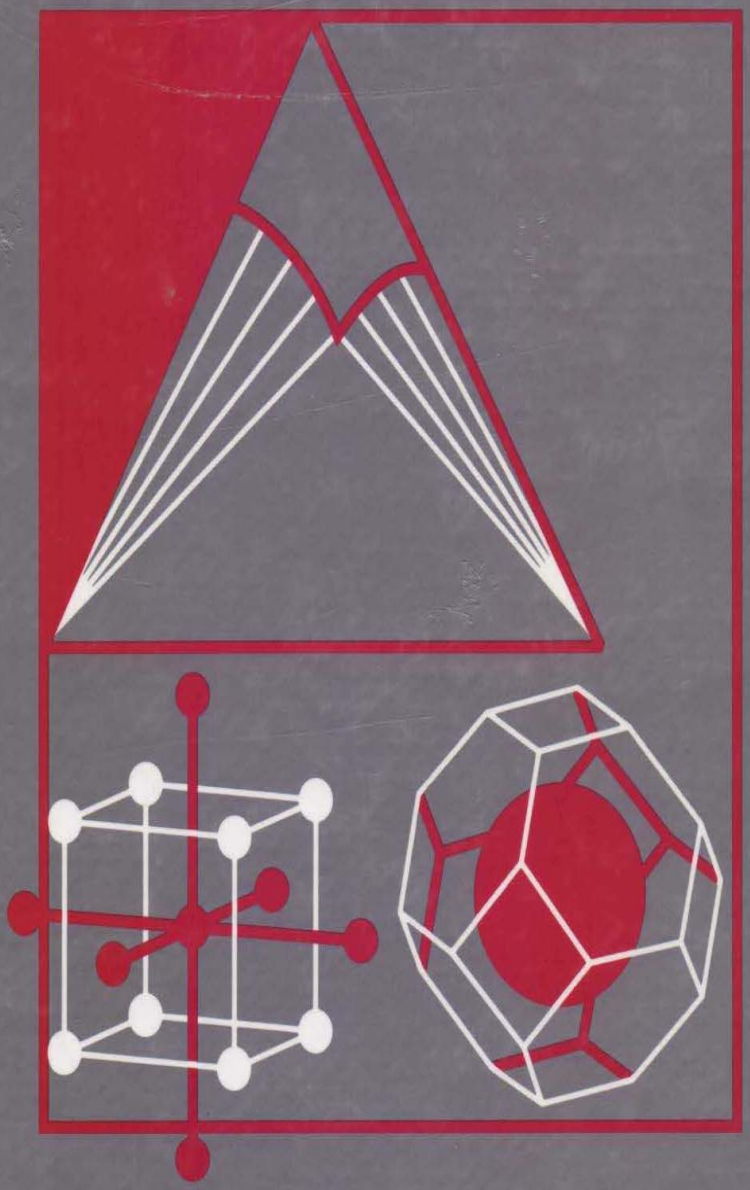
The Physical Chemistry *of* Solids



R.J. Borg *and* G.J. Dienes

Contents

Preface xi

Chapter 1
Crystallography and Structure of the Elements 1

1. Symmetry 2
2. Lattices 6
3. Bravais Lattices 7
4. Crystal Systems 7
5. Space Groups 10
6. Miller Indices 10
7. The Unit Cell 14
8. Crystal Structures of the Metallic Elements 15
9. Covalently Bonded Elements 25

Exercises 36
Additional Reading 37

Chapter 2
Thermodynamic Equations of State 39

1. Thermodynamic Functions 39
2. Equations of State 43
3. The Effect of Pressure on Heat Capacity 48
4. The Effects of Pressure Upon S, E, and G 52

5. Matter at Extremely High Temperatures and Pressures 56
Exercises 62
Additional Reading 63

Chapter 3
The Vibrational Properties of Solids 65

1. The Grüneisen Constant 65
2. The Einstein Heat Capacity 69
3. Normal Vibrational Modes 71
4. The Spectrum of the Normal Modes 75
5. The Debye Model of the Heat Capacity 79
6. The Electronic Specific Heat 82
7. Anharmonicity 84
8. Optical Vibrations 85

Exercises 88
Additional Reading 90

Chapter 4
Potential Functions 91

1. Isolated Two-Body Systems 92
2. Generalized Potential Functions 101
3. Some Applications of the Potential Functions 108

Exercises 116
Additional Reading 117

Chapter 5
Ionic Crystals 119

1. The Madelung Constant and Lattice Energies 120
2. The Repulsive Potential 124
3. The Born–Haber Cycle 130
4. The Kapustinskii Equations 135
5. Entropies of Solid Compounds 138
6. The Size of Ions 141
7. Ionic Packing and Crystal Structure 148
8. Complex Ionic Crystals—Pauling's Rules 153
9. Electronegativity: Ionic Bonds 154
10. Some Important Ionic Structures 159

Exercises 176
Additional Reading 178

Chapter 6
Quantum Mechanical Principles and the Covalent Bond 179

1. The Schrödinger Equation 179
2. Atomic Wave Functions 189
3. The Covalent Bond 195
4. Ligand Fields 214

Exercises 225
Additional Reading 226

Chapter 7
Covalent Crystals 229

1. Covalent Radii 229
2. The Silicates 232
3. Silicate Minerals 243
4. Thermodynamics of Semiconduction 250
5. Electrons in a Periodic Potential 255
6. Elemental Intrinsic Semiconductors 269
7. Compound Semiconductors 270
8. Extrinsic Semiconductors 273
9. Graphite 274
10. Intercalate Compounds 276
11. Electron-Deficient Elements and Compounds 280

Exercises 284
Additional Reading 284

Chapter 8
Metallic Crystals 287

1. The Band Model 288
2. The Metallic Bond 290
3. The Pseudopotential 299
4. Metallic Solid Solutions 302
5. Intermediate Phases 305
6. Metallic Compounds 320

Exercises 321
Additional Reading 321

Chapter 9
Polyphase Equilibrium 323

1. Ideal Solutions 323
2. The Liquid–Solid Phase Diagram for Ideal Binary Solutions 327

3. Nonideal Solutions 331
4. Phase Separation 335
5. Equilibrium Among Phases 336
6. The Phase Rule 339
7. Phase Diagram for Single-Component Systems 340
8. Binary Phase Diagrams—Construction and Nomenclature 345
9. The Lever Law 349
10. Eutectics 350
11. Complex Phase Reactions 353
12. Free-Energy Diagrams 355
13. Ternary Systems 357
Exercises 364
Additional Reading 366

Chapter 10
Thermodynamics of Heterogeneous Equilibria 367

1. Partial Pressure, Fugacity, and Thermodynamic Activity 367
2. Activities Derived from Phase Diagrams 370
3. Henry's Law 372
4. Phase Separation 376
5. The Equilibrium Constant 376
6. Solid–Gas Reactions 378
7. Equilibrium between Compounds and Gases 381
Exercises 384
Additional Reading 386

Chapter 11
The Chemistry of Interfaces 387
1. Surface Free Energy 388
2. The Chemical Potential as a Function of Surface Curvature 390
3. The Gibbs Adsorption Isotherm 393
4. The Segregation of Impurities at Interfaces 395
5. The Langmuir Adsorption Isotherm 397
6. The BET Isotherm 400
7. The Rate and Mechanism of Thermal Desorption 403
8. Coupled Adsorption and Bulk Diffusion 405
9. Chemisorption—Chemical Bonding to Surfaces 408
10. Effects of Surface Structure 415
11. Surface Reactions—Carbon 417
Exercises 419
Additional Reading 421

Chapter 12
Crystal Defects 423

1. Definitions and Classification 423
2. Thermodynamics of Point Defects in Monoatomic Solids 425
3. Defects in Ionic Crystals 431
4. Defects in Semiconductors 433
5. Formation Energies of Vacancies and Interstitial Atoms 435
6. Defect Complexes 437
7. Experimental Determination of Crystal Defect Parameters 440

Exercises 445
Additional Reading 447

Chapter 13
Diffusion in Solids 449

1. Basic Phenomenological Equations 449
2. Mechanisms 455
3. Temperature Dependence and Activation Energies 456
4. The Correlation Coefficient 461
5. Representative Experimental Results 463
6. Defect Reactions 474

Exercises 484
Additional Reading 486

Chapter 14
Phase Transitions 489

1. Melting 490
2. Order–Disorder Transitions 498
3. Magnetic Order 510
4. Spinodal Decomposition 518
5. Precipitation by Nucleation and Growth 521
6. Martensitic Transformations 525
7. Glasses 530
8. The Photographic Process 538

Exercises 540
Additional Reading 542

Appendix A
van der Waals Forces 545

Appendix B
The Grüneisen Constants 549

Appendix C
Zero-Point Energy of the Harmonic Oscillator 553

Appendix D
Partial Differential Equations and Boundary Value Problems: The Vibrating String 557

Appendix E
Polarization Catastrophe and the Shell Model 561

Appendix F
Operators 565

Appendix G
The Uncertainty Principle 569

Appendix H
Euler's Equation and Thermodynamics 571

Author Index 574
Subject Index 578