OXFORD

ELEMENTS of Physical Chemistry

PETER ATKINS & JULIO DE PAULA

7th edition

Fundamental constants

Quantity	Symbol	Value	Power of 10	Units
Speed of light	c	2.997 924 58	10^{8}	m s^{-1}
Elementary charge	e	1.602 176 621	10^{-19}	C
Planck's constant	h	6.626 070 040	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 571 800	10^{-34}	J s
Boltzmann's constant	k	1.380 648 52	10^{-23}	J K^{-1}
Avogadro's constant	N_A	6.022 140 857	10^{23}	mol^{-1}
Gas constant	$R = N_A k$	8.314 459 8		J K^{-1} mol^{-1}
Faraday's constant	$F = N_A e$	9.648 533 289	10^{4}	C mol^{-1}
Mass				
electron	m_e	9.109 383 52	10^{-31}	kg
proton	m_p	1.672 621 898	10^{-27}	kg
neutron	m_n	1.674 927 471	10^{-27}	kg
atomic mass constant	m_u	1.660 539 040	10^{-27}	kg
Vacuum permeability	μ_0	4π	10^{-7}	J s^2 C^{-2} m^{-1}
Vacuum permittivity	$\varepsilon_0 = 1/\mu_0 c^2$	8.854 187 817	10^{-12}	J^{-1} C^2 m^{-1}
	$4\pi\varepsilon_0$	1.112 650 056	10^{-10}	J^{-1} C^2 m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 009 994	10^{-24}	J T^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.050 783 699	10^{-27}	J T^{-1}
Proton magnetic moment	μ_p	1.410 606 787	10^{-26}	J T^{-1}
g-Value of electron	g_e	2.002 319 304		
Magnetogyric ratio				
electron	$\gamma_e = -g_e e/2m_e$	–1.001 159 652	10^{10}	C kg^{-1}
proton	$\gamma_p = 2\mu_p/\hbar$	2.675 222 004	10^{8}	C kg^{-1}
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/e^2 m_e$	5.291 772 107	10^{-11}	m
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^{\,2}$	1.097 373 157	10^{5}	cm^{-1}
	hcR_∞/e	13.605 692 53		eV

* The values quoted here were extracted in February 2016 from the National Institute of Standards and Technology (NIST) website (search term: physical constants).

Elements of Physical Chemistry

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7th EDITION

OXFORD
UNIVERSITY PRESS

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Great Clarendon Street, Oxford, OX2 6DP
United Kingdom

Oxford University Press is a department of the University of Oxford.
It furthers the University's objective of excellence in research, scholarship,
and education by publishing worldwide. Oxford is a registered trade mark of
Oxford University Press in the UK and in certain other countries

Fourth edition 2005
Fifth edition 2009
Sixth edition 2013
Impression: 1

Published in the United States of America by Oxford University Press
198 Madison Avenue, New York, NY 10016, United States of America

British Library Cataloguing in Publication Data
Data available

Library of Congress Control Number: 2016953953

ISBN 978–0–19–872787–3 (UK Edition)
ISBN 978–0–19–879670–1 (US Edition)

Printed in Italy by L.E.G.O. S.p.A.

Using this book to master physical chemistry

Organizing the information

Innovative new structure

Instead of being organized into chapters, the material is now presented as short 'Topics', which are collected into 15 'Focus' sections. At the beginning of each Focus, the relationships between the different Topics are discussed, to show you the connections between different areas of physical chemistry and help you see the bigger picture. Each Topic opens with three questions: why is it important? What is the key idea? And what do you need to know already to understand the material? While the Topics – and Focuses – are interconnected, each Topic is also readable as a stand-alone unit, and can therefore be read in any order.

> **➤ Why do you need to know this material?**
>
> Energy is central to almost every explanation in chemistry, and is defined in terms of work. This Topic also introduces some fundamental definitions of the concepts used in thermodynamics.
>
> **➤ What is the key idea?**
>
> One procedure for transferring energy is by doing work, the process of moving against an opposing force.
>
> **➤ What do you need to know already?**
>
> You need to be familiar with the definition of work, which is summarized in *The chemist's toolkit* 7, and the perfect gas equation (Topic 1A). Integration methods are summarized in *The chemist's toolkit* 8.

The prologue: Energy, temperature, and chemistry

You should first read this brief introduction to the Boltzmann distribution, as it introduces basic concepts that are used throughout the text.

Checklist of key concepts

The principal concepts introduced in each Topic are summarized in a checklist at the end of each one.

> **Checklist of key concepts**
>
> ☐ 1 A **spectrometer** is an instrument that detects the characteristics of radiation absorbed, emitted, or scattered by atoms and molecules.
>
> ☐ 2 In **emission spectroscopy**, an atom or molecule undergoes a transition from a state of high energy to a state of lower energy, and emits the excess energy as a photon.
>
> ☐ 3 In **absorption spectroscopy**, the net absorption of incident radiation is monitored as the frequency is varied.

Resource section

Thermodynamic, kinetic, and spectroscopic data help you to understand trends in chemical and physical properties and become familiar with the magnitudes of properties. However, long tables can break up the flow of the text and be hard to find, so where appropriate they have been collected at the end of the book.

A note on good practice

The 'notes on good practice' have been written to help you avoid making common mistakes. They encourage you to conform to the international language of science adopted by the International Union of Pure and Applied Chemistry (IUPAC).

> **A note on good practice** Write ΔU for the change in internal energy because it is the difference between the final and initial values. You should not write Δq or Δw because it is meaningless to refer to a 'difference of heat' or a 'difference of work': q and w are the quantities of energy transferred as heat and work, respectively, that result in the change ΔU.

Getting to grips with the mathematics

Annotated equations and equation labels

We have annotated many equations so that you can follow how they are developed. A red label takes you across the equals sign: it is a reminder of the substitution used, an approximation made, or the terms that have been assumed constant. A red annotation is a reminder of the significance of an individual term in an expression. Many of the equations are also labelled to highlight their significance. We sometimes colour a collection of numbers or symbols to show how they carry from one line to the next.

$$\Delta V = \overbrace{V_f}^{n_f RT/p_{ex}} - \overbrace{V_i}^{n_i RT/p_{ex}} \overset{n_f - n_i = \Delta n_g}{=} \frac{RT\Delta n_g}{p_{ex}}$$

Justifications

Mathematical development is an intrinsic part of physical chemistry, and to achieve full understanding you need to see how a particular expression is derived and if any assumptions have been made.

Justification 2D.1

Heat transfers at constant pressure

Consider a system open to the atmosphere so that its pressure p is constant and equal to the external pressure p_{ex}. From eqn 3b

$$\Delta H = \Delta U + p\Delta V \overset{p = p_{ex}}{=} \Delta U + p_{ex}\Delta V$$

However, the change in internal energy is given by eqn 1 of Topic 2C ($\Delta U = w + q$) with $w = -p_{ex}\Delta V$ (provided the system does no other kind of work). Therefore

Chemist's toolkits

The chemist's toolkits provide succinct reminders of the mathematical concepts and techniques that you will need in order to understand a particular derivation, and appear just where they are likely to be most helpful to you.

The chemist's toolkit 7 Work and energy

Work, w, is done when a body is moved against an opposing force. If that force is constant, then the magnitude of the work done, $|w|$, is the product of the magnitude of the force, F, and the distance, d, through which the body is moved:

$$|w| = Fd \qquad \text{Work done against an opposing force}$$

Mechanical work is done on a body when it is raised through a vertical distance against the force of gravity.

Becoming a problem solver

Brief illustrations

Brief illustrations are short examples of how to use the equations introduced in the text. Each Brief illustration is accompanied by a 'self-test' question, which you can use to monitor your progress.

Brief illustration 2B.2 Electrical heating

If a current of 10.0 A from a 12 V supply is passed through a heater for 300 s, then the energy supplied as heat to the calorimeter is

$$q_{cal} = (10.0\ \mathrm{A}) \times (12\ \mathrm{V}) \times (300\ \mathrm{s}) = 3.6 \times 10^4\ \overbrace{\mathrm{A\,V\,s}}^{1\,\mathrm{A\,V\,s}\,=\,1\,\mathrm{J}} = +36\ \mathrm{kJ}$$

Self-test 2B.3

For how long must the same current be passed for the energy transferred to reach +100 kJ?

Answer: 13 min 53 s

Examples

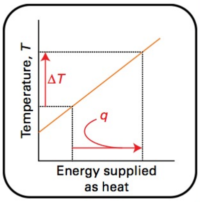
In each Example we suggest how to 'Collect your thoughts' by organizing the information in a problem and then finding its solution. An accompanying simple diagram illustrates the problem-solving process. Use the 'self-tests' following each Example to check that you have mastered the concepts being introduced.

Example 2B.1

Calculating a temperature change from the heat capacity

Suppose a 1.0 kW kettle contains 1.0 kg of water and is turned on for 100 s. By how much does the temperature of the water change if all the heat is transferred to the water?

Collect your thoughts You can suppose initially that the water is not heated so much that it boils, but you will have to verify that once the calculation has been carried out. The calculation hinges on being able to use the data to calculate the energy supplied to the



Questions at the end of each Focus

The **Exercises** allow you to assess your grasp of the material that has just been introduced, and are based on a specific Topic. **Discussion questions** are designed to help you think about the material conceptually before tackling more complex numerical questions. **Problems** are more challenging questions based on the material in the Focus. **Projects** require you to explore specific ideas in more detail. Projects involving calculus are indicated by the symbol **‡**.

Solutions manual

The accompanying *Solutions Manual* [ISBN: 978-019-879865-1 (UK Edition); 978-019-880225-9 (US Edition)] provides full, detailed solutions to the Discussion questions, Exercises, Problems, and Projects.

Online Resource Centre

The Online Resource Centre to accompany *Elements of Physical Chemistry* seventh edition provides a number of useful teaching and learning resources for lecturers and students.

The site can be accessed at:
www.oxfordtextbooks.co.uk/orc/echem7e/

Student resources:

Impact sections

The 'Impact' sections show how the principles of physical chemistry developed in the book are being applied to a selection of modern problems in a variety of disciplines.

Multiple choice questions

A bank of auto-marking multiple choice questions, with worked-out solutions, is provided for each Focus. Make the most of these questions to cement your knowledge and use them to draw your attention to areas where you need further study.

Answers to end-of-Focus exercises

Final numerical answers are provided to the end-of-Focus exercises.

Password protected resources available for registered adopters:

Figures and Tables of data

If you wish to use the figures or tables in a lecture you may do so without charge (but not for commercial purposes without specific permission). Almost all are available in PowerPoint® format.

Test bank

A ready-made, electronic testing resource is provided, which is fully customizable and contains feedback for students.

Preface

We want our readers to have an instructive and enjoyable experience. With that guiding principle in mind we have developed a new presentation that provides flexibility for the instructor and accessibility for the student.

Gone are chapters. In their place we have *Focuses*, which gather together major areas of physical chemistry. Gone are chapter sections. In their place we have *Topics*, which describe discrete aspects of the material in the Focus. The division of a Focus into Topics that can, in principle, be re-ordered or simply omitted according to the judgement, needs, and inclination of the instructor, gives great flexibility when matching the text to the course. Of course, we would not regard some sequences as appropriate, but we leave that judgement to the instructor. For the student, the material is broken up into smaller fragments, which should help to make the subject more accessible than when confronted with a big new subject spread over dozens of pages. We provide a succession of hills rather than a single mountain range. We also consider the use of Topics to reduce a student's apprehension when some are omitted by the instructor.

We are aware that a possible criticism of this approach is the loss of intellectual cohesion. With that in mind, each Focus begins with a preamble in which the development in the Topics is outlined and their interdependence explained.

On a smaller scale, we have put ourselves into what we imagine to be the mind of the student, who sometimes cannot see the point of a particular subject. Each Topic opens with the kind of question a student is likely to ask: *What is the importance of this material?* We then give a brief (but not exhaustive) indication of why it is worth paying attention. Then there is the other typical, but often unarticulated question: *What do we need to know already?* Here we make suggestions about the material that would be useful, and sometimes essential, to know while working through the Topic.

Many of the innovations introduced in earlier editions that users have found useful have been retained, sometimes with elaboration. For instance, we are fully aware of the fear that mathematics inspires, and have added more steps and a different and more helpful kind of annotation to the equations. *The chemist's toolkits*, the mathematical tools necessary at that point, have been enhanced: they are intended to remind the reader of various techniques and concepts (including some from introductory chemistry and physics). The *Worked Examples* have been redeveloped to help students acquire a systematic approach to setting up the solution by having a section called *Collect your thoughts* in each one.

Some of the Toolkits replace the *Foundations* section of earlier editions. We consider that appropriate, as the reminder is there at the point of use rather than as a probably forgotten prelude. In its place we have a *Prologue* which establishes, with a very light touch, three important concepts that pervade the whole of chemistry: energy, temperature, and the Boltzmann distribution. With that material in mind, much of physical chemistry falls into place. We do not see the Prologue as a Topic in its own right, but more as a window for viewing much of what follows (where all three concepts are elaborated).

As always in the preparation of a new edition we have relied heavily on advice from users throughout the world, our numerous translators into other languages, and colleagues who have given their time in the reviewing process. For this edition we have collected comments from student panels, and we are very grateful to them for putting us so closely in touch with their attitudes, difficulties, and needs. We would particularly like to thank David Smith, of Bristol University, for the care with which he reviewed the drafts and his extensive work on the end-of-chapter Exercises, which he reviewed in detail and augmented where he felt it appropriate.

Our publishers have, as always, been a pleasure to work with, and supportive throughout.

PWA
JdeP

About the authors

Peter Atkins is a fellow of Lincoln College in the University of Oxford and the author of about seventy books for students and a general audience. His texts are market leaders around the globe. A frequent lecturer in the United States and throughout the world, he has held visiting professorships in France, Israel, Japan, China, and New Zealand. He was the founding chairman of the Committee on Chemistry Education of the International Union of Pure and Applied Chemistry and was a member of IUPAC's Physical and Biophysical Chemistry Division.

Julio de Paula is Professor of Chemistry at Lewis & Clark College. A native of Brazil, Professor de Paula received a B.A. degree in chemistry from Rutgers, The State University of New Jersey, and a Ph.D. in biophysical chemistry from Yale University. His research activities encompass the areas of molecular spectroscopy, biophysical chemistry, and nanoscience. He has taught courses in general chemistry, physical chemistry, biophysical chemistry, instrumental analysis, and writing. He is the recipient of a Henry Dreyfus Teacher-Scholar Award, and has been named a Cottrell Scholar by the Research Corporation for Science Advancement.

Acknowledgements

The authors have received a great deal of help during the preparation and production of this text and wish to thank all their colleagues who have made such thought-provoking and useful suggestions. In particular, we wish to record publicly our thanks to:

Christine Aikens, Kansas State University
William Alexander, University of Memphis
Chris Amodio, University of Surrey
Alexander Angerhofer, University of Florida
Dmitri Babikov, Marquette University
Kyle Backstrand, Viterbo University
Thilo Behrends, Utrecht University
Petia Bobadova-Parvanova, Rockhurst University
Terry Brack, Hofstra University
Jorge N. Chacón, University of the West of Scotland
Andres Cisneros, Wayne State University
Anders Ericsson, Uppsala University
Brian Frink, Lakeland College
Qingfeng Ge, Southern Illinois University
Robert Glinski, Tennessee Technological University
Fiona Gray, University of St Andrews
Gerhard Groebner, Umeå University
Alex Grushow, Rider University
Jan Gryko, Jacksonville State University
Anton Guliaev, San Francisco State University
Todd Hamilton, Georgetown College
Lisandro Hernandez de la Pena, Kettering University
Grant Hill, University of Sheffield
Jonathan Howse, University of Sheffield
Meez Islam, Teesside University
Jeffrey Joens, Florida International University
Kameron Jorgensen, Texas A&M International University
Peter Karadakov, University of York
Yu Kay Law, Indiana University East
Arthur Low, Tarleton State
Mike Lyons, Trinity College Dublin
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David McGarvey, Keele University
Christine Morales, Emporia State University
Ross Nord, Eastern Michigan University
Maria Pacheco, Buffalo State College
Peter Palenchar, Villanova University
Martin Paterson, Heriot-Watt University
Stephen Price, University College London
Subrayal Reddy, University of Surrey
John Reilly, Florida Gulf Coast University
Marina Roginskaya, East Tennessee State University
Richard Schwenz, University of Northern Colorado
Jon Serra, West Liberty University
Yinghong Sheng, Florida Gulf Coast University
Justin Stace, Belmont University
Robert Stolk, Utrecht University of Applied Sciences
Bradley Stone, San Jose State University
Alex Volkov, Oakwood University
Barry L. Westcott, Central Connecticut State University
Chris Wiebe, University of Winnipeg
Darren Williams, Sam Houston State University

We are greatly indebted to Michael Clugston, who read the proofs with a great deal of care and attention, so saving us from much public embarrassment.

Brief contents

Full contents

Conventions

To avoid intermediate rounding errors, but to keep track of values in order to be aware of values and to spot numerical errors, we display intermediate results as *n.nnn*… and normally round the calculation only at the final step.

Blue terms are used when we want to identify a term in an equation. An entire quotient, numerator/denominator, is coloured blue if the annotation refers to the entire term, not just to the numerator or denominator separately.

List of *The chemist's toolkits*

List of tables

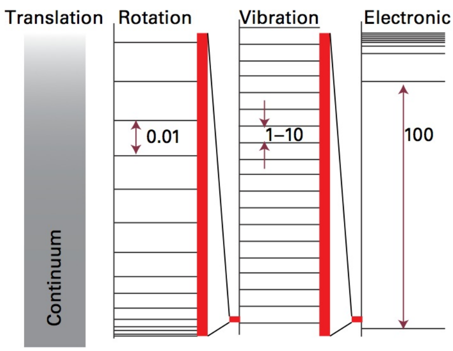
List of Impacts

The *Impacts* are available at www.oxfordtextbooks.co.uk/orc/echem7e/.

Energy, temperature, and chemistry

The concept of energy occurs throughout chemistry. Some reactions release energy; others absorb it. Bond formation is accompanied by a lowering of energy; bond breaking requires energy. Almost every structure and almost every reaction can be discussed in terms of energy, and the precise meaning of the term and its role will emerge in the course of this text.

One very important feature of energy that should be kept in mind at all times is that, except in certain cases, the energy of an object (specifically an atom or molecule) cannot have an arbitrary value. That is, energy is *quantized*, restricted to certain values. The separation between these 'energy levels' depends on the type of motion responsible for the energy and on the characteristics of the object, such as its mass. The first illustration summarizes the relative sizes of the characteristic energy separations for four types of molecular motion: 'translation' refers to the motion through space of a molecule in a large container, 'rotation' is motion around an axis through the molecule, 'vibration' is a periodic distortion of the molecule (for example, the stretching of bonds or bending of bond angle), and 'electronic' denotes the energies of electrons in the molecule. (Only the relative sizes of the energy separations are shown, the text will develop their actual sizes.)

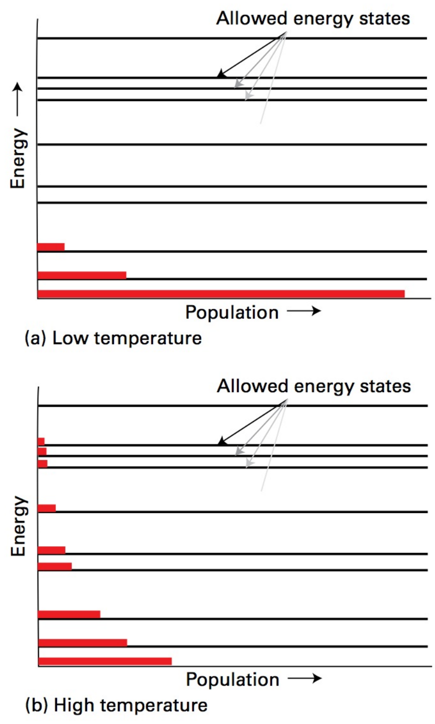


The energy level separations typical of translational, rotational, vibrational, and electronic motion. Only the relative sizes of the energy separations are shown.

In a typical sample of matter, the atoms or molecules occupy these levels, with most molecules in the lower energy states and progressively fewer at higher energies. The states are populated in accord with the 'Boltzmann distribution', which gives the population, N_i, of any state of the system regardless of its origin (whatever the substance and whether it is due to translation, rotation, vibration, or any other mode of motion) in terms of the energy of the state, ε_i, and the absolute temperature, T:

$$N_i \propto e^{-\varepsilon_i/kT}$$

In this expression, k is a fundamental constant now called Boltzmann's constant (it is listed inside the front cover). The second illustration shows two typical consequences of this expression, the red bars indicating the relative population of each state, one at low temperature, the other at high temperature. The Boltzmann distribution clarifies the meaning of 'temperature', for it is seen to be the single parameter that governs the spread of populations over the available energy states.



The Boltzmann distribution of populations for a system at two temperatures. (a) At low temperatures, most molecules are in states of low energy. (b) At high temperatures, some molecules can populate states of high energy.

As can be seen from the second illustration, at low temperature, most molecules are in states of low energy. This feature is hugely important for chemistry, as it means that few molecules have enough energy to change by breaking bonds and forming new compounds: at low temperatures matter survives unchanged. However, at high temperatures some molecules have such high energy that they can undergo change. This feature is also hugely important for chemistry, for it enables chemical reaction. Thus, the Boltzmann distribution underlies the two major aspects of chemistry: the persistence of structure and the possibility of change. Its consequences will be seen throughout this text.