

## CONTENTS

Preface	<i>page</i> xiii
Online Resources and Exercises	xvii
<b>1 What Is Thermodynamics?</b>	
1.1 Introduction	1
1.2 What Is the Problem?	1
1.3 A Mechanical Analogy	2
1.4 Thermodynamic Potentials	5
1.5 Idealization in Thermodynamics	7
1.6 Limitations of the Thermodynamic Model	8
1.7 Summary	9
Exercises	9
Additional Problems	10
<b>2 Defining Our Terms</b>	
2.1 Something Is Missing	11
2.2 Systems	11
2.3 Equilibrium	15
2.4 State Variables	20
2.5 Phases, Components, and Species	22
2.6 Processes	23
2.7 Notation	31
2.8 Time as a Thermodynamic Variable	33
2.9 Thermodynamics and Natural Systems	34
2.10 Summary	35
Exercises	36
Additional Problems	37
<b>3 The First Law of Thermodynamics</b>	
3.1 Temperature and Pressure Scales	38
3.2 Internal Energy	39
3.3 Energy Transfers	42
3.4 The First Law of Thermodynamics	44
3.5 Work	45
3.6 Heat	55
3.7 How Far Have We Got?	61
3.8 The Model Again	61

## Contents

3.9	Summary	63
	Exercises	64
	Additional Problems	65
<b>4</b>	<b>The Second Law of Thermodynamics</b>	
4.1	Introduction	66
4.2	The Problem Restated	66
4.3	Thermodynamic Potentials	68
4.4	Entropy	70
4.5	The Fundamental Equation	74
4.6	The $U$ – $S$ – $V$ Surface	75
4.7	Applicability of the Fundamental Equation	77
4.8	Constraints and Metastable States	78
4.9	The Energy Inequality Expression	81
4.10	Entropy and Heat Capacity	84
4.11	A More Useful Thermodynamic Potential	90
4.12	Gibbs and Helmholtz Functions as Work	95
4.13	Open Systems	98
4.14	The Meaning of Entropy	101
4.15	The End of the Road	104
4.16	Summary	104
	Exercises	106
	Additional Problems	107
<b>5</b>	<b>Getting Data</b>	
5.1	Introduction	110
5.2	What to Measure?	111
5.3	Solution Calorimetry	113
5.4	The Third Law	118
5.5	The Problem Resolved	121
5.6	Data at Higher Temperatures	127
5.7	Data at Higher Pressures	131
5.8	Summary	132
	Exercises	133
	Additional Problems	134
<b>6</b>	<b>Some Simple Applications</b>	
6.1	Introduction	137
6.2	Simple Phase Diagrams	137
6.3	The Slope of Phase Boundaries	141
6.4	Another Example	144
6.5	Summary	148
	Exercises	148
	Additional Problems	149

## Contents

<b>7</b>	<b>Solutions</b>	
	7.1 Introduction	150
	7.2 Measures of Concentration	150
	7.3 Properties of Ideal Solutions	153
	7.4 Ideal Solution Laws	155
	7.5 Ideal Solution Equations	160
	7.6 Real Solutions	167
	7.7 Solution Volumes	168
	7.8 Next Step – The Activity	173
	7.9 Summary	173
	Exercises	174
	Additional Problems	175
<b>8</b>	<b>Fugacity and Activity</b>	
	8.1 Fugacity	177
	8.2 Activity	180
	8.3 Standard States and Activity Coefficients	184
	8.4 Activities and Standard States: An Overall View	187
	8.5 Summary	190
	Exercises	191
	Additional Problems	192
<b>9</b>	<b>The Equilibrium Constant</b>	
	9.1 Reactions in Solution	195
	9.2 Reactions at Equilibrium	196
	9.3 The Most Useful Equation in Thermodynamics	198
	9.4 Special Meanings for $K$	203
	9.5 $K$ in Solid–Solid Reactions	207
	9.6 Change of $K$ with Temperature I	210
	9.7 The Amino Acid Example Again	215
	9.8 Some Conventions Regarding Components	218
	9.9 Summary	222
	Exercises	222
	Additional Problems	226
<b>10</b>	<b>Rock–Water Systems</b>	
	10.1 Real Problems	231
	10.2 Is the Sea Saturated with Calcium Carbonate?	231
	10.3 Determining the IAP – Speciation	234
	10.4 Combining the IAP and the $K_{sp}$	241
	10.5 Mineral Stability Diagrams	243
	10.6 Summary	249
	Exercises	250
	Additional Problems	251

## Contents

<b>11</b>	<b>Redox Reactions</b>	
11.1	Introduction	257
11.2	Electron Transfer Reactions	257
11.3	The Role of Oxygen	258
11.4	A Simple Electrolytic Cell	259
11.5	The Nernst Equation	263
11.6	Some Necessary Conventions	265
11.7	Measuring Activities	268
11.8	Measuring Redox Conditions	270
11.9	<i>Eh</i> –pH Diagrams	274
11.10	Oxygen Fugacity	278
11.11	Summary	281
	Exercises	283
	Additional Problems	287
<b>12</b>	<b>Phase Diagrams</b>	
12.1	What Is a Phase Diagram?	293
12.2	The Phase Rule	294
12.3	Unary Systems	296
12.4	Binary Systems	303
12.5	Ternary Systems	327
12.6	Summary	336
	Exercises	336
	Additional Problems	340
<b>13</b>	<b>Affinity and Extent of Reaction</b>	
13.1	Introduction	343
13.2	Quasistatic Processes	343
13.3	The Extent of Reaction Variable	344
13.4	Components and Species Again	348
13.5	The Affinity	349
13.6	Conclusion	355
13.7	Final Comment	355
	Exercises	357
	Additional Problems	357
	<b>APPENDICES</b>	
	Appendix A Constants and Numerical Values	359
	Appendix B Standard State Thermodynamic Properties of Selected Minerals and Other Compounds	361
	Appendix C Answers to Exercises	375
	References	403
	Index	408

## ONLINE MATERIALS: ADDITIONAL CHAPTERS FROM THE SECOND EDITION

Available at [www.cambridge.org/thermodynamics](http://www.cambridge.org/thermodynamics)

<b>10</b>	<b>Real Solutions</b>	
10.1	Introduction	1
10.2	Solution Volumes	1
10.3	The Infinite Dilution Standard State	12
10.4	Excess Properties	13
10.5	Enthalpy and Heat Capacity	20
10.6	Gibbs Energies	28
10.7	Margules Equations	35
10.8	Beyond Margules	39
10.9	The Gibbs–Duhem Equation	39
10.10	Summary	41
<b>11</b>	<b>The Phase Rule</b>	
11.1	Introduction	42
11.2	Derivation of the Phase Rule	42
11.3	Components and Species	45
11.4	Duhem’s Theorem	50
11.5	Buffered Systems	53
11.6	Summary	57
<b>13</b>	<b>Equations of State</b>	
13.1	Introduction	58
13.2	The Ideal Gas	58
13.3	Two Kinds of EoS	63
13.4	Cubic Equations of State	63
13.5	The Virial Equation	69
13.6	Thermal Equations of State	74
13.7	Other Equations of State	81
13.8	Summary	83
<b>14</b>	<b>Solid Solutions</b>	
14.1	Introduction	85
14.2	Solid Solutions	86
14.3	Activity Coefficients in Solid Solutions	92
14.4	Summary	109

**Online Materials: Additional Chapters from the Second Edition**

<b>15</b>	<b>Electrolyte Solutions</b>	
15.1	Introduction	111
15.2	Activities of Electrolyte Components	111
15.3	Numerical Values for Single-Ion Properties	123
15.4	The Debye–Hückel Theory	127
15.5	Activity Coefficients of Neutral Molecules	134
15.6	Ion Association, Ion Pairs and Complexes	135
15.7	The Pitzer Equations	137
15.8	The HKF Model for Aqueous Electrolytes	138
15.9	Comparison of Pitzer and HKF Models	140
	<b>The van 't Hoff Equilibrium Box</b>	143
1.1	Introduction	143
1.2	The Affinity	144
1.3	The Two Kinds of Work	145
1.4	Irreversible Work	151
1.5	Summary	155
	<b>Topics in Mathematics</b>	156
C.1	Differentials and Derivatives	156
C.2	Partial Derivatives and Total Differentials	159
C.3	Integration	159
C.4	Single-Valued and Continuous Functions	160
C.5	Exact and Inexact Differentials	161
C.6	Homogeneous Functions	163
C.7	Euler's Theorem for Homogeneous Functions	164
C.8	Legendre Transforms	165
C.9	All Components in All Phases	170
C.10	Chemical Potentials of Dilute Components	175
C.11	The Bursting Balloon	176
	References	178