

Contents

Preface to First Edition *xv*

Preface to Second Edition *xix*

| | | |
|----------|--|-----------|
| 1 | Introduction | <i>1</i> |
| 1.1 | Overview | <i>1</i> |
| 1.2 | Decoding Complexity in Chemical Kinetics | <i>2</i> |
| 1.3 | Three Types of Chemical Kinetics | <i>2</i> |
| 1.3.1 | Applied Kinetics | <i>3</i> |
| 1.3.2 | Detailed Kinetics | <i>3</i> |
| 1.3.3 | Mathematical Kinetics | <i>3</i> |
| 1.4 | Challenges and Goals. How to Kill Chemical Complexity | <i>4</i> |
| 1.4.1 | “Gray-Box” Approach | <i>4</i> |
| 1.4.2 | Analysis of Kinetic Fingerprints | <i>5</i> |
| 1.4.3 | Non-steady-state Kinetic Screening | <i>6</i> |
| 1.5 | What Our Book is Not About. Our Book Among Other Books on Chemical Kinetics | <i>6</i> |
| 1.6 | The Logic in the Reasoning of This Book | <i>7</i> |
| 1.7 | How Chemical Kinetics and Mathematics are Interwoven in This Book | <i>7</i> |
| 1.8 | History of Chemical Kinetics | <i>8</i> |
| | References | <i>12</i> |
| 2 | Chemical Reactions and Complexity | <i>17</i> |
| 2.1 | Introduction | <i>17</i> |
| 2.2 | Elementary Reactions and the Mass-Action Law | <i>19</i> |
| 2.2.1 | Homogeneous Reactions | <i>19</i> |
| 2.2.2 | Heterogeneous Reactions | <i>21</i> |
| 2.2.3 | Rate Expressions | <i>22</i> |
| 2.3 | The Reaction Rate and Net Rate of Production of a Component – A Big Difference | <i>23</i> |
| 2.4 | Dimensions of the Kinetic Parameters and Their Orders of Magnitude | <i>24</i> |

| | | |
|----------|--|-----------|
| 2.5 | Conclusions | 26 |
| | Nomenclature | 26 |
| | References | 28 |
| 3 | Kinetic Experiments: Concepts and Realizations | 29 |
| 3.1 | Introduction | 29 |
| 3.2 | Experimental Requirements | 29 |
| 3.3 | Material Balances | 30 |
| 3.4 | Classification of Reactors for Kinetic Experiments | 31 |
| 3.4.1 | Steady-state and Non-steady-state Reactors | 31 |
| 3.4.2 | Transport in Reactors | 31 |
| 3.4.3 | Ideal Reactors | 32 |
| 3.4.3.1 | Batch Reactor | 32 |
| 3.4.3.2 | Continuous Stirred-tank Reactor | 33 |
| 3.4.3.3 | Plug-flow Reactor | 34 |
| 3.4.4 | Ideal Reactors with Solid Catalyst | 34 |
| 3.4.4.1 | Batch Reactor | 34 |
| 3.4.4.2 | Continuous Stirred-tank Reactor | 35 |
| 3.4.4.3 | Plug-flow Reactor | 35 |
| 3.4.4.4 | Pulse Reactor | 35 |
| 3.4.5 | Determination of the Net Rate of Production | 36 |
| 3.5 | Formal Analysis of Typical Ideal Reactors | 36 |
| 3.5.1 | Batch Reactor | 36 |
| 3.5.1.1 | Irreversible Reaction | 36 |
| 3.5.1.2 | Reversible Reaction | 38 |
| 3.5.1.3 | How to Distinguish Parallel Reactions from Consecutive Reactions | 40 |
| 3.5.2 | Steady-state Plug-flow Reactor | 43 |
| 3.5.3 | Non-steady-state Continuous Stirred-tank Reactor | 43 |
| 3.5.3.1 | Irreversible Reaction | 43 |
| 3.5.3.2 | Reversible Reaction | 44 |
| 3.5.4 | Thin-zone TAP Reactor | 45 |
| 3.6 | Kinetic-model-free Analysis | 46 |
| 3.6.1 | Steady State | 46 |
| 3.6.2 | Non-steady State | 47 |
| 3.6.2.1 | Continuous Stirred-tank Reactor | 47 |
| 3.6.2.2 | Plug-flow Reactor | 48 |
| 3.7 | Diagnostics of Kinetic Experiments in Heterogeneous Catalysis | 49 |
| 3.7.1 | Gradients at Reactor and Catalyst-pellet Scale | 49 |
| 3.7.2 | Experimental Diagnostics and Guidelines | 49 |
| 3.7.2.1 | Test for External Mass-transfer Effect | 51 |
| 3.7.2.2 | Test for Internal Mass-transport Effect | 51 |
| 3.7.2.3 | Guidelines | 52 |
| 3.7.3 | Theoretical Diagnostics | 52 |
| 3.7.3.1 | External Mass Transfer | 53 |
| 3.7.3.2 | External Heat Transfer | 54 |
| 3.7.3.3 | Internal Mass Transport | 56 |

| | | |
|----------|---|-----------|
| 3.7.3.4 | Internal Heat Transport | 59 |
| 3.7.3.5 | Non-steady-state Operation | 59 |
| | Nomenclature | 59 |
| | References | 62 |
| 4 | Chemical Book-keeping: Linear Algebra in Chemical Kinetics | 65 |
| 4.1 | Basic Elements of Linear Algebra | 65 |
| 4.2 | Linear Algebra and Complexity of Chemical Reactions | 67 |
| 4.2.1 | Atomic Composition of Chemical Components: Molecules “Consist of” Atoms | 68 |
| 4.2.1.1 | Molecular Matrix | 68 |
| 4.2.1.2 | Linear Algebra and Laws of Mass Conservation | 68 |
| 4.2.1.3 | Key Components and Their Number | 70 |
| 4.2.2 | Stoichiometry of Chemical Reactions: Reactions “Consist of” Chemical Components | 72 |
| 4.2.2.1 | Stoichiometric Matrix | 72 |
| 4.2.2.2 | Difference and Similarity Between the Conservation Law for Chemical Elements and the Kinetic Mass-Conservation Law | 74 |
| 4.2.2.3 | Similarity and Difference Between the Number of Key Components and the Number of Key Reactions | 74 |
| 4.2.3 | Detailed Mechanism of Complex Reactions: Complex Reactions “Consist of” Elementary Reactions | 75 |
| 4.2.3.1 | Mechanisms and Horiuti Numbers | 75 |
| 4.2.3.2 | Matrices and Independent Routes of Complex Reactions | 80 |
| 4.3 | Concluding Remarks | 83 |
| 4.A | Book-Keeping Support in Python/SymPy | 83 |
| 4.A.1 | Skeleton Code Generation | 83 |
| 4.A.2 | Matrix Augmentation and Reduction | 84 |
| | Nomenclature | 88 |
| | References | 90 |
| 5 | Steady-State Chemical Kinetics: A Primer | 93 |
| 5.1 | Introduction to Graph Theory | 93 |
| 5.2 | Representation of Complex Mechanisms as Graphs | 94 |
| 5.2.1 | Single-route Mechanisms | 95 |
| 5.2.2 | Single-route Mechanism with a Buffer Step | 97 |
| 5.2.3 | Two-route Mechanisms | 97 |
| 5.2.4 | Number of Independent Reaction Routes and Horiuti’s Rule | 99 |
| 5.3 | How to Derive the Reaction Rate for a Complex Reaction | 101 |
| 5.3.1 | Introduction | 101 |
| 5.3.2 | Kinetic Cramer’s Rule and Trees of the Chemical Graph | 104 |
| 5.3.3 | Forward and Reverse Reaction Rates | 110 |
| 5.3.4 | Single-route Linear Mechanism – General Case | 111 |
| 5.3.5 | How to Find the Kinetic Equation for the Reverse Reaction: The Horiuti–Boreskov Problem | 112 |
| 5.3.6 | What About the Overall Reaction – A Provocative Opinion | 114 |

| | | |
|----------|---|------------|
| 5.4 | Derivation of Steady-State Kinetic Equations for a Single-Route Mechanism – Examples | 116 |
| 5.4.1 | Two-step Mechanisms | 117 |
| 5.4.1.1 | Michaelis–Menten Mechanism | 117 |
| 5.4.1.2 | Water–Gas Shift Reaction | 118 |
| 5.4.1.3 | Liquid-phase Hydrogenation | 119 |
| 5.4.2 | Three-step Mechanisms | 120 |
| 5.4.2.1 | Oxidation of Sulfur Dioxide | 120 |
| 5.4.2.2 | Coupling Reaction | 121 |
| 5.4.3 | Four-step Mechanisms | 122 |
| 5.4.4 | Five-step Mechanisms | 124 |
| 5.4.5 | Single-route Linear Mechanisms with a Buffer Step | 125 |
| 5.5 | Derivation of Steady-State Kinetic Equations for Multi Route Mechanisms: Kinetic Coupling | 126 |
| 5.5.1 | Cycles Having a Common Intermediate | 127 |
| 5.5.2 | Cycles Having a Common Step | 129 |
| 5.5.3 | Cycles Having Two Common Steps | 130 |
| 5.5.4 | Different Types of Coupling Between Cycles | 131 |
| | Nomenclature | 132 |
| | References | 133 |
| 6 | Steady-state Chemical Kinetics: Machinery | 137 |
| 6.1 | Analysis of Rate Equations | 137 |
| 6.1.1 | Dependence of Parameters on Temperature and Number of Identifiable Parameters | 138 |
| 6.1.2 | Simplifying Assumptions | 140 |
| 6.1.2.1 | Fast Step | 140 |
| 6.1.2.2 | Rate-limiting Step | 141 |
| 6.1.2.3 | Quasi-equilibrated Step(s) | 141 |
| 6.1.2.4 | Irreversible Step(s) | 142 |
| 6.1.2.5 | Dependence of the Reaction Rate on Concentrations | 143 |
| 6.2 | Apparent Kinetic Parameters: Reaction Order and Activation Energy | 143 |
| 6.2.1 | Definitions | 143 |
| 6.2.2 | Two-step Mechanism of an Irreversible Reaction | 145 |
| 6.2.2.1 | Apparent Partial Reaction Order | 145 |
| 6.2.2.2 | Apparent Activation Energy | 146 |
| 6.2.3 | More Examples | 147 |
| 6.2.3.1 | Apparent Partial Reaction Order | 147 |
| 6.2.3.2 | Apparent Activation Energy | 152 |
| 6.2.4 | Some Further Comments | 153 |
| 6.3 | How to Reveal Mechanisms Based on Steady-state Kinetic Data | 154 |
| 6.3.1 | Assumptions | 154 |
| 6.3.2 | Direct and Inverse Problems of Kinetic Modeling | 155 |
| 6.3.3 | Minimal and Non-minimal Mechanisms | 155 |
| 6.3.3.1 | Two-step Catalytic Mechanisms | 156 |
| 6.3.3.2 | Three-step Catalytic Mechanisms | 156 |

| | | |
|----------|---|------------|
| 6.3.3.3 | Four-step Catalytic Mechanisms | 157 |
| 6.3.3.4 | Five-step Catalytic Mechanisms | 158 |
| 6.3.3.5 | Summary | 158 |
| 6.3.4 | What Kind of Kinetic Model Do We Need to Describe Steady-state Kinetic Data and to Decode Mechanisms? | 159 |
| 6.3.4.1 | Kinetic Resistance | 159 |
| 6.3.4.2 | Analysis of the Kinetic Resistance in Identifying and Decoding Mechanisms and Models | 160 |
| 6.3.4.3 | Concentration Terms of the Kinetic Resistance and Structure of the Detailed Mechanism | 160 |
| 6.3.4.4 | Principle of Component Segregation | 164 |
| 6.4 | Concluding Remarks | 165 |
| | Nomenclature | 166 |
| | References | 167 |
| 7 | Linear and Nonlinear Relaxation: Stability | 169 |
| 7.1 | Introduction | 169 |
| 7.1.1 | Linear Relaxation | 171 |
| 7.1.2 | Relaxation Times and Steady-state Reaction Rate | 173 |
| 7.1.2.1 | Relaxation Times and Kinetic Resistance | 173 |
| 7.1.2.2 | Temkin's Rule. Is it Valid? | 174 |
| 7.1.3 | Further comments | 176 |
| 7.2 | Relaxation in a Closed System – Principle of Detailed Equilibrium | 177 |
| 7.3 | Stability – General Concept | 180 |
| 7.3.1 | Elements of the Qualitative Theory of Differential Equations | 180 |
| 7.3.2 | Local Stability – Rigorous Definition | 182 |
| 7.3.3 | Local Stability – System with two Variables | 184 |
| 7.3.3.1 | Real Roots | 186 |
| 7.3.3.2 | Imaginary Roots | 187 |
| 7.3.4 | Self-sustained Oscillations and Global Dynamics | 188 |
| 7.4 | Simplifications of Non-steady-state Models | 190 |
| 7.4.1 | Abundance and Linearization | 190 |
| 7.4.2 | Fast Step – Equilibrium Approximation | 191 |
| 7.4.3 | Rate-limiting Step Approximation | 191 |
| 7.4.4 | Quasi-steady-state Approximation | 192 |
| | Nomenclature | 198 |
| | References | 200 |
| 8 | Nonlinear Mechanisms: Steady State and Dynamics | 203 |
| 8.1 | Critical Phenomena | 203 |
| 8.2 | Isothermal Critical Effects in Heterogeneous Catalysis: Experimental Facts | 205 |
| 8.2.1 | Multiplicity of Steady States | 205 |
| 8.2.2 | Self-sustained Oscillations of the Reaction Rate in Heterogeneous Catalytic Reactions | 207 |
| 8.2.3 | Diversity of Critical Phenomena and Their Causes | 207 |

| | | |
|----------|---|------------|
| 8.3 | Ideal Simple Models: Steady State | 209 |
| 8.3.1 | Parallel and Consecutive Adsorption Mechanisms | 209 |
| 8.3.2 | Impact Mechanisms | 210 |
| 8.3.3 | Simplest Mechanism for the Interpretation of Multiplicity of Steady States | 212 |
| 8.3.4 | Hysteresis: Influence of Reaction Reversibility | 218 |
| 8.3.5 | Competition of Intermediates | 223 |
| 8.4 | Ideal Simple Models: Dynamics | 227 |
| 8.4.1 | Relaxation Characteristics of the Parallel Adsorption Mechanism | 227 |
| 8.4.2 | Catalytic Oscillators | 234 |
| 8.4.2.1 | Simplest Catalytic Oscillator | 234 |
| 8.4.2.2 | Relaxation of Self-sustained Oscillation: Model | 239 |
| 8.4.2.3 | Other Catalytic Oscillators | 239 |
| 8.4.3 | Fine Structure of Kinetic Dependences | 242 |
| 8.5 | Structure of Detailed Mechanism and Critical Phenomena: Relationships | 244 |
| 8.5.1 | Mechanisms Without Interaction Between Intermediates | 245 |
| 8.5.2 | Horn–Jackson–Feinberg Mechanism | 247 |
| 8.6 | Nonideal Factors | 250 |
| 8.7 | Conclusions | 251 |
| | Nomenclature | 251 |
| | References | 253 |
| 9 | Kinetic Polynomials | 263 |
| 9.1 | Linear Introduction to the Nonlinear Problem: Recap | 263 |
| 9.2 | Nonlinear Introduction | 266 |
| 9.3 | Principles of the Approach: Quasi-Steady-State Approximation. Mathematical Basis | 267 |
| 9.3.1 | Introduction | 267 |
| 9.3.2 | Examples | 269 |
| 9.4 | Kinetic Polynomials: Derivation and Properties | 270 |
| 9.4.1 | Resultant Reaction Rate: A Necessary Mathematical Basis | 270 |
| 9.4.2 | Properties of the Kinetic Polynomial | 272 |
| 9.4.3 | Examples of Kinetic Polynomials | 273 |
| 9.4.3.1 | Impact Mechanism | 273 |
| 9.4.3.2 | Adsorption Mechanism | 274 |
| 9.5 | Kinetic Polynomial: Classical Approximations and Simplifications | 276 |
| 9.5.1 | Rate-limiting Step | 276 |
| 9.5.2 | Vicinity of Thermodynamic Equilibrium | 278 |
| 9.5.3 | Thermodynamic Branch | 279 |
| 9.6 | Application of Results of the Kinetic-polynomial Theory: Cycles Across an Equilibrium | 282 |
| 9.7 | Critical Simplification | 289 |
| 9.7.1 | Critical Simplification: A Simple Example | 289 |
| 9.7.2 | Critical Simplification and Limitation | 295 |

| | | |
|-----------|---|------------|
| 9.7.3 | Principle of Critical Simplification: General Understanding and Application | 296 |
| 9.8 | Concluding Remarks | 297 |
| 9.A | Appendix | 298 |
| | Nomenclature | 299 |
| | References | 301 |
| 10 | Temporal Analysis of Products: Principles, Applications, and Theory | 307 |
| 10.1 | Introduction | 307 |
| 10.2 | Characteristics of TAP | 309 |
| 10.2.1 | The TAP Experiment | 309 |
| 10.2.2 | Description and Operation of a TAP Reactor System | 310 |
| 10.2.3 | Basic Principles of TAP | 312 |
| 10.3 | Position of TAP Among Other Kinetic Methods | 314 |
| 10.3.1 | Uniformity of the Active Zone | 315 |
| 10.3.1.1 | Continuous Stirred-tank Reactor | 315 |
| 10.3.1.2 | Plug-flow Reactor | 315 |
| 10.3.1.3 | TAP Reactor | 315 |
| 10.3.2 | Domain of Conditions | 315 |
| 10.3.3 | Possibility of Obtaining Relevant Kinetic Information | 316 |
| 10.3.4 | Relationship Between Observed Kinetic Characteristics and Catalyst Properties | 316 |
| 10.3.5 | Model-Free Kinetic Interpretation of Data | 317 |
| 10.3.6 | Summary of the Comparison | 318 |
| 10.3.7 | Applications of TAP | 318 |
| 10.4 | Qualitative Analysis of TAP Data: Examples | 318 |
| 10.4.1 | Single-pulse TAP Experiments | 319 |
| 10.4.2 | Pump-probe TAP Experiments | 322 |
| 10.4.3 | Multipulse TAP Experiments | 324 |
| 10.5 | Quantitative TAP Data Description. Theoretical Analysis | 326 |
| 10.5.1 | One-Zone Reactor | 327 |
| 10.5.1.1 | Diffusion Only | 327 |
| 10.5.1.2 | Irreversible Adsorption | 330 |
| 10.5.1.3 | Reversible Adsorption | 331 |
| 10.5.2 | Two- and Three-Zone Reactors | 332 |
| 10.5.3 | Thin-Zone TAP Reactor Configuration | 333 |
| 10.5.4 | Moment-Based Quantitative Description of TAP Experiments | 336 |
| 10.5.4.1 | Moments and Reactivities | 336 |
| 10.5.4.2 | From Moments to Reactivities | 342 |
| 10.5.4.3 | Experimental Procedure | 345 |
| 10.5.4.4 | Summary | 348 |
| 10.6 | Kinetic Monitoring: Strategy of Interrogative Kinetics | 348 |
| 10.6.1 | State-by-state Kinetic Monitoring. Example: Oxidation of Furan | 348 |
| 10.6.2 | Strategy of Interrogative Kinetics | 352 |

| | | |
|-----------|---|------------|
| 10.7 | Theoretical Frontiers | 353 |
| 10.7.1 | Global Transfer Matrix Equation | 353 |
| 10.7.2 | Y Procedure | 354 |
| 10.7.2.1 | Principles of the Solution | 355 |
| 10.7.2.2 | Exact Mathematical Solution | 358 |
| 10.7.2.3 | How to Reconstruct the Active Zone Concentration and Net Rate of Production in Practice | 359 |
| 10.7.2.4 | Numerical Experiments | 361 |
| 10.7.2.5 | Summary of the Y Procedure | 364 |
| 10.7.3 | Probabilistic Theory of Single-particle TAP Experiments | 366 |
| 10.8 | Conclusions: What Next? | 367 |
| | Nomenclature | 368 |
| | References | 371 |
| 11 | Joint Kinetics | 383 |
| 11.1 | Events and Invariances | 383 |
| 11.2 | Single Reaction | 384 |
| 11.2.1 | Batch Reactor | 384 |
| 11.2.1.1 | Basics | 384 |
| 11.2.1.2 | Point of Intersection | 386 |
| 11.2.1.3 | Swapping the Equilibrium | 387 |
| 11.2.2 | Continuous Stirred-tank Reactor | 388 |
| 11.2.2.1 | Basis | 388 |
| 11.2.2.2 | Point of Intersection | 388 |
| 11.2.3 | Invariances | 389 |
| 11.3 | Multiple Reactions | 391 |
| 11.3.1 | Events: Intersections and Coincidences | 391 |
| 11.3.2 | Mathematical Solutions of Kinetic Models | 393 |
| 11.3.2.1 | Batch Reactor | 393 |
| 11.3.2.2 | Continuous Stirred-tank Reactor | 394 |
| 11.3.3 | First Stage: Occurrence of Single Kinetic Events | 394 |
| 11.3.4 | Second Stage: Coincidences: Ordering Events by Pairs | 397 |
| 11.3.5 | End Products Intersection: Intersection of B and C | 402 |
| 11.3.6 | Invariances | 403 |
| | Nomenclature | 405 |
| | References | 406 |
| 12 | Decoding the Past | 407 |
| 12.1 | Chemical Time and Intermediates. Early History | 407 |
| 12.2 | Discovery of Catalysis and Chemical Kinetics | 407 |
| 12.3 | Guldberg and Waage's Breakthrough | 409 |
| 12.4 | Van't Hoff's Revolution: Achievements and Contradictions | 409 |
| 12.4.1 | Undisputable Achievements | 409 |
| 12.4.2 | Contradictions | 410 |
| 12.5 | Post-Van't Hoff Period: Reaction is Not a Single-act Drama | 411 |
| 12.6 | All-in-all Confusion. Attempts at Understanding | 411 |
| 12.7 | Out of Confusion: Physicochemical Understanding | 412 |

| | | |
|-----------|---|------------|
| 12.8 | Towards Mathematical Chemical Kinetics | 414 |
| | Nomenclature | 418 |
| | References | 419 |
| 13 | Decoding the Future | 425 |
| 13.1 | A Great Achievement, a Great Illusion | 425 |
| 13.2 | A New Paradigm for Decoding Chemical Complexity | 426 |
| 13.2.1 | Advanced Experimental Kinetic Tools | 427 |
| 13.2.2 | New Mathematical Tools. Chemical Kinetics and Mathematics | 428 |
| | References | 430 |
| | Index | 433 |

