Problem of reduction of reaction mechanisms in plasma chemistry

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Abstract: Processes in chemically active plasmas were studied by the combination of experiment and computer simulation. The simulation technique was the macroscopic kinetic approach. As resulting sets of equations consisted of several hundreds of ordinary differential equations, a reduction technique resulting in the reduction of both chemical reactions and active species was suggested. This technique was applied on N2/CH4 and O2 plasma.

Keywords: chemical kinetics, reduction, plasma chemistry, hydrocarbons, oxygen

1. Introduction

In many application areas the algorithms of chemical kinetics are used – in combustion, reactive transport, air pollution modelling, plasma chemistry, etc. In order to increase the efficiency of modelling, in present time more sophisticated detailed models are being developed and analyzed. However, accurate models that correctly predict the studied chemical processes are typically extremely complex and involve a large number of reacting species. Therefore, it is desirable to reduce models complexity without significant loss of their preciseness.

From the mathematical point of view the kinetic equations describing the studied chemical process represent set of ordinary differential equations for time dependencies of concentrations of individual species

\[ \frac{dn_i}{dt} = g_i(n_1, ..., n_m, t) . \]

A large number of elementary reactions can occur among the species; some of these reactions are fast and some are slow and these multiple time scales cause severe stiffness of the resulting set of equations.

Reduction methods decrease the size and complexity of systems of kinetic equations and in this way reduce the stiffness and improve the performance of computer codes. The aim of simplified kinetics modelling is to derive the simplest reaction system which retains the essential features of the full system.

Over the years, a large number of reduction methods have been proposed. These methods can be divided into three groups [1]:

(i) Reduced mechanisms using quasi-steady-state and partial equilibrium assumptions.
(ii) Reduction of the number of reacting species and reactions.
(iii) Mathematical representations based on the time-scale separation.

The problem of obtaining a reduced model for the chemical kinetics problem has been considered by a number of authors. The classical chemical kinetics reduction approaches such as the Quasi-Steady-State Approximation (QSSA) [2], [3] or the Partial Equilibrium Approximation (PEA) [4], have generally relied on experience and intuition to identify the quasi-steady state species and the fast reactions. Another classical technique is a sensitivity analysis (e.g. [5]-[8]). The sensitivity analysis studies the change in the species concentration for small perturbations of the rate constants of chemical reactions in the model. If a reaction is slow and unimportant, it can be identified in this way.

Further reduction was attempted using the methods of time-scale separation [9], [10]. Modern model reduction methods are based typically on time scale analysis and range from the computational singular perturbation (CSP) method [11], intrinsic low-dimensional manifolds (ILDM) [12] to ideas from integer optimization [1]. Apart of methods making the explicit use of time scale separation, powerful geometrical approaches to simplification of chemical kinetics have been suggested [13]. The former methods are essentially based on the identification of a suitable projection vector basis of the phase space, which is related to the system's dynamics, and which, relying on a sufficient separation between fast and slow time scales, defines a decomposition of such space into a fast and slow subspace.

In last years a special attention is devoted to modern approaches based on the slow invariant manifold. In [14] various techniques for the construction of these manifolds are discussed and results compared with the CSP method.

2. Reduction in plasma chemistry

In our laboratories the discharges in hydrocarbons and in oxygen containing mixtures have been studied for a long time – e.g. [15], [16]. In order to compare mechanisms in gaseous chemistry under different discharge conditions, a computer experiment was prepared. The technique of simulations for both groups of discharges was the same. Models consisted of large
number of reactions between neutral, charged and excited species. The rate coefficients of these reactions depended on experimental conditions – electron and gas temperature, etc. Further influence of experimental conditions was included into spatial concentrations of some species. These data were derived from the probe measurements and from the emission-optical spectroscopy.

For the solution of models a macroscopic kinetic approach was used. The complete set of balance equations describes the conservation of individual species and consists of creation and lost processes due to chemical reactions in plasma as well as of drift and diffusion terms and results in set of partial differential equations. However, when taking into account our experimental conditions, both the drift and diffusion can be neglected compared to the influence of chemical reactions and we obtained the standard set of ordinary differential equations

\[
\frac{\text{d}n_i}{\text{d}t} = A_i(n_1, \ldots n_m) - B_i(n_1, \ldots n_m), \quad i = 1, \ldots, m,
\]

where \( n_i \) is the concentration of the \( i \)-th specie and \( m \) the total number of species in the studied mechanism. The creation processes \( A_i \) and the loss processes \( B_i \) consist of the terms \( \pm k_j \times n_a \times n_b \) and \( \pm k_j \times n_a \times n_b \times n_c \), for reactions of the first, second and third order, respectively. The rate coefficients \( k_j \) may depend on gas or electron temperature thus may depend on the time \( t \) or on the position in the discharge.

However, the complete reaction schemes for discharges in hydrocarbons as well as in oxygen consist of several hundreds of chemical reactions (see Sections 3 and 4) resulting in very stiff sets of equations; therefore a reduction method to simplify the system of kinetic equations must be applied.

Our reduction technique belongs to the group (ii) Reduction of the number of reacting species and reactions. The technique is based on the comparison of reaction rates. First it is necessary to reorder the list of chemical reactions according to their importance in the studied plasma chemical process. For this purpose two quantities were introduced:

- Differential weight factor of the \( i \)-th reaction \( w_i(t) \), i.e. the sum of absolute values of all terms \( k_j \times n_a \times n_b \) (as well as \( k_j \times n_a \times n_b \times n_c \)) with the same rate coefficient \( k_j \).

- Integral weight factor of the \( i \)-th reaction \( W_i(\infty) \), i.e. the integral of \( w_i(t) \) for times between 0 and \( t \).

Both the differential and integral weight factors characterise the speed of each reaction in each time of the kinetic calculations. While the differential weight factors can be used for the discussion of the importance of different reaction channels in various time periods, the integral weight factors \( W_i(\infty) \) characterise the importance of given reaction in the complete reaction mechanism. When the list of chemical reactions is reordered according to corresponding values \( W_i(\infty) \), we can preserve only reactions with highest integral weights. The number of reactions in simplified model depends on the demanded accuracy of the model (see Fig.2).

However, the described reduction procedure reduces not only the number of chemical reactions but also the number of species in the simplified model. Therefore, if we are interested in the behaviour of the most important species only, the reduction procedure can be applied as it was described above. But if we are interested in some globally non-important specie, corresponding reactions must be added back in the simplified model.

3. \( \text{N}_2/\text{CH}_4 \) plasma

The conversion of methane in more suitable products is one of challenging problems of plasma chemistry. The kinetics of methane decomposition in various plasma mixtures – in \( \text{N}_2/\text{CH}_4, \text{H}_2/\text{CH}_4 \), etc. – has been studied for several decades. The experimental techniques used for the decomposition of methane into simpler hydrocarbons are based either on the processing in active discharges or in flowing afterglow conditions. The advantage of the last technique is better controlled energy of individual species in plasma, so this technique is better suited for efficient gaseous chemistry. Contrary to that, the decomposition of methane in active discharges is often used for the preparation of carbon-containing thin films.

In our experiments performed in UPMC we studied the physical and chemical processes in \( \text{N}_2/\text{CH}_4 \) flowing afterglow. The methane was mixed with the nitrogen activated in the microwave discharge downstream the discharge reactor and various techniques were used for the study of gas parameters (pressure, flows and temperature along the discharge tube), characteristics of charged species (spatial dependence of electron concentration and temperature measured by means of probe diagnostics, optical characteristics of afterglow plasma measured by optical emission spectroscopy) and resulting stable products (by gas chromatography) [15].

The kinetic mechanism of methane decomposition both in active discharge and in flowing afterglow conditions was analysed by the computer experiment based on a macroscopic kinetic approach. The first version of the model consisted from 166 chemical reactions between 46 active species – electrons, neutral and excited input gases, hydrocarbons, nitriles and other nitrogen-containing species, both radicals and stable products. The final version of the model included 274 reactions between 50 charged and neutral species.

The resulting set of ordinary partial equations was solved with the help of a semi-implicit extrapolation method (Bulirsch-Stoer) [17]. Results of the simulation can be seen in Fig.1.
As the complete set of equations is rather stiff, the above described reduction method was used. In Fig.2 the influence of the decreasing number of equations in simplified model on the preciseness of simulation is demonstrated. The flow of carbon atoms in the simplified model of afterglow conditions is shown in Fig.3.

4. O₂ and O₂/Ar plasma

Similar study was performed in the oxygen plasma. The experimental conditions correspond to the positive column of dc glow discharge. The measurements were performed in laboratory of CU. The plasma consisted of oxygen both pure and in the mixture with rare gases. For the study of plasma properties optical, probe and microwave diagnostics were used. Some of these experimental results can be found in [16].

The model of the active oxygen and oxygen-argon discharges consisted of 196 reactions between 17 kinds of particles – electrons, neutral species (O, O₂, O₃), charged species (O⁺, O₂⁺, O₃⁺, O⁵⁺, O⁵⁻, O₃⁻, O₄⁻) and excited species (O(1S), O(1D), O₂(a¹∆), O₂(b¹Σ), O₂). When the oxygen-argon mixture was studied, several more species were added (Ar, Ar⁺, Ar²⁺). The model was again based on a macroscopic kinetic approach and was solved by the semi-implicit extrapolation method. The results of simulation performed for E/n = 80 Td with the help of a complete model are shown in Fig.4.

The analysis of the complete set of reactions from the point of view of possible reduction of the reaction set was performed and it was found that reaction could be divided into two groups:
- some reactions are highly important and influence the plasma composition profoundly
- while the other reactions have only a small influence on the final concentration of active species.
As an example of derived results, the reactions important for the creation and loss of main negative specie O\(^-\) together with their relative importance are
\[
\begin{align*}
O + O^- & \rightarrow O_2 + e \quad 96.1 \text{ %} \quad - \\
O_2 + e & \rightarrow O + O^- \quad 75.5 \text{ %} \quad + \\
e + O_2(a^1\Delta) & \rightarrow O + O^- \quad 23.3 \text{ %} \quad + \\
O^- + O_2(a^1\Delta) & \rightarrow O_3 + e \quad 2.3 \text{ %} \quad - \\
O^- + O_2(a^1\Delta) & \rightarrow O + O_2^- \quad 0.75 \text{ %} \quad - \\
e + O_2(b^1\Sigma) & \rightarrow O + O^- \quad 0.72 \text{ %} \quad +
\end{align*}
\]
These results depend on the plasma parameters – see e.g. our another contribution [18]. The presented data correspond again to 80 Td.

5. Discussion
During the analysis of chemical kinetics in both active and afterglow plasma of oxygen and hydrocarbon containing mixtures it was found, that suggested rather simple reduction mechanism can be used for the analysis of moderate sized plasma chemical systems.

In the study of two types of discharges in N\(_2\)/CH\(_4\) mixture it was found that, contrary to active discharges, where the role of charged species is very important, in the afterglow conditions the role of charged particles is unsubstantional compared to excited species both during the initialisation of methane decomposition and during further conversion into stable products.

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References