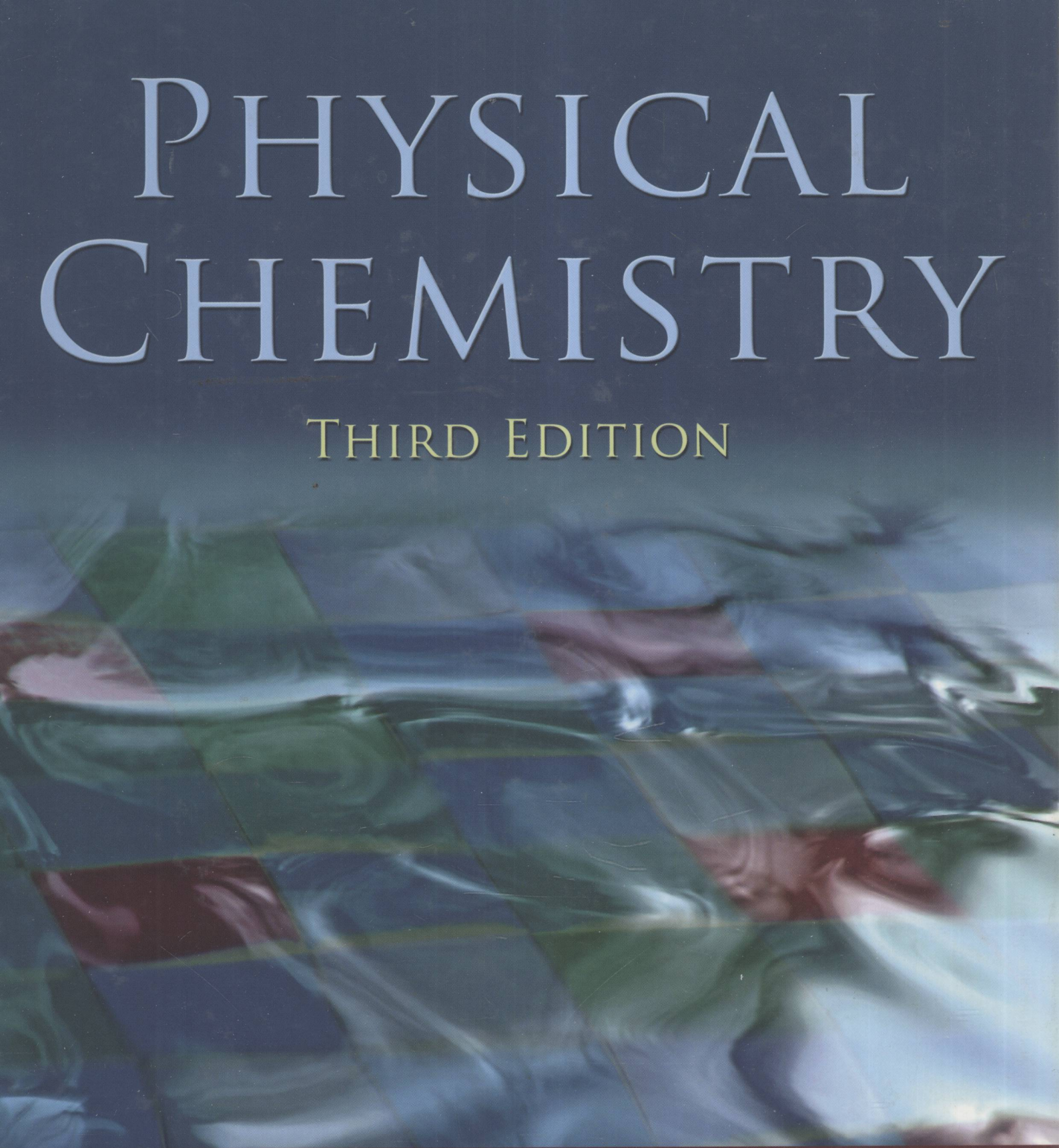
PHYSICAL CHEMISTRY

THIRD EDITION



ROBERT G. MORTIMER

Physical Chemistry

Third Edition

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Academic Press is an imprint of Elsevier

Cover Design: Eric DeCicco
Cover Image: © iStockphoto

Elsevier Academic Press
30 Corporate Drive, Suite 400, Burlington, MA 01803, USA
525 B Street, Suite 1900, San Diego, CA 92101-4495, USA
84 Theobald's Road, London WC1X 8RR, UK

This book is printed on acid-free paper. ♾

Library of Congress Catalog-in-Publishing Data
Mortimer, Robert G.
Physical chemistry / Robert G. Mortimer. – 3rd ed.
p. cm.
Includes bibliographical references and index.
ISBN 978-0-12-370617-1 (hardcover : alk. paper)
1. Chemistry, Physical and theoretical. I. Title.
QD453.2.M67 2008
541–dc22

2008007675

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN-13: 978-0-12-370617-1

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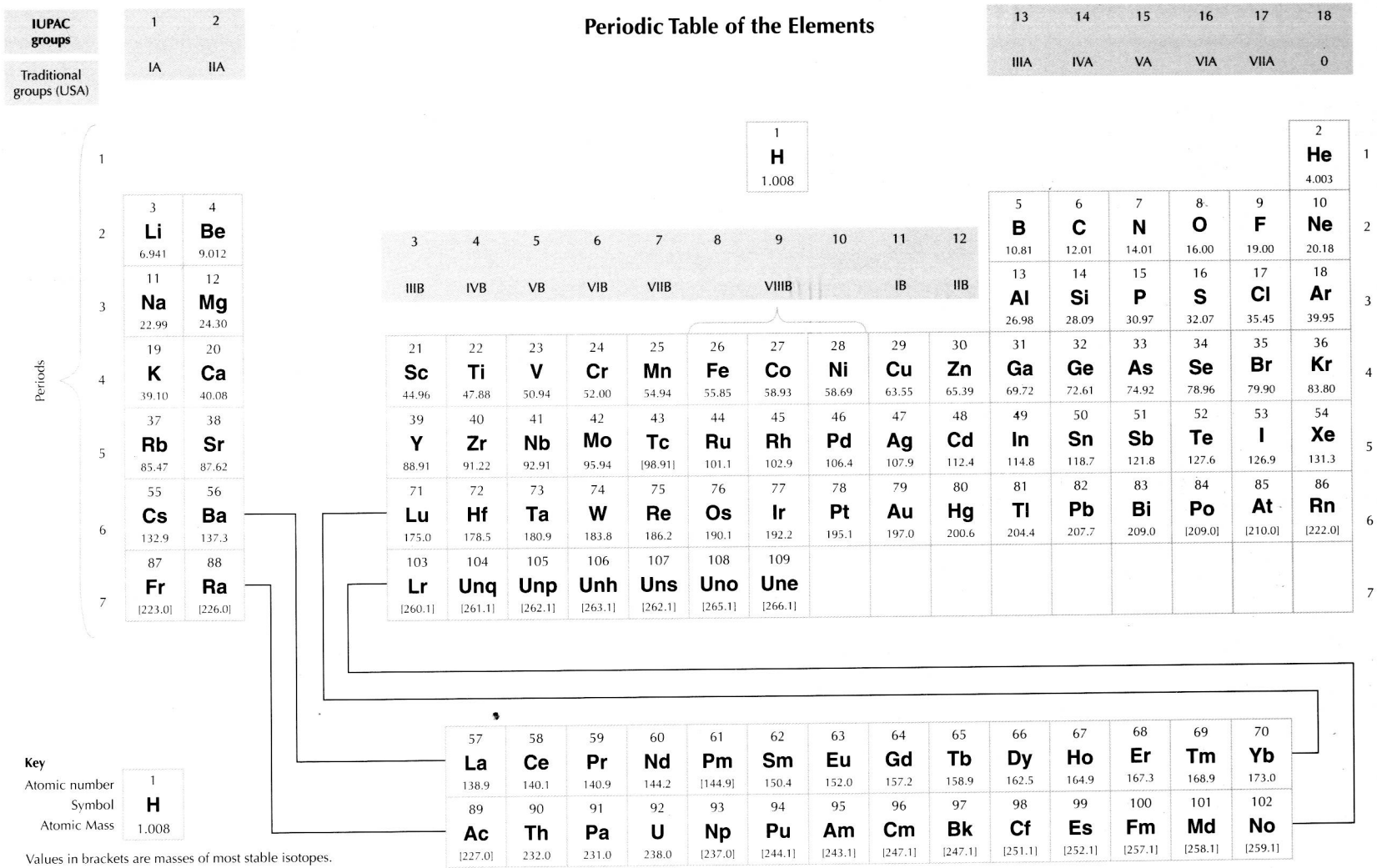
Printed in Canada
08 09 10 9 8 7 6 5 4 3 2 1

Periodic Table of the Elements



Values in brackets are masses of most stable isotopes.

List of Numerical Tables in Appendix A

Physical Chemistry

Third Edition

To my wife, Ann,
and to my late father, William E. Mortimer,
who was responsible for my taking my first chemistry course

Preface

This is the third edition of a physical chemistry textbook designed for a two-semester undergraduate physical chemistry course. The physical chemistry course is often the first opportunity that a student has to synthesize descriptive, theoretical, and mathematical knowledge about chemistry into a coherent whole. To facilitate this synthesis, the book is constructed about the idea of defining a system, studying the states in which it might be found, and analyzing the processes by which it can change its state.

The book is divided into four parts. The first part focuses on the macroscopic properties of physical systems. It begins with the descriptive study of gases and liquids, and proceeds to the study of thermodynamics, which is a comprehensive macroscopic theory of the behavior of material systems. The second part focuses on dynamics, including gas kinetic theory, transport processes, and chemical reaction kinetics. The third part presents quantum mechanics and spectroscopy. The fourth part presents the relationship between molecular and macroscopic properties of systems through the study of statistical mechanics. This theory is applied to the structure of condensed phases. The book is designed so that the first three parts can be studied in any order, while the fourth part is designed to be a capstone in which the other parts are integrated into a cohesive whole.

In addition to the standard tables of integrals and numerical values of various properties, the book contains several appendices that expand on discussions in the body of the text, such as more detailed discussions of perturbation theory, group theory, and several mathematical topics. Each chapter begins with a statement of the principal facts and ideas that are presented in the chapter. There is a summary at the end of each chapter to assist in synthesizing the material of each chapter into a coherent whole. There are also marginal notes throughout the chapters that present biographical information and some comments. 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 each section are designed to provide practice in applying techniques and insights obtained through study of the chapter.

Answers to all of the numerical exercises and to the odd-numbered numerical problems are placed in Appendix K. A solutions manual, with complete solutions to all exercises and all odd-numbered problems, is available from the publisher. An instructor's manual with solutions to the even-numbered problems is available on-line to instructors. The instructor can choose whether to allow students to have access to the solutions manual, but can assign even-numbered problems when he or she wants the students to work problems without access to solutions.

The author encourages students and instructors to comment on any part of the book; please send comments and suggestions to the author's attention.

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Acknowledgments

The writing of the first edition of this book was begun during a sabbatical leave from Rhodes College, and continued during summer grants from the Faculty Development Committee of Rhodes College. It is a pleasure to acknowledge this support.

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.

I have benefited from the expert advice of many reviewers. These include:

Jonas Goldsmith	Bryn Mawr College
Jason D. Hofstein	Sienna College
Daniel Lawson	University of Michigan–Dearborn
Jennifer Mihalick	University of Wisconsin–Oshkosh
Cynthia M. Woodbridge	Hillsdale College

and the reviewers of the previous editions. 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. The errors that remain are my responsibility, not theirs.

I wish to thank the editorial staff of Elsevier/Academic Press for their guidance and help during a rather long and complicated project, and also wish to thank Erica Ellison, who was a valuable consultant. I thank my wife, Ann, for her patience, love, and support during this project.

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}	$6.02214 \times 10^{23}\ \mathrm{mol}^{-1}$
Bohr magneton	β_e	$9.27402 \times 10^{-24}\ \mathrm{J\,T}^{-1}$
Boltzmann constant	k_B	$1.38066 \times 10^{-23}\ \mathrm{J\,K}^{-1}$
Electron g-factor	g_e	2.0023193044
Electron mass	m_e	$9.10939 \times 10^{-31}\ \mathrm{kg}$
Elementary charge	e	$1.602177 \times 10^{-19}\ \mathrm{C}$
Faraday constant	F	$96485.3\ \mathrm{C\,mol}^{-1}$
molar gas constant	R	$8.3145\ \mathrm{J\,K}^{-1}\ \mathrm{mol}^{-1}$
neutron mass	m_n	$1.674929 \times 10^{-27}\ \mathrm{kg}$
Newtonian constant of gravitation	G	$6.673 \times 10^{-11}\ \mathrm{m}^3\ \mathrm{kg}^{-1}\ \mathrm{s}^{-2}$
Nuclear magneton	β_N	$5.050787 \times 10^{-27}\ \mathrm{J\,T}^{-1}$
Permeability of vacuum	μ_0	$4\pi \times 10^{-7}\ \mathrm{N\,A}^{-2}$ (exact) $12.566370614 \times 10^{-7}\ \mathrm{N\,A}^{-2}$
Permittivity of vacuum	ε_0	$8.8545187817 \times 10^{-12}\ \mathrm{C}^2\ \mathrm{N}^{-1}\ \mathrm{m}^{-2}$ (exact)
Planck constant	h	$6.62608 \times 10^{-34}\ \mathrm{J\,s}$
Proton mass	m_p	$1.672623 \times 10^{-27}\ \mathrm{kg}$
Rydberg constant	$\mathscr{R}_\infty$	$10973731.53\ \mathrm{m}^{-1}$
	$hc\mathscr{R}$	13.60570 eV
Speed of light in vacuum	c	$299792458\ \mathrm{m\,s}^{-1}$ (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	101,325 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	Υ	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

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