

Fundamentals of Chemical Kinetics

S. R. Logan

*Reader in Chemistry
University of Ulster*



Longman

Contents

Preface xi

Acknowledgements xiii

1 THE EMPIRICAL FRAMEWORK OF CHEMICAL KINETICS 1

- 1.1 Introduction 1
- 1.2 The rate equation 3
- 1.3 Integrated rate equations 5
- 1.4 Reaction half-life and mean lifetime 9
- 1.5 The determination of reaction order 12
- 1.6 Effect of temperature on reaction rates 17
- Suggested reading 21
- Problems 21

2 THE EXPERIMENTAL STUDY OF REACTION KINETICS 24

- 2.1 Minimum requirements for the study of chemical kinetics 24
- 2.2 The evolution of techniques for monitoring reaction progress 25
- 2.3 The application of spectrophotometry to chemical kinetics 27
- 2.4 Electrical conductivity and dilatometry 30
- 2.5 Techniques for the gas phase 31
- 2.6 Modern experimental techniques 33
- 2.7 The evaluation of the rate constant 35
- Suggested reading 38
- Problems 38

3 REACTION MECHANISM AND REACTION ORDER 40

- 3.1 An elementary reaction and the molecularity 40
- 3.2 Consecutive reaction processes 42
- 3.3 Formation of an intermediate complex 45
- 3.4 The "third body" effect in atom recombination 47
- 3.5 Parallel reactions 50
- 3.6 Reactant participating in equilibria 53
- 3.7 Opposing reactions 55
- 3.8 Isotopic exchange reactions 58

- Suggested reading 61
Problems 62
- 4 THEORIES OF BIMOLECULAR REACTIONS 65**
- 4.1 The Collision Theory 65
4.2 Transition State Theory 70
4.3 The theory of diffusion-controlled reactions in solution 78
Suggested reading 84
Problems 85
- 5 THE INTERPRETATION OF BIMOLECULAR REACTIONS IN SOLUTION 86**
- 5.1 Solvent effects on reaction rates 86
5.2 Applied hydrostatic pressure 87
5.3 Dielectric permittivity 90
5.4 Ionic strength 91
5.5 Linear free energy relationships 94
5.6 Kinetic isotope effects 96
5.7 Electron transfer reactions in solution 101
Suggested reading 105
Problems 106
- 6 UNIMOLECULAR GAS PHASE REACTIONS 109**
- 6.1 The kinetic results 109
6.2 The Lindemann mechanism 111
6.3 The RRK (or Kassel) theory 114
6.4 The RRKM theory 118
Suggested reading 121
Problems 121
- 7 CHAIN REACTIONS 123**
- 7.1 Linear chain reactions 123
7.2 Pyrolysis reactions involving chain mechanisms 126
7.3 Chain polymerisation: free radical processes 129
7.4 Chain polymerisation: ionic processes 131
7.5 Less simple linear chain reactions 135
7.6 Branching chains and explosion phenomena 138
Suggested reading 143
Problems 143
- 8 HETEROGENEOUS CATALYSIS 146**
- 8.1 Introduction 146
8.2 Chemisorption and the chemisorbed state 146
8.3 The Langmuir adsorption isotherm 148
8.4 Reactions on a catalyst surface 151
8.5 Catalytic exchange of alkanes with deuterium 153

- 8.6 The catalytic oxidation of carbon monoxide 156
- 8.7 Catalytic synthesis and decomposition of ammonia 158
- 8.8 The criterion for a good catalyst 161
- 8.9 Catalysis in industry 162
- Suggested reading 164
- Problems 165

- 9 HOMOGENEOUS CATALYSIS 167**
 - 9.1 Gas phase catalysis 167
 - 9.2 Catalysis in solution 169
 - 9.3 Catalysis by acids 171
 - 9.4 Catalysis by bases 174
 - 9.5 Autocatalysis 177
 - 9.6 Oscillating reactions 179
 - 9.7 Catalysis by enzymes 184
 - 9.8 Enzyme inhibitors 187
 - Suggested reading 189
 - Problems 190

- 10 RELAXATION AND OTHER ADVANCED TECHNIQUES 192**
 - 10.1 Introduction 192
 - 10.2 Relaxation techniques: experimental aspects 196
 - 10.3 More complex reaction systems 199
 - 10.4 NMR spectroscopy 202
 - 10.5 Electrochemical methods 206
 - Suggested reading 209
 - Problems 210

- 11 PHOTOCHEMISTRY AND RADIATION CHEMISTRY 212**
 - 11.1 Initial effects of light absorption 212
 - 11.2 Photochemical kinetics 215
 - 11.3 Flash photolysis 224
 - 11.4 Primary effects of ionising radiations 228
 - 11.5 Radiation chemistry of aqueous solutions 229
 - 11.6 Pulse radiolysis 232
 - Suggested reading 236
 - Problems 236

- 12 REACTION DYNAMICS 239**
 - 12.1 Introduction 239
 - 12.2 Studies using crossed molecular beams 240
 - 12.3 Energy distribution within the reaction products 242
 - 12.4 Ion-molecule reactions 245
 - 12.5 Dynamics of ion-molecule reactions 248
 - Suggested reading 251

X Contents

APPENDIX A 252

APPENDIX B 254

ANSWERS TO THE PROBLEMS 256

INDEX 258

INDEX OF CHEMICAL REACTIONS 263