

Contents

Chapter 1	First Law	1
1.1	System and Surroundings	1
1.2	Energy Transfer	2
1.3	Energy of a System	4
1.4	Energy as a State Function	5
1.5	Work	5
1.6	The Closed System	7
1.7	Notation	8
1.8	Intensive and Extensive Properties	9
1.9	The Open System	10
1.10	Enthalpy	11
1.11	Steady State	11
1.12	Heat Capacity at Constant Volume	12
1.13	Heat Capacity at Constant Pressure	13
1.14	Adiabatic Flow Through a Valve: Joule–Thomson Expansion	16
1.15	Equations of State	17
1.16	Nonideal Gases	22
1.17	Adiabatic Compression or Expansion	26
1.18	Enthalpies of Formation	29
1.19	Enthalpy Changes in Chemical Reactions	31
1.20	Adiabatic Temperature Change in Chemical Reactions	34
<i>References</i>		38
<i>Problems</i>		38

Chapter 2 Second Law 45

2.1	Entropy as a State Function	46
2.2	Entropy Not Conserved	49
2.3	Open System Entropy Balance	50
2.4	Adiabatic, Reversible, Steady State System	50
2.5	Heat Engines	51
2.6	Diagrammatic Representation	54
2.7	Refrigerators	55
2.8	Heat Pumps	57
2.9	Entropy Changes	57
2.10	Entropy Changes in Chemical Reactions and the Third Law	60
<i>References</i>		62
<i>Problems</i>		62

Chapter 3 Property Relationships 67

3.1	The Property Relation	69
3.2	The Functions F and G	70
3.3	Chemical Potentials	71
3.4	Partial Molar Quantities	73
3.5	Property Relations Derived from U , H , F , and G	75
3.6	Ideal Gas	78
3.7	Entropy of Mixing	78
3.8	Heat Capacity	80
3.9	Variation of Heat Capacity	81
3.10	Isentropic Pressure–Temperature Relationship	82
3.11	Isentropic Compression of Solids	83
3.12	Thermoelastic Effect	84
3.13	Compressibility	87
3.14	Magnetic Effects	89
<i>References</i>		93
<i>Problems</i>		93

Chapter 4 Equilibrium 97

4.1	Condition of Equilibrium	98
4.2	Barometric Equation	100
4.3	Phase Equilibria	101
4.4	Special Case: Closed System, Constant Volume	103
4.5	First-Order Transitions: Variation of Equilibrium Pressure with Temperature	104
4.6	Clapeyron Equation in Vapor Equilibria	107

4.7	Variation of Vapor Pressure of a Condensed Phase with Total Applied Pressure	109
4.8	Variation of Vapor Pressure with Particle Size	111
4.9	Second-Order Transitions	112
4.10	Superconductivity: An Example	114
<i>References</i>		116
<i>Problems</i>		116

Chapter 5 Chemical Equilibrium **119**

5.1	Thermodynamic Activity	119
5.2	Chemical Equilibrium	122
5.3	Gaseous Equilibria	123
5.4	Solid–Vapor Equilibria	125
5.5	Sources of Information on ΔG°	127
5.6	Ellingham Diagrams	130
5.7	Variation of Equilibrium Constant with Temperature	135
5.8	Gases Dissolved in Metals (Sievert's Law)	138
5.9	Chemical Equilibrium and Adiabatic Flame Temperatures	139
<i>References</i>		144
<i>Problems</i>		144

Chapter 6 Electrochemistry **149**

6.1	Electrochemical Cell	150
6.2	Nomenclature	151
6.3	Calculation of Cell Voltage	152
6.4	Direction of Reaction	153
6.5	Half-Cell Reactions	154
6.6	Variation of Voltage with Concentration: Nernst Equation	156
6.7	Pourbaix Diagrams	156
6.8	Concentration Cells	159
6.9	Oxygen Pressure Determination	161
6.10	Temperature Dependence of Voltage	162
6.11	Electrochemical Potential	162
<i>References</i>		164
<i>Problems</i>		164

Chapter 7 Solutions **169**

7.1	Thermodynamic Activity	169
7.2	Partial Molar Quantities	171
7.3	Relative Partial Molar Quantities	173

xii Contents

7.4	Entropy of Mixing: Ideal Solution	174
7.5	Enthalpy of Mixing: Ideal Solution	174
7.6	Graphical Representation	175
7.7	Nonideal Solutions	178
7.8	Gibbs–Duhem Relation	181
7.9	Dilute Solutions and Colligative Properties	183
7.10	Integrating the Gibbs–Duhem Equation	184
7.11	Regular Solutions	186
7.12	Regular Solutions: Atomistic Interpretation	188
7.13	Polymer Solutions	190
7.14	Osmotic Pressure	192
	<i>References</i>	195
	<i>Problems</i>	195

Chapter 8 **Phase Rule** **199**

8.1	Phases	199
8.2	Components	200
8.3	Specifying a System	200
8.4	Equilibrium Conditions	201
8.5	Gibbs Phase Rule	201
8.6	One-Component System	201
8.7	Examples	202
8.8	Phase Rule for Condensed Systems	204
	<i>Problems</i>	205

Chapter 9 **Phase Diagrams** **207**

9.1	Freezing Point Depression	208
9.2	The Lever Rule	211
9.3	Simple Eutectic Diagram	213
9.4	Cooling Curves	214
9.5	Complete Miscibility	216
9.6	Immiscibility	220
9.7	Spinodal Points	222
9.8	Peritectic Phase Diagrams	224
9.9	Compounds	225
9.10	Ternary Diagrams	225
	<i>References</i>	234
	<i>Problems</i>	234

Chapter 10 Statistical Thermodynamics 245

10.1	Average Velocity of Gas Molecules	246
10.2	Macrostates and Microstates	249
10.3	Isolated Systems and the Boltzmann Hypothesis	252
10.4	The Third Law	254
10.5	Systems at Constant Temperature	255
10.6	Information and Entropy	256
10.7	Boltzmann Distribution	258
10.8	Degeneracy	262
10.9	Partition Function	263
10.10	Distinguishability of Particles	264
10.11	Ideal Gas	265
10.12	Maxwell–Boltzmann Distribution: Ideal Gas	267
10.13	Fermi–Dirac Distribution	270
10.14	Heat Capacity of Solids	274
10.15	Molecular Weight Distribution in Polymers	278
10.16	Entropy of Mixing of Polymer Solutions	284
<i>References</i>		287
<i>Appendix 10.A: Proof that $\beta = 1/kT$</i>		287
<i>Problems</i>		288

Appendix Background 293

Units

A.1	Length	294
A.2	Mass and Amount of Material	294
A.3	Time	294
A.4	Electric Current	295
A.5	Temperature	295
A.6	Force	296
A.7	Pressure	296
A.8	Volume	296
A.9	Energy	296
A.10	Power	297
A.11	Composition	297
A.12	Checking Units	298

Mathematical Manipulation

A.13	Logarithms	299
A.14	Differentials	300
A.15	Partial Derivatives	300

xiv Contents

A.16	Total Differential	301
A.17	Factorials	301
A.18	Homogeneous Functions	302
A.19	Lagrange Method of Undetermined Multipliers	302
	Exercises in Unit Conversions	306
Index		309