

Contents

1	Beginnings	1
1.1	Introduction	1
1.2	Heat and Motion	2
1.3	The Laws	4
1.3.1	First Law	4
1.3.2	Second Law	7
1.4	Modern Directions	9
1.5	Summary	10
	Exercises	10
2	Formulation	13
2.1	Introduction	13
2.2	Systems and Properties	13
2.2.1	Systems	13
2.2.2	Boundaries	14
2.2.3	Properties and States	15
2.2.4	Surfaces and States	15
2.2.5	Quasistatic Processes	16
2.2.6	Properties and Processes	16
2.3	Properties and the Laws	17
2.3.1	Temperature	18
2.3.2	Internal Energy	19
2.3.3	Entropy	24
2.4	Combining the Laws	29
2.5	Summary	30
	Exercises	31
3	Mathematical Background	41
3.1	Introduction	41
3.2	Exact Differentials	42
3.3	Integration	44

3.4	Differential Relationships	46
3.5	Variable Transformations	47
3.5.1	From Points to Tangent Lines	47
3.5.2	Surfaces and Contours	49
3.5.3	General Legendre Transformation	51
3.6	Summary	52
	Exercises	52
4	Thermodynamic Potentials	55
4.1	Introduction	55
4.2	The Fundamental Surface	55
4.3	The Four Potentials	56
4.3.1	Internal Energy	56
4.3.2	Transformations	60
4.3.3	The Helmholtz Energy	60
4.3.4	The Enthalpy	63
4.3.5	Gibbs Energy	66
4.4	Relations Among Potentials	68
4.5	Maxwell Relations	69
4.6	Intensive and Extensive Variables	71
4.7	Variable Composition	72
4.7.1	Single Components	72
4.7.2	Mixing	75
4.7.3	Gibbs-Duhem Equation	79
4.8	The Gibbs Formulation	80
4.9	Summary	81
	Exercises	82
5	Structure of the Potentials	85
5.1	Introduction	85
5.1.1	General Curvature Relationships	85
5.2	Gibbs-Helmholtz Equations	86
5.3	Curvatures of the Fundamental Surface	89
5.3.1	Caloric Properties and Curvatures	89
5.3.2	Mechanical Properties and Curvatures	90
5.3.3	Curvatures of the Potentials	91
5.3.4	From Curvatures to Potentials	92
5.4	Mechanical and Caloric Consistency	94
5.5	Summary	94
	Exercises	95
6	Laboratory Measurements	97
6.1	Introduction	97
6.2	Temperature	98
6.2.1	International Scale	98

6.2.2	Fixed Points	98
6.2.3	Thermometers	100
6.3	Pressure	100
6.3.1	Electronic Pressure Measurement	100
6.3.2	Resonant Pressure Sensors	102
6.3.3	Piston Gauges	102
6.3.4	Low Pressure	103
6.4	Density	104
6.4.1	Magnetic Suspension	104
6.4.2	Two-Sinker Densimeter	105
6.4.3	Single-Sinker Densimeter	105
6.4.4	Vibrating Bodies	106
6.5	Speed of Sound	106
6.6	Calorimetry	107
6.6.1	AC Calorimetry	107
6.6.2	Differential Scanning Calorimetry	108
6.6.3	Nanocalorimetry	109
6.6.4	Cryogenics	110
6.6.5	High Temperatures	110
6.7	Summary	111
7	The Third Law	113
7.1	Introduction	113
7.2	Nernst's Hypothesis	113
7.3	Unattainability of Absolute Zero	115
7.3.1	Limits on H and G	117
7.4	Consequences of the Third Law	117
7.4.1	Coefficient of Expansion	117
7.4.2	Specific Heats	117
7.5	Summary	118
	Exercises	119
8	Models of Matter	121
8.1	Introduction	121
8.2	The Ideal Gas	121
8.2.1	Ideal Gas Kinetic Theory	122
8.2.2	Kinetic Theory with Collisions	127
8.2.3	Collisional Models	128
8.3	Van der Waals Fluid	130
8.3.1	Van der Waals Model	131
8.3.2	Condensation	133
8.3.3	Van der Waals and Maxwell	133
8.3.4	Critical Point and Constants	138
8.4	Beyond van der Waals	139
8.4.1	Compressibility	139

8.4.2	Virial Expansion	141
8.4.3	Redlich-Kwong Equation of State	144
8.5	Summary	145
	Exercises	146
9	Statistical Mechanics	151
9.1	Introduction	151
9.2	Gibbs' Statistical Mechanics	151
9.3	Ensembles of Systems	152
9.4	Phase Space	154
9.4.1	Concept	154
9.4.2	μ - Space	155
9.4.3	Γ -Space	155
9.4.4	Relationship of μ - to Γ -Space	156
9.4.5	Volumes in Phase Space	158
9.5	Ensemble Averages	159
9.6	Coefficient of Probability	160
9.6.1	Nonequilibrium	160
9.6.2	Equilibrium	161
9.7	Thermodynamics of Ensembles	162
9.7.1	Canonical Ensemble	162
9.7.2	Microcanonical Ensemble	165
9.8	Information Theory	173
9.9	Potential Energies	174
9.10	Equipartition Principle	175
9.11	Applications	178
9.11.1	Sackur-Tetrode Equation	178
9.11.2	Mixing	180
9.11.3	Experiment	181
9.12	Molecular Partition Function	184
9.13	Spinless Gases	187
9.13.1	Vibration	188
9.13.2	Rotation	189
9.13.3	Electronic	191
9.13.4	Molecular Partition	194
9.13.5	Applications	194
9.14	Summary	197
	Exercises	198
10	Quantum Statistical Mechanics	203
10.1	Introduction	203
10.2	Particles with Spin	203
10.3	General Treatment	205
10.3.1	Grand Canonical Ensemble	205
10.3.2	Bose Gas	208

10.3.3	Structureless Bose Gas	210
10.3.4	Bose-Einstein Condensation	213
10.4	Fermi Gas	219
10.4.1	Structureless Fermi Gas	220
10.4.2	Degenerate Fermi Gas	223
10.5	Summary	228
	Exercises	228
11	Irreversibility	231
11.1	Introduction	231
11.2	Entropy Production	231
11.2.1	General	231
11.2.2	Forces and Flows	233
11.2.3	Phenomenological Laws	235
11.2.4	Onsager Symmetry	236
11.3	Sources of Entropy Production	237
11.3.1	Mixing	237
11.3.2	Membrane Transport	238
11.3.3	Chemical Reactions	243
11.4	Minimum Entropy Production	254
11.5	Summary	255
	Exercises	255
12	Stability	259
12.1	Introduction	259
12.2	Entropy	260
12.3	The Potentials	261
12.4	Form and Stability	262
12.4.1	Fundamental Relationships	262
12.4.2	Transformed Relationships	267
12.5	Summary	269
	Exercises	270
13	Equilibrium of Chemical Reactions	271
13.1	Introduction	271
13.2	Stability of Reactions	271
13.3	Chemical Potential	274
13.3.1	Ideal Gases	274
13.3.2	Nonideal Caloric Effects	276
13.3.3	Nonideal Collisional Effects	277
13.4	Fugacity	279
13.5	Activities and Mass Action	281
13.5.1	In Nonideal Gases	281
13.5.2	In Ideal Gases	283
13.6	Temperature Dependence	284

13.7	Model Systems	286
13.7.1	Van der Waals Fluid	287
13.7.2	Virial Approximation	287
13.7.3	Mixtures of Nonideal Gases	290
13.8	Coupled Reactions	291
13.9	Chemical Affinity	292
13.10	Summary	294
	Exercises	294
14	Chemical Kinetics	299
14.1	Introduction	299
14.2	Kinetic Equations	299
14.3	Collision Rates	301
14.4	Activated Complex	303
14.5	Transition State Theory	306
14.5.1	Microscopic TST	308
14.5.2	Macroscopic TST	314
14.6	Specific Reactions	315
14.6.1	Lindemann Mechanism	315
14.6.2	Enzyme Kinetics	319
14.7	Summary	322
	Exercises	323
15	Solutions	327
15.1	Introduction	327
15.2	Thermodynamic Equilibrium in Solutions	327
15.3	Chemical Potential of a Solution	329
15.4	Empirical Laws	331
15.5	Ideal Solutions	334
15.5.1	Ideal Solutions	334
15.5.2	Lewis-Randall Ideal Solutions	334
15.6	Activity Coefficient	336
15.7	Excess and Mixing Properties	337
15.8	Summary	339
	Exercises	339
16	Heterogeneous Equilibrium	341
16.1	Introduction	341
16.2	Gibbs Phase Rule	341
16.3	Phase Transitions	344
16.3.1	Van der Waals Fluid	344
16.3.2	Maxwell Construction	347
16.3.3	Above the Critical Point	348
16.4	Coexistence Lines	349
16.5	Phase Transition Classification	353

- 16.6 Binary Systems 354
 - 16.6.1 General Binary System 354
 - 16.6.2 Liquid-Gas 355
 - 16.6.3 Solid-Liquid 357
- 16.7 Summary 358
- Exercises 359
 - A.1 The Ideal Gas 361
 - A.2 Second Law Traditional Treatment 364
 - A.3 Liouville Theorem 368
 - A.4 Lagrange Undetermined Multipliers 369
 - A.5 Maximizing $W(\mathbf{Z}^*)$ 370
 - A.6 Microcanonical Volumes 371
 - A.7 Carathéodory's Principle 372
 - A.8 Jacobians 378
 - A.8.1 Definition 378
 - A.8.2 Differential Relations 379
 - A.8.3 Inverse Transformation 380
 - A.8.4 Reversing Orders 381
- References** 389
- Index** 397

