

CONTENTS

Acknowledgments	xv
Introduction	xvii
Part I PHASE DIAGRAMS AND THERMODYNAMICS	
Chapter 1 Introduction	3
References	8
List of Websites	8
Chapter 2 Thermodynamics Fundamentals	9
2.1 The First and Second Laws of Thermodynamics	10
2.2 Enthalpy	13
2.3 Gibbs Energy	16
2.4 Equilibrium and Chemical Reactions	18
2.5 Measuring Gibbs Energy, Enthalpy and Entropy	25
2.6 Gibbs Energy of a Pure Compound as a Function of Temperature	27
2.7 Auxiliary Functions	28
2.8 The Chemical Potential	29
2.9 Some Other Useful Thermodynamic Equations	30
Reference	31
List of Websites	31
Chapter 3 The Gibbs Phase Rule	33
3.1 The Phase Rule and Binary Temperature-Composition Phase Diagrams	35
3.2 Other Examples of Applications of the Phase Rule	38
Reference	40

Chapter 4 Fundamentals of the Thermodynamics of Solutions	41
4.1 Gibbs Energy of Mixing	41
4.2 Tangent Construction	43
4.3 Partial Molar Properties	43
4.4 Relative Partial Molar Properties	44
4.5 Activity	46
4.6 Ideal Raoultian Solutions	46
4.7 Excess Properties	48
4.8 Activity Coefficients	49
4.9 Regular Solution Theory	50
4.10 Multicomponent Solutions	52
References	52
List of Websites	52
Chapter 5 Thermodynamic Origin of Phase Diagrams	53
5.1 Temperature-Composition Phase Diagrams in Systems with Complete Solid and Liquid Miscibility	53
5.2 Binary Pressure-Composition Phase Diagrams	58
5.3 Minima and Maxima in Two-Phase Regions	59
5.4 Miscibility Gaps	61
5.5 Simple Eutectic Systems	63
5.6 Thermodynamic Origin of Simple Binary Phase Diagrams Illustrated by Regular Solution Theory	65
5.7 Immiscibility—Montectics	67
5.8 Intermediate Phases	70
5.9 Limited Mutual Solubility—Ideal Henrian Solutions	73
5.10 Henry's Law, Raoult's Law and Standard States	76
5.11 Single Ion Activities	78
5.12 The "Activity" of a Solution	79
5.13 Geometry of Binary Temperature-Composition Phase Diagrams	80

5.14 Effects of Grain Size, Coherency, and Strain Energy	83
References	84
List of Websites	84
Chapter 6 Ternary Temperature-Composition Phase Diagrams	85
6.1 The Ternary Composition Triangle	85
6.2 Ternary Space Model	86
6.3 Polythermal Projections of Liquidus Surfaces	88
6.4 Ternary Isothermal Sections	91
6.5 Ternary Isopleths (Constant Composition Sections)	95
6.6 First-Melting (Solidus) Projections of Ternary Systems	97
6.7 Phase Diagram Projections in Quaternary and Higher-Order Systems	99
References	102
List of Websites	102
Chapter 7 General Phase Diagram Sections	103
7.1 Corresponding Potentials and Extensive Variables	104
7.2 The Law of Adjoining Phase Regions	105
7.3 Nodes in Phase Diagram Sections	107
7.4 Zero Phase Fraction Lines	108
7.5 Choice of Variables to Ensure That Phase Diagram Sections are Single-Valued	110
7.6 Corresponding Phase Diagrams	114
7.7 The Thermodynamics of General Phase Diagram Sections	118
7.8 Interpreting Phase Diagrams of Oxide Systems and Other Systems Involving Two or More Oxidation States of a Metal	122
7.9 Choice of Components and Choice of Variables	127
7.10 Phase Diagrams of Reciprocal Systems	128
7.11 Choice of Variables to Ensure Straight Tie-Lines	129
7.12 Other Sets of Corresponding Variable Pairs	130
7.13 Extension Rules for Polythermal Liquidus Projections	131

7.14 Phase Fraction Lines	131
References	131
List of Websites	131
Chapter 8 Equilibrium and Scheil-Gulliver Solidification	133
8.1 Equilibrium Solidification	133
8.2 General Nomenclature for Invariant and Other Reactions	134
8.3 Quasi-Invariant Reactions	135
8.4 Nonequilibrium Scheil-Gulliver Solidification	136
8.5 Scheil-Gulliver Constituent Diagrams	137
References	148
List of Websites	148
Chapter 9 Paraequilibrium Phase Diagrams and Minimum Gibbs Energy Diagrams	149
9.1 The Geometry of Paraequilibrium Phase Diagram Sections	150
9.2 Minimum Gibbs Energy Phase Diagrams	155
References	158
Chapter 10 Second-Order and Higher-Order Transitions	159
10.1 Equations for Thermodynamic Properties due to Magnetic Ordering	163
References	164
List of Websites	164
Chapter 11 Phase Diagrams of Systems With an Aqueous Phase	165
11.1 Evaporation Paths	165
11.2 <i>Eh</i> -pH Diagrams	167
11.3 True Aqueous Phase Diagrams	172
References	182
List of Websites	182

Chapter 12 Bibliography on Phase Diagrams	183
12.1 Phase Diagram Compilations	183
12.2 Further Reading	184
References	184
List of Websites	185
Part II THERMODYNAMIC MODELING OF SOLUTIONS	
Chapter 13 Introduction	189
List of Websites	191
Chapter 14 Single-Lattice Random-Mixing (Bragg-Williams—BW) Models	193
14.1 Ideal Raoultian Solutions	194
14.2 Regular Solution Theory: Binary Systems	195
14.3 Polynomial Expansion of the Excess Gibbs Energy: Binary Systems	196
14.4 Solutions With Two or More Sublattices But With Only One Sublattice of Variable Composition	200
14.5 Solutions With Limited Solubility: Lattice Stabilities	201
14.6 Darken's Quadratic Formalism	202
14.7 Introduction to Coupled Thermodynamic/Phase Diagram Optimization: Binary Systems	203
14.8 Multicomponent Systems	207
14.9 Liquid Solutions: Coordination Equivalent Fractions	219
14.10 Wagner's Interaction Parameter Formalism and the Unified Interaction Parameter Formalism	222
14.11 Thermal Vacancies	226
References	226
Chapter 15 Multiple-Sublattice Random-Mixing (Bragg-Williams—BW) Models	229
15.1 Case of a Two-Sublattice (A,B)(X,Y) Solution	231

15.2	Activities of the End-Members	239
15.3	The Compound Energy Formalism (CEF)	240
15.4	Asymmetric Molten Ionic Solutions: Temkin Model	249
	References	252
	List of Websites	252
Chapter 16	Single-Lattice Models With Short-Range Ordering (SRO)	253
16.1	Associate Models	257
16.2	The Modified Quasichemical Model (MQM)	260
16.3	Second-Nearest-Neighbor Short-Range Ordering in Ionic Liquids	272
16.4	Short-Range Ordering and Positive Deviations From Ideal Mixing	274
16.5	Approximating Short-Range Ordering with a Polynomial Expansion	277
16.6	Modified Quasichemical Model—Multicomponent Systems ..	278
16.7	The MQM Equations in Closed Explicit Form	286
16.8	Combining Bragg-Williams and MQM Models in One Multicomponent Database	287
16.9	Comparison of the Bragg-Williams, Associated and Modified Quasichemical Models in Predicting Ternary Properties From Binary Properties	288
16.10	The Two-Sublattice “Ionic Liquid” Model	292
	References	293
	List of Websites	294
Chapter 17	Modeling Short-Range Ordering With Two Sublattices ..	295
17.1	Introduction	295
17.2	Definitions, Coordination Numbers	296
17.3	Formal Treatment of Quadruplets as “Complexes” or Molecules”	300
17.4	Gibbs Energy Equation	303

17.5	The Configurational Entropy	305
17.6	Second-Nearest-Neighbor Interaction Terms	308
17.7	Summary of Model	314
17.8	Sample Calculations	317
	References	318
Chapter 18	Some Applications	319
18.1	Molten Oxide Solutions	319
18.2	Order-Disorder Transitions	333
18.3	Liquid Solutions With More Than One Composition of Short-Range Ordering	341
18.4	Deoxidation Equilibria in Steel	342
18.5	Magnetic Contributions to the Thermodynamic Properties of Solutions	346
18.6	Limiting Liquidus Slope in Dilute Solutions	346
	References	349
	List of Websites	350

EXERCISES

Chapter 19	Exercises With Solutions	351
19.1	Exercises	351
19.2	Solutions to Exercises	363
	Index	377