

Contents

<i>Preface</i>	vii
1. Introduction	1
2. Temperature, Work, and Heat	9
2.1 Temperature	9
2.1.1 Centigrade (Celsius) Scale	12
2.1.2 Fahrenheit Scale	14
2.1.3 Absolute Temperature Scale and Ideal Gas Thermometer	14
2.2 Pressure	18
2.3 Work	19
2.4 Heat	25
2.5 Reversible Processes and Reversible Work	28
3. The First Law of Thermodynamics	31
3.1 Equivalence of Heat and Energy	31
3.2 The First Law of Thermodynamics	33
3.3 Enthalpy	36
3.3.1 Differential Forms for Enthalpy	37
3.3.2 The Difference in Isobaric and Isochoric Heat Capacities for Ideal Gases	39
3.4 Work and Heat of Isothermal Reversible Expansion . . .	40
3.5 Work of Adiabatic Expansion	40
3.6 Heat Capacity and Heat Change	41

3.7	Thermochemistry	44
3.7.1	Heat of Reaction	44
3.7.2	Standard States and Heat of Formation	45
3.7.3	Hess's Law	46
3.7.4	Kirchhoff's Equation	49
3.8	Mathematical Notes	50
3.8.1	Exact Differentials	51
3.8.2	Chain Relations	52
3.8.3	Jacobians	54
4.	The Second Law of Thermodynamics	57
4.1	Carnot Cycle	60
4.2	Carnot's Theorem	65
4.3	Thermodynamic Temperature	70
4.4	Entropy and Calortropy	72
4.4.1	Clausius Inequality	72
4.4.2	Entropy	74
4.4.3	Calortropy	76
4.4.4	Inequalities of Entropy and Calortropy	79
4.5	Carnot's Theorem and Real Gases	85
4.6	Examples of Other Cycles	88
4.6.1	Rankine Cycle	88
4.6.2	Otto Cycle	88
4.6.3	Diesel Cycle	89
4.7	Calculation of Entropy Change	90
4.7.1	Phase Transition and Entropy Change	90
4.7.2	Entropy Changes of an Ideal Gas	91
4.8	Free Energies	93
4.8.1	Helmholtz Free Energy	93
4.8.2	Gibbs Free Energy	93
4.9	Maxwell's Relations	93
5.	Equilibrium Conditions and Thermodynamic Stability	103
5.1	Inequalities	103
5.2	Equilibrium Conditions	106
5.3	Stability of Equilibrium	112

6.	The Third Law of Thermodynamics	115
7.	Thermodynamics of Mixtures and Open Systems	121
7.1	Chemical Potentials	121
7.1.1	The Gibbs Theory	121
7.1.2	Alternative Consideration	123
7.1.3	Fundamental Relations for Open Systems	124
7.2	Partial Molar Properties	125
7.3	Measurement of Partial Molar Properties	130
7.3.1	Method of Intercepts	131
7.3.2	Direct Method	132
7.3.3	Method of Apparent Molar Property	133
7.3.4	Density Dependence of \bar{M}_i	133
8.	Heterogeneous Equilibria	135
8.1	Equilibrium Conditions for a Multiphase System	135
8.1.1	Mechanical Equilibrium	137
8.1.2	Thermal Equilibrium	139
8.1.3	Material Equilibrium	140
8.2	Gibbs Phase Rule	143
8.3	One-Component, Two-Phase Systems	144
8.3.1	Vapor Pressure and Measurement of Δh	147
8.3.2	Ramsay–Young Rule	148
8.4	Two-Component Systems	151
9.	Thermodynamics of Real Fluids	159
9.1	Constitutive Equations	159
9.1.1	Ideal Gas Equation of State	161
9.1.2	Caloric Equation of State	161
9.1.3	Ratio of Specific Heats and Compressibility	162
9.1.4	Sound Wave Velocity and Polytropic Ratio	163
9.2	Virial Equation of State	166
9.3	van der Waals Equation of State	168
9.4	Law of Corresponding States	172
9.5	Thermodynamic Functions	173
9.5.1	Reversible Work	174
9.5.2	Heat Change in Isothermal Expansion	175

9.5.3	Standard States	176
9.5.4	Enthalpy	177
9.5.5	Internal Energy	181
9.5.6	Entropy	184
	9.5.6.1 Real Gases	185
	9.5.6.2 Substances in Condensed Phase	187
9.5.7	Gibbs Free Energy	188
9.6	Fugacity	189
9.7	Joule–Thomson Experiment	193
9.8	Liquefaction of Gases	198
9.9	Entropy Surface	200
	9.9.1 Ideal Gas	201
	9.9.2 van der Waals Gas	202
10.	Canonical Equation of State	205
10.1	Canonical Equation of State	206
10.2	Reduced Variables	208
10.3	Reduced Canonical Equation of State	210
10.4	Models for the GvdW Parameters	211
	10.4.1 Subcritical Regime	211
	10.4.2 Supercritical Regime	213
10.5	Reduced Chemical Potential	213
10.6	Specific Heat	215
10.7	Virial and Joule–Thomson Coefficients	216
	10.7.1 Virial Coefficients	217
	10.7.2 Joule–Thomson Coefficient	218
	10.7.3 Asymptotic Behavior of the Second Virial Coefficient	219
10.8	Stability Conditions of Mechanical and Material Equilibria	219
	10.8.1 Classical Definition of Critical Point	219
	10.8.2 Extended Definition	220
10.9	Critical Properties of Fluids	222
	10.9.1 Critical Point	222
	10.9.2 Critical Isotherm for Pressure	223
	10.9.3 Spinodal Curve	225
	10.9.4 Excess Chemical Potential	227

10.9.5	Liquid–Vapor Coexistence Curve	231
10.9.5.1	Equilibrium Conditions	231
10.9.5.2	Coexistence Curve	232
10.9.6	Excess Heat Capacity	235
10.9.7	Isothermal Compressibility	237
10.10	Quadratic Model	238
10.10.1	Subcritical Regime	238
10.10.2	Supercritical Regime	240
10.10.3	Critical Point	241
10.10.4	Critical Isotherms	242
10.10.5	Spinodal Curve	242
10.11	Concluding Remarks	243
11.	Thermodynamics of Real Gas Mixtures	247
11.1	Chemical Potentials for Mixtures	247
11.2	Entropy of Mixing	253
11.3	Heat of Mixing	256
11.4	Activity and Activity Coefficient	257
11.5	Canonical Equation of State for a Mixture	260
12.	Chemical Equilibria	265
12.1	A Single Reaction	265
12.2	Coupled Chemical Reactions	268
12.3	Chemical Reactions in a Multiphase System	269
12.4	Equilibrium Constant	271
12.5	van't Hoff Equation	273
12.6	Equilibrium Constant for Real Gases	276
13.	Thermodynamics of Solutions	279
13.1	Chemical Potentials of Solutions	279
13.2	Ideal Solutions	283
13.3	Raoult's Law	286
13.4	Two-Component, Two-Phase Equilibrium Reconsidered	289
13.5	Margules Expansions	293
13.6	Regular Solutions	295
13.7	Real Solutions	298

13.8	Osmotic Coefficient of Bjerrum	303
13.9	Determination of Activity Coefficients	307
13.9.1	Vapor Fugacity	308
13.9.2	Freezing Point Depression	308
13.9.3	Boiling Point Elevation	313
13.9.4	Osmotic Pressure	317
13.9.5	Solubility	319
14.	Thermodynamics of Surfaces	323
14.1	Dividing Surface	324
14.2	Gibbs Relation for Interface	325
14.3	Nearly Planar Surface and Surface Tension	331
14.4	Gibbs–Duhem Relation for Interface	334
14.5	Location of the Dividing Surface and Surface Tension	335
14.6	Gibbs Phase Rule Including Interface	336
14.7	Thermodynamics of Interface	337
14.7.1	Invariance of Derivatives to the Position of the Dividing Surface	337
14.7.2	Various Thermodynamic Relations for Interface	339
14.7.3	Liquid–Vapor Equilibrium	340
14.7.3.1	Density Dependence of γ	340
14.7.3.2	Temperature Dependence of γ	342
15.	Electrolyte Solutions	345
15.1	Mean Activity and Mean Activity Coefficient	346
15.2	Isopiestic Method	348
15.3	Activity Coefficient from Freezing Point Measurement	351
15.4	Activity Coefficient from Osmotic Pressure Measurement	352
16.	Debye–Hückel Theory of Strong Electrolyte Solutions	355
16.1	Ionic Atmosphere	356
16.2	Mean Potential and the Excess Free Energy	357

17.	Galvanic Cells and Electromotive Forces	363
17.1	Reversible Galvanic Cells and Reversible Electrodes . . .	363
17.2	Electrochemical Potentials	364
17.3	Galvanic Cells Without Liquid Junction	366
17.3.1	Cell Diagrams and the Sign Convention	367
17.4	Fuel Cells	371
17.5	Donnan Membrane Equilibrium	376
18.	Thermodynamics of Electric and Magnetic Fields	379
18.1	Dielectrics in Electrostatic Field	379
18.2	Field Dependence of Thermodynamic Quantities	384
18.2.1	Electrostriction	384
18.2.2	Electrocaloric Effects	385
18.3	Static Magnetic Fields	387
18.3.1	Magnetostriction	389
18.3.2	Magnetocaloric Effects	389
19.	Thermodynamics of Nonequilibrium Processes	393
19.1	Extended Gibbs Relation for Calortropy	393
19.1.1	Differential Form for Calortropy	395
19.1.2	Variables in the Tangent Manifold	398
19.1.2.1	Nonequilibrium Effect on Temperature	399
19.1.2.2	Nonequilibrium Effect on Pressure	400
19.1.2.3	Nonequilibrium Effect on Chemical Potentials	400
19.1.2.4	Nonequilibrium Effect on Equilibrium Constants	402
19.2	Flow of a Non-Newtonian Liquid	403
19.2.1	Velocity Profile of Flow in a Rectangular Channel	404
19.2.1.1	The Case of $p_x = 0$	406
19.2.1.2	The Case of $p_x \neq 0$	407
19.2.2	Non-Newtonian Viscosity	409
19.3	Chemical Oscillations and Pattern Formation	412

Appendix A	Local Form of Energy Conservation Law	425
Appendix B	Various Coefficients Used in Chapter 10	431
B.1	Coefficients of $\Pi^{(i)}(x_{sk}, t)$	431
B.2	Coefficients P_{ij}	432
B.3	Coefficients $\hat{\Pi}_j^{(i)}(t)$	433
B.4	Coefficients of the Spinodal Equations	436
<i>Index</i>		441