Contents

1. Classical Thermodynamics 1
1.1 Basic Laws of Classical Thermodynamics 1
1.2 Classical Equilibrium Thermodynamics 4
1.3 Nonequilibrium Thermodynamics in Classical Thermodynamics 8
1.4 Criteria of Change Direction and Limitation 10
1.5 Relationship Between Gibbs Free Energy and Temperature or Pressure 11
1.6 Chemical Potential and Its Relationship with Temperature and Pressure 13
1.7 Change of Gibbs Free Energy in Chemical Reactions 17
1.8 Limitation to the Applicability of Classical Thermodynamics 21

2. Fundamentals of Modern Thermodynamics 23
2.1 Modern Formulation of Basic Thermodynamic Laws 24
2.2 Some Basic Concepts in Nonequilibrium Thermodynamics 26
2.2.1 Irreversibility of Change with Time 27
2.2.2 Equilibrium State, Stationary State and Nonequilibrium State 27
2.2.3 Reversible and Irreversible Processes 28
2.3 Assumption of Local Equilibrium 29
2.4 Calculation of Entropy 31
2.5 Systematization of Modern Thermodynamics 35
2.6 Onsager's Reciprocity Relation 40
2.7 Entropy Production Minimization Principle 45
2.8 Prigogine's Dissipative Structures 47
2.8.1 Bénard's Pattern 47
2.8.2 Laser Emission 48
2.8.3 Chemical Oscillation 51

3. High-Pressure Synthesis and Low-Pressure Vapor Growth of Diamond Seeds 53
3.1 Early History of Diamond Synthesis 53
3.2 Thermodynamic Predictions 55
3.3 Success of the High-Pressure Process 57
3.4 Early Exploration of Low-Pressure Vapor Growth of Diamond Seeds 64
3.5 Thermodynamic Conditions for Crystal Growth from the Vapor Phase 65
3.5.1 Supersaturation Degree 65
3.5.2 Nucleation Barrier 66
3.6 Diamond Seed Growth from the Vapor Phase 71

4. Activated Low-Pressure Diamond Growth from the Vapor Phase 75
4.1 Success of Activated Low-Pressure Vapor Growth Process 75
4.2 Setup of Activated Low-Pressure Growth from the Vapor Phase 79
4.3 Preferential Etching Kinetic Model of SAH 85
4.4 Kinetic Control Model 86
4.5 Some Thermodynamic Theoretical Models of the 1980s 89
4.5.1 Quasiequilibrium Model 90
4.5.2 Surface Reaction Thermodynamic Model 94
4.5.3 Defect-Induced Stabilization Model 96

5. Reaction Coupling Model 99
5.1 Chemical Pump Model 99
5.1.1 Mechanism of the Chemical Pump 100
5.1.2 Chemical Pump Reaction 103
5.2 Calculation of the Chemical Pump Effect 104
5.3 Reaction Coupling Model 109
5.4 Thermodynamic Data for Activated Graphite 112
5.5 New Concept of Nonequilibrium (Stationary) Phase Diagrams 116
5.6 Nonequilibrium Nondissipation Principle 119
5.7 Calculation of Nonequilibrium Phase Diagrams 122
5.8 Some Results and Discussions 125
5.9 Morphology of Diamond Crystals and Orientation of Diamond Films 132

6. Nonequilibrium Phase Diagrams of C-H, C-O and Other Binary Systems 139
6.1 *T*-*X* Nonequilibrium Phase Diagrams for C-H Binary Systems 139
6.2 *T*-*p*-*X* Nonequilibrium Phase Diagrams for C-H and C-O Binary Systems 146
6.3 Nonequilibrium Phase Diagrams for Other Binary Systems 150

7. Nonequilibrium Phase Diagrams of C-H-O and Other Ternary Systems 153
7.1 Bachmann's Empirical Phase Diagram for the C-H-O System 154
7.2 Projective Nonequilibrium Phase Diagrams for C-H-O Systems 157
7.3 Influences of T and p Ranges on C-H-O Ternary Phase Diagrams 161
7.4 Cross-Sectional Nonequilibrium Phase Diagrams for C-H-O Ternary Systems 165
7.5 Nonequilibrium Phase Diagrams for C-H-X Ternary Systems 169

8. Further Discussions on Some Debates 173
8.1 Coupled Reaction in Biochemistry 174
8.2 The Seventy-Year Controversy About Reaction Coupling in Chemistry 178
8.3 Quantitative Verification of Reaction Coupling in Inanimate Systems 185
8.4 Reaction Barrier in Synthetic Diamond Processes 195
8.4.1 "Unified Barrier" Model 195
8.4.2 Thermodynamic Coupling Effect and Catalytic Effect . 196
8.4.3 Analysis of Calculated Results and Conclusions 203
8.5 Other Thermodynamic Discussions on Activated CVD Diamond 209
8.5.1 Charged Cluster Model 209
8.5.2 Other Thermodynamic Discussions 211

9. Other Applications and Summary 213
9.1 Nonequilibrium Phase Diagrams for the Activated CVD cBN Process 213
9.2 Modern Thermodynamics for Belousov–Zhabotinsky Reactions 217
9.3 A Characteristic of Life: Drawing Negative Entropy from its Environment 219

9.4 Some Similarities of Reaction Coupling in Biological and Inanimate Systems 224
9.5 Some Conclusions, Further Development and Prospects 228

References 237

Index 251