Contents

Preface XI

1	Introduction 1	
1.1	Green Chemistry and Sustainable Development	1

- 1.1.1 What Is 'Green Chemistry'? 2
- 1.1.2 Quantifying Environmental Impact: Efficiency, E-Factors, and Atom Economy 4
- 1.1.3 Just How 'Green' Is This Process? 6
- 1.1.4 Product and Process Life-Cycle Assessment (LCA) 10
- 1.2 What Is Catalysis and Why Is It Important? 12
- 1.2.1 Homogeneous Catalysis, Heterogeneous Catalysis, and Biocatalysis: Definitions and Examples 14

V

- 1.2.2 Connecting Catalysis and Sustainability: Saving Resources by Using Catalytic Cycles 20
- 1.2.3 Industrial Example: the BHC Ibuprofen Process 22
- 1.3 Tools in Catalysis Research 24
- 1.3.1 Catalyst Synthesis and Testing Tools 24
- 1.3.2 Catalyst Characterisation Tools 27
- 1.3.3 Modelling/Mechanistic Studies Tools 28
- 1.4 Exercises 30 References 38 Further Reading 41

2 The Basics of Catalysis 43

- 2.1 Catalysis Is a Kinetic Phenomenon 43
- 2.1.1 Reaction Rates, Reaction Orders, Rate Equations and Rate-Determining Steps 45
- 2.1.2 The Reaction Profile and the Reaction Coordinate 49
- 2.1.3 Zero-Order, First-Order and Second-Order Kinetics 52
- 2.1.4 Langmuir–Hinshelwood Kinetics 58
- 2.1.5 The Steady-State Approximation *61*
- 2.1.6 Michaelis–Menten Kinetics 62
- 2.1.7 Consecutive and Parallel First-Order Reactions 66

- VI Contents
 - 2.1.8 Pre-equilibrium, 'Catalyst Reservoirs', and Catalyst Precursors 67
 - 2.2 Practical Approaches in Kinetic Studies 70
 - 2.2.1 Initial Reaction Rates and Concentration Effects 70
 - 2.2.2 Creating Pseudo-Order Conditions 71
 - 2.2.3 What You See vs. What You Get 72
 - 2.2.4 Learning from Stoichiometric Experiments 73
 - 2.3 An Overview of Some Basic Concepts in Catalysis 74
 - 2.3.1 Catalyst-Substrate Interactions and Sabatier's Principle 74
 - 2.3.2 Catalyst Deactivation, Sintering, and Thermal Degradation 75
 - 2.3.3 Catalyst Inhibition 78
 - 2.4 Exercises 79

References 85

3 Homogeneous Catalysis 89

- 3.1 Metal Complex Catalysis in the Liquid Phase 90
- 3.1.1 Elementary Steps in Homogeneous Catalysis 91
- 3.1.2 Structure-Activity Relationships in Homogeneous Catalysis 100
- 3.1.3 Asymmetric Homogeneous Catalysis 106
- 3.1.4 Industrial Examples 109
- 3.2 Homogeneous Catalysis without Metals 117
- 3.2.1 Classic Acid/Base Catalysis 117
- 3.2.2 Organocatalysis 117
- 3.3 Scaling Up Homogeneous Reactions: Pros and Cons 119
- 3.3.1 Catalyst Recovery and Recycling 120
- 3.3.2 Immobilised Complexes and Ship-In-A-Bottle Catalysts 122
- 3.4 'Click Chemistry' and Homogeneous Catalysis 122
- 3.5 Exercises 124 References 131

4 Heterogeneous Catalysis 137

- 4.1 Classic Gas/Solid Systems 139
- 4.1.1 The Concept of the Active Site 141
- 4.1.2 Model Catalyst Systems 143
- 4.1.3 Real Catalysts: Promoters, Modifiers, and Poisons 144
- 4.1.4 Preparation of Solid Catalysts: Black Magic Revealed 146
- 4.1.5 Selecting the Right Support 154
- 4.1.6 Catalyst Characterisation 157
- 4.1.7 The Catalytic Converter: an Example from Everyday Life 166
- 4.1.8 Surface Organometallic Chemistry *168*
- 4.2 Liquid/Solid and Liquid/Liquid Catalytic Systems 171
- 4.2.1 Aqueous Biphasic Catalysis 171
- 4.2.2 Fluorous Biphasic Catalysis 173
- 4.2.3 Biphasic Catalysis Using Ionic Liquids 175
- 4.2.4 Phase-Transfer Catalysis 176

4.3 Advanced Process Solutions Using Heterogeneous Catalysis 178

Contents VII

- 4.3.1 The BP AVADA Ethyl Acetate Process 178
- 4.3.2 The CB&I Lummus/Albemarle AlkyClean Process 179
- 4.3.3 The IFP and Yellowdiesel Processes for Biodiesel Production 180
- 4.3.4 The ABB Lummus/UOP SMART Process 184
- 4.4 Exercises 186 References 196

5 Biocatalysis 205

- 5.1 The Basics of Enzymatic Catalysis 206
- 5.1.1 Terms and Definitions the Bio Dialect 206
- 5.1.2 Active Sites and Substrate Binding Models 210
- 5.1.3 Intramolecular Reactions and Proximity Effects 212
- 5.1.4 Common Mechanisms in Enzymatic Catalysis 213
- 5.2 Applications of Enzyme Catalysis 215
- 5.2.1 Whole-Cell Systems vs. Isolated Enzymes 216
- 5.2.2 Immobilised Enzymes: Bona Fide Heterogeneous Catalysis 218
- 5.2.3 Replacing 'Conventional Routes' with Biocatalysis 221
- 5.2.4 Combining 'Bio' and 'Chemo' Catalysis 223
- 5.3 Developing New Biocatalysts: Better than Nature's Best 225
- 5.3.1 Prospecting Natural Diversity 226
- 5.3.2 Rational Design 226
- 5.3.3 Directed Evolution 227
- 5.4 Non-enzymatic Biocatalysts 229
- 5.4.1 Catalytic Antibodies (Abzymes) 229
- 5.4.2 Catalytic RNA (Ribozymes) 230
- 5.5 Industrial Examples 232
- 5.5.1 High-Fructose Corn Syrup: 11 Million Tons per Year 232
- 5.5.2 The Mitsubishi Rayon Acrylamide Process 233
- 5.5.3 The BMS Paclitaxel Process 235
- 5.5.4 The Tosoh/DSM Aspartame Process 236
- 5.6 Exercises 237 References 243

6 Computer Applications in Catalysis Research 249

- 6.1 Computers as Research Tools in Catalysis 249
- 6.2 Modelling of Catalysts and Catalytic Cycles 251
- 6.2.1 A Short Overview of Modelling Methods 251
- 6.2.2 Simplified Model Systems vs. Real Reactions 253
- 6.2.3 Modelling Large Catalyst Systems Using Classical Mechanics 254
- 6.2.4 In-Depth Reaction Modelling Using Quantum Mechanics 256
- 6.3 Predictive Modelling and Rational Catalyst Design 258
- 6.3.1 Catalysts, Descriptors, and Figures of Merit 259
- 6.3.2 Three-Dimensional (3D) Descriptors of Homogeneous Catalysts 260
- 6.3.3 Two-Dimensional (2D) Descriptors of Homogeneous Catalysts 263
- 6.3.4 Descriptors of Heterogeneous (Solid) Catalysts 267

VIII Contents

- 6.3.5 Predictive Modelling in Biocatalysis 271
- 6.3.6 Generating Virtual Catalyst Libraries in Space A 272
- 6.3.7 Understanding Catalyst Diversity 273
- 6.3.8 Virtual Catalyst Screening: Connecting Spaces A, B, and C 276
- 6.4 An Overview of Data Mining Methods in Catalysis 277
- 6.4.1 Principal Components Analysis (PCA) 279
- 6.4.2 Partial Least-Squares (PLS) Regression 281
- 6.4.3 Artificial Neural Networks (ANNs) 283
- 6.4.4 Classification Trees 284
- 6.4.5 Model Validation: Separating Knowledge from Garbage 284

6.5 Exercises 287

References 291

Index 297