

Tamás Turányi · Alison S. Tomlin

Analysis of Kinetic Reaction Mechanisms

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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

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 Mavrouniotis 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.

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Chapter 2

Reaction Kinetics Basics

Abstract This chapter provides an introduction to the basic concepts of reaction kinetics simulations. The level corresponds mainly to undergraduate teaching in chemistry and in process, chemical and mechanical engineering. However, some topics are discussed in more detail and depth in order to underpin the later chapters. The section “parameterising rate coefficients” contains several topics that are usually not present in textbooks. For example, all reaction kinetics textbooks discuss the pressure dependence of the rate coefficients of unimolecular reactions, but usually do not cover those of complex-forming bimolecular reactions. The chapter contains an undergraduate level introduction to basic simplification principles in reaction kinetics. The corresponding sections also discuss the handling of conserved properties in chemical kinetic systems and the lumping of reaction steps.

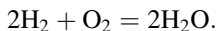
2.1 Stoichiometry and Reaction Rate

2.1.1 Reaction Stoichiometry

In this section, we begin by explaining the formulation of chemical reaction mechanisms and the process of setting up chemical rate equations from stoichiometric information and elementary reaction rates.

First, we assume that a chemical process can be described by a single *stoichiometric equation*. The stoichiometric equation defines the molar ratio of the reacting species and the reaction products. This equation is also called the *overall reaction equation*. Real chemical systems corresponding to such a single chemical reaction, that is, when the reactants react with each other forming products immediately, are in fact very rare. In most cases, the reaction of the reactants produces intermediates, these intermediates react with each other and the reactants, and the final products are formed at the end of many coupled reaction steps. Each of the individual steps is called an *elementary reaction*. Within elementary reactions, there is no macroscopically observable intermediate between the reactants and the products. This point is now illustrated for the case of hydrogen oxidation, but similar examples could be cited across many different application fields.

The overall reaction equation of the production of water from hydrogen and oxygen is very simple:



We can see that this overall reaction balances the quantities of the different elements contained in the reactants and products of the reaction. Reaction stoichiometry describes the 2:1:2 ratio of hydrogen, oxygen and water molecules in the above equation. From a stoichiometric point of view, a chemical equation can be rearranged, similarly to a mathematical equation. For example, all terms can be shifted to the right-hand side:

$$0 = -2\text{H}_2 - 1\text{O}_2 + 2\text{H}_2\text{O}.$$

Let us denote the formulae of the chemical species by the vector $\mathbf{A} = (A_1, A_2, A_3)$ and the corresponding multiplication factors by vector $\mathbf{v} = (v_1, v_2, v_3)$. In this case, $A_1 = \text{“H}_2\text{”}$, $A_2 = \text{“O}_2\text{”}$, $A_3 = \text{“H}_2\text{O”}$ and $v_1 = -2$, $v_2 = -1$, $v_3 = +2$. The corresponding general stoichiometric equation is

$$0 = \sum_{j=1}^{N_s} v_j A_j, \quad (2.1)$$

where N_s is the number of species. The general stoichiometric equation of any chemical process can be defined in a similar way, where v_j is the *stoichiometric coefficient* of the j th species and A_j is the formula of the j th species in the overall reaction equation. The stoichiometric coefficients are negative for the reactants and positive for the products. The stoichiometric coefficients define the ratios of the reactants and products. Therefore, these are uncertain according to a scalar multiplication factor. This means that by multiplying all stoichiometric coefficients with the same scalar, the resulting chemical equation refers to the same chemical process. Thus, chemical equations $0 = -2\text{H}_2 - 1\text{O}_2 + 2\text{H}_2\text{O}$ and $0 = -1\text{H}_2 - \frac{1}{2}\text{O}_2 + 1\text{H}_2\text{O}$ (or using the traditional notation, $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ and $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$, respectively) represent the same chemical process. Also, the order of the numbering of the species is arbitrary. We show here the stoichiometric coefficients for an overall reaction step, but the same approach is taken for each of the elementary steps of a detailed chemical scheme. In general, for elementary reaction steps within a chemical mechanism, the stoichiometric coefficients are integers.

There are many chemical processes for which a single overall reaction equation that describes the stoichiometry of the process cannot be found. For example, the oxidation of hydrocarbons sourced from exhaust gases in the troposphere cannot be described by a single overall reaction equation. Many types of hydrocarbons are emitted to the troposphere, and their ratio changes dependent on the type of

pollution source. Therefore, no single species can be identified as reactants or products.

Let us now think about the time-dependent behaviour of a chemical system and how we might describe it using information from the kinetic reaction system. The simplest practical case here would be one or more reactants reacting in a well-mixed vessel to form one or more products over time. In this case, if the molar concentration Y_j of the j th species is measured at several consecutive time points, then by applying a finite-difference approach, the *production rate* of the j th species dY_j/dt can be calculated. The rate of a chemical reaction defined by stoichiometric equation (2.1) is the following:

$$r = \frac{1}{v_j} \frac{dY_j}{dt}. \quad (2.2)$$

Reaction rate r is independent of index j . This means that the same reaction rate is obtained when the production rate of any of the species is measured. However, the reaction rate depends on the stoichiometric coefficient, and therefore, the reaction rate depends on a given form of the stoichiometric equation.

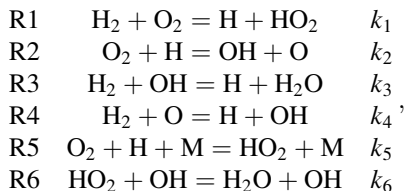
Within a narrow range of concentrations, the reaction rate r can always be approximated by the following equation:

$$r = k \prod_{j=1}^{N_S} Y_j^{\alpha_j}, \quad (2.3)$$

where the positive scalar k is called the *rate coefficient*, the exponents α_j are positive real numbers or zero, the operator Π means that the product of all terms behind it should be calculated and N_S is the number of species. In the case of some reactions, the form of Eq. (2.3) is applicable over a wide range of concentrations. When the reaction rate is calculated by Eq. (2.3), molar concentrations (i.e. the amount of matter divided by volume with units such as mol cm^{-3}) should always be used. The rate coefficient k is independent of the concentrations but may depend on temperature, pressure and the quality and quantity of the nonreactive species present (e.g. an inert dilution gas or a solvent). This is the reason why the widely used term *rate constant* is not preferred and *rate coefficient* is a more appropriate term. The exponent α_j in Eq. (2.3) is called the *reaction order with respect to species A_j* .

The sum of these exponents $\left(\alpha = \sum_{j=1}^{N_S} \alpha_j \right)$ is called the *overall order of the reaction*. In the case of an overall reaction equation such as $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$, the order α_j is usually not equal to the stoichiometric coefficient v_j because of the intermediate steps that are involved in the overall reaction. For elementary reactions, the reaction orders of the reactions and the absolute value of the stoichiometric coefficients of the reactants are commonly mathematically the same.

As stated above, intermediates are formed within most reaction systems, and hence, in order to define the time-dependent dynamics of a system accurately, a reaction model should include steps where such intermediates are formed from reactants and then go on to form products. For example, detailed reaction mechanisms for the oxidation of hydrogen [see e.g. Ó Conaire et al. (2004), Konnov (2008), Hong et al. (2011), Burke et al. (2012), Varga et al. (2015)] contain not only the reactants (H_2 and O_2) and the product (H_2O) but also several intermediates (H , O , OH , HO_2 , H_2O_2), which are present in the 30–40 reaction steps considered. Any hydrogen combustion mechanism should contain the following reaction steps:



where species M represents any species present in the mixture and will be further discussed in the next section.

The number of elementary reaction steps within a kinetic reaction mechanism can typically vary from ten to several ten thousands, depending on the chemical process, the reaction conditions and the required detail and accuracy of the chemical kinetic model. Each elementary reaction step i can be characterised by the following stoichiometric equation:

$$\sum_j v_{ij}^L A_j = \sum_j v_{ij}^R A_j, \quad (2.4)$$

where the stoichiometric coefficients on the left-hand side (v_{ij}^L) and the right-hand side (v_{ij}^R) of an elementary reaction step should be distinguished. The stoichiometric coefficient belonging to species i in a reaction step can be obtained from the equation $v_{ij} = v_{ij}^R - v_{ij}^L$. The left-hand side stoichiometric coefficients v_{ij}^L should be positive integers, whilst the right-hand side stoichiometric coefficients v_{ij}^R are positive integers for elementary reactions and can be positive or negative, integer or real numbers for reaction steps that were obtained by the combination (“lumping”) of several elementary reactions. Therefore, the overall stoichiometric coefficients v_{ij} can also be any numbers (positive or negative figures; integers or real numbers). Elements v_{ij}^L , v_{ij}^R and v_{ij} constitute the left-hand side, the right-hand side and the overall *stoichiometric matrix*, respectively.

To emphasise the analogy with mathematical equations, so far the equality sign ($=$) was always used for chemical equations. From now on, arrows will be used for one-way or irreversible chemical reactions (like $\text{A} \rightarrow \text{B}$). Reversible reactions will be denoted by double arrows (like $\text{A} \rightleftharpoons \text{B}$).

A detailed *kinetic reaction mechanism* contains the stoichiometric equations of type (2.4) and the corresponding rate coefficient for each reaction step. These rate coefficients can be physical constants that are valid for the conditions of the reactions (e.g. temperature, pressure) or functions that can be used to calculate the value of the rate coefficient applicable at the actual temperature, pressure, gas composition, etc. The physical dimension of the rate coefficient depends on the overall order of the reaction step. When the order of the reaction step is 0, 1, 2 or 3, the dimension of the rate coefficient is $\text{concentration} \times (\text{time})^{-1}$, $(\text{time})^{-1}$, $(\text{concentration})^{-1} \times (\text{time})^{-1}$ or $(\text{concentration})^{-2} \times (\text{time})^{-1}$, respectively.

2.1.2 Molecularity of an Elementary Reaction

The reaction steps in the mechanism of a homogeneous gas-phase reaction are usually *elementary reactions*, that is, the stoichiometric equation of the reaction step corresponds to real molecular changes. The molecularity of an elementary reaction is the number of **molecular entities** involved in the molecular encounter. Thus, an elementary reaction can be *unimolecular* or *bimolecular*. Some books on chemical kinetics also discuss termolecular reactions (Raj 2010), but three molecular entities colliding at the same time is highly improbable (Drake 2005). What are often referred to as termolecular reactions actually involve the formation of an energetically excited reaction intermediate in a bimolecular reaction which can then collide with a third molecular entity (e.g. a molecule or radical).

In a unimolecular reaction, only one reaction partner species is changed. Examples include photochemical reactions (e.g. $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$, where $h\nu$ represents a photon) and unimolecular decomposition such as the decomposition of fuel molecules in combustion or pyrolysis. In such reactions, the fuel molecule decomposes as a result of collision with another molecule that does not change chemically during the molecular event (e.g. $\text{C}_3\text{H}_8 + \text{N}_2 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_5 + \text{N}_2$). The rearrangement of a molecule such as the isomerisation of gas-phase molecules and the fluctuation of the structure of a protein from one conformation to another are also results of such so-called nonreactive collisions (Bamford et al. 1969).

Most elementary reactions are bimolecular, when two particles (molecules, radicals, ions) meet and both particles change chemically. Bimolecular reactions can be either direct bimolecular reactions (e.g. $\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}$) or complex-forming bimolecular reactions (e.g. $\text{O}_2 + \text{H} \rightarrow \text{HO}_2^*$ and $\text{HO}_2^* + \text{M} \rightarrow \text{HO}_2 + \text{M}$). In direct bimolecular reactions, the products are formed in a single step. The product of a complex-forming bimolecular reaction is a highly energised intermediate (in this case, a vibrationally excited HO_2 radical) that has to lose the excess energy in another collision with any other particle called a *third-body* M. This third body can be a molecule of the bath gas (in most experiments argon or nitrogen) or any other species of the reaction system. A more detailed description on how the reaction steps involving third bodies are treated is presented in Sect. 2.2.2.

In this section, we have discussed elementary reaction steps, but there are many reaction mechanisms where the reaction steps are not elementary reactions, but lumped reactions. This is very common, for example, in solution-phase kinetics and will be discussed in detail later.

The distinction between molecularity and order is an important one. It is therefore important that the terms unimolecular reaction and first-order reaction, and bimolecular reaction and second-order reaction are not synonyms. The first term refers to a type of molecular change whilst the second one to the type of applicable rate equation governed by the observed dependence of reaction rates on concentration.

2.1.3 Mass Action Kinetics and Chemical Rate Equations

The rates of elementary reactions can be calculated by assuming the rule of *mass action kinetics*. According to the chemical kinetic *law of mass action* (Waage and Guldberg 1864)

$$r_i = k_i \prod_j^{N_S} Y_j^{\nu_{ij}^L}, \quad (2.5)$$

where r_i and k_i are the rate and the rate coefficient, respectively, of reaction step i , and Y_j is the molar concentration of species j . Equation (2.5) looks similar to Eq. (2.3), but here the exponent is not an empirical value (the reaction order), but the corresponding stoichiometric coefficient. When the law of mass action is valid, the overall order of reaction step i is equal to $\sum_j \nu_{ij}^L$. In many cases, the law of mass

action is assumed to be also applicable for non-elementary reaction steps, but it is not always the case that a lumped reaction follows the law of mass action. Note that in textbooks of general chemistry, the term “law of mass action” is used in an entirely different context. In general chemistry, the law of mass action means that a chemical equilibrium can be shifted towards the products by adding reactants and towards the reactants by adding products to the reacting mixture.

The *kinetic system of ordinary differential equations (ODEs)* defines the relationship between the production rates of the species and rates of the reaction steps r_i :

$$\frac{dY_j}{dt} = \sum_i^{N_R} \nu_{ij} r_i; \quad j = 1, 2, \dots, N_S. \quad (2.6)$$

Equation (2.6) can also be written in a simpler form using the vector of concentrations \mathbf{Y} , the stoichiometric matrix $\boldsymbol{\nu}$ and the vector of the rates of reaction steps \mathbf{r} :

$$\frac{d\mathbf{Y}}{dt} = \boldsymbol{\nu}\mathbf{r}. \quad (2.7)$$

This means that the number of equations in the kinetic systems of ODEs is equal to the number of species in the reaction mechanism. These equations are coupled and therefore can only be solved simultaneously. It is also generally true that in order to accurately represent the time-dependent behaviour of a chemical system, the ODEs should be based on the chemical mechanism incorporating intermediate species and elementary reaction steps rather than the overall reaction equation which contains only reactants and products. We will see later in Chap. 7 that one aim of chemical mechanism reduction is to limit the number of required intermediates within the mechanism in order to reduce the number of ODEs required to accurately represent the time-dependent behaviour of key species.

An analogous equation to Eq. (2.6) can be written when other concentration units are used, e.g. mass fractions or mole fractions [see, e.g. Warnatz et al. (2006)], but Eq. (2.5) is applicable only when the “amount of matter divided by volume” concentration units are used. The amount of matter can be defined, e.g., in moles or molecules, whilst volume is usually defined in dm^3 or cm^3 units.

In adiabatic systems or in systems with a known heat loss rate, usually temperature is added as the $(N_S + 1)$ th variable of the kinetic system of ODEs. The differential equation for the rate of change of temperature in a closed spatially homogeneous reaction vessel is given as

$$C_p \frac{dT}{dt} = \sum_{i=1}^{N_R} \Delta_r H_i^\ominus r_i - \frac{\chi S}{V} (T - T_0), \quad (2.8)$$

where T is the actual temperature of the system, T_0 is the ambient temperature (e.g. the temperature of the lab), C_p is the constant pressure heat capacity of the mixture, $\Delta_r H_i^\ominus$ is the standard molar reaction enthalpy of reaction step i , S and V are the surface and the volume of the system, respectively, and χ is the heat transfer coefficient between the system and its surroundings. The change in temperature can be calculated together with the change in concentrations as part of the coupled ODE system. In the examples used throughout the book, the variables of the kinetic differential equations will be species concentrations only, but in all cases, the ODE can be easily extended to include the equation for temperature.

The kinetic system of ODEs and its initial values together provide the following initial value problem:

$$\frac{d\mathbf{Y}}{dt} = \mathbf{f}(\mathbf{Y}, \mathbf{k}), \quad \mathbf{Y}(t_0) = \mathbf{Y}_0. \quad (2.9)$$

From a mathematical point of view, the kinetic system of ODEs is first-order and usually nonlinear, since it contains first-order derivatives with respect to time and the time derivative is usually a nonlinear function of concentrations. In general,

each species participates in several reactions; therefore, the production rates of the species are coupled. The rates of the reaction steps can be very different and may span many (even 10–25) orders of magnitude. Such differential equations are called stiff ODEs. The stiffness of the kinetic ODEs and related problems will be discussed in detail in Sect. 6.7.

In theory, if a laboratory experiment is repeated say one hour later than the first execution, then the same concentration–time curves should be obtained (ignoring experimental error for now). Accordingly, the time in the kinetic system of differential equations is not the wall-clock time, but a relative time from the beginning of the experiment. Such a differential equation system is called an *autonomous system of ODEs*. In other cases, such as in atmospheric chemical or biological circadian rhythm models, the actual physical time is important, because a part of the parameters (the rate coefficients belonging to the photochemical reactions) depend on the strength of sunshine, which is a function of the absolute time. In this case, the kinetic system of ODEs is *nonautonomous*.

Great efforts are needed even in a laboratory to achieve a homogeneous spatial distribution of the concentrations, temperature and pressure of a system, even in a small volume (a few mm³ or cm³). Outside the confines of the laboratory, chemical processes always occur under spatially inhomogeneous conditions, where the spatial distribution of the concentrations and temperature is not uniform, and transport processes also have to be taken into account. Therefore, reaction kinetic simulations frequently include the solution of partial differential equations that describe the effect of chemical reactions, material diffusion, thermal diffusion, convection and possibly turbulence. In these partial differential equations, the term \mathbf{f} defined on the right-hand side of Eq. (2.9) is the so-called chemical source term. In the remainder of the book, we deal mainly with the analysis of this chemical source term rather than the full system of model equations.

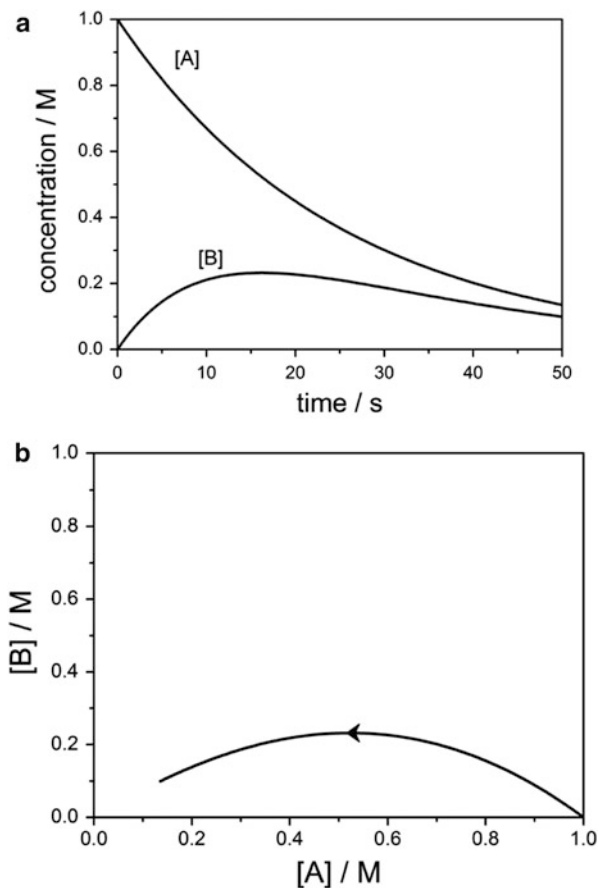
In the following chapters, the Jacobian matrix

$$\mathbf{J} = \frac{\partial \mathbf{f}(\mathbf{Y}, \mathbf{k})}{\partial \mathbf{Y}} = \left\{ \frac{\partial f_i}{\partial Y_j} \right\} \quad (2.10)$$

will be frequently used. It can be of great use in the mechanism reduction process, forming the basis of local sensitivity analysis of each species in the mechanism, as discussed in Chap. 5. It will also prove useful in the analysis of timescales present in the kinetic system which may form a further basis for model reduction (see Chap. 6). If the reaction mechanism consists of zeroth-order and first-order reaction steps only, then the elements of the Jacobian are constant real numbers. In all other cases, the elements of the Jacobian depend on the concentration vector \mathbf{Y} . The normalised form of the Jacobian $\tilde{\mathbf{J}} = \left\{ \frac{Y_j}{f_i} \frac{\partial f_i}{\partial Y_j} \right\}$ is also frequently used.

The elements of matrix $\mathbf{F} = \frac{\partial \mathbf{f}(\mathbf{Y}, \mathbf{k})}{\partial \mathbf{k}} = \left\{ \frac{\partial f_i}{\partial k_j} \right\}$ contain the derivative of the right-hand side of the ODE with respect to the parameters. This matrix can also be used in a normalised form: $\tilde{\mathbf{F}} = \left\{ \frac{k_j}{f_i} \frac{\partial f_i}{\partial k_j} \right\}$.

Fig. 2.1 Results of the simulation of the reaction system $A \rightarrow B \rightarrow C$ (a) concentration–time curves; (b) trajectory in the space of concentrations



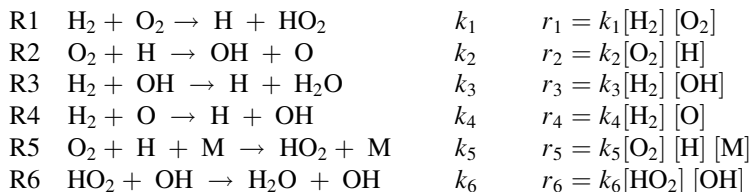
The solution of the initial value problem described by Eq. (2.9) can be visualised so that the calculated concentrations are plotted as a function of time as shown in Fig. 2.1a. Another possibility is to explore the solution in the space of concentrations as in Fig. 2.1b. In this case, the axes are the concentrations and the time dependence is not indicated. The actual concentration set is a point in the space of concentrations. The movement of this point during the simulation outlines a curve in the space of concentrations, which is called the *trajectory* of the solution. This type of visualisation is often referred to as visualisation in *phase space*. In a closed system, the trajectory starts from the point that corresponds to the initial value and after a long time ends up at the equilibrium point. In an open system where the reactants are continuously fed into the system and the products are continuously removed, the trajectory may end up at a stationary point, approach a closed curve (a limit cycle in an oscillating system) or follow a strange attractor in a chaotic system. It is not the purpose of this book to discuss dynamical systems analysis of chemical models in detail, and the reader is referred to the book of Scott for an excellent treatment of this topic (Scott 1990).

If the mechanism consists of only first-order reaction steps, then the kinetic system of ODEs always has a solution which can be expressed in the form of mathematical functions (Rodiguin and Rodiguina 1964). Such a solution is called *analytical* in science and engineering and *symbolic* in the literature of mathematics and computer science. The analytical solution of small reaction mechanisms, consisting of mixed first-order and second-order steps, can also be found in the chapter of Szabó (1969) and the reaction kinetics chapter of Atkins' Physical Chemistry textbook (Atkins and de Paula 2009). However, in most practical cases, for larger coupled kinetic systems, finding analytical solutions is not possible without seeking simplifications of the chemistry representation. In most cases therefore, numerical solutions of the kinetic differential equations (2.9) are sought.

Reaction kinetic models can be simulated not only on a deterministic basis by solving the kinetic system of differential equations but also via the simulation of stochastic models (Érdi et al. 1973; Bunker et al. 1974; Érdi and Tóth 1976; Gillespie 1976, 1977; Tóth and Érdi 1978; Kraft and Wagner 2003; Gillespie 2007; Li et al. 2008; Tomlin et al. 1994). If the system contains many molecules, then the two solutions usually (but not always) provide identical solutions (Kurtz 1972). If the system contains few molecules, which frequently occurs in biological systems, then the stochastic solution can be qualitatively different from the deterministic one (Arányi and Tóth 1977). Stochastic chemical kinetic modelling is discussed in detail in a recent monograph (Érdi and Lente 2014).

2.1.4 Examples

The first example for the creation of the kinetic system of ODEs will be based on a skeleton hydrogen combustion mechanism. Using the law of mass action, the rates r_1 to r_6 of the reaction steps can be calculated from the species concentrations and rate coefficients



Here [M] is the sum of the concentrations of all species present. The species that are jointly denoted by M may have a different effective concentration than their actual physical concentration based on how effective their collisions are in making reaction R5 proceed (see Sect. 2.2.2).

The calculation of the production rates is based on Eq. (2.6). For example, the hydrogen atom H is produced in reaction steps 1, 3 and 4 ($\nu = +1$), it is consumed in reaction steps 2 and 5 ($\nu = -1$), and it is not present in reaction step 6 ($\nu = 0$). The

line of the kinetic system of ODEs, corresponding to the production of H is the following:

$$\frac{d[H]}{dt} = +1r_1 - 1r_2 + r_3 + 1r_4 - 1r_5 + 0r_6,$$

or

$$\frac{d[H]}{dt} = k_1[H_2][O_2] - k_2[O_2][H] + k_3[H_2][OH] + k_4[H_2][O] - k_5[O_2][H][M].$$

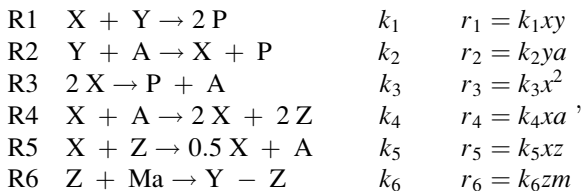
In a similar way, the production of water can be described by the following equations:

$$\frac{d[H_2O]}{dt} = +1r_3 + 1r_6,$$

or

$$\frac{d[H_2O]}{dt} = k_3[H_2][OH] + k_6[HO_2][OH].$$

Let us now consider a more complex mechanism, where the stoichiometric coefficients are not only -1 , 0 or $+1$. Whilst the hydrogen oxidation example is very simple, the next example contains all possible complications. We now illustrate the formulation of the kinetic ODEs and their related matrices on an example based on the well-known Belousov–Zhabotinskii (BZ) reaction. The BZ reaction has been highly studied as an example of non-equilibrium thermodynamics where a nonlinear chemical oscillator can easily be established in a simple reaction vessel and illustrated by a simple colour change. The starting mixture consists of potassium bromate, malonic acid and a cerium (IV) salt in an acidic solution. A simplified mechanism of the BZ oscillating reaction (Belousov 1959; Zhabotinsky 1964; Belousov 1985) was elaborated by Field et al. (1972). The Oregonator model (Field and Noyes 1974) was based on this mechanism. A newer version (Turányi et al. 1993) of the reaction steps within the Oregonator model is the following:



where X, Y, Z, A, P and Ma indicate species $HBrO_2$, Br^- , Ce^{4+} , BrO_3^- , $HOBr$ and malonic acid, respectively. The corresponding small italic letter denotes the molar

concentration of the species and k_1, \dots, k_6 the rate coefficients of the reaction steps. The rates of the reaction steps (r_1, \dots, r_6) can be calculated using the kinetic law of mass action [Eq. (2.5)] even though not all reactions in this reduced scheme could be classified as elementary reaction steps. Note, for example, that reactions 5 and 6 do not contain positive whole integers as stoichiometric coefficients on the right-hand side. The concentrations of species BrO_3^- (A) and malonic acid (Ma) are much higher than those of the others, and these concentrations are practically constant (this is termed the pool chemical approximation, and it is detailed in Sect. 2.3.1). Note that HOBr (P) is considered as a nonreactive product.

In the models of formal reaction kinetics, a species is called an *internal species* if its concentration change is important for the simulation of the reaction system. These species are denoted by letters from the end of the Latin alphabet (X, Y, Z). The concentrations of the *external species* are either constant or change slowly in time (A and Ma) (pool chemical) or have no effect on the concentrations of the other species (P).

According to this model, the rates of change of the concentrations of HBrO_2 (X), Br^- (Y) and Ce^{4+} (Z) in a well-mixed closed vessel are described by the following system of ODEs:

$$\begin{aligned}\frac{dx}{dt} &= -1r_1 + 1r_2 - 2r_3 + 1r_4 - 0.5r_5, \\ \frac{dy}{dt} &= -1r_1 - 1r_2 + 1r_6, \\ \frac{dz}{dt} &= +2r_4 - 1r_5 - 2r_6.\end{aligned}$$

In each equation, on the right-hand side in each term, the rate of the reaction step is multiplied by the change in the number of moles in the corresponding chemical equation. For example, one mole of species X is consumed in reaction step 1 (therefore, the change in the number of moles is -1); in reaction step 2, one mole of X is produced ($+1$); and in step 3, two moles are consumed (-2). In reaction step 4, one mole of X is consumed and two moles are produced; therefore, the change in the number of moles is $+1$.

Inserting the terms for the reaction rates $r_1 - r_6$ into the equations above gives

$$\begin{aligned}\frac{dx}{dt} &= -k_1xy + k_2ya - 2k_3x^2 + k_4xa - 0.5k_5xz, \\ \frac{dy}{dt} &= -k_1xy - k_2ya + k_6zm, \\ \frac{dz}{dt} &= 2k_4xa - k_5xz - 2k_6zm.\end{aligned}$$

Some remarks should be made concerning the equations above. Species concentration c_i has to be present in all negative terms on the right-hand side of the

equation dc_i/dt . A negative term without concentration c_i is called a *negative cross effect* (Érdi and Tóth 1989). A first-order ordinary system of differential equations with polynomial right-hand side can be related to a reaction mechanism if and only if it does not contain a negative cross-effect term. When the reaction step is obtained by lumping from several elementary reaction steps, then the same species may appear on both sides of the chemical equations (see reaction steps 4, 5 and 6). For the calculation of the rates of the reaction steps using the kinetic law of mass action [see Eq. (2.5)], only the left-hand side stoichiometric coefficients have to be considered. However, for the construction of the kinetic system of ODEs [Eq. (2.6)], the difference between the right- and left-hand side stoichiometric coefficients, that is, the change of the number of moles in the reaction step, has to be taken into account. The left-hand side stoichiometric coefficients v_j^B are always positive integers, whilst the kinetic system of ODEs can still be easily constructed if the right-hand side stoichiometric coefficients v_j^I are arbitrary real numbers, i.e. these can be negative numbers or fractions. Such reaction steps can be obtained by lumping several elementary reaction steps. The topic of lumping will be discussed in detail in Sect. 7.7. Furthermore, since the pool chemical approximation has been invoked for the concentration of species Ma, the rate of reaction 6 becomes a *pseudo-first-order* reaction since m is in fact constant.

Let us determine the matrices \mathbf{J} and \mathbf{F} belonging to the kinetic system of ODEs above. These two types of matrices will be used several dozen times in the following chapters. For example, the Jacobian is used within the solution of stiff differential equations (Sect. 6.7), the calculation of local sensitivities (Sect. 5.2) and in timescale analysis (Sect. 6.2), whilst matrix \mathbf{F} is used for the calculation of local sensitivities (Sect. 5.2). Carrying out the appropriate derivations, the following matrices are obtained:

$$\mathbf{J} = \begin{pmatrix} \frac{\partial \frac{dx}{dt}}{\partial x} & \frac{\partial \frac{dx}{dt}}{\partial y} & \frac{\partial \frac{dx}{dt}}{\partial z} \\ \frac{\partial \frac{dy}{dt}}{\partial x} & \frac{\partial \frac{dy}{dt}}{\partial y} & \frac{\partial \frac{dy}{dt}}{\partial z} \\ \frac{\partial \frac{dz}{dt}}{\partial x} & \frac{\partial \frac{dz}{dt}}{\partial y} & \frac{\partial \frac{dz}{dt}}{\partial z} \end{pmatrix} = \begin{pmatrix} -k_1y - 4k_3x + k_4a - 0.5k_5z & -k_1x + k_2a & -0.5k_5x \\ & -k_1y & -k_1x - k_2a & k_6m \\ & 2k_4a - k_5z & 0 & -k_5x - 2k_6m \end{pmatrix},$$

$$\mathbf{F} = \begin{pmatrix} \frac{\partial \frac{dx}{dt}}{\partial k_1} & \frac{\partial \frac{dx}{dt}}{\partial k_2} & \frac{\partial \frac{dx}{dt}}{\partial k_3} & \frac{\partial \frac{dx}{dt}}{\partial k_4} & \frac{\partial \frac{dx}{dt}}{\partial k_5} & \frac{\partial \frac{dx}{dt}}{\partial k_6} \\ \frac{\partial \frac{dy}{dt}}{\partial k_1} & \frac{\partial \frac{dy}{dt}}{\partial k_2} & \frac{\partial \frac{dy}{dt}}{\partial k_3} & \frac{\partial \frac{dy}{dt}}{\partial k_4} & \frac{\partial \frac{dy}{dt}}{\partial k_5} & \frac{\partial \frac{dy}{dt}}{\partial k_6} \\ \frac{\partial \frac{dz}{dt}}{\partial k_1} & \frac{\partial \frac{dz}{dt}}{\partial k_2} & \frac{\partial \frac{dz}{dt}}{\partial k_3} & \frac{\partial \frac{dz}{dt}}{\partial k_4} & \frac{\partial \frac{dz}{dt}}{\partial k_5} & \frac{\partial \frac{dz}{dt}}{\partial k_6} \\ -xy & ya & -2x^2 & xa & -0.5xz & 0 \\ -xy & -ya & 0 & 0 & 0 & zm \\ 0 & 0 & 0 & 2xa & -xz & -2zm \end{pmatrix}.$$

The examples above indicate some further rules. The main diagonal of the Jacobian contains mainly negative numbers. An element of the main diagonal of the Jacobian can be positive only if the corresponding reaction is a single-step autocatalytic reaction, like $A + X \rightarrow B + 2 X$ (*cf.* reaction step R4 above). Matrix \mathbf{F} is in general a sparse matrix, since most of its elements are zero. The elements of \mathbf{F} that are nonzero can be obtained from the expressions for the reaction rates r_1, \dots, r_6 in a way that multiplication of the appropriate rate coefficient k is omitted.

2.2 Parameterising Rate Coefficients

2.2.1 Temperature Dependence of Rate Coefficients

An important part of specifying a chemical reaction mechanism is providing accurate parameterisations of the rate coefficients. In liquid phase and in atmospheric kinetics, the temperature dependence of rate coefficient k is usually described by the *Arrhenius equation*:

$$k = A \exp(-E/RT) \quad (2.11)$$

where A is the pre-exponential factor or A -factor, E is the activation energy, R is the gas constant and T is temperature. The dimension of quantity E/R is temperature, and therefore, E/R is called the *activation temperature*. This equation is also referred to as the “classic” or “original” Arrhenius equation. If the temperature dependence of the rate coefficient can be described by the original Arrhenius equation, then plotting $\ln(k)$ as a function of $1/T$ (*Arrhenius plot*) gives a straight line. The slope of this line is $-E/R$, and the intercept is $\ln(A)$. Figure 2.2a shows such an Arrhenius plot.

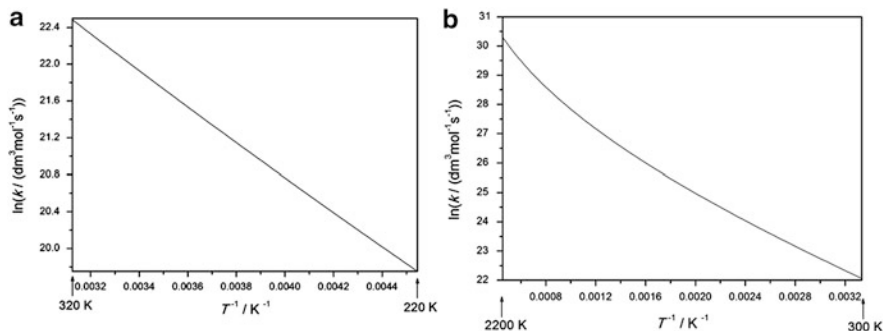


Fig. 2.2 Arrhenius plot of the temperature dependence of the rate coefficient of reaction $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$. (a) Temperature range 220 K to 320 K; (b) temperature range 300 K to 2,200 K

In high-temperature gas-phase kinetic systems, such as combustion and pyrolytic systems, the temperature dependence of the rate coefficient is usually described by the *modified Arrhenius equation*:

$$k = AT^n \exp(-E/RT). \quad (2.12)$$

This equation is also called the *extended Arrhenius equation*. An alternative notation is $k = BT^n \exp(-C/RT)$, which emphasises that the physical meaning of parameters B and C is not equal to the pre-exponential factor and activation energy, respectively. If the temperature dependence of a rate coefficient can only be described by a modified Arrhenius equation and not in the classic form, then a curved line is obtained in an Arrhenius plot (see Fig. 2.2b).

If the temperature dependence of the rate coefficient is described by the modified Arrhenius equation, then the activation energy changes with temperature. The activation energy at a given temperature can be calculated from the slope of the curve, i.e. the derivative of the temperature function with respect to $1/T$. If the temperature dependence is defined using the equation $k = BT^n \exp(-C/RT)$, then the temperature dependent activation energy is given by

$$\begin{aligned} E_a(T) &= -R \left(\frac{d \ln\{k\}}{d(1/T)} \right) = -R \left(\frac{d(\ln\{B\} + n \ln\{T\} - C/RT)}{d(1/T)} \right) \\ &= -R \left(\frac{d \left(\ln\{B\} - n \ln \left\{ \frac{1}{T} \right\} - C/RT \right)}{d(1/T)} \right) = nRT + C. \end{aligned} \quad (2.13)$$

For some gas-phase kinetic elementary reactions, the temperature dependence of the rate coefficient is described by the power function $k = AT^n$. This can also be

considered as a truncated form of the extended Arrhenius equation. Another type of unusual temperature dependence is when there are two different routes from the reactants to the products; therefore, the temperature dependence of the reaction step in a wide temperature range is described by the sum of two Arrhenius expressions: $k = A_1 T^{n_1} \exp(-E_1/RT) + A_2 T^{n_2} \exp(-E_2/RT)$. An example is the case of reaction $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$ (Burke et al. 2013).

Reaction $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ is the major consumption reaction of methane in the troposphere, where the typical temperature extremes are 220 K (-53°C) and 320 K ($+47^\circ\text{C}$). In this 100 K temperature range, the temperature dependence of the rate coefficient can be described accurately with a 2-parameter Arrhenius equation as shown in Fig. 2.2a. The same reaction is important in methane flames, where this reaction is one of the main consuming reactions of the fuel molecules. In a methane flame, the temperature is changing between 300 K (room temperature or laboratory temperature) and 2,200 K, which is the typical maximum temperature of a laminar premixed methane–air flame. When representing the temperature dependence of the rate coefficient within this wide temperature range in an Arrhenius plot, the obtained function is clearly curved (see Fig. 2.2b). This example shows that the temperature dependence of the same rate coefficient can be well described by the original Arrhenius expression within a narrow (less than 100 K) temperature range, but only with the extended Arrhenius expression within a wide (several hundred Kelvin) temperature range. However, the temperature dependence of some rate coefficients can be characterised by the original Arrhenius equation within a very wide temperature range. One example is the reaction $\text{I} + \text{H}_2 \rightarrow \text{HI} + \text{H}$, where the experimentally determined rate coefficients could be fitted using the original Arrhenius equation over the temperature range 230 K to 2,605 K, even though the rate coefficient changed by about 30 orders of magnitude (Michael et al. 2000).

2.2.2 Pressure Dependence of Rate Coefficients

The rate coefficients of thermal decomposition or isomerisation reactions of several small organic molecules have been found to be pressure dependent at a given temperature. A model reaction was the isomerisation of cyclopropane yielding propene. The rate coefficient of the reaction was found to be first-order and pressure independent at high pressures whilst second-order and linearly dependent on pressure at low pressures. These types of observations were interpreted by Lindemann et al. (1922) and Hinshelwood by assuming that the molecules of cyclopropane (C) are colliding with any of the other molecules present in the system (*third body*, denoted by M) producing rovibrationally excited cyclopropane molecules (C^*). These molecules can then isomerise (transform into another molecule with the same atoms but with a different arrangement) yielding propene (P), or further collisions may convert the excited cyclopropane molecules back to non-excited ones: $\text{C} + \text{M} \rightleftharpoons \text{C}^* + \text{M}$ and $\text{C}^* \rightarrow \text{P}$. This model allowed the interpretation of changing order with pressure (Pilling and Seakins 1995). Later research