

Uncertainty analysis and reduction of chemical kinetic models

Summary of the PhD thesis of

Tibor Nagy

Eötvös Loránd University (ELTE), Faculty of Science
PhD School in Chemistry

Head of the PhD School:
Prof. György Inzelt, DSc

PhD programme in theoretical and physical chemistry, and study of the structure of matter

Head of the programme:
Prof. Péter Surján, DSc

ELTE Institute of Chemistry, Laboratory for Chemical Kinetics

Supervisor:
Prof. Tamás Turányi, DSc

Budapest, 2009

I. Introduction

One of the success stories of our time is the application of complex reaction mechanisms for the solution of academic and industrial problems. Chemical reactions are usually composed of several hundreds or even thousands of reaction steps. Reaction kinetic parameters of most reaction steps can be investigated experimentally, separately from the other steps. In the case of other reaction steps, methods of theoretical chemistry can provide the rate parameters. Annually, several hundred publications report the determinations of rate parameters of elementary reactions. These rate parameters are collected in databases, which are available through the Internet. Also, several groups are working on the production of collections of evaluated chemical kinetics data. These evaluated databases recommended parameters for the description of the temperature and pressure dependence of the rate coefficients of elementary reactions, usually based on several independent measurements and theoretical calculations. These databases also contain recommendations on the temperature dependence of the uncertainties of the rate coefficients. Based on the primary publications on the kinetics of elementary reactions and the chemical kinetic databases, detailed reaction mechanisms can be created for the description of complex chemical reactions.

Computer simulations based on detailed reaction mechanisms can be used to acquire new chemical information. For example, such simulations may provide the concentrations of minor components that could not be measured directly due to technical limitations. Kinetic analysis of the mechanisms may provide information on the main reaction paths and the interaction of the various processes.

Computer simulations based on detailed reaction mechanisms are increasingly used in environmental protection and technology. One way for the development of the production of computer chips is the improvement of the technology of chemical vapour deposition (CVD), based on simulations. Reaction kinetics of more and more processes in the chemical industry is determined with the resolution of elementary reactions. Based on simulations using detailed reaction mechanisms, the yield of the final product can be maximized with the simultaneous suppression of the production of harmful by-products. The recently developed car engines have a better fuel economy and emit fewer pollutants, due to the computer aided design that take into account the chemistry of combustion. Furnaces and combustors are designed and modified using the detailed combustion mechanisms. Using models of atmospheric chemistry, the effect of the emission of various pollutants can be calculated, and the consequence of the

increase or decrease of emission can be investigated. Recently, publications in systems biology discussed how new medical drugs could be designed based on the biochemical kinetic model of human diseases.

Advancements are needed in two areas to make detailed reaction mechanisms more applicable in practical simulations. First, parameters of all chemical kinetic models are uncertain and therefore the simulation results are also uncertain. The result of a simulation is really useful, if it also includes an assessment of the uncertainty of the simulation result. Second, computer models based on large detailed reaction mechanisms consume much computer time and are usually not applicable for the simulation of spatially inhomogeneous systems. It is therefore important to convert the original model to a reduced one, which provides almost the same simulation results for the important species, but much faster. This thesis reports advancements in both areas.

II. Aims

- 1 Temperature-dependence of the rate coefficients can be described by the extended Arrhenius equation $k = AT^n \exp(-E/RT)$, or using its reduced forms, the original Arrhenius equation $k = A \exp(-E/RT)$ or equation $k = AT^n$. Chemical kinetics databases contain the recommended Arrhenius parameters and also information on the temperature-dependent uncertainties of the rate coefficients for several thousand reactions, but usually do not provide information on the uncertainty of the Arrhenius parameters. One of the aims of my work was to elaborate a method for the calculation of the uncertainty of the Arrhenius parameters based on the available uncertainty information given in the chemical kinetics databases.
- 2 The first step of the reduction of large reaction mechanisms is the identification of redundant species and reaction steps. The reduced mechanism should provide almost identical simulation results for the important species. Several methods have been suggested for the selection of redundant species and reaction steps, usually via the investigation of the right hand side of the kinetic system of differential equations. My aim was to find a more effective way for this type of mechanism reduction.
- 3 Reduced mechanisms obtained by the identification and elimination of redundant species and reaction steps are still too large for many practical purposes and further reduction is

needed based on time scale analysis. In this approach, processes according to the time scale of simulation are resolved only, and the much faster and much slower processes are handled in a special way. Traditional methods, like QSSA, fast equilibrium assumption and pool component approximation use this approach. There are related recent methods, like CSP or ILDM, which use the eigenvalue–eigenvector decomposition of the Jacobian of the kinetic system of differential equations. In such studies, the Jacobian is usually assumed to be diagonalizable. My aim was to investigate the determination of time scales in chemical kinetic systems from a wider perspective.

III. New scientific results

1 Uncertainty of Arrhenius parameters

- 1.1 A relation was derived between the temperature dependence of the variance of a rate coefficient and the temperature independent covariance matrix of the Arrhenius parameters. This relation defines the possible temperature dependence of the variance of a rate coefficient.
- 1.2 In chemical kinetics databases, the uncertainties of rate coefficients are defined in three different ways. The “combustion chemistry type” handling defines properly the uncertainties of Arrhenius parameters only in rare exceptional cases. Depending on the number of temperatures where the uncertainties are given, in most cases the uncertainties are not defined unambiguously, while in other cases the uncertainty information is not self-consistent. In atmospheric chemistry, the IUPAC and the JPL data collections define the uncertainties of rate coefficients differently. The uncertainty definition of the IUPAC database is correct, but implicitly assumes unit correlation between A and E . Using the uncertainty definition of JPL, very different joint probability density function (*pdf*) can be determined below and above temperature 298 K, thus a unique temperature independent joint *pdf* cannot be determined.
- 1.3 If the joint *pdf* of the Arrhenius parameters correspond to a multivariate normal distribution, then the rate coefficient has a normal distribution at all temperatures. If the *pdf* of the rate coefficient is truncated at values k_{\min} and k_{\max} , then the joint *pdf* of the Arrhenius parameters will correspond to a truncated normal distribution.

- 1.4 Based on the equations derived, elements of the temperature independent covariance matrix of the Arrhenius parameters can be fitted to the uncertainty information provided in the chemical kinetics databases. If the kinetics database does not contain unambiguous uncertainty information, then a joint *pdf* of the Arrhenius parameters can be constructed that is not in contradiction with the uncertainty information of the database. The method was presented using the evaluated kinetic data for reactions $\text{O}+\text{N}_2\text{O}\rightarrow\text{NO}+\text{NO}$, $\text{N}+\text{OH}\rightarrow\text{NO}+\text{H}$, $\text{HO}_2+\text{C}_3\text{H}_5\rightarrow\text{C}_3\text{H}_6+\text{O}_2$, $\text{O}+\text{C}_2\text{H}_4\rightarrow\text{products}$, and $\text{O}(\text{}^1\text{D})+\text{H}_2\text{O}\rightarrow\text{OH}+\text{OH}$.
- 1.5 We recommend that the chemical kinetics databases should publish the covariance matrix of the Arrhenius parameters instead of the information on the temperature dependent uncertainties of rate parameters. The former means 3 parameters for a two-parameter Arrhenius equation and 6 parameters for a three-parameter Arrhenius equation. In uncertainty analysis studies carried out so far in changing temperature chemical kinetic simulations, always the uncertainty of parameter *A* was considered, which meant that the uncertainties of parameters *n* and *E* were assumed to be zero in an unrealistic way. Using the joint *pdf* of the Arrhenius parameters, as defined in this thesis, more realistic uncertainty analysis of chemical kinetic systems will be possible.

2 Reduction of reaction mechanisms based on simulation error minimization

- 2.1 The Simulation Error Minimization Connectivity Method (SEM-CM) was developed for the identification of redundant species in a reaction mechanism. As a first step, the species that are considered as important should be selected. Based on the analysis of the normed Jacobian, species groups are identified that can form a consistent mechanism when added to the group of important species. Simulations are carried out with all generated mechanisms; the mechanisms and the corresponding simulation errors are recorded in a database. The simulation error is defined as the deviation of simulation results, obtained with the full and the reduced mechanisms. If even the smallest recorded error is greater than an acceptable threshold, then new species groups are added to the mechanism having the smallest error. This way a series of reaction mechanisms can be obtained, with increasing size and decreasing simulation error. For any predefined threshold a reduced mechanism can be identified that contains almost optimally mini-

imum number of species; however, this mechanism may still contain redundant reactions.

- 2.2 The method of “Principal Component Analysis of Matrix F with Simulation Error Minimization” (SEM-PCAF) was elaborated for the identification of redundant reactions in a mechanism. Starting from the mechanism obtained in the previous step, the PCAF method is applied with systematically varied thresholds. The obtained reaction mechanisms, the corresponding simulation errors, and the CPU time needed for the simulations are recorded in a database. Using this database, a mechanism can be selected that produces almost identical simulation results compared to those of the full mechanism, while requiring much less CPU time for the simulations.
- 2.3 A large reaction mechanism consisting of 6874 reaction steps of 345 species, describing the partial oxidation of methane to high conversion, was investigated. Using this example, the joint application of methods SEM-CM and SEM-PCAF was demonstrated to be a very efficient method for the reduction of large reaction mechanisms. The aim was the reproduction of the concentration–time profiles of the 12 large concentration species at conditions of industrial relevance with 5% maximum error. The joint application of methods SEM-CM and SEM-PCAF resulted in a reduced mechanism having 246 reaction steps of 47 species. The simulation using this reduced mechanism is 116 times faster than using the original full mechanism.
- 2.4 Based on the original publications, several methods were encoded that were recently suggested for the identification redundant species and reactions in large reaction mechanisms. These methods included the Directed Relation Graph (DRG), the two-step DRG, DRGASA, DRGEP and the extended DRGEP techniques. In all cases the deviations of the simulation results obtained with the full and the reduced mechanisms were investigated as a function of the size of the reduced mechanism. The latter was characterized with the number of species in the reduced mechanism. Our newly developed method proved to be the most effective, since it resulted in the smallest reduced mechanism at any required simulation error threshold.

3 Time scale analysis of chemical kinetic models

- 3.1 If the Jacobian of the kinetic system of differential equations does not have multiple eigenvalues, or if the geometric multiplicity of the eigenvalue is equal to its algebraic multiplicity, then the time scales can be properly defined by the eigenvalues. If the geometric multiplicity of the eigenvalue is less than its algebraic multiplicity, then the eigenvalue itself does not define a time scale. This so-called degenerate case has not been discussed in the literature.
- 3.2 The Jordan decomposition of the Jacobian of the kinetic system of differential equations was applied for the determination of the time scales of chemical kinetic systems. Within a linear approximation, it characterizes properly the time scales in all cases. In the degenerate case, the decay of a concentration perturbation does not follow a sum of purely exponential functions, but some member-functions are products of an exponential and a power function term. According to the parameters of this member-function, the corresponding time scale can be shorter or longer than those of defined by the eigenvalue.
- 3.3 If two reaction steps in a mechanism have identical rate coefficients, then the corresponding Jacobian may have degenerate eigenvalues, as it was demonstrated on a simple example. In detailed tropospheric chemical models, there are many chemically similar species. Usually identical rate coefficients (called “generic rate coefficients”) are assigned to the similar reactions of these species, due to the lack of rate data. Similar generic rate coefficients are usually applied in models of low-temperature combustion. At the investigation of the models of these chemical systems, the Jacobian may have degenerate eigenvalues and therefore the timescales defined on the basis of the Jordan decomposition may have significance.

Publications and conference presentations

Publications related to the dissertation

1. T. Nagy, T. Turányi
Reduction of very large reaction mechanisms using methods based on simulation error minimization
Combustion and Flame, **156**, 417–428 (2009)
impact factor: 2.184
2. T. Nagy, T. Turányi
Relaxation of concentration perturbation in chemical kinetic systems
Reaction Kinetics and Catalysis Letters, **96**, 269–278 (2009)
impact factor: 0.584
3. T. Nagy, T. Turányi
Uncertainty of Arrhenius parameters
J. Phys. Chem. A, to be submitted
4. I. Gy. Zsély, T. Nagy, J. M. Simmie, H. J. Curran
Reduction of a detailed kinetic model for the ignition of methane/propane mixtures at gas turbine conditions using simulation error minimization methods
Combustion and Flame, to be submitted

Conference proceedings

1. I. Lagzi, T. Nagy, T. Turányi, L. Haszpra, A. S. Tomlin
Simulation of the formation and spread of photochemical air pollution in Hungary
Proceedings of the Conference on Modelling Fluid Flow (CMFF'03), pp. 495-500
September 3 - 6, 2003, Budapest, Hungary
2. I. Gy. Zsély, T. Nagy, J. M. Simmie, H. J. Curran
Reduction of detailed kinetic model for the ignition of natural gas mixtures at gas turbine conditions
Proceedings of the Fourth European Combustion Meeting, Vienna, Austria, 14-17
April 2009
3. T. Nagy, T. Turányi
Mechanism reduction based on simulation error minimization
Proceedings of the Second International Workshop on Model Reduction in Reacting Flows, pp. 115-118
March 30 – April 1, 2009, University of Notre Dame, Indiana, USA

Presentations on international conferences

1. T. Nagy, T. Turányi, M. J. Pilling
A reduced mechanism for the tropospheric degradation of isoprene
Nonlinear phenomena in chemistry; ESF REACTOR workshop
24-27 January, 2003, Budapest, Hungary
(poster)
2. I. Lagzi, T. Nagy, T. Turányi., L. Haszpra, A. S. Tomlin
Simulation of the formation and spread of photochemical air pollution in Hungary
Conference on Modelling Fluid Flow (CMFF'03)
3-6 September, 2003, Budapest, Hungary
(lecture)
3. Á. Kramarics, T. Nagy, I. Gy. Zsély, T. Turányi
Reduction of very large reaction mechanisms: the example of fuel-cell gas kinetics
5th International Conference on Sensitivity Analysis of Model Output (SAMO)
18-22 June, 2007, Budapest, Hungary
(poster)
4. T. Nagy, I. Gy. Zsély, T. Turányi
Reduction of very large reaction mechanisms using methods based on simulation error minimization.
32nd International Symposium on Combustion
3-8 August, 2008, Montreal, Canada
(poster)
5. T. Nagy, I. Gy. Zsély, T. Turányi
Reduction of very large reaction mechanisms using methods based on simulation error minimization.
Austrian - Croatian - Hungarian Combustion Meeting (ACH2008)
3 October, 2008, Sopron, Hungary
(poster)
6. T. Nagy, T. Turányi
Mechanism reduction based on simulation error minimization
Second International Workshop on Model Reduction in Reacting Flows
March 30 – April 1, 2009, University of Notre Dame, Indiana, USA
(lecture)
7. I. Gy. Zsély, T. Nagy, J. M. Simmie, H. J. Curran
Reduction of a Detailed Kinetic Model for the Ignition of Natural Gas Mixtures at Gas Turbine Conditions
Fourth European Combustion Meeting (ECM2009)
14-17 April, 2009, Vienna, Austria
(poster)

Lectures on Hungarian conferences

1. T. Nagy
Az izoprén légköri lebomlási mechanizmusának egyszerűsítése
(Simplification of the atmospheric degradation mechanism of isoprene)
Workshop of the "MTA Reakciókinetikai és Fotokémiai Munkabizottság"
20-21 October, 2005, Gyöngyöstarján
(lecture)
2. T. Nagy, Á. Kramarics, I. Gy. Zsély, T. Turányi
Metán tüzelőanyagú szilárd oxidos tüzelőanyag-elemek anódterében lejátszódó reakciók mechanizmusának vizsgálata
(Investigation of the mechanism of reactions occurring in the anode channel of methane-fuelled SOFCs)
Workshop of the "MTA Reakciókinetikai és Fotokémiai Munkabizottság"
25-26 October, 2007, Gyöngyöstarján
(lecture)