Table of contents

Preface xiii

Foreword by *Marc-Olivier Coppens* xv

Foreword by *Umit S. Ozkan* xvii

About the Authors and Acknowledgments xix

List of Symbols xxi

About the Companion Website xxvii

1 Rate Concept and Species Conservation Equations in Reactors 1

1.1 Reaction Rates of Species in Chemical Conversions 1

1.2 Rate of a Chemical Change 3

1.3 Chemical Reactors and Conservation of Species 6

1.4 Flow Reactors and the Reaction Rate Relations 8

1.5 Comparison of Perfectly Mixed Flow and Batch Reactors 9

1.6 Ideal Tubular Flow Reactor 10

1.7 Stoichiometric Relations Between Reacting Species 13

1.7.1 Batch Reactor Analysis 13

1.7.2 Steady-Flow Analysis for a CSTR 13

1.7.3 Unsteady Perfectly Mixed-Flow Reactor Analysis 14

Problems and Questions 15

References 18

2 Reversible Reactions and Chemical Equilibrium 19

2.1 Equilibrium and Reaction Rate Relations 19

2.2 Thermodynamics of Chemical Reactions 21

2.3 Different Forms of Equilibrium Constant 23

2.4 Temperature Dependence of Equilibrium Constant and Equilibrium Calculations 25

Problems and Questions 33

References 34

3 Chemical Kinetics and Analysis of Batch Reactors 35

3.1 Kinetics and Mechanisms of Homogeneous Reactions 35

3.2 Batch Reactor Data Analysis 39

3.2.1 Integral Method of Analysis 41

3.2.1.1 First-Order Reaction 41

3.2.1.2 *n*th-Order Reaction and Method of Half-Lives 43

3.2.1.3 Overall Second-Order Reaction Between Reactants A and B 44

3.2.1.4 Second-Order Autocatalytic Reactions 48

3.2.1.5 Zeroth-Order Dependence of Reaction Rate on Concentrations 50

3.2.1.6 Data Analysis for a Reversible Reaction 51

3.2.2 Differential Method of Data Analysis 52

3.3 Changes in Total Pressure or Volume in Gas-Phase Reactions 54

Problems and Questions 56

References 61

4 Ideal-Flow Reactors: CSTR and Plug-Flow Reactor Models 63

4.1 CSTR Model 63

4.1.1 CSTR Data Analysis 67

4.2 Analysis of Ideal Plug-Flow Reactor 69

4.3 Comparison of Performances of CSTR and Ideal Plug-Flow Reactors 71

4.4 Equilibrium and Rate Limitations in Ideal-Flow Reactors 72

4.5 Unsteady Operation of Reactors 76

4.5.1 Unsteady Operation of a Constant Volume Stirred-Tank Reactor 76

4.5.2 Semi-batch Reactors 77

4.6 Analysis of a CSTR with a Complex Rate Expression 79

Problems and Questions 81

References 85

5 Multiple Reactor Systems 87

5.1 Multiple CSTRs Operating in Series 87

5.1.1 Graphical Method for Multiple CSTRs 91

5.2 Multiple Plug-Flow Reactors Operating in Series 93

5.3 CSTR and Plug-Flow Reactor Combinations 94

Problems and Questions 96

References 98

6 Multiple Reaction Systems 99

6.1 Selectivity and Yield Definitions 100

6.2 Selectivity Relations for Ideal Flow Reactors 101

6.3 Design of Ideal Reactors and Product Distributions for Multiple Reaction Systems 104

6.3.1 Parallel Reactions 104

6.3.2 Consecutive Reactions 110

Problems and Questions 113

References 116

7 Heat Effects and Non-isothermal Reactor Design 117

7.1 Heat Effects in a Stirred-Tank Reactor 118

7.2 Steady-State Multiplicity in a CSTR 121

7.3 One-Dimensional Energy Balance for a Tubular Reactor 126

7.4 Heat Effects in Multiple Reaction Systems 131

7.4.1 Heat Effects in a CSTR with Parallel Reactions 131

7.4.2 Heat Effects in a CSTR with Consecutive Reactions 132

7.4.3 Energy Balance for a Plug-Flow Reactor with Multiple Reactions 133

7.5 Heat Effects in Multiple Reactors and Reversible Reactions 133

7.5.1 Temperature Selection and Multiple Reactor Combinations 133

7.5.1.1 Endothermic-Reversible Reactions in a Multi-stage Reactor System 141

7.5.2 Cold Injection Between Reactors 147

7.5.3 Heat-Exchanger Reactors 149

Problems and Questions 150

Case Studies 154

References 160

8 Deviations from Ideal Reactor Performance 161

8.1 Residence Time Distributions in Flow Reactors 161

8.2 General Species Conservation Equation in a Reactor 163

8.3 Laminar Flow Reactor Model 166

8.4 Dispersion Model for a Tubular Reactor 168

8.5 Prediction of Axial Dispersion Coefficient 172

8.6 Evaluation of Dispersion Coefficient by Moment Analysis 174

8.7 Radial Temperature Variations in Tubular Reactors 175

8.8 A Criterion for the Negligible Effect of Radial Temperature Variations on the Reaction Rate 177

8.9 Effect of L/d_t Ratio on the Performance of a Tubular Reactor and Pressure Drop 179

Problems and Questions 180

Exercises 181

References 182

9 Fixed-Bed Reactors and Interphase Transport Effects 185

9.1 Solid-Catalyzed Reactions and Transport Effects within Reactors 185

9.2 Observed Reaction Rate and Fixed-Bed Reactors 187

9.3 Significance of Film Mass Transfer Resistance in Catalytic Reactions 189

9.4 Tubular Reactors with Catalytic Walls 191

9.4.1 One-Dimensional Model 192

9.4.2 Two-Dimensional Model 193

9.5 Modeling of a Non-isothermal Fixed-Bed Reactor 194

9.6 Steady-State Multiplicity on the Surface of a Catalyst Pellet 196

Exercises 197

References 198

10 Transport Effects and Effectiveness Factor for Reactions in Porous Catalysts 199

10.1 Effectiveness Factor Expressions in an Isothermal Catalyst Pellet 199

10.2 Observed Activation Energy and Observed Reaction Order 205

10.3 Effectiveness Factor in the Presence of Pore-Diffusion and Film Mass Transfer Resistances 208

10.4 Thermal Effects in Porous Catalyst Pellets 210

10.5 Interphase and Intrapellet Temperature Gradients for Catalyst Pellets 215

10.6 Pore Structure Optimization and Effectiveness Factor Analysis for Catalysts with Bi-modal Pore-Size Distributions 217

10.7 Criteria for Negligible Transport Effects in Catalytic Reactions 221

10.7.1 Criteria for Negligible Diffusion and Heat Effects on the Observed Rate of Solid-Catalyzed Reactions 221

10.7.2 Relative Importance of Concentration and Temperature Gradients in Catalyst Pellets 222

10.7.3 Intrapellet and External Film Transport Limitations 225

10.7.4 A Criterion for Negligible Diffusion Resistance in Bidisperse Catalyst Pellets 225

10.8 Transport Effects on Product Selectivities in Catalytic Reactions 226

10.8.1 Film Mass Transfer Effect 226

10.8.2 Pore-Diffusion Effect 227

Problems and Questions 228

Exercises 229

References 233

11 Introduction to Catalysis and Catalytic Reaction Mechanisms 235

11.1 Basic Concepts in Heterogeneous Catalysis 235

11.2 Surface Reaction Mechanisms 237

11.3 Adsorption Isotherms 241

11.4 Deactivation of Solid Catalysts 244

Exercises 246

References 246

12 Diffusion in Porous Catalysts 247

12.1 Diffusion in a Capillary 247

12.2 Effective Diffusivities in Porous Solids 251

12.3 Surface Diffusion 252

12.4 Models for the Prediction of Effective Diffusivities 253

12.4.1 Random Pore Model 253

12.4.2 Grain Model 254

12.5 Diffusion and Flow in Porous Solids 254

12.6 Experimental Methods for the Evaluation of Effective Diffusion Coefficients 255

12.6.1 Steady-State Methods 255

12.6.2 Dynamic Methods 256

12.6.3 Single-Pellet Moment Method 257

Exercises 259

References 259

13 Process Intensification and Multifunctional Reactors 261

13.1 Membrane Reactors 262

13.1.1 Modeling of a Membrane Reactor 263

13.1.2 General Conservation Equations and Heat Effects in a Membrane Reactor 265

13.2 Reactive Distillation 266

13.2.1 Equilibrium-Stage Model 267

13.2.2 A Rate-Based Model for a Continuous Reactive Distillation Column 269

13.3 Sorption-Enhanced Reaction Process 270

13.4 Monolithic and Microchannel Reactors 275

13.4.1 Microchannel Reactors 278

13.5 Chromatographic Reactors 279

13.6 Alternative Energy Sources for Chemical Processing 279

13.6.1 Microwave-Assisted Chemical Conversions 280

13.6.2 Ultrasound Reactors 282

13.6.3 Solar Energy for Chemical Conversion 282

References 283

14 Multiphase Reactors 285

14.1 Slurry Reactors 285

14.2 Trickle-Bed Reactors 289

14.3 Fluidized-Bed Reactors 290

References 294

15 Kinetics and Modeling of Non-catalytic Gas–Solid Reactions 295

15.1 Unreacted-Core Model 296

15.2 Deactivation and Structural Models for Gas–Solid Reactions 299

15.3 Chemical Vapor Deposition Reactors 302

Exercises 305

References 307

Appendix A Some Constants of Nature 309

Appendix B Conversion Factors 311

Appendix C Dimensionless Groups and Parameters 313

Index 315