

Reduced Reaction Kinetics

Chemked – A Program for Chemical Kinetics of Gas-Phase Reactions

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Introduction

Realistic description of many industrial plants and natural processes requires detailed knowledge of associated reaction chemistry. For some classes of the problems the reaction mechanisms were developed and widely used for the numerical modelling. These mechanisms can involve hundreds of species and thousands of reactions. However, it is now recognized that the information body required for description of a reacting system depends not only on the physical-chemical properties of the system but also on the goal of the investigation.

For example, when studying properties of a fuel, we can be interested in both global properties (such as gas temperature, ignition delay time, or burning velocity) and emission of hazardous impurities. The available detailed reaction sets can include a great number of reactions involving hazardous species with low concentrations. This information is excessively detailed for description of the global properties. Hence the user must have a tool for reduction of the detailed reaction mechanism without losses of accuracy in description of the general characteristics. In addition, the replacement of the detailed reaction set with a simplified one decreases the body of output data and allows users to better understand the processes in the reacting system.

1. Reduction Method

There are several classes of methods for reduction of reaction mechanisms. We will not give a review of these methods; the detailed discussion you can find in the literature. Here we present only the information that is necessary for understanding the operation of Chemked -II of reduced reaction kinetics.

The Chemked -II program of reduced reaction kinetics has the following main features.

- The program is a postprocessor tool for creation of reduced reaction mechanisms. By this is meant that the reduced mechanism is formed from a detailed reaction mechanism using results of detailed solutions.
- The program selects important reactions with the directed relation graph (DRG) method [1]. The procedure is similar to a procedure for skeletal mechanism generation from the works [2, 3]. However, in contrast to [2, 3], where the graph of important species was created, Chemked -II generates a graph of important reactions. The list of important species is generated simultaneously; these species are reactants or produces of the important reactions.
- Criteria for selection of the important reactions employ elementary reaction fluxes averaged over time intervals.

Remark -----

In the work [3], an advanced version of the DRG method was proposed; the version uses generalized coupling coefficients based on error propagation. In [3], the procedure of creation of a reduced mechanism has two stages. At the first stage, a graph of important species is built on a basis of the detailed set of reactions. At the second stage, the important reactions are found for each important species. The final reaction set of the reduced mechanism is the union of reaction subsets of the important species. This procedure is not fully consistent due to difference between the final reaction set and the reactions set, which is used for prediction of the important species. Perhaps an iterative procedure can remove the inconsistency; but it leads to significant complication of the method.

Thus the following steps must be done for creation of a reduced reaction mechanism.

1. An existing reaction mechanism is chosen as a detailed reaction mechanism. As a rule, this mechanism consists of a great number of species and reactions.
2. A problem of reaction chemistry is solved with the detailed reaction mechanism for particular initial conditions.
3. The results obtained with the detailed reaction mechanism are used for formation of a particular reduced reaction mechanism. Before starting the formation process, the user must define the following control parameters.
 - Specify species, which are believed to be important for the consideration; we will call these species and/or temperature as ‘targets’.
 - For the targets and non-targets, enter selection parameters a_k , which define accuracy of the reaction selection, (Figure 1.1), these values are set on the interval $[0,1]$ (for details, see Appendix).
 - Specify lengths of the time intervals for averaging of the reaction fluxes. These values are defined in terms of computational steps Δn of the detailed solution; where Δn is an integer on the interval $[1, N]$, N is the total number of computational steps of the detailed solution.

Remark -----

The smaller a_k is, the more reactions involving the k th species are included in the list of important reactions. If a_k is 0, all reactions involving the k th species are included in the list. If a_k is 1, a branch of the graph is not continued, when the k th species appear in this branch.

Computational time needed for preparing a reduced mechanism is proportional to the number of time intervals. The computational time can be reduced, when setting $\Delta n > 1$. But contents of the reduced mechanism can be varied as well depending on the Δn value.

4. The selection procedure is shown schematically in Figure 1.1. The procedure is performed on each time interval. The process starts from targets; all the targets are included in a list of important species. The first step selects a subset of reactions that are important for production of the targets. These reactions are included in a list of important reactions. Any additional species, which appear in the important reactions, are included in the species list. The next step selects reactions that are important for production of the new species. The procedure will be repeated until no new species appear. Thus a graph of reactions will be created, where each link is important for production/consumption of reactants or products in the previous link.

The selection process is repeated on each time interval until the end of total time interval will be achieved. The important reactions and species are cumulated, and the final lists form a particular reduced reaction mechanism.

5. The created mechanism is particular; that is, it is applicable to certain gas parameters, for example, to certain temperature and pressure. In order to create mechanism for a domain of parameters, particular reduction mechanisms must be created for separated points within this domain and then the particular mechanisms must be united [2].

In the following section, sample problems are presented, which demonstrate the capability of Chemked -II for creation of reduced reaction mechanisms.

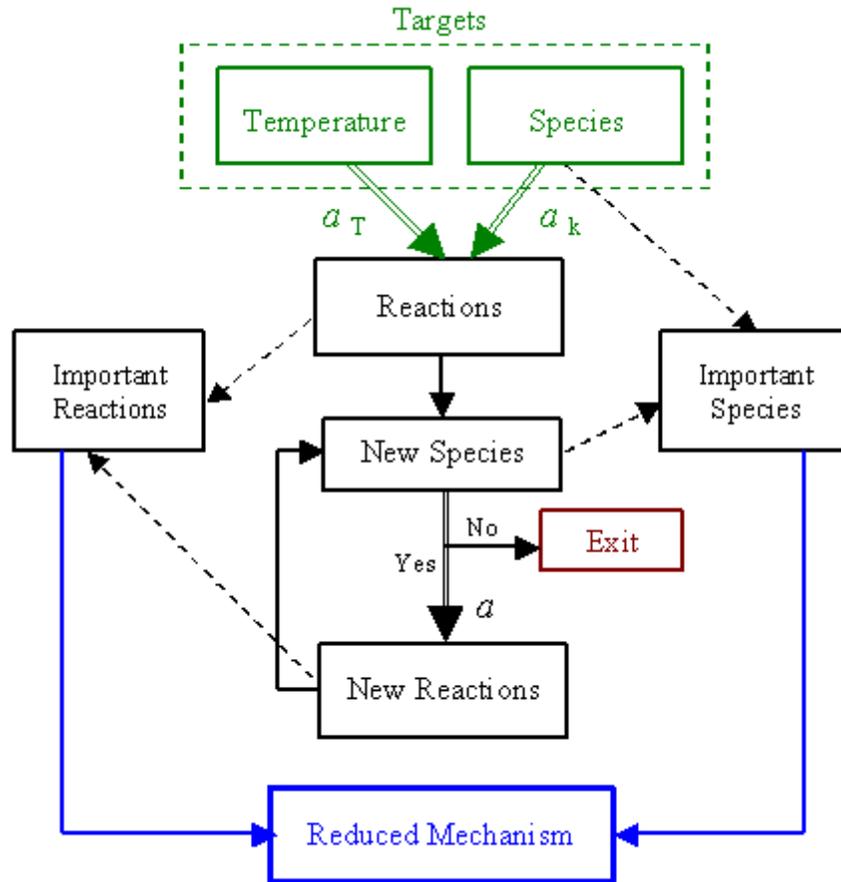


Fig. 1.1. Selection of important species and reactions on a single time interval

2. Sample Problems

2.1 Hydrogen-Air Reaction Mechanism (CHEMKIN II/III)

This sample is prepared for testing Chemked -II of reduced reaction kinetics. A reaction set from the CHEMKIN II/III test problem [4] has been chosen as a detailed reaction mechanism. The set contains 23 reactions and 11 species; the species and reaction lists are presented in Tables 2.2 – 2.3 and are denoted as Mech#0. With the tools of Chemked -II two reduced reaction mechanisms are created and verified, the results are presented below.

Before starting the program of reduced reaction kinetics, a solver file, which contains a solution for the detailed reaction mechanism Mech#0, must be prepared. For the detailed and reduced mechanisms the numerical solutions were performed for identical initial conditions.

Input values:

Fixed pressure problem, pressure $P=1$ atm,

Initial temperature $T_0=1000\text{K}$

Initial mole fractions: $[\text{H}_2]_0 : [\text{O}_2]_0 : [\text{N}_2]_0 = 1 : 3 : 0.1$

2.1.1 Reduced reaction mechanism with NO production (Mech#1)

This reduced reaction mechanism was formed with Chemked -II, using the solution of the detailed reaction mechanism and selection parameters from Table 2.1. The reduced mechanism contains 14 reactions and 10 species (Tables 2.2 and 2.3).

Profiles of the temperature and the NO concentration are shown in Figures 2.1 and 2.2. In these figures, the relative errors arising due to reduction of the reaction mechanism are depicted as well. Note that the error of NO concentration has a noticeable maximum at about 50 μsec . This maximum is seen for some other species as well and is related with a time shift of the region of intensive chemical processes. The concentrations of radicals in the vicinity of the maximum are usually small.

2.1.2 Reduced reaction mechanism without NO production (Mech#2)

Selection parameters of this mechanism are shown in Table 2.1. We call your attention to the N_2 selection parameter; it is equal to 1. By this is meant that a branch of the graph will be broken, if the N_2 species appear in this branch. For the reaction set discussed, this condition excludes all reactions with the N element but the N_2 species are kept in the initial conditions. As a result the reaction mechanism with 11 reactions and 8 species will be created (Tables 2.2 and 2.3).

Profiles of the O and N concentrations are shown in Figure 2.3. The temperature profile and its errors are identical to that from Figure 2.1. These results illustrate a good agreement between data obtained with Mech#0 and Mech#2 mechanisms.

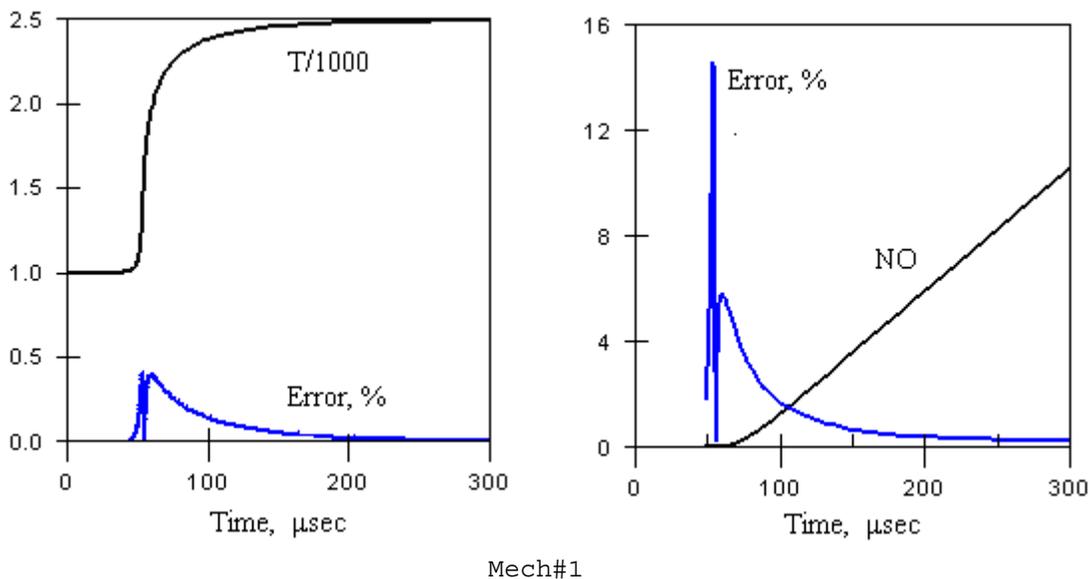


Fig. 2.1 Temperature, $T(\text{K})/1000$ and relative error, %
Fig. 2.2. NO concentration, $\text{mol}/\text{cm}^3 \times 1.E+11$ and relative error, %

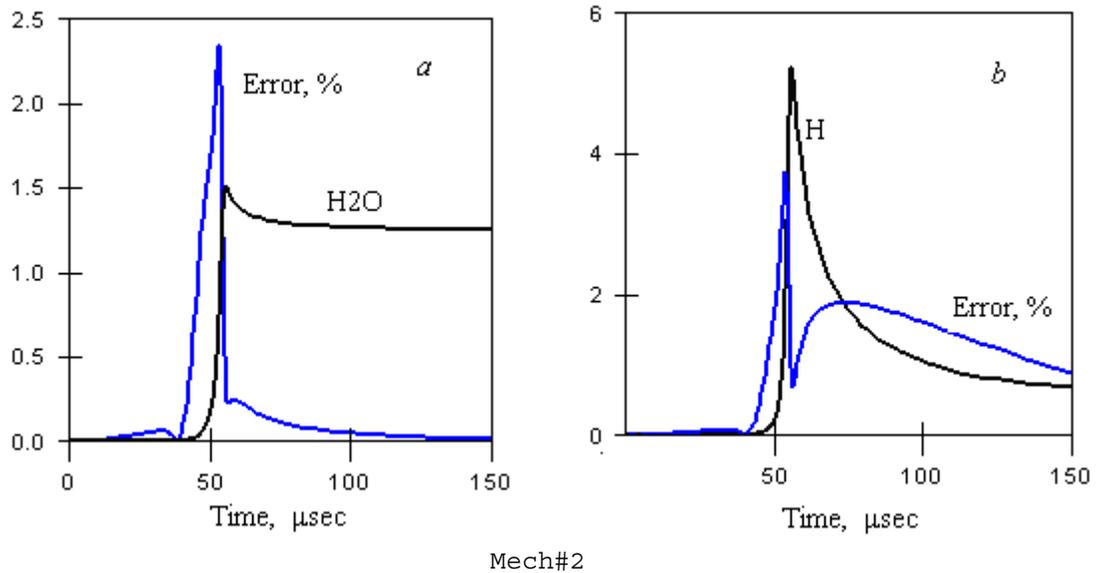


Fig. 2.3. Specie concentration and relative error, %.
a – H₂O concentration, mol/cm³ × 1.E+6, *b* – H concentration, mol/cm³ × 1.E+7.

Table 2.1 Targets and selection parameters

	Temperature	H2	O2	N2	NO	Others	Δn
Mech#1	0.1	0.1	0.1	0.1	0.1	0.3	1
Mech#2	0.1	0.1	0.1	1.0		0.3	1

Note. Here and further the species with non-zero initial concentrations are highlighted.

Table 2.2 Species pools of reaction mechanisms

	H	H2	H2O	H2O2	HO2	O	O2	OH	N	N2	NO
Mech#0	*	*	*	*	*	*	*	*	*	*	*
Mech#1	*	*	*		*	*	*	*	*	*	*
Mech#2	*	*	*		*	*	*	*		*	

Table 2.3 Contents of reaction mechanisms

Reaktion	Mech#0	Mech#1	Mech#2
1. $\text{H}_2 + \text{O}_2 \rightleftharpoons \text{OH} + \text{OH}$	*	*	*
2. $\text{OH} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{H}$	*	*	*
3. $\text{O} + \text{OH} \rightleftharpoons \text{O}_2 + \text{H}$	*	*	*
4. $\text{O} + \text{H}_2 \rightleftharpoons \text{OH} + \text{H}$	*	*	*
5. $\text{H} + \text{O}_2 + \text{M} \rightleftharpoons \text{HO}_2 + \text{M}$	*	*	*
6. $\text{OH} + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{O}_2$	*	*	*
7. $\text{H} + \text{HO}_2 \rightleftharpoons \text{OH} + \text{OH}$	*	*	*
8. $\text{O} + \text{HO}_2 \rightleftharpoons \text{O}_2 + \text{OH}$	*	*	*
9. $\text{OH} + \text{OH} \rightleftharpoons \text{O} + \text{H}_2\text{O}$	*	*	*
10. $\text{H} + \text{H} + \text{M} \rightleftharpoons \text{H}_2 + \text{M}$	*		
11. $\text{H} + \text{H} + \text{H}_2 \rightleftharpoons \text{H}_2 + \text{H}_2$	*		
12. $\text{H} + \text{H} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{H}_2\text{O}$	*		
13. $\text{H} + \text{OH} + \text{M} \rightleftharpoons \text{H}_2\text{O} + \text{M}$	*	*	*
14. $\text{H} + \text{O} + \text{M} \rightleftharpoons \text{OH} + \text{M}$	*		
15. $\text{O} + \text{O} + \text{M} \rightleftharpoons \text{O}_2 + \text{M}$	*		
16. $\text{H} + \text{HO}_2 \rightleftharpoons \text{H}_2 + \text{O}_2$	*	*	*
17. $\text{HO}_2 + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O}_2 + \text{O}_2$	*		
18. $\text{H}_2\text{O}_2 \rightleftharpoons \text{OH} + \text{OH}$	*		
19. $\text{H}_2\text{O}_2 + \text{H} \rightleftharpoons \text{HO}_2 + \text{H}_2$	*		
20. $\text{H}_2\text{O}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{HO}_2$	*		
21. $\text{O} + \text{N}_2 \rightleftharpoons \text{NO} + \text{N}$	*	*	
22. $\text{N} + \text{O}_2 \rightleftharpoons \text{NO} + \text{O}$	*	*	
23. $\text{OH} + \text{N} \rightleftharpoons \text{NO} + \text{H}$	*	*	

2.2. Methane-Air Reaction Mechanism (GRI-Mech 3.0)

This sample illustrates the program capability for selection of a subsystem from a large reaction set in order to use the subsystem for description of a particular chemical process. For this purpose the thermal decomposition of ethane (C_2H_6) behind reflected shock wave is considered. This process has been used in the work [5] for production of methyl radicals (CH_3), whose UV absorption at high temperature was measured. Here only one experimental run will be examined: gas mixture 200 ppm C_2H_6/Ar , post-shock temperature $T_5=2070$ K and pressure $P_5=1.399$ atm. The experimental trace of the CH_3 mole fraction is presented in Figure 2.4. In the work [5], the GRI-Mech 3.0 reaction mechanism [6] with some modifications was used for description of the experimental data. A computed profile (1) is shown in Figure 2.4, it describes excellently the experiment.

Here for the purposes of illustration the original version of the GRI-Mech 3.0 mechanism is used without modifications. The CH_3 profile (2) obtained with the original version is shown in Figure 2.4. We believe that the discrepancy between calculation and experiment is not great. The original GRI-Mech 3.0 mechanism contains 325 reactions and 53 species that consist of H, C, N, O and Ar atoms. For description of the C_2H_6 chemistry only the subsystem of H, C and Ar atoms is required. With Chemked -I tool this subsystem is easily selected; the corresponding reaction mechanism contains 46 reactions and 18 species. Nevertheless, this mechanism can be also excessively detailed for description of the reacting system discussed. Chemked-II of the reduced reaction kinetics allows the user to examine the reaction mechanism and to select important species and reactions that well describe the C_2H_6 decomposition.

The procedure for creation of reduced reaction mechanism is described above (Section 1) and has the following main steps.

1. The problem of C_2H_6 decomposition is solved with the Chemked solver using the full original GRI-Mech 3.0 reaction mechanism. In the discussed experiment, very high-diluted mixture of C_2H_6 in Ar was used. Under these conditions the approximation of fixed pressure and fixed temperature is applicable.

Input values:

Fixed pressure and fixed temperature problem, $P_5=1.399$ atm, $T_5=2070$ K.

Initial gas mixture: 200 ppm C_2H_6/Ar .

2. Calculation results obtained with the GRI-Mech 3.0 reaction mechanism are entered in the program of reduced reaction kinetics. Additionally, the list of targets and corresponding selection parameters must be specified; this information is presented in Table 2.4.

Table 2.4 Targets and selection parameters

C2H6	CH3	AR	Others	Δn
0.1	0.1	1	0.3	1

Note. The selection parameter for Ar is set 1 in order to make sure that all the species with non-zero initial conditions will be included in the species list of the reduced mechanism.

After processing the input information the reduced reaction mechanism was created. The mechanism contains 22 reactions and 14 species; the computational time for preparing the mechanism is less than 1 sec. The sizes of reaction mechanisms discussed here are accumulated in Table 2.5.

Table 2.5. Sizes of reaction mechanisms

Reaction mechanism	Reactions	Species
Full GRI-Mech 3.0	325	53
The H, C, Ar subsystem	46	18
Reduced mechanism	22	14

Now the C_2H_6 decomposition chemistry can be calculated, using the reduced mechanism. The deviation from the results of the GRI-Mech 3.0 mechanism is not great; errors are shown in Figure 2.5 (profile 3).

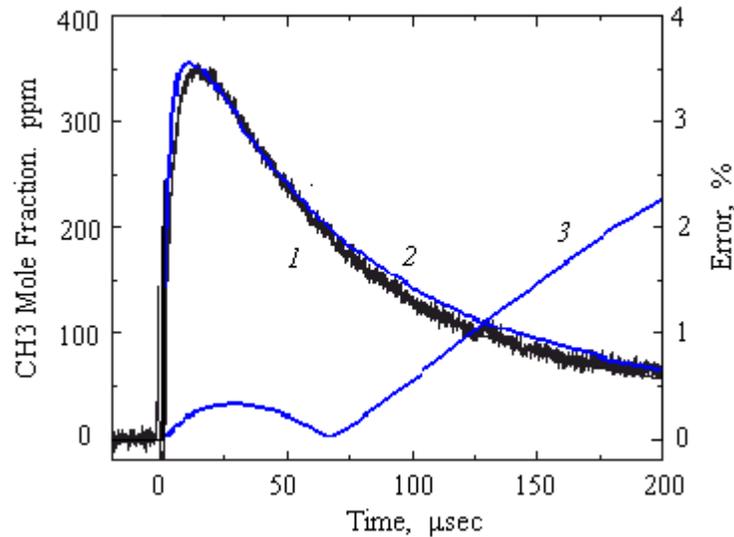


Fig.2.4. Measured and calculated CH_3 profiles behind reflected shock wave; 200 ppm C_2H_6/Ar , $P_5=1.399$ atm, $T_5=2070$ K.

- 1- calculation from [5] with a modified GRI-Mech 3.0 reaction mechanism, the profile merges with the experimental trace.
- 2- this calculation with the original GRI-Mech 3.0 reaction mechanism.
- 3 - error due to reduction of the reaction mechanism.

In addition, the use of reduced reaction mechanism reduces the work on examination of the numerical results. In particular, the reactions, which are important for the CH_3 production and consumption, can be quickly displayed in a diagram with the help of the Chemked -II tools. An example of the diagram is shown in Figure 2.5.

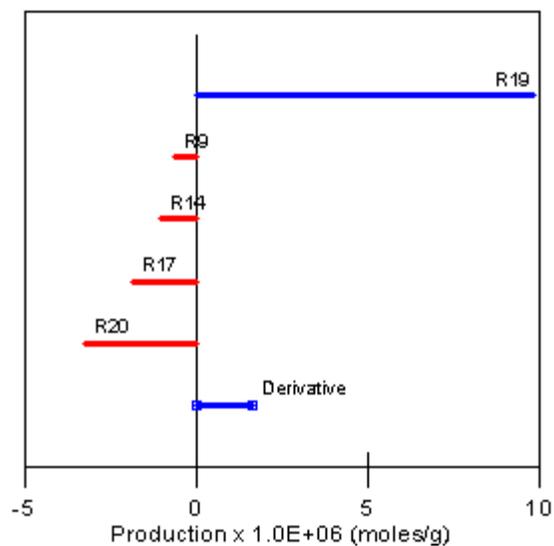


Fig.2.5. Important reactions for CH₃ production

Time interval 0.00E+00 - 2.0E-04 sec

No	Reaction	Production
19	CH ₃ + CH ₃ + M\$ <=> C ₂ H ₆ + M\$	9.80E-06
9	C + CH ₃ <=> H + C ₂ H ₂	-6.60E-07
14	CH ₂ + CH ₃ <=> H + C ₂ H ₄	-1.05E-06
17	CH ₂ (s) + H ₂ <=> CH ₃ + H	-1.86E-06
20	CH ₃ + CH ₃ <=> H + C ₂ H ₅	-3.27E-06
	Sum	2.95E-06
	Derivative	1.62E-06

Note. In the reaction list, the sum of reaction contributions differs from the total CH₃ production because only important reactions are presented.

2.3. Ethylene and Acetylene Oxidation at High Temperature [7]

These samples demonstrate the capabilities of Chemked-II for processing large reaction mechanisms. For this purpose a kinetic model of ethylene and acetylene oxidation from [7] has been chosen as a detailed reaction mechanism; it consists of 529 reversible reactions and 75 species. This mechanism was extensively tested against a variety of combustion data. It has been shown that most of the experimental data are well predicted by the mechanism.

2.3.1 Acetylene–Oxygen–Argon Mixture

Here a reduced mechanism will be created for conditions of an experiment from the work [8]. In this work, the acetylene oxidation behind reflected shock wave has been considered; a measured profile of CO₂ concentration is shown in Figure 2.6 (symbols). These data, among others, has been used in [7] for comparison with calculations (Figure 2.6, profile 1). As noted in [7], this prediction was not satisfactory.

The reflected shock wave has a complex structure and its exact description requires generally a very sophisticated technique. Nevertheless, in specific cases there are simple descriptions based on approximation of fixed density or fixed pressure. There are reasons to believe that in the discussed case, where the highly diluted mixture was used, the constant pressure approach is more preferable (see an example of pressure profile in Figure 2.8).

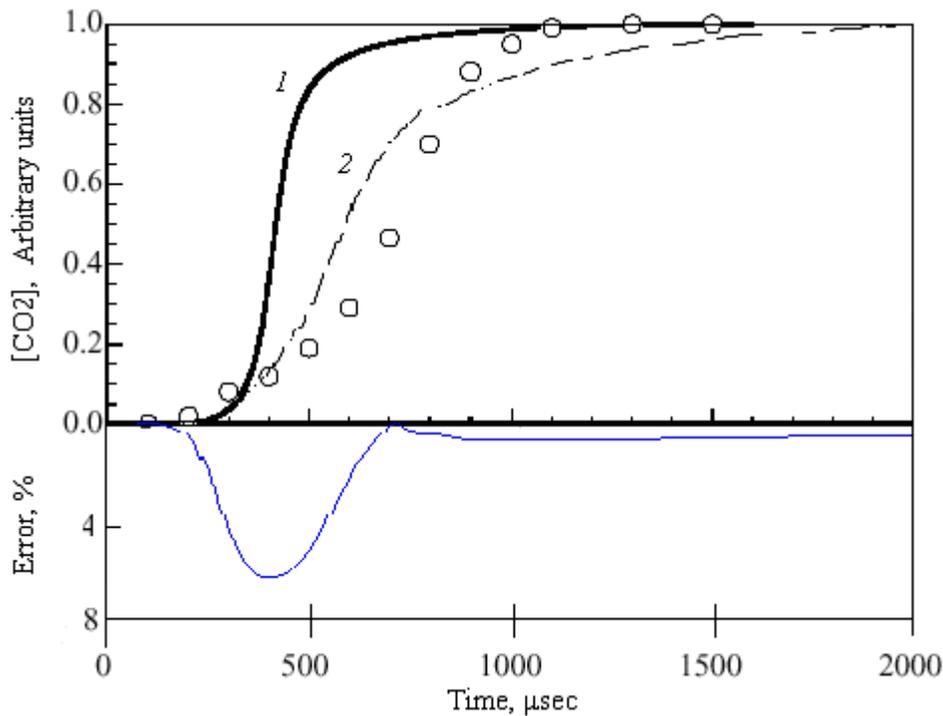


Fig.2.6. Comparison of experimental [8] (symbols) and computed (lines) CO₂ profiles behind reflected shock wave; C₂H₂ – 2%, O₂ – 2.5%, Ar – 95.5%, P₅=1.33 atm, T₅=1179 K.

Upper: 1– calculation [7] at constant density, 2 – this calculation at constant pressure.

Lower: errors due to reduction of reaction mechanism.

The procedure for creation of reduced reaction mechanism is described above (Section 1) and has the following main steps.

1. A problem of C_2H_2 oxidation behind reflected shock wave must be solved with the Chemked solver using the detailed reaction mechanism [7]. As mentioned above, in this case the fixed pressure approximation can be employed. The post-shock gas parameters are taken as initial conditions of the problem.

Input values:

Fixed pressure problem, $P_5=1.33$ atm.

Initial temperature: $T_5=1179$ K.

Initial gas mixture: $C_2H_2 - 2\%$, $O_2 - 2.5\%$, $Ar - 95.5\%$.

2. Calculation results obtained with the detailed mechanism are entered in the program of reduced reaction kinetics. Additionally, the list of targets and corresponding selection parameters must be specified; this information is presented in Table 2.6.

Table 2.6. Targets and selection parameters

Temperature	C2H2	O2	AR	CO2	Others	Δn
0,025	0,5	0,5	1	0.1	0.8	2

After processing the input information the reduced reaction mechanism was created; the mechanism contains 163 reactions and 51 species, the computational time for preparing the mechanism is about 5 sec.

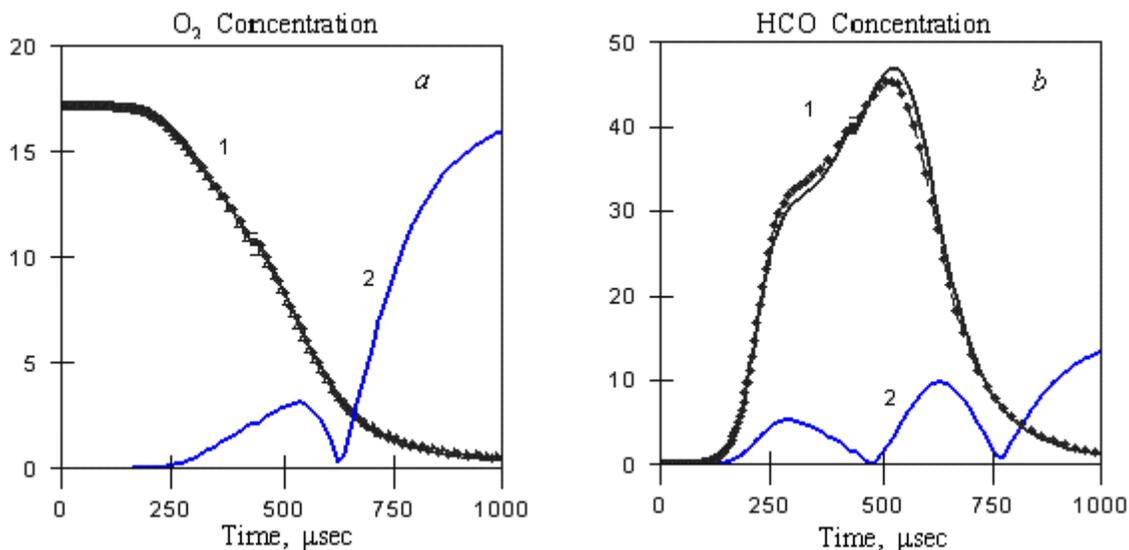


Fig. 2.7. Concentration of non-target species, calculations with detailed (lines) and reduced (symbols) reaction mechanisms.

a) 1 – O_2 concentration, $mol/cm^3 \times 5.E+07$, 2 – relative error, %

b) 1 – HCO concentration, $mol/cm^3 \times 1.E+12$, 2 – relative error, %

The results obtained with the detailed reaction mechanism (profile 2) and experiments (symbols) are shown in Figure 2.6. It is seen that the experimental data are well predicted by the fixed pressure approximation. For

comparison the fixed density calculations [7] (profile 1) is also presented. The CO₂ profile has been calculated with the reduced mechanism as well. The results fall very closely to the profile 2; errors due to mechanism reduction are shown in the same figure.

In Figure 2.7, the profiles of non-target species are shown. It follows from the figures that the reduced model predicts well also some non-targets.

2.3.2 Ethylene–Oxygen–Argon Mixture

This example illustrates the capability of Chemked –II for creating reduced reaction mechanism, which will be valid on a temperature interval. The discussed here mechanism of ethylene and acetylene oxidation from [7] is chosen as a detailed reaction mechanism. The calculations are performed for conditions of experiments [9] where ignition delay time in the C₂H₄ / O₂ / Ar mixtures has been measured.

The experiments [9] were conducted in a shock- tube facility. The ignition delay time τ_{ign} were measured behind reflected shock waves for different pressures, temperatures and C₂H₄ / O₂ / Ar mixtures. The ignition process was monitored by observing UV light emission from the OH radicals, which are produced in the reacting region. The emission was registered by two detectors; one located at endwall and the other at the sidewall of the shock tube. Figure 2.8 presents typical experimental sidewall data; here the light emission is converted to concentration of the OH* emitted state. In the same figure, definition of characteristic times of the ignition process is given as well. The ignition delay time τ_{ign} is defined as the intersection between a line corresponding to the maximum slope and the initial concentration.

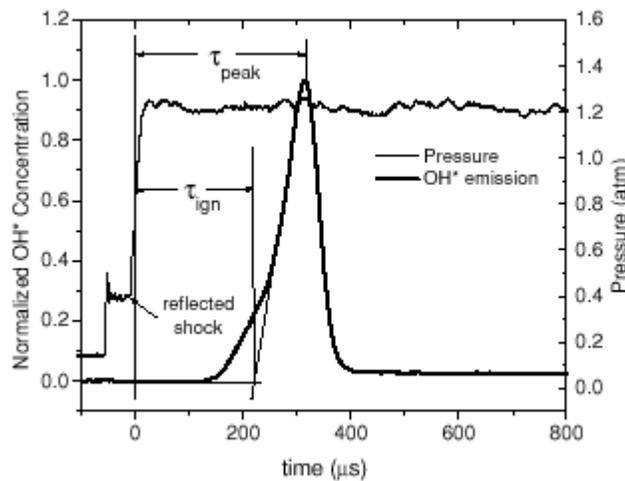


Fig. 2.8. Typical experimental profiles [9] obtained from the sidewall and scheme for definition of ignition delay time

Appearances of the sidewall and endwall emission traces are different. The sidewall data (Figure 2.8) more exactly represent the temporal evolution of the process. However in the work [9], the endwall data are accepted as a more correct source for description of the ignition because the gas near the end wall is immune to gas dynamic effects. Figure 2.9 presents the τ_{ign} values (symbols) obtained with endwall data for the gas mixture C₂H₄ – 0.5%, O₂ – 1.5 %, Ar – 98%, pressure $P_5 = 1.07$ atm and on the temperature interval 1223 – 1733 K.

Remark -----

In the work [9], the raw signals of the endwall detectors were directly used for calculation of ignition delay times. We believe that this procedure causes errors in τ_{ign} values. For this reason, the comparison to experiments in the Figure 2.9 has most likely a qualitative character. The detailed discussion of this subject can be found at [10].

In the same figure, the τ_{ign} calculated values from [9] (solid line) are shown as well; these values were obtained with the detailed mechanism [7] that has been extended with a reaction subsystem for description of kinetics of the OH* emitted state.

The numerical simulation provides more ways for definition of the ignition delay time. First of all, the ignition process is characterized by the temperature elevation, and the temperature profiles versus time can be used for the τ_{ign} determination. The calculated procedure is schematically shown in Figure 2.10; it is similar to the procedure from [9] (Figure 2.8).

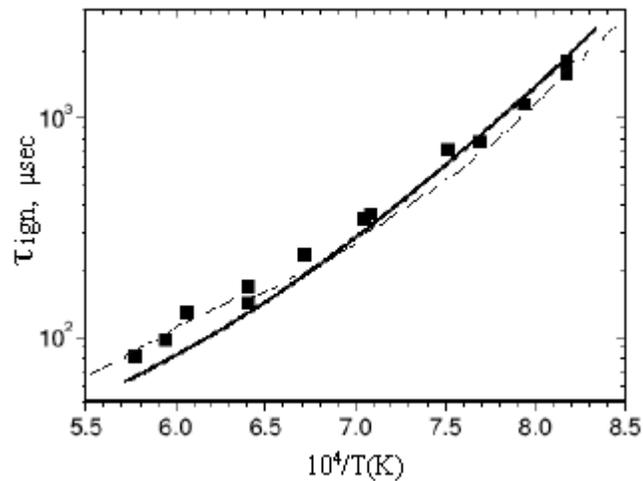


Fig. 2.9. Ignition delay time; experimental (symbols) and computed (solid line) data from [9], dotted line – this calculation. C₂H₄ – 0.5%, O₂ – 1.5 %, Ar – 98%, P₅ = 1.07 atm.

The goal of the following investigation is to create a reduced reaction mechanism that can be valid on the temperature interval, for which the data in Figure 2.9 are obtained. We will call this mechanism as “united reduced reaction mechanism”.

The united reduced reaction mechanism is formed as follows.

1. A problem of C₂H₄ oxidation must be solved with the Chemked solver using the detailed reaction mechanism [7] without extensions and modifications. The approximation of the fixed pressure is used; the post-shock gas parameters are taken as initial conditions of the problem.

Input values:

Fixed pressure problem, P₅=1.07 atm

Initial temperature: T₅ = 1223 – 1733 K.

Initial gas mixture: C₂H₄ – 0.5%, O₂ – 1.5%, Ar – 98.5%.

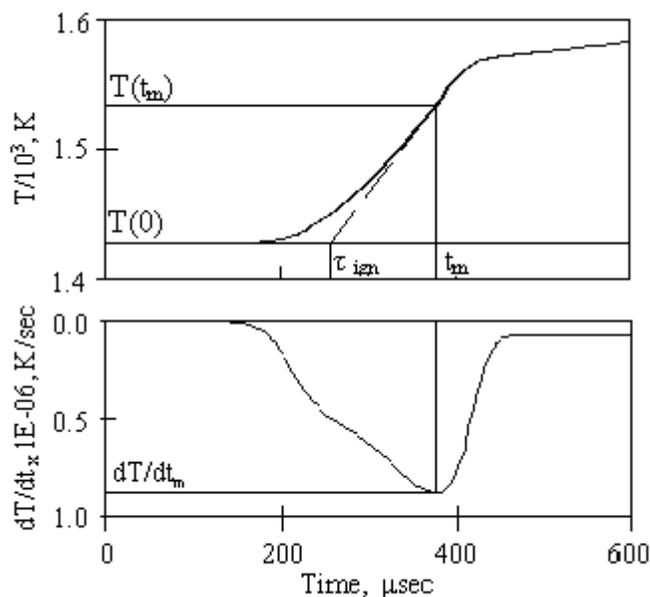


Fig. 2.10. Typical computed profiles and scheme for definition of ignition delay time.
 $C_2H_4 - 0.5\%$, $O_2 - 1.5\%$, $Ar - 98\%$, $T_5 = 1428\text{ K}$, $P_5 = 1.07\text{ atm}$.

A number of solutions were performed for the temperature interval considered. These numerical results were processed in terms of the procedure shown in Figure 2.10 to determine the $\tau_{\text{ign d}}$ values. The resulting curve is presented in Figure 2.9 (dotted line); these data are in good agreement with the experimental and calculated data from [9].

2. Three solutions at temperatures 1250, 1428, and 1667 K ($T/10^4 = 8, 7$ and 6 respectively) are chosen as reference solutions. Separately from each reference solution the program of reduced reaction kinetics forms a particular reduced mechanism. List of targets and corresponding selection parameters used for the mechanism formation are presented in Table 2.7. In the same table, sizes of the created mechanisms are shown as well.

In order to test the reduced reaction mechanisms the ignition delay times $\tau_{\text{ign r}}$ were calculated. These data and the $\tau_{\text{ign d}}$ values obtained with the detailed mechanism are compared in Table 2.7. As is seen, the difference between $\tau_{\text{ign d}}$ and $\tau_{\text{ign r}}$ is not great (less than 5%), despite the great reduction of the numbers of reactions and species. Note that the number of important species and reactions increases in the low-temperature region. Examples of temperature profiles obtained with detailed and particular reduced mechanisms are shown in Figure 2.11.

Table 2.7 Parameters of particular reduced reaction mechanisms

$T/10^4$	Temperature	C_2H_4	O_2	AR	Others	Reactions	Species	$\tau_{\text{ign d}}$	$\tau_{\text{ign r}}$
6	0,2	0,5	0,5	1	0.8	68	32	97	102
7	0.15	0,5	0,5	1	0.8	91	41	247	241
8	0.1	0.5	0.5	1	0.8	122	49	1063	1037

Note. Here $\tau_{\text{ign d}}$ and $\tau_{\text{ign r}}$ denote ignition delay times calculated with the detailed and reduced reaction mechanisms respectively.

3. The united reduced reaction mechanism, which is valid on the total temperature interval considered, can be formed through uniting the particular reduced mechanisms. The uniting has been performed with the Chemked -I tools; the mechanism consists of 132 reactions and 50 species. It is obvious that the united mechanism predicts the ignition delay time much more closely to the detailed calculations.

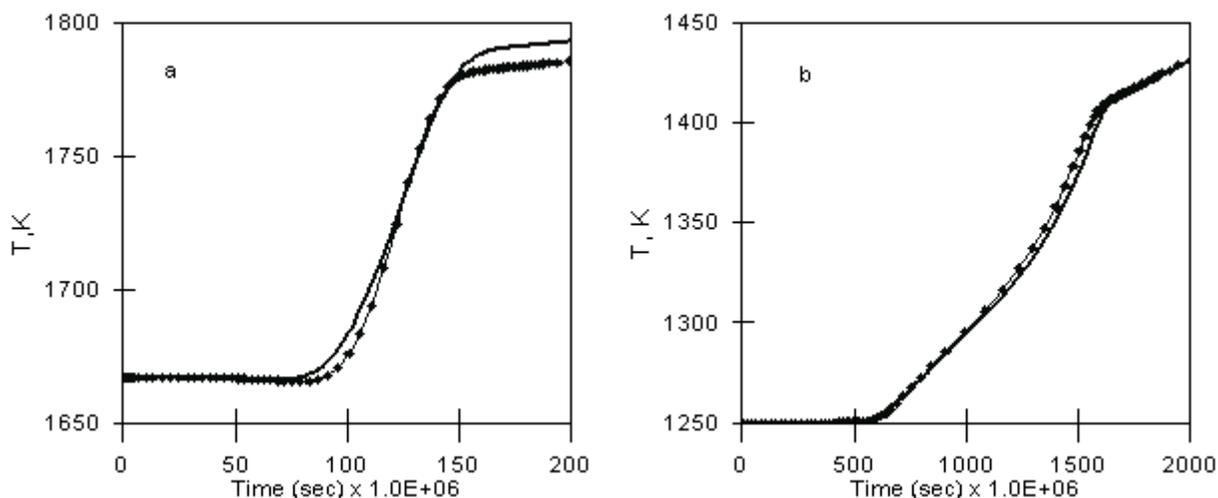


Figure 2.11. Calculated temperature profiles; $a - T_5 = 1667 \text{ K}$, $b - T_5 = 1250 \text{ K}$.
 $\text{C}_2\text{H}_4 - 0.5\%$, $\text{O}_2 - 1.5 \%$, $\text{Ar} - 98\%$, $P_5 = 1.07 \text{ atm}$.

Solid line – detailed reaction mechanism, symbols – particular reduced reaction mechanism.

Remark -----

The number of species in detailed and reduced reaction mechanisms can be different. Because of this the equilibrium gas parameters (temperature and species concentrations) are different as well (see, for example, Figure 2.11a).

3. Conclusion

The directed relation graph method, used here for generation of sets of important reactions and species, has been found to be effective in description of some reacting systems. The method is simply implemented and requires no special preliminary preparation. Additionally, the method is fast acting; for example, reduction of the Ethylene/Acetylene/Oxygen mixture (529 reactions and 75 species) on PC requires 5-10 sec.

However, the implemented here version has drawbacks due to imperfection of the final stage of the process. The program does not give any conclusion about accuracy and suitability of the reduced model as a whole. In Chemked -II, required size of the reduced mechanism is achieved by variation of the selection parameters a_k , and errors due to mechanism reduction are evaluated by direct comparison of the detailed and reduced calculations. On the basis of this information the user himself must do the decision about applicability of the reduced mechanism.

It should be noted that examples of the reduced reaction mechanisms presented in this work are not optimal; they are used only for illustration of the method. In principle, the optimisation problem can be solved in the frame of the approach used here. Then the problem is formulated as follows. For a given detailed reaction mechanism a reduced mechanism must be created with a minimal reaction set and/or a minimal species pool. The movement to the optimal state is performed by variation of the selection parameters a_k subject to a condition that the target errors must be less than user-specified tolerances.

Appendix. Selecting Important Reactions

Here we present a criterion that is used for selecting important reactions in building reduced reaction mechanisms (Section 1). We start from the mass conservation equation:

$$\frac{d \{Z_k\}}{dt} = \sum_j r_{kj} , \quad (\text{A.1})$$

where t is time, $\{Z_k\}$ is the molar contents of k th species per gram of gas mixture, r_{kj} is rate production of the k th species in j th reaction. Integration of Eq.(A.1) with respect to t over a time interval $[t_1, t_2]$ gives

$$\begin{aligned} \{Z_k\}_{t_2} - \{Z_k\}_{t_1} &= \sum_j W_{kj}(t_1, t_2) \\ W_{kj}(t_1, t_2) &= \int_{t_1}^{t_2} r_{kj} dt \end{aligned} \quad (\text{A.2})$$

Set of the W_{kj} values is a basis for definition of important reactions for production (consumption) of the k th species on a time interval $[t_1, t_2]$.

Now we introduce new values: $A_{kj} = \text{abs}(W_{kj})$. For the k th species, the A_{kj} values are sorted in ascending order and thus each A_{kj} correlates with the B_{kl} value from the ascending sequence. Note that $B_{kl+1} \geq B_{kl}$, where l is the number of a sequence term. The following expression can be formed from the B_{kl} values.

$$a_k = \frac{\sum_{l=1}^n B_{kl}}{\sum_{l=1}^N B_{kl}} , \quad (\text{A.3})$$

where the summations are over the sequence terms, N is the total number of the sequence terms (or the total number of reactions involving the k th species), a_k is a parameter. The expression (A.3) can be considered as an equation in n and is used as a criterion for selecting reactions. For given a_k , the number n defines the boundary between unimportant and important reactions; the reactions with the numbers $l > n$ are important. The criterion can be changed, choosing different a_k values on the interval $[0, 1]$.

References

- [1] A.B. Bendtsen, P. Glarborg, K. Dam-Johansen, Visualization methods in analysis of detailed chemical kinetics modelling. *Computers and Chemistry* **25**(2), pp 161-170, (2001).
- [2] T.F Lu and C.K. Law, A directed relation graph method for mechanism reduction, *Proceedings of the Combustion Institute* **30**, pp 1333-1341, (2005).
- [3] P. Pepiot and H. Pitsch. Systematic reduction of large chemical mechanisms. 4th Joint Meeting of the U.S. Sections of the Combustion Institute, Philadelphia, PA, (2005).
- [4] R.J. Kee, F.M. Rupley, J.A. Miller, M.E. Coltrin, J.F. Grcar, E. Meeks, H.K. Moffat, A.E. Lutz, G. Dixon-Lewis, M.D. Smooke, J. Warnatz, G.H. Evans, R.S. Larson, R.E. Mitchell, L.R. Petzold, W.C. Reynolds, M. Caracotsios, W.E. Stewart, P. Glarborg, C. Wang, and O. Adigun, *CHEMKIN Collection*, Release 3.6, Reaction Design, Inc., San Diego, CA (2000).
- [5] M.A. Oehlschlaeger, D.F. Davidson, R.K. Hanson, High-temperature UV absorption of methyl radicals behind shock waves. *Journal of Quantitative Spectroscopy & Radiative Transfer* **92**, pp 393–402, (2005).
- [6] GRI-Mech 3.0, The Gas Research Institute.
http://www.me.berkeley.edu/gri_mech/
- [7] H. Wang and A. Laskin, A comprehensive kinetic model of Ethylene and Acetylene oxidation at high temperatures, Dept. of Mechanical Engineering, Univ. of Delaware, Internal Report, Newark, (1998).
http://ame-www.usc.edu/research/combustion/combustionkinetics/c2_download.html
- [8] Y. Hidaka, K. Hattori, T. Okuno, K. Inami, T. Abe and T. Koike, Shock-tube and modeling study of acetylene pyrolysis and oxidation. *Combustion and Flame* **107**, No 4, pp 401-417, (1996).
- [9] D.M. Kalitan, J.M. Hall and E.L. Petersen, Ignition and oxidation of Ethylene-Oxygen-diluent mixtures with and without silane. *Journal of Propulsion and Power* **21**, No. 6, pp 1045 – 1056, (2005).
- [10] M. Jelezniak and I. Jelezniak. Use of radical emission for determination of ignition delay times behind reflected shocks, (2007).
http://www.jelezniak.de/Mark/chemical_reactions/ignition_delay_times.pdf