Contents

Preface xvii

I Fundamental Principles and Equations for a Closed System 1

1. First Law 2
   1.1. Enunciation of the First Law 2
   1.2. State Functions and Perfect Differentials 2
   1.3. Heat Capacities and Enthalpy 4
   1.4. Standard States 6
   1.5. Heats of Reactions 8
   1.6. Heats of Formation 11
2. Second Law 12
   2.1. Enunciation of the Second Law 12
   2.2. Entropy as a Measure of Irreversibility and Degradation 14
   2.3. Criteria of Equilbrium 14
   2.4. Useful Relationships 17
   2.5. Perfect Gases 17
   2.6. Relation Between C_p and C_v 20
3. Third Law 21
   3.1. Enunciation of the Third Law 21
   3.2. Experimental Verification 22
   3.3. Interpretation 23
   3.4. Consequences 24
   3.5. Estimates of Heat Capacities and Entropies 25
4. Application to the Stability of Phases for One-Component Systems 34
   4.1. Gibbs Free Energy Function 36
   4.2. Clausius–Clapeyron Equation 35
   4.3. Triple Points 39
   4.4. Critical Points 40
5. Summary 43

Problems 44

References 47

Selected Bibliography 47

II Fundamental Principles and Equations for an Open System 49
1. Introduction of the Chemical Potential 50
2. Extensive Properties 51
3. Partial Molar Properties 53
3.1. Definitions and Relationships 53
3.2. Graphical Representation: The Method of Intercepts 54
3.3. Constant Volume Conditions 58
3.4. Independent Variables 59
4. Derivation of the Conditions for Equilibrium in a Heterogeneous System 61
4.1. Preliminary Example 61
4.2. General Case 62
5. Application of the Conditions for Equilibrium in a Heterogeneous System 66
5.1. Example 66
5.2. Common Tangent Construction 67
5.3. Phase Rule 68
Problems 69
References 70
Selected Bibliography 70

III Stability 71
1. Stable and Unstable Equilibria 72
2. General Discussion of Stability Conditions with Respect to Infinitesimal Fluctuations 73
3. Stability Criteria for Infinitesimal Composition Fluctuations 74
3.1. First Method 75
3.2. Second Method 76
4. Spinodal Line and Critical Point 80
4.1. Case of a Regular Solution 82
4.2. General Case 83
5. Stability Function ψ 86
6. Thermodynamic Calculations Associated with the Nucleation and Growth of Precipitates 89
6.1. Free Energy Changes 89
6.2. Selection of the Displacement Variable 92
6.3. Driving Forces 93
Problems 95
References 96

IV Chemical Potentials, Fugacities, and Activities 97
1. Chemical Potential of a Single Component 98
1.1. Perfect Gas 98
1.2. Real Gases; the Fugacity Function 99
1.3. Solids and Liquids 102

2. Mixture of Ideal Gases 103
2.1. Definition 103
2.2. Interpretation 104
2.3. Fugacities 104
3. Fugacities in a Mixture of Real Gases 106
3.1. Ideal Solution of Imperfect Gases 106
4. Solid and Liquid Solutions; the Activity Function 107
5. Partial Vapor Pressure of a Solute 109
6. Composition Dependence of the Activity Under Conditions of Constant Volume 110
Problems 111
References 112

V Chemical Reactions 113
1. Case of a Single Chemical Reaction 114
1.1. General Treatment 114
1.2. Example 117
1.3. Effect of Temperature and Pressure 118
2. Le Chatelier–Braun Principle 120
3. Case of Simultaneous Reactions 122
3.1. General Treatment 122
3.2. Example: Composition of the Gas Phase of a Furnace 127
3.3. Example: Decomposition of Silica 130
4. Application to Oxygen and Sulfur Potential Diagrams 132
5. Application to Some Important Metallurgical Equilibria 137
5.1. Boudouard Reaction 137
5.2. Dissociation of Carbon Dioxide 140
5.3. Reduction of Iron Oxides 141
6. Remarks on the Progress Variables 143
6.1. Change of Basis 143
6.2. Coupled Reactions 145
Problems 147
References 150
Selected Bibliography 150

VI Binary Solutions 151
1. Thermodynamic Functions of Mixing 152
2. Ideal Solution 154
3. Excess Properties 155
4. Raoult's and Henry's Laws 158
4.1. Definitions 158
4.2. Raoult's Law as a Consequence of Henry's Law 160
4.3. Henry's Zeroth Order and First Order Laws 161
5. Integration of the Gibbs–Duhem Equation 163
Problems 166
References 167

VII Thermodynamic Formalisms Associated with Binary Metallic Solutions 169
1. Dilute Solutions 170
1.1. Approximation of a Series by a Polynomial 170
1.2. Application to $\ln \gamma_2$*; Free Energy Interaction Coefficients* 172
1.3. Enthalpy and Entropy Interaction Coefficients 174
1.4. Application of the Gibbs–Duhem Equation 175
2. Use of Polynomials Across the Composition Range 176
3. Composition Coordinates and Standard States for the Measure of the Activity Function 179
3.1. Change of Reference State 179
3.2. Composition Coordinates 180
3.3. Raoultian Standard State and Mole Fraction Composition Coordinate 181
3.4. Henrian Standard State and Mole Fraction Composition Coordinate 181
3.5. Henrian Standard State and Weight Percent Composition Coordinate 183
4. Interaction Coefficients Based on a Weight Percent Composition Coordinate 184
4.1. Free Energy Interaction Coefficients 184
4.2. Enthalpy and Entropy Interaction Coefficients 185
5. Application to Chemical Reactions 187
5.1. Notation 187
5.2. Solubility of Gases 187
5.3. Henrian Standard States and the Calculation of ΔG° 188
Problems 191
References 194

VIII Binary Phase Diagrams 195
1. General Features 196
2. Ideal and Nearly Ideal Systems 200
3. Minima and Maxima 204
4. Eutectic Points 207
5. Peritectic Points 211
6. Correspondences Between Various Types of Phase Diagrams 214
7. Complex Phase Diagrams 215
8. Calculation of Phase Diagrams 219
8.1. Numerical Techniques for the Calculation of Phase Boundaries 219
8.2. Slopes and Curvatures of Phase Boundaries 221
8.3. Calculation of the Boundaries in the Vicinity of Some Invariant Points 223
8.4. Example of Application of the Numerical Techniques 227
8.5. Calculation of the Thermodynamic Parameters of a Phase 228
Problems 229
References 231
Selected Bibliography 232

IX Analytic Expressions for the Thermodynamic Functions of Dilute Multicomponent Metallic Solutions 235
1. Raoult's and Henry's Laws for Multicomponent Solutions 236
2. Dilute Ternary Solutions 237
2.1. Approximation of a Series by a Polynomial 237
2.2. Application to $\ln \gamma_2$*; Free Energy Interaction Coefficients* 238
2.3. Enthalpy and Entropy Interaction Coefficients 240
2.4. Qualitative Atomistic Interpretation of the Interaction Coefficients 241
2.5. Reciprocal Relations Between Interaction Coefficients 243
2.6. Examples of Application 247
3. Dilute Multicomponent Solutions 252
3.1. Second Order Free Energy Interaction Coefficients 252
3.2. Reciprocal Relationships 253
4. Interaction Coefficients on a Weight Percent Basis 255
5. Application to Deoxidation Reactions 257
Problems 259
References 262

X Multicomponent Solutions and Phase Diagrams 263
1. General Features of Ternary Phase Diagrams 264
1.1. Graphical Representation 264
1.2. Examples of Ternary Phase Diagrams 267
1.3. Lever Rule 271
1.4. Four-Phase Equilibria 273
2. Notes on the Graphical Representation of Multicomponent Phase Diagrams 274
3. Representation and Calculation of Gibbs Free Energies 276
3.1. Analytic Representation of the Integral Gibbs Free Energy 277
3.2. Analytic Representation of Activities 282
3.3. Graphical Integration of the Gibbs–Duhem Equation 283
4. Calculation of Multicomponent Phase Diagrams 285
4.1. Formulation of the Conditions for Equilibrium Between Two Phases by Direct Minimization of the Gibbs Free Energy 286
4.2. Stepwise Calculation of an Isothermal Section 287
4.3. Slopes of the Phase Boundaries at Infinite Dilution of Component m 289
4.4. Conclusions 291
Problems 293
References 293
Selected Bibliography 294

XI Stability of Multicomponent Solutions and Effects of a Third Component on Some Invariant Points of Binary Systems 297
1. Stability Conditions for a Multicomponent Solution 298
1.1. Derivation 298
1.2. Existence of a Most Restrictive Condition 301

2. Stability Function ψ 304
2.1. Definition 304
2.2. Applications 306
3. Critical Lines and Surfaces 309
3.1. Analytic Derivation 309
3.2. Effects on a Binary Critical Point of Small Additions of a Third Component 312
4. Effect of Small Additions of a Third Component on the Eutectic and Peritectic Temperatures of Binary Systems 315
4.1. Analytic Derivation 315
4.2. Alternative Forms and Consequences 317
4.3. Examples 320
4.4. Conclusions 324
Problems 325
References 326

XII Thermodynamic Functions Associated with Compounds 329
1. Stoichiometric and Nonstoichiometric Compounds 330
2. Chemical Potential of a Compound 332
2.1. Binary Systems 332
2.2. Multicomponent Systems 336
3. Activity of a Compound 339
3.1. Reference States 339
3.2. Composition Dependence 340
4. Applications 342
5. Summary 343
Problems 344
References 344

XIII Surfaces and Surface Tensions 345
1. Fundamental Equations 347
1.1. Temperature and Chemical Potentials at the Interface 347
1.2. Model System 349
1.3. Surface Tension 350
1.4. Equilibrium Conditions for the Pressures 352
2. Mechanical Equivalence of the Model System 353
2.1. General Procedure and Definition of the Surface Tension 353
2.2. Case of a Cylindrical Surface of Constant Curvature 354
3. Gibbs Adsorption Equation 359
4. Surface Tension and the Thermodynamic Potential Ω 360
4.1. Thermodynamic Equations 360
4.2. Surfaces of Solids 361

5. Variance of a Two-Phase System and Effects of the Interface's Curvature 362
5.1. Variance of a Two-Phase System 362
5.2. Effect of Curvature on the Vapor Pressure of a Pure Species 363
5.3. Effect of Curvature on the Boiling Point of a Pure Species 364
5.4. Effect of Curvature on the Solubility of a Pure Species 365
5.5. Effect of Curvature on the Chemical Potential of a Solute 365
5.6. Remarks 366
6. Equilibrium Shape of a Crystal 368
6.1. Geometric Description of a Crystal 368
6.2. Wulff's Relationships 369
6.3. Wulff Plots 370
7. The Equation of Laplace for a Crystal 372
8. Equilibrium at a Line of Contact of Three Phases 373
8.1. Condition for Equilibrium 373
8.2. Contact Angle 374
8.3. Phase Distribution in a Polycrystalline Solid 375
8.4. Torque Component in Grain Boundaries 375
9. Representative Values of Interfacial Tensions 380
10. Summary 383
Problems 384
References 385
Selected Bibliography 386

XIV Adsorption 389
1. Surface Excess Quantities and the Position of the Dividing Surface 391
2. Relative Adsorptions 392
2.1. Definition 392
2.2. Simplified Form 393
3. Relative Functions and the Gibbs Adsorption Equation 395
4. Reduced Adsorptions 396
5. Alternative Thermodynamic Treatment of a Planar Interface 397
5.1. Invariance with Respect to the Boundaries of the Surface Layer 398
5.2. Choice of the Two Dependent Variables X and Y 399
6. Perfect Solution Model of an Interface 400
6.1. Definition 400
6.2. Consequences 401
7. Mixtures of Two Metals 403
8. Surface-Active Species 405
8.1. Dilute Solutions 405
8.2. Saturation Stage 406
8.3. Models of Adsorption 408
8.4. Remarks 413

9. Derivation of the Adsorption Functions from Surface Tension Data in Ternary Systems 414
9.1. Direct Method 415
9.2. Method of Whalen, Kaufman, and Humenik 418
9.3. Graphic-Analytic Method 419
9.4. Analytic Method 420
10. Adsorption in Multicomponent Solutions 422
10.1. Adsorption Interaction Coefficient $\xi_i^{(j)}$ 423
10.2. Examples 424
11. Heats of Adsorption and Effect of the Temperature on the Surface Tension 425
11.1. Standard State and Standard Heats of Adsorption 425
11.2. Isosteric Heat of Adsorption 426
11.3. Physical and Chemical Adsorptions 429
11.4. Effect of Temperature on the Surface Activity 429
12. Summary 430
Problems 432
References 434

XV Statistical Models of Substitutional Metallic Solutions 437
1. Introduction 438
2. Ideal Solution 439
3. Regular Solution 441
4. Quasi-Chemical Approximation 446
4.1. Assumptions of the Model 446
4.2. Derivation 447
4.3. Test of the Model and Discussion 450
5. Central Atoms Model 452
5.1. General Features of the Model 452
5.2. Possible Expressions for the Individual Partition Function q 453
5.3. Probabilities Associated with Different Configurations and Thermodynamic Functions 455
5.4. Quasi-Regular Solution 458
5.5. Correlation Between Excess Enthalpy and Entropy 461
5.6. Assumptions and Discussion 463
6. Multicomponent Solutions 469
6.1. Regular and Quasi-Regular Solutions 469
6.2. Quasi-Chemical Approximations 472
7. Conclusions 473
Problems 474
References 474

XVI Statistical Models of Interstitial Metallic Solutions 477
1. Introduction 478
2. Ideal Interstitial Solution 478
3. Central Atoms Model of a Binary Interstitial Solution 482
3.1. Derivation of the Model 482
3.2. Linear Variation of a Central Atom's Potential Energy 485

3.3. Application to the Iron–Carbon System 486
3.4. Comparison with Other Models 488
4. Central Atoms Model of an Interstitial Solute in a Multicomponent System 491
4.1. Preliminary Definitions and Parameters 492
4.2. Ternary Solution of Two Substitutional Components and One Interstitial Component 493
4.3. Ternary Solution of Two Interstitial Solutes 495
4.4. Quaternary Solution of Two Substitutional and Two Interstitial Components 498
4.5. Quaternary Solution of Three Substitutional Components and One Interstitial Component 499
4.6. Multicomponent Solutions 501
5. Conclusions 502
Problems 504
References 504

Appendix 1. Units, Useful Constants, and Conversion Factors 507
Appendix 2. Atomic Weights and the Periodic Table 509
Appendix 3. Standard Enthalpies and Gibbs Free Energies of Formation at 298°K for Selected Compounds 511
Appendix 4. JANAF Tables for CO, CO_2, H_2, H_2O, N_2, and O_2 515
Appendix 5. Interaction Coefficients for Liquid Iron at 1600°C 523
Answers to Problems 535
List of Symbols 559
Author Index 563
Subject Index 569