CHEMICAL REACTION NETWORKS

A Graph-Theoretical Approach

Oleg N. Temkin

Lomonosov Academy of Fine Chemical Technology, Moscow

Andrew V. Zeigarnik

Lomonosov Academy of Fine Chemical Technology, Moscow

Danail Bonchev

Higher Institute of Chemical Technology in Burgas and Texas A & M University, Galveston, Texas



CRC Press Boca Raton New York London Tokyo

Contents

	Introduction	1
1	Graph Theory Assistance in Studies of Elementary	
	Steps of Complex Reactions	7
	1.1. The Concept of an Elementary Step	7
	1.2. A Reaction as a Combinatorial Object	10
	1.3. Enumeration of Reaction Classes	12
	1.3.1. Analytical Enumeration Using Pólya's Enumeration	
	Theorem	12
	1.3.2. Constructive Enumeration	19
	1.4. Topological Heuristics	23
	1.5. Other Heuristics	27
	References and Notes	31
2	Reaction Mechanisms and Networks	41
	2.1. Application of Graph Theory to Reaction Networks:	
	An Overview of Different Methods and Events	41
	2.1.1. Linear Mechanisms in Terms of Linear Networks	42
	2.1.2. Any Mechanisms in Terms of Linear Networks	44
	2.1.3. Any Mechanisms in Terms of Nonlinear Networks	48
	2.1.4. Relationships between Different Graph-Theoretical Models	53
	2.2. Linear Reaction Networks	59
	2.2.1. Basic Definitions	59
	2.2.2. Classification, Coding, and Enumeration of Linear	
	Reaction Networks	66
	2.2.3. Computer-Assisted Generation of Specific Linear Networks	87
	2.2.4. Graphical Methods for the Derivation of Rate Laws	98
	2.3. Nonlinear Reaction Networks	121
	2.3.1. Elementary Reactions in Terms of Stoichiometry	121
	2.3.2. Exact Determination of Nonlinear Networks.	122

2.3.3.	Stoichiometric Relationships in Nonlinear	
	Reaction Networks	127
2.3.4.	The Algorithm and Computer Program GERM	
	for the Search for Simple Submechanisms	134
2.3.5.	The Structure of the Solution to the Equation	
	$\mathbf{B}(SI)^{\mathrm{T}}\gamma = 0$ in which γ Is Unknown	137
2.3.6.	The Material Balance in Reaction Networks	143
2.3.7.	Applications of Simple Submechanisms and Nonlinear	
	Networks	147
2.3.8.	An Alternative Approach to the Choice of Intermediates	148
References	and Notes	151

 165
 170
 175
 175
 175
 177
 185
 187
 189
 193
 196
· · · · · · · · · · · · · · · · · · ·

4	Complexity	y of Reaction Mechanisms	199
	4.1. Introd	uction	199
	4.2. Comp	lexity of Chemical Graphs	201
	4.2.1.	Shannon's Entropy Measures of Graph Complexity	201
	4.2.2.	Topological Indexes as Potential Complexity Measures	204
	4.2.3.	Combined Graph Complexity Measures	206
	4.3. Kineti	c Complexity Index for Linear Reaction Networks	209
	4.3.1.	Complexity of Kinetic Graphs	209
	4.3.2.	Formulas for the Spanning Trees and Algebraic	
		Complements in Kinetic Graphs.	211
	4.3.3.	Standard Tables with the Complexities of All	
		Topologically Distinct Four-Route Mechanisms	
		Having Two to Six Intermediates	213
	4.3.4.	Trends Increasing Mechanistic Complexity	213
	4.3.5.	Isocomplexity	228
	4.3.6.	Complexity of Networks with Pendant Vertexes	235
	4.4. Stoich	nometric Complexity Index for Reaction Networks	236
	4.4.1.	Background.	236

4.4.2. Mathematical Formalism	237
4.4.3. Calculation Methodology for Linear Networks	239
4.4.4. Influence of Principal Complexity Factors	
and Properties of the Index	240
4.4.5. Concluding Remarks.	248
References and Notes	249

5	Topological Structure of a Mechanism and Its Kinetic Analysis	253
	5.1. Topological Structure of a Mechanism and the Structure	
	of Its Kinetic Model	253
	5.2. Analysis of Conjugation Nodes	260
	5.3. Topological Structure of Mechanisms and "Dimensionless" Bate Equations	268
	References and Notes.	272

•

Subject Index

.

275