

The late F. A. Cotton would certainly not have appreciated the title of this book, and in particular the use of the word “cluster” to describe simple coordination complexes without metal–metal bonds. This is probably the only criticism that could be made about this book: Richard Winpenny could have found a better title! However, if one does not like the title of the book, that is certainly not a reason to dislike its contents. This new book succeeds in its aim to be a complementary volume to the *Molecular Nanomagnets* textbook by Dante Gatteschi, Roberta Sessoli, and Jacques Villain. Master and PhD students, as well as researchers in the field of molecule-based magnetism, will be delighted to read this book and to use it as a reference source in their research work and future papers.

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- [1] J. Mervis, *Science* **2012**, 336, 22.  
[2] G. Aromi, E. K. Brechin, *Structure and Bonding* **2006**, 122, 1–67.

**Kinetics of Chemical Reactions**

This book was written by two authors from different schools: Prof. Marin was educated in the tradition of the thermodynamics and kinetics school of the Low Countries as well as that of the American school (Prof. Boudart). On the other hand, Gregory Yablonsky had his training in the Soviet-Russian catalysis school (Profs. Mikhail Slin’ko and Georgij Borekov). He was also a prominent member of the Russian chemico-mathematical team that included Alexander Gorban, Valerij Bykov, Vladimir Elokhn, and Mark Lazman. The different backgrounds of the authors are reflected in the book. Another welcome aspect is that the book also includes many results from Soviet science, which are not widely known.

The book is divided into 12 chapters. The first chapter describes the approach adopted. Three types of chemical kinetics are covered: applied kinetics, detailed kinetics, and mathematical kinetics. The goal of applied kinetics is to obtain kinetic relationships for the design of efficient catalytic processes and reactors. The study of detailed kinetics is aimed at reconstructing the detailed

mechanism of a reaction, based on kinetic and non-kinetic (adsorption, desorption, spectrometric) data. Quantum-chemical methods are not taken into account. Mathematical kinetics deals with the analysis of various mathematical, mostly deterministic, models that are used in chemical kinetics. The book focuses on the correspondence between observed kinetic behavior and “hidden” detailed mechanisms, and presents it as the main problem of chemical kinetics. The chapter ends with a short review of the history of kinetics.

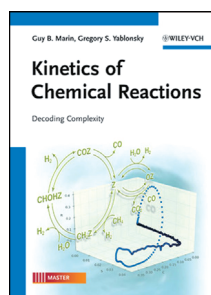
The second chapter introduces fundamental definitions of concepts such as elementary reactions and homogeneous expressions, and explains the difference between the reaction rate and the net rate of formation of a product. A reference to the *IUPAC Gold Book* is given.

The third chapter presents material and heat balances for the standard types of chemical reactors, followed by an analysis of some important types of reaction schemes taking place in those reactors. In particular, the ability to distinguish between parallel and consecutive reactions based on kinetic fingerprints is discussed. A subsection is devoted to the question of whether it is possible to extract the values of the rate of chemical transformation without any assumptions about the kinetic model. The chapter ends with complex diagnostics of kinetic experiments in heterogeneous catalysis.

Linear algebraic methods in chemical kinetics are discussed in the fourth chapter, which presents three main matrices for describing complex chemical transformations: the molecular and stoichiometric ones, and a matrix of Horiuti numbers. Some mathematical methods of linear algebra, for example the solution of systems of linear equations, are discussed. The approaches are then used for finding key components and key reactions, and other techniques of stoichiometry such as the use of Horiuti numbers are described.

Graph theory as a tool for easily solving mathematical theoretical problems of chemical kinetics are introduced in Chapter 5. Complex reaction networks can be represented by a method that is an advanced modification of already known graphical methods (King–Altman, Volkenstein–Gol’dshstein, and Horiuti–Temkin), with a focus on “kinetics–mechanism” relationships. Some very useful examples showing how to find the reaction rate for a complex mechanism are presented. The famous Horiuti–Borekov problem of how to find the rate equation for the reverse reaction, when one knows the expression for the forward reaction and the equilibrium coefficient of the overall reaction, is explained and solved in the general case for linear mechanisms.

The so-called “gray-box” approach for revealing complex reaction mechanisms is introduced in



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Decoding Complexity. By  
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Yablonsky. Wiley-VCH, Wein-  
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Chapter 6. Within the “gray-box” approach, a general structuralized form of the steady-state rate equation for the complex reaction is described. This method is based on solid thermodynamic grounds, and guarantees thermodynamically consistent kinetic models. A sub-section that describes how to reveal mechanisms on the basis of steady-state kinetic data is particularly useful for experimentalists, as this is not usually discussed in the chemical engineering literature. Some examples explain the method.

Time-dependent kinetic equations are considered in Chapter 7. The relaxation behavior of linear sets of equations and the stability of these systems are investigated, followed by concepts such as local stability and the analysis of global dynamics. Approximate methods such as the quasi-steady-state approximation and the rate-limiting step method are described and their limitations are discussed.

Chapter 8 continues the subject of time-dependence problems, and discusses phenomena associated with nonlinear mechanisms, such as self-sustained oscillation of the reaction rate in heterogeneous catalytic reactions, multiplicities, and slow relaxations. The Lotka–Volterra equations, the Turner–Sales–Maple model, CO oxidation over Pt(110), and the Horn–Jackson–Feinberg mechanism serve as illustrative examples. A detailed analysis of the 3-step adsorption mechanism (Langmuir–Hinshelwood), with no assumptions about the equilibrium of adsorption steps, is given. As early as the mid-1970s, the Russian scientists Yablonsky and Bykov showed rigorously that this mechanism is the simplest one that permits the multiplicity of steady states. Later, this mechanism or similar ones became extremely popular for explaining critical phenomena.

Chapter 9 introduces a concept originally proposed by Lazman and Yablonsky in the 1980s, namely the kinetic polynomial, which is an implicit function of the reaction rate. The kinetic polynomial is the most generalized form of the rate equation for a complex reaction. It is suitable for the kinetic description of different catalytic mechanisms, both linear and nonlinear. The commonly used Langmuir–Hinshelwood and Hougen–Watson

equations are particular cases of the kinetic polynomial. Several examples of kinetic polynomials are given, in particular for the CO oxidation and water-gas shift reactions. Also a solution of the Horiuti–Borakov problem is presented for some nonlinear cases.

Chapter 10 presents an extensive review of the advanced pulse-response method for non-steady-state characterization of catalysts, as proposed by Gleaves in 1988. This so-called “temporal analysis of products” (TAP) method is also considered as a versatile tool for the analysis of complex kinetics of heterogeneous catalytic reactions. Recent advances in the theory and application of TAP are discussed. This approach can be described as a “third kinetic strategy” alongside traditional catalytic experiments in continuous stirred tank reactors or plug-flow reactors and surface science experiments. Various strategies for the evaluation of kinetic experiments are given, including a comprehensive “interrogative kinetics” diagram. Procedures for solving data obtained with the three-zone TAP reactor are given.

The last two chapters describe the history of chemical kinetics and expected future developments.

To sum up, this book is the first to give an overview of the formal decoding of reaction mechanisms based on kinetic data. Decoding complexity is presented as the inherent feature of chemical kinetics. The book provides a unique combination of reports on kinetics developments in the West and those in the former Soviet Union. The latter are, for the most part, widely ignored in the West. Many of the approaches presented may be useful for the evaluation of experimental results. As the authors mention in their introduction, this is not an encyclopedia or a textbook on chemical kinetics, but it can be a complementary book in graduate courses on chemical kinetics for chemical engineers and chemists. The text is clearly written and well organized.

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