

Concise Chemical Thermodynamics

Third Edition

A.P.H. PETERS

The first two editions of *Concise Chemical Thermodynamics* proved to be a very popular introduction to a subject many undergraduate students perceive to be difficult due to the underlying mathematics. With its concise explanations and clear examples, the text has for the past 40 years clarified for countless students one of the most complicated branches of science. Following in the tradition of its predecessors, this *Third Edition* continues to offer a practical, example-based exploration of a critical topic, maintaining academic rigor but eschewing complicated calculations.

Updated to reflect new concerns in the 21st century, this edition now includes

- An extensive outlook on the world's current energy consumption and the role of renewable energy in the future
- An example of an exothermic reaction through a discussion of the Mond process for extracting and purifying nickel
- The use of Mathcad® to calculate a plot of Gibbs energy for a reaction mixture versus the extent of reaction
- An explanation of the Lambda sensor, which reduces vehicle emissions
- The use of FactSage software to calculate and describe the production of silicon in an arc (oven) furnace

This latest edition reworks problems that have proven to be the most difficult for students and adds several new ones to further amplify complex areas. The book also provides an updated list of suggested readings. Keeping pace with new technology and the shift in emphasis to green chemistry, this volume provides an up-to-date treatment of a foundational topic.



CRC Press

Taylor & Francis Group
an informa business

www.crcpress.com

ISBN: 978-1-4398-1332-4
90000



781439 813324

Contents

Preface.....	ix
Preface to the Second Edition.....	xi
Preface to the First Edition.....	xiii
Author.....	xv
Symbols and Abbreviations.....	xvii
Chapter 1 Energy.....	1
1.1 The Realm of Thermodynamics.....	1
1.1.1 Energy Bookkeeping.....	2
1.1.2 Nature's Driving Forces.....	6
1.2 Setting the Scene: Basic Ideas.....	7
1.2.1 System and Surroundings.....	7
1.2.2 Functions of State.....	7
1.2.3 Mechanical Work and Expanding Gases.....	8
1.2.4 The Absolute Temperature Scale.....	9
1.3 Forms of Energy and Their Interconversion.....	11
1.4 Forms of Renewable Energy.....	17
1.4.1 Solar Energy.....	17
1.4.2 Wind Energy.....	18
1.4.3 Hydroelectric Power.....	18
1.4.4 Geothermal Energy.....	19
1.4.5 Biomass Energy.....	19
References.....	19
Problems.....	20
Chapter 2 The First Law of Thermodynamics.....	21
2.1 Statement of the First Law.....	21
2.1.1 Reversible Expansion of an Ideal Gas.....	23
2.1.2 Constant-Volume Processes.....	23
2.1.3 Constant-Pressure Processes.....	24
2.2 A New Function: Enthalpy.....	24
2.2.1 Relationship between ΔH and ΔU	25
2.3 Uses and Conventions of ΔH	26
2.3.1 Enthalpy Change of Reaction.....	26
2.3.2 Standard Enthalpies of Formation.....	27
2.3.3 The Many Uses of $\Delta_f H^0$ Data.....	29
References.....	35
Problems.....	35

Chapter 3	Thermochemistry	39
3.1	Calorimetry.....	39
3.1.1	Bomb Calorimeters.....	39
3.1.2	Differential Scanning Calorimetry.....	43
3.2	Concepts of Heat Capacity.....	44
3.2.1	Combustion and Flame Temperatures.....	49
3.2.2	Variation of Reaction Enthalpies with Temperature.....	51
3.3	Bond Energies.....	53
3.3.1	Average Bond Dissociation Energies.....	54
	References.....	57
	Problems.....	57
Chapter 4	Spontaneous Changes	59
4.1	Everyday Processes.....	59
4.2	Exothermicity: A Possible Criterion.....	60
4.2.1	Spontaneous Exothermic Processes.....	60
4.2.2	Spontaneous Processes Involving No Heat Change.....	60
4.2.3	Endothermic Processes.....	62
4.3	The Second Driving Force.....	62
	Problems.....	63
Chapter 5	Entropy	65
5.1	Measurement of Entropy.....	65
5.1.1	The Second Law of Thermodynamics.....	65
5.1.2	Reversibility and Entropy.....	66
5.1.2.1	Isothermal Expansion of Gases.....	67
5.1.2.2	Reversible Transfer of Heat.....	67
5.1.2.3	An Irreversible Change.....	69
5.1.3	Changes in Entropy with Temperature.....	71
5.1.4	An Adiabatic Compression.....	71
5.2	Absolute Entropies.....	72
5.2.1	The Third Law of Thermodynamics.....	72
5.2.2	ΔS for Phase Changes.....	74
5.3	The Direction of Time.....	77
	Reference.....	77
	Problems.....	77
Chapter 6	Free Energy: The Arbiter	81
6.1	Processes in Isolated Systems.....	81
6.2	Gibbs Free Energy, G	83
6.3	Gibbs Free Energy and Maximum Work.....	84
6.4	Some Processes in Terms of Gibbs Free Energy.....	86
6.4.1	Adsorption Processes.....	86

6.4.2	Evaporation Phenomena.....	86
6.4.3	Endothermic Chemical Processes.....	88
6.4.4	Exothermic Chemical Process.....	90
6.5	Standard Free Energy Changes.....	91
	Reference.....	91
	Problems.....	92
Chapter 7	Chemical Equilibrium.....	95
7.1	Preamble.....	95
7.2	Variation of G with Gas Pressure.....	96
7.2.1	Chemical Potential, μ	97
7.2.2	Pressure and Chemical Potential for Ideal Gases.....	102
7.2.3	Chemical Potential for Real Gases.....	103
7.2.4	Activity.....	106
7.3	The Active Mass of Pure Liquids and Solids.....	107
7.4	Activity of Materials in Solution.....	108
7.4.1	Solvents.....	108
7.4.2	Solutes or Minor Components.....	108
7.5	A Summing Up: Activity as a Unifying Concept.....	109
7.6	Practical Aspects of Activity.....	109
7.7	Equilibrium and the Reaction Isotherm.....	110
7.8	Summary.....	116
	References.....	116
	Problems.....	116
Chapter 8	Equilibrium Experiments and Their Interpretation.....	121
8.1	The Reaction Isochore Equation.....	121
8.1.1	Le Chatelier Up to Date.....	124
8.2	Applications of the Isochore Equation.....	124
8.2.1	Vaporization Processes.....	125
8.2.2	The Decomposition of the Compound $\text{Fe}(\text{OH})_3$	127
8.2.3	The High-Temperature Dissociation of Water Vapor.....	129
8.3	The Clapeyron Equation.....	131
8.4	Summary.....	132
	References.....	133
	Problems.....	133
Chapter 9	Electrochemical Cells.....	137
9.1	Electrochemical Cells.....	137
9.2	Cell Energetics.....	140
9.3	Standard Electrode Potentials.....	142
9.4	Variation of Cell Electromotive Force with Activity.....	145
9.4.1	Ionic Activities.....	149
9.4.2	Analysis of Electromotive Force Data to Find E^0	150

9.5	Variation of Electromotive Force with Temperature	152
	References.....	156
	Problems	156
Chapter 10	Free Energy and Industrial Processes	161
10.1	Free Energies as a Function of Temperature	161
10.1.1	The Gibbs-Helmholtz Equation	161
10.1.2	The Integrated Form of the Gibbs-Helmholtz Equation	162
10.1.3	Tabulated Forms of Free Energy.....	163
10.2	The Synthesis of Ethanol	164
10.2.1	Equilibrium Calculations	164
10.2.2	Use of Activity Coefficients	166
10.3	Ellingham Diagrams.....	168
10.3.1	Corrosion Prevention.....	172
10.3.2	Electrolysis of Alumina.....	173
10.3.3	Thermal Reduction of Magnesia.....	173
10.3.4	Titanium and the Kroll Process	175
10.3.5	Silicon Metal Production.....	177
10.4	Summary.....	178
	References.....	178
	Problems	179
Chapter 11	Computational Thermochemistry	181
11.1	Calculation of an Adiabatic Flame Temperature.....	181
11.2	Precipitation of Carbide and Nitride Phases from Dilute Solution in Alloy Steel.....	185
11.3	CVD Production of Ultrapure Silicon	186
11.4	Processing of Wastes from the Aluminum Electrolytic Furnace	188
11.5	Production of Metallurgical-Grade Silicon in an Arc (Oven) Furnace.....	189
11.6	Summary.....	191
	References.....	192
Appendix I	193
Appendix II	195
Appendix III	197
Answers	203
Suggested Further Reading	209
Index	211