

Introduction

1.1 Overview

Chemistry is a complex science, especially for chemists. The etymology of the word “chemistry,” the science of matter and its transformations, is a debatable issue [1]. It is very likely that it has been borrowed from the ancient name for Egypt, “Keme” the birthplace of alchemy. The word “complex” comes from the Latin word “complexus” the past participle of “complecti” (to entwine, encircle, compass, infold), from “com” (together) and “plectere” (to weave, braid).

Decoding complexity is considered one of the main scientific problems of the twenty-first century. In chemistry, this process of decoding aims at explaining the temporal evolution of a multicomponent chemical mixture. In this book, depending on the context, there are three different meanings of “time”:

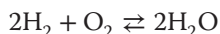
1. *“Clock” time, or astronomic time, or “external” time of the system, t :* This time relates to the change of chemical composition observed during some time interval.
2. *“Internal” or “intrinsic” time:* Typically, we consider this time when we are talking about the hierarchy of times of different chemical processes or reactions. For a first-order reaction, the intrinsic time, that is, the timescale at which the reaction occurs, is the reciprocal value of its rate coefficient that has the dimension per second.
3. *Residence time:* This time reflects the “transport time” of a chemical process, for example, in a plug-flow reactor (PFR) (see Chapter 3).

An excellent collection of the different meanings of time can be found in Ref. [2].

Formally, the non-steady-state model for a chemical process in a closed system (batch reactor) is identical to the steady-state model for the same chemical process in an open system in which the longitudinal profile of the chemical composition is taken into account, but the radial profile is neglected (see Chapter 3 for more details). In the latter model, the space time, which is proportional to the residence time, corresponds to astronomical time in the model for the batch reactor.

In the description of chemical complexity, the first key words are “many components,” “many reactions” and “change,” that is, a multicomponent chemical mixture changes in time and space. For example, in the homogeneous gas-phase

oxidation of hydrogen



there are as much as nine different components and as much as 60 reactions involved. See Chapter 2 for more details.

In heterogeneous reactions, for example gas–solid reactions, the situation becomes even more complicated. Rephrasing Lewis Carroll’s saying from *Alice in Wonderland*, “curiouser and curiouser,” one can say “complexier and complexier.” Over 90% of industrial chemical reactions occur with solid catalysts that can dramatically accelerate these reactions. Many catalysts are multicomponent solids, for example, mixed transition metal oxides on some support used in the selective oxidation of hydrocarbons. Catalysts can exist in different states that depend on the oxidation degree, water content, bulk structure, and so on. These states have different physicochemical properties and different abilities to accelerate reactions. Moreover, the catalyst composition changes in time under the influence of the reaction medium. This is the level of chemical complexity that needs to be decoded.

1.2 Decoding Complexity in Chemical Kinetics

Immediately, many questions regarding this decoding arise:

1. What are we going to decode?
2. Based on which experimental characteristics are we going to decode?
3. In which terms are we going to decode?

In this book, our answers are the following:

1. We are going to decode data mostly related to heterogeneous catalytic reactions.
2. We are going to decode these data based on experimental characteristics obtained during kinetic experiments, that is, measurements of rates of transformation of chemical components.
3. We are going to try and interpret these kinetic data based on the concept of *reaction mechanism* (or *detailed mechanism*), a detailed description of the steps leading from reactants to products of the reaction, which includes intermediates.

We consider this decoding to be an inherent feature of chemical kinetics, which can be defined as the science of rates and mechanisms of chemical reactions. One can hardly overestimate the role of chemical kinetics, both in understanding the “generative” character of chemical reactions and in designing new chemical processes and reactors.

1.3 Three Types of Chemical Kinetics

Presently, chemical kinetics is an area comprising challenges and adventures, in which at least four sciences overlap: chemistry, physics, chemical engineering,

and mathematics. In fact, contemporary chemical kinetics itself is a complex combination of different areas. Depending on the goal of a kinetic analysis, one may distinguish between applied kinetics, detailed kinetics, and mathematical kinetics.

1.3.1 Applied Kinetics

The goal of applied kinetics is to obtain kinetic dependences for the design of efficient catalytic processes and reactors. Kinetic dependences are dependences of the rates of chemical transformations on reaction conditions, that is, temperature, pressure, concentrations, and so on. When expressed mathematically, these dependences are called *kinetic models*. A kinetic model is the basis of the mathematical simulation of a chemical process. A series of models needs to be developed for the simulation of a catalytic reactor: kinetic model → model of catalyst pellet → model of catalyst bed → model of reactor. In this hierarchy of models, introduced by Boreskov and Slin'ko [3], the kinetic model represents the initial level, the foundation. No technologically interesting description of a chemical reactor can be given without reference to a kinetic model. Applied kinetic models are, as a rule, stationary; they are based on kinetic data obtained at steady-state conditions.

During the past 25 years, a lot of attention has been paid to the problem of selecting the best catalyst via so-called “combinatorial catalysis” procedures, which involve simultaneous steady-state testing of many different catalyst samples. However, the technique and methodology for precise kinetic catalyst characterization is still far from being complete, in particular for catalyst characterization at non-steady-state conditions. Such characterization is a critical issue in the design of a new generation of catalysts.

1.3.2 Detailed Kinetics

The study of detailed kinetics is aimed at reconstructing the *detailed mechanism* of a reaction, based on kinetic and non-kinetic (adsorption, desorption, spectrometric, etc.) data. The concept of a detailed mechanism may be used in a broad as well as a narrow sense. In its application to catalytic reactions, one should specify reactants, products, intermediates, reaction steps, surface properties, adsorption patterns, and so on.

In the practice of chemical kinetics, detailed kinetics is often used in a more narrow sense, as a set of elementary reaction steps. Each elementary step consists of a forward and a reverse elementary reaction, whose kinetic dependences are governed by the *mass-action law*.

1.3.3 Mathematical Kinetics

Mathematical kinetics deals with the analysis of various mathematical models that are used in chemical kinetics. As a rule, these are deterministic models consisting of a set of algebraic, ordinary differential or partial differential equations. There are also stochastic models that are based on Monte Carlo methods, for

modeling adsorption or surface-catalytic reactions, reaction–diffusion processes in the catalyst pellet or in the catalyst bed, and so on.

Problems related to mathematical kinetics may be either direct kinetic problems or inverse kinetic problems. A direct kinetic problem requires the analysis of a given kinetic model, either steady-state or non-steady-state, with known kinetic parameters. In contrast, solving an inverse kinetic problem involves reconstructing the kinetic dependences and estimating their parameters based on experimental kinetic data, either steady-state or non-steady-state.

1.4 Challenges and Goals. How to Kill Chemical Complexity

We will address all three types of chemical kinetics mentioned. However, the focus will be on one big issue, which can be defined as “the correspondence between observed kinetic behavior and ‘hidden’ detailed mechanisms.” This general problem will be posed and solved using the following three approaches to “killing chemical complexity”:

1. thermodynamically consistent “gray-box” approach
2. analysis of kinetic fingerprints
3. non-steady-state kinetic screening.

1.4.1 “Gray-Box” Approach

Within the “gray-box” approach, a general structuralized form of the steady-state rate equation of the complex reaction is presented for linear reaction mechanisms [4, 5] and for nonlinear reaction mechanisms, the so-called “kinetic polynomial” [6]. In Chapters 5 and 6, we will show how this equation contains some terms that can be written easily without any knowledge about the detailed mechanism, and only based on the overall equation of the complex reaction, including only reactants and products and no intermediates.

For example, for a single-route multistep (complex) reaction, the numerator of the steady-state rate relationship can be presented independently of the details of the mechanism, that is, *mechanism-free*, based only on the *driving force* for the reaction. All of the information regarding the mechanism is “hidden” in the denominator of the rate expression. However, this denominator is not very sensitive to the mechanism of the complex reaction. One needs to use a special experimental procedure, in particular involving the feeding of chemical mixtures containing products of the reaction, to be able to distinguish between different mechanisms and extract the corresponding parameters.

Nevertheless, this approach is not statistical modeling of the “black-box” type, as the kinetic models concerned are consistent from a thermodynamic point of view; if the reaction rate equals zero, the driving force equals zero as well, so thermodynamic relationships are fulfilled. That is why we call this approach a gray-box approach. In fact, it is a rigorous generalization of the

results presented in the 1930s and 1940s by Horiuti, Boreskov, and Hougen and Watson.

In Chapter 9, it is shown how the gray-box approach works for a general nonlinear mechanism, in which more than one intermediate can participate in an elementary reaction. There, the steady-state reaction rate, r , is presented implicitly as a polynomial in reaction rate, concentrations, and temperature: the kinetic polynomial $f(r, c, T) = 0$. Typically, all terms of this polynomial are powers of the steady-state reaction rate with the exception of the free term, which is proportional to the driving force. At equilibrium conditions all terms containing r vanish, while the free term becomes equal to zero as well. Therefore, even in this nonlinear case, such a representation of the rate is consistent from a thermodynamic point of view.

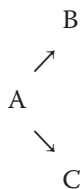
The kinetic polynomial can be comprehended as the most general steady-state rate dependence. The known Langmuir–Hinshelwood, Hougen–Watson, and Horiuti–Boreskov rate expressions are particular cases of this implicit rate expression.

1.4.2 Analysis of Kinetic Fingerprints

The goal of the analysis of kinetic fingerprints [4, 5] is to find features and characteristics of observed kinetic behavior, based on which it is possible to resolve the detailed mechanism, its class or its family, and to determine its characteristics. Most chemical kineticists and chemical engineers know exactly how to distinguish the consecutive mechanism



from the parallel mechanism



If a maximum in the concentration of B is observed during the temporal change, the mechanism is clearly consecutive. Thus, this maximum in the concentration of B is a fingerprint of the consecutive mechanism. The more such fingerprints we have, the easier it is to resolve the mechanism, and such detective work in the style of Sherlock Holmes has to be developed further and further.

The developed theory [4] provides a fingerprint based just on the experimental observation of isothermal critical phenomena such as multiplicity of steady-state reaction rates, reaction-rate oscillations, and so on. If such phenomena are observed, it means that, assuming that the mass-action law is valid, the detailed mechanism must include a step in which different surface intermediates, for example, adsorbed oxygen and adsorbed carbon monoxide,

interact. A well-known example of such a mechanism is the so-called adsorption mechanism or Langmuir–Hinshelwood mechanism. The kinetic model corresponding to this mechanism is studied in detail in Chapter 8.

In 1798, Georges Cuvier, who played a major role in establishing comparative anatomy and paleontology, wrote: “Today comparative anatomy has reached such a point of perfection, that, after inspecting a single bone, one can often determine the class and sometimes even the genus of the animal to which it belonged.” Our goal with respect to chemical kinetics is the same.

1.4.3 Non-steady-state Kinetic Screening

Non-steady-state kinetic screening can be based on the technique of Temporal Analysis of Products (TAP), invented by Gleaves at Monsanto in 1988 [7]. A rigorous theoretical development of this approach, which can be termed “chemical calculus,” was subsequently started by Gleaves et al. [8].

The main revolutionary idea of TAP is to treat the catalyst by a series of pulses of very small intensity relative to the amount of catalyst, so that the change of the catalyst composition caused by every pulse is insignificant. However, a precise mass-spectroscopic technique allows monitoring of changes in the composition of the pulsed chemical mixture at the exit of the catalyst bed. Upon applying a large series of such pulses, the catalyst composition changes significantly in a controlled manner. Therefore, a sequence of *infinitesimal* steps produces a *finite* change of the catalyst activity, hence the term “chemical calculus”; see Chapter 10 for more details.

Non-steady-state kinetic screening using the TAP technique has gained considerable popularity since its introduction. Nowadays, no less than 15 groups in different parts of the world (United States; Belgium, France, Germany, Spain, and United Kingdom in Europe; and China, Japan, and Thailand in Asia) are using this technique [9–11].

1.5 What Our Book is Not About. Our Book Among Other Books on Chemical Kinetics

To avoid raising false expectations, it is important to state the areas that are *not* covered in this book. First of all, this book is *not* an encyclopedia or a textbook on chemical kinetics or catalysis. It is *not* about the law of elementary chemical reactions, *nor* does it reflect the progress in the understanding of detailed mechanisms of catalytic reactions or the development of industrial catalytic processes. *Neither* is it about computer modeling of complex chemical reactions, although some results of such modeling are presented.

There are excellent books in contemporary literature covering these topics. Regarding kinetic dependences of elementary reactions, we recommend the monograph by Zhdanov [12]. For books on general chemical kinetics see for example Laidler [13], Boudart and Djega-Mariadassou [14], Houston [15], van Santen and Niemantsverdriet [16] and Masel [17]. Recommended books

on theoretical and practical concepts of catalysis are those by Thomas and Thomas [18], Bond [19], van Santen and Neurock [20, 21], Chorkendorff and Niemantsverdriet [22], and last, but not least, Dumesic et al. [23]. Some recent books on applied catalytic kinetics include the well-written monograph by Murzin and Salmi [24] and the book by Vannice [25]. Many aspects of modeling the kinetics of complex reactions are presented in a recent monograph [26], in particular in the chapter by Green [27].

In this book, some of these aspects are touched upon, but only briefly or as illustrations. As mentioned previously, our focus is on presenting a general strategy and methodology for decoding complex kinetic behavior using the approaches described in Section 1.4. Some features of this new “paradigm” were formulated in the 1980s and 1990s [4, 5, 8, 23, 28–30], and in an interesting book by Temkin [31], published in 2008. In this book, we present a much updated version of this strategy, which is still under construction.

1.6 The Logic in the Reasoning of This Book

This book’s logic can be presented as the sequence of building blocks as illustrated in Figure 1.1.

1.7 How Chemical Kinetics and Mathematics are Interwoven in This Book

Chemical kinetics is certainly an intrinsic area of chemistry. However, it can also be viewed as a bridge between chemistry, chemical engineering, and physics on

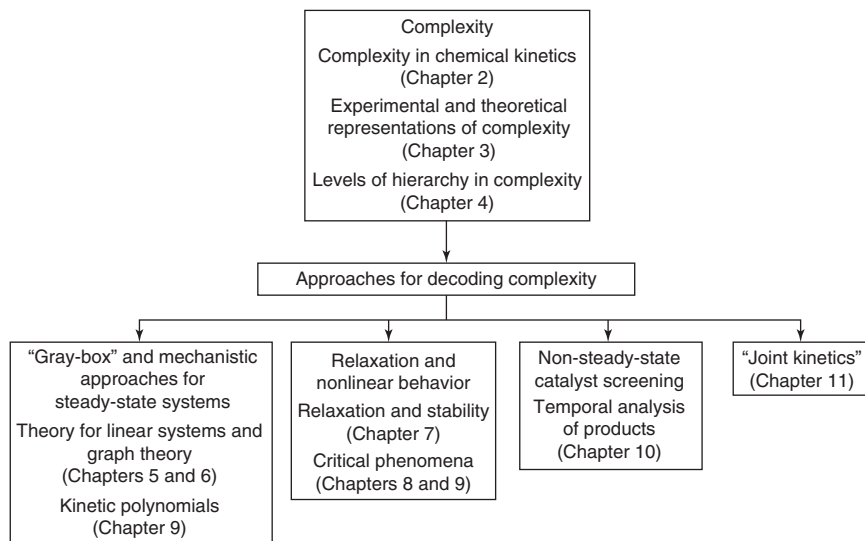


Figure 1.1 Building blocks of this book.

one side and mathematics on the other. That is why we have presented several mathematical concepts, the understanding of which is absolutely necessary for the contemporary researcher working or going to work in this area. These concepts include “linear algebra” (Chapter 4), “graph theory” (Chapters 5 and 6), “ordinary differential equations” and “stability theory” (Chapters 7 and 8), “algebraic models” (Chapter 8) and “partial differential equations” (Chapter 10).

In all these cases we have tried to present the concepts making a compromise between “scrupulously mathematically accurate” and “chemically clear” in favor of the chemical comprehension using many illustrative examples.

The one exception is the concept of the “kinetic polynomial,” which is described in Chapter 9. We illustrate an efficient application of kinetic polynomials to the analysis of critical behavior of catalytic reactions (“critical simplification”) and the behavior of reversible catalytic reactions on “both sides of the equilibrium.” The style of reasoning in these sections is not the same as in the rest of the book; the compromise is in favor of mathematics. Many details of mathematical derivations can be found in Ref. [4].

1.8 History of Chemical Kinetics

Chemical kinetics has manifested itself as an inherent part of chemistry. It also has a large impact on other scientific areas. For instance, after its discovery, the concept of chain reactions was immediately used in nuclear physics in the 1930s.

Table 1.1 presents the sequence of the most important events in the history of chemical kinetics. It is impossible to describe all of the achievements in one book, and so we had to be selective.

Catalysis as a concept was introduced as early as 1835 by Berzelius [33, 34] in order to explain decomposition and transformation reactions observed by various investigators, such as Döbereiner and Davy; see, for example, Ref. [32]. Berzelius assumed that catalysts possess special powers that can influence the affinity of chemical substances. A definition that is still valid today is due to Ostwald (1895): “A catalyst accelerates a chemical reaction without affecting the position of the equilibrium.”

In 1850, Wilhelm performed the first kinetic experiments and showed that the rates of chemical reactions are dependent on the concentrations of the reactants [35]. In 1864, Guldberg and Waage formulated the first correct quantitative law, known as the mass-action law [32, 36, 49]. An event of great importance was the publication, in 1884, of van’t Hoff’s “*Études de Dynamique Chimique*” [37, 50]. van’t Hoff received the first Nobel Prize in Chemistry in 1901.

Since the time of Ostwald, designing chemical reactors and processes has been impossible without kinetic analysis. Two of the earliest examples are ammonia synthesis and ammonia oxidation. Nowadays, the development of new reactors and processes is based on a preliminary kinetic characterization, including the development of kinetic models. A kinetic analysis has become the first and one of the last stages in technological decision making. For a chemical process to be interesting in practice, the reaction rate and selectivity need to be sufficiently high.

Table 1.1 Important events in the development of chemical kinetics in the nineteenth and twentieth century.

When?	What?	Who?
1810s–1820s	Catalysis discovered as a means for a dramatic increase of chemical productivity	Döbereiner, Davy, and others [32]
1830s	Catalysis distinguished as a special phenomenon	Berzelius [33, 34]
1850s	Concept of chemical reaction rate formulated based on data of catalytic reactions	Wilhelmy [35]
1860s	Mass-action law proposed based on catalytic esterification data	Waage and Guldberg [36]
1880s–1890s	Formulation of a “natural classification of reactions” (uni-, bi-, and termolecular) with corresponding dependences using data of non-catalytic reactions	van’t Hoff [37]
	Catalysis is explained as a purely kinetic phenomenon	Ostwald
	Principle of independence of reactions	Ostwald
	Concept of reaction mechanisms arises	Schönbein
1900s–1910s	Constraints on kinetic coefficients, “Wegscheider’s paradox”	Wegscheider [38]
	Discovery of chain reactions	Bodenstein
	Cyclic sequence of reactions, catalytic cycle	Christiansen
	Quasi-steady-state hypothesis	Chapman and Underhill [39], Bodenstein
	Gas–solid catalysis occurs on the <i>surface</i> of the solid catalyst, not in the gas phase or in the bulk of the catalyst	Langmuir
1920s–1930s	Discovery of branching chain reactions	Semenov [40], Hinshelwood [41]
	Concept of active catalyst sites	Taylor [42]
	Discoveries in enzyme adaptation and bacterial genetics	Monod [43]
	Development of the Onsager reciprocal relationships	Onsager [44, 45]
1950s–1960s	Analysis of multistep catalytic reactions	Christiansen
	Studies of fast reactions by the relaxation technique	Eigen
	Discovery of oscillating reactions	Belousov, Zhabotinsky
1970s–1980s	Concept of turnover frequency	Boudart [46, 47]
	Development of models for thermodynamics of irreversible processes	Prigogine [48]
1980s–1990s	Novel observation techniques in heterogeneous catalytic kinetics	Ertl, Somorjai

Steady-state chemical reactors for ammonia synthesis and oxidation of sulfur dioxide have been designed based on the classical kinetic models by Temkin and Boreskov, respectively. Nowadays, in non-steady-state catalytic technology one attempts to use kinetic models based on detailed mechanistic knowledge. Examples worth mentioning are

- automotive catalytic processes, which by definition are non-steady-state processes – see for example Ref. [51];
- reverse-flow processes developed by Matros [52, 53], in which the direction of the flow through the catalyst bed is periodically reversed;
- oxidation–reduction processes for selective hydrocarbon oxidation, in which the solid oxidation catalyst is transported from the reduction to the oxidation stage [54, 55];
- circulating fluidized-bed reactors, specifically risers [56];
- total oxidation of hydrocarbons by metal oxides, that is, so-called chemical looping combustion (CLC), the goal of which is minimization of carbon dioxide emissions (see, for example Ref. [57]).

During the twentieth century, three important chemical discoveries were made based on pure or modified kinetic paradigms, namely branching chain reactions by Semenov [40] and Hinshelwood [41], enzyme adaptation and bacterial genetics via kinetic methods by Monod [43], and oscillating reactions by Belousov [58]. Zhabotinsky [59] later refined Belousov's work.

In 1931, Onsager [44, 45] published generalizations to the reciprocal relations introduced in the nineteenth century by Kelvin and Helmholtz. He deduced his famous equations, known as the “Onsager reciprocal relationships,” starting from the concept of detailed equilibrium: at equilibrium, each elementary reaction should be equilibrated by its reverse reaction (see also Ref. [60]). There is also a connection between Onsager's relationships and results originating from the analysis of cyclic catalytic mechanisms. Onsager remarked that “chemists apply a very interesting approach,” referring to the paper [38] in which Wegscheider showed that for any chemical reaction cycle the product of the equilibrium constants around the cycle is equal to one.

From the 1940s onward, two main trends in chemical kinetics have been distinguished. The first trend is related to the precise characterization of chemical activity, or catalyst activity, through kinetic experiments. In the 1940s, a battery of completely new and/or very much improved kinetic devices and methods were invented and accepted by kineticists, namely the continuous-stirred-tank reactor (CSTR), the PFR, and the differential PFR.

Temkin [61, 62], Denbigh [63, 64], Berty [65], and Carberry [66] can be named as pioneers of steady-state kinetic experiments. Bennett [67–69], and Kobayashi and Kobayashi [70] can be considered the founders of non-steady-state kinetic experiments in catalysis.

By the 1940s, the concept of active sites proposed by Taylor [42] in the 1920s had become widespread. Taylor suggested that catalytic reactions do not occur everywhere on the catalyst surface, but only on specific sites, the so-called active sites, which may be few and isolated from each other. In the 1960s, based on this idea of active sites, Boudart proposed the concept of the turnover

frequency (TOF) [46, 47]. Boudart denoted TOF (dimension per second) as the rate of reaction with respect to the number of active sites, which was typically measured in separate adsorption experiments. This concept immediately became extremely popular in the area of catalysis, both theoretical and applied.

In the 1950s and 1960s, Eigen developed a novel experimental technique for kinetic studies of very fast reactions; see, for example, Ref. [71]. Finally, in 1988, Gleaves proposed the non-steady-state TAPs reactor [7, 8].

The second trend in chemical kinetics is a series of attempts at developing a theory that allows decoding the chemical complexity. Several authors created different versions of such a theory: Horiuti [72–77], Boreskov [3], and Temkin [78–80] in heterogeneous catalysis and King and Altman [81] and Volkenstein and Goldstein [82, 83] in enzyme kinetics. King and Altman, Volkenstein and Goldstein, and Temkin used graph theory as an efficient mathematical tool.

In the 1970s and 1980s, Prigogine used oscillating chemical reactions as a starting point for the development of mathematical models of irreversible thermodynamics for states far removed from equilibrium, including the concept of dissipative structures [48, 84, 85]. At about the same time, the first versions of a rigorous theory were shaped out, which enabled the revealing of a link between observed kinetic behavior and the detailed mechanisms of complex reactions. Such theories were developed by a group at the Minnesota University (Aris, Amundson, Horn, and Feinberg) and by the Siberian chemico-mathematical team (Gorban, Yablonskii, Bykov, and Elokhin).

In the 1980s and 1990s, Ertl, of the Fritz-Haber Institute, applied novel observation techniques – in particular low-energy-electron-diffraction (LEED), ultraviolet photoelectron spectroscopy (UPS), and scanning tunneling microscopy (STM) – in detailed kinetic studies of the catalytic ammonia synthesis over iron and the oxidation of carbon monoxide over platinum. Ertl analyzed the phenomena of kinetic oscillations over platinum and surface dissipative structures and developed the nonlinear models proposed by the Siberian and Minnesota teams in the 1970s and 1980s in more detail.

Ertl was awarded the 2007 Nobel Prize in Chemistry. Presently, it is the last “kinetic” Nobel Prize in a series: Jacobus Henricus van’t Hoff (1901), Svante Arrhenius (1903), Wilhelm Ostwald (1909), Irving Langmuir (1932), Cyril Hinshelwood and Nikolay Semenov (1956), Jacques Monod (1965), Manfred Eigen (1967), Lars Onsager (1968), Ilya Prigogine (1977), Dudley Herschbach, Yuan Lee and John Polanyi (1986) Yves Chauvin, Robert Grubbs and Richard Schrock (2005), and Gerhard Ertl (2007).

Other notable names are Evstigneev, who made a large contribution to the development of the kinetic graph theory [86], Clarke [87], who developed an efficient graph algorithm for testing critical phenomena in chemical reactions, and Vol’pert, Khudyaev and Ivanova (Chernogolovka) [88, 89], who gave rigorous mathematical proofs of solutions to several problems in chemical kinetics. Decoding the kinetic complexity of enzyme reactions in terms of graph theory has recently been described in detail by O. Temkin et al. [30, 31].

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