c_0 for the initial concentrations. Simulation of spatially homogeneous reaction systems is not problematic today and such studies are of vital importance for understanding the chemical details of kinetic problems. However, applying large reaction mechanisms the chemical essence of the problems are usually covered by the great number of redundant species and reactions.

Modelling of spatially inhomogeneous systems include the solution of the kinetic differential equations several thousand times using different initial conditions. In case of such systems the simulation of chemical reactions require much more computer time than the description of the effect of advection and diffusion. The smaller the reaction mechanism applied, the less computer time is needed for the kinetic simulation of a spatially inhomogeneous system.

Frequently a general purpose large mechanism is applied for a well-defined special task. In this case a reduced mechanism is required which replaces the complete mechanism in a narrower temperature, pressure or concentration range or gives information about the behaviour of less species.

It is evident that a reduction of large reaction mechanisms are often required. Reduction means the identification of a smaller subset of reactions which still describes accurately the problem to be modelled.

Efficient methods for mechanism reduction have not been developed of far. In the next section methods, published in the literature for partial mechanism reduction, will be reviewed. Then a new method for a complete mechanism reduction is presented and it is illustrated by the reduction of a 98-step alkane pyrolysis reaction mechanism to a 38 step reduced mechanism.

Some existing methods for mechanism reduction

Mechanism reductions are usually carried out by using either the concept of sensitivities or the concept of reaction rates. A recent review¹, which contains about 170 references, describes the sensitivity methods and details their applications in chemical kinetics. Local concentration sensitivity analysis is the most widely used sensitivity method. Local sensitivity coefficients refer to only the effect of an infinitesimal parameter change and they do not carry information about the consequence of setting the value of a parameter to zero, which is the case in mechanism reduction. Therefore a reaction may not be eliminated on the basis that its sensitivity is small regarding to all important species of a mechanism. However, sensitivity analysis is applicable for the identification of redundant reactions. Hwang² stated explicitly first, that a reaction is eliminable, if its sensitivity is small with respect to *each species* of the reaction system at any time of the interval considered. In this way the redundancy of reactions are investigated one by one. Progress was made, when the importance of reaction groups was studied^{3,4} by the principal component analysis of the lognormed concentration sensitivity matrix \tilde{S} . The principal component analysis of matrix $\tilde{S} = \{\partial \ln c_i / \partial \ln k_j\}$ is based on the eigenvalue-eigenvector analysis of the cross-product matrix $\tilde{S}^T \tilde{S}$. The higher eigenvector elements of the higher eigenvalues of matrix $\tilde{S}^T \tilde{S}$ correspond to the important parameters, while the eigenvectors carry information about the connection of reactions.

An alternative way for the search of redundant reactions is based on the investigation of reaction rates. Several such methods have been published in the literature of chemical kinetics and they differ from each other in the rates investigated (e.g. rate of elementary reactions, rate of production of important radicals and so on) and in the way of comparison of these rates. A non-complete list of such methods are given in the introduction of article ⁵. The only systematic method among these seems to be the investigation of the contribution of each reaction to the rate of production of *each species* of the mechanism at several reaction times. This procedure is called the rate-of-production analysis ⁶ or screening analysis ⁷. This method has been recommended for mechanism reduction ⁸. The drawbacks of the application of this method are that a different threshold value has to be found to each species and that the application of this method requires considerable human effort in case of a large mechanism.

A mathematically better established and more comfortable way of the use of rate information is rate sensitivity analysis ⁵. This method is based on the principal component analysis of the lognormalized algebraic rate sensitivity matrix. This matrix can be computed easily by

$$\tilde{F} = \{ \partial \ln f_i / \partial \ln k_j \} = \{ v_{ij} R_j / f_i \}$$

where v_{ij} is the stoichiometric number of species j in reaction i , R_j designates the rate of reaction j and f_i is the rate of production of species i . An element of matrix \tilde{F} is the ratio of the rate of formation or consumption of species i in reaction j and the net rate of concentration change of species i .

As in case of the principal component analysis of the local concentration sensitivity matrix, the principal component analysis of matrix \tilde{F} reveals those parameter groups, which can be eliminated. Rate analysis has been successfully applied to the reduction of reaction mechanisms ⁵.

The common feature of the methods described above is that they consider each species equally important. The consequence is that they can not be applied to weeding out species and therefore the reduced mechanism will also contain the reactions of redundant species. When a complete mechanism reduction is required, redundant species have to be identified first.

Identification of redundant species

The aim of most kinetic modelling studies is to describe properly the concentration changes of certain species which are considered important. Another objective of a study can be the reproduction of some kinetic features of the reaction, as for instance the maximum concentration of species, the corresponding reaction time, the length of induction period, or the period time of an oscillating reaction.

Chemical species can be classified into three categories :

IMPORTANT SPECIES are those for which the accurate reproduction of the concentration profiles follows directly from the aim of the investigation. The decision which species and/or features are considered important depends on the objective of the modeling.

NECESSARY SPECIES are those for which realistic concentrations are required in order to calculate accurate concentration profiles for the important species or to reproduce important features.

REDUNDANT SPECIES are those which may be omitted from the mechanism without jeopardizing the aims of the modeling.

Two methods are proposed below for the identification of redundant species.

Method 1. Identification of redundant species via reduced models.

A consequence of the kinetic law of mass action is that if a species has no consuming reactions, the change of its concentration has no influence on the concentrations of other species. Therefore a species is redundant if the elimination of all of its consuming reactions does not cause significant deviation from the solution of the full model, regarding important species and/or features. This test has to be carried out by investigating each species which is not important. However, a species may be redundant even if the elimination of its consuming reactions causes significant changes. This is the situation, when a species is formed by fast reversible reactions and if the concentration of this species is low and it is therefore not a significant reservoir of matter. If all consuming reactions of this species are eliminated, the concentration of it will increase significantly, maybe causing a simultaneous change of the concentration of important species. Hence those species, which were not found to be redundant, have to be reinvestigated by eliminating simultaneously their fast forming and consuming reactions. This second procedure may reveal further redundant species.

Method 2. Identification of redundant species via the investigation of the Jacobian.

Change of the concentration of a species changes the rates of those reactions in which this species is a reactant. A direct effect will be a change in the concentration of species which are reactants or products of these reactions. The primary concentration changes then may cause the change of the concentration of other species.

A species may be considered redundant if its concentration change has no significant effect on the rate of production of important species. An element of the normed Jacobian $\partial \ln f_i / \partial \ln c_j$ is a measure of such an effect ⁹. This coefficient represents the percentage change of the rate of production of species i caused by the percentage change of c_j . The influence of the change of the concentration of species i on the rate of production of an N -membered group of important species can be taken into account by the sum of squares of normalized Jacobian elements:

$$B_i = \sum_{n=1}^N (\partial \ln f_n / \partial \ln c_i)^2$$

This measure is very similar to the overall sensitivity, which has been used for the interpretation of concentration sensitivity ³ and rate sensitivity ⁵ matrices.

The higher the B_i value of a non-important species, the greater is its *direct* effect on important species. However, there are necessary species, which are linked to the important species through other necessary species. Therefore the group of necessary species have to be identified by an iteration procedure. The best ranked species on the basis of the B_i values are also considered in the summation, then the B_i values are recalculated and the procedure is repeated again and again. As important and necessary species form a definite group, vector B will converge. Redundant species are those, which are not included in the summation at the end.

The first method requires the preparation and simulation of a number of reduced models. The number of simulations is in the order of the number of species. The results obtained

directly express the consequence of the elimination of a species.

The second method is less effective, as some redundant species which are formed in fast reversible reactions can not be identified if they are connected by fast reactions to a necessary species. The effect on important features cannot be studied in this way, either. This method requires only a single simulation of the full model, but the procedure has to be repeated at several concentration sets. The major flaw of this procedure is that the threshold limits in the range of B_i values at the distinction of necessary and redundant species are arbitrary. However, this method can be used to study the change of categories of necessary and redundant species as the reaction proceeds.

A recommended method for the reduction of large reaction mechanisms

The above methods for the identification of redundant species can be combined with any of the methods for mechanism reduction described above. The most effective of them, regarding both the computer time requirements and the size of the reduced mechanism seems to be the principal component analysis of the rate sensitivity matrix. If the important and necessary species are considered in the objective function of the analysis, a reduced model is obtained which describes properly the important features and/or the concentration changes of important species. Hence a complete mechanism reduction can be carried out as described below:

1. First the objective of the study should be clearly established. This determines the important species and/or kinetic features of the system.

2. The next step is the identification of necessary species using the first method described in the previous section.

3. Identification of important reactions follows by performing principal component analysis of matrix \bar{F} with important and necessary species in the objective function. Note, that fast reversible reactions of some redundant species are pretended to be important. However, these redundant reactions have been identified in the previous step. Therefore the list of important reactions are given as the result of steps 2 and 3.

4. Finally, redundant species and redundant reactions are omitted from the mechanism and the solutions of the kinetic equations for the reduced and for the full schemes are compared.

Example: reduction of an alkane pyrolysis mechanism

Edelson and Allara¹⁰ proposed a 98-step mechanism of 36 species for the low-temperature pyrolysis of propane and *n*-butane at low conversions. This mechanism, reproduced in Table I, was selected from a 500-step model by competitive kinetic considerations. The procedure did not result in a compact mechanism as there were no formation steps for five species (1,5-heptadiene, C_4H_7 , 2- C_5H_{10} , 2- C_6H_{12} , and C_4H_6) in the mechanism and therefore the rate of reactions 6, 74, 76, 78, 82, 86, 87, 96, and 98 were zero at any time. Hence the mechanism of Edelson and Allara really consists of 89 reactions of 31 species.

Table I. - Steps of the Edelson-Allara alkane pyrolysis mechanism and significance of reactions at the circumstances of our investigations (see text).

No	Reaction	Importances						
		at different reaction times						
		1	2	3	4	5	6	7
1.	$C_3H_8 \longrightarrow CH_3 \cdot + C_2H_5 \cdot$	■	■	■	■	■	■	■
2.	$1-C_4H_8 \longrightarrow CH_3 \cdot + C_3H_5 \cdot$							□
3.	$1-C_5H_{10} \longrightarrow C_2H_5 \cdot + C_3H_5 \cdot$							□
4.	$1-C_6H_{12} \longrightarrow 1-C_3H_7 \cdot + C_3H_5 \cdot$							□
5.	$(C_3H_5)_2 \longrightarrow C_3H_5 \cdot + C_3H_5 \cdot$						■	■
6.	$1,5\text{-heptadiene} \longrightarrow C_3H_5 \cdot + C_4H_7 \cdot$							
7.	$n-C_4H_{10} \longrightarrow CH_3 \cdot + 1-C_3H_7 \cdot$							
8.	$n-C_4H_{10} \longrightarrow C_2H_5 \cdot + C_2H_5 \cdot$							
9.	$H_2 + CH_3 \cdot \longrightarrow H \cdot + CH_4$							■
10.	$H_2 + C_2H_5 \cdot \longrightarrow H \cdot + C_2H_6$							■
11.	$C_3H_8 + H \cdot \longrightarrow 1-C_3H_7 \cdot + H_2$	■	■	■	■	■	■	■
12.	$C_3H_8 + CH_3 \cdot \longrightarrow 1-C_3H_7 \cdot + CH_4$	■	■	■	■	■	■	■
13.	$C_3H_8 + C_2H_5 \cdot \longrightarrow 1-C_3H_7 \cdot + C_2H_6$	■	■	■	■	■	■	■
14.	$C_3H_8 + 2-C_3H_7 \cdot \longrightarrow C_3H_8 + 1-C_3H_7 \cdot$		■	■	■	■	■	■
15.	$C_3H_8 + 1-C_3H_7 \cdot \longrightarrow C_3H_8 + 2-C_3H_7 \cdot$			■	■	■	■	■
16.	$C_3H_8 + C_3H_5 \cdot \longrightarrow 1-C_3H_7 \cdot + C_3H_6$			■	■	■	■	■
17.	$C_3H_6 + H \cdot \longrightarrow C_3H_5 \cdot + H_2$	■	■	■	■	■	■	■
18.	$C_3H_8 + H \cdot \longrightarrow 2-C_3H_7 \cdot + H_2$	■	■	■	■	■	■	■
19.	$C_3H_8 + CH_3 \cdot \longrightarrow 2-C_3H_7 \cdot + CH_4$	■	■	■	■	■	■	■
20.	$C_3H_8 + C_2H_5 \cdot \longrightarrow 2-C_3H_7 \cdot + C_2H_6$	■	■	■	■	■	■	■
21.	$C_3H_8 + C_3H_5 \cdot \longrightarrow 2-C_3H_7 \cdot + C_3H_6$			■	■	■	■	■
22.	$H_2 + C_2H_5 \cdot \longrightarrow H \cdot + C_2H_6$							■

Table I. - (Continued).

74.	$C_3H_5 \cdot + C_4H_7 \cdot \longrightarrow 1,5\text{-heptadiene}$					
75.	$CH_3 \cdot + C_2H_5 \cdot \longrightarrow C_3H_8$					
76.	$CH_3 \cdot + C_4H_7 \cdot \longrightarrow 2\text{-}C_5H_{10}$					
77.	$C_2H_5 \cdot + C_2H_5 \cdot \longrightarrow n\text{-}C_4H_{10}$	□	□	□		□
78.	$C_2H_5 \cdot + C_4H_7 \cdot \longrightarrow 2\text{-}C_6H_{12}$					
79.	$H \cdot + 2\text{-}C_3H_7 \cdot \longrightarrow C_3H_6 + H_2$					
80.	$CH_3 \cdot + 1\text{-}C_3H_7 \cdot \longrightarrow C_3H_6 + CH_4$					
81.	$CH_3 \cdot + 2\text{-}C_3H_7 \cdot \longrightarrow C_3H_6 + CH_4$			■	■	■
82.	$CH_3 \cdot + C_4H_7 \cdot \longrightarrow C_4H_6 + CH_4$					
83.	$C_2H_5 \cdot + 2\text{-}C_3H_7 \cdot \longrightarrow C_3H_6 + C_2H_6$					
84.	$1\text{-}C_3H_7 \cdot + 2\text{-}C_3H_7 \cdot \longrightarrow C_3H_6 + C_3H_8$					
85.	$2\text{-}C_3H_7 \cdot + 2\text{-}C_3H_7 \cdot \longrightarrow C_3H_6 + C_3H_8$			■	■	■
86.	$2\text{-}C_3H_7 \cdot + C_4H_7 \cdot \longrightarrow C_4H_6 + C_3H_8$					
87.	$C_3H_5 \cdot + C_4H_7 \cdot \longrightarrow C_4H_6 + C_3H_6$					
88.	$C_3H_5 \cdot + C_2H_5 \cdot \longrightarrow C_2H_4 + C_3H_6$					
89.	$C_3H_5 \cdot + 1\text{-}C_3H_7 \cdot \longrightarrow C_3H_6 + C_3H_6$					□
90.	$C_3H_5 \cdot + 2\text{-}C_3H_7 \cdot \longrightarrow C_3H_6 + C_3H_6$				■	■
91.	$C_2H_5 \cdot + 2\text{-}C_3H_7 \cdot \longrightarrow C_3H_8 + C_2H_4$				□	□
92.	$1\text{-}C_3H_7 \cdot + 2\text{-}C_3H_7 \cdot \longrightarrow C_3H_8 + C_3H_6$					□
93.	$CH_3 \cdot + C_2H_5 \cdot \longrightarrow C_2H_4 + CH_4$				□	□
94.	$C_2H_5 \cdot + C_2H_5 \cdot \longrightarrow C_2H_4 + C_2H_6$					□
95.	$C_2H_5 \cdot + 2\text{-}C_4H_9 \cdot \longrightarrow 2\text{-}C_4H_8 + C_2H_6$	□	□	□	□	□
96.	$C_2H_5 \cdot + C_4H_7 \cdot \longrightarrow C_4H_6 + C_2H_6$					
97.	$C_2H_5 \cdot + 2\text{-}C_4H_9 \cdot \longrightarrow n\text{-}C_4H_{10} + C_2H_4$					
98.	$C_2H_5 \cdot + C_4H_7 \cdot \longrightarrow C_2H_4 + \text{olefin}$					

Edelson and Allara considered propane and the main products of the pyrolysis as important ones: C_3H_8 , H_2 , CH_4 , C_3H_6 , C_2H_4 , C_2H_6 . They characterized the effect of a small change of parameters on the concentration of the important species by heuristic ranks, calculated from concentration sensitivities. Applying the terms introduced in review Ref. 1, they determined the tuning importance of reactions considering a six-member group of species. This information is usually not applicable for mechanism reduction and Edelson and Allara did not use it for this purpose, either. However, elimination of reactions with zero ranks (see Table I in Ref. 10, "Global Sensitivity Rating" of factor A, propane) gave a 52-step reduced mechanism and, as it is shown in the third column of Table II, concentrations of the important species calculated from this reduced model agree very well with the solution of the full model.

Our calculations were carried out at 817.16 K temperature and 1.912×10^{-3} mol dm $^{-3}$ initial propane concentration in accordance with article Ref. 10. The initial concentrations of other species were zero. The mechanism was investigated at reaction times 10^{-4} s, 10^{-3} s, 10^{-2} s, 10^{-1} s, 1s, 5s, 100s. The longest reaction time corresponds to 2% propane conversion. The same six species were considered to be important like in the study of Edelson and Allara. The necessary species were determined by both methods given in section 3.

In the original mechanism there are four non-important species (2- C_4H_8 , 2-Me-propane, 2-Me-butane, 2-Me-pentane) which have only formation reactions and therefore they need not be considered among the necessary species. All the

remaining non-important species were investigated by the first method and the results are summarized in Table III. Large deviation (indicated by letter L) means that at 100s the deviation between the reduced and the full model is greater than 1% (typical deviations are several orders of magnitude), while small deviation (letter S) indicates deviations smaller than 1% (typically 10^{-3} %). Nine redundant species were identified by eliminating the consuming reactions. The remaining species were investigated one by one further by eliminating all of their consuming and producing reactions. In this test five additional species (1- C_4H_9 ., 2- C_4H_9 ., 2-Me-1-propyl., 3-Me-1-butyl., and 4-Me-2-pentyl radicals) proved to be redundant. So the result of the first method is that of the 31 species, originally present in the mechanism, only seven species (CH_3 ., C_2H_5 ., C_3H_5 ., $(C_3H_5)_2$, 1- C_3H_7 ., 2- C_3H_7 ., and H.) are necessary besides the six important species.

Applying Method 2, the Jacobian was investigated separately at each time. It is apparent from Table IV, that the higher is the conversion, the more species are necessary for the description of the concentration of important species. At the highest conversion, at 100. s, the following species were found to be necessary: CH_3 ., C_2H_5 ., C_3H_5 ., $(C_3H_5)_2$, 1- C_3H_7 ., 2- C_3H_7 ., H., 1- C_4H_9 ., 2- C_4H_9 ., 2-Me-1-propyl., 3-Me-1-butyl., and 4-Me-2-pentyl. These results are in accordance with the outcomes of Method 1, when only the consuming steps were omitted.

Redundant reactions were identified by the principal component analysis of the normed rate sensitivity matrix \bar{F} calculated at each time. Reactions were considered to be

Table II. – Comparison of the solutions of the full and of the various reduced models at 100s. The three species groups separated by dashed lines are the important, the necessary, and the redundant species.

Species	concentrations [mole dm ⁻³]			
	89 steps 31 species	52 steps 23 species	70 steps 31 species	38 steps 13 species
C ₃ H ₈	1.874E-03	-0.00048	-0.0045	-0.0093
H ₂	2.125E-05	0.14	0.33	0.57
CH ₄	1.628E-05	0.14	0.35	0.59
C ₃ H ₆	2.122E-05	0.14	0.32	0.55
C ₂ H ₄	1.589E-05	0.14	0.34	0.58
C ₂ H ₆	4.581E-07	0.25	0.65	0.44

CH ₃ ·	3.425E-11	0.06	0.37	0.08
C ₂ H ₅ ·	1.213E-11	0.13	0.60	0.61
C ₃ H ₅ ·	6.624E-10	0.15	0.56	0.37
(C ₃ H ₅) ₂	6.561E-08	0.37	1.11	1.28
1-C ₃ H ₇ ·	4.635E-12	0.06	-0.15	-0.43
2-C ₃ H ₇ ·	1.298E-10	0.07	0.35	0.08
H·	8.175E-14	0.04	0.29	-0.01

1-C ₄ H ₉ ·	2.291E-16	---	0.91	---
2-C ₄ H ₉ ·	9.274E-15	---	0.69	---
2-Me-1-propyl·	5.072E-15	---	0.69	---
3-Me-1-butyl·	3.024E-15	---	0.69	---
4-Me-2-pentyl·	2.195E-15	---	0.67	---
1-C ₄ H ₈	4.054E-08	0.37	0.92	---
1-C ₅ H ₁₀	4.760E-09	0.42	1.17	---
1-C ₆ H ₁₂	2.510E-09	11.90	0.59	---
n-C ₄ H ₁₀	6.983E-10	-3.43	1.51	---
1-C ₅ H ₁₁ ·	4.466E-17	0.27	0.92	---
2-C ₅ H ₁₁ ·	8.031E-16	0.27	0.92	---
1-C ₆ H ₁₃ ·	7.770E-10	---	0.34	---
2-C ₆ H ₁₃ ·	5.017E-09	15.81	0.34	---
2-Me-1-butyl·	2.210E-16	---	0.92	---
2-C ₄ H ₈	1.045E-14	---	1.28	---
2-Me-propane	1.474E-08	0.37	0.77	---
2-Me-butane	1.256E-09	0.36	0.95	---
2-Me-pentane	1.007E-09	0.36	0.56	---

important if they corresponded to a significant eigenvector element (greater than 10^{-2}) of a principal component characterized by a large eigenvalue (greater than 10^{-4}). If all species were considered in the analysis (i.e. all species were taken into account in the objective function of the method) reactions, denoted by squares (either empty or filled) in Table I were found to be important. These reactions form a 70-step reduced mechanism and the solution of this mechanism is in good

agreement with the solution of the full model considering each species as it is apparent from the fourth column of Table II.

Reactions, significant for the thirteen important and necessary species were identified by applying the principal component analysis of matrix \tilde{F} in such a way that only these species were considered in the objective function of the method. The

Table III. - Identification of redundant species by Method I.

Species	Consuming steps omitted	Consuming and producing steps omitted	Decision
CH ₃ ·	L	L	necessary
C ₂ H ₅ ·	L	L	necessary
C ₃ H ₅ ·	L	L	necessary
(C ₃ H ₅) ₂	L	L	necessary
1-C ₃ H ₇ ·	L	L	necessary
2-C ₃ H ₇ ·	L	L	necessary
H.	L	L	necessary

1-C ₄ H ₉ ·	L	S	redundant
2-C ₄ H ₉ ·	L	S	redundant
2-Me-1-propyl	L	S	redundant
3-Me-1-butyl.	L	S	redundant
4-Me-2-pentyl.	L	S	redundant
1-C ₄ H ₈	S	-	redundant
1-C ₅ H ₁₀	S	-	redundant
1-C ₆ H ₁₂	S	-	redundant
n-C ₄ H ₁₀	S	-	redundant
1-C ₅ H ₁₁ ·	S	-	redundant
2-C ₅ H ₁₁ ·	S	-	redundant
1-C ₆ H ₁₃ ·	S	-	redundant
2-C ₆ H ₁₃ ·	S	-	redundant
2-Me-1-butyl.	S	-	redundant
2-C ₄ H ₈	-	-	redundant
2-Me-propane	-	-	redundant
2-Me-butane	-	-	redundant
2-Me-pentane	-	-	redundant

L: large deviation; S: small deviation

analysis pretended to be important the fast consuming and producing reactions of radicals 1-C₄H₉, 2-C₄H₉, 2-Me-1-propyl, 3-Me-1-butyl, and 4-Me-2-pentyl, e.g. reactions 38, 39, 40, 41, 42, 50, 51, 52, 55, and 56 as well. This problem is associated with the study of reaction rates. If concentration sensitivities had been investigated as for instance by the principal component analysis of matrix \tilde{S} , these reactions would have shown to be redundant. However, the identification of these pseudo-important reactions does not require the application of the more time consuming concentration sensitivity analysis, as these reactions have proved to be redundant during the search for redundant species by Method 1. Note, that these reactions can be identified⁹ by merely the principal component analysis of the rate sensitivity matrix as they form separated reaction groups characterised by very high eigenvalues.

Reactions, which are significant steps of the important and necessary species, are denoted by filled squares in Table I and they form a completely reduced mechanism. In our case this reduced mechanism consists of 13 species and 38 reactions.

The deviation of its solution from that of the full model for all important and necessary species is about half percent even at the highest conversion (see the fifth column in Table II). Redundant species have not to be considered as dynamic variables. However, some of them (1-C₄H₈, 1-C₅H₁₀, n-C₄H₁₀, 2-C₅H₁₁·, 2-C₆H₁₃·, 2-Me-propane, 2-Me-pentane) are on the right hand side of important reactions and it is possible to assess their concentrations from the reduced model as well. Although it was not required, the deviation between the solutions of the full and of the reduced models is small for all redundant species except for radical 2-C₅H₁₁.

The solution of this reduced model requires only 12% of the running time of the full model. The main reason of this significant decrease of computer time requirement is that the stiffness of differential equations of the kinetic system decreased due to the elimination of species having short lifetimes. Another reason is that the size of the Jacobian, to be triangularized in each step, also decreased. Finally, the elimination of reactions makes faster the calculation of the

Table IV. — Identification of necessary species at each time by the investigation of the Jacobian.

Species	Reaction times						
	1	2	3	4	5	6	7
	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1.	5.	100. s
CH ₃ ·	■	■	■	■	■	■	■
C ₂ H ₅ ·	■	■	■	■	■	■	■
C ₃ H ₅ ·					■	■	■
(C ₃ H ₅) ₂							■
1-C ₃ H ₇ ·	■	■	■	■	■	■	■
2-C ₃ H ₇ ·	■	■	■	■	■	■	■
H.	■	■	■	■	■	■	■
1-C ₄ H ₉ ·							■
2-C ₄ H ₉ ·					■	■	■
2-Me-1-propyl.					■	■	■
3-Me-1-butyl.						■	■
4-Me-2-pentyl.						■	■
1-C ₄ H ₈							
1-C ₅ H ₁₀							
1-C ₆ H ₁₂							
n-C ₄ H ₁₀							
1-C ₅ H ₁₁ ·							
2-C ₅ H ₁₁ ·							
1-C ₆ H ₁₃ ·							
2-C ₆ H ₁₃ ·							
2-Me-1-butyl.							
2-C ₄ H ₈							
2-Me-propane							
2-Me-butane							
2-Me-pentane							

right hand side of kinetic differential equation and the calculation of the Jacobian.

Conclusions

Large reaction mechanisms are frequently applied on several areas where the results of chemical kinetics are utilized in practice, especially in the modeling of atmospheric and combustion systems. There is a need for a systematic procedure for the identification of redundant species and reactions as reduced mechanisms are better applicable for understanding of the chemical essence of problems and the simulation of them require less computer time. The latter is important mainly in the modelling of spatially inhomogeneous systems.

An algorithm is provided in this paper for a complete mechanism reduction. The effectiveness of the method is illustrated by the reduction of a 98-step mechanism to a 38-steps mechanism, while the deviation between the solutions of the two models is about half percent for all important species.

Note. All calculations in this article were carried out by program package KINAL¹¹. Those, who are interested in receiving the Fortran 77 language programs are requested to send a blank 5 1/4" floppy disk.

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