# Table of Contents

**Preface** V

**Symbols and Definitions** XIII

1 **Introduction** 1

1.1 Scope 1
1.2 Historical Remarks 6
1.3 Four Basic Kinetic Situations 10
  1.3.1 Homogeneous Reactions: Point Defect Relaxation 10
  1.3.2 Steady State Flux of Point Defects in a Binary Compound 12
  1.3.3 The Kinetics of an Interface Reaction 14
  1.3.4 Kinetics of Compound Formation: \( A + B = AB \) 16

References 18

2 **Thermodynamics of Point Defects** 19

2.1 Introduction 19
2.2 Thermodynamics of Crystals 21
  2.2.1 Phenomenological Approach 21
  2.2.2 Remarks on Statistical Thermodynamics of Point Defects 27
2.3 Some Practical Aspects of Point Defect Thermodynamics 31
2.4 Point Defects in Solid Solutions 38
2.5 Conclusions 40

References 41

3 **One- and Two-Dimensional Defects in Crystals** 43

3.1 Introduction 43
3.2 Dislocations 43
  3.2.1 Strain, Stress, and Energy 43
  3.2.2 Kinetic Effects Due to Dislocations 48
3.3 Grain Boundaries 50
  3.3.1 Structure and Energy of Grain Boundaries 50
  3.3.2 Phase Boundaries in Solids 54
3.4 Mobility of Dislocations, Grain Boundaries, and Phase Boundaries 57

References 60

4 **Basic Kinetic Concepts and Situations** 61

4.1 Introduction 61
  4.1.1 Systematics of Solid State Chemical Processes 61
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>The Concepts of Irreversible Thermodynamics</td>
<td>63</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Structure Element Fluxes</td>
<td>66</td>
</tr>
<tr>
<td>4.3</td>
<td>Diffusion</td>
<td>68</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Introduction</td>
<td>68</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Fickian Transport</td>
<td>70</td>
</tr>
<tr>
<td>4.3.3</td>
<td>Chemical Diffusion</td>
<td>71</td>
</tr>
<tr>
<td>4.4</td>
<td>Transport in Ionic Solids</td>
<td>75</td>
</tr>
<tr>
<td>4.4.1</td>
<td>Introduction</td>
<td>75</td>
</tr>
<tr>
<td>4.4.2</td>
<td>Transport in Binary Ionic Crystals AX</td>
<td>78</td>
</tr>
<tr>
<td>4.4.3</td>
<td>First Order Kinetics</td>
<td>75</td>
</tr>
<tr>
<td>4.5</td>
<td>Transport Across Phase Boundaries</td>
<td>82</td>
</tr>
<tr>
<td>4.5.1</td>
<td>Introduction. Equilibrium Phase Boundaries</td>
<td>82</td>
</tr>
<tr>
<td>4.5.2</td>
<td>Non-Equilibrium Phase Boundaries</td>
<td>84</td>
</tr>
<tr>
<td>4.6</td>
<td>Transport in Semiconductors; Junctions</td>
<td>85</td>
</tr>
<tr>
<td>4.6.1</td>
<td>Introduction</td>
<td>85</td>
</tr>
<tr>
<td>4.6.2</td>
<td>The (p-n) Junction</td>
<td>86</td>
</tr>
<tr>
<td>4.7</td>
<td>Basic Rate Equations for Homogeneous Reactions</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>Kinetics and Dynamics. Local Equilibrium</td>
<td>95</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>95</td>
</tr>
<tr>
<td>5.1.1</td>
<td>Linear Response</td>
<td>99</td>
</tr>
<tr>
<td>5.1.2</td>
<td>Transition State</td>
<td>101</td>
</tr>
<tr>
<td>5.1.3</td>
<td>Brownian Motion</td>
<td>103</td>
</tr>
<tr>
<td>5.2</td>
<td>Kinetic Parameters and Dynamics</td>
<td>107</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Phenomenological Coefficients and Kinetic Theory</td>
<td>107</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Correlation of Atomic Jumps</td>
<td>109</td>
</tr>
<tr>
<td>5.2.3</td>
<td>Conductivity of Ionic Crystals: Frequency Dependence</td>
<td>112</td>
</tr>
<tr>
<td>5.2.4</td>
<td>Diffusive Motion and Phonons</td>
<td>116</td>
</tr>
<tr>
<td>5.3</td>
<td>Relaxation of Irregular Structure Elements</td>
<td>117</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Introduction</td>
<td>117</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Relaxation of Structure Elements in Nonstoichiometric Compounds</td>
<td>118</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Relaxation of Intrinsic Disorder</td>
<td>119</td>
</tr>
<tr>
<td>5.4</td>
<td>Defect Equilibration During Interdiffusion</td>
<td>123</td>
</tr>
<tr>
<td>5.4.1</td>
<td>The Atomistics of Interdiffusion</td>
<td>123</td>
</tr>
<tr>
<td>5.4.2</td>
<td>The Kirkendall Effect</td>
<td>125</td>
</tr>
<tr>
<td>5.4.3</td>
<td>Local Defect Equilibration During Interdiffusion</td>
<td>127</td>
</tr>
<tr>
<td>5.4.4</td>
<td>Interdiffusion of Heterovalent Compounds</td>
<td>133</td>
</tr>
<tr>
<td>5.5</td>
<td>References</td>
<td>135</td>
</tr>
</tbody>
</table>

6 Heterogeneous Solid State Reactions 137
6.1 Introduction 137
6.2 Nucleation and Initial Growth 138
  6.2.1 Introductory Remarks 138
  6.2.2 Nucleation Kinetics 140
  6.2.3 Early Growth 143
6.3 Compound Formation 146
  6.3.1 Formation Kinetics of Double Salts 146
  6.3.2 Formation of Multiphase Products 153
6.4 Displacement Reactions 155
6.5 Powder Reactions 157
  6.5.1 General 157
  6.5.2 Self-Propagating Exothermic Powder Reactions 158
6.6 Interface Rate Control 160
6.7 Thermal Decomposition of Solids 162
References 163

7 Oxidation of Metals 165
  7.1 Introduction 165
  7.2 Wagner's Theory of Metal Oxidation 166
  7.3 Non-Parabolic Rate Laws 171
  7.4 Alloy Oxidation 175
  7.4.1 The Morphological Stability of Boundaries During Metal Oxidation 176
  7.5 Some Practical Aspects of High Temperature Corrosion 179
References 181

8 Solids in Thermodynamic Potential Gradients 183
  8.1 Introduction 183
  8.2 Multicomponent Solids in Chemical Potential Gradients 184
  8.3 Kinetic Decomposition of Compounds in Chemical Potential Gradients 189
  8.4 Cross Effects 191
  8.5 Demixing Under Non-Hydrostatic Stress 198
  8.6 Demixing in Temperature Gradients (Ludwig-Soret Effect) 200
  8.7 Demixing in Multiphase Systems 202
  8.8 Multiphase Systems in Electric Fields 204
References 207

9 Internal Reactions 209
  9.1 Introduction 209
  9.2 Internal Oxidation of Metals 211
  9.3 Internal Reactions in Nonmetallic Systems 213
  9.3.1 Internal Oxidation in Nonmetallic Solid Solutions 213
  9.3.2 Internal Reduction in Nonmetallic Solutions 217
# Table of Contents

## 12.3 Diffusive Transformations 304
12.3.1 First-Order Transformation with Small Composition Changes 305
12.3.2 Spinodal Decomposition 308
References 312

## 13 Reactions in Solids Under Irradiation 315
13.1 Introduction 315
13.2 Particle Irradiation 317
13.2.1 Basic Concepts 317
13.2.2 Radiation Effects in Halides (Radiolysis) 320
13.2.3 Radiation Effects in Metals 321
13.3 Photon Irradiation 324
13.3.1 Basic Concepts 324
13.3.2 Radiation Effects in Halides (Photolysis) 326
13.3.3 Ag Based Photography 327
References 328

## 14 Influence of Mechanical Stress 331
14.1 Introduction 331
14.2 Thermodynamic Considerations 332
14.2.1 Thermodynamics of Stressed Solids 332
14.2.2 Thermodynamics of Stressed Solids with Only Immobile Components 335
14.3 Transport in Stressed Solids 336
14.3.1 Introductory Remarks 336
14.3.2 The Influence of Stress on Heterogeneous Reactions $A + B = AB$ 337
14.3.3 Transport in Inhomogeneously Stressed Crystals 338
14.4 Creep and Fracture 342
14.4.1 Introductory Remarks 342
14.4.2 Creep 342
14.4.3 Fracture 347
14.4.4 Toughening of Crystals by Phase Transformations 349
14.5 Tribochemistry 351
References 353

## 15 Transport and Reactions in Special Systems 355
15.1 Introduction 355
15.2 Silicates 356
15.2.1 Introductory Remarks 356
15.2.2 Transport in Silicates 357
15.2.3 Order-Disorder Reactions 363
15.2.4 The Role of Hydrogen in Silicates 364
15.2.5 Silicate Glasses 365
# Table of Contents

15.3 Fast Ion Conductors 368  
15.3.1 Introductory Remarks 368  
15.3.2 Halides 370  
15.3.3 $\text{Ag}_2\text{S} (\text{Ag}_2\text{Se, Ag}_2\text{Te})$ 372  
15.3.4 Oxides: Stabilized Zirconia 374  
15.3.5 $\beta$-Alumina 377  
15.3.6 Proton Conductors 379  
15.4 Hydrides 380  
15.4.1 Introductory Remarks 380  
15.4.2 Phase Equilibria 382  
15.4.3 Kinetics of Hydride Formation and Decomposition 383  
15.5 Molecular (Organic) Crystals 386  
15.5.1 Introductory Remarks 386  
15.5.2 Diffusion in Molecular Crystals 388  
15.5.3 Conducting Polymers 389  

References 391

16 Appendix: Experimental Methods for *In-situ* Investigations 393  
16.1 Introduction 393  
16.2 Thermogravimetry, -manometry, -volumetry, -analysis 395  
16.2.1 Thermogravimetry 395  
16.2.2 Thermomanometry, Thermovolumetry 396  
16.2.3 Thermal Analysis 397  
16.3 Electrochemical Measurements 398  
16.3.1 Introductory Remarks 398  
16.3.2 Chemical Potential Sensors 399  
16.4 Spectroscopic Methods: Nuclear Spectroscopy 402  
16.4.1 Introduction 402  
16.4.2 Physical Background 404  
16.4.3 *In-situ* Application, Examples 408  
16.5 Spectroscopic Methods: Electromagnetic Spectroscopy (IR, VIS, UV, X-ray) 412  
16.5.1 Introduction 412  
16.5.2 Physical Background 412  
16.5.3 *In-situ* Application, Examples 413  
16.6 Particle Spectroscopy 415  
16.6.1 Introduction 415  
16.6.2 Physical Background 416  
16.6.3 Examples 417  
References 419

Epilogue 421

Subject Index 423

Author Index 431