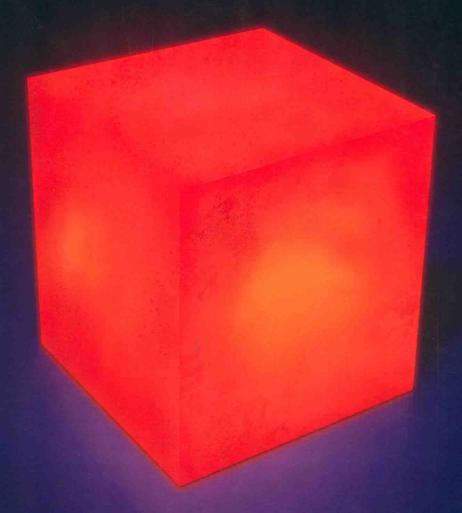
Atkins' PHYSICAL CHEMISTRY

10th Edition



Peter Atkins | Julio de Paula

Atkins' PHYSICAL CHEMISTRY

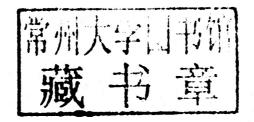
Tenth edition

Peter Atkins

Fellow of Lincoln College, University of Oxford, Oxford, UK

Julio de Paula

Professor of Chemistry, Lewis & Clark College, Portland, Oregon, USA







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

© Peter Atkins and Julio de Paula 2014

The moral rights of the authors have been asserted

9th Edition copyright 2010 8th Edition copyright 2006 7th Edition copyright 2002

Impression: 1

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, without the prior permission in writing of Oxford University Press, or as expressly permitted by law, by licence or under terms agreed with the appropriate reprographics rights organization. Enquiries concerning reproduction outside the scope of the above should be sent to the Rights Department, Oxford University Press, at the address above

You must not circulate this work in any other form and you must impose this same condition on any acquirer

British Library Cataloguing in Publication Data
Data available

ISBN 978-0-19-969740-3

Printed and bound in China by C&C Offset Printing Co. Ltd

QR Code images are used throughout this book. QR Code is a registered trademark of DENSO WAVE INCORPORATED. If your mobile device does not have a QR Code reader try this website for advice www.mobile-barcodes.com/qr-code-software.

Links to third party websites are provided by Oxford in good faith and for information only. Oxford disclaims any responsibility for the materials contained in any third party website referenced in this work.

FUNDAMENTAL CONSTANTS

Constant	Symbol		Value		
			Power of 10	Units	
Speed of light	с	2.997 924 58*	10^{8}	$\mathrm{m}\ \mathrm{s}^{-1}$	
Elementary charge	e	1.602 176 565	10^{-19}	C	
Planck's constant	h	6.626 069 57	10^{-34}	J s	
	$h=h/2\pi$	1.054 571 726	10^{-34}	J s	
Boltzmann's constant	k	1.380 6488	10^{-23}	$J K^{-1}$	
Avogadro's constant	$N_{ m A}$	6.022 141 29	10^{23}	mol^{-1}	
Gas constant	$R = N_A k$	8.314 4621		$J\ K^{-1}\ mol^{-1}$	
Faraday's constant	$F = N_A e$	9.648 533 65	10^{4}	C mol ⁻¹	
Mass					
Electron	$m_{\rm e}$	9.109 382 91	10^{-31}	kg	
Proton	$m_{ m p}$	1.672 621 777	10-27	kg	
Neutron	$m_{ m n}$	1.674 927 351	10^{-27}	kg	
Atomic mass constant	$m_{ m u}$	1.660 538 921	10^{-27}	kg	
Vacuum permeability	$\mu_{\scriptscriptstyle 0}$	$4\pi^*$	10 ⁻⁷	$J s^2 C^{-2} m^{-1}$	
Vacuum permittivity	$\varepsilon_0 = 1/\mu_0 c^2$	8.854 187 817	10^{-12}	$J^{-1} C^2 m^{-1}$	
	$4\piarepsilon_0$	1.112 650 056	10^{-10}	$J^{-1} C^2 m^{-1}$	
Bohr magneton	$\mu_{\mathrm{B}} = e\hbar/2m_{\mathrm{e}}$	9.274 009 68	10^{-24}	$J T^{-1}$	
Nuclear magneton	$\mu_{\rm N} = e\hbar/2m_{\rm p}$	5.050 783 53	10^{-27}	$J T^{-1}$	
Proton magnetic moment	$\mu_{ m p}$	1.410 606 743	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	$\gamma_{\rm p} = 2\mu_{\rm p}/\hbar$	2.675 222 004	10^{8}	C kg ⁻¹	
Bohr radius	$a_0 = 4\pi \varepsilon_0 \hbar^2 / e^2 m_e$	5.291 772 109	10^{-11}	m	
Rydberg constant	$\tilde{R}_{\infty} = m_{\rm e}e^4/8h^3c\varepsilon_0^2$	1.097 373 157	105	cm^{-1}	
	$hc ilde{R}_{\infty}/e$	13.605 692 53		eV	
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 352 5698	10^{-3}		
	α^{-1}	1.370 359 990 74	10^{2}		
Second radiation constant	$c_2 = hc/k$	1.438 777 0	10^{-2}	m K	
Stefan-Boltzmann constant	$\sigma = 2\pi^5 k^4 / 15h^3 c^2$	5.670 373	10^{-8}	$W m^{-2} K^{-4}$	
Standard acceleration of free fall	g	9.806 65*		$\mathrm{m}~\mathrm{s}^{-2}$	
Gravitational constant	\overline{G}	6.673 84	10^{-11}	$N m^2 kg^{-2}$	

^{*} Exact value. For current values of the constants, see the National Institute of Standards and Technology (NIST) website.

Useful relations

At 298.15 K

RT	$2.4790kJmol^{-1}$	RT/F	25.693 mV
RT ln 10/F	59.160 mV	kT/hc	207.225 cm ⁻¹
kT/e	25.693 meV	$V_{\rm m}^{\oplus}$	2.4790×10^{-2}
			$m^3 \text{ mol}^{-1}$

24.790 dm³ mol⁻¹

Selected units*

1 N	$1 \mathrm{kg}\mathrm{m}\mathrm{s}^{-2}$	1 J	$1 \text{ kg m}^2 \text{ s}^{-2}$
1 Pa	$1 kg m^{-1} s^{-2}$	1 W	$1 \mathrm{J s^{-1}}$
$1\mathrm{V}$	1 J C ⁻¹	1 A	$1 \mathrm{C} \mathrm{s}^{-1}$
1 T	$1 kg s^{-2} A^{-1}$	1 P	$10^{-1}\mathrm{kg}\mathrm{m}^{-1}\mathrm{s}^{-1}$
1 S	$1 \Omega^{-1} = 1 A V^{-1}$		

^{*} For multiples (milli, mega, etc.), see the Resource section

Conversion factors

 θ /°C=T/K-273.15*

1 eV	$1.602\ 177 \times 10^{-19} \text{J}$	1 cal	4.184* J
	$96.485kJmol^{-1}$		

8065.5 cm⁻¹

1 atm 101.325* kPa 1 cm⁻¹ 1.9864×10⁻²³ J 760* Torr

2 225 (4×10=30 C --- 1 Å

 $3.335 64 \times 10^{-30} \text{ C m}$ 1 Å 10^{-10} m^*

1D

Mathematical relations

 π =3.141 592 653 59 ... e=2.718 281 828 46 ...

Logarithms and exponentials

$$\ln x + \ln y + \dots = \ln xy \dots \quad \ln x - \ln y = \ln(x/y)$$

$$a \ln x = \ln x^a \qquad \qquad \ln x = 1$$

(ln 10) lo

 $(\ln 10) \log x = (2.302585...)$

 $\log x$

 $e^{x}e^{y}e^{z}...=e^{x+y+z+...}$ $e^{x}/e^{y}=e^{x-y}$

 $(e^x)^a = e^{ax} \qquad \qquad e^{\pm ix} = \cos x \pm i \sin x$

Series expansions

$$e^{x} = 1 + x + \frac{x^{2}}{2!} + \frac{x^{3}}{3!} + \cdots$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \dots \quad \ln x = (x-1) - \frac{(x-1)^2}{2} + \frac{(x-1)^3}{3} - \dots$$

$$\frac{1}{1+x} = 1 - x + x^2 - \frac{1}{1-x} = 1 + x + x^2 + \dots$$

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \cdots$$
 $\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \cdots$

Derivatives; for Integrals, see the Resource section

$$d(f+g) = df + dg$$

$$d(fg) = f dg + g df$$

$$d\frac{f}{g} = \frac{1}{g}df - \frac{f}{g^2}dg$$
 $\frac{df}{dt} = \frac{df}{dg}\frac{dg}{dt}$ for $f = f(g(t))$

$$\left(\frac{\partial y}{\partial x}\right)_z = 1/\left(\frac{\partial x}{\partial y}\right)_z \qquad \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1$$

$$\frac{\mathrm{d}x^n}{\mathrm{d}x} = nx^{n-1} \qquad \qquad \frac{\mathrm{d}e^{ax}}{\mathrm{d}x} = ae^{ax} \qquad \qquad \frac{\mathrm{d}\ln(ax)}{\mathrm{d}x} = \frac{1}{x}$$

$$\mathrm{d}f = g(x, y)\mathrm{d}x + h(x, y)\mathrm{d}y$$
 is exact if $\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$

Greek alphabet*

 Θ , θ theta

Α, α	alpha	I, t	iota	P, p	rho
Β, β	beta	Κ, κ	kappa	Σ, σ	sigma
Γ, γ	gamma	Λ, λ	lambda	Τ, τ	tau
Δ, δ	delta	M,μ	mu	Υ, υ	upsilon
Ε, ε	epsilon	Ν, ν	nu	Φ, φ	phi
Ζ, ζ	zeta	Ξ, ξ	xi	X, χ	chi
H, η	eta	О, о	omicron	Ψ, ψ	psi

^{*} Oblique versions (α , β , ...) are used to denote physical observables.

 Π, π pi

 Ω , ω omega

^{*} Exact value

PREFACE

This new edition is the product of a thorough revision of content and its presentation. Our goal is to make the book even more accessible to students and useful to instructors by enhancing its flexibility. We hope that both categories of user will perceive and enjoy the renewed vitality of the text and the presentation of this demanding but engaging subject.

The text is still divided into three parts, but each chapter is now presented as a series of short and more readily mastered *Topics*. This new structure allows the instructor to tailor the text within the time constraints of the course as omissions will be easier to make, emphases satisfied more readily, and the trajectory through the subject modified more easily. For instance, it is now easier to approach the material either from a 'quantum first' or a 'thermodynamics first' perspective because it is no longer necessary to take a linear path through chapters. Instead, students and instructors can match the choice of Topics to their learning objectives. We have been very careful not to presuppose or impose a particular sequence, except where it is demanded by common sense.

We open with a *Foundations* chapter, which reviews basic concepts of chemistry and physics used through the text. Part 1 now carries the title *Thermodynamics*. New to this edition is coverage of ternary phase diagrams, which are important in applications of physical chemistry to engineering and materials science. Part 2 (*Structure*) continues to cover quantum theory, atomic and molecular structure, spectroscopy, molecular assemblies, and statistical thermodynamics. Part 3 (*Change*) has lost a chapter dedicated to catalysis, but not the material. Enzyme-catalysed reactions are now in Chapter 20, and heterogeneous catalysis is now part of a new Chapter 22 focused on surface structure and processes.

As always, we have paid special attention to helping students navigate and master this material. Each chapter opens with a brief summary of its Topics. Then each Topic begins with three questions: 'Why do you need to know this material?', 'What is the key idea?', and 'What do you need to know already?'. The answers to the third question point to other Topics that we consider appropriate to have studied or at least to refer to as background to the current Topic. The *Checklists* at the end of each

Topic are useful distillations of the most important concepts and equations that appear in the exposition.

We continue to develop strategies to make mathematics, which is so central to the development of physical chemistry, accessible to students. In addition to associating *Mathematical background* sections with appropriate chapters, we give more help with the development of equations: we motivate them, justify them, and comment on the steps taken to derive them. We also added a new feature: *The chemist's toolkit*, which offers quick and immediate help on a concept from mathematics or physics.

This edition has more worked *Examples*, which require students to organize their thoughts about how to proceed with complex calculations, and more *Brief illustrations*, which show how to use an equation or deploy a concept in a straightforward way. Both have *Self-tests* to enable students to assess their grasp of the material. We have structured the end-of-chapter *Discussion questions*, *Exercises*, and *Problems* to match the grouping of the Topics, but have added Topicand Chapter-crossing *Integrated activities* to show that several Topics are often necessary to solve a single problem. The *Resource section* has been restructured and augmented by the addition of a list of integrals that are used (and referred to) throughout the text.

We are, of course, alert to the development of electronic resources and have made a special effort in this edition to encourage the use of web-based tools, which are identified in the *Using the book* section that follows this preface. Important among these tools are *Impact* sections, which provide examples of how the material in the chapters is applied in such diverse areas as biochemistry, medicine, environmental science, and materials science.

Overall, we have taken this opportunity to refresh the text thoroughly, making it even more flexible, helpful, and up to date. As ever, we hope that you will contact us with your suggestions for its continued improvement.

> PWA, Oxford JdeP, Portland

USING THE BOOK

For the tenth edition of *Atkins' Physical Chemistry* we have tailored the text even more closely to the needs of students. First, the material within each chapter has been re-organized into discrete topics to improve accessibility, clarity, and flex-

ibility. Second, in addition to the variety of learning features already present, we have significantly enhanced the mathematics support by adding new Chemist's toolkit boxes, and checklists of key concepts at the end of each topic.

Organizing the information

➤ Innovative new structure

Each chapter has been reorganized into short topics, making the text more readable for students and more flexible for instructors. Each topic opens with a comment on why it is important, a statement of the key idea, and a brief summary of the background needed to understand the topic.

➤ Why do you need to know this material?

Because chemistry is about matter and the changes that it can undergo, both physically and chemically, the properties of matter underlie the entire discussion in this book.

➤ What is the key idea?

The bulk properties of matter are related to the identities

> Notes on good practice

Our *Notes on good practice* will help you avoid making common mistakes. They encourage conformity to the international language of science by setting out the conventions and procedures adopted by the International Union of Pure and Applied Chemistry (IUPAC).

applicable only to perfect gases (and other idealized systems) are labelled, as here, with a number in blue.

A note on good practice Although the term 'ideal gas' is almost universally used in place of 'perfect gas', there are reasons for preferring the latter term. In an ideal system the interactions between molecules in a mixture are all the same. In a perfect gas not only are the interactions all the same but they are in fact zero. Few, though, make this useful distinction.

Equation A.5, the perfect gas equation, is a summary of three empirical conclusions, namely Boyle's law $(p \approx 1/V \text{ at})$

Resource section

The comprehensive *Resource section* at the end of the book contains a table of integrals, data tables, a summary of conventions about units, and character tables. Short extracts of these tables often appear in the topics themselves, principally to give an idea of the typical values of the physical quantities we are introducing.

RESOURCE SECTION

Contents

1 Common integrals 964 2 Units 965 3 Data 966 4 Character tables 996

Checklist of concepts

A Checklist of key concepts is provided at the end of each topic so that you can tick off those concepts which you feel you have mastered.

Checklist of concepts

- ☐ 1. The **entropy** acts as a signpost of spontaneous change.
- ☐ 2. Entropy change is defined in terms of heat transactions (the Clausius definition).
- ☐ 3. The Boltzmann formula defines absolute entropies in terms of the number of ways of achieving a configuration.

Presenting the mathematics

Justifications

Mathematical development is an intrinsic part of physical chemistry, and to achieve full understanding you need to see how a particular expression is obtained and if any assumptions have been made. The Justifications are set off from the text to let you adjust the level of detail to meet your current needs and make it easier to review material.

Justification 3A.1 Heating accompanying reversible adiabatic expansion

This Justification is based on two features of the cycle. One feature is that the two temperatures T_h and T_c in eqn 3A.7 lie on the same adiabat in Fig. 3A.7. The second feature is that the energy transferred as heat during the two isothermal stages

$$q_{\rm h} = nRT_{\rm h} \ln \frac{V_{\rm B}}{V_{\rm A}}$$
 $q_{\rm c} = nRT_{\rm c} \ln \frac{V_{\rm D}}{V_{\rm C}}$

We now show that the two volume ratios are related in a very simple way. From the relation between temperature and volume for reversible adiabatic processes (VT^{t} =constant, Topic 2D):

Chemist's toolkits

New to the tenth edition, the Chemist's toolkits are succinct reminders of the mathematical concepts and techniques that you will need in order to understand a particular derivation being described in the main text.

The chemist's toolkit A.1 Quantities and units

The result of a measurement is a physical quantity that is reported as a numerical multiple of a unit:

physical quantity = numerical value × unit

It follows that units may be treated like algebraic quantities and may be multiplied, divided, and cancelled. Thus, the expression (physical quantity)/unit is the numerical value (a dimensionless quantity) of the measurement in the specified

Mathematical backgrounds

There are six Mathematical background sections dispersed throughout the text. They cover in detail the main mathematical concepts that you need to understand in order to be able to master physical chemistry. Each one is located at the end of the chapter to which it is most relevant.

Mathematical background 1 Differentiat

Two of the most important mathematical techniques in the physical sciences are differentiation and integration. They occur throughout the subject, and it is essential to be aware of the procedures involved.

MB1.1 Differentiation: definitions

Differentiation is concerned with the slopes of functions, such as the rate of change of a variable with time. The formal definition of the **derivative**, df/dx, of a function f(x) is

> Annotated equations and equation labels

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

$$w = -nRT \int_{V_i}^{V_f} \frac{\mathrm{d}V}{V} \stackrel{\text{Integral A.2}}{\widehat{=}} -nRT \ln \frac{V_f}{V_i}$$

$$Perfect gas, reversible, isothermal expansion (2A.9)$$

Checklists of equations

You don't have to memorize every equation in the text. A checklist at the end of each topic summarizes the most important equations and the conditions under which they apply.

Checklist of equations

Property	Equation
Compression factor	$Z = V_{\rm m}/V_{\rm m}^{\circ}$
Virial equation of state	$pV_m = RT(1 + B/V_m + C/V_m^3 + \cdots)$
van der Waals equation of state	$p = nRT/(V - nb) - a(n/V)^2$
Reduced variables	$X_{\rm r} = X_{\rm m}/X_{\rm c}$

Setting up and solving problems

Brief illustrations

A Brief illustration shows you how to use equations or concepts that have just been introduced in the text. They help you to learn how to use data, manipulate units correctly, and become familiar with the magnitudes of properties. They are all accompanied by a Self-test question which you can use to monitor your progress.

Brief illustration 1C.5 Corresponding states

The critical constants of argon and carbon dioxide are given in Table 1C.2. Suppose argon is at 23 atm and 200 K, its reduced pressure and temperature are then

$$p_{\rm r} = \frac{23 \, \text{atm}}{48.0 \, \text{atm}} = 0.48$$
 $T_{\rm r} = \frac{200 \, \text{K}}{150.7 \, \text{K}} = 1.33$

For carbon dioxide to be in a corresponding state, its pressure and temperature would need to be

$$p=0.48\times(72.9 \text{ atm})=35 \text{ atm}$$
 $T=1.33\times304.2 \text{ K}=405 \text{ K}$

Self-test 1C.6 What would be the corresponding state of ammonia?

Answer: 53 atm, 539 K

Worked examples

Worked *Examples* are more detailed illustrations of the application of the material, which require you to assemble and develop concepts and equations. We provide a suggested method for solving the problem and then implement it to reach the answer. Worked examples are also accompanied by *Self-test* questions.

Example 3A.2 Calculating the entropy change for a composite process

Calculate the entropy change when argon at 25 °C and 1.00 bar in a container of volume 0.500 dm³ is allowed to expand to 1.000 dm³ and is simultaneously heated to 100 °C.

Method As remarked in the text, use reversible isothermal expansion to the final volume, followed by reversible heating at constant volume to the final temperature. The entropy change in the first step is given by eqn 3A.16 and that of the second step, provided C_V is independent of temperature, by eqn 3A.20 (with C_V in place of C_D). In each case we need to

Discussion questions

Discussion questions appear at the end of every chapter, where they are organized by topic. These questions are designed to encourage you to reflect on the material you have just read, and to view it conceptually.

Exercises and Problems

Exercises and Problems are also provided at the end of every chapter, and organized by topic. They prompt you to test your understanding of the topics in that chapter. Exercises are designed as relatively straightforward numerical tests whereas the problems are more challenging. The Exercises come in related pairs, with final numerical answers available on the book's Online Resource Centre for the 'a' questions. Final numerical answers to the odd-numbered problems are also available on the Online Resource Centre.

Integrated activities

At the end of most chapters, you will find questions that cross several topics and chapters, and are designed to help you use your knowledge creatively in a variety of ways. Some of the questions refer to the Living graphs in the Online Resource Centre, which you will find helpful for answering them.

Solutions manuals

Two solutions manuals have been written by Charles Trapp, Marshall Cady, and Carmen Giunta to accompany this book.

The Student's Solutions Manual (ISBN 9780198708001) provides full solutions to the 'a' exercises and to the odd-numbered problems.

TOPIC 3A Entropy

Discussion questions

3A.1 The evolution of life requires the organization of a very large number of molecules into biological cells. Does the formation of living organisms violate the Second Law of thermodynamics? State your conclusion clearly and present detailed arguments to support it.

3A.2 Discuss the significance of the terms 'dispersal' and 'disorder' in the context of the Second Law.

Exercises

3A.1(a) During a hypothetical process, the entropy of a system increases by 125 J K⁻¹ while the entropy of the surroundings decreases by 125 J K⁻¹. Is the process spontaneous?

3A.1(b) During a hypothetical process, the entropy of a system increases by $105 \, \mathrm{J} \, \mathrm{K}^{-1}$ while the entropy of the surroundings decreases by $95 \, \mathrm{J} \, \mathrm{K}^{-1}$. Is the process spontaneous?

3A.2(a) A certain ideal heat engine uses water at the triple point as the hot source and an organic liquid as the cold sink. It withdraws 10.00 kJ of heat from the hot source and generates 3.00 kJ of work. What is the temperature of the organic liquid?

3A.2(b) A certain ideal heat engine uses water at the triple point as the hot source and an organic liquid as the cold sink. It withdraws 2.71 kJ of heat from the hot source and generates 0.71 kJ of work. What is the temperature of the organic liquid?

The *Instructor's Solutions Manual* provides full solutions to the 'b' exercises and to the even-numbered problems (available to download in the Online Resource Centre for registered adopters of the book only).

ONLINE RESOURCE CENTRE

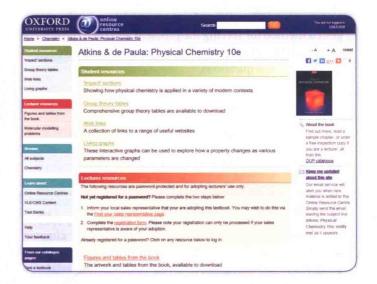
The Online Resource Centre to accompany Atkins' Physical Chemistry provides a number of useful teaching and learning resources for students and lecturers.

The site can be accessed at:

www.oxfordtextbooks.co.uk/orc/pchem10e/

Lecturer resources are available only to registered adopters of the textbook. To register, simply visit the site and follow the link to the registration form.

Student resources are openly available to all, without registration.





Materials on the online resource centre include:

'Impact' sections

'Impact' sections show how physical chemistry is applied in a variety of modern contexts. New for this edition, the Impacts are linked from the text by QR code images. Alternatively, visit the URL displayed next to the QR code image.

Group theory tables

Comprehensive group theory tables are available to download.

Web links

This collection of links to a range of useful websites is organized by chapter to aid navigation.

Figures and tables from the book

Lecturers can find the artwork and tables from the book in ready-to-download format. These may be used for lectures without charge (but not for commercial purposes without specific permission).

Molecular modelling problems

PDFs containing molecular modelling problems can be downloaded, designed for use with the Spartan Student™ software. However they can also be completed using any modelling software that allows Hartree-Fock, density functional, and MP2 calculations.

Living graphs

These interactive graphs can be used to explore how a property changes as various parameters are changed.

ACKNOWLEDGEMENTS

A book as extensive as this could not have been written without significant input from many individuals. We would like to reiterate our thanks to the hundreds of people who contributed to the first nine editions. Many people gave their advice based on the ninth edition, and others, including students, reviewed the draft chapters for the tenth edition as they emerged. We wish to express our gratitude to the following colleagues:

Oleg Antzutkin, Luleå University of Technology

Mu-Hyun Baik, Indiana University — Bloomington Maria G. Benavides, *University of Houston — Downtown* Joseph A. Bentley, Delta State University Maria Bohorquez, Drake University Gary D. Branum, Friends University Gary S. Buckley, Cameron University Eleanor Campbell, University of Edinburgh Lin X. Chen, Northwestern University Gregory Dicinoski, University of Tasmania Niels Engholm Henriksen, Technical University of Denmark Walter C. Ermler, University of Texas at San Antonio Alexander Y. Fadeev, Seton Hall University Beth S. Guiton, University of Kentucky Patrick M. Hare, Northern Kentucky University Grant Hill, University of Glasgow Ann Hopper, Dublin Institute of Technology Garth Jones, University of East Anglia George A. Kaminsky, Worcester Polytechnic Institute Dan Killelea, Loyola University of Chicago Richard Lavrich, College of Charleston Yao Lin, University of Connecticut

Tony Masiello, California State University — East Bay

Lida Latifzadeh Masoudipour, California State University — Dominquez Hills Christine McCreary, University of Pittsburgh at Greensburg Ricardo B. Metz, University of Massachusetts Amherst Maria Pacheco, Buffalo State College Sid Parrish, Jr., Newberry College Nessima Salhi, Uppsala University Michael Schuder, Carroll University Paul G. Seybold, Wright State University John W. Shriver, University of Alabama Huntsville Jens Spanget-Larsen, Roskilde University Stefan Tsonchev, Northeastern Illinois University A. L. M. van de Ven, Eindhoven University of Technology Darren Walsh, University of Nottingham Nicolas Winter, Dominican University Georgene Wittig, Carnegie Mellon University Daniel Zeroka, Lehigh University

Because we prepared this edition at the same time as its sister volume, *Physical Chemistry: Quanta, matter, and change*, it goes without saying that our colleague on that book, Ron Friedman, has had an unconscious but considerable impact on this text too, and we cannot thank him enough for his contribution to this book. Our warm thanks also go to Charles Trapp, Carmen Giunta, and Marshall Cady who once again have produced the *Solutions manuals* that accompany this book and whose comments led us to make a number of improvements. Kerry Karukstis contributed helpfully to the Impacts that are now on the web.

Last, but by no means least, we would also like to thank our two commissioning editors, Jonathan Crowe of Oxford University Press and Jessica Fiorillo of W. H. Freeman & Co., and their teams for their encouragement, patience, advice, and assistance.

18

								Lanthanoids (lanthanides) Actinoids (actinides)
VIIA Heim	4.00 1s ²	10 Ne neon 20.18	18 Ar argon 39.95 3s ² 3p ⁶	36 Kr krypton 83.80 48 ² 4p ⁶	54 Xe xenon 131.29 5s ² 5p ⁶	86 Rn radon (222) 6s ² 6p ⁶	118	
7 2					- e			
_	VIIA						V 117	70 Yb ytterbium 173.04 4f ¹⁴ 6s ² 102 No nobelium (259) 5f ¹⁴ 7s ²
16	NAIN AIN	8 0 oxygen 16.00 2s ² 2p ⁴	16 S sulf ur 32.06 38 ² 3p ⁴	34 Se selenium 78.96 48²4p⁴	52 Te tellunium 127.60 5825p ⁴	84 Po polonium (209) (826p ⁴	116 LV livermorium ?	69 Tm thalium 168.93 4f ¹³ 6s ² 10.1Md to endlevium (258)
15	> 4>	7 N nitrogen 14.01 2s ² 2p ³	15 P phosphons 30.97 38 ² 3p ³	33 As arsenic 74.92 48 ² 4p ³	51 Sb antimony 121.76 58 ² 5p ³	83 Bi bismuth 208.98 6s ² 6p ³	115	
4	≥ NA	6 C carbon 12.01 2s ² 2p ²	14 Si silicon 28.09 3s ² 3p ²	32 Ge germa nium 72.64 48 ² 4p ²	50 Sn tin 118.71 58 ² 5p ²	82 Pb lead 207.2 68 ² 6p ²	114FV flerovium ? 7s ² 7p ²	
13	 	B oron).81	AI minim .98	31 Ga gallium ge 69.72 48²4p¹	49 In Eningium indium 114.82 1 58.5p1	T mm - do		67 Ho holmium 164.93 4f ¹¹ 6s ² 99 Es eins teinium (252) 5f ¹¹ 7s ²
,	_	2s 2s 2s					Cium 113	66 Dy dysprosium 162.50 4f°06s² 98 Cf 251) 5f°07s²
			12 IIB	30 Zn zinc 65.41 3d ¹⁰ 4s ²	48 Cd cadmium 7 112.41 4d ¹⁰ 5s ²	80 Hg mercuy 7 200.59 5d ¹⁰ 6s ²	112 Cn copernicium ? 6d ¹⁰ 7s ²	65 Tb terbium 158.93 4F'6s ² 97 Bk berkelium (247)
			_ 8	29Cu copper 63.55 3d ¹⁰ 4s ¹	47 Ag silver 107.87 4d ¹⁰ 5s ¹	79 Au gold 196.97 5d ¹⁰ 6s ¹	111 Rg noentgenium (272) 6d ⁹ 78 ²	64 Gd gadolinium 157.25 1 4f'5d'6s' 96 Cm curium (247) 5f'6d'7s²
			10	28 Ni nickel 58.69 3d84s ²	46 Pd palladium 106.42 4d ¹⁰	78 Pt platinum 195.08 5496s ¹	110 Ds armstadtiun (271) 6d87s ²	
			9	27 Co cobalt 58.93	45 Rh thodium 102.90 448581	77 r irdium 92.22 5d ⁷ 6s ²	109 Mt 1 meinerium de (266) 6d ⁷ 7s ²	63 Eu europian 151.96 4f'6s² 95 Am americium (243) 5f'7s²
				26 Fe 2 iron 55.84 5 3464s ²	44 Ru 4 101.07 101.07 4 4d ⁷ 5s ¹	76 Os 7 osmium 190.23 115 5466s ²	08 HS 10 hassium me (265) (66°75°2	62 Sm samarium 150.36 4f ⁶ 6s ² 94 Pu plutonium (244) 5f ⁶ 7s ²
- H	1.0079		ω <u> </u>				(-	61 Pm (145) 4f6s ² 4f6s ² 93 Np neptunium (237) 5f ² 6d ¹ 7s ²
	Period 1		7 VIIB	25 mam 54 3d	43 techno (9) 4d ⁵	75 their	107Bh bohrium (262) 6d ⁵ 7s ²	60 Nd (67424) 144.24 4146.82 92 U 10 10 10 10 10 10 10 10 10 1
	Pel		0 × NB	24 Cr chromium 52.00 3d ⁵ 4s ¹	42 Mo molybde num 95.94 4d ⁵ 5s ¹	74 W tungsten 183.84 546s ²	106 Sg seaborgium (263) 6d ⁴ 7s ²	
			VB <	23 V vanadium 50.94 3d ³ 4s ²	41 Nb miobium 92.91 44 ⁴ 5s ¹	73 Ta tantalum 180.95 5d ³ 6s ²	105 Db dubnium (262) 6d ³ 7S ²	59 Pr 140.91 41.682 91 Pa protactinium 231.04 51.664782
			4 N	Ti ium 87 48 ²	40 Zr zirconium 91.22 4d ² 5s ²	72 Hf hafnium 178.49 15426s2	104 Rf 1 utherfordium (261) 6d ² 7s ²	58 Ce carium 140.12 4f'5d'6s² 90 Th thorium 232.04 6d²7s²
								9
			E 3	21Sc scandium 44.96 3d ¹ 4s ²	39 Y yutium 888.91 4415s ²	57 La lanthan um 138.91 5d¹6s²	89 Ac actinium (227) 6d ¹ 7s ²	
2	= ≦	4 Be beryllium 9.01	12 Mg magnesium 24.31 38 ²	20 Ca calcium 40.08 48 ²	38 Sr strontium 87.62 58 ²	56 Ba barium 137.33 68 ²	88 Ra radium (226) 7s ²	s weights) r of r of en as as ally
_	<u>- ⊴</u>	3 Li lithium 6.94 2s ¹	11 Na sodium 22.99 3s ¹	19 K potassium 39.10 4s ¹	37 Rb nubidium 85.47 5s ¹	55 Cs caesium 132.91 6s ¹	87 Fr francium (223) 7s ¹	ies (atomic he number figures giv e regarded most natura amples
Group		2	w	boin	2	9		Molar masses (atomic weights) quoted to the number of significant figures given here can be regarded as typical of most naturally occurring samples

FULL CONTENTS

List of tables	xxiv		
List of chemist's toolkits	xxvi		
Foundations	1	1A.2 Equations of state	32
A Matter	2	(a) The empirical basis	32
A.1 Atoms	2	(b) Mixtures of gases	35
(a) The nuclear model	2	Checklist of concepts	36
(b) The periodic table	2	Checklist of equations	36
(c) lons	3	Tania 10. The binestic model	27
A.2 Molecules	3	Topic 1B. The kinetic model	37
(a) Lewis structures	3	1B.1 The model	37
(b) VSEPR theory	4	(a) Pressure and molecular speeds	37
(c) Polar bonds	4	(b) The Maxwell–Boltzmann distribution of speeds	39
A.3 Bulk matter	5	(c) Mean values 1B.2 Collisions	40
(a) Properties of bulk matter	5	(a) The collision frequency	42
(b) The perfect gas equation	6		42
Checklist of concepts	7	(b) The mean free path	43
Checklist of equations	8	Checklist of concepts	44
		Checklist of equations	44
B Energy	9	Tonis 16 Pool gases	45
B.1 Force	9	Topic 1C Real gases	45
(a) Momentum	9	1C.1 Deviations from perfect behaviour	45
(b) Newton's second law of motion	10	(a) The compression factor (b) Virial coefficients	46
B.2 Energy: a first look	11	(c) Critical constants	47
(a) Work	11	1C.2 The van der Waals equation	48
(b) The definition of energy	11	(a) Formulation of the equation	48
(c) The Coulomb potential energy	12	(b) The features of the equation	50
(d) Thermodynamics	14	(c) The principle of corresponding states	52
B.3 The relation between molecular and bulk properties	15		53
(a) The Boltzmann distribution	15	Checklist of concepts	
(b) Equipartition	17	Checklist of equations	53
Checklist of concepts	17	Discussion questions, exercises, and problems	54
Checklist of equations	18		
5 W		Mathematical background 1 Differentiation and	
C Waves	19	integration	59
C.1 Harmonic waves	19		
C.2 The electromagnetic field	20	CHAPTER 2 The First Law	63
Checklist of concepts	21	Topic 2A Internal energy	64
Checklist of equations	22	2A.1 Work, heat, and energy	65
Discussion questions and exercises	23	(a) Operational definitions	65
Discussion questions and exercises		(b) The molecular interpretation of heat and work	66
		2A.2 The definition of internal energy	66
PART 1 Thermodynamics	27	(a) Molecular interpretation of internal energy	67
CHARTER 1 The properties of cases	20	(b) The formulation of the First Law	67
CHAPTER 1 The properties of gases	29	2A.3 Expansion work	68
Topic 1A The perfect gas	30	(a) The general expression for work	68
1A.1 Variables of state	30	(b) Expansion against constant pressure	69
(a) Pressure	30	(c) Reversible expansion	70
(b) Temperature	31	(d) Isothermal reversible expansion	70

2A.4 Heat transactions	71	3A.3 The entropy as a state function	117
(a) Calorimetry	71	(a) The Carnot cycle	118
(b) Heat capacity	72	(b) The thermodynamic temperature	120
Checklist of concepts	74	(c) The Clausius inequality	120
Checklist of equations	74	3A.4 Entropy changes accompanying specific processes	121
Checkist of equations	2.77	(a) Expansion	121
Topic 2B Enthalpy	75	(b) Phase transitions	122
2B.1 The definition of enthalpy	75	(c) Heating	123
(a) Enthalpy change and heat transfer	75	(d) Composite processes	124
(b) Calorimetry	76	Checklist of concepts	124
2B.2 The variation of enthalpy with temperature	77		
(a) Heat capacity at constant pressure	77	Checklist of equations	125
(b) The relation between heat capacities	79	Topic 3B The measurement of entropy	120
		3B.1 The calorimetric measurement of entropy	120
Checklist of concepts	79	3B.2 The Third Law	12
Checklist of equations	79	(a) The Nernst heat theorem	12
Table 20 Thermal American	00		
Topic 2C Thermochemistry	80	(b) Third-Law entropies	129
2C.1 Standard enthalpy changes	80	Checklist of concepts	130
(a) Enthalpies of physical change	81	Checklist of equations	130
(b) Enthalpies of chemical change	82		
(c) Hess's law	83	Topic 3C Concentrating on the system	13
2C.2 Standard enthalpies of formation	84	3C.1 The Helmholtz and Gibbs energies	13
(a) The reaction enthalpy in terms of enthalpies of forma	tion 85	(a) Criteria of spontaneity	13
(b) Enthalpies of formation and molecular modelling	85	(b) Some remarks on the Helmholtz energy	13:
2C.3 The temperature dependence of reaction enthalpies	86	(c) Maximum work	133
2C.4 Experimental techniques	87	(d) Some remarks on the Gibbs energy	134
(a) Differential scanning calorimetry	87	(e) Maximum non-expansion work	13.
(b) Isothermal titration calorimetry	88	3C.2 Standard molar Gibbs energies	130
Checklist of concepts	88	(a) Gibbs energies of formation	130
Checklist of equations	89	(b) The Born equation	137
		Checklist of concepts	138
Topic 2D State functions and exact differentials	90	Checklist of equations	138
2D.1 Exact and inexact differentials	90	Checkist of equations	13.
2D.2 Changes in internal energy	91	Topic 3D Combining the First and Second Laws	140
(a) General considerations	91	3D.1 Properties of the internal energy	140
(b) Changes in internal energy at constant pressure	93	(a) The Maxwell relations	14
2D.3 The Joule–Thomson effect	95	(b) The variation of internal energy with volume	14
(a) Observation of the Joule–Thomson effect	95	3D.2 Properties of the Gibbs energy	14:
(b) The molecular interpretation of the Joule–Thomson		(a) General considerations	14:
		(b) The variation of the Gibbs energy with temperature	14
Checklist of concepts	98	(c) The variation of the Gibbs energy with pressure	14
Checklist of equations	99	(d) The fugacity	
Total OF A Patricular Section	100		14
Topic 2E Adiabatic changes	100	Checklist of concepts	148
2E.1 The change in temperature	100	Checklist of equations	14
2E.2 The change in pressure	101	Discussion questions, exercises, and problems	149
Checklist of concepts	102	Discussion questions, exercises, una problems	1913
Checklist of equations	102	CHAPTER 4 Physical transformations of	
Discussion questions, exercises, and problems	103	pure substances	154
		Topic 4A Phase diagrams of pure substances	155
Mathematical background 2 Multivariate calculus	109	4A.1 The stabilities of phases	15
		(a) The number of phases	15
CHAPTER 3 The Second and Third Laws	112	(b) Phase transitions	15
Topic 3A Entropy	113	(c) Thermodynamic criteria of phase stability	15
3A.1 The Second Law	113	4A.2 Phase boundaries	15
3A.2 The definition of entropy	115	(a) Characteristic properties related to phase transitions	15
(a) The thermodynamic definition of entropy	115	(b) The phase rule	15
(b) The statistical definition of entropy	116	4A.3 Three representative phase diagrams	16
(b) The statistical definition of entropy	110	This initial representative priore didylands	10

(a) Carbon dioxide	160	5C.2 Temperature-composition diagrams	206
(b) Water	161	(a) The distillation of mixtures	206
(c) Helium	162	(b) Azeotropes	207
Checklist of concepts	162	(c) Immiscible liquids	208
Checklist of equations	163	5C.3 Liquid-liquid phase diagrams	208
Checkist of equations	103	(a) Phase separation	208
Topic 4B Thermodynamic aspects of phase transitions	164	(b) Critical solution temperatures	209
4B.1 The dependence of stability on the conditions	164	(c) The distillation of partially miscible liquids	21
(a) The temperature dependence of phase stability	165	5C.4 Liquid-solid phase diagrams	212
(b) The response of melting to applied pressure	165	(a) Eutectics	212
(c) The vapour pressure of a liquid subjected to pressure	166	(b) Reacting systems	214
4B.2 The location of phase boundaries	167	(c) Incongruent melting	214
(a) The slopes of the phase boundaries	167	Checklist of concepts	215
(b) The solid-liquid boundary	168	Checklist of equations	215
(c) The liquid-vapour boundary	169		
(d) The solid-vapour boundary	170	Topic 5D Phase diagrams of ternary systems	216
4B.3 The Ehrenfest classification of phase transitions	171	5D.1 Triangular phase diagrams	210
(a) The thermodynamic basis	171	5D.2 Ternary systems	21
(b) Molecular interpretation	172	(a) Partially miscible liquids	21
Checklist of concepts	173	(b) Ternary solids	218
Checklist of equations	173	Checklist of concepts	219
Discussion questions, exercises, and problems	174	Topic 5E Activities	220
		5E.1 The solvent activity	22
CHAPTER 5 Simple mixtures	178	5E.2 The solute activity	22
Topic 5A The thermodynamic description of mixtures	180	(a) Ideal-dilute solutions	22
SA.1 Partial molar quantities	180	(b) Real solutes	22
(a) Partial molar volume	181	(c) Activities in terms of molalities	22
(b) Partial molar Gibbs energies	182	(d) The biological standard state	22
(c) The wider significance of the chemical potential	183	5E.3 The activities of regular solutions	22
(d) The Gibbs-Duhem equation	183	Checklist of concepts	22
5A.2 The thermodynamics of mixing	184	Checklist of equations	22
(a) The Gibbs energy of mixing of perfect gases	185		
(b) Other thermodynamic mixing functions	186	Topic 5F The activities of ions	22
5A.3 The chemical potentials of liquids	187	5F.1 Mean activity coefficients	22
(a) Ideal solutions	187	(a) The Debye-Hückel limiting law	22
(b) Ideal-dilute solutions	188	(b) Extensions of the limiting law	22
Checklist of concepts	190	5F.2 The Debye-Hückel theory	22
Checklist of equations	190	(a) The work of charging	22
		(b) The potential due to the charge distribution	22
Topic 5B The properties of solutions	192	(c) The activity coefficient	23
5B.1 Liquid mixtures	192	Checklist of concepts	23
(a) Ideal solutions	192	Checklist of equations	23
(b) Excess functions and regular solutions	193	Discussion supertions avanties and problems	233
58.2 Colligative properties	195	Discussion questions, exercises, and problems	23.
(a) The common features of colligative properties	195	CHAPTER 6 Chemical equilibrium	24
(b) The elevation of boiling point	196 197	Topic 6A The equilibrium constant	24
(c) The depression of freezing point	198	6A.1 The Gibbs energy minimum	24
(d) Solubility (e) Osmosis	199	(a) The reaction Gibbs energy	24
		(b) Exergonic and endergonic reactions	24
Checklist of concepts	201	6A.2 The description of equilibrium	24
Checklist of equations	201	(a) Perfect gas equilibria	24
Topic 5C Phase diagrams of binary systems	202	(b) The general case of a reaction	24
5C.1 Vapour pressure diagrams	202	(c) The relation between equilibrium constants	25
(a) The composition of the vapour	202	(d) Molecular interpretation of the equilibrium constant	25
(b) The interpretation of the diagrams	203	Checklist of concepts	25
(c) The lever rule	205	Checklist of equations	25

Topic 6B The response of equilibria to the conditions	254	Topic 7C The principles of quantum theory	299
6B.1 The response to pressure	254	7C.1 Operators	299
6B.2 The response to temperature	255	(a) Eigenvalue equations	299
(a) The van 't Hoff equation	256	(b) The construction of operators	300
(b) The value of K at different temperatures	257	(c) Hermitian operators	302
Checklist of concepts	258	(d) Orthogonality	303
Checklist of equations	258	7C.2 Superpositions and expectation values	304
		7C.3 The uncertainty principle	305
Topic 6C Electrochemical cells	259	7C.4 The postulates of quantum mechanics	308
6C.1 Half-reactions and electrodes	259	Checklist of concepts	308
6C.2 Varieties of cells	260	Checklist of equations	308
(a) Liquid junction potentials	261		
(b) Notation	261	Discussion questions, exercises, and problems	310
6C.3 The cell potential	261	Mathematical background 3 Complex numbers	314
(a) The Nernst equation	262	Mathematical background 5 Complex numbers	314
(b) Cells at equilibrium	264	CHAPTER 8 The quantum theory of motion	316
6C.4 The determination of thermodynamic functions	264	Topic 8A Translation	317
Checklist of concepts	265	8A.1 Free motion in one dimension	317
Checklist of equations	266	8A.2 Confined motion in one dimension	318
		(a) The acceptable solutions	318
Topic 6D Electrode potentials	267	(b) The properties of the wavefunctions	320
6D.1 Standard potentials	267	(c) The properties of observables	321
(a) The measurement procedure	268	8A.3 Confined motion in two or more dimensions	322
(b) Combining measured values	269	(a) Separation of variables	322
6D.2 Applications of standard potentials	269	(b) Degeneracy	324
(a) The electrochemical series	269	8A.4 Tunnelling	324
(b) The determination of activity coefficients	270		
(c) The determination of equilibrium constants	270	Checklist of concepts	327
Checklist of concepts	271	Checklist of equations	328
Checklist of equations	271	Topic 8B Vibrational motion	329
discussion questions, exercises, and problems	272	8B.1 The harmonic oscillator	329
iscussion questions, exercises, and problems	2/2	(a) The energy levels	330
المراجعة الم		(b) The wavefunctions	331
ART 2 Structure	279	8B.2 The properties of oscillators	333
HAPTER 7 Introduction to quantum theory	281	(a) Mean values	334
		(b) Tunnelling	335
Topic 7A The origins of quantum mechanics	282	Checklist of concepts	336
7A.1 Energy quantization	282	Checklist of equations	336
(a) Black-body radiation	282		
(b) Heat capacities	285	Topic 8C Rotational motion	337
(c) Atomic and molecular spectra	286 287	8C.1 Rotation in two dimensions	337
7A.2 Wave-particle duality (a) The particle character of electromagnetic radiation	287	(a) The qualitative origin of quantized rotation	337
(b) The wave character of particles	289	(b) The solutions of the Schrödinger equation	338
		(c) Quantization of angular momentum	340
Checklist of concepts	290	8C.2 Rotation in three dimensions	342
Checklist of equations	291	(a) The wavefunctions	342
Topic 7B Dynamics of microscopic systems	292	(b) The energies	344
		(c) Angular momentum	345
78.1 The Schrödinger equation 78.2 The Born interpretation of the wavefunction	292 293	(d) Space quantization	345
(a) Normalization	295	(e) The vector model	346
(b) Constraints on the wavefunction	296	Checklist of concepts	347
(c) Quantization	296	Checklist of equations	347
7B.3 The probability density	297		
Checklist of concepts	298	Discussion questions, exercises, and problems	349
		Mathematical background 4 Differential equations	354
Checklist of equations	298	mathematical background 4 Differential equations	334