

Table of Contents

Volume 1

1 Thermodynamic Systems : Definitions -----	1
1.1 Introduction -----	1
1.2 Interactions of Thermodynamic Systems with their Environment -----	2
1.3 System in a State of Equilibrium -----	3
1.4 Thermal reservoir. Heat Source. -----	4
1.5 Diathermal and Adiabatic Enclosures -----	4
1.6 State Function and State Variables. Intensive and Extensive Variables. -----	4
1.6.1 Definitions and Properties -----	4
1.6.2 Isobaric Coefficient of Thermal Expansion. Isothermal Compressibility Coefficient -----	6
1.7 Change of a State Variable as the Result of a Thermodynamic Process -----	7
1.7.1 General Process -----	7
1.7.2 Cyclic Process -----	8
1.7.3 Expansion and Compression of a Gas -----	9
1.7.4 Mathematical Properties of a State Function -----	10
1.8 Reversible and Irreversible Processes -----	11
1.9 Equation of State -----	11
2 Work -----	13
2.1 Introduction -----	13
2.2 Sign Convention -----	13
2.3 Mechanical Work -----	14
2.3.1 Definition -----	14
2.3.2 Work and Volume Change -----	15
2.3.3 Examples -----	16
2.4 Electrical Work -----	18
2.5 Various Forms of Energy -----	19
2.6 Various Expressions for Work -----	20
3 First Law of Thermodynamics -----	21
3.1 Introduction -----	21
3.2 The Joule Experiment -----	22
3.3 Internal Energy. First Law -----	22
3.3.1 General Aspects. Expression of the First Law of Thermodynamics -----	22
3.3.2 Application to a Closed System -----	23
3.4 Internal Energy – A Look at the Molecular Scale -----	25
4 Second Law of Thermodynamics -----	27
4.1 Spontaneous Processes. Illustration at the Molecular Scale -----	27
4.1.1 Spatial rearrangement -----	27

4.1.2 Heat Transfer-----	28
4.1.3 A First Glance at Entropy -----	29
4.2 First Formulation of the Second Law-----	31
4.3 Carnot Cycle. Heat Engine. Thermodynamic Temperature -----	32
4.3.1 Carnot Cycle. Operation of an Engine -----	32
4.3.2 Reversible Cycles of Two Distinct Systems-----	33
4.3.3 Definition of the Thermodynamic Temperature -----	34
4.4 Entropy. Reversible and Irreversible Processes -----	35
4.4.1 Definition -----	35
4.4.2 Entropy is a State Function -----	36
4.4.3 Implications of the Second Law towards Entropy and Spontaneity of Processes -----	38
4.4.4 System in Contact with a Single Thermal Reservoir-----	41
4.4.5 System in Contact with Several Thermal Reservoirs -----	42
4.4.6 Other Formulations of the Second Law. Equilibrium Condition -----	43
4.4.7 Thermal Equilibrium-----	43
4.4.8 Differential Expression for the Internal Energy of a Closed System -----	45
4.4.9 Maximum Usable Work during a Process -----	46
4.4.10 Entropy Change during a Monothermal Expansion of an Ideal Gas-----	47
4.5 Carnot Cycle of an Ideal Gas -----	50
4.5.1 Isothermal (Reversible) Process of an Ideal Gas -----	50
4.5.2 Reversible Adiabatic Process of an Ideal Gas -----	51
4.5.3 Properties of the Cycle-----	52
4.6 Heat Engines, Refrigerators, Heat Pumps-----	55
4.6.1 Thermal Machines -----	55
4.6.2 Efficiency of an Engine -----	55
4.6.3 Refrigerator, Air Conditioner, Heat Pump -----	56
4.7 Internal Combustion Engine -----	58
4.7.1 The Otto Cycle or Beau de Rochas Cycle-----	58
4.7.2 Efficiency of an Engine -----	59
4.8 Other Examples-----	60
4.8.1 Stirling Cycle-----	60
4.8.2 Joule Cycle-----	63
5 Auxiliary Functions : Enthalpy, Helmholtz Energy, Gibbs Energy -----	65
5.1 Introduction -----	65
5.2 Closed Systems -----	66
5.2.1 Constant Volume Process (Isochoric Process) -----	66
5.2.2 Constant Pressure Process (Isobaric Process) -----	67
5.3 Characteristic Variables. Fundamental Equations. Open Systems -----	68

5.3.1	Generalities	68
5.3.2	Internal Energy	69
5.3.3	Enthalpy	70
5.3.4	Helmholtz Function (Helmholtz Energy, Free Energy)	70
5.3.5	Gibbs Function (Gibbs Energy, Free Enthalpy)	71
5.3.6	Chemical Potential. Summary	72
5.4	Maxwell's Relations	73
5.5	Thermodynamic Equation of State	75
5.5.1	General Case	75
5.5.2	Equation of State for an Ideal Gas	77
5.6	Properties of C_p and C_V	78
5.6.1	Relation between C_p and C_V	78
5.6.2	Variation of C_V with Volume and of C_p with Pressure	80
5.7	Physical Meaning of the Auxiliary Functions	81
5.7.1	Helmholtz Function (Free Energy, Helmholtz Energy)	81
5.7.2	Gibbs Function (Gibbs Energy, Free Enthalpy)	84
5.7.3	Spontaneous Evolution of a System. Equilibrium Condition	86
6	Pure Substances and Mixtures : Molar Quantities and Partial Molar Quantities	89
6.1	Homogeneous Functions and their Properties	89
6.2	Extensive Variables : Essential Property	90
6.3	Intensive Variables	91
6.4	Explicit Expressions for Various Extensive Variables	93
6.5	Gibbs-Duhem Equation	95
6.6	Partial Molar Quantities	96
6.6.1	Definition	96
6.6.2	Relation between Partial Molar Quantities	97
6.6.3	Pure Substance	98
6.6.4	Other Relations	98
6.7	Measurement of Partial Molar Volumes	100
7	Thermodynamics of Gases	105
7.1	Pure Ideal Gas	105
7.1.1	Chemical Potential of a Pure Ideal Gas	105
7.1.2	Selection of the Standard State Pressure	106
7.1.3	Mathematical Expressions of other Thermodynamic Functions of Ideal Gases	106
7.1.4	Entropy Change of an Ideal Gas due to a Change of State	107
7.2	Mixtures of Ideal Gases	108
7.2.1	Basic Properties, Ideal Gas Mixture	108
7.2.2	Entropy of Mixing, Gibbs and Helmholtz Energy of Mixing of Two Ideal Gases Forming an Ideal Gas Mixture	110

7.2.3 Irreversible Mixing of Two Ideal Gases -----	113
7.2.4 Chemical Potential of an Ideal Gas in an Ideal Gas Mixture of Two Gases -----	113
7.2.5 Several Gases, Partial Molar Quantities, Functions of Mixing-----	114
7.3 Pure Real Gases-----	116
7.3.1 Molecular Interactions in Real Gases -----	116
7.3.2 Chemical Potential of a Pure Real Gas-----	118
7.3.3 Fugacity Coefficient of a Pure Real Gas -----	119
7.3.4 The Virial Equation-----	119
7.3.5 The van der Waals Equation of State-----	120
7.3.6 Joule–Thomson Effect-----	124
7.4 Mixtures of Real Gases-----	127
7.4.1 Chemical Potential of a Real Gas in a Mixture-----	127
7.4.2 Variables of Mixing for Real Gases -----	128
7.5 Ideal Mixtures of Gases-----	130
7.5.1 General Remarks -----	130
7.5.2 The Lewis–Randall Rule -----	132
8 Systems Made up of Several Phases with No Chemical Reaction -----	133
8.1 Introduction -----	133
8.2 Differential Expressions of State Functions-----	134
8.2.1 Fundamental Relations -----	134
8.2.2 Chemical Potentials at Equilibrium -----	135
8.2.3 General Expressions for Open Systems-----	136
8.3 Spontaneous Transfer of a Species from One Phase to Another -----	137
8.4 The Phase Rule-----	138
8.5 Equilibrium of Two Phases of a Pure Substance -----	139
8.5.1 The Clapeyron Equation -----	139
8.5.2 Equilibrium between a Gaseous Phase and a Condensed Phase (Liquid or Solid) of a Pure Substance -----	141
8.5.3 Schematic Representation of some of the Thermodynamic Functions in the Vicinity of a Phase Change -----	142
8.5.4 Effect of an Inert Gas on the Vapor Pressure of a Pure Substance-----	144
8.5.5 Effect of Temperature on the Latent Heat of Phase Change and on the Equilibrium Pressure-----	145
8.6 Phase Diagram of a Pure Substance -----	146
8.6.1 The Solid Exists in only One Crystalline Form -----	146
8.6.2 The Solid May Exist in Several Crystalline Forms -----	150
Problems and Solutions Chapters 1 through 8-----	153
Index	

Volume 2

9 Energetics of Chemical Reactions -----	271
9.1 Introduction -----	271
9.2 The Extent of Reaction -----	272
9.3 Variables of Reaction -----	273
9.3.1 Gibbs Energy of Reaction (Free Enthalpy of Reaction) -----	273
9.3.2 Spontaneous Reaction. Equilibrium -----	274
9.3.3 Systems where Several Reactions can Take Place Simultaneously -----	274
9.3.4 Other Variables of Reaction -----	276
9.3.5 Standard Variables of Reaction -----	276
9.3.6 Standard Variables of Formation -----	278
9.4 Hess's Law -----	280
9.4.1 Content -----	280
9.4.2 Application -----	280
9.4.3 Generalization -----	282
9.4.4 Example -----	282
9.5 Kirchoff's Equation -----	284
9.6 Effect of Temperature on the Entropy of Reaction and the Gibbs Energy of Reaction -----	286
9.7 Conversion of Chemical Energy into Work -----	288
9.7.1 Any Form of Work -----	288
9.7.2 Work other than Work due to Volume Change -----	289
9.7.3 Batteries -----	290
9.7.4 Lead Storage Battery -----	291
9.8 Effect of the Choice of the Standard State Pressure on the Tabulated Thermodynamic Values -----	293
9.8.1 Justification of the Choice -----	293
9.8.2 Useful Relations -----	294
9.8.3 Ideal Gases -----	294
9.8.4 Real Gases -----	296
9.8.5 Condensed Phase -----	296
9.8.6 System with one Gas Phase and Several Condensed Phases -----	296
9.9 Variables of Combustion -----	297
10 Chemical Equilibria -----	299
10.1 Introduction -----	299
10.2 Spontaneous Reaction and Equilibrium Condition -----	299
10.3 Change in $G(\xi)$ with the Extent of Reaction -----	300
10.3.1 General Expression for a Mixture of Reacting Ideal Gases -----	300
10.3.2 Schematic Representation -----	302
10.4 Affinity -----	303
10.5 Law of Mass Action for a Mixture of Gases -----	304
10.5.1 General Case -----	304

10.5.2 Other Forms of the Law of Mass Action -----	305
10.6 Chemical Equilibrium in the Presence of Pure Condensed Phases-----	307
10.6.1 Chemical Potential of a Pure Condensed Phase. Activity-----	307
10.6.2 Law of Mass Action for Heterogeneous Systems-----	308
10.7 Independent Reactions -----	310
10.7.1 General Remarks -----	310
10.7.2 Number and Nature of Independent Reactions-----	311
10.7.3 Verifying the Independence of Reactions -----	315
10.7.4 Consequences on Equilibrium and the Law of Mass Action -----	317
10.8 Phase Rule for Systems with Chemical Reactions -----	317
10.8.1 Demonstration -----	317
10.8.2 Examples of the Use of the Phase Rule-----	318
10.9 Effect of Temperature on the Equilibrium Constant -----	319
10.10 Displacement Laws of Equilibria-----	321
10.10.1 Effect of Temperature -----	321
10.10.2 Effect of Pressure-----	322
10.10.3 Effect of Volume-----	323
10.10.4 Effect of the Addition of an Inert Gas -----	323
10.10.5 Effect of an Excess in One of the Reacting Species at Constant Pressure-----	324
10.11 Reduction of Iron Oxides-----	327
10.11.1 Introduction and Method -----	327
10.11.2 Reduction by Carbon Monoxide -----	328
10.11.3 Reduction by Hydrogen-----	333
11 Thermodynamics of Perfect and Ideal Solutions -----	337
11.1 Introduction-----	337
11.2 Perfect Solution-----	340
11.2.1 Isothermal Diagram-----	340
11.2.2 Isobaric Representation -----	342
11.3 Mixing Properties of Ideal Solutions-----	343
11.4 Effect of Pressure and Temperature on Liquid Vapor Equilibria -----	344
11.5 Depression of the Freezing Temperature of a Solvent in the Presence of a Solute-----	345
11.6 Elevation of the Boiling Temperature of a Solvent in the Presence of a Solute -----	347
11.7 Osmotic Pressure -----	348
12 Thermodynamics of Non Ideal Solutions -----	351
12.1 Introduction-----	351
12.2 Variables and Excess Variables of Mixing -----	352
12.3 Effect of Temperature and Pressure on the Activity Coefficient-----	353

12.4 Standard State – Convention I for the Activity Coefficient	354
12.5 Applications of the Gibbs–Duhem Equation	356
12.5.1 Relation between Activity Coefficients in Binary Systems	356
12.5.2 Equilibrium Shift. Azeotropy	357
12.6 Isothermal Diagram	360
12.7 Isobaric Diagram	361
12.8 Standard State – Convention II for the Activity Coefficient	362
12.9 Liquid – Liquid Extraction	366
12.10 Other Composition Scales and Standard States	367
12.10.1 Molality	367
12.10.2 Concentration	369
12.11 Law of Mass Action for Liquid Phase Systems	369
12.12 Electrolytes	371
12.12.1 General Considerations	371
12.12.2 Chemical Potential of Ions in Solution	372
12.12.3 Dissociation Equilibrium	373
12.12.4 Hydrogen Ion Convention for Aqueous Solutions	374
12.12.5 Electrode Potential	376
13 Statistical Mechanics	377
13.1 Introduction	377
13.2 Statistical Models	379
13.2.1 Maxwell–Boltzmann Statistics	379
13.2.2 Bose–Einstein Statistics	380
13.2.3 Fermi–Dirac Statistics	381
13.2.4 Illustration of the Different Statistics in a Simple Case	381
13.2.5 Dilute Systems. Corrected Boltzons	382
13.3 Stirling’s Approximations	383
13.4 Microcanonical Ensemble	384
13.5 Thermodynamic Functions for a System of Corrected Boltzons	386
13.6 A Simple System	388
13.6.1 Energy Levels for a Particle in a Box	388
13.6.2 Expression for the Partition Function	389
13.6.3 Expressions for the Thermodynamic Functions	390
13.7 Internal Degrees of Freedom	391
13.8 Microcanonical Partition Functions	392
13.8.1 Translational Partition Function	392
13.8.2 Vibrational Partition Function	392
13.8.3 Rotational Partition Function for Diatomic Molecules	394
13.8.4 Rotational Partition Function for Polyatomic Molecules	395
13.8.5 Electronic Partition Function	395

13.9 Canonical Ensemble-----	396
13.10 Canonical Partition Function for Independent Particles -----	400
13.10.1 Independent Distinguishable Particles -----	400
13.10.2 Independent Indistinguishable Particles -----	401
13.11 Heat Capacities of a Crystal -----	401
13.11.1 Introduction -----	401
13.11.2 Einstein Model-----	401
13.11.3 Debye Model -----	403
13.12 Evaluation of Entropies -----	405
13.13 Third Law of Thermodynamics-----	406
13.14 Implications of the Third Law -----	407
13.14.1 Heat Capacities -----	407
13.14.2 Effect of Pressure and Volume on Entropy at 0 K-----	407
13.14.3 Helmholtz Energy and Gibbs Energy at 0 K ----	407
13.14.4 Agreement with Statistical Thermodynamics -----	408
Problems and Solutions Chapters 9 through 13 -----	409
Appendix -----	535
A.1 Legendre Transform -----	535
A.1.1 Mathematical Considerations -----	535
A.1.2 Application to Thermodynamic Functions -----	536
A.2 Lagrange Multipliers -----	537
A.2.1 Single Constraint -----	537
A.2.2 Multiple Constraints -----	538
Bibliography -----	541
Textbooks-----	541
Handbooks and Tables-----	542
Articles -----	542
Index	