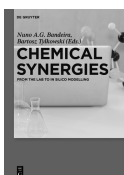


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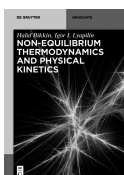
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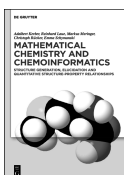
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Chemical Complexity via Simple Models

MODELICS

DE GRUYTER

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Preface

The idea of writing this book was born in 2015 during the International Conference “Mathematics in (Bio)Chemical Kinetics and Engineering” (MACKiE-2015), held in Ghent (Belgium). Professors Valeriy Bykov and Grigoriy (Gregory) Yablonsky were colleagues who worked closely at the Boreskov Institute of Catalysis (Novosibirsk, Russia) for more than a decade in the 1970s to 1980s. They established the Siberian chemico-mathematical team – together with Alexander Gorban and Vladimir Elokhin. They co-authored many books and articles related to the area of the mathematical modeling of chemical processes. Dr Svetlana Tsybenova joined this activity later in the 1990s, enhancing its computational and applied aspects.

After graduating from Novosibirsk State University in 1968, Valeriy Bykov started his scientific career in the Department of Mathematical Modeling at the Boreskov Institute of Catalysis. Professor Mikhail Slin’ko and Dr Albert Fedotov were his scientific supervisors. In 1985, Valeriy Bykov received his degree of Doctor of Physics and Mathematics (Physical Chemistry) from the Institute of Chemical Physics in Chernogolovka.

Gregory Yablonsky also worked in the same Department of Mathematical Modeling at the Boreskov Institute of Catalysis (Novosibirsk), first as a post-graduate student and then as a researcher. Professor Mikhail Slin’ko was also his supervisor. In 1989, Gregory Yablonsky received his degree of Doctor of Science (Physical Chemistry) from the Boreskov Institute.

Svetlana Tsybenova graduated from Krasnoyarsk State Technical University in 1996 and received her PhD in Technical Sciences from the same university in 1999. In 2011, she received the degree of Doctor of Physics and Mathematics (Physical Chemistry) from Bashkir State University, Ufa; her being adviser was Professor Semyon Spivak.

In 1978, there was a remarkable moment in this story when a scientific delegation from the USA, the three prominent professors Rutherford Aris, Dan Luss, and Harmon Ray, visited the Boreskov Institute in Novosibirsk. This was a starting point for Soviet–American cooperation in mathematical chemistry. Unfortunately, this cooperation met many political obstacles. Nonetheless, it became a significant stimulus for a fruitful exchange of information and ideas.

Over the last 50 years, the main directions and approaches have been determined in mathematical chemistry, both theoretical and applied. Discoveries of new experimental facts, i.e., the rate of hysteresis, chemical oscillations, chaos, etc, created new challenges in decoding the complexity of chemical reactions. Batteries of mathematical models distinguished by the level of complexity and assumed factors have been developed for imitating complex chemical behavior.

“Battery of models”, “zoo of models”, or “market of models” – different metaphors can be used. Nevertheless, the real alternative in contemporary modeling is between the model taken from the “market” and that produced by the individual “tailor”.

Certainly, a suit from the tailor is more elegant; however, it is much cheaper and faster to buy a suit in a supermarket and adapt it if necessary.

An optimal strategy of modeling can be formulated as follows:

1. to develop typical (“simple”) models for describing the phenomena of our interest;
2. to adapt them to concrete phenomena or processes.

A special question arose: what is the *simplest* model to describe newly discovered critical phenomena? This book is devoted to *basic models*, which can be used as building blocks for constructing the mathematical models of complex chemical processes. We call the methodology of selecting and analyzing these models “*modelics*”. Our book is focused on *simple nonlinear models*.

Generally, the concepts of “simplicity” and the “simple model” are complex. Einstein’s advice was: “Make everything as simple as possible but not simple.” On the other hand, Leonardo da Vinci said: “Simplicity is the ultimate sophistication.” So, when working with simplicity, we move through the “gray zone” between science, art, and philosophy, and the inscription on the gates is: “Less is more!”

The authors express their gratitude to the colleagues who provided them with help at various times and in different situations: Professors Sergey Varfolomeev, Bair Bal’zhinimaev, Alexander Gorban’, Semyon Spivak, Aizek Volpert, Konstantin Shkadinskii, Sergey Reshetnikov, Georgij Malinetskii, and Zulhair Mansurov.

Finally, we would like to thank our beloved ones for their support and understanding.

Valeriy Bykov, Moscow, 2017

Svetlana Tsybenova, Moscow, 2017

Gregory Yablonsky, St. Louis, 2017

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Part I: **General part**

1 Introduction. How to describe complex processes using simple models: Modelics

In contemporary scientific folklore, there is a legend which is transferred from one book to another one. At the end of the 1950s there was a meeting organized on an important and highly secret project, say on the possible constructing of military bases on the Moon. One intellectual from the Rand Corporation (“highbrow” or even “egghead”) presented an invited talk involving many formulas and numbers. A general from the Pentagon interrupted him: “Excuse me, sir! What is a source of your information?” – “What do you mean, sir?” “How do you know all these estimates, equations, numbers etc.” – The scientist replied immediately: “Sir, we have a model!”, and the general was completely satisfied by this statement.

1.1 Model...modeling...

Today, on August 30, 2017, Google presented these numbers

Model	5,600,000,000
Modeling	553,000,000
Energy	1,690,000,000
Force	1,600,000,000
Physical model	650,000,000
Physical energy	819,000,000
Physical force	41,700,000
Mathematical modeling	4,870,000
Mathematical model	10,100,000

Clearly “*modeling*” and “*model*” are terms extremely popular in science and engineering.

It is easy to define modeling as the study of processes using models. However, what is a *model* in “hard sciences”?

There are many definitions of this term which pretend to be rigorous to some extent. We prefer the following one:

Object **M** is a model of object **A** with respect to a certain group of characteristics (properties), if **M** is constructed (or chosen) to simulate **A** in accordance with these characteristics.

In physics, chemistry, and biology (“hard sciences”) and psychology and sociology (“soft sciences”), mathematical models are symbolic descriptions which represent the different dependencies of process characteristics or/and material properties in terms of controlled parameters (temperature, pressure, composition, electrical con-

ductivity, etc.). A mathematical model can be a number, a geometrical image, a function, a set of equations, etc.

What should we know before “constructing” any model? First, its basic elements, secondly, its main principles and laws, and thirdly, the algorithm for the model construction.

“Complex” and “simple” are key words in the development of models. The word “complex” comes from the Latin *complexus*, past participle of *complecti* (to entwine, encircle, compass, infold), from *com* (together) and *plectere* (to weave, braid). This concept reflects the multilevel and multicomponent structure of the world. The concept of “simplicity” is deep as well. There are different meanings of this term, positive and negative. St. Augustine said “Ignorance and stupidity are given the names of simplicity and innocence”. Etymologically, “simple” originated in the medical science of the Dark Ages as related to a medicine made from one constituent, especially from one plant.

In contemporary science, “simplicity” is about the ability to understand or explain in an easy way with a minimum of assumed concepts, and, finally, about elegance and parsimony. When we are talking about simplicity, we always remember “Occam’s razor”, the principle of simplicity: “the simpler explanation is usually better” (William of Ockham was a Franciscan friar, a philosopher of the 14th century). It is not true in general, however it is a good starting point of reasoning.

In real science and modeling, the “Holy Grail” is the model which represents an efficient compromise between “complexity” and “simplicity”: Simple, but not too simple; complex, but not too complex. This compromise is determined by two primary characteristics of the model, i.e., its goal and its number of assumed variables.

1.2 Top-down and bottom-up

In modeling, two different strategies can be distinguished, *top-down* and *bottom-up*.

The *top-down approach* became possible and popular since the start of the computer era. In this approach a “large” complex model constructed, say via combinatorial methods, is decomposed into “small” simple submodels in accordance with some hierarchy. In chemistry and chemical engineering, the kinetic model is a foundation of the mathematical modelling of chemical reactions, reactors, and processes [1–3]. There exists a hierarchy of models of complex catalytic process: kinetic model, catalyst pellet model, catalyst bed model, contact reactor model, aggregate model, and, finally, model of the chemical plant. In this hierarchy of models, the kinetic model is the first level. None of the calculations that are of interest for chemical technology are carried out without kinetic models. For dynamic (kinetic) models of physicochemical processes, the basic elements are chemical substances and elementary acts; the main laws are the mass-action-law and surface-action-law; one of the algorithms for model construction is the quasi-steady-state method. Later we’ll explain it in more detail.

The bottom-up approach is opposite to the *top-down* one. It starts from a “seed” simple submodel, combining it with another simple model “model-by-model”), and, finally, developing the model of a complex multilevel material or process.

Summing up, in the top-down modeling, simple models are obtained by the decomposition of a complex model. Such models approximate complex behavior in a certain parametric or temporal domain. The bottom-up methods take simple submodels as the initial ones. In any case, in both approaches, *top-down* or *bottom-up*, the simple models are unavoidable elements of modeling. Moreover, it is obvious that the simple models are more reliable for wide application in the “modeling industry” than the complex ones because of the amount and quality of information. In some situations, simple models exhibit very complex properties. However, knowing the properties of simple models we will be able to achieve an understanding which is a final goal of modeling, not just a calculated number.

Simple nonlinear models are the center of our interest. These models must reflect the main features of the chemical system studied, with the goal “not numbers, but understanding”. For example, if the rate hysteresis is experimentally observed, the corresponding simplest kinetic model must be nonlinear and have a dimension of 2 including the special nonlinear term of “xy” type.

If the chemical self-oscillations of the chemical rate are found, the simplest mathematical model must be nonlinear as well and have a dimension of 3. If complex spatiotemporal structures occur, it is necessary to use a “reaction–diffusion” model with mass-action-law nonlinearity.

Our experience shows that with a well-developed system of basic models, it is much easier to construct and understand the specific mathematical model of the real process.

That is why this book is focused on the analysis of typical simple models using a special term, *modelics*, for modeling via simple models.

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2 Categorization of models

2.1 Physical framework of model design

Models of closed, open and semiopen systems.

Local and global models.

Time in modeling. Steady-state and non-steady-state models

Models differ by the factors and processes which they reflect. In fact, the goal of a model is a description of the specific processes based on reasonable assumptions and considering certain factors.

In model design, the key words are: *open* and *closed*; *local* and *global*; *steady state* and *non-steady-state*. As known from thermodynamics, systems can be classified as either open or closed, depending on whether there is exchange of matter with the surroundings. Closed systems can exchange energy with the surroundings, but they cannot exchange matter, while open systems can exchange either matter and energy or only matter. Semiopen (or semiclosed) systems also exist, in which only some type of material is exchanged with the surroundings. In chemical kinetics and engineering, the closed reactor is better known as the batch reactor and the open reactor as the continuous-flow reactor. In the pulse reactor, a small quantity of a chemical substance is injected into the reactor.

The general equation, which reflects the material balance for any component in any system, open or closed, can be represented qualitatively as follows:

$$\begin{array}{lcl} \text{temporal change of} & = & \text{transport} \\ \text{amount of component} & & \text{change} \quad + \quad \text{change due to} \\ & & \text{reaction} \end{array} \quad (2.1)$$

in which the temporal change of the amount of component, often termed *accumulation*, is its change with respect to time at a fixed position, the transport change is the change caused by motion of the component and the reaction change is the change caused by chemical reaction. It is the model of a non-steady-state process (*non-steady-state model*), $dc_i/dt \neq 0$, where c_i is the concentration of i -th component, t is time.

If the temporal change is assumed to be zero, $dc_i/dt = 0$, the differential (2.1) is transformed to an algebraic equation. It becomes *the steady-state model*, i.e., the model of the steady-state process.

Rigorously speaking, (2.1) is the so-called *continuity equation* (see the classical monograph by Bird, Stewart, and Lightfoot [1]) with two terms, which are the “transport term” and “chemical term”, respectively. All isothermal models represent different cases of this continuity equation. The chemical term is *local*, reflecting the changes at the given place of space. The transport term is *global*, corresponding to the exchange between different places of space. Equation (2.1) can be used for the classification and

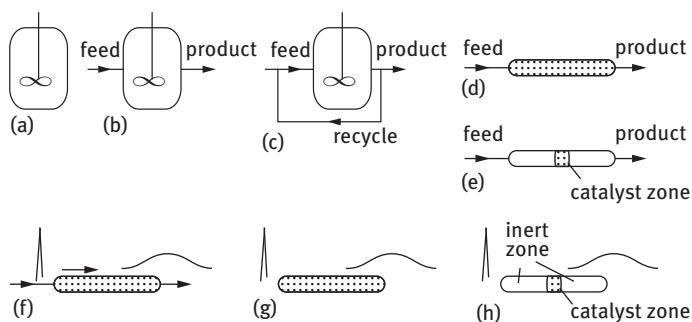


Fig. 2.1: Reactors for kinetic experiments. (a) batch reactor; (b) continuous stirred-tank reactor; (c) continuous-flow reactor with recirculation; (d) plug-flow reactor; (e) differential plug-flow reactor; (f) convectional pulse reactor; (g) diffusional pulse reactor or TAP reactor; (h) thin-zone TAP reactor

qualitative description of different types of systems and reactors [2–5]. All isothermal models represent different cases of this continuity equation.

Figure 2.1 shows schematic representations of several reactor types which are widely used for purposes of chemical engineering. These reactors are supplied by typical simple models with corresponding names, and these models are models of applied kinetics

2.1.1 Models of transport

Typically, transport processes are quite complicated, including at least two types of processes: convection and diffusion.

For convection, the molar flow rate F_i ($\text{mol} \cdot \text{s}^{-1}$) of a component i is determined as the product of the total volumetric flow rate q_V ($\text{m}^3 \cdot \text{s}^{-1}$) and the concentration of the component c_i ($\text{mol} \cdot \text{m}^{-3}$):

$$F_i = q_V c_i. \quad (2.2)$$

For diffusion, in the simplest case the molar flow rate of a component is determined in accordance with Fick's first law:

$$F_i = -D_i A \frac{dc_i}{dz}, \quad (2.3)$$

where D_i is a diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$), A is the cross-sectional area of the reactor available for fluid flow (m^2), and z is the axial reactor coordinate (m).

Pure convection or pure diffusion are examples of well-defined regimes. These hydrodynamic regimes with their corresponding mathematical descriptions are used as “measuring sticks” for extracting the intrinsic kinetic dependencies of chemically active materials, adsorbents, catalysts, membranes, etc.

In the model describing a batch reactor, the transport change term is completely absent. In perfectly mixed convectional systems and reactors, the “transport change”

can be represented as the difference of convectional molar flow rates, $q_{V0}c_{i0} - q_Vc_i$, where q_{V0} and q_V are the inlet and outlet volumetric flow rates and c_{i0} and c_i are the inlet and outlet concentrations, or $q_V(c_{i0} - c_i)$ if $q_V = q_{V0}$.

In purely diffusional systems and reactors, the “transport change” in the simplest case can be represented as the difference between diffusional flow rates in and out, F_{i0} and F_i . Both flow rates are written in accordance with Fick’s first law:

$$F_{i0} = -D_iA \left. \frac{dc_i}{dz} \right|_z, \quad F_i = -D_iA \left. \frac{dc_i}{dz} \right|_{z+\Delta z}. \quad (2.4)$$

Then,

$$F_{i0} - F_i = \left(-D_iA \left. \frac{dc_i}{dz} \right|_z \right) - \left(-D_iA \left. \frac{dc_i}{dz} \right|_{z+\Delta z} \right) = D_iA \frac{d^2c_i}{dz^2} \Delta z. \quad (2.5)$$

2.1.2 The batch reactor

In an ideal batch reactor, i.e., a non-steady-state closed reactor with perfect mixing, (2.1) becomes

$$\begin{array}{ccc} \text{temporal change of} & = & \text{change due to} \\ \text{amount of component} & & \text{reaction} \end{array} \quad (2.6)$$

The simplest mathematical model for the temporal change of any component in a batch reactor of constant reaction volume is

$$\frac{dc_i}{dt} = R_i = v_i r, \quad (2.7)$$

where R_i is the net rate of production of the component per unit reaction volume ($\text{mol m}^{-3} \text{s}^{-1}$), v_i is the so-called stoichiometric coefficient, and r is the reaction rate ($\text{mol m}^{-3} \text{s}^{-1}$).

For a reversible reaction, the reaction rate is a combination of the rates of the forward and reverse reactions:

$$r = r^+ - r^-. \quad (2.8)$$

The state in which $dc/dt = 0$ is called equilibrium. In this state $r = r^+ - r^-$ and $r^+ = r^-$.

2.1.3 The continuous stirred-tank reactor

A continuous stirred-tank reactor (CSTR) is an open reactor with perfect mixing (gradientless reactor) and only convective flow. This mixing can be achieved not only by internal but also by external recirculation. The material balance for any component in a non-steady-state CSTR can be written as

$$\frac{dc_i}{dt} = R_i + \frac{q_{V0}c_{i0} - q_Vc_i}{V} \quad (2.9)$$

with V the reaction volume (m^3). At steady state, the net rate of production of component i can be determined from

$$R_i = -\frac{q_{V0}c_{i0} - q_V c_i}{V} . \quad (2.10)$$

If $q_V = q_{V0}$, (2.10) can be expressed as

$$R_i = -\frac{q_{V0}(c_{i0} - c_i)}{V} = -\frac{c_{i0} - c_i}{\tau} , \quad (2.11)$$

where $\tau = V/q_{V0}$ is the space time (s). It is denoted as space time because its definition involves a spatial variable, V , which distinguishes it from the “astronomic” time. It corresponds to the average residence time in an isothermal CSTR.

2.1.4 The plug-flow reactor

In an ideal plug-flow reactor (PFR), it is assumed that perfect uniformity is achieved in the direction perpendicular to that of the flow, i.e., in the radial direction. Axial diffusion effects are also neglected. The composition of the fluid phase varies along the reactor, so the material balance for any component must be made for a differential element:

$$dV \frac{dc_i}{dt} = R_i dV - q_V dc_i . \quad (2.12)$$

In a more rigorous form, (2.12) can be written as a partial differential equation:

$$dV \frac{\partial c_i}{\partial t} = R_i dV - q_V \frac{\partial c_i}{\partial z} dz . \quad (2.13)$$

Using $q_V = uA$ and $dV = Adz$, where u is the superficial fluid velocity (m s^{-1}), (2.13) can be written as

$$\frac{\partial c_i}{\partial t} = R_i - u \frac{\partial c_i}{\partial z} . \quad (2.14)$$

or

$$\frac{\partial c_i}{\partial t} + \frac{\partial c_i}{\partial \tau} = R_i \quad (2.15)$$

with $\tau = z/u$.

For the steady-state case, $\partial c_i / \partial t = 0$ and the model equation for an ideal PFR can be expressed by the ordinary differential equation

$$\frac{dc_i}{d\tau} = R_i , \quad (2.16)$$

which remarkably is identical to the expression for a batch reactor, (2.7). The only difference is the meaning of the term time used. In the model for the batch reactor, the time is the time of the experimental observation or “astronomic time”, whereas the time in the model for the plug-flow reactor is the space time, τ .

2.1.5 The pulse reactor

The pulse reactor is, by definition, the non-steady-state system. In a pulse reactor, which typically contains a fixed active zone, e.g., catalytic material, a small amount of a component is injected into the reactor during a small interval. In a conventional pulse reactor, the component is pulsed into an inert steady carrier-gas stream. The relaxation of the outlet composition following the perturbation by this pulse provides information about the mechanism of complex chemical process.

In the TAP reactor, created by John Gleaves in the 1980s [5], no carrier gas stream is used and the component is pulsed directly into the reactor. Transport only occurs by Knudsen diffusion, in which gas molecules collide with the wall, not with other molecules. In a thin-zone temporal-analysis-of-products reactor (TZTR) [6], the active material (catalyst) is located only within a narrow zone. The net rate of production in the catalyst zone of the TZTR is the difference between two diffusional flow rates at the boundaries of the thin active zone divided by the mass of catalyst in the reactor:

$$R_{W,i} = \frac{F_i(t) - F_{i0}(t)}{W_{\text{cat}}} . \quad (2.17)$$

This is analogous to the case of the steady-state CSTR, in which the reaction rate is given by the difference between convectational flow rates.

2.2 How to simplify complex models? Principles of simplification

This section is devoted to approaches of simplification of chemico-mathematical models. Many of them have been categorized in the recent monograph by Constales et al. [7] Most of this activity is performed for *models of detailed kinetics (microkinetics)*, i.e., models based on a detailed chemical mechanism.

In science and engineering, simplification is not only a method for the easy and efficient analysis of processes, but it also is a necessary step in understanding their behavior. In many cases, “to understand” means “to simplify”. Now the main question is: “Which separate process or set of processes are responsible for the observed characteristics?” Frequently, simplification is defined as a reduction of the “original” set of system factors (processes, variables, parameters) to the “essential” set for revealing the behavior of the system, observed through real or virtual (computer) experiments. Every simplification must be correct. In physical science and chemical engineering, the answer to this question very much depends on the details of the reaction mechanism and on the temporal domain that we are interested in.

As a basis of simplification, many physicochemical and mathematical principles/methods/approaches or their efficient combination are used, such as fundamental laws of mass conservation and energy conservation, the dissipation principle, the principle of the detailed equilibrium, etc. Based on these concepts, many advanced methods of simplification of complex chemical models have been developed [3, 4].

In the mathematical sense, simplification can be defined as “model reduction”, that is, the rigorous or approximate representation of complex models by simpler ones. For example, in a certain domain of parameters or times, a model of partial differential equations (“diffusion-reaction” model) is approximated by a model of differential equations, or a model of differential equations is approximated by a model of algebraic equations, etc. See also [8–11].

2.2.1 Physicochemical assumptions of simplification of chemico-mathematical models

Typically, assumptions are made on substances, on reactions and their parameters, on transport-reaction characteristics and experimental procedures as well. Presenting these assumptions, we follow the monograph by Constaes et al. [7].

2.2.1.1 Assumptions on substances

1. Abundance of some substances in comparison with others, so their amount/concentration can be assumed to be constant during the process, either steady state or non-steady state. For example, in aqueous-phase reactions, the water concentration is often taken as a parameter in kinetic reaction models.
2. Insignificant change of some substance amount/concentration in comparison with its initial amount/concentration during a non-steady-state process. For example, in pulse-response experiments under high vacuum conditions in a temporal-analysis-of-products (TAP) reactor the total number of catalytic active sites is much larger than the amount of gas molecules injected in one pulse. Therefore, the concentration of active catalyst sites may be assumed to remain approximately equal during a pulse-response experiment.
3. Dramatic increase of the concentration/temperature at the very beginning of a process in a batch reactor or at the inlet of a continuous-flow reactor, typically is presented by a delta function or step function.
4. Complete conversion of some substances in time during the process or at the very end (the final section) of the chemical reactor.
5. Gaussian distribution of the chemical composition regarding some physicochemical properties, e.g., the molecular weight of polymers.
6. Assumptions on intermediates of complex chemical reactions:
 - (a) Abundance of some intermediates. Frequently, the concentrations of many intermediates are very small compared to the concentrations of others. At the limit, only one intermediate dominates. For heterogeneous catalysis, the term “most abundant reaction intermediate” (MARI) is used. This term introduced by Boudart means the only important surface intermediate on the catalyst surface under reaction conditions.

- (b) Quasi-steady state (QSS) for some intermediates. Some intermediates can be in a quasi-steady state, or pseudo-steady state (PSS). In the literature, the meanings of the terms “pseudo” and “quasi” are a bit different. “Pseudo” is from Greek, meaning “false” or “not real(ly)” and is typically used for situations where deception is deliberate. “Quasi” is from Latin, meaning “almost”, “as if” or “as it were”. It is often used to describe something that for the most part behaves like something else, but not completely. Hence, we prefer to use “quasi” to describe this type of (non)steady state.

A quasi-steady-state assumption relates to reaction intermediates whose rate of change follows the time evolution of the concentrations of other species. Per the quasi-steady-state assumption the rates of production and consumption of intermediates are approximately equal, so their net rate of production is approximately equal to zero.

Two typical uses of the quasi-steady-state assumption are in:

1. Gas-phase chain reactions (e.g., oxidation reactions) are propagated by free radicals, that is, species having an unpaired electron (H, O, OH, etc.). The kinetic parameters of reactions in which these short-lived, highly reactive free radicals participate are much larger than the kinetic parameters of reactions involving other species. Their concentration in the quasi-steady state is necessarily small.
2. Gas-solid catalytic reactions occur through catalytic surface intermediates. These are not necessarily short-lived, but their concentrations are much smaller than the concentrations of reactants and products of the overall reaction. Therefore, the kinetic dependencies of the surface intermediates are governed by the concentrations of the gaseous species. A similar reasoning holds for enzyme-catalyzed biochemical reactions, in which the number of active enzyme sites is small compared to the number of substrate and product molecules.

2.2.1.2 Assumptions on (processes) reactions and their parameters

Assumption on irreversibility of processes (reaction steps):

1. All Processes (reaction steps) are irreversible, i.e., strong irreversibility or
2. Some processes (reaction steps) are irreversible, i.e., weak reversibility.

Rigorously speaking, all reaction steps are reversible. If the rate of the forward reaction is much larger than that of the reverse reaction, we consider the reaction step to be irreversible. If in a sequence of steps, say in a heterogeneous catalytic cycle, at least one step is irreversible, the overall reaction can be irreversible.

Assumption on “rate-limiting or rate-determining step”:

In a sequence of reaction steps there usually are “fast” steps and “slow” steps. The kinetic parameters of the slow steps are much smaller than those of the fast steps, reversible or irreversible, and kinetic dependencies are governed by these small pa-

rameters. If there is only a single slow step, this is called the rate-limiting or rate-determining step. However, this is not a rigorous definition of the “rate-limiting-step” concept, which remains a subject of permanent fierce discussions [8, 10, 12]. In their paper [12], Kozuch, and Martin express a provocative opinion on this subject.

Assumption of “quasi equilibrium” or “fast equilibrium”:

If in a sequence of steps both the forward and reverse reactions of some reversible steps are much faster than other reaction steps, the assumption can be made that the forward and reverse reactions of such fast steps occur at approximately equal rates, i.e., are at equilibrium. Typically, this assumption is justified by the fact that the kinetic parameters of these fast steps are much larger than the kinetic parameters of the other, slow steps. For many chemical systems, the assumption of quasi equilibrium is complimentary to the assumption of a rate-limiting step; if one step is considered to be rate limiting, other, reversible, steps can be assumed to be at equilibrium.

Assumption of equality or similarity of chemical activity:

Based on a preliminary analysis some groups of species with identical or similar chemical functions or activities can be distinguished, e.g., a family of hydrocarbons of similar activity can be represented by just one hydrocarbon. This is the so-called lumping procedure.

Additional assumptions on parameters:

1. Assumption of equality of parameters of some steps, e.g., kinetic parameters of some adsorption steps or even coefficients of all irreversible reactions are equal.
2. Assumption of “fast step”, that is, the kinetic parameter of a certain step is assumed to be much larger than the kinetic parameters of other steps.
3. Assumption regarding the hierarchy of kinetic parameters, e.g., in catalytic reactions adsorption coefficients are usually much larger than the kinetic parameters of reactions between different surface intermediates.

Principle of critical simplification:

In accordance with this principle (Yablonsky et al., [13]), the behavior near critical points, for instance ignition or extinction points in catalytic combustion reactions, is governed by the kinetic parameters of only one reaction – adsorption for ignition and desorption for extinction – which is not necessarily the rate-limiting one.

2.2.1.3 Assumptions on transport-reaction characteristics

1. Assumption of continuity of flow. When a fluid is in motion, it must move in such a way that mass is conserved.
2. Assumption of uniformity of chemical composition, and/or temperature, and/or gas pressure in a chemical reactor.

3. Assumption of transport limitation, i.e., an assumption under which a model only comprising transport can be used (fast reaction and slow transport, in particular diffusion limitation).
4. Assumption of kinetic limitation, i.e., an assumption under which a model only including reaction can be used (fast advection or fast diffusion and slow reaction, kinetic limitation).

2.2.1.4 Assumptions on experimental procedures

1. Assumption of insignificant change of the system characteristics during an experiment involving a small perturbation of the system, i.e., a state-defining experiment.
2. Assumption of controlled change of the system characteristics during an experiment, i.e., a state-altering experiment.
3. Assumption of instantaneous change, i.e., instantaneous injection of a reactant into a chemical reactor.
4. Assumption of linear change of the controlled parameter, e.g., a linear temperature increase during thermodesorption.

2.2.1.5 Combining assumptions

It should be noted that some physicochemical assumptions are overlapping and some are complimentary. For example, if some steps are fast, we automatically assume that other steps are slow. In the simplest case – the two-step mechanism – the assumption of a fast first step is identical to the assumption of a rate-limiting second step. Assumptions on the abundance of species and rate-limiting steps can be made both for reversible and irreversible reaction steps. In contrast, the quasi-equilibrium assumption cannot be applied to a set of reaction steps that are all reversible. Sometimes many assumptions, not just one or two, are used for the development of a model. An example is the Michaelis–Menten model that is well known in biocatalysis. In this model,

1. The total amount of active enzyme sites is much smaller than the amounts of liquid-phase substrate (S) and product (P). Because of that quasi-steady-state behavior of the enzyme species (free enzyme E and substrate-bound enzyme ES) is observed.
2. The first step ($E + S \rightleftharpoons ES$) is assumed to be reversible, while the second step ($ES \rightarrow P + E$) is assumed to be irreversible.
3. The kinetic parameters of the first step are assumed to be much larger than those of the second step, i.e., the first step is fast and the second step is slow.

Therefore, there are two simultaneous assumptions, i.e., the assumption of quasi-equilibrium of the first step and the assumption that the second step is rate-limiting.

2.3 Mathematical concepts of simplification in chemical kinetics

A primary analysis of different types of mathematical simplifications was done in the monograph by Constales et al. [7]. In modeling, it is not enough to represent assumptions or simplifications expressed in a verbal way. Physicochemical assumptions have to be translated into the language of mathematics. In 1963, Kruskal [14] introduced a special term for this activity, “asymptotology”. See Gorban et al. [8] for a detailed analysis. Mathematical models should be developed based on assumptions with a clear physicochemical basis. Every physicochemical assumption has a domain of its correct application, and this domain must be validated. Typically, this is done using the “full” model that includes the “partial” model, the validity of which is tested. The partial model is generated asymptotically from the full model and the correctness of this asymptotic procedure must be proven [10]. As stressed by Gorban et al. [8] “... often we do not know the rate constants for complex networks, and kinetics that is ruled by orderings rather than by exact values of rate constants may be very useful in practically frequent situations when the values of the various reaction constants are unknown or poorly known”.

A mathematical analysis founded on the basic laws of physics, e.g., laws of thermodynamics, may provide us with an understanding of “tricks” of which the physicochemical meaning was previously unclear or even with a formulation of new fundamental concepts. The lumping procedure, a commonly-used approach to reduce the number of chemical species and reactions to be handled by grouping together species having similar chemical functions or activities into one pseudo-component or lump, was theoretically grounded and realized by Wei and Prater [15] and Wei and Kuo [16]. Complex chemical behavior that was discovered in chemical systems in the 1950s–1970s, such as bistability, oscillations, chaotic behavior, etc. has been understood only by transferring and adapting the concepts of the mathematical dynamic theory (stability, bifurcation, catastrophes, chaos, etc.). Maas and Pope [11] efficiently used the mathematical technique of manifolds for understanding combustion processes. At the same time, many mathematical tools applied to chemical problems still remain “purely mathematical”, not having a special chemical content, e.g., many methods of statistical analysis, sensitivity analysis, etc.

2.3.1 Mathematical status of the quasi-steady-state (QSS) approximation

In chemico-mathematical modeling, revealing the rigorous mathematical status of the quasi-steady-state approximation was one of the most challenging problems. This assumption was introduced into chemistry at the very beginning of the twentieth century. However, it was clarified only about fifty years later via the mathematical theory of singular perturbations, and even now this knowledge is not sufficiently widespread within the chemical and chemical engineering community. One can say that this ap-

proximation is the most applied and the least understood. It can be called “*the most complicated simplification*”.

First, the quasi-steady state is not a steady state; it is a special type of non-steady state. The popular version of the quasi-steady-state approximation can be formulated as follows. During a chemical process, the concentrations of both species present in large amounts, usually the controllable and observed species, and species present in small amounts (intermediates such as radicals and surface intermediates), usually the uncontrollable and unobserved species, change in time. In the quasi-steady-state approximation, the concentrations of the intermediates become functions of the concentrations of the observed abundant species; they “adapt” to the concentrations of the observed species as if they were steady-state concentrations.

Within the traditional mathematical QSS-procedure, three steps can be distinguished:

1. Write the non-steady-state model, that is, a set of ordinary differential equations for both the observed species and the unobserved intermediates;
2. Then replace the differential equations for the intermediates with the corresponding algebraic equations by setting their rates of production equal to their rates of consumption, so that the net rate of production is zero, which in the case of catalytic surface intermediates translates into putting:

$$\frac{d\theta_j}{dt} = 0 ,$$

where θ_j is the normalized concentration of surface intermediate j , and then solving these equations, such that the concentrations of intermediates are expressed as a function of the concentrations of the observed species and temperature. In fact, solving this set of equations is quite easy for linear models, but for nonlinear models this may not be so simple;

3. Finally, expressions for the reaction rates of the observed species can be constructed terms of the reactant and product concentrations of the overall reaction only.

The rigorous mathematical theory of quasi-steady-state approximation is the following. A complex reaction mechanism consisting of a combination of subsystems related to the observed variables x and unobserved variables y can be described by the general model:

$$\begin{aligned} \frac{dx}{dt} &= f(x, y) , \\ \frac{dy}{dt} &= g(x, y) . \end{aligned}$$

The subsystems are called subsystems of “slow” and “fast” motion, respectively. The mathematical validity of the quasi-steady-state approximation can be illustrated by

scaling the original set of equations and writing it in dimensionless form as

$$\begin{aligned}\frac{d\bar{x}}{dt} &= f(\bar{x}, \bar{y}), \\ \varepsilon \frac{d\bar{y}}{dt} &= g(\bar{x}, \bar{y}),\end{aligned}$$

in which ε is the so-called “small parameter” ($\varepsilon \ll 1$). At the limit $\varepsilon \rightarrow 0$, this system transforms into the so-called “degenerated” set of equations

$$\begin{aligned}\frac{d\bar{x}}{dt} &= f(\bar{x}, \bar{y}), \\ 0 &= g(\bar{x}, \bar{y}).\end{aligned}$$

Different actual systems generate the small parameter ε in different ways, and Yablonskii et al. [3] have indicated different scenarios for reaching quasi-steady-state regimes. For example, in homogeneous chain reactions, the small parameter is a ratio of rate coefficients. It arises because the reactions in which unstable and thus short-lived free radicals participate are much faster than the other reactions.

In heterogeneous gas-solid catalytic systems, the small parameter is the ratio of the total amount of surface intermediates $n_{t,int}$ to the total amount of reacting gas molecules $n_{t,g}$ which are present in the reactor. Summing up the theoretical analysis of the quasi-steady-state problem, we can distinguish two types of behavior:

1. a quasi-steady state caused by a difference in kinetic parameters (rate-parametric QSS);
2. a quasi-steady state caused by a difference in mass balances of species (mass-balance QSS).

2.3.2 Limits of simplification: optimal model

Every simplification has a limit. Please remember: Simple, but not too simple; complex, but not too complex. Obviously, the level of minimal complexity depends on the amount of available information. In the literature, the corresponding model is termed a “minimal”, or “optimal”, or “rational”, or “skeleton” model. See the concept of the minimal mechanism described by Marin and Yablonsky [4]. The question answered was: “What is the minimum number of steps of the detailed mechanism?”. Certainly, this number is not smaller than two because otherwise there would not be a catalytic cycle, which should include not smaller than two steps. E.g., for the Michaelis–Menten mechanism with one substrate (S) and one product (P), the minimal mechanism has two steps, not more. Then the properties of the minimal mechanism are summarized in a very simple way, depending on whether the number of reactant molecules in the overall reaction is larger or smaller than or equal to the number of product molecules. If the number of reactant molecules is bigger than the number of product molecules,

the number of steps is equal to the number of reactant molecules. Similarly, if the number of product molecules is bigger than the number of reactant molecules, the number of steps is equal to the number of product molecules. Based on the minimal mechanism, the minimal kinetic model will be constructed.

There is no a general theory how to determine the “optimal model”. In every concrete case, such a model is generated via special systematic studies.

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Part II: **Chemical modelics**

3 Basic models of chemical kinetics

This chapter is devoted to a gallery of mathematical models which describe the critical phenomena of a pure chemical, nonthermal nature. Nonlinearity of systems is caused by reaction mechanisms, which are nonlinear. In typical cases, these systems are systems of ordinary differential equations with right parts which contain nonlinearities of type $X_m Y_n$. As shown in [1, 2], the presence of interaction steps of various substances (e.g., $X + Y \rightarrow$) is a necessary condition for multiplicity of steady states. Sufficient conditions of their occurrence can be determined by different factors: the presence of competition in the different stages (their different kinetic order), the presence of so-called buffer steps, the nonideality of elementary processes, the ratio of special parameters, etc. One of the most important kinetic characteristics is the presence of autocatalytic stages of type $A + Z \rightarrow 2Z$ in a reaction mechanism. We must say that such stages are present in the abstract mechanisms of chemical reactions studied in the works of I. Prigogine and his school [3–5]. These are all sorts of “oregonator”, “brusselator”, etc. The formal model of O. Rossler [6] also contains members which can be interpreted as the autocatalysis.

The models with the autocatalysis are the simplest models in sense of their degree of nonlinearity and the number of phase variables. Catalytic schemes of transformations which do not contain autocatalytic stages are more realistic, but they lead to systems of larger numbers of variables. The main complicating factors as a flow of the system, the presence of two or more types of active centers (multifunctional catalysis), and chemical nonideality are studied here. Main results of the analytical study are accompanied by graphical pictures. In particular, each model is characterized by its parametric portrait, where bifurcation curves divide the all parameter region into subregions of parameters with different number and type of stability of steady states.

3.1 Equations of chemical kinetics and a scheme of parametric analysis

3.1.1 Experimental background

Recently the research area of critical phenomena in kinetics has increased considerably. The discovery and study of such effects have a long history [7]. The beginning of a modern step is considered to be the detection by B.P. Belousov and the study by A.M. Zhabotinsky of oscillations in the oxidation reaction of malonic acid by bromine (catalysis – ions of the cerium) [8, 9]. It should be noted that publications on experimental studies of oscillation modes of chemical reactions appear in the beginning of the last century [7]. However, only this reaction (now called the B.Z.-reaction) has

caused a surge of attention among chemists, physicists, biologists and mathematicians.

Homogeneous systems are more simple than heterogeneous ones. Therefore, a study of homogeneous models will facilitate the understanding of the character of chemical oscillations [10]. Overviews of the main part of the experimental works on the Belousov–Zhabotinsky reaction and its modifications are presented in the book [8]. However, a single comprehensive mathematical model is not built. There is a significant number of kinetic models describing individual properties of these systems with varying degrees of detail. It seems to us that in this case there is a certain contradiction between the “want to know all” and “select the most important factors”.

Lately, oscillatory reactions occurring in the gas phase have been investigated [11, 12] intensively. One of the most studied isothermal systems is the reaction of oscillatory oxidation of carbon monoxide. Gas-phase oscillators can be divided into isothermal and thermokinetic types. The first of them are characterized by nonlinearities of a nonthermal nature, which correspond to the presence of nonlinear stages in the reaction mechanism. The nonlinear nature of thermokinetic oscillations due to nonlinear dependence (in the simplest case the Arrhenius equation) of the reaction rate on temperature.

I. Prigogine’s scientific school introduced a significant contribution to the development of understanding and interpretation of complex dynamic behavior of open chemical systems far from thermodynamic equilibrium [3–5]. A brief review of relevant models is given in [6].

Critical phenomena were discovered in many heterogeneous catalytic reactions, some of which have important application value to chemical technology. G.K. Boreskov, M.G. Slinko and employees studied a hydrogen oxidation reaction on nickel, palladium and platinum. They found that different values of the stationary reaction rate correspond to the same composition of the gas phase in definite region of parameters [13–25]. Since the early 70s there has been a new wave of intensive experimental and theoretical studies of critical effects in heterogeneous catalysis. It was the first cycle of works by M.G. Slinko and his disciples [26–34].

Critical phenomena in oxidation reactions of CO over Pt/Al₂O₃ and platinum wires are described in the works of E. Wicke (see, e.g., [27]). In these works, the authors showed that the multiplicity of steady states is due to the nonlinearity of the rate of formation and spending of intermediates on the catalyst surface. An important conclusion of E. Wicke and coauthors is that the cause of a complex dynamic behavior of a reaction lies in the complex chemistry of the processes on the catalyst surface. E. Wicke’s line was continued by G. Eigenberger. To describe auto-oscillations of the rate of a catalytic reaction, he used the “buffer” step. Reversible stages of the formation of nonreactive able forms of oxygen or inert substance were added to E. Wicke’s scheme. The “buffer” step performs the role of “feedback”, but this step has allowed G. Eigenberger to describe the oscillations of rates obtained in experiments. [35]

The existence of kinetic auto-oscillations in heterogeneous reactions has been shown in the works of M.G. Slinko, V.D. Belyaev, and others [36–38]. The main nonlinear factor was accepted as the dependence of the activation energy on the degree of coverage of the catalyst surface by one of the intermediates. The mathematical models were built using this.

In the works of V.V. Barelko and A.S. Zhukov isothermal effects were investigated in a number of heterogeneous catalytic reactions with the help of a device they created, allowing them to exclude the influence of the thermal factor [39–42].

The number of works devoted to nonstationary processes in catalysis is constantly growing. To represent time a great deal of experimental data on the phenomena of self-organization in heterogeneous catalysis has been accumulated. Critical phenomena were observed for many heterogeneous oxidation reactions of hydrogen, carbon monoxide, carbon monoxide, nitrogen, and sulfur dioxide [27]. Such metals as platinum, palladium, iridium, and nickel are used in all works as a catalyst. Authors mainly consider the multiplicity of steady states and auto-oscillations [45–68].

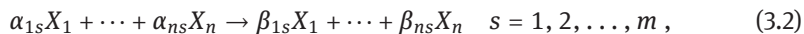
In our book the central theme is a theme associated with the building and analysis of so-called basic mathematical models of critical phenomena of both thermal and nonthermal nature. In a sense they are the simplest models describing the multiplicity of steady states (triggers) and auto-oscillations (oscillators). The concept of basic models, developed by us, primarily supposes an understanding of the studied phenomenon. Then, a detailed description is created. The basic models are the kinds of blocks which must be put in the foundation of each detailed model. At this step we achieve not only a qualitative but also a quantitative description of the complex nonlinear and dynamic properties of the studied processes.

3.1.2 Equations of chemical kinetics

The equations of chemical kinetics are written as follows [1]. First, the list of substances is set as

$$X_1, X_2, \dots, X_n, \quad (3.1)$$

and the list of reactions becomes



where α_{1s}, β_{1s} are stoichiometric coefficients.

Further, the rates of stages in scheme (3.2) are defined:

$$w_s = w_s(T, \mathbf{x}), \quad s = 1, 2, \dots, m, \quad (3.3)$$

where T is temperature and $\mathbf{x} = (x_1, x_2, \dots, x_n)$ is a vector of the concentrations of the substances (3.1).

The most simple kinetic functions (3.3) satisfy the law of mass action:

$$w_s(T, \mathbf{x}) = k_s(T) x_1^{\alpha_{1s}} \cdots x_n^{\alpha_{ns}}. \quad (3.4)$$

The temperature dependencies are defined by Arrhenius:

$$k_s(T) = k_s^0 \exp\left(-\frac{E}{RT}\right), \quad s = 1, 2, \dots, m.$$

The law of conservation of mass in a nonstationary case at $T = \text{const}$ takes the form

$$\frac{dx_i}{dt} = \sum_{s=1}^m \gamma_{is} w_s, \quad i = 1, 2, \dots, n, \quad (3.5)$$

where $\gamma_{is} = \beta_{is} - \alpha_{is}$.

The equation of chemical kinetics (3.5) can be written down in compact vector form:

$$\frac{d\mathbf{x}}{dt} = \mathbf{\Gamma} \mathbf{w}(T, \mathbf{x}), \quad (3.6)$$

where $\mathbf{w} = (w_1, w_2, \dots, w_m)$ is a vector of the rates of the stages. The stoichiometric matrix $\mathbf{\Gamma} = ((\gamma_{is}))$ is such that the law of conservation of mass is performed for (3.5):

$$B_j: \quad \sum_{i=1}^n m_{ij} x_i = b_j, \quad j = 1, 2, \dots, l,$$

where b_j are the quantities of balances and m_{ij} are quantities proportional to the number of atoms of the j -th type contained in the i -th substance X_i .

The system (3.6) is defined in the polyhedron of the reaction in which the conditions of nonnegativity and balances are set B_j :

$$\mathbf{M} = \{x: x \geq 0, x \in B_j\}.$$

The model (3.6) represents a system in which no exchange of substances occurs with the environment. It can be a chemically reacting closed system or an open system far from equilibrium due to the persistence of some part of the reagent.

Thus, the basic model of chemical kinetics is a system of nonlinear differential equations (3.6) in the general case, in which the right-hand sides are formed according to the mechanism of transformations. General analysis of models of type (3.6) is given in [1]. Here we only note that a necessary condition for the multiplicity of steady states is the presence in the mechanism of the reaction stages of interaction of various substances. If there are no such stages, the behavior of (3.6) will be quasithermodynamic. For all initial conditions from the polyhedron reactions all solutions of the dynamic model (3.6) for $t \rightarrow \infty$ will approach a single stationary state. The equations of chemical kinetics (3.6) are a special case of dynamical systems of the general type. In the simplest case, the right-hand sides of equations (3.6) are polynomials in the phase variables $x_1, \dots, x_n$.

However, they have sufficient commonality. Multitudes of equations of chemical kinetics are everywhere dense in the set of dynamical systems. The probability of this assertion is very high because on any finite time interval, any sufficiently smooth dynamical system can be approximated with any prescribed accuracy by a dynamical system whose right-hand sides represent finite Taylor series. After that you can use E.M. Korzukhin's theorem [8] on the possibility of approximating a dynamical system with polynomial right-hand sides by a system of equations of chemical kinetics.

3.1.3 Scheme of parametric analysis

Here, we briefly describe a scheme of parametric analysis of a dynamical system. The investigated real process usually occurs under certain external conditions, which can be characterized by some parameter values. These parameters are included in the appropriate kinetic model, which is a system of ordinary differential equations of the form

$$\dot{x}_i = f_i(x_1, \dots, x_n, p_1, \dots, p_m), \quad i = 1, \dots, n, \quad (3.7)$$

where x_i are phase variables (temperature and concentration of substances) and p_j , $j = 1, \dots, m$, are parameters which can be varied within certain limits. Parameters are usually chosen as thermal, physical and geometrical characteristics of a real process, such as temperature and concentrations of substances at the inlet to the reactor, their initial values, the volume of the reactor, and so on.

The first step in the parametric analysis of system (3.7) is the definition of its steady states. For model (3.7) the steady states are solutions of the system of equations

$$f_i(x_1, \dots, x_n, p_1, \dots, p_m) = 0, \quad i = 1, \dots, n, \quad (3.8)$$

in the unknown variables $x_1, \dots, x_n$. If system (3.8) can be solved in explicit form

$$x_i = \varphi_i(p_1, \dots, p_m), \quad i = 1, \dots, n,$$

we obtain the required parameter dependencies of steady states on parameters. Generally, if we cannot solve (3.8) in explicit form, the steady states and their dependencies on parameters should be found by rather hard computational procedures. However, the system of stationarity equations often can be reduced to one equation by elementary transformations

$$F(x, p_1, \dots, p_m) = 0, \quad (3.9)$$

where x is one of the phase coordinates x_i . The nonlinear equation (3.9) may have multiple solutions, which leads to a multiplicity of steady states. Variation of p_j , $j = 1, \dots, m$, in this case leads to the hysteresis of stationary dependencies on parameter.

The second step of the procedure of parametric analysis of system (3.7) is the investigation of the stability of steady states. It is necessary to form the Jacobian matrix

with elements:

$$a_{ij} = \frac{\partial f_i}{\partial x_j}(x^*), \quad i, j = 1, \dots, n,$$

where the value x^* is responsible for a steady state. The stability of steady states is determined by the eigenvalues λ_i , $i = 1, \dots, n$, of the Jacobian matrix. If all λ_i have nonzero real part, the steady state will be rude. Its stability is determined by the sign of $\text{Re } \lambda_i$.

An important step of parametric analysis is the construction of the parametric dependencies of $\varphi_i(p_1, \dots, p_m)$. In the general case this task is related to the solution of nonlinear systems with parameters. Computing and software tools for their solution are presented in [69–79]. In the study of specific systems it is sometimes possible to significantly simplify the procedure of constructing the parametric dependencies. Our experience shows that the parameters in the stationary equation (3.9) are generally such that you can write the parametric dependencies from (3.9) in explicit form.

$$p_j = \eta_j(x), \quad j = 1, \dots, m,$$

where x is varied. Thus, it is possible to obtain the function which is the reverse of the required parametric dependence $x = \varphi(\text{integer})$, $j = 1, \dots, m$. If, for example, the functions $\eta_j(x)$ are given in graphical form, the function $\varphi(\text{integer})$ will be obtained simply by inverting the coordinates x and p_j .

If one of the parameters, for example, p_1 , is changed, there exist its special (bifurcation) values for which the number and stability of steady states is changed. Changing the second parameter p_2 leads to the result that in the (p_1, p_2) plane the bifurcation values of p_1 describe some curves which are bifurcation curves. In the simple case of dynamical systems ($n = 2$) there are two basic bifurcation curves on the plane: the curve of multiplicity of steady states L_Δ and the neutrality curve L_σ . The stability of steady states is determined by the roots of the second order characteristic equation

$$\lambda^2 - \sigma\lambda + \Delta = 0,$$

where $\sigma = a_{11} + a_{22}$ and $\Delta = a_{11}a_{22} - a_{12}a_{21}$. Let's take the two parameters p_1, p_2 , and plot L_Δ, L_σ in the plane of these parameters. The boundaries of the region of the multiplicity of steady states is defined as a solution of the system

$$F(x, p_1, p_2) = 0,$$

$$\Delta(x, p_1, p_2) = 0,$$

which can be represented in the form

$$p_2 = \xi_2(x),$$

$$p_1 = \xi_1(x, \xi_2(x)),$$

where x is the changed value.

To plot the curve of neutrality L_σ , the stationarity equation must be added by the condition

$$\sigma(x, p_1, p_2) = 0.$$

From this condition the equation for the curve of neutrality can be often written in explicit form

$$\begin{aligned} p_2 &= \xi_2(x), \\ p_1 &= \xi_3(x, \xi_2(x)). \end{aligned}$$

Analysis of mutual location of curves L_Δ, L_σ in the plane (p_1, p_2) allows us to define the parametric portrait of the system. Curves L_Δ, L_σ allow for any values of the selected parameters to determine the number and stability of the steady states.

Useful information about the possible dynamic behavior of solutions of model (3.7) gives the plotting of phase portraits. The plotting of the phase portrait of system (3.7) for each given set of parameters from the selected region on the parametric portrait is performed by using numerical integration of (3.7) with different initial data. Each region of the parametric portrait matches its own type of phase portrait. The enumeration of all possible types of phase portraits is a rather time-consuming task [78]. However, in some specific cases, such a complete study is possible [79–83].

Complete representation of the dynamics of system (3.7) is given by time dependencies $x_i = x_i(t, p_1, \dots, p_m)$. The solutions $x_i(t)$ are usually found by numerical integration of differential equations (3.7) for a fixed set of parameters p_j . Technical difficulties are present, and here they are connected first of all with the “rigidity” of the system of ordinary differential equations (3.7).

Consider a system of nonlinear equations with a parameter:

$$\mathbf{f}(\mathbf{x}, \alpha) = 0, \quad (3.10)$$

where $\mathbf{x}$ is a vector of unknowns, α is a parameter, and $\mathbf{f}$ is a vector function. The system (3.10) implicitly specifies the dependence:

$$\mathbf{x} = \mathbf{x}(\alpha). \quad (3.11)$$

Plotting this dependence is the main goal of a parametric analysis of the solutions of system (3.10). The general scheme of the method of parameter continuation [73, 78] is as follows. Using the substitution (3.11) in (3.10) and differentiating the resulting identities we have

$$\mathbf{J} \frac{d\mathbf{x}}{d\alpha} + \frac{\partial \mathbf{f}}{\partial \alpha} \equiv 0, \quad (3.12)$$

where $\mathbf{J}$ is the Jacobian matrix of system (3.10):

$$\mathbf{J} = \frac{\partial \mathbf{f}}{\partial \mathbf{x}}(\mathbf{x}, \alpha). \quad (3.13)$$

We consider the identity (3.12) as a system of linear equations for $d\mathbf{x}/d\alpha$. The equations of motion for the parameter can be gotten from the identity (3.12).

$$\frac{d\mathbf{x}}{d\alpha} = -\mathbf{J}^{-1} \frac{\partial \mathbf{f}}{\partial \alpha}. \quad (3.14)$$

The required parametric dependence of $\mathbf{x}(\alpha)$ is the solution of a system of ordinary differential equations (3.14) for some given initial data

$$\mathbf{x}(\alpha_0) = \mathbf{x}^0.$$

The specificity of system (3.14) is that at the bifurcation points of solutions of (3.10) the Jacobian matrix $\mathbf{J}$ is special. Therefore, for the numerical integration of (3.14) we proceed to the parameterization by the arc length of the curve $\mathbf{x}(\alpha)$ in the appropriate space of dimension $\dim \mathbf{x} + 1$. Note that for the integration of system (3.14) special methods should be applied, including those based on the calculation of the Jacobian matrix [78]. In this case, you must have the partial derivatives $\frac{\partial}{\partial \mathbf{x}} (\mathbf{J}^{-1} \frac{\partial \mathbf{f}}{\partial \mathbf{x}})$, and that leads to additional technical difficulties. System (3.14) is often written on the basis of the solution of (3.12), for example by the Gauss method relative to $d\mathbf{x}/d\alpha$. When solving (3.14) a problem of getting sufficient accuracy initial data appears. All of this suggests that the numerical implementation of the method of parameter continuation is a rather time-consuming computational task. The degree of its complexity depends essentially on the dimension of system (3.10). The computational cost is significantly reduced by lowering, if possible, the number of equations in (3.10) due to the exclusion of some variables.

Consider the special case when the original system (3.10) can be reduced to one equation

$$g(x, \alpha) = 0,$$

where g is a scalar function of one argument x and parameter α . Similarly to (3.12) from differentiating the identity $g(x(\alpha), \alpha) \equiv 0$ we have

$$\frac{dx}{d\alpha} = -\frac{\partial g}{\partial \alpha} / \frac{\partial g}{\partial x} \quad (3.15)$$

or

$$\frac{d\alpha}{dx} = -\frac{\partial g}{\partial x} / \frac{\partial g}{\partial \alpha}. \quad (3.16)$$

The required parametric dependence $x(\alpha)$ or the inverse dependence $\alpha(x)$ is found by numerical integration of one of the equations (3.15) or (3.16). Equation (3.15) or (3.16) is integrated (at moving on a curve $x(\alpha)$) depending on a value of the right side of the equation. At the turning points $(\partial g / \partial x)$ or $(\partial g / \partial \alpha)$ is zero. Therefore, the following inequality can be accepted by the selection condition of motion on α or on x

$$\left| \frac{\partial g}{\partial \alpha} / \frac{\partial g}{\partial x} \right| < 1. \quad (3.17)$$

In the numerical integration of the equations (3.15) or (3.16), there must be an “inversion” of the system, i.e., the transition from equation (3.15) to equation (3.16) or on the contrary depending on the implementation of (3.17). The integrator must include verification of the value of the right side of (3.15) or (3.16) and implement this inversion for