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.

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

$$2H_2 + O_2 = 2H_2O.$$

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:

$$0 = -2H_2 - 1\,O_2 + 2H_2O.$$

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 $\boldsymbol{\nu} = (\nu_1, \nu_2, \nu_3)$. In this case, $A_1 =$ "H_2", $A_2 =$ "O_2", $A_3 =$ "H_2O" and $\nu_1 = -2$, $\nu_2 = -1$, $\nu_3 = +2$. The corresponding general stoichiometric equation is

$$0 = \sum_{j=1}^{N_S} \nu_j A_j, \tag{2.1}$$

where N_S is the number of species. The general stoichiometric equation of any chemical process can be defined in a similar way, where ν_j is the *stoichiometric coefficient* of the jth species and A_j is the formula of the jth 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 $0 = -2H_2 - 1O_2 + 2H_2O$ and $0 = -1H_2 - ½\ O_2 + 1H_2O$ (or using the traditional notation, $2H_2 + O_2 = 2H_2O$ and $H_2 + ½O_2 = H_2O$, 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 jth species is measured at several consecutive time points, then by applying a finite-difference approach, the *production rate* of the jth species $\mathrm{d}Y_j/\mathrm{d}t$ can be calculated. The rate of a chemical reaction defined by stoichiometric equation (2.1) is the following:

$$r = \frac{1}{\nu_j}\frac{\mathrm{d}Y_j}{\mathrm{d}t}. \tag{2.2}$$

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:

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

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 $\left(\alpha = \sum_{j=1}^{N_\mathrm{S}} \alpha_j\right)$ is called the *overall order of the reaction*. In the case of an overall reaction equation such as $2\mathrm{H}_2 + \mathrm{O}_2 = 2\mathrm{H}_2\mathrm{O}$, the order α_j is usually not equal to the stoichiometric coefficient ν_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:

$$
\begin{array}{lcl}
\mathrm{R1} & \mathrm{H_2 + O_2 = H + HO_2} & k_1 \\
\mathrm{R2} & \mathrm{O_2 + H = OH + O} & k_2 \\
\mathrm{R3} & \mathrm{H_2 + OH = H + H_2O} & k_3 \\
\mathrm{R4} & \mathrm{H_2 + O = H + OH} & k_4\,{}^{\prime} \\
\mathrm{R5} & \mathrm{O_2 + H + M = HO_2 + M} & k_5 \\
\mathrm{R6} & \mathrm{HO_2 + OH = H_2O + OH} & k_6
\end{array}
$$

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:

$$\sum_j v_{ij}^L \mathrm{A}_j = \sum_j v_{ij}^R \mathrm{A}_j, \tag{2.4}$$

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 $\mathrm{A} \rightarrow \mathrm{B}$). Reversible reactions will be denoted by double arrows (like $\mathrm{A} \rightleftarrows \mathrm{B}$).

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 concentration × $(\text{time})^{-1}$, $(\text{time})^{-1}$, $(\text{concentration})^{-1} \times (\text{time})^{-1}$ 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. $NO_2 + h\nu \rightarrow NO + O$, 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. $C_3H_8 + N_2 \rightarrow CH_3 + C_2H_5 + N_2$). 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. $H_2 + OH \rightarrow H + H_2O$) or complex-forming bimolecular reactions (e.g. $O_2 + H \rightarrow HO_2{}^*$ and $HO_2{}^* + M \rightarrow HO_2 + M$). 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)

$$r_i = k_i \prod_{j}^{N_\mathrm{S}} Y_j^{\nu_{ij}^L}, \tag{2.5}$$

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:

$$\frac{\mathrm{d}Y_j}{\mathrm{d}t} = \sum_{i}^{N_\mathrm{R}} \nu_{ij} r_i; \quad j = 1, 2, \ldots, N_\mathrm{S}. \tag{2.6}$$

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 $\mathbf{r}$:

$$\frac{\mathrm{d}\mathbf{Y}}{\mathrm{d}t} = \boldsymbol{\nu}\mathbf{r}. \tag{2.7}$$

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 $(N_\mathrm{S}+1)$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

$$C_\mathrm{p}\frac{\mathrm{d}T}{\mathrm{d}t} = \sum_{i=1}^{N_R} \Delta_\mathrm{r} H_i^{\ominus} r_i - \frac{\chi S}{V}(T - T_0), \tag{2.8}$$

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, $\Delta_\mathrm{r} H_i^{\ominus}$ 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:

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

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* ODE*s*. 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 mm^3 or cm^3). 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 **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

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

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 **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: $\tilde{\mathbf{F}} = \left\{ \frac{k_j}{f_i} \frac{\partial f_i}{\partial k_j} \right\}$.

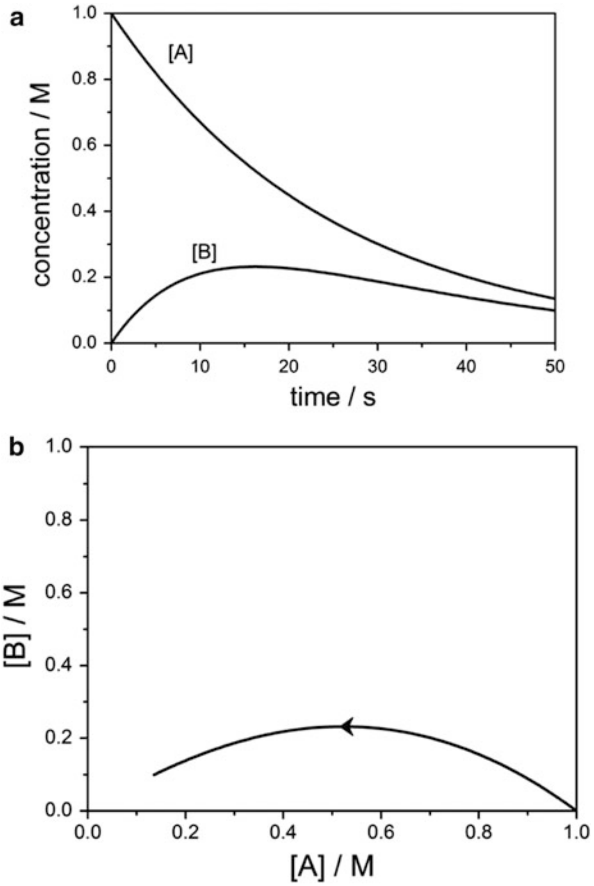


Fig. 2.1 Results of the simulation of the reaction system A → B → C (**a**) concentration–time curves; (**b**) trajectory in the space of concentrations

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

R1	$H_2 + O_2 \rightarrow H + HO_2$	k_1	$r_1 = k_1[H_2]\,[O_2]$
R2	$O_2 + H \rightarrow OH + O$	k_2	$r_2 = k_2[O_2]\,[H]$
R3	$H_2 + OH \rightarrow H + H_2O$	k_3	$r_3 = k_3[H_2]\,[OH]$
R4	$H_2 + O \rightarrow H + OH$	k_4	$r_4 = k_4[H_2]\,[O]$
R5	$O_2 + H + M \rightarrow HO_2 + M$	k_5	$r_5 = k_5[O_2]\,[H]\,[M]$
R6	$HO_2 + OH \rightarrow H_2O + OH$	k_6	$r_6 = k_6[HO_2]\,[OH]$

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:

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

or

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

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

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

or

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

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:

R1	$\mathrm{X + Y \rightarrow 2\,P}$	k_1	$r_1 = k_1xy$
R2	$\mathrm{Y + A \rightarrow X + P}$	k_2	$r_2 = k_2ya$
R3	$\mathrm{2\,X \rightarrow P + A}$	k_3	$r_3 = k_3x^2$
R4	$\mathrm{X + A \rightarrow 2\,X + 2\,Z}$	k_4	$r_4 = k_4xa$,
R5	$\mathrm{X + Z \rightarrow 0.5\,X + A}$	k_5	$r_5 = k_5xz$
R6	$\mathrm{Z + Ma \rightarrow Y - Z}$	k_6	$r_6 = k_6zm$

where X, Y, Z, A, P and Ma indicate species $\mathrm{HBrO_2}$, $\mathrm{Br^-}$, $\mathrm{Ce^{4+}}$, $\mathrm{BrO_3}^-$, HOBr and malonic acid, respectively. The corresponding small italic letter denotes the molar concentration of the species and $k_1,\ldots, k_6$ the rate coefficients of the reaction steps. The rates of the reaction steps ($r_1,\ldots,r_6$) 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:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -1r_1 + 1r_2 - 2r_3 + 1r_4 - 0.5r_5,$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = -1r_1 - 1r_2 + 1r_6,$$

$$\frac{\mathrm{d}z}{\mathrm{d}t} = +2r_4 - 1r_5 - 2r_6.$$

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

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -k_1xy + k_2ya - 2k_3x^2 + k_4xa - 0.5k_5xz,$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = -k_1xy - k_2ya + k_6zm,$$

$$\frac{\mathrm{d}z}{\mathrm{d}t} = 2k_4xa - k_5xz - 2k_6zm.$$

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 $\mathrm{d}c_i/\mathrm{d}t$. 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 ν_j^B are always positive integers, whilst the kinetic system of ODEs can still be easily constructed if the right-hand side stoichiometric coefficients ν_j^J 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 **J** and **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 **F** is used for the calculation of local sensitivities (Sect. 5.2). Carrying out the appropriate derivations, the following matrices are obtained:

$$\mathbf{J} = \left\{ \begin{array}{ccc} \frac{\partial \frac{dx}{dt}}{\partial x} & \frac{\partial \frac{dx}{dt}}{\partial y} & \frac{\partial \frac{dx}{dt}}{\partial z} \\ \frac{\partial \frac{dy}{dt}}{\partial x} & \frac{\partial \frac{dy}{dt}}{\partial y} & \frac{\partial \frac{dy}{dt}}{\partial z} \\ \frac{\partial \frac{dz}{dt}}{\partial x} & \frac{\partial \frac{dz}{dt}}{\partial y} & \frac{\partial \frac{dz}{dt}}{\partial z} \end{array} \right\}$$

$$= \left\{ \begin{array}{ccc} -k_1 y - 4k_3 x + k_4 a - 0.5k_5 z & -k_1 x + k_2 a & -0.5k_5 x \\ -k_1 y & -k_1 x - k_2 a & k_6 m \\ 2k_4 a - k_5 z & 0 & -k_5 x - 2k_6 m \end{array} \right\},$$

$$\mathbf{F} = \left\{ \begin{matrix} \dfrac{\partial \frac{\mathrm{d}x}{\mathrm{d}t}}{\partial k_1} & \dfrac{\partial \frac{\mathrm{d}x}{\mathrm{d}t}}{\partial k_2} & \dfrac{\partial \frac{\mathrm{d}x}{\mathrm{d}t}}{\partial k_3} & \dfrac{\partial \frac{\mathrm{d}x}{\mathrm{d}t}}{\partial k_4} & \dfrac{\partial \frac{\mathrm{d}x}{\mathrm{d}t}}{\partial k_5} & \dfrac{\partial \frac{\mathrm{d}x}{\mathrm{d}t}}{\partial k_6} \\ \dfrac{\partial \frac{\mathrm{d}y}{\mathrm{d}t}}{\partial k_1} & \dfrac{\partial \frac{\mathrm{d}y}{\mathrm{d}t}}{\partial k_2} & \dfrac{\partial \frac{\mathrm{d}y}{\mathrm{d}t}}{\partial k_3} & \dfrac{\partial \frac{\mathrm{d}y}{\mathrm{d}t}}{\partial k_4} & \dfrac{\partial \frac{\mathrm{d}y}{\mathrm{d}t}}{\partial k_5} & \dfrac{\partial \frac{\mathrm{d}y}{\mathrm{d}t}}{\partial k_6} \\ \dfrac{\partial \frac{\mathrm{d}z}{\mathrm{d}t}}{\partial k_1} & \dfrac{\partial \frac{\mathrm{d}z}{\mathrm{d}t}}{\partial k_2} & \dfrac{\partial \frac{\mathrm{d}z}{\mathrm{d}t}}{\partial k_3} & \dfrac{\partial \frac{\mathrm{d}z}{\mathrm{d}t}}{\partial k_4} & \dfrac{\partial \frac{\mathrm{d}z}{\mathrm{d}t}}{\partial k_5} & \dfrac{\partial \frac{\mathrm{d}z}{\mathrm{d}t}}{\partial k_6} \end{matrix} \right\}$$

$$= \left\{ \begin{matrix} -xy & ya & -2x^2 & xa & -0.5xz & 0 \\ -xy & -ya & 0 & 0 & 0 & zm \\ 0 & 0 & 0 & 2xa & -xz & -2zm \end{matrix} \right\}.$$

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 $\mathrm{A} + \mathrm{X} \rightarrow \mathrm{B} + 2\ \mathrm{X}$ (*cf.* reaction step R4 above). Matrix **F** is in general a sparse matrix, since most of its elements are zero. The elements of **F** that are nonzero can be obtained from the expressions for the reaction rates $r_1, \ldots,$ 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:*

$$k = A \exp(-E/RT) \tag{2.11}$$

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.

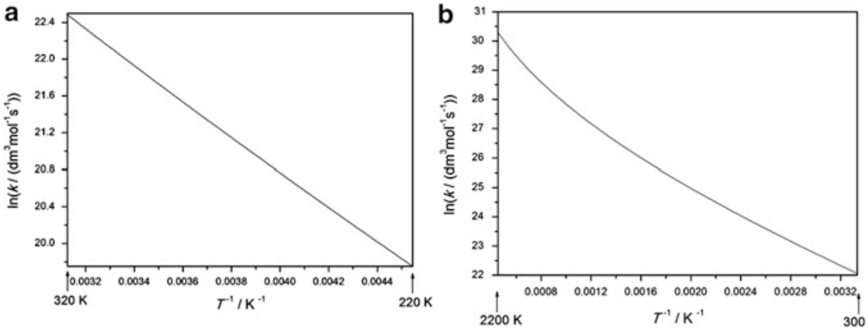


Fig. 2.2 Arrhenius plot of the temperature dependence of the rate coefficient of reaction $CH_4 + OH \rightarrow CH_3 + H_2O$. (**a**) Temperature range 220 K to 320 K; (**b**) temperature range 300 K to 2,200 K

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:*

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

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

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

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 $HO_2 + OH = H_2O + O_2$ (Burke et al. 2013).

Reaction $CH_4 + OH \rightarrow CH_3 + H_2O$ is the major consumption reaction of methane in the troposphere, where the typical temperature extremes are 220 K (−53 °C) and 320 K (+47 °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 $I + H_2 \rightarrow HI + H$, 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: $C + M \rightleftarrows C^* + M$ and $C^* \rightarrow P$. This model allowed the interpretation of changing order with pressure (Pilling and Seakins 1995). Later research confirmed that the basic idea was correct. However, it was shown that the collisions create excited reactant species having a wide range of rovibrational energies. The cyclopropane molecules can move up and down on an energy ladder, and the rate coefficient of isomerisation depends on the energy of the excited reactant.

The isomerisation of cyclopropane has limited practical importance, but the pressure-dependent decomposition or isomerisation of many molecules and radicals proved to be very important in combustion and atmospheric chemistry. In these elementary reactions, only a single species undergoes chemical transformation, and therefore, these are called *unimolecular reactions*. For example, the decomposition of H_2O_2 is a very important reaction for the combustion of hydrogen, syngas and hydrocarbons. Due to collisions with any species present in the mixture, the rovibrational energy level of the H_2O_2 molecule can move up and down on the energy ladder (see Fig. 2.3a). Molecules having an energy level higher than a threshold can decompose to the OH radical and the rate of decomposition is energy dependent.

At intermediate pressures, the reaction rate of unimolecular reactions is neither second-order nor first-order. The apparent first-order rate coefficient in this pressure region (*fall-off region*) can be calculated using the *Lindemann approach* (Gilbert et al. 1983; Pilling and Seakins 1995; Atkins and de Paula 2009). Arrhenius rate parameters are required for both the low- and high-pressure limiting cases, and the Lindemann formulation blends them to produce a pressure-dependent rate expression. The low-pressure rate coefficient is given by the expression:

$$k_0 = A_0 T^{n_0} \exp\left(\frac{-E_0}{RT}\right) \tag{2.14}$$

and the high-pressure rate coefficient by the expression:

$$k_\infty = A_\infty T^{n_\infty} \exp\left(\frac{-E_\infty}{RT}\right). \tag{2.15}$$

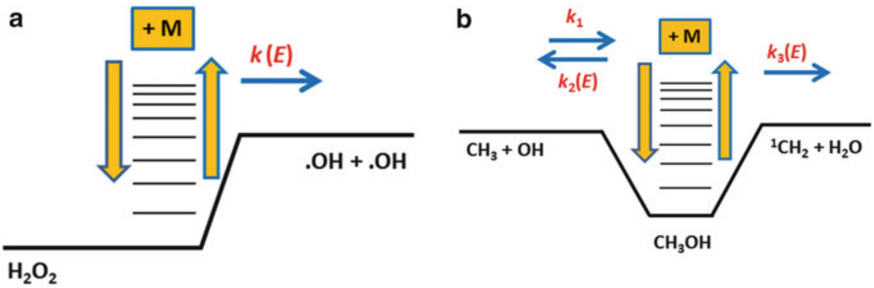


Fig. 2.3 Schematic energy diagram of two reaction systems: (**a**) $H_2O_2 \rightleftarrows 2OH$; (**b**) $CH_3 + OH \rightleftarrows CH_3OH$ and $CH_3 + OH \rightleftarrows {}^1CH_2 + H_2O$

The apparent first-order rate coefficient at any pressure can be calculated by the expression:

$$k = k_{\infty}\left(\frac{P_r}{1 + P_r}\right)F. \tag{2.16}$$

In the equation above, $F = 1$ in the Lindemann approach and the reduced pressure P_{r} is given by

$$P_{\mathrm{r}} = \frac{k_0[\mathrm{M}]}{k_{\infty}}, \tag{2.17}$$

where M is the third body. When calculating the effective concentration of the third body, the *collision efficiencies* m_{y_i} are also taken into account:

$$[\mathrm{M}] = \sum_i m_{y_i}[Y_i]. \tag{2.18}$$

In the case of the example reaction of H_2O_2 decomposition, the effective concentration of the third body is calculated by Metcalfe et al. (2013) as $[\mathrm{M}] = 5.00[\mathrm{H_2O}] + 5.13[\mathrm{H_2O_2}] + 0.8[\mathrm{O_2}] + 2.47[\mathrm{H_2}] + 1.87[\mathrm{CO}] + 1.07[\mathrm{CO_2}] + 0.67[\mathrm{Ar}] + 0.43[\mathrm{He}]+$ the sum of the concentrations of all other species. Since N_2 is a commonly used *bath gas* within experiments, it often makes up the majority of the colliding species concentrations. N_2 is therefore assumed to have unit collision efficiency, and those of the other species are compared against it. In the reaction $H_2O_2(+M) \rightleftarrows 2OH\ (+M)$, species that have similar molecular energy levels to the rovibrationally excited H_2O_2 molecules (like H_2O_2 and H_2O) have large collision efficiencies, whilst noble gases have typically small collision efficiencies. The general trend is that larger molecules with more excitable rovibrational frequencies have larger collision efficiency factors. There are few measurements that specifically address third-body efficiency factors, and these values can be quite uncertain (Baulch et al. 2005). The third-body efficiency factors can also be considered as temperature dependent (Baulch et al. 2005), but even an approximate parameterisation is hindered by the lack of appropriate experimental data. The effective third-body concentration continuously changes during the course of a reaction according to the change of the mixture composition.

The Lindeman equation does not describe properly the pressure dependence of the rate coefficient, and it can be improved by the application of the pressure and temperature dependent parameter F. In the Troe formulation (Gilbert et al. 1983), F is represented by a more complex expression:

$$\log F = \log F_{\mathrm{cent}} \left[1 + \left[\frac{\log P_{\mathrm{r}} + c}{n - d(\log P_{\mathrm{r}} + c)} \right]^2 \right]^{-1}, \tag{2.19}$$

with $c = -0.4 - 0.67 \log F_{\mathrm{cent}}$, $n = -0.75 - 1.271 \log F_{\mathrm{cent}}$, $d = 0.14$ and

$$F_{\mathrm{cent}} = (1 - \alpha)\exp\left(-\frac{T}{T^{***}}\right) + \alpha \exp\left(-\frac{T}{T^{*}}\right) + \exp\left(-\frac{T^{**}}{T}\right) \tag{2.20}$$

so that four extra parameters, α, T^{***}, T^{*} and T^{**}, must be defined in order to represent the fall-off curve with *Troe parameterisation*.

In several cases, the pressure dependence in the fall-off region is described by temperature-independent F_{cent}, but still keeping the Troe representation. For example, for the reaction $H + O_2(+M) = HO_2$ (+M), Ó Conaire et al.(2004) provided the following Troe parameters: $\alpha = 0.5$, $T^{***} = 1.0 \times 10^{-30}$, $T^{*} = 1.0 \times 10^{+30}$ and $T^{**} = 1.0 \times 10^{+100}$. At combustion temperatures ($T = 700 - 2{,}500$ K), the exponential terms are approximately $\exp(-10^{33}) \approx 0$, $\exp(-10^{-27}) \approx \exp(0) = 1$ and $\exp(-10^{97}) \approx 0$; therefore, using these Troe parameters in Eq. (2.20) gives a temperature-independent $F_{\mathrm{cent}} = 0.5$.

Figure 2.4 shows the change of the apparent first-order rate coefficient k^{uni} with pressure for the reaction $H_2O_2 \rightleftarrows 2OH$ at $T = 1{,}000$ K. Using log–log axes (Fig. 2.4a), it is clear that when applying both the Lindemann approach ($F = 1$) and the Troe parameterisation, the calculated apparent rate coefficient converges to the low-pressure limit and the high-pressure limit rate coefficient at low and high pressures, respectively. However, closely approaching the high-pressure limit requires very high pressures of about 10^5 bar. Figure 2.4b uses non-logarithmic axes and shows that at pressures characteristic for an internal combustion engine (1–60 bar), the rate coefficient cannot be approximated well with the low-pressure limit. In addition, the Lindemann and Troe equations provide very different rate

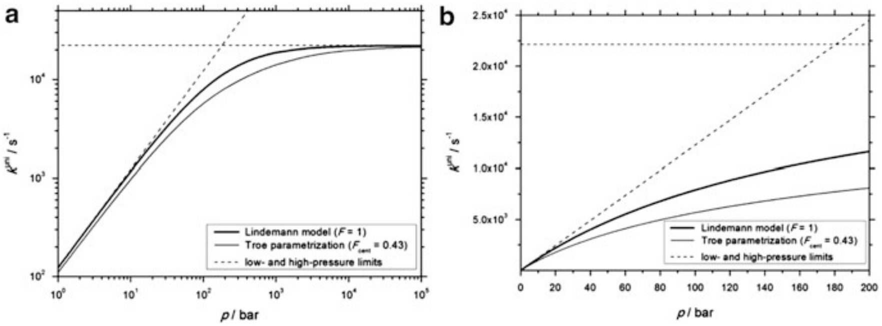


Fig. 2.4 The change of the apparent first-order rate coefficient k^{uni} with pressure for reaction $H_2O_2 \rightleftarrows 2OH$ at temperature $T = 1{,}000$ K using bath gas N_2. The source of data is the article of Troe (2011); (**a**) logarithmic axes and (**b**) non-logarithmic axes

coefficients. The rate coefficient k^{uni} corresponding to the low-pressure limit is a linear function of pressure on both the log–log and non-logarithmic plots.

Not only the rate coefficients of unimolecular reactions may have pressure dependence. The other category of reactions with pressure-dependent rate coefficients is those of *complex-forming bimolecular reactions*. An example of such a pressure-dependent reaction is the reaction of OH with CH_3 radicals, which is important both in combustion and atmospheric chemistry. The reaction first produces a rovibrationally excited CH_3OH molecule, which may decompose to many directions (such as product channels $CH_3O + H$, $CH_2OH + H$, $HCOH + H_2$, $HCHO + H_2$), but the main products are the stabilisation product CH_3OH and decomposition products singlet methylene and water; $^1CH_2 + H_2O$ (Jasper et al. 2007). As Fig. 2.3b shows, the excited CH_3OH molecule can lose the extra energy in collisions and stabilise as a thermally equilibrated CH_3OH molecule, can decompose back to radicals OH and CH_3 or can decompose forward to species $^1CH_2$ and H_2O. The rate coefficients of the decomposition channels depend on the energy level of the CH_3OH molecule, and decomposition is possible only above an energy threshold. At very high pressures, the collisions with the molecules present in the gas mixture are frequent. Therefore, almost all excited CH_3OH molecules get stabilised. Consequently, the reaction can be described with stoichiometry $CH_3 + OH \rightleftarrows CH_3OH$, and it is a second-order reaction. The corresponding rate coefficient k_∞ is called the high-pressure limit. At low pressures, the reaction is third-order and mainly proceeds via $CH_3 + OH + M \rightleftarrows {}^1CH_2 + H_2O + M$. The corresponding third-order rate coefficient k_0 is called the low-pressure limit. Within the fall-off region, the apparent second-order rate coefficient of reaction $CH_3 + OH$ (+M) $\rightleftarrows$ CH_3OH (+M) increases with pressure.

The pressure dependence of the apparent second-order rate coefficient can be calculated by Equations (2.14) to (2.20). Figure 2.5 shows the change of the apparent second-order rate coefficient k^{bi} with pressure for reaction $CH_3 + OH \rightleftarrows CH_3OH$ at temperature $T = 1{,}000$ K. Again, the figure with log–log

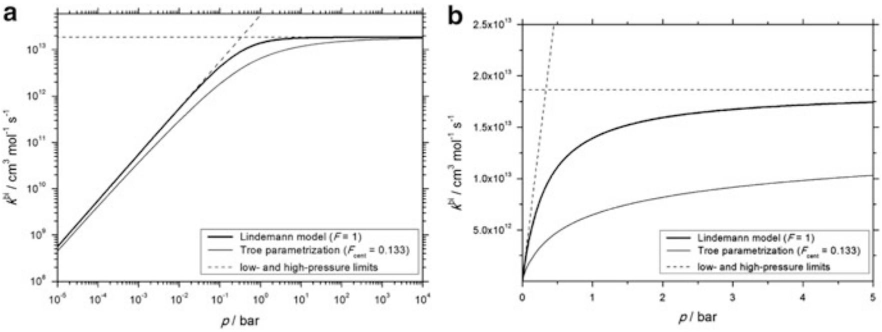


Fig. 2.5 The change in apparent second-order rate coefficient k^{bi} with pressure for reaction $CH_3 + OH \rightleftarrows CH_3OH$ at temperature $T = 1{,}000$ K using bath gas He. The source of data is the article of De Avillez Pereira et al. (1997); (**a**) logarithmic axes and (**b**) non-logarithmic axes

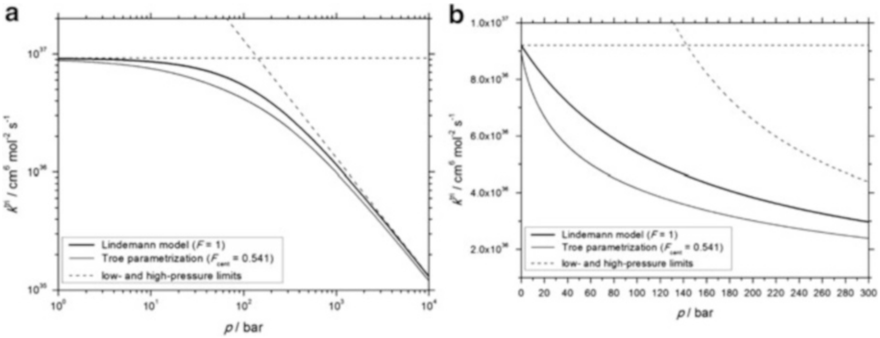


Fig. 2.6 The change in apparent third-order rate coefficient k^{tri} with pressure for reaction $CH_3 + OH \rightleftarrows {}^1CH_2 + H_2O$ at temperature $T = 1{,}000$ K using bath gas He. The source of data is the article of De Avillez Pereira et al. (1997); (**a**) logarithmic axes and (**b**) non-logarithmic axes

axes (a) shows that the rate coefficient approaches the limits at extremes pressures, whilst the figure with non-logarithmic axes (b) indicates that in the pressure range of 0–5 bar, the apparent second-order rate coefficient significantly changes with pressure using both the Lindemann and Troe formulations.

The apparent third-order rate coefficient of reaction $CH_3 + OH$ (+M) $\rightleftarrows {}^1CH_2 + H_2O$ (+M) decreases with pressure. Rate coefficient k' of the decomposition of the excited species can be calculated in the following way:

$$k' = k_0 \left(\frac{1}{1 + P_{\mathrm{r}}} \right) F. \tag{2.21}$$

Figure 2.6 shows the change of the apparent third-order rate coefficient k^{tri} with pressure for this reaction channel at temperature $T = 1{,}000$ K. Again, the figure with the log–log axes (a) shows the approach of the limiting rate coefficients, whilst the non-logarithmic plot (b) indicates the significant change in rate coefficient at engine conditions of about of 1 to 60 bar. It is interesting to note that the k^{tri} corresponding to the high-pressure limit is a linear function of pressure on the log–log plot, but it is a curved function on the non-logarithmic plot, which is a characteristic of functions $\log(a) - \log(x)$ and a/x , respectively.

The Troe equation and the similar SRI equation (Stewart et al. 1989) can accurately represent the fall-off region only for single-well potential energy surfaces (Venkatech et al. 1997). For more complicated elementary reactions, the difference between the theoretically calculated rate coefficient and the best Troe fit can be as high as 40 %. A series of fitting formulae for the parameterisation of the fall-off curves are discussed in Zhang and Law (2009, 2011). In some mechanisms, the pressure dependence is given by the so-called log p formalism [see e.g. Zádor et al. (2011)] :

$$\ln\{k\} = \ln\{k_i\} + (\ln\{k_{i+1}\} - \ln\{k_i\})\frac{\ln\{p\} - \ln\{p_i\}}{\ln\{p_{i+1}\} - \ln\{p_i\}}. \tag{2.22}$$

Here k is the rate coefficient belonging to pressure p, whilst the (p_i, k_i) pairs are a series of tabulated rate coefficients, defined by Arrhenius parameters, belonging to different pressures. Hence, this is an interpolation method which is linear in log p. Usually the rate coefficient at a given pressure will follow the extended Arrhenius formulation, but this need not be the same at different pressures making the log p formulation more flexible than the Troe formulation. Differences in third-body efficiencies can also be accounted for each collider separately, but the log p formalism is not compatible with the effective concentration formalism [see Eq. (2.18)]. Another possible approach is the application of Chebyshev polynomials to represent the temperature and pressure dependencies of the apparent rate coefficients (Venkatech et al. 1997). Whilst this may be more accurate in some cases than using interpolation based on a limited number of pressures, care should be taken not to extrapolate the use of Chebyshev polynomials outside the range in which they were fitted. Further discussion of the handling of pressure-dependent reactions can be found in Pilling and Seakins (1995) and Carstensen and Dean (2007).

2.2.3 Reversible Reaction Steps

In theory, all thermal elementary reactions are reversible, which means that the reaction products may react with each other to reform the reactants. Within the terminology used for reaction kinetics simulations, a reaction step is called irreversible, either if the backward reaction is not taken into account in the simulations or the reversible reaction is represented by a pair of opposing irreversible reaction steps. These irreversible reactions are denoted by a single arrow "→". Reversible reaction steps are denoted by the two-way arrow symbol within the reaction step expression "⇄". In such cases, a forward rate expression may be given either in the Arrhenius or pressure-dependent forms, and the reverse rate is calculated from the thermodynamic properties of the species through the equilibrium constants. Hence, if the forward rate coefficient k_{f_i} is known, the reverse rate coefficient can be calculated from

$$k_{r_i} = \frac{k_{f_i}}{K_{c_i}}, \tag{2.23}$$

where K_{c_i} is the equilibrium constant expressed in molar concentrations. K_{c_i} is obtained from the thermodynamic properties of the species.

In combustion systems, thermodynamic properties are often calculated from 14 fitted polynomial coefficients called the NASA polynomials for each species (Burcat 1984). Seven are used for the low-temperature range T_{low} to T_{mid} and seven for the high-temperature range T_{mid} to T_{high}. Typical values are $T_{\mathrm{low}} = 300$ K, $T_{\mathrm{mid}} = 1{,}000$ K and $T_{\mathrm{high}} = 5{,}000$ K. The polynomial coefficients are determined by fitting to tables of thermochemical or thermodynamic properties, which are either measured values or calculated using theoretical methods and statistical thermodynamics (Goos and Lendvay 2013). The polynomial coefficients can then be used to evaluate various properties at a given temperature (T), such as standard molar heat capacity ($C_{\mathrm{p}}^{\ominus}$), enthalpy ($H^{\ominus}$) and entropy ($S^{\ominus}$) as follows:

$$\frac{C_{\mathrm{p}}^{\ominus}}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4, \tag{2.24}$$

$$\frac{H^{\ominus}}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T}, \tag{2.25}$$

$$\frac{S^{\ominus}}{R} = a_1 \ln\{T\} + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7, \tag{2.26}$$

where the a_n parameters are the NASA polynomial coefficients, and R is the universal gas constant. The standard molar reaction enthalpy ($\Delta_{\mathrm{r}}H_j^{\ominus}$) and entropy ($\Delta_{\mathrm{r}}S_j^{\ominus}$) can be calculated from the following equations:

$$\frac{\Delta_{\mathrm{r}}S_j^{\ominus}}{R} = \sum_{i=1}^{I} v_{ij}\frac{S_i^{\ominus}}{R}, \tag{2.27}$$

$$\frac{\Delta_{\mathrm{r}}H_j^{\ominus}}{RT} = \sum_{i=1}^{I} v_{ij}\frac{H_i^{\ominus}}{RT}. \tag{2.28}$$

The equilibrium constant K in terms of normalised pressures $p/p^{\ominus}$ is then obtained from

$$\Delta_{\mathrm{r}}G^{\ominus} = -RT\ln K, \tag{2.29}$$

$$K = \exp\left(\frac{\Delta_{\mathrm{r}}S^{\ominus}}{R} - \frac{\Delta_{\mathrm{r}}H^{\ominus}}{RT}\right). \tag{2.30}$$

The equilibrium constant in concentration units K_{c} is related to the equilibrium constant in normalised pressure units K by the following:

$$K_{\mathrm{c}} = K\left(\frac{p^{\ominus}}{RT}\right)^{\Delta\nu}, \tag{2.31}$$

where $p^{\ominus}$ is the standard pressure and $\Delta\nu = \sum_i \nu_i$ is the sum of stoichiometric coefficients. Remember that the stoichiometric coefficients of the products and reactants have positive and negative signs, respectively. In this way, the reverse rate coefficient for a thermal reaction can be defined by its forward rate coefficient and the appropriate NASA polynomials for the component species within the reaction.

2.3 Basic Simplification Principles in Reaction Kinetics

Simplification of a kinetic mechanism or the kinetic system of ODES is often required in order to facilitate finding solutions to the resulting equations and can sometimes be achieved based on *kinetic simplification principles*. In most cases, the solutions obtained are not exactly identical to those from the full system of equations, but it is usually satisfactory for a chemical modeller if the accuracy of the simulation is better than the accuracy of the measurements. For example, usually better than 1 % simulation error for the concentrations of the species of interest when compared to the original model is appropriate. Historically, simplifications were necessary before the advent of computational methods in order to facilitate the analytical solution of the ODEs resulting from chemical schemes. We begin here by discussing these early simplification principles. In later chapters, we will introduce more complex methods for chemical kinetic model reduction that may perhaps require the application of computational methods.

The following four kinetic simplification principles may provide a nearly identical solution compared to the original system of equations if applied appropriately: (i) the pool chemical approximation, (ii) the pre-equilibrium approximation, (iii) the rate-determining step and (iv) the quasi-steady-state approximation. An alternative approach, where the kinetic system of ODEs can be formulated to have fewer variables than the number of species, is based on the application of conserved properties, and this topic is discussed in Sect. 2.3.5. Decreasing the number of calculated variables based on conserved properties is different from the previous four principles, because in this case, the number of variables is decreased without an approximation and without losing any information. The last subsection deals with the lumping of reaction steps based on previously introduced principles.

2.3.1 The Pool Chemical Approximation

The *pool chemical approximation* (also called the *pool component approximation*) is applicable when the concentration of a reactant species is much higher than those of the other species, and therefore the concentration change of this species is considered to be negligible throughout the simulation period. For example, a second-order reaction step $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$ can be converted to first-order, if concentration b of reactant B is almost constant during the simulations. In this way, the product $k' = k\,b$ of concentration b and rate coefficient k is practically constant; therefore, the second-order expression can be converted to a first-order one: $\mathrm{d}c/\mathrm{d}t = k\,a\,b = k'\,a$. In this special case, the pool chemical approximation is called the *pseudo-first-order approximation* and k' is the *pseudo-first-order* rate coefficient.

2.3.2 The Pre-equilibrium Approximation

The *pre-equilibrium approximation* (PEA; also called the *partial equilibrium approximation* or *fast–equilibrium approximation*) is applicable when the species participating in a pair of fast-equilibrium reactions are consumed by slow reactions. After the onset of an equilibrium, the rates of the *forward* and *backward reactions* become equal to each other, and therefore the ratios of the concentrations of the participating species can be calculated from the stoichiometry of the reaction steps and the equilibrium constant. According to the pre-equilibrium approximation, if the rates of the equilibrium reactions are much higher than the rates of the other reactions consuming the species participating in the equilibrium reactions, then the concentrations of these species are determined, with good approximation, by the equilibrium reactions only.

As an example, let us consider the equilibrium reaction $A \rightleftarrows B$. The corresponding rate coefficients are k_1 and k_2, and the equilibrium constant is denoted by $K = k_1/k_2$. In the case of an onset of equilibrium, the rates of the opposing reactions are identical: $k_1 a = k_2 b$, and therefore, $b = k_1/k_2 a = Ka$. Now consider the reaction system $A \rightleftarrows B \rightarrow C$, where species B is consumed by a slow reaction with a small rate coefficient k_3 compared to k_1 and k_2. In this case, we can still assume that $b = Ka$ is a good approximation, and thus, $\mathrm{d}c/\mathrm{d}t = k_3 b$, $\mathrm{d}c/\mathrm{d}t = k_3 K a$. Therefore, the concentration of B is not required in order to calculate the rate of production of C as long as the rate coefficients are known.

A common example of such a situation is the enzyme-substrate reaction involved in biochemical pathways. In this type of reaction, an enzyme E binds to a substrate S to produce an enzyme-substrate intermediate ES, which then forms the final product P:

$$E + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} E + P.$$

Here the rate of production of the final product (usually an essential biomolecule) can be derived using the pre-equilibrium approximation to be

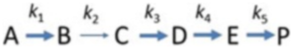
$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_2 \frac{k_1}{k_{-1}} [\mathrm{E}][\mathrm{S}] = k_2 K [\mathrm{E}][\mathrm{S}],$$

where the square brackets indicate the molar concentrations of the given species.

Another common situation is when a large organic molecule isomerises in a fast–equilibrium reaction to a low-concentration, more reactive form, and this more reactive species is consumed by a slow reaction. Using the equation $\mathrm{d}c/\mathrm{d}t = k_3 K a$ means that the rate equation contains the less reactive organic species that is present in higher concentration and therefore can be measured more easily.

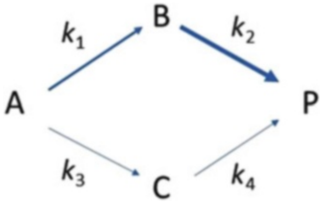
2.3.3 Rate-Determining Step

Even in the case of large reaction mechanisms, the production rate of a reactant or final product of the overall chemical reaction may depend mainly on the rate coefficient of a single reaction step. This reaction step is called the *rate-determining step*. If we have sequential first-order reactions, then the reaction step having the smallest rate coefficient is the rate-determining one. In this case, the production rate of the final product is equal to the rate coefficient of the rate-determining step multiplied by the concentration of the reactant of this reaction step. In this example



if $k_2 \ll k_1$, k_3, k_4, k_5, then $\mathrm{d}p/\mathrm{d}t \approx k_2 b$.

In the case of an arbitrary mechanism, the rate-determining step is characterised by the fact that increasing its rate coefficient increases the production rate of the product significantly. However, in general, this may not be the reaction step having the smallest rate coefficient. For example, when species P is produced from species A in parallel pathways, then the rate coefficient of the rate-determining step may be relatively high. In the example below, rate coefficient k_1 belonging to the rate-determining step is relatively large if k_3, $k_4 \ll k_1 \ll k_2$:



In the general case, we have to investigate how a small change of rate coefficient k_j changes the production rate $d y_i/d t$ of product Y_i. This effect appears in the local rate sensitivity coefficient $\partial(\mathrm{d}c_i/\mathrm{d}t)/\partial k_j$ (see Sect. 5.2). If this coefficient is much higher for reaction j than for the other reaction steps, then reaction j is the rate-determining step of the production of species i (Turányi 1990).

2.3.4 The Quasi-Steady-State Approximation (QSSA)

The *quasi-steady-state approximation* (QSSA) is also called the Bodenstein principle, after one of its first users (Bodenstein 1913). As a first step, species are selected that will be called quasi-steady-state (or QSS) species. The QSS-species are usually highly reactive and low-concentration intermediates, like radicals. The production rates of these species are set to zero in the kinetic system of ODEs. The corresponding right-hand sides form a system of algebraic equations. These algebraic equations can be used to calculate the concentrations of the QSS-species from the concentrations of the other (non-QSS) species. The system of ODEs for the non-QSS-species and the system of algebraic equations for the QSS-species together form a coupled system of differential algebraic equations. For the successful application of the QSSA, the solution of this coupled system of differential algebraic equations should be very close to those of the original system of kinetic ODEs. In some cases, the system of algebraic equations can be solved separately, that is, the concentrations of all QSS-species can be calculated from (explicit) algebraic equations. The calculated QSS-species concentrations can then be used in the system of kinetic ODEs for the remaining species. In this case, following the application of the QSSA, the kinetic system of ODEs is transformed to a smaller system of ODEs having fewer variables. The background to the QSSA is that in chemical kinetic models, the timescales involved usually span quite a wide range (see Sect. 6.2).

As an example, consider the following reaction sequence where B is a QSS-species linking reactant A to product C:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \overset{k_2}{\rightarrow} \mathrm{C}.$$

If the QSSA is applied to B, then we assume:

$$\frac{\mathrm{d}[B]}{\mathrm{d}t} = 0 \tag{2.32}$$

so that

$$k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] - k_2[\mathrm{B}] = 0. \tag{2.33}$$

Therefore,

$$[\mathrm{B}] = \frac{k_1}{k_{-1} + k_2}[\mathrm{A}]. \tag{2.34}$$

Hence,

$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k_2[\mathrm{B}] = \frac{k_1 k_2 [\mathrm{A}]}{k_{-1} + k_2} = k^{'}[\mathrm{A}], \tag{2.35}$$

where

$$k^{'} = \frac{k_1 k_2}{k_{-1} + k_2}. \tag{2.36}$$

Therefore, the above set of reactions can be replaced by a single reaction of the form:

$$\mathrm{A} \rightarrow \mathrm{C} \tag{2.37}$$

with the effective rate coefficient k' defined in Eq. (2.36). The quantitative kinetic involvement of intermediate B in the overall reaction is encapsulated in k', but the species has been removed from the mechanism. Should the concentration of B be required, it can be calculated from the expression (2.34), but usually the concentrations of the QSS-species are not required in practical applications. Therefore, the method constitutes their complete removal from the scheme, thus reducing the overall number of variables in the model and also usually its stiffness since the range of timescales remaining has been reduced .

Whilst it is quite straightforward to comprehend the applicability of the previous three basic kinetic simplification principles, the QSSA is not so easy to understand. For example, it may seem strange that the solution of a coupled system of algebraic differential equations can be very close to the system of ODEs. Another surprising feature is that the concentrations of QSS-species can vary substantially over time; for example, the QSSA has found application in oscillating systems (Tomlin et al. 1992). The key to the success of the QSSA is the proper selection of the QSS-species based on the error induced by its application. The interpretation of the QSSA and the error induced by the application of this approximation will be discussed fully in Sect. 7.8.

2.3.5 Conserved Properties

As noted above, the consideration of conserved properties allows the kinetic system of ODEs to contain fewer variables than the number of species. However, it is an exact transformation, and therefore it is usually handled separately from the rules above which are based on approximations.

In many reaction mechanisms, there are *conserved properties*. The simplest conserved property occurs when the sum of the molar concentrations is constant. This is obtained when the volume is constant and for each reaction step $0 = \sum_j \nu_{ij}^{J} - \nu_{ij}^{B}$, that is, the change of the number of moles is zero for each reaction step.

In a closed chemical system, the chemical reactions do not change the moles of elements, and therefore the number of moles of each element is a conserved property. Other conserved properties include the total enthalpy in an adiabatic system or the charge in an electrochemical system. Another way of referring to a conserved property is as a *reaction invariant* (Gadewar et al. 2001). If an atomic group remains unchanged during the reaction steps, then its number of moles is also a conserved property (*conserved moiety*). Such a conserved moiety may be, for example, the adenosine group, and the sum of species AMP, ADP and ATP may remain constant in a closed biochemical system (Vallabhajosyula et al. 2006).

The presence of conserved elements and conserved moieties cause linear dependence between the rows of the stoichiometric matrix $\boldsymbol{\nu}$ and decrease the rank of the stoichiometric matrix. In most cases, the number of species N_S is much less than the number of reaction steps N_R, that is, $N_\mathrm{S} < N_\mathrm{R}$. If the stoichiometric matrix $\boldsymbol{\nu}$ has N_R rows and N_S columns, and conserved properties are not present, then the rank of the stoichiometric matrix is usually N_S. If N_C conserved properties are present, then the rank of the stoichiometric matrix is $N = N_\mathrm{S} - N_\mathrm{C}$. In this case, the original system of ODEs can be replaced by a system of ODEs having N variables, since the other concentrations can be calculated from the computed concentrations using algebraic relations related to the conserved properties.

2.3.6 Lumping of Reaction Steps

In some cases, without much mathematical background, common sense rules can be applied to the simplification of reaction mechanisms by lumping the reaction steps. For example, reaction steps having common reactants can be lumped together:

$$\begin{array}{ll} \mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D} & 0.4k \\ \mathrm{A} + \mathrm{B} \rightarrow \mathrm{E} + \mathrm{F} & 0.6k \end{array}$$

Such reactions are common in detailed mechanisms. The usual terminology is that reaction "A + B → products" is a *multichannel reaction* that has two *reaction channels*, one resulting in products C + D and the other products E + F. The overall rate coefficient of the reaction is therefore k, whilst the *channel ratio* is 0.4:0.6. A synonym of the term channel ratio is the *branching ratio*. Following the rules for the creation of the kinetic system of differential equations, the two chemical equations above result in exactly the same terms when starting from the single chemical equation below:

$$\mathrm{A} + \mathrm{B} \rightarrow 0.4\,\mathrm{C} + 0.4\,\mathrm{D} + 0.6\,\mathrm{E} + 0.6\,\mathrm{F} \qquad k$$

The number of reaction steps in the mechanism is decreased by one, but since lumping of the reaction steps resulted in exactly the same set of ODEs, there is no gain in simulation speed. Nevertheless, the lumping of multichannel reactions as above is common in atmospheric chemical mechanisms, because it may clarify the main reaction routes for the user.

Reaction steps can also be lumped using the principle of a rate-determining step (see Sect. 2.3.3). Let us consider the following two reactions:

$$\begin{array}{lll} \mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D} & r_1 = k_1 ab & \text{slow} \\ \mathrm{D} + \mathrm{E} \rightarrow \mathrm{F} & r_2 = k_2 de & \text{fast} \end{array} .$$

The first, slow reaction, is the rate-determining step, and therefore, the rate of the lumped reaction obtained by merging these two reactions can be calculated by the equation $r = k_1ab$. If we want to keep the mass action kinetics formalism, then on the left-hand side of the lumped reaction should be $A + B$. During the course of these two reactions, A, B and E are consumed; C and F are produced. Equal amounts of D are consumed and produced; therefore, D should not be present in the lumped equation. Species E is consumed, but since it is not part of the rate-determining step, it should not be present on the left-hand side of the chemical equation. Therefore, it appears on the right-hand side, with a -1 stoichiometric coefficient. The lumped reaction is the following:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{F} - \mathrm{E} \qquad r = k_1ab.$$

Using the rules of mass action kinetics, (almost) the same equations can be derived for the production rates of all species but D. The presence of a negative stoichiometric coefficient is perhaps surprising at first glance, but there are several lumped atmospheric chemical mechanisms (Gery et al. 1989) that contain negative stoichiometric coefficients on the right-hand side of some chemical equations.

One result of the reaction lumping above is the removal of the highly reactive species D. This means that a fast timescale was removed from the system, and the stiffness of the corresponding ODE system was decreased. The calculation of lifetimes of species is discussed in Sect. 6.2. Reaction lumping based on timescales may remove species and decrease stiffness, and thus may lead to increases in simulation speed. For example, its application was successful for the further reduction of a skeletal scheme describing *n*-heptane oxidation in Peters et al. (2002). This will be discussed more fully in connection with the application of the QSSA in Sect. 7.8.6.

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