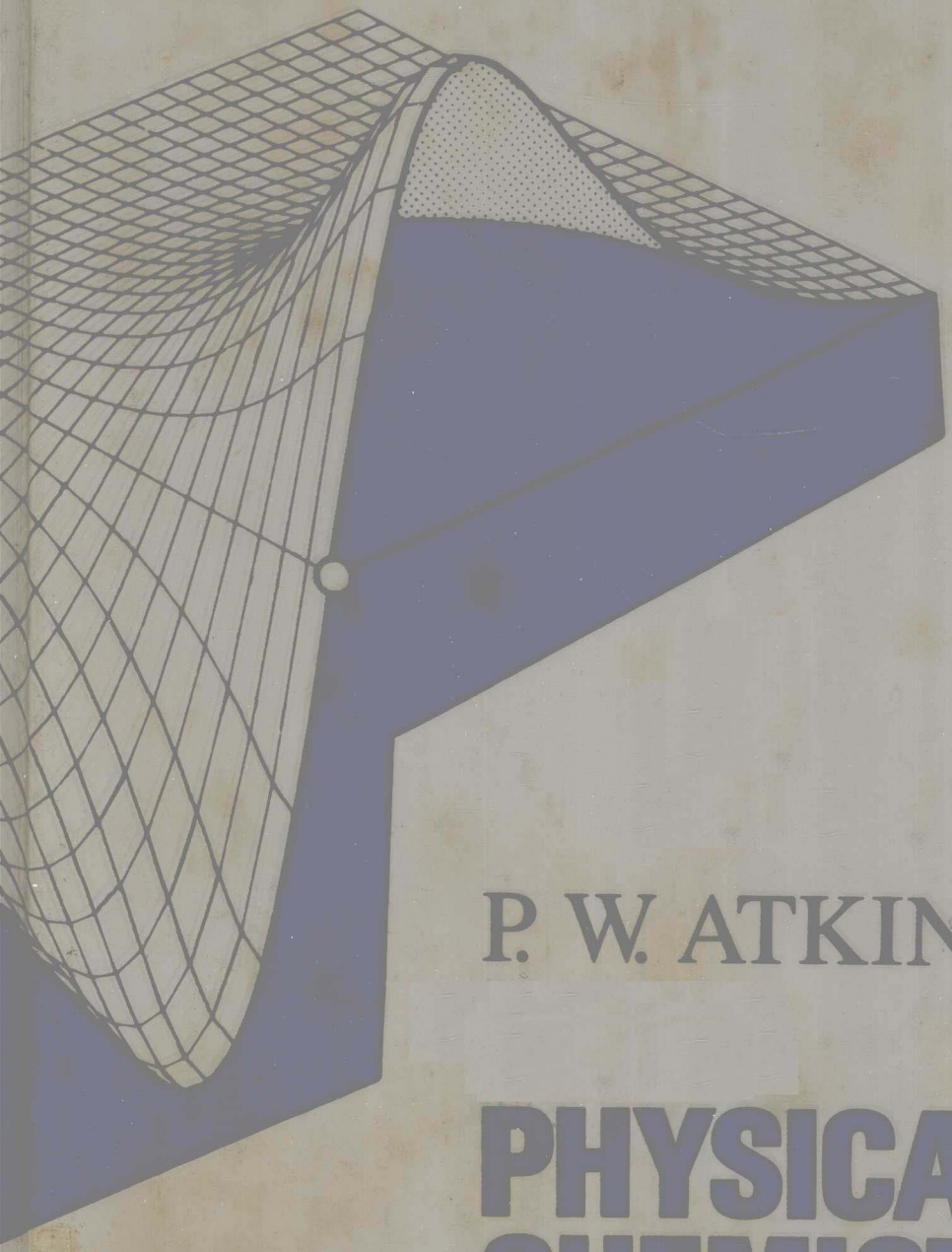
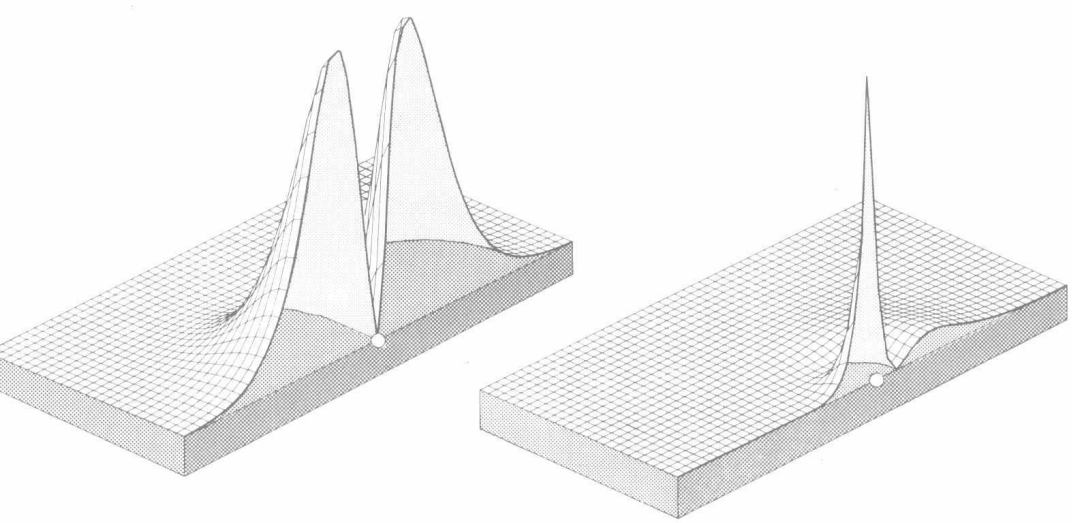


P. W. ATKINS

PHYSICAL CHEMISTRY

Second Edition

Physical Chemistry



W. H. Freeman and Company
New York San Francisco

Library of Congress Cataloging in Publication Data

Atkins, P. W. (Peter William), 1940-
Physical chemistry.

Includes bibliographies and indexes.
1. Chemistry, Physical and theoretical. I. Title.
QD453.2.A88 1982 541.3 81-15260
ISBN 0-7167-1381-0 AACR2

Printed in the United States of America

4 5 6 7 8 9 MP 1 0 8 9 8 7 6 5 4

Published in Great Britain
by Oxford University Press

USEFUL RELATIONS

At 298.15 K

$RT = 2.4789 \text{ kJ mol}^{-1}$

$RT/F = 0.025\,693 \text{ V}$

$2.3026\ RT/F = 0.059\,15 \text{ V}$

$kT/hc = 207.223 \text{ cm}^{-1}$

$V_m^{\ominus} = RT/p^{\ominus} = 2.446\,5 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1} = 24.465 \text{ dm}^3 \text{ mol}^{-1}$

T/K	100.00	298.15	500.00	1000	1500	2000
(kT/hc)/cm^{-1}	69.50	207.223	347.51	695.03	1042.54	1390.06

$p^{\ominus} = 101.325 \text{ kPa} = 1.013\,25 \times 10^5 \text{ N m}^{-2}$

$p^{\ominus} \triangleq 1 \text{ atm} \triangleq 760 \text{ mmHg}$ 1 mmHg $\triangleq$ 133.322 N m^{-2}

1 eV $\triangleq 1.602\,189 \times 10^{-19}$ J

96.485 kJ mol^{-1}

8065.5 cm^{-1}

1000 cm^{-1} $\triangleq 1.986 \times 10^{-20}$ J

11.96 kJ mol^{-1}

0.1240 eV

$hc = 1.986\,48 \times 10^{-23} \text{ J cm}$ $hc/k = 1.438\,79 \times 10^{-2} \text{ m K}$

$g/\text{m s}^{-2} = 9.806\,4 - 0.025\,9 \cos\{2(\text{latitude})\} \approx 9.811$ at 50°

1 cal = 1 cal$_{th}$ $\triangleq$ 4.184 J 1 debye = 1 D $\triangleq 3.335\,64 \times 10^{-30}$ C m

N = J m^{-1} $\triangleq 10^5$ dyn W = J s^{-1} T = J C^{-1} s m^{-2}

J $\triangleq 10^7$ erg A = C s^{-1} J = A V s

MATHEMATICAL INFORMATION

$\ln \equiv \log_e$ $\lg \equiv \log_{10}$ $\ln x = (\ln 10) \lg x = 2.302\,585 \lg x$

$\pi = 3.141\,592\,653\,59$ $e = 2.718\,281\,828\,46$

$=$ equals

$\approx$ approximately equals

$\equiv$ identical to

$\triangleq$ corresponds to

$\stackrel{\text{def}}{=}$ equal by definition to

$\sim$ asymptotically equal to

GENERAL DATA

Speed of light	c	$2.997925 \times 10^{8}\ \mathrm{m\,s^{-1}}$
Charge of proton (Charge on the electron is $-e$)	e	$1.60219 \times 10^{-19}\ \mathrm{C}$
Faraday constant	$F = eL$	$9.64846 \times 10^{4}\ \mathrm{C\,mol^{-1}}$
Boltzmann constant	k	$1.38066 \times 10^{-23}\ \mathrm{J\,K^{-1}}$
Gas constant	$R = kL$	$8.31441\ \mathrm{J\,K^{-1}\,mol^{-1}}$
		$1.98720\ \mathrm{cal\,K^{-1}\,mol^{-1}}$
		$8.20575 \times 10^{-2}\ \mathrm{dm^3\ atm\,K^{-1}\,mol^{-1}}$
Planck constant	h	$6.62618 \times 10^{-34}\ \mathrm{J\,s}$
	$\hbar = h/2\pi$	$1.05459 \times 10^{-34}\ \mathrm{J\,s}$
Avogadro constant	L	$6.02205 \times 10^{23}\ \mathrm{mol^{-1}}$
Atomic mass unit	$\mathrm{u} = 10^{-3}\ \mathrm{kg}/(L\ \mathrm{mol})$	$1.66056 \times 10^{-27}\ \mathrm{kg}$
Mass of electron	m_e	$9.10953 \times 10^{-31}\ \mathrm{kg}$
proton	m_p	$1.67265 \times 10^{-27}\ \mathrm{kg}$
neutron	m_n	$1.67495 \times 10^{-27}\ \mathrm{kg}$
nuclide	$m = M_r\mathrm{u}$	$1.66056 \times 10^{-27} \times M_r\ \mathrm{kg}$
Vacuum permittivity	ε_0	$8.854188 \times 10^{-12}\ \mathrm{J^{-1}\,C^2\,m^{-1}}$
	$4\pi\varepsilon_0$	$1.112650 \times 10^{-10}\ \mathrm{J^{-1}\,C^2\,m^{-1}}$
Vacuum permeability (Note that $\varepsilon_0\mu_0 = 1/c^2$)	μ_0	$4\pi \times 10^{-7}\ \mathrm{J\,s^2\,C^{-2}\,m^{-1}}$
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.27408 \times 10^{-24}\ \mathrm{J\,T^{-1}}$
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.05082 \times 10^{-27}\ \mathrm{J\,T^{-1}}$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.29177 \times 10^{-11}\ \mathrm{m}$
Rydberg constant	$R_\infty = m_e e^4/8h^2\varepsilon_0{}^2$	$2.179908 \times 10^{-18}\ \mathrm{J}$
	R_∞/hc	$1.097373 \times 10^{5}\ \mathrm{cm^{-1}}$
Gravitational constant	G	$6.6720 \times 10^{-11}\ \mathrm{N\,m^2\,kg^{-2}}$

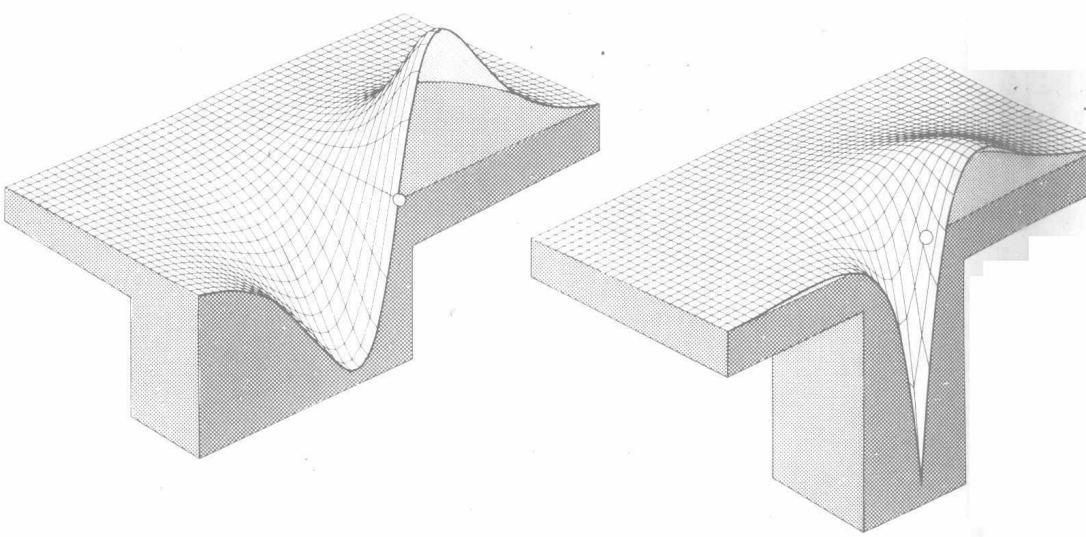
PREFIXES

p	n	μ	m	c	d	k	M	G
pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

Physical Chemistry

P. W. ATKINS

Second Edition



Preface to the Second Edition

In preparing the second edition of this book I have taken into account the advice I have received from readers throughout the world. The principal changes include a revised introduction to thermodynamics, a strengthening of the sections on quantum theory and molecular structure, and an entirely new chapter on macromolecules. I have also brought up to date the sections on X-ray diffraction, magnetic resonance, and surface chemistry. Wherever possible I have simplified the notation and the presentation, particularly in the sections on electrochemistry. The chapters on statistical thermodynamics have been restructured into a simpler form. Every section of the original edition has been reconsidered in order to improve the presentation, introduce modern material, or to simplify the notation without loss of rigour. The illustrations have been revised and the visual presentation of the material has been improved in a variety of ways, including the use of computer graphics in a novel format. All the Tables, Problems, Examples, and Further Reading entries have been reconsidered in detail. Throughout the revision, however, I have aimed to retain the level of presentation of the first edition, and to preserve its style and approach.

I owe a considerable debt to all those who wrote to me with comments either on the first edition or on the draft of the second. Extensive sections of the latter were commented on by W. J. Albery (London), A. D. Buckingham (Cambridge), A. J. B. Cruickshank (Bristol), A. A. Denio (Wisconsin), R. A. Dwek (Oxford), A. H. Francis and T. M. Dunn (Michigan), D. A. King (Liverpool), G. Lowe (Oxford), M. L. McGlashan (London), J. Murto (Helsinki), M. J. Pilling (Oxford), C. K. Prout (Oxford), H. Reiss (UCLA), H. S. Rossotti (Oxford), J. S. Rowlinson (Oxford), W. A. Wakeham (London), D. H. Whiffen (Newcastle), J. S. Winn (Berkeley), and M. Wolfsberg (Irvine) and I am grateful to them all. I should also like to thank the following, who made particularly helpful comments on the first edition, and whose remarks have been built into this: M. D. Archer (Cambridge), L. Brewer (Berkeley), D. H. Everett (Bristol), D. Husain (Cambridge), R. M. Lynden-Bell (Cambridge), I. M. Mills (Reading), and A. D. Pethybridge (Reading), as well as those others whom I have acknowledged privately. The correspondence with my translators, K. P. Butin (Moscow), G. Chambaud (Paris), H. Chihara (Osaka), M. Guardo (Bologna), and A. Höpfner (Heidelberg), has been a particularly fruitful source of advice.

Finally, I should like to thank Judith Adam, who helped to prepare this edition, Caron Crisp, who typed it accurately and always on time, Daniel James, who provided the computer graphics, and the officers of both Oxford University Press and W. H. Freeman and Co. who, as always, have done so much by way of support and encouragement.

Oxford 1981 P.W.A.

Preface to the First Edition

Authors should not preach to teachers. Textbooks should be flexible and adaptable, yet have a strong story-line. I have tried to conform to these demands by dividing the text into three parts, *Equilibrium*, *Structure*, and *Change*. Each part begins in an elementary way, drawing on the others only weakly. Of course they rapidly get tangled up with each other—as they should because the subject is a unity—but teachers will be able to match the text to their own needs without unduly burdening the student. The student, I hope, will be enticed to read his way into chemistry's web of interdependencies, and will find that he can master them without getting confused.

Physical chemistry possesses its mathematics for a purpose: there has to be enough mathematical spine in the subject to enable our ideas on the behaviour of molecules and systems to stand up to experimental verification. Ideas that cannot be tested do not belong to science. Nevertheless, in an introductory treatment the ideas must not be overborne by the mathematics. In this text I show how physical ideas can be developed mathematically, and I take care to interpret the mathematical statements I make. Only where the mathematics and the chemistry lose sight of each other is physical chemistry a difficult subject, so I try never to let that happen.

These views have led me to a further organization of the text. In several places I have treated a subject in two parts, as 'Concepts' and as 'Machinery'. The former establishes the ideas, while the latter extends and develops them more mathematically. This is the arrangement I have adopted for the First and Second Laws of thermodynamics and, later on in Part 2, for statistical thermodynamics. The 'Concepts' chapters emphasize the underlying physics and let the reader understand the conceptual basis of the subject; the 'Machinery' chapters let him discover the ramifications of these ideas and show him how to apply them to chemical problems.

Throughout the text I have used a series of worked *Examples*. These serve two purposes. The first is to show how calculations are actually done: an example with all its detailed working can save pages of explanation and give the reader a much clearer impression of what is involved, and a sense of reality. Their second purpose is to introduce a remark to extend the text, or to stimulate the reader's imagination and interest. Apart from the *Examples* there are the *Problems* at the end of each chapter. I have included a lot of simple ones as well as a number that require more time and effort, and occasionally access to a small computer. Many are based on recent literature. I do not expect readers to do all of them, but I have provided a large number so that teachers can be selective. The answers to most Problems will be found at the end of the book. Virtually

all necessary data are given in the Tables, and the Table Index on p. 1083 should permit quick location of any item. SI units are used throughout, but I have sprinkled a selection of others through the text in order to keep older literature accessible. *Boxes* serve to collect results of arguments or to summarize handy information. *Appendices* contain detailed developments or background that would have encumbered the main text with too much detail or too many equations.

A book such as this could not have appeared without the sustained help of a number of people. Chapters from an early draft were read and criticized by Professor G. Allen (University of London), Dr M. H. Freemantle (University of Jordan), Professor P. J. Gans (New York University), Dr R. J. Hunter (University of Sydney), Professor L. G. Pedersen (University of North Carolina), Professor D. W. Pratt (University of Pittsburg), Dr D. J. Waddington (University of York), Dr S. M. Walker (University of Liverpool), and Professor R. W. Zuehlke (University of Bridgeport). From their remarks grew the second draft, which in turn owes a considerable debt to others. W. H. Freeman and Company of San Francisco played a key role in having the book extensively reviewed and in making sure that it would fit the requirements of courses in North America. They obtained comments and advice from Professor H. C. Andersen (Stanford University), Professor J. Simons (University of Utah), and Professor R. C. Stern (Lawrence Livermore Laboratory). I owe a particular debt of gratitude to Professor Stern who made penetrating remarks on almost every word, or so it seemed; to Miss A. J. MacDermott (University of Oxford) who read the whole and criticized acutely; and to Mr S. P. Keating (University of Oxford), who worked hard and thoughtfully on many of the Problems. After such global assistance there appears to be little left to which the author can attach his name, except to the apologies for the errors that may remain.

I would also like to pay tribute to the officers of the Oxford University Press, who have suffered without public complaint the intrusions of a pernickity and local author. The sustained good humour of our relations made the whole exercise most agreeable. In particular, though, I must thank Dr M. G. Rodgers, whose wise advice, in the form of enthusiasm tempered by selective discouragement, is in no small part responsible for the eventual appearance of this book.

Finally, I thank my wife and my daughter for suffering, again without complaint, the brutishness to which authors sink in order to create something they hope is worthwhile.

Oxford 1977 P.W.A.

Units and notation

SI units are used throughout, but the atmosphere (atm) is retained as a very convenient unit of pressure. The adoption of SI leads to the appearance of unfamiliar units in only two cases. First, pm (picometer, 10^{-12} m or 0.01 ångström) is used as the unit of length for molecules: with this choice molecular dimensions and bond lengths are of the order of 100 pm and decimal points conveniently disappear. Secondly, dm^3 ($1000\,cm^3$, 1 litre) is used as the unit of volume, unless cm^3 or m^3 are more convenient. The replacement of the litre by dm^3 may take a little getting used to, but it simplifies the numerical working of equations. Simply remember that $1\,dm^3$ is exactly the same as $1\,l$.

Some interconversions, and some commonly encountered notational differences are listed below. Others are listed inside the front cover.

Units

$1\,l \equiv 1\,dm^3 \equiv 1000\,cm^3 \equiv 10^{-3}\,m^3$

1 molar, $1M \equiv 1\,mol\,l^{-1} \equiv 1\,mol\,dm^{-3}$

$100\,pm \equiv 1.00$ ångström $\equiv 10^{-8}\,cm \equiv 10^{-10}\,m$

$1\,atm = 760\,Torr = 760\,mmHg = 1.013\,25 \times 10^5\,N\,m^{-2}$.

Notation

U, internal energy. Some texts use E.

G, Gibbs function. Some texts use F.

A, Helmholtz function. Some texts use F.

L, Avogadro's constant. Some texts use N_A, $\mathcal{N}_A$, or N_0.

$p^\ominus$ denotes a pressure of 1 atm (101.325 kPa).

$m^\ominus$ denotes a molality of $1\,mol\,kg^{-1}$.

Contents