Chapter 1
Introduction

Abstract Chemical processes can be described by detailed kinetic reaction mechanisms consisting of several hundreds or even thousands of reaction steps. Such reaction mechanisms are used in many fields of science and technology, including combustion, atmospheric chemistry, environmental modelling, process engineering, and systems biology. This book describes methods for the analysis of reaction mechanisms that are applicable in all these fields. The book will address topics such as the importance of model evaluation as well as the need for model reduction under situations where the kinetic model is coupled with models describing complex physical processes where computational expense becomes a critical issue. It includes topics such as: the basic foundations of chemical kinetic models; methods for the automatic generation of kinetic mechanisms; sources of thermodynamic and kinetic data; methods for uncertainty and sensitivity analysis; timescale analyses; similarities in model sensitivities; and chemical model reduction. Within the introduction we discuss the motivations behind the text as well as providing a brief summary of key reference texts on similar topics from the current literature.

Chemical processes can be described by detailed kinetic reaction mechanisms consisting of several hundreds or even thousands of reaction steps. Detailed reaction mechanisms are used in many fields of science and technology, including combustion, atmospheric chemistry, environmental modelling, process engineering and systems biology. This book describes methods for the analysis of reaction mechanisms that are applicable in all these fields. The reasons for analysis may vary. It may be important to determine the key reaction steps that drive the overall reactivity of the chemical system or the production of key species. It may also be necessary to include the chemical mechanism within a larger model describing, for example, a reactive flow problem. In this case, the smallest version of the mechanism describing key kinetic features may be required in order to meet the limitations of the computational requirements. Mechanism reduction techniques can identify the core reactions in a large mechanism and the application of reduced mechanisms may speed up the simulations, allowing engineering optimisations. It may also be important to determine the predictability of any model which incorporates the chemical mechanism and therefore to assess the confidence that can be placed in simulation results. Uncertainty analysis allows the calculation of the uncertainty of simulation results based on the users' best knowledge of the input

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parameters, potentially putting an error bar on model predictions. Sensitivity analysis can provide the subsequent identification of the most important parameters driving model uncertainty. These methods can form a key part of the process of model evaluation and improvement.

This book is a monograph for researchers and engineers dealing with detailed kinetic reaction mechanisms and also a textbook for graduate students of related courses in chemistry, mechanical engineering, environmental science and biology. We include biology, since nowadays even biological and biochemical processes such as the *cell cycle*, *metabolism networks* and *molecular signal transfer* can be described by detailed reaction mechanisms (Klipp et al. 2005, 2009). Reaction kinetic formalism is also used in some ecological models. The best-known example is the *Lotka – Volterra model* (Lotka 1910, 1920; Volterra 1926), which describes the dynamics of a biological system consisting of an interaction of a predator and a prey. This model was originally suggested by Lotka to describe autocatalytic chemical reactions, but the same equations were later interpreted to model predator–prey interactions. Érdi and Tóth (1989) also claim that reaction kinetic formalisms are frequently used as a metalanguage in many other fields. The methods described in this book are all applicable for the analysis of non-chemical models that use chemical kinetic formalism. Moreover, many of the methods should be applicable without substantial modifications, for the analysis of any model based on differential equations used in physics, chemistry, biology or economics.

Several reviews dealing with the topics of this book have previously been published. The book chapter of Tomlin et al. (1997) discusses many relevant papers that were published up to 1995 that dealt with mathematical and computational methods used for the automatic creation, analysis and reduction of detailed reaction mechanisms in combustion. Several journal review articles have also subsequently been published (Okino and Mavrovouniotis 1998; Ross and Vlad 1999; Law et al. 2003; Law 2007; Ross 2008; Lu and Law 2009; Pope 2013; Stagni et al. 2014) that discuss various available methods for the analysis and reduction of reaction mechanisms. The book chapter of Goussis and Maas also confers several mechanism reduction methods, especially those that are related to turbulent combustion modelling (Goussis and Maas 2011). Mathematical modelling of chemical reactions was discussed in the book of Érdi and Tóth (1989). Mechanism reduction methods based on invariant manifolds are described in the book of Gorban and Karlin (2005). Volume 42 of series Comprehensive Chemical Kinetics (Carr 2007) contains several related reviews dealing with topics such as an introduction to chemical kinetics and the construction and optimisation of reaction mechanisms. Part IV [Chaps. 16 to 19; (Tomlin and Turányi 2013a, b; Maas and Tomlin 2013; Turányi and Tomlin 2013)] of a book on the development of detailed chemical kinetic models for cleaner combustion (Battin-Leclerc et al. 2013) deals with several topics of this book, including methods for mechanism reduction and uncertainty analysis.

The various methods used for sensitivity analysis are discussed in several recent reviews (Saltelli et al. 2005, 2006, 2012; Saltelli and Annoni 2010; Zi 2011; Tomlin 2013; Wang and Sheen 2015), a monograph (Saltelli et al. 2000) and two

textbooks (Saltelli et al. 2004, 2008). This book aims to bring together and update the discussion of a wide range of techniques available for the analysis of chemical kinetic mechanisms and to guide the user on the most appropriate techniques for different classes of problems.

References

Battin-Leclerc, F., Blurock, E., Simmie, J. (eds.): Development of Detailed Chemical Kinetic Models for Cleaner Combustion. Springer, Heidelberg (2013)

Carr, R.W. (ed.): Modeling of Chemical Reactions. Elsevier, Amsterdam (2007)

Érdi, P., Tóth, J.: Mathematical Models of Chemical Reactions. Princeton University Press, Princeton (1989)

Gorban, A., Karlin, I.V.: Invariant Manifolds for Physical and Chemical Kinetics. Springer, Berlin (2005)

Goussis, D.A., Maas, U.: Model reduction for combustion chemistry. In: Echekki, T., Mastorakos, E. (eds.) Turbulent Combustion Modeling, pp. 193–220. Springer, New York (2011)

Klipp, E., Herwig, R., Kowald, A., Wierling, C., Lehrach, H.: Systems Biology in Practice. Wiley-VCH, Weinheim (2005)

Klipp, E., Liebermeister, W., Wierling, C., Kowland, A., Lehrach, H., Herwig, R.: Systems Biology: A Textbook. Wiley-VCH Verlag, Weinheim (2009)

Law, C.K.: Combustion at a crossroads: status and prospects. Proc. Combust Inst. **31**, 1–29 (2007)

Law, C.K., Sung, C.J., Wang, H., Lu, T.F.: Development of comprehensive detailed and reduced reaction mechanisms for combustion modeling. AIAA J. **41**, 1629–1646 (2003)

Lotka, A.J.: Contribution to the theory of periodic reaction. J. Phys. Chem. **14**, 271–274 (1910)

Lotka, A.J.: Analytical note on certain rhythmic relations in organic systems. Proc. Natl. Acad. Sci. U. S. A. **6**, 410–415 (1920)

Lu, T., Law, C.K.: Toward accommodating realistic fuel chemistry in large-scale computations. Prog. Energy Combust. Sci. **35**, 192–215 (2009)

Maas, U., Tomlin, A.S.: Time-scale splitting-based mechanism reduction. In: Battin-Leclerc, F., Blurock, E., Simmie, J. (eds.) Development of Detailed Chemical Kinetic Models for Cleaner Combustion, pp. 467–484. Springer, Heidelberg (2013)

Okino, M.S., Mavrovouniotis, M.L.: Simplification of mathematical models of chemical reaction systems. Chem. Rev. **98**, 391–408 (1998)

Pope, S.B.: Small scales, many species and the manifold challenges of turbulent combustion. Proc. Combust. Inst. **34**, 1–31 (2013)

Ross, J.: Determination of complex reaction mechanisms. Analysis of chemical, biological and genetic networks. J. Phys. Chem. A **112**, 2134–2143 (2008)

Ross, J., Vlad, M.O.: Nonlinear kinetics and new approaches to complex reaction mechanisms. Ann. Rev. Phys. Chem. **50**, 51–78 (1999)

Saltelli, A., Annoni, P.: How to avoid a perfunctory sensitivity analysis. Environ. Model. Software **25**, 1508–1517 (2010)

Saltelli, A., Scott, M., Chen, K. (eds.): Sensitivity Analysis. Wiley, Chichester (2000)

Saltelli, A., Tarantola, S., Campolongo, F., Ratto, M.: Sensitivity Analysis in Practice. A Guide to Assessing Scientific Models. Wiley, Chichester (2004)

Saltelli, A., Ratto, M., Tarantola, S., Campolongo, F.: Sensitivity analysis for chemical models. Chem. Rev. **105**, 2811–2828 (2005)

Saltelli, A., Ratto, M., Tarantola, S., Campolongo, F.: Sensitivity analysis practices: strategies for model-based inference. Reliab. Eng. Syst. Saf. **91**, 1109–1125 (2006)

Saltelli, A., Ratto, M., Andres, T., Campolongo, F., Cariboni, J., Gatelli, D., Saisana, M., Tarantola, S.: Global Sensitivity Analysis: The Primer. Wiley, New York (2008)

Saltelli, A., Ratto, M., Tarantola, S., Campolongo, F.: Update 1 of: sensitivity analysis for chemical models. Chem. Rev. **112**, PR1–PR21 (2012)

Stagni, A., Cuoci, A., Frassoldati, A., Faravelli, T., Ranzi, E.: Lumping and reduction of detailed kinetic schemes: an effective coupling. Ind. Eng. Chem. Res. **53**, 9004–9016 (2014)

Tomlin, A.S.: The role of sensitivity and uncertainty analysis in combustion modelling. Proc. Combust. Inst. **34**, 159–176 (2013)

Tomlin, A.S., Turányi, T.: Investigation and improvement of reaction mechanisms using sensitivity analysis and optimization. In: Battin-Leclerc, F., Blurock, E., Simmie, J. (eds.) Development of Detailed Chemical Kinetic Models for Cleaner Combustion, pp. 411–445. Springer, Heidelberg (2013a)

Tomlin, A.S., Turányi, T.: Mechanism reduction to skeletal form and species lumping. In: Battin-Leclerc, F., Blurock, E., Simmie, J. (eds.) Development of Detailed Chemical Kinetic Models for Cleaner Combustion, pp. 447–466. Springer, Heidelberg (2013b)

Tomlin, A.S., Turányi, T., Pilling, M.J.: Mathematical tools for the construction, investigation and reduction of combustion mechanisms. In: Pilling, M.J., Hancock, G. (eds.) Low-temperature Combustion and Autoignition. Comprehensive Chemical Kinetics, vol. 35, pp. 293–437. Elsevier, Amsterdam (1997)

Turányi, T., Tomlin, A.S.: Storage of chemical kinetic information. In: Battin-Leclerc, F., Blurock, E., Simmie, J. (eds.) Development of Detailed Chemical Kinetic Models for Cleaner Combustion, pp. 485–512. Springer, Heidelberg (2013)

Volterra, V.: Variazioni e fluttuazioni del numero d'individui in specie animali conviventi. Mem. Acad. Lincei Roma **2**, 31–113 (1926)

Wang, H., Sheen, D.A.: Combustion kinetic model uncertainty quantification, propagation and minimization. Prog. Energy Combust. Sci. **47**, 1–31 (2015)

Zi, Z.: Sensitivity analysis approaches applied to systems biology models. IET Syst. Biol. **5**, 336–346 (2011)