

Contents

Foreword	v
Preface	vii
List of Symbols	xiii
1. Regular Symbols	xiii
2. Greek Symbols	xv
3. Subscripts	xvi
1. Introduction	1
2. Definitions and Concepts	5
2.1 Stoichiometric Coefficients	5
2.2 Extent of Reaction	5
2.3 Rate of Reaction	6
2.4 Turnover Frequency or Specific Activity	6
2.5 Selectivity	8
2.6 Structure-Sensitive and Structure-Insensitive Reactions	8
2.7 Elementary Step and Rate Determining Step (RDS)	8
2.8 Reaction Pathway or Catalytic Cycle	10
2.9 Most Abundant Reaction Intermediate (MARI)	11
2.10 Chain Reactions	11
2.11 Reaction Rates in Reactors	11
2.12 Metal Dispersion (Fraction Exposed)	12
2.13 Metal-Support Interactions (MSI)	12
References	13
3. Catalyst Characterization	14
3.1 Total (BET) Surface Area	15
3.2 Pore Volume and Pore Size Distribution	17
3.2.1 Hg Porosimetry Method	17
3.2.2 N ₂ Desorption Method	18
3.2.3 Overall Pore Size Distribution	18
3.3 Metal Surface Area, Crystallite Size, and Dispersion	19

3.3.1	Transmission Electron Microscopy (TEM).....	19
3.3.2	X-Ray Techniques	20
3.3.2.1	Line Broadening of X-Ray Diffraction (XRD) Peaks	20
3.3.2.2	Extended X-Ray Absorption Fine Structure (EXAFS).....	22
3.3.3	Magnetic Measurements	23
3.3.4	Chemisorption Methods	23
3.3.4.1	H ₂ Chemisorption.....	23
3.3.4.2	CO Chemisorption	28
3.3.4.3	O ₂ Chemisorption.....	30
3.3.4.4	H ₂ –O ₂ Titration Techniques	31
3.3.5	Relationships Between Metal Dispersion, Surface Area, and Crystallite Size	32
	References.....	33
	Problems.....	35
4.	Acquisition and Evaluation of Reaction Rate Data.....	38
4.1	Types of Reactors.....	38
4.1.1	Batch Reactor.....	38
4.1.2	Semi-Batch Reactor	42
4.1.3	Plug-Flow Reactor (PFR).....	42
4.1.4	Continuous Flow Stirred-Tank Reactor (CSTR).....	49
4.2	Heat and Mass Transfer Effects	51
4.2.1	Interphase (External) Gradients (Damköhler Number)	52
4.2.1.1	Isothermal Conditions	52
4.2.1.2	Nonisothermal Conditions.....	55
4.2.2	Intraphase (Internal) Gradients (Thiele Modulus).....	56
4.2.2.1	Isothermal Conditions	56
4.2.2.2	Nonisothermal Conditions.....	61
4.2.2.3	Determining an Intraphase (Internal) Effectiveness Factor from a Thiele Modulus	61
4.2.3	Intraphase Gradients (Weisz-Prater Criterion).....	63
4.2.3.1	Gas-Phase or Vapor-Phase Reactions	63
4.2.3.2	Liquid-Phase Reactions	67
4.2.4	Other Criteria to Verify the Absence of Mass and Heat Transfer Limitations (The Madon-Boudart Method)	77
4.2.5	Summary of Tests for Mass and Heat Transfer Effects	80
	References.....	82
	Problems.....	84

5. Adsorption and Desorption Processes	87
5.1 Adsorption Rate	87
5.2 Desorption Rate	90
5.3 Adsorption Equilibrium on Uniform (Ideal) Surfaces-Langmuir Isotherms	91
5.3.1 Single-Site (Nondissociative) Adsorption	92
5.3.2 Dual-Site (Dissociative) Adsorption	92
5.3.3 Derivation of the Langmuir Isotherm by Other Approaches	95
5.3.4 Competitive Adsorption	97
5.4 Adsorption Equilibrium on Nonuniform (Nonideal) Surfaces	98
5.4.1 The Freundlich Isotherm	98
5.4.2 The Temkin Isotherm	99
5.5 Activated Adsorption	101
References	103
Problems	104
6. Kinetic Data Analysis and Evaluation of Model Parameters for Uniform (Ideal) Surfaces	106
6.1 Transition-State Theory (TST) or Absolute Rate Theory	107
6.2 The Steady-State Approximation (SSA)	113
6.3 Heats of Adsorption and Activation Barriers on Metal Surfaces: BOC-MP/UBI-QEP Method	117
6.3.1 Basic BOC-MP/UBI-QEP Assumptions	118
6.3.2 Heats of Atomic Chemisorption	120
6.3.3 Heats of Molecular Chemisorption	121
6.3.4 Activation Barriers for Dissociation and Recombination on Metal Surfaces	130
6.4 Use of a Rate Determining Step (RDS) and/or a Most Abundant Reaction Intermediate (MARI)	133
6.5 Evaluation of Parameter Consistency in Rate Expressions for Ideal Surfaces	134
References	136
Problems	137
7. Modeling Reactions on Uniform (Ideal) Surfaces	141
7.1 Reaction Models with a RDS – Unimolecular Surface Reactions	142
7.2 Reaction Models with a RDS – Bimolecular Surface Reactions	156
7.3 Reaction Models with a RDS – Reactions between an Adsorbed Species and a Gas-Phase Species	170
7.4 Reaction Models with no RDS	171
7.4.1 A Series of Irreversible Steps – General Approach	175

7.4.2	Redox Reactions: The Mars-van Krevelen Rate Law	183
7.5	Data Analysis with an Integral Reactor	185
7.6	Occurrence of a Very High Reaction Order	191
	References	193
	Problems	195
8.	Modeling Reactions on Nonuniform (Nonideal) Surfaces	208
8.1	Initial Models of a Nonuniform Surface	208
8.2	Correlations in Kinetics	209
8.3	Formalism of a Temkin Surface	210
8.4	Consequences of Temkin's Model	213
8.4.1	Adsorption Isotherms	214
8.4.2	Kinetic and Catalytic Behavior	215
	References	222
	Problems	222
9.	Kinetics of Enzyme-Catalyzed Reactions	223
9.1	Single-Substrate Reactions	223
9.2	Dual-Substrate Reactions	228
	References	231
	Problems	231
	Subject Index	234