MARK LADD

物理化学导论 第3版

INTRODUCTION TO PHYSICAL CHEMISTRY

THIRD EDITION

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Introduction to physical chemistry

3rd Edition

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The third edition of this book has been completely revised. It is intended for first- and second-year undergraduates in chemistry, and for undergraduates in other science and engineering subjects which require an understanding of chemistry.

The author gives more attention to the solid and liquid states than is found in most other books on physical chemistry, and introduces topics such as computer simulation and quasicrystals. Each chapter concludes with a set of problems designed to lead the reader to familiarity with the subject and its application in new situations. Computer programs designed to assist the reader are downloadable from the Worldwide Web (www.cup.cam.ac.uk). Detailed solutions to the problems are available on the same internet, while brief answers are contained within the book itself. Stereoviews are presented for three-dimensional structures and instructions for viewing them are provided. The book assumes only pre-degree mathematics, and special mathematical and other topics are contained in appendices.

This modern text on physical chemistry will be of interest to undergraduate students in chemistry and also to students in other areas of science and engineering requiring a familiarity with the subject.

PREFACE

This book is a complete revision of an earlier work of the same title by the author and his late colleague, Dr W H Lee. It is intended to meet the requirements of students in their first and second years of a degree course in chemistry, or in those sciences for which chemistry forms a significant part, and so to prepare the ground for more advanced final-year studies in this subject.

The mathematical arguments that have been employed in the book should lie within the scope of any chemistry degree student, who will have studied mathematics to A-level, or its equivalent, at least. Physical chemistry is not a nonmathematical subject: any attempt to make it appear so will probably detract from the elegance that attends those approaches that have served this subject well. Some less familiar mathematical topics are discussed in appendices.

Each chapter has been provided with a set of problems designed to enhance the reader's appreciation of the subject matter and its application to new situations. A suggested scheme for solving problems has been given in Appendix 1. The ready availability of computers means that much more extensive data sets can be handled than would be reasonable with hand calculators.

To this end, a number of computer programs has been written, as outlined in Appendix 1. They have been made available on the Worldwide Web internet and may be accessed at web site www.cup.cam.ac.uk; the set of programs, with notes, may be obtained also from the author. The reader is encouraged to make full use of these facilities. The set of programs includes the derivation of point groups and practical point-group recognition, which have been used successfully by the author in teaching these subjects over many years, and the calculation of Madelung constants, in addition to other, more numerical procedures.

The detailed solutions to the problems are available on the same web site, while brief answers are provided within the book itself.

The SI system of units is used throughout the book. However, there are several instances, for example, wavenumber (cm^{-1}) or ionization energy (eV), for which current practice demands that these alternative units should, at least, appear. Competency in more than one system of units will enhance the reader's appreciation of the subject and its literature.

In the sections that discuss three-dimensional topics, such as Bravais lattices and crystal structures, many illustrations have been provided as stereoscopic views and directions for viewing them are given in Appendix 2. Sections on liquid structure, quasicrystals and Wigner–Seitz cells have been introduced, in order to broaden the scope of the treatment of the subject of physical chemistry.

The author is most appreciative of those publishers and authors who have given their permission to reproduce those illustrations that carry the appropriate acknowledgements. The author is very greatly indebted to colleagues who have assisted in the preparation of this

book: to Professor S F A Kettle, Professorial Fellow at the University of East Anglia, for reading the work in manuscript and for making a number of helpful suggestions; to Professor J R Jones, Head of the Department of Chemistry at the University of Surrey, for a careful reading of the book in proof, thereby eliminating some unforced errors; and finally to the publishers for their assistance and cooperation in bringing the work to a state of completion. Any infelicities that might remain are the sole responsibility of the author.

Mark Ladd

Note added at proof

The reader is cautioned to distinguish carefully between the italic 'vee' and the Greek ***nu***. An example of their occurrence together is in equation (A3.5), p. 458, where the first of these characters is a 'vee'.

PHYSICAL CONSTANTS AND OTHER NUMERICAL DATA

These data have been selected, or derived, from the compilation of E R Cohen and B N Taylor, *J. Phys. Chem. Ref. Data* (1988) **17**, 1795–1803; the values are reported in SI units. The figures in parentheses after each value represent the standard deviation to be applied to its last two digits; the values of c and ϵ_0 are *defined*. Although the data are presented here with their full precision, we shall rarely need to employ more than about the first four or five significant figures.

Speed of light in a vacuum	c	2.99792458	$\times 10^{8}$	$m\ s^{-1}$
Permittivity of a vacuum	ϵ_0	8.854187817	$\times 10^{-12}$	$F\ m^{-1}$
Permeability of a vacuum	μ_0	4π	$\times 10^{-7}$	$H\ m^{-1}$
Planck constant	h	6.6260755(40)	$\times 10^{-34}$	$J\ Hz^{-1}$
Elementary charge	e	1.60217733(49)	$\times 10^{-19}$	C
Avogadro constant	L	6.0221367(36)	$\times 10^{23}$	mol^{-1}
Atomic mass unit	u	1.6605402(10)	$\times 10^{-27}$	kg
Bohr magneton	μ_B	9.2740154(31)	$\times 10^{-24}$	J T
Rydberg constant	R_∞	1.0973731534(13)	$\times 10^{7}$	m^{-1}
Rydberg constant for hydrogen	R_H	1.0967758772(13)	$\times 10^{7}$	m^{-1}
Bohr radius	a_0	5.29177249(24)	$\times 10^{-11}$	m
Boltzmann constant	k_B	1.380658(12)	$\times 10^{-23}$	$J\ K^{-1}$
Molar gas constant	$\mathscr{R}$	8.314510(70)		$J\ K^{-1}\ mol^{-1}$
		0.0820577(7)		$dm^3\ atm\ K^{-1}\ mol^{-1}$
Molar volume of ideal gas at 273.15 K and 101 325 Pa	V_m	22.41410(19)	$\times 10^{-3}$	$m^3\ mol^{-1}$
Compton wavelength (electron)	λ_c	2.42631058(22)	$\times 10^{-12}$	m
Rest mass of electron	m_e	9.1093897(54)	$\times 10^{-31}$	kg
Rest mass of proton	m_p	1.6726231(10)	$\times 10^{-27}$	kg
Rest mass of neutron	m_n	1.6749286(10)	$\times 10^{-27}$	kg
Reduced mass of proton and electron pair	μ	9.1044313(54)	$\times 10^{-31}$	kg
Faraday	$\mathscr{F}$	9.6485309(29)	$\times 10^{3}$	$C\ mol^{-1}$
Ice-point temperature	T_{ice}	273.1500(01)		K

(Farad $F = C\ V^{-1}$; Tesla $T = 10^4$ G (gauss) $= J\ C^{-1}\ m^{-2}\ s$; Henry $H = J\ C^{-2}\ s^2$)

Some of the more important additional units are listed below.

Length

1 Å (ångström unit) $= 10^{-10}$ m $= 10$ nm

Energy
1 eV (electronvolt)≡1.60217733(49)×10^{-19} J
1 cal (calorie)=4.184 J≡96.485309(29) kJ mol^{-1}
1 cm^{-1}≡1.9864673(4)×10^{-23} J≡1.1962568(5)×10^{-2} kJ mol^{-1}
Pressure
1 atm (atmosphere)=101 325 Pa (N m^{-2})=760 Torr≡760 mmHg
Dipole moment
1 D (debye)=3.33564×10^{-30} C m

PREFIXES TO UNITS

The following prefixes to units are in common use.

femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
f	p	n	μ	m	c	d	k	M	G
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

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