

# Contents

## Part I Foundations of Thermodynamics

<b>1</b>	<b>Historical Introduction</b>	3
<b>2</b>	<b>Basic Concepts and Definitions</b>	7
2.1	Concept of Thermodynamic Equilibrium	7
2.1.1	System and Surroundings	9
2.1.2	State Parameters and State Functions	10
2.1.3	Thermodynamic Processes	11
2.1.4	Calculation of Physical Quantities in Quasi-static Processes	14
2.2	Extensive Parameters of State	17
2.2.1	Volume	17
2.2.2	Amount of Substance	18
2.2.3	Internal Energy	19
2.3	Intensive Parameters of State	20
2.3.1	Pressure	21
2.3.2	Temperature	23
2.3.3	Chemical Potential	27
2.4	Equations of State	29
2.4.1	Ideal Gas	29
2.4.2	Van der Waals Gas	31
2.4.3	Photon Gas	31
2.4.4	Equations of State in Terms of Intensive Parameters	32
2.5	Exercises	33
<b>3</b>	<b>Internal Energy, Work and Heat</b>	39
3.1	First Law of Thermodynamics	39
3.2	Isochoric Process	41
3.2.1	Heat Capacity at Constant Volume	42
3.3	Isobaric Process	43
3.3.1	Heat Capacity at Constant Pressure	43
3.4	Adiabatic Process	44

3.4.1	Reversible Adiabatic Process . . . . .	44
3.4.2	Irreversible Adiabatic Process at Constant Pressure . . . . .	45
3.5	Isothermal Process . . . . .	47
3.5.1	Reversible Isothermal Process . . . . .	47
3.5.2	Irreversible Isothermal Process at Constant Pressure . . . . .	47
3.6	Evaporation of Liquids . . . . .	48
3.7	Chemical Reaction . . . . .	49
3.8	Exercises . . . . .	51
<b>4</b>	<b>Entropy and Irreversibility of Thermodynamic Processes . . . . .</b>	<b>57</b>
4.1	Second Law of Thermodynamics . . . . .	57
4.1.1	Entropy Maximum Principle for Isolated Systems . . . . .	60
4.2	Conditions of Thermodynamic Equilibrium . . . . .	61
4.2.1	Thermal Equilibrium . . . . .	61
4.2.2	Mechanical Equilibrium . . . . .	65
4.2.3	Equilibrium with Respect to the Matter Flow . . . . .	65
4.3	Entropy as a Function of State Parameters . . . . .	67
4.3.1	Fundamental Relation of Thermodynamics . . . . .	67
4.3.2	Euler Relation . . . . .	68
4.3.3	Entropy of the Ideal Gas . . . . .	70
4.3.4	Relation Between Entropy and Heat Capacity . . . . .	71
4.4	Changes in Entropy in Reversible Processes . . . . .	72
4.4.1	Isothermal Process . . . . .	72
4.4.2	Isochoric and Isobaric Processes . . . . .	73
4.4.3	Evaporation of Liquids . . . . .	74
4.5	Heat Devices . . . . .	75
4.5.1	Heat Engine and the Carnot Cycle . . . . .	75
4.5.2	Efficiency of the Carnot Cycle and Thermodynamic Temperature . . . . .	77
4.5.3	Refrigerator and the Heat Pump . . . . .	79
4.5.4	Other Thermodynamic Cycles . . . . .	81
4.6	Changes in Entropy in Irreversible Processes . . . . .	82
4.6.1	Irreversible Flow of Heat . . . . .	82
4.6.2	Free Gas Expansion . . . . .	84
4.6.3	Irreversible Chemical Reaction . . . . .	85
4.7	Third Law of Thermodynamics . . . . .	85
4.8	Exercises . . . . .	86
<b>5</b>	<b>Thermodynamic Potentials . . . . .</b>	<b>89</b>
5.1	Legendre Transformation of the Internal Energy and Entropy . . . . .	89
5.1.1	Definition of the Legendre Transformation . . . . .	90
5.1.2	Helmholtz Free Energy . . . . .	92
5.1.3	Enthalpy . . . . .	93
5.1.4	Gibbs Free Energy . . . . .	93
5.1.5	Grand Thermodynamic Potential . . . . .	95
5.1.6	Massieu Functions . . . . .	96

5.2	Natural Variables . . . . .	96
5.2.1	Equivalent Representations of the Fundamental Relation . .	97
5.2.2	Thermodynamic Potentials for the Ideal Gas . . . . .	98
5.3	Free-Energy Minimum Principle . . . . .	100
5.3.1	Systems at Constant Temperature . . . . .	100
5.3.2	Systems at Constant Temperature and Pressure . . . . .	102
5.4	Examples of Application of Thermodynamic Potentials . . . . .	105
5.4.1	Rules of Calculation of Some Partial Derivatives . . . . .	105
5.4.2	Maxwell Relations . . . . .	106
5.4.3	Second Partial Derivatives of the Internal Energy and Thermodynamic Potentials . . . . .	107
5.4.4	Reversible Adiabatic Process . . . . .	111
5.4.5	Free Gas Expansion . . . . .	112
5.4.6	Joule–Thomson Process . . . . .	113
5.5	Intrinsic Stability of a System . . . . .	115
5.6	Exercises . . . . .	117

## Part II Phase Transitions

<b>6</b>	<b>Phase Transitions in Pure Substances . . . . .</b>	<b>123</b>
6.1	Concept of Phase . . . . .	123
6.2	Classification of Phase Transitions . . . . .	124
6.2.1	First-Order Phase Transitions . . . . .	124
6.2.2	Continuous Phase Transitions . . . . .	125
6.2.3	Ehrenfest Classification . . . . .	127
6.3	Conditions of Phase Coexistence . . . . .	127
6.3.1	Two-Phase Coexistence . . . . .	127
6.3.2	Three-Phase Coexistence . . . . .	131
6.4	Phase Diagrams . . . . .	132
6.4.1	Phase Diagram of a Typical Substance . . . . .	132
6.4.2	Phase Diagram of Water . . . . .	134
6.4.3	Phase Diagram of $^4\text{He}$ . . . . .	135
6.5	Two-Phase Coexistence Lines . . . . .	138
6.5.1	Clapeyron Equation . . . . .	138
6.5.2	Solid–Liquid Coexistence . . . . .	139
6.5.3	Liquid–Gas Coexistence . . . . .	140
6.5.4	Solid–Gas Coexistence . . . . .	140
6.6	Liquid–Vapour Two-Phase Region . . . . .	140
6.7	Van der Waals Equation of State . . . . .	143
6.7.1	Maxwell Construction . . . . .	145
6.7.2	Principle of Corresponding States . . . . .	146
6.8	Exercises . . . . .	148
<b>7</b>	<b>Mixtures . . . . .</b>	<b>151</b>
7.1	Basic Concepts and Relations . . . . .	151
7.1.1	Definitions . . . . .	151

7.1.2	Internal Energy . . . . .	153
7.1.3	Thermodynamic Potentials . . . . .	154
7.2	Intrinsic Stability of a Mixture . . . . .	156
7.3	Partial Molar Quantities and Functions of Mixing . . . . .	160
7.3.1	Partial Molar Quantities . . . . .	160
7.3.2	Relations Between Partial Molar Quantities . . . . .	162
7.3.3	Functions of Mixing . . . . .	163
7.4	Mixture of Ideal Gases . . . . .	164
7.4.1	Dalton's Law . . . . .	164
7.4.2	Chemical Potential of a Component . . . . .	165
7.4.3	Functions of Mixing for Ideal Gases . . . . .	166
7.5	Ideal Mixture . . . . .	167
7.6	Real Mixtures . . . . .	168
7.6.1	Fugacity . . . . .	168
7.6.2	Activity . . . . .	170
7.6.3	Dilute Solutions . . . . .	172
7.6.4	Excess Functions . . . . .	175
7.7	Phase Rule . . . . .	176
7.8	Exercises . . . . .	177
<b>8</b>	<b>Phase Equilibrium in Ideal Mixtures . . . . .</b>	<b>181</b>
8.1	Liquid–Gas Equilibrium . . . . .	181
8.1.1	Raoult's Law . . . . .	181
8.1.2	Liquid–Vapour Phase Diagram at Constant Temperature . . . . .	183
8.1.3	Lever Rule . . . . .	185
8.1.4	Liquid–Vapour Phase Diagram at Constant Pressure . . . . .	185
8.1.5	Boiling Point of a Solution . . . . .	186
8.1.6	Solubility of Gases in Liquids. Henry's Law . . . . .	189
8.1.7	Ostwald Absorption Coefficient . . . . .	190
8.2	Liquid–Solid Equilibrium . . . . .	191
8.2.1	Freezing Point of a Solution . . . . .	191
8.2.2	Solubility of Solids in Liquids . . . . .	193
8.2.3	Simple Eutectic . . . . .	194
8.3	Osmotic Equilibrium . . . . .	196
8.4	Colligative Properties . . . . .	197
8.4.1	Vapour Pressure Depression . . . . .	197
8.4.2	Boiling Point Elevation . . . . .	197
8.4.3	Freezing Point Depression . . . . .	197
8.4.4	Osmotic Pressure . . . . .	198
8.5	Exercises . . . . .	198
<b>9</b>	<b>Phase Equilibrium in Real Mixtures . . . . .</b>	<b>201</b>
9.1	Liquid–Vapour Equilibrium . . . . .	201
9.1.1	Deviations From Raoult's Law . . . . .	201
9.1.2	Simple Solutions . . . . .	202
9.1.3	Zeotropic and Azeotropic Mixtures . . . . .	204

9.1.4	Zeotropic Mixtures . . . . .	206
9.1.5	Azeotropic Mixtures . . . . .	207
9.1.6	Derivation of Equations for the Bubble Point and Dew Point Isotherms and Isobars . . . . .	208
9.2	Liquid Solutions with Miscibility Gap . . . . .	210
9.2.1	Miscibility Curve and Critical Temperatures . . . . .	210
9.2.2	Miscibility Gap in Simple Solutions . . . . .	213
9.3	Liquid–Vapour Equilibrium in Presence of Miscibility Gap . . . .	216
9.4	Liquid–Solid Equilibrium and Solid Solutions . . . . .	218
9.5	Exercises . . . . .	220

### Part III Chemical Thermodynamics

<b>10</b>	<b>Systems with Chemical Reactions . . . . .</b>	<b>225</b>
10.1	Condition of Chemical Equilibrium . . . . .	225
10.1.1	Enthalpy of Reaction . . . . .	227
10.2	Effect of External Perturbation on Chemical Equilibrium . . . . .	228
10.2.1	Effect of Temperature . . . . .	228
10.2.2	Effect of Pressure . . . . .	229
10.2.3	Le Chatelier–Braun Principle . . . . .	230
10.3	Law of Mass Action for Ideal Gases . . . . .	231
10.3.1	Effect of Temperature on the Equilibrium Constant . . . . .	233
10.3.2	Effect of Pressure on the Equilibrium Constant . . . . .	233
10.4	Thermochemistry . . . . .	234
10.4.1	Hess' Law . . . . .	234
10.4.2	Standard Enthalpy of Formation . . . . .	235
10.4.3	Kirchhoff Equation . . . . .	237
10.5	Phase Rule for Chemical Systems . . . . .	238
10.6	Exercises . . . . .	240
<b>11</b>	<b>Electrochemical Systems . . . . .</b>	<b>245</b>
11.1	Electrolyte Solutions . . . . .	245
11.1.1	Dissociation . . . . .	245
11.1.2	Chemical Potential of the Electrolyte . . . . .	246
11.1.3	Debye–Hückel Limiting Law . . . . .	248
11.2	Aqueous Solutions of Acids and Bases . . . . .	250
11.2.1	Brønsted–Lowry Theory of Acids and Bases . . . . .	250
11.2.2	pH of a Solution . . . . .	251
11.2.3	Dissociation Constant . . . . .	252
11.3	Electrochemical Cells . . . . .	253
11.3.1	Daniell Cell . . . . .	253
11.3.2	Galvanic and Electrolytic Cells . . . . .	255
11.4	Reversible Cell . . . . .	256
11.4.1	Work of Chemical Reaction . . . . .	256
11.4.2	Nernst Equation . . . . .	257

11.4.3 Half-Cell Potential . . . . .	259
11.4.4 Standard Hydrogen Electrode . . . . .	260
11.5 Exercises . . . . .	261
<b>Solutions</b> . . . . .	265
Exercises of Chapter 2 . . . . .	265
Exercises of Chapter 3 . . . . .	280
Exercises of Chapter 4 . . . . .	289
Exercises of Chapter 5 . . . . .	297
Exercises of Chapter 6 . . . . .	303
Exercises of Chapter 7 . . . . .	310
Exercises of Chapter 8 . . . . .	315
Exercises of Chapter 9 . . . . .	320
Exercises of Chapter 10 . . . . .	323
Exercises of Chapter 11 . . . . .	331
<b>References</b> . . . . .	337
<b>Index</b> . . . . .	339



<http://www.springer.com/978-94-007-2998-8>

Thermodynamics for Chemists, Physicists and  
Engineers

Hołyst, R.; Poniewierski, A.

2012, XVI, 344 p., Hardcover

ISBN: 978-94-007-2998-8