

Contents

Preface to the Two-Volume Series	xiii
Preface to the First Volume	xxi
CHAPTER 1: Introduction	1
1.1 Thermodynamics — A Pre-eminent Example of an Exact Science	1
1.2 The Language of Thermodynamics	3
1.2a The Thermodynamic System	3
1.2b Isolated, Closed, and Adiabatic Systems: Surroundings and the Universe	4
1.2c Components and Mixtures	5
1.2d Chemical Processes	7
1.3 Thermodynamic Variables	8
1.3a Number of moles (n)	9
1.3b Volume (V)	9
1.3c Pressure (p)	10
1.3d Temperature (T)	10
The Zeroth Law of Thermodynamics	11
Temperature Scales	11
The Thermodynamic or Kelvin Temperature Scale	11
The Absolute Temperature Scale	11
The International Temperature Scale — ITS-90	12
1.3e Internal Energy (U)	14
1.3f Entropy (S)	17
1.3g Enthalpy (H)	19
1.3h Helmholtz Free Energy (A)	20
1.3i Gibbs Free Energy (G)	21
1.4 The Mathematics of Thermodynamics	22
1.4a The Pfaffian Differential and the Test for Exactness	22
1.4b Relationships Between Exact Differentials	24

1.5	Derivation of Thermodynamic Equations using the Properties of the Exact Differential	28
1.5a	Examples of the Application of Exact Differential Relationships	29
1.6	Calculation of Changes in the Thermodynamic Variable	32
1.7	Use of Units	33
	References	36
CHAPTER 2: The First and Second Laws of Thermodynamics		37
2.1	The First Law of Thermodynamics	37
2.1a	Work	38
2.1b	Calculation of Work	40
	The Isobaric Process	41
	The Isochoric Process	42
	The Isothermal Process	42
	The Reversible Process	44
2.1c	Calculation of Heat	48
	Heat Capacity	48
	Relationships between U , H , q , C_p , and C_V	52
2.1d	Calculation of q for Other Processes	56
2.2	The Second Law of Thermodynamics	56
2.2a	The Carnot Cycle: A Hypothetical Engine of Fundamental Importance	58
2.2b	The Kelvin Temperature and Its Role in Calculating an Entropy Change	60
2.2c	The Second Law Expressed in Terms of an Entropy Change	62
2.2d	Carathéodory and Pfaffian Differentials	63
	Pfaffian Differential Expressions With Two Variables	64
	Pfaffian Differential Expressions with Three or More Variables and the Conditions for the Existence of an Integrating Denominator	67
2.2e	The Carathéodory Principle and Inaccessible States	68
2.2f	The Identification of the Absolute (Ideal Gas) Temperature as the Integrating Denominator	71
2.2g	Entropy Changes for Reversible and Irreversible Paths	78
2.2h	Calculation of an Entropy Change	82
	Calculation of ΔS for the Reversible Isothermal Expansion of an Ideal Gas	83

	Calculation of ΔS for the Reversible Adiabatic Expansion	83
	Calculation of ΔS for the Isobaric Temperature Change	83
	Calculation of ΔS for the Isochoric Temperature Change	84
	Calculation of ΔS for the Reversible (Equilibrium) Phase Change	84
	Calculation of ΔS for the Mixing of Ideal Gases at Constant T and p	85
	2.2i Entropy and Disorder	89
2.3	Implications of the Laws	90
	2.3a The Laws of Thermodynamics and Cyclic Engines	94
	References	102
CHAPTER 3: Thermodynamic Relationships and Applications		105
3.1	The Gibbs Equations	106
3.2	Partial Differential Relationships	107
	3.2a The Gibbs–Helmholtz Equation	113
	3.2b Observations About the Differential Relationships	114
3.3	Applications of the Differential Relationships	118
	3.3a Examples of the Application of the Differential Relationships	120
	3.3b Difference Between C_p and C_V	129
	3.3c The Reversible Adiabatic Expansion or Compression	131
	3.3d The Carnot Cycle	135
	3.3e The Joule–Thomson Expansion	139
3.4	Relationship Between Free Energy and Work	145
	References	153
CHAPTER 4: The Third Law and Absolute Entropy Measurements		155
4.1	Verification of the Third Law	163
4.2	Exceptions to the Third Law	167
4.3	Implications and Applications of the Third Law	177
	4.3a Attainment of Perfect Order at Low Temperatures	177
	4.3b Limiting Values for Thermal Properties at Zero Kelvin	182
	Coefficient of Expansion	182
	Temperature Gradient of Pressure	183

	Heat Capacity	183
	G_0 and H_0	184
4.4	Production of Low Temperatures and the Inaccessibility of Absolute Zero	184
4.4a	Production of Low Temperatures	184
	Joule–Thomson Expansion and Evaporation	
	Techniques	184
	Adiabatic Demagnetization	185
	Nuclear Alignment	186
	Laser Cooling	186
4.4b	Inaccessibility of Absolute Zero	188
4.5	Thermodynamic Functions	189
	References	200
CHAPTER 5: The Chemical Potential and Equilibrium		203
5.1	Composition as a Variable	203
5.2	The Chemical Potential	204
5.3	Partial Molar Properties	208
5.4	The Gibbs–Duhem Equation	213
5.5	Determination of Partial Molar Properties	214
5.5a	Numerical Methods	215
5.5b	Analytical Methods Using Molality	217
5.5c	Analytical Methods Using Mole Fractions	219
5.5d	Calculations of Partial Molar Properties From Apparent Molar Properties	222
5.6	Criteria for Equilibrium	225
5.6a	Criterion for Phase Equilibrium	231
5.6b	The Gibbs Phase Rule	237
5.6c	The Clapeyron Equation	238
5.6d	Criterion for Chemical Equilibrium	240
	References	246
CHAPTER 6: Fugacity, Activity, and Standard States		247
6.1	Fugacity	247
6.1a	Definition of Fugacity	247
6.1b	Determination of Fugacities	249
6.1c	Fugacity for Pure Condensed Phases	259
6.1d	Effect of Pressure and Temperature on the Vapor Fugacity	260
	Change of Fugacity With Pressure	260
	Change of Fugacity With Temperature	261

6.1e	Fugacity in a Mixture	262
	Fugacity of a Component in a Gaseous Mixture	263
	Fugacity in Liquid Mixtures: Raoult's Law and Henry's Law	268
	a. Raoult's Law and the Ideal Solution	268
	b. Henry's Law	273
	c. The Duhem–Margules Equation	276
6.2	The Activity	279
6.2a	Effect of Pressure on Activity	280
6.2b	Effect of Temperature on Activity	281
6.3	Standard States	282
6.3a	Choice of Standard States	283
	Standard State of a Gas	283
	Standard States for Pure Solids and Pure Liquids	285
	Standard State of a Solvent in a Mixture	287
	Standard States of Solutes in Solution	290
6.4	Activities of Electrolyte Solutions	294
6.4a	Activities and Standard States of Strong Electrolytes	295
6.4b	Activities of Strong Unsymmetrical Electrolytes	301
6.5	Determination of Activity	304
6.5a	Activity from Vapor Pressure Measurements	304
6.5b	Activities from Freezing Point and Boiling Point Measurements	305
6.5c	Activity from Isopiestic Methods	309
6.5d	Solute Activities From Measurement of Partition Coefficients	311
6.5e	Calculation of the Activity of One Component From That of the Other	313
	References	322

CHAPTER 7: The Thermodynamic Properties of Solutions 325

7.1	Change in the Thermodynamic Properties of Nonelectrolyte Solutions due to the Mixing Process	325
7.1a	Change in Thermodynamic Properties Resulting from the Formation of Ideal Solutions	326
7.1b	Excess Thermodynamic Functions	328
	Nonpolar + Nonpolar Mixtures	330
	Polar + Nonpolar Mixtures	330
	Mixtures with Hydrogen Bonding	331
	Excess Volume Comparison	332

7.2	Calculation of the Thermodynamic Properties of Strong Electrolyte Solutes: The Debye–Hückel Theory	333
7.2a	Derivation of the Activity Coefficient Equations	335
7.2b	Comparison of the Debye–Hückel Prediction with Experimental Values	343
7.2c	The Debye–Hückel Prediction of the Osmotic Coefficient	345
7.2d	The Debye–Hückel Prediction of Thermal and Volumetric Properties of the Solute	348
7.3	Relative Partial Molar and Apparent Relative Partial Molar Thermal Properties	350
7.3a	Relative Partial Molar Enthalpies	350
7.3b	Calculation of ΔH from Relative Partial Molar Enthalpies	352
7.3c	Relative Apparent Molar Enthalpy	356
7.3d	Determination of Relative Apparent Molar Enthalpies	358
7.3e	Relative Partial Molar Heat Capacities	363
7.3f	Relative Apparent Molar Heat Capacity	365
7.4	The Osmotic Pressure	367
7.4a	Osmosis	373
	References	382
CHAPTER 8: The Equilibrium Condition Applied to Phase Equilibria		383
8.1	Phase Equilibria for Pure Substances	385
8.1a	The Phase Diagram and the Gibbs Phase Rule	385
8.1b	Solid + Liquid Equilibrium	387
8.1c	Equilibrium Involving a Condensed Phase and the Vapor Phase	389
	The Clausius–Clapeyron Equation	389
8.1d	Vapor + Liquid Equilibrium: The Critical Point	392
8.1e	Solid + Solid Phase Transitions	399
	First-Order Phase Transitions	402
8.2	Phase Equilibria for Mixtures	405
8.2a	Vapor + Liquid Equilibrium	406
8.2b	Liquid + Liquid Equilibrium	413
8.2c	Solid + Liquid Equilibrium	418
	Effect of Pressure on Solid + Liquid Equilibrium	422
	Solid + Liquid Equilibria in Less Ideal Mixtures	424
	References	433

CHAPTER 9: The Equilibrium Condition Applied to Chemical Processes	435
9.1 The Equilibrium Constant	435
9.1a Alternate Forms of the Equilibrium Constant	437
9.1b Effect of Pressure and Temperature on the Equilibrium Constant	443
The Effect of Pressure	443
The Effect of Temperature	446
9.2 Enthalpies and Gibbs Free Energies of Formation	448
9.2a Determination of Standard Enthalpies and Gibbs Free Energies of Formation	450
Enthalpies of Formation	450
Gibbs Free Energies of Formation	456
9.2b Enthalpies of Formation and Gibbs Free Energies of Formation of Ions in Solution	457
9.3 Examples of Chemical Equilibrium Calculations	464
9.4 Electrochemical Cells	475
9.4a Thermodynamic Applications of Electrochemical Cells	479
Measurement of E° and Activities	479
Measurement of Equilibrium Constants	487
References	496
CHAPTER 10: Statistical Thermodynamics	497
10.1 Energy Levels of an Ideal Gas Molecule	497
Translational Energy Levels	498
Rotational Energy Levels	499
Vibrational Energy Levels	502
Electronic Energy Levels	505
10.2 Distribution of Energy Among Energy Levels	507
10.3 The Boltzmann Distribution Law	514
10.3a Evaluation of α	517
10.3b Evaluation of β	518
10.4 The Partition Function	523
10.5 Relationship Between the Partition Function and the Thermodynamic Properties	528
10.6 Evaluation of the Partition Function for the Ideal Gas	534
10.6a Translational Partition Function	536
10.6b Rotational Partition Function	538
10.6c Vibrational Partition Function	540
10.6d Electronic Partition Function	541

10.7	Calculation of the Thermodynamic Properties of the Ideal Gas	543
10.7a	Examples of the Derivation of the Contribution to the Thermodynamic Properties	544
	Translational Contribution to Entropy	544
	Translational and Rotational Contributions to Enthalpy for a Linear Molecule	548
	Vibrational Contribution to the Gibbs Free Energy for a Linear Diatomic Molecule	549
	Calculation of Thermodynamic Properties	549
10.7b	Corrections to Table 10.4 for Diatomic Molecules	555
	Rotational Partition Function Corrections	556
	Anharmonicity and Nonrigid Rotator Corrections	557
10.7c	Contributions of Internal Rotation to the Thermodynamic Properties	564
	Free Rotation ($kT \gg V_0$)	566
	Hindered Rotation ($kT \approx V_0$)	568
10.8	Calculation of the Thermodynamic Properties of Solids	569
10.8a	The Einstein Heat Capacity Equation	569
10.8b	The Debye Heat Capacity Equation	572
10.8c	Contribution to the Heat Capacity of Solids from Low-lying Electronic Levels: The Schottky Effect	580
	References	592
APPENDIX 1: Mathematics for Thermodynamics		593
A1.1	Operations with Derivatives and Integrals	593
A1.2	Total Differentials and Relationships Between Partial Derivatives	594
A1.3	Intensive and Extensive Variables	598
A1.4	State Functions and Exact Differentials; Inexact Differentials and Line Integrals	599
	A1.4a State Functions	599
	A1.4b Exact and Inexact Differentials	604
	A1.4c Line Integrals	605
A1.5	Pfaffian Differentials	608
	A1.5a Pfaffian Differential Expressions in Three Dimensions	609
	A1.5b Maxwell Relations in Three Dimensions	609

A1.5c	Differential Equations, Solution Curves, and Solution Surfaces	610
A1.5d	Pfaffian Differential Expressions in Two Dimensions	611
A1.6	Euler's Theorem	612
A1.7	Graphical Integrations	613
A1.7a	The Trapezoidal Rule	613
A1.7b	Simpson's Rule	614
A1.8	Stirling's Approximation	615
APPENDIX 2: The International Temperature Scale of 1990		617
A2.1	Fixed Points	619
A2.2	Choice of Thermometer	619
A2.2a	Temperature Interval 0.65 to 5.0 K	619
A2.2b	Temperature Interval 3.0 to 24.5561 K	620
A2.2c	Temperature Interval 13.8033 to 1234.93 K	620
A2.3	The Deviation Function	622
A2.4	Measurement of Temperatures Above 1234.93 K	624
A2.5	Correction of Existing Data to ITS-90	624
APPENDIX 3. Equations of State for Gases		627
A3.1	The Ideal Gas	627
A3.2	The Virial Equation	627
A3.3	The Virial Equation Explicit in Pressure	629
A3.4	Other Equations of State	629
A3.5	Cubic Equations of State	631
A3.5a	Comparison of Cubic Equations of State	631
APPENDIX 4: Calculations from Statistical Thermodynamics		639
Table A4.1	Thermodynamic Functions of an Ideal Gas	640
Table A4.2	Moments of Inertia and Rotational Constants of Some Common Molecules	642
Table A4.3	Fundamental Vibrational Frequencies of Some Common Molecules	644
Table A4.4	Electronic Energy Levels of some Common Molecules or Atoms With Unpaired Electrons	646
Table A4.5	Anharmonic Oscillator and Nonrigid Rotator Corrections	646

610	Table A4.6	Contributions to the Thermodynamic Properties Due to Internal Rotation	648
611	Table A4.7	The Debye Thermodynamic Functions Expressed in Terms of θ_D/T	651
612	A1.6	Euler's Theorem	544
613	A1.7a	Exponential Integrals	545
614	A1.8	Stirling's Approximation	549
615		Calculation of Thermodynamic Properties	549
617		Corrections to Table 4.01 of 1990	
619	A2.1	Fixed Points	555
619	A2.2	Choice of Thermometric	
619	A2.2a	Temperature Interval 0.05 to 2.0 K	557
620	A2.2b	Temperature Interval 2.0 to 24.561 K	
620	A2.2c	Temperature Interval 24.561 to 1234.93 K	564
622	A2.3	The Deviation Function	566
624	A2.4	Measurement of Temperatures Above 1234.93 K	567
624	A2.5	Correction of Existing Data to ITS-90	569
627	10.8a	The Entropy Capacity	569
627	10.8b	The Debye Heat Capacity Equation	572
627	10.8c	Equation of State for Gaseous	
627	A3.1	The Ideal Gas	585
627	A3.2	The Virial Equation	592
629	A3.3	The Virial Equation Explicit in Pressure	
629	A3.4	Other Equations of State	
631	A3.5	Cubic Equations of State	595
631	A3.5a	Comparison of Cubic Equations of State	595
639	A1.3	Calculations from Statistical Thermodynamics	595
640	A1.4	Thermodynamic Functions of Ideal Gases	
642	Table A4.2	Moments of Inertia and Rotational Constants of Some Common Molecules	595
644	Table A4.3	Fundamental Vibrational Frequencies of Some Common Molecules	596
646	Table A4.4	Electronic Energy Levels of Some Common	599
646	Table A4.5	Anharmonic Oscillator and Nonrigid Rotor	603
646		and	605