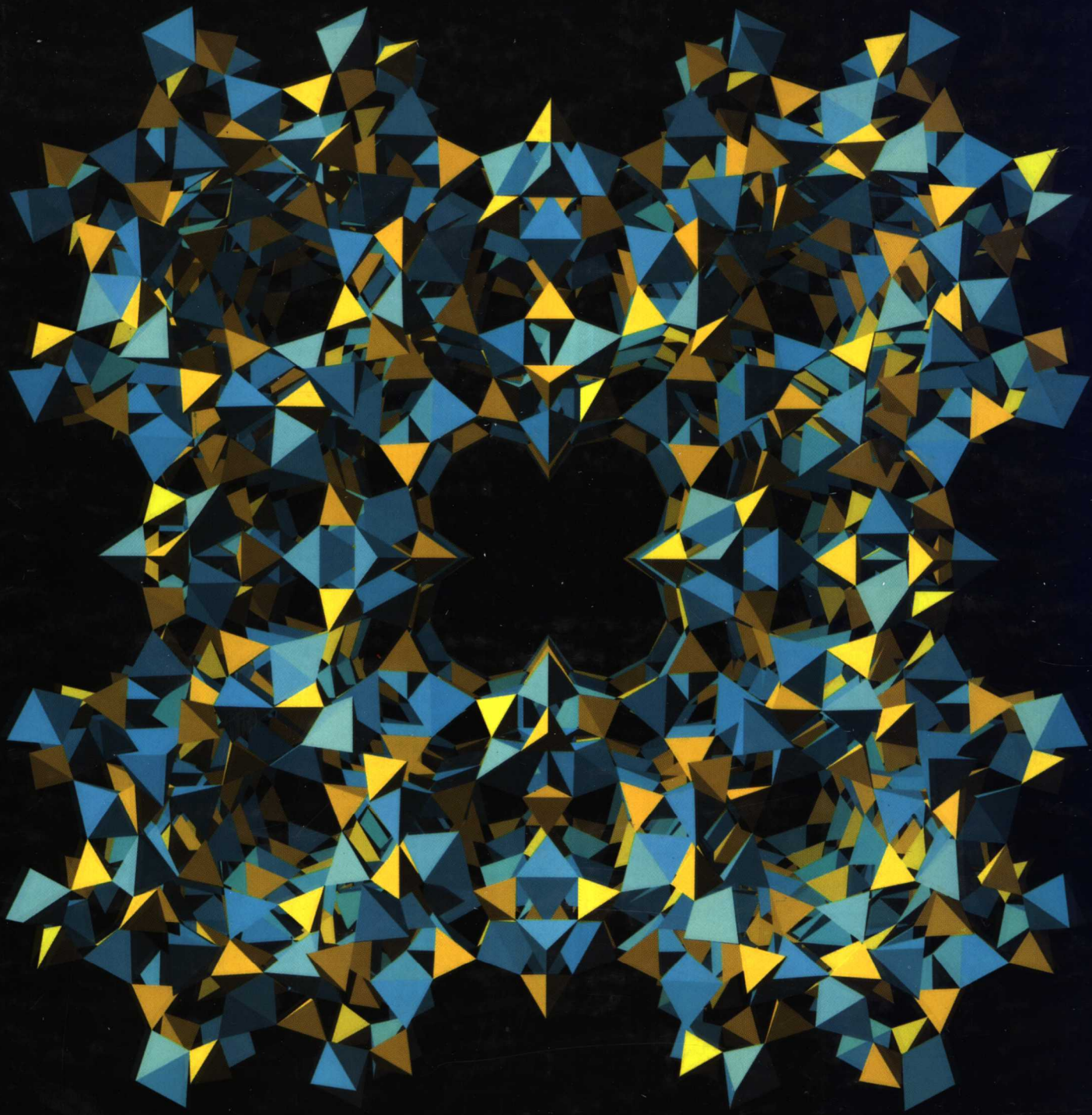

PHYSICAL CHEMISTRY

SECOND EDITION

ROBERT G. MORTIMER

Physical Chemistry

Second Edition

ROBERT G. MORTIMER
Rhodes College

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To my teachers of physical chemistry:

the late Norman Bauer
Norman Davidson
the late Henry Eyring
the late Joe Mayer
Robert Mazo
and Lowell Tensmeyer

Preface

The physical chemistry course is the course in which most chemistry students first have the opportunity to synthesize what they have learned in mathematics, physics, and chemistry courses into a coherent pattern of knowledge. The topics of the traditional physical chemistry course can be grouped into several areas: (1) The study of the macroscopic properties of systems of many atoms or molecules; (2) The study of the processes which systems of many atoms or molecules can undergo; (3) the study of the properties of individual atoms and molecules, and (4) the study of the relationship between molecular and macroscopic properties.

The different portions of the book cover different parts of physical chemistry, as follows:

Chapter 1: Introduction to the macroscopic description of large systems.
Chapters 2–9: Thermodynamics and its applications
Chapters 10–13: Nonequilibrium processes
Chapters 14–20: Quantum mechanics and its applications
Chapter 21: Statistical mechanics—the bridge between mechanics and thermodynamics
Chapter 22: The structure of solids and liquids
Chapter 23: Some theories of nonequilibrium processes

The book is constructed so that several different sequences of these topic areas are possible with a minimum of adjustments. Four sequences which should be practical are:

I. As written
II. Ch. 1–9, Ch. 14–20, Ch. 10–13, Ch. 21–23
III. Ch. 1, Ch. 14–20, Ch. 2–9, Ch. 10–13, Ch. 21–23
IV. Ch. 1, Ch. 10–13, Ch. 2–9, Ch. 14–23.

If time does not permit covering the entire book, chapters 22 and 23 can be omitted without loss of continuity.

The book contains several appendixes, designed to improve the usefulness of the book. All of the tables of numerical data in the book are collected into Appendix A. Appendix B is a brief survey of some useful mathematics. Appendix C is a table of integrals and some information about the error function. Appendix D is a brief survey of classical mechanics. Appendix E contains some derivations of thermodynamic formulas. Appendix F presents information about special mathematical functions encountered in quantum mechanics. Appendix G contains a derivation of a formula used in perturbation theory in quantum mechanics. Appendix H is a discussion of the Hückel method of quantum mechanics. Appendix I discusses the matrix representation

of symmetry groups. Appendix J is a list of symbols used in the book. Appendix K contains answers to selected numerical exercises and problems.

Each chapter has a list of the principal facts and ideas that are presented in the chapter, as well as objectives for the student. There is also a summary to assist in synthesizing the material of each chapter into a coherent whole. There are also marginal notes throughout the chapters to provide biographical information about some of the important people who originated the ideas that are presented in the book and to assist the student in following the flow of topics in the chapter. Each chapter contains examples that illustrate various kinds of calculations, as well as exercises placed within the chapter. Both these exercises and the problems at the end of the chapter are designed to provide practice in applying techniques and insights obtained through study of the chapter.

The author welcomes feedback from students and instructors; please send your comments and suggestions to the author's attention.

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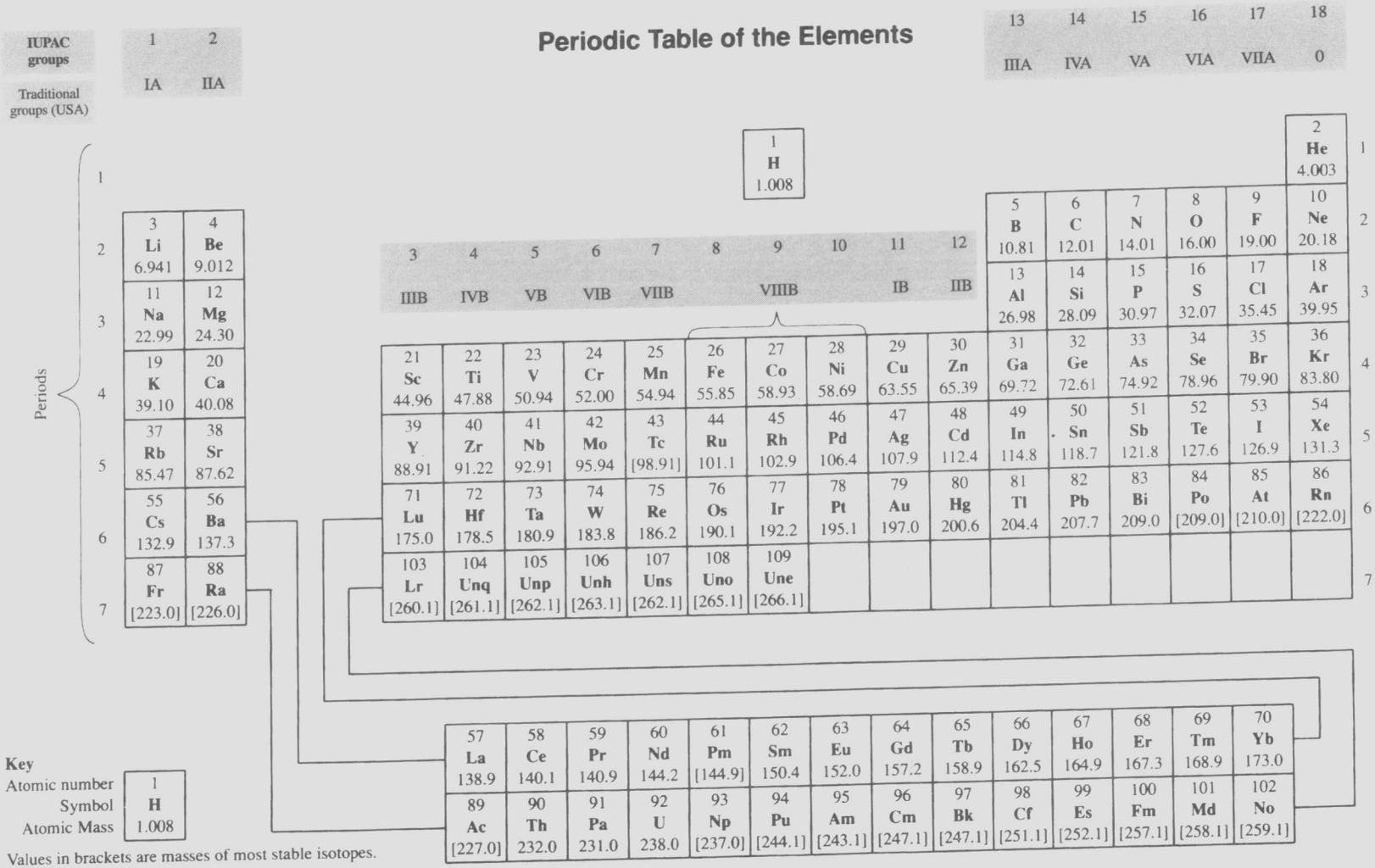
It has been my pleasure to have studied with many dedicated and proficient teachers, and I acknowledge their influence, example, and inspiration. I am also grateful for the privilege of working with students, whose efforts to understand the workings of the physical universe make teaching the most desirable of all professions.

While writing this edition of this book, I have benefited from the expert advice of many reviewers:

Robert L. Carter	University of Massachusetts Boston
Peter Gold	Pennsylvania State University
James House	Illinois State University
Jaan Laane	Texas A & M University
Jack Opdycke	University of San Diego
J. Bevan Ott	Brigham Young University
Kim Salt	Claremont Colleges

All of these reviewers gave sound advice, and some of them went beyond the call of duty in searching out errors and unclarities and in suggesting remedies. I continue to be grateful to the reviewers who assisted with the first edition of this book. The errors which remain are my responsibility, not the responsibility of the reviewers.

I wish to thank the editorial staff at Harcourt/Academic Press for their guidance and help during a rather long and complicated project.


Periodic Table of the Elements
IUPAC groups
Traditional groups (USA)
1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8
9 VIIIB
10
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 0
Periods
1 H 1.008
2 He 4.003
3 Li 6.941
4 Be 9.012
5 B 10.81
6 C 12.01
7 N 14.01
8 O 16.00
9 F 19.00
10 Ne 20.18
11 Na 22.99
12 Mg 24.30
13 Al 26.98
14 Si 28.09
15 P 30.97
16 S 32.07
17 Cl 35.45
18 Ar 39.95
19 K 39.10
20 Ca 40.08
21 Sc 44.96
22 Ti 47.88
23 V 50.94
24 Cr 52.00
25 Mn 54.94
26 Fe 55.85
27 Co 58.93
28 Ni 58.69
29 Cu 63.55
30 Zn 65.39
31 Ga 69.72
32 Ge 72.61
33 As 74.92
34 Se 78.96
35 Br 79.90
36 Kr 83.80
37 Rb 85.47
38 Sr 87.62
39 Y 88.91
40 Zr 91.22
41 Nb 92.91
42 Mo 95.94
43 Tc [98.91]
44 Ru 101.1
45 Rh 102.9
46 Pd 106.4
47 Ag 107.9
48 Cd 112.4
49 In 114.8
50 Sn 118.7
51 Sb 121.8
52 Te 127.6
53 I 126.9
54 Xe 131.3
55 Cs 132.9
56 Ba 137.3
71 Lu 175.0
72 Hf 178.5
73 Ta 180.9
74 W 183.8
75 Re 186.2
76 Os 190.1
77 Ir 192.2
78 Pt 195.1
79 Au 197.0
80 Hg 200.6
81 Tl 204.4
82 Pb 207.7
83 Bi 209.0
84 Po [209.0]
85 At [210.0]
86 Rn [222.0]
87 Fr [223.0]
88 Ra [226.0]
103 Lr [260.1]
104 Unq [261.1]
105 Unp [262.1]
106 Unh [263.1]
107 Uns [262.1]
108 Uno [265.1]
109 Une [266.1]
57 La 138.9
58 Ce 140.1
59 Pr 140.9
60 Nd 144.2
61 Pm [144.9]
62 Sm 150.4
63 Eu 152.0
64 Gd 157.2
65 Tb 158.9
66 Dy 162.5
67 Ho 164.9
68 Er 167.3
69 Tm 168.9
70 Yb 173.0
89 Ac [227.0]
90 Th 232.0
91 Pa 231.0
92 U 238.0
93 Np [237.0]
94 Pu [244.1]
95 Am [243.1]
96 Cm [247.1]
97 Bk [247.1]
98 Cf [251.1]
99 Es [252.1]
100 Fm [257.1]
101 Md [258.1]
102 No [259.1]
Key
Atomic number
Symbol
Atomic Mass
1 H 1.008
Values in brackets are masses of most stable isotopes.

Fundamental Constants and Conversion Factors

From E. R. Cohen and B. N. Taylor, *The 1986 Adjustment of the Fundamental Physical Constants, CODATA Bulletin Number 63*, November 1986

Quantity	Symbol	Value
Avogadro constant	N_{Av}	6.02214×10^{23} mol^{-1}
Bohr magneton	β_e	9.27402×10^{-24} J T^{-1}
Boltzmann constant	k_B	1.38066×10^{-23} J K^{-1}
electron g-factor	g_e	2.0023193044
electron mass	m_e	9.10939×10^{-31} kg
elementary charge	e	1.602177×10^{-19} C
Faraday constant	F	96485.3 C mol^{-1}
molar gas constant	R	8.3145 J K^{-1} mol^{-1}
neutron mass	m_n	1.674929×10^{-27} kg
Newtonian constant of gravitation	G	6.673×10^{-11} m^3 kg^{-1} s^{-2}
nuclear magneton	β_N	5.050787×10^{-27} J T^{-1}
permeability of vacuum	μ_0	$4\pi \times 10^{-7}$ N A^{-2} (exact)
		$12.566370614 \times 10^{-7}$ N A^{-2}
permittivity of vacuum	ε_0	$8.8545187817 \times 10^{-12}$ C^2 N^{-1} m^{-2}
Planck constant	h	6.62608×10^{-34} J s
proton mass	m_p	1.672623×10^{-27} kg
Rydberg constant	$\mathfrak{R}_\infty$	10973731.53 m^{-1}
	$hc\mathfrak{R}_\infty$	13.60570 eV
	$\mathfrak{R}_H$	10967758.1 m^{-1}
	$hc\mathfrak{R}_H$	13.5983 eV
speed of light in vacuum	c	299792458 m s^{-1} (exact)

Prefixes for SI Units

factor	prefix	abbreviation	factor	prefix	abbreviation
10^{-1}	deci	d	10	deca	da
10^{-2}	centi	c	10^2	hecto	h
10^{-3}	milli	m	10^3	kilo	k
10^{-6}	micro	μ	10^6	mega	M
10^{-9}	nano	n	10^9	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P
10^{-18}	atto	a	10^{18}	exa	E

Conversion Factors for Non-SI Units

unit	abbreviation	value
atmosphere	atm	101325 Pa (definition)
torr	torr	133.322 Pa $= \frac{1}{760}$ atm
atomic mass unit	amu	1.66054×10^{-27} kg
bar	bar	1×10^{5} Pa
electron volt	eV	1.602178×10^{-19} J
poise	P	0.1 kg m^{-1} s^{-1}
liter	L	1×10^{-3} $m^3 = 1$ dm^3
angstrom	Å	1×10^{-10} m
debye	D	3.335641×10^{-30} C m
calorie	cal	4.184 J (definition)
inch	in	0.0254 m (definition)
pound	lb	0.4536 kg

The Greek Alphabet

A	α	alpha	I	ι	iota	P	ρ	rho
B	β	beta	K	κ	kappa	Σ	σ	sigma
Γ	γ	gamma	Λ	λ	lambda	T	τ	tau
Δ	δ	delta	M	μ	mu	Y	υ	upsilon
E	ε	epsilon	N	ν	nu	Φ	ϕ	phi
Z	ζ	zeta	Ξ	ξ	xi	X	χ	chi
H	η	eta	O	o	omicron	Ψ	ψ	psi
Θ	θ	theta	Π	π	pi	Ω	ω	omega

List of Numerical Tables in the Appendix

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