


OXFORD

# ELEMENTS

## of Physical Chemistry

PETER ATKINS & JULIO DE PAULA

A central image of a glass beaker containing a vibrant blue liquid. The liquid is bubbling, and a thick, white, smoke-like vapor rises from the top of the beaker, spreading out on the surface below. The background is black, making the blue and white elements stand out. The beaker has measurement markings on its side, including 50, 100, and 150.

7th edition



# Fundamental constants

Quantity	Symbol	Value	Power of 10	Units
Speed of light	$c$	2.997 924 58	$10^8$	$\text{m s}^{-1}$
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	$10^{-23}$	$\text{J K}^{-1}$
Avogadro's constant	$N_A$	6.022 140 857	$10^{23}$	$\text{mol}^{-1}$
Gas constant	$R = N_A k$	8.314 459 8		$\text{J K}^{-1} \text{mol}^{-1}$
Faraday's constant	$F = N_A e$	9.648 533 289	$10^4$	$\text{C mol}^{-1}$
<b>Mass</b>				
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	$\mu_0$	$4\pi$	$10^{-7}$	$\text{J s}^2 \text{C}^{-2} \text{m}^{-1}$
Vacuum permittivity	$\epsilon_0 = 1/\mu_0 c^2$	8.854 187 817	$10^{-12}$	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
	$4\pi\epsilon_0$	1.112 650 056	$10^{-10}$	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 009 994	$10^{-24}$	$\text{J T}^{-1}$
Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.050 783 699	$10^{-27}$	$\text{J T}^{-1}$
Proton magnetic moment	$\mu_p$	1.410 606 787	$10^{-26}$	$\text{J T}^{-1}$
$g$ -Value of electron	$g_e$	2.002 319 304		
<b>Magnetogyric ratio</b>				
electron	$\gamma_e = -g_e e/2m_e$	-1.001 159 652	$10^{10}$	$\text{C kg}^{-1}$
proton	$\gamma_p = 2\mu_p/\hbar$	2.675 222 004	$10^8$	$\text{C kg}^{-1}$
Bohr radius	$a_0 = 4\pi\epsilon_0 \hbar^2 / e^2 m_e$	5.291 772 107	$10^{-11}$	m
Rydberg constant	$R_\infty = m_e e^4 / 8h^3 c \epsilon_0^2$	1.097 373 157	$10^5$	$\text{cm}^{-1}$
	$hcR_\infty/e$	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

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# 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  $\Delta U$  for the change in internal energy because it is the difference between the final and initial values. You should not write  $\Delta q$  or  $\Delta w$  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  $\Delta U$ .

## 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.

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

$n_f - n_i = \Delta n_g$

### 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  $p_{\text{ex}}$ . From eqn 3b

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

$p = p_{\text{ex}}$

However, the change in internal energy is given by eqn 1 of Topic 2C ( $\Delta U = w + q$ ) with  $w = -p_{\text{ex}} \Delta V$  (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:

$$|w| = Fd$$

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

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

#### 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



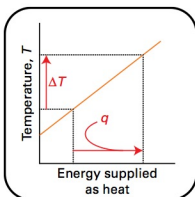
**Examples**

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/](http://www.oxfordtextbooks.co.uk/orc/echem7e/)

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## 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.

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## 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 re-developed 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.



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# Brief contents

	Conventions	xxii
	List of <i>The chemist's toolkits</i>	xxiii
	List of tables	xxiv
	List of Impacts	xxvi
	Energy, temperature, and chemistry	1
FOCUS 1	The properties of gases	3
FOCUS 2	The First Law of thermodynamics	37
FOCUS 3	The Second Law of thermodynamics	87
FOCUS 4	Physical transformations	115
FOCUS 5	Chemical change	175
FOCUS 6	Chemical kinetics	249
FOCUS 7	Quantum theory	315
FOCUS 8	Atomic structure	355
FOCUS 9	The chemical bond	389
FOCUS 10	Molecular interactions	427
FOCUS 11	Molecular spectroscopy	447
FOCUS 12	Statistical thermodynamics	499
FOCUS 13	Magnetic resonance	523
FOCUS 14	Macromolecules and aggregates	547
FOCUS 15	Solids	571
	<b>Resource section</b>	603
Index		617





# Full contents

Conventions	xxii	<b>FOCUS 2</b>	
List of <i>The chemist's toolkits</i>	xxiii	<b>The First Law of thermodynamics</b>	<b>37</b>
List of tables	xxiv		
List of Impacts	xxvi		
<b>Energy, temperature, and chemistry</b>	<b>1</b>		
<b>FOCUS 1</b>			
<b>The properties of gases</b>	<b>3</b>		
<b>1A The perfect gas</b>	<b>4</b>	<b>2A Work</b>	<b>39</b>
1A.1 The perfect gas equation of state	6	2A.1 Systems and surroundings	40
1A.2 Using the perfect gas law	9	2A.2 Expansion work	41
1A.3 Mixtures of gases: partial pressures	10	2A.3 Reversible expansion	43
CHECKLIST OF KEY CONCEPTS	12	CHECKLIST OF KEY CONCEPTS	46
<b>1B The kinetic model of gases</b>	<b>13</b>	<b>2B Heat</b>	<b>47</b>
1B.1 The pressure of a gas according to the kinetic model	13	2B.1 Conventions	47
1B.2 The root-mean-square speed of gas molecules	16	2B.2 Heat capacity	48
1B.3 The Maxwell distribution of speeds	16	2B.3 Calorimetry	49
1B.4 Diffusion and effusion	18	2B.4 Heat influx during expansion	51
1B.5 Molecular collisions	19	CHECKLIST OF KEY CONCEPTS	51
CHECKLIST OF KEY CONCEPTS	22	<b>2C Internal energy</b>	<b>52</b>
<b>1C Real gases</b>	<b>23</b>	2C.1 The internal energy	52
1C.1 Molecular interactions	24	2C.2 The internal energy as a state function	53
1C.2 The critical temperature	24	2C.3 Changes in the internal energy	53
1C.3 The compression factor	26	2C.4 The molecular basis of the internal energy	55
1C.4 The virial equation of state	27	CHECKLIST OF KEY CONCEPTS	56
1C.5 The van der Waals equation of state	28	<b>2D Enthalpy</b>	<b>57</b>
1C.6 The liquefaction of gases	30	2D.1 The definition of enthalpy	58
CHECKLIST OF KEY CONCEPTS	32	2D.2 Changes in enthalpy	58
<b>Exercises, discussion questions, problems, and projects</b>	<b>33</b>	2D.3 The temperature dependence of the enthalpy	59
		CHECKLIST OF KEY CONCEPTS	61
		<b>2E Physical change</b>	<b>62</b>
		2E.1 The enthalpy of phase transition	62
		2E.2 Ionization and electron attachment	66
		CHECKLIST OF KEY CONCEPTS	68
		<b>2F Chemical change</b>	<b>69</b>
		2F.1 Bond dissociation	69
		2F.2 Enthalpies of combustion	71
		2F.3 The combination of reaction enthalpies	73
		2F.4 Standard enthalpies of formation	74
		2F.5 The variation of reaction enthalpy with temperature	76
		CHECKLIST OF KEY CONCEPTS	78
		<b>Exercises, discussion questions, problems, and projects</b>	<b>79</b>

## FOCUS 3

**The Second Law of thermodynamics 87****3A Entropy 88**

3A.1 The direction of spontaneous change 88

3A.2 Entropy and the Second Law 89

3A.3 Heat engines, refrigerators, and heat pumps 90

CHECKLIST OF KEY CONCEPTS 92

**3B Entropy changes 93**

3B.1 The entropy change accompanying a change in volume 93

3B.2 The entropy change accompanying a change in temperature 94

3B.3 The entropy change accompanying a phase transition 96

3B.4 Entropy changes in the surroundings 98

CHECKLIST OF KEY CONCEPTS 99

**3C Absolute entropy 100**

3C.1 The Third Law of thermodynamics 100

3C.2 The molecular interpretation of entropy 102

3C.3 Residual entropy 104

CHECKLIST OF KEY CONCEPTS 105

**3D The Gibbs energy 106**

3D.1 The standard reaction entropy 106

3D.2 The spontaneity of chemical reactions 107

3D.3 Focusing on the system 107

3D.4 Properties of the Gibbs energy 108

CHECKLIST OF KEY CONCEPTS 110

Exercises, discussion questions, problems, and projects 111

## FOCUS 4

**Physical transformations 115****4A The thermodynamics of transition 117**

4A.1 The condition of stability 117

4A.2 The variation of Gibbs energy with pressure 118

4A.3 The variation of Gibbs energy with temperature 120

4A.4 The Gibbs–Helmholtz equation 122

CHECKLIST OF KEY CONCEPTS 123

**4B Phase diagrams of pure substances 124**

4B.1 Phase boundaries 124

4B.2 The location of phase boundaries 126

4B.3 Characteristic points 130

4B.4 The phase rule 131

4B.5 Phase diagrams of typical materials 133

CHECKLIST OF KEY CONCEPTS 135

**4C Partial molar quantities 136**

4C.1 Partial molar volume 136

4C.2 The chemical potential 137

4C.3 Spontaneous mixing 139

CHECKLIST OF KEY CONCEPTS 141

**4D Solutions 142**

4D.1 Ideal solutions 142

4D.2 The chemical potential of the solvent 144

4D.3 Ideal–dilute solutions 145

4D.4 The chemical potential of the solute 147

4D.5 Real solutions: activities 149

CHECKLIST OF KEY CONCEPTS 150

**4E Colligative properties 151**

4E.1 The modification of boiling and freezing points 151

4E.2 Osmosis 154

CHECKLIST OF KEY CONCEPTS 157

**4F Phase diagrams of mixtures 158**

4F.1 Mixtures of volatile liquids 158

4F.2 Liquid–liquid phase diagrams 160

4F.3 Liquid–solid phase diagrams 162

4F.4 Zone refining 164

4F.5 The Nernst distribution law 165

CHECKLIST OF KEY CONCEPTS 166

Exercises, discussion questions, problems, and projects 167

## FOCUS 5

**Chemical change 175****5A The thermodynamics of reaction 177**

5A.1 The reaction Gibbs energy 177

5A.2 The variation of  $\Delta_r G$  with composition 179

5A.3 Reactions at equilibrium 180

5A.4 The standard reaction Gibbs energy 183

CHECKLIST OF KEY CONCEPTS 184

**5B The equilibrium constant 185**

5B.1 The composition at equilibrium 185

5B.2 The equilibrium constant in terms of concentration 187

5B.3	The molecular interpretation of equilibrium constants	188	5J.3	The variation of potential with pH	235
	CHECKLIST OF KEY CONCEPTS	189	5J.4	The electrochemical series	236
<b>5C Response to conditions</b>		<b>190</b>	5J.5	The combination of standard potentials	237
5C.1	The effect of temperature	190	5J.6	Thermodynamic data from standard potentials	237
5C.2	The effect of compression	192		CHECKLIST OF KEY CONCEPTS	238
5C.3	The presence of a catalyst	194	<b>Exercises, discussion questions, problems, and projects</b>		<b>239</b>
	CHECKLIST OF KEY CONCEPTS	194			
<b>5D Proton transfer equilibria</b>		<b>195</b>	<b>FOCUS 6</b>		
5D.1	Brønsted–Lowry theory	195	<b>Chemical kinetics</b>		<b>249</b>
5D.2	Protonation and deprotonation	196			
	CHECKLIST OF KEY CONCEPTS	201	<b>6A Empirical chemical kinetics</b>		<b>251</b>
<b>5E Polyprotic acids</b>		<b>202</b>	6A.1	The definition of rate	251
5E.1	Successive deprotonation	202	6A.2	Experimental techniques	252
5E.2	Speciation	202		CHECKLIST OF KEY CONCEPTS	255
	CHECKLIST OF KEY CONCEPTS	205	<b>6B Rate laws</b>		<b>256</b>
<b>5F Acid–base equilibria of salts in water</b>		<b>206</b>	6B.1	The rate constant	256
5F.1	The pH of salt solutions	206	6B.2	Reaction order	258
5F.2	Acid–base titrations	208	6B.3	The determination of the rate law	259
5F.3	Buffer action	211		CHECKLIST OF KEY CONCEPTS	261
	CHECKLIST OF KEY CONCEPTS	212	<b>6C Integrated rate laws</b>		<b>262</b>
<b>5G Solubility equilibria</b>		<b>213</b>	6C.1	Zeroth-order reactions	262
5G.1	The solubility constant	213	6C.2	First-order reactions	262
5G.2	The common-ion effect	214	6C.3	Second-order reactions of the type $A \rightarrow$ products	264
5G.3	The effect of added salts on solubility	215	6C.4	Second-order reactions of the type $A + B \rightarrow$ products	265
	CHECKLIST OF KEY CONCEPTS	216	6C.5	Half-lives	267
<b>5H Ions in solution</b>		<b>217</b>		CHECKLIST OF KEY CONCEPTS	268
5H.1	Mean activity coefficients	218	<b>6D The temperature dependence of reaction rates</b>		<b>269</b>
5H.2	The Debye–Hückel theory	219	6D.1	The Arrhenius parameters	269
5H.3	The migration of ions	220	6D.2	Collision theory of gas-phase reactions	272
	CHECKLIST OF KEY CONCEPTS	223	6D.3	Transition-state theory	274
<b>5I Electrochemical cells</b>		<b>224</b>		CHECKLIST OF KEY CONCEPTS	276
5I.1	Half-reactions and electrodes	225	<b>6E The approach to equilibrium</b>		<b>277</b>
5I.2	Reactions at electrodes	227	6E.1	Equilibria and rates	277
5I.3	Varieties of cell	229	6E.2	Relaxation	279
5I.4	The cell reaction	230		CHECKLIST OF KEY CONCEPTS	280
5I.5	The cell potential	230	<b>6F Reaction mechanisms</b>		<b>281</b>
	CHECKLIST OF KEY CONCEPTS	232	6F.1	Elementary reactions	281
<b>5J Standard potentials</b>		<b>233</b>	6F.2	The formulation of rate laws	282
5J.1	The contributions of individual electrodes	233	6F.3	Consecutive reactions	283
5J.2	Equilibrium constants from standard potentials	234	6F.4	Pre-equilibrium	284

6F5	The steady-state approximation	284	<b>7D Rotation</b>	<b>340</b>
6F6	The rate-determining step	286	7D.1	Rotation in two dimensions 341
6F7	Kinetic control	286	7D.2	Rotation in three dimensions 343
6F8	Unimolecular reactions	287	CHECKLIST OF KEY CONCEPTS	346
CHECKLIST OF KEY CONCEPTS		288	<b>7E Vibration</b>	<b>347</b>
<b>6G Reactions in solution</b>		<b>289</b>	7E.1	The harmonic oscillator 347
6G.1	Activation control and diffusion control	289	7E.2	The quantum mechanical treatment 348
6G.2	Diffusion	290	CHECKLIST OF KEY CONCEPTS	350
CHECKLIST OF KEY CONCEPTS		294	<b>Exercises, discussion questions, problems, and projects</b>	<b>351</b>
<b>6H Homogeneous catalysis</b>		<b>295</b>	<b>FOCUS 8</b>	
6H.1	The Michaelis–Menten mechanism of enzyme catalysis	295	<b>Atomic structure</b>	<b>355</b>
6H.2	The analysis of rates of enzyme-catalysed reactions	297	<b>8A Hydrogenic atoms</b>	<b>356</b>
CHECKLIST OF KEY CONCEPTS		299	8A.1	The permitted energies of hydrogenic atoms 356
<b>6I Heterogeneous catalysis</b>		<b>300</b>	8A.2	Quantum numbers 359
6I.1	Physisorption and chemisorption	301	8A.3	The s orbitals 362
6I.2	Adsorption isotherms	302	8A.4	The p and d orbitals 365
6I.3	Mechanisms of surface-catalysed reactions	305	CHECKLIST OF KEY CONCEPTS	367
CHECKLIST OF KEY CONCEPTS		306	<b>8B Many-electron atoms</b>	<b>368</b>
<b>Exercises, discussion questions, problems, and projects</b>		<b>307</b>	8B.1	The orbital approximation 368
<b>FOCUS 7</b>			8B.2	Electron spin 369
<b>Quantum theory</b>		<b>315</b>	8B.3	The Pauli principle 370
<b>7A The emergence of quantum theory</b>		<b>316</b>	8B.4	Penetration and shielding 370
7A.1	The evidence for discrete energies	317	8B.5	The building-up principle 372
7A.2	The evidence for radiation as particles	319	8B.6	The occupation of d orbitals 373
7A.3	The evidence for particles as waves	320	8B.7	The configurations of cations and anions 373
CHECKLIST OF KEY CONCEPTS		322	8B.8	Self-consistent field orbitals 374
<b>7B The dynamics of microscopic systems</b>		<b>323</b>	CHECKLIST OF KEY CONCEPTS	374
7B.1	The Schrödinger equation	323	<b>8C Periodic trends of atomic properties</b>	<b>375</b>
7B.2	The Born interpretation	326	8C.1	Atomic and ionic radii 375
7B.3	The uncertainty principle	328	8C.2	Ionization energy and electron affinity 377
CHECKLIST OF KEY CONCEPTS		330	CHECKLIST OF KEY CONCEPTS	379
<b>7C Translation</b>		<b>331</b>	<b>8D Atomic spectroscopy</b>	<b>380</b>
7C.1	Motion in one dimension	331	8D.1	The spectra of hydrogenic atoms 380
7C.2	Tunnelling	335	8D.2	The energies of many-electron atoms 381
7C.3	Motion in two dimensions	336	8D.3	Spin–orbit coupling 383
CHECKLIST OF KEY CONCEPTS		339	8D.4	Selection rules for many-electron atoms 385
			CHECKLIST OF KEY CONCEPTS	385
			<b>Exercises, discussion questions, problems, and projects</b>	<b>386</b>

**FOCUS 9****The chemical bond 389****9A Valence bond theory 391**

9A.1	Diatomic molecules	392
9A.2	Polyatomic molecules	394
9A.3	Promotion and hybridization	395
9A.4	Resonance	398
9A.5	The language of valence bond theory	399
	CHECKLIST OF KEY CONCEPTS	400

**9B Molecular orbital theory: homonuclear diatomics 401**

9B.1	The construction of molecular orbitals	401
9B.2	Bonding and antibonding orbitals	403
9B.3	Inversion symmetry	404
9B.4	The chemical bond in molecular orbital theory	404
9B.5	Many-electron homonuclear diatomics	406
9B.6	The configurations of Period 2 homonuclear diatomics	408
9B.7	The criteria for building molecular orbitals	409
	CHECKLIST OF KEY CONCEPTS	410

**9C Molecular orbital theory: heteronuclear diatomics 411**

9C.1	Polar bonds	411
9C.2	The formulation of molecular orbitals	412
9C.3	Molecular orbital diagrams	414
	CHECKLIST OF KEY CONCEPTS	415

**9D Molecular orbital theory: polyatomic molecules 416**

9D.1	The molecular orbitals of H <sub>2</sub> O	416
9D.2	The Hückel method	417
9D.3	The molecular orbitals of benzene	420
9D.4	Computational chemistry	421
	CHECKLIST OF KEY CONCEPTS	423

**Exercises, discussion questions, problems, and projects 424**

**FOCUS 10****Molecular interactions 427****10A Electric properties of molecules 428**

10A.1	Electric dipole moments	428
10A.2	Dipole moments of polyatomic molecules	429
10A.3	Polarizabilities	431
	CHECKLIST OF KEY CONCEPTS	432

**10B Interactions between molecules 433**

10B.1	Interactions between partial charges	433
10B.2	Charge–dipole interactions	434
10B.3	Dipole–dipole interactions	435
10B.4	Dipole–induced dipole interactions	437
10B.5	Dispersion interactions	437
10B.6	Hydrogen bonding	439
10B.7	The hydrophobic effect	440
10B.8	Modelling the total interaction	440
	CHECKLIST OF KEY CONCEPTS	442

**Exercises, discussion questions, problems, and projects 443**

**FOCUS 11****Molecular spectroscopy 447****11A General features of molecular spectroscopy 449**

11A.1	Spectrometers	450
11A.2	Absorption and emission	451
11A.3	Raman scattering	455
11A.4	Linewidths	455
	CHECKLIST OF KEY CONCEPTS	457

**11B Rotational spectroscopy 458**

11B.1	The rotational energy levels of molecules	458
11B.2	Forbidden and allowed rotational states	462
11B.3	Populations at thermal equilibrium	463
11B.4	Microwave spectroscopy	464
11B.5	Rotational Raman spectra	466
	CHECKLIST OF KEY CONCEPTS	467

**11C Vibrational spectroscopy 468**

11C.1	The vibrations of molecules	468
11C.2	Vibrational transitions	470
11C.3	Anharmonicity	471
11C.4	Vibrational Raman spectra of diatomic molecules	471
11C.5	The vibrations of polyatomic molecules	472
11C.6	Vibration–rotation spectra	474
11C.7	Vibrational Raman spectra of polyatomic molecules	475
	CHECKLIST OF KEY CONCEPTS	476

**11D Electronic spectroscopy 477**

11D.1	Ultraviolet and visible spectra	477
11D.2	Specific types of transitions	479

11D.3	Analysis of mixtures by electronic spectroscopy	480		
11D.4	Photoelectron spectroscopy	481		
	CHECKLIST OF KEY CONCEPTS	483		
<b>11E</b>	<b>The decay of excited states</b>	<b>484</b>		
11E.1	Fluorescence and phosphorescence	485		
11E.2	Mechanism of decay of excited states	487		
11E.3	Quenching	488		
11E.4	Resonance energy transfer	490		
	CHECKLIST OF KEY CONCEPTS	491		
	<b>Exercises, discussion questions, problems, and projects</b>	<b>492</b>		
<b>FOCUS 12</b>				
<b>Statistical thermodynamics</b>		<b>499</b>		
<b>12A</b>	<b>The Boltzmann distribution</b>	<b>500</b>		
12A.1	The population of states	500		
12A.2	The general form of the Boltzmann distribution	501		
12A.3	The origins of the Boltzmann distribution	502		
	CHECKLIST OF KEY CONCEPTS	503		
<b>12B</b>	<b>The partition function</b>	<b>504</b>		
12B.1	The interpretation of the partition function	504		
12B.2	The molecular partition function	506		
12B.3	The translational partition function	506		
12B.4	The rotational partition function	508		
12B.5	The vibrational partition function	509		
12B.6	The electronic partition function	510		
12B.7	The significance of the molecular partition function	510		
	CHECKLIST OF KEY CONCEPTS	511		
<b>12C</b>	<b>The origin of thermodynamic properties</b>	<b>512</b>		
12C.1	The internal energy	512		
12C.2	The heat capacity	514		
12C.3	The entropy	515		
12C.4	The Gibbs energy	516		
12C.5	The equilibrium constant	517		
	CHECKLIST OF KEY CONCEPTS	519		
	<b>Exercises, discussion questions, problems, and projects</b>	<b>520</b>		
			<b>FOCUS 13</b>	
			<b>Magnetic resonance</b>	<b>523</b>
			<b>13A</b>	<b>Nuclear magnetic resonance</b>
			13A.1	Nuclei in magnetic fields
			13A.2	The resonance condition
			13A.3	The technique
				CHECKLIST OF KEY CONCEPTS
			<b>13B</b>	<b>The information in NMR spectra</b>
			13B.1	The chemical shift
			13B.2	The fine structure
			13B.3	The origin of spin–spin splitting
			13B.4	Spin relaxation
			13B.5	Conformational conversion and chemical exchange
				CHECKLIST OF KEY CONCEPTS
			<b>13C</b>	<b>Electron paramagnetic resonance</b>
			13C.1	Electrons in magnetic fields
			13C.2	The technique
			13C.3	The $g$ -value
			13C.4	Hyperfine structure
				CHECKLIST OF KEY CONCEPTS
				<b>Exercises, discussion questions, problems, and projects</b>
				<b>544</b>
			<b>FOCUS 14</b>	
			<b>Macromolecules and aggregates</b>	<b>547</b>
			<b>14A</b>	<b>Biological and synthetic macromolecules</b>
			14A.1	Average molar masses
			14A.2	Models of structure
			14A.3	Random coils
			14A.4	Polypeptides and polynucleotides
			14A.5	The prediction of structure
			14A.6	Mechanical properties of polymers
			14A.7	Thermal properties of polymers
				CHECKLIST OF KEY CONCEPTS
			<b>14B</b>	<b>Mesophases and disperse systems</b>
			14B.1	Liquid crystals
			14B.2	Classification of disperse systems
			14B.3	Surface, structure, and stability
			14B.4	The electric double layer
			14B.5	Liquid surfaces and surfactants
				CHECKLIST OF KEY CONCEPTS
				<b>Exercises, discussion questions, problems, and projects</b>
				<b>568</b>

**FOCUS 15****Solids****571****15A Crystal structure****572**

15A.1 The identification of crystal planes 573

15A.2 The determination of structure 575

15A.3 Bragg's law 577

15A.4 Experimental techniques 577

CHECKLIST OF KEY CONCEPTS 580

**15B Bonding in solids****581**

15B.1 Metallic solids 581

15B.2 Ionic solids 584

15B.3 The electronic structure of metallic and ionic solids 586

15B.4 The energetics of bonding in ionic solids 587

15B.5 Molecular solids 590

15B.6 Covalent networks 591

CHECKLIST OF KEY CONCEPTS 592

**15C The properties of solids****593**

15C.1 Electrical properties 593

15C.2 Superconductivity 595

15C.3 Optical properties 595

15C.4 Solid-state lasers 596

15C.5 Magnetic properties 597

CHECKLIST OF KEY CONCEPTS 599

Exercises, discussion questions, problems, and project

**600****Resource section****603****Part 1 Common integrals****604****Part 2 Units****605****Part 3 Data****607**

## Index

**617**

# 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.mmm...* 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*

Number	Topic	Title	
1	1A	Quantities and units	5
2	1A	Linear relations and graphs	7
3	1B	Momentum and force	15
4	1B	Exponential and Gaussian functions	17
5	1C	Differentiation	23
6	1C	Power series and expansions	31
7	2A	Work and energy	39
8	2A	Integration	44
9	2B	Electrical charge, current, power, and energy	50
10	3C	Logarithms	104
11	4A	The rules of differentiation	123
12	4D	Measures of concentration	148
13	5B	Quadratic equations	187
14	5H	The Coulomb potential	217
15	5H	Resistance and conductance	221
16	5I	Oxidation numbers	225
17	6G	Partial derivatives	292
18	7A	Electromagnetic waves	316
19	7B	Ordinary differential equations	324
20	7B	Operators	325
21	7C	Partial differential equations	338
22	7D	Angular momentum	340
23	7D	Vectors	345
24	8D	Addition and subtraction of vectors	382
25	9A	The Lewis theory of covalent bonding	391
26	9A	The VSEPR model	391
27	9D	Simultaneous equations	419
28	13A	Magnetic fields	525

# List of tables

Table 1A.1	The gas constant in various units	6
Table 1A.2	The molar volumes of gases at standard ambient temperature and pressure (SATP: 298.15 K and 1 bar)	9
Table 1B.1	Collision cross-sections of atoms and molecules	21
Table 1C.1	The critical temperatures of gases	26
Table 1C.2	van der Waals parameters of gases	29
Table 2B.1	Heat capacities of common materials	49
Table 2D.1	Temperature dependence of heat capacities	60
Table 2E.1	Standard enthalpies of transition at the transition temperature	63
Table 2E.2	First and second (and some higher) standard enthalpies of ionization, $\Delta_{\text{ion}}H^\ominus/(\text{kJ mol}^{-1})$	66
Table 2E.3	Standard electron gain enthalpies of the main-group elements, $\Delta_{\text{eg}}H^\ominus/(\text{kJ mol}^{-1})$	68
Table 2F1	Selected bond enthalpies at 298.15 K, $\Delta H(\text{AB})/(\text{kJ mol}^{-1})$	70
Table 2F2	Mean bond enthalpies at 298.15 K, $\Delta H_{\text{b}}/(\text{kJ mol}^{-1})$	71
Table 2F3	Standard enthalpies of combustion at 298.15 K	72
Table 2F4	Reference states of some elements	75
Table 2F5	Standard enthalpies of formation at 298.15 K	75
Table 3B.1	Entropies of vaporization at 1 atm and the normal boiling point	97
Table 3C.1	Standard molar entropies of some substances at 298.15 K	102
Table 4B.1	Vapour pressures	129
Table 4B.2	Critical constants	130
Table 4D.1	Henry's law constants for gases dissolved in water at 25 °C	146
Table 4D.2	Activities and standard states	149
Table 4E.1	Cryoscopic and ebullioscopic constants	152
Table 5A.1	Thermodynamic criteria of spontaneity	181
Table 5A.2	Standard Gibbs energies of formation at 298.15 K	183
Table 5D.1	Acidity and basicity constants at 298.15 K	198
Table 5E.1	Successive acidity constants of polyprotic acids at 298.15 K	203
Table 5G.1	Solubility constants at 298.15 K	214
Table 5H.1	Ionic conductivities, $\lambda/(\text{mS m}^2 \text{ mol}^{-1})$ , at 298.15 K	221
Table 5H.2	Ionic mobilities in water, $u/(10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1})$ , at 298.15 K	223
Table 5I.1	Varieties of electrodes	228
Table 5J.1	Standard potentials at 298.15 K	234

Table 6A.1	Kinetic techniques for fast reactions	253
Table 6B.1	Kinetic data for first-order reactions	257
Table 6B.2	Kinetic data for second-order reactions	257
Table 6C.1	Integrated rate laws	268
Table 6D.1	Arrhenius parameters	270
Table 6G.1	Diffusion coefficients at 25 °C, $D/(10^{-9} \text{ m}^2 \text{ s}^{-1})$	291
Table 6G.2	Coefficients of viscosity at 25 °C, $\eta/(10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})$	294
Table 7E.1	Harmonic oscillator wavefunctions	349
Table 8A.1	Hydrogenic wavefunctions	360
Table 8C.1	Atomic radii of main-group elements, $r/\text{pm}$	376
Table 8C.2	Ionic radii, $r/\text{pm}$	377
Table 8C.3	First ionization energies of main-group elements, $I/\text{eV}$	377
Table 8C.4	Electron affinities of main-group elements, $E_{\text{ea}}/\text{eV}$	378
Table 9A.1	Hybrid orbitals	397
Table 9C.1	Electronegativities of the main-group elements	412
Table 10A.1	Dipole moments, polarizabilities, and polarizability volumes	429
Table 10B.1	Potential energy of molecular interactions	433
Table 10B.2	Lennard-Jones parameters for the (12,6)-potential	441
Table 11B.1	Moments of inertia	459
Table 11C.1	Properties of diatomic molecules	471
Table 11D.1	Colour, frequency, and energy of light	477
Table 13A.1	Nuclear constitution and the nuclear spin quantum number	524
Table 13A.2	Nuclear spin properties	525
Table 14A.1	Interactions in macromolecules	554
Table 14B.1	Surface tensions of liquids at 293 K	565
Table 15A.1	The essential symmetries of the seven crystal systems	573
Table 15B.1	Radius ratio and crystal type	585
Table 15B.2	Ionic radii, $r/\text{pm}$	585
Table 15B.3	Lattice enthalpies, $\Delta H_{\text{L}}^{\ominus}/(\text{kJ mol}^{-1})$	588
Table 15B.4	Madelung constants	590
Table 15C.1	Magnetic susceptibilities at 298 K	598

# List of Impacts

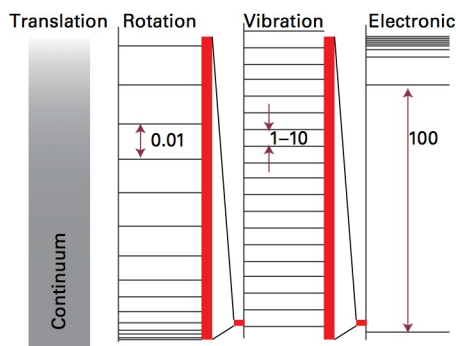
The *Impacts* are available at [www.oxfordtextbooks.co.uk/orc/echem7e/](http://www.oxfordtextbooks.co.uk/orc/echem7e/).

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- IMPACT 8 ON MEDICINE: Molecular recognition and drug design
- IMPACT 9 ON ENVIRONMENTAL SCIENCE: Climate change
- IMPACT 10 ON MEDICINE: Magnetic resonance imaging
- IMPACT 11 ON BIOCHEMISTRY: Biological membranes
- IMPACT 12 ON BIOCHEMISTRY: X-ray crystallography of biological macromolecules

# 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.)



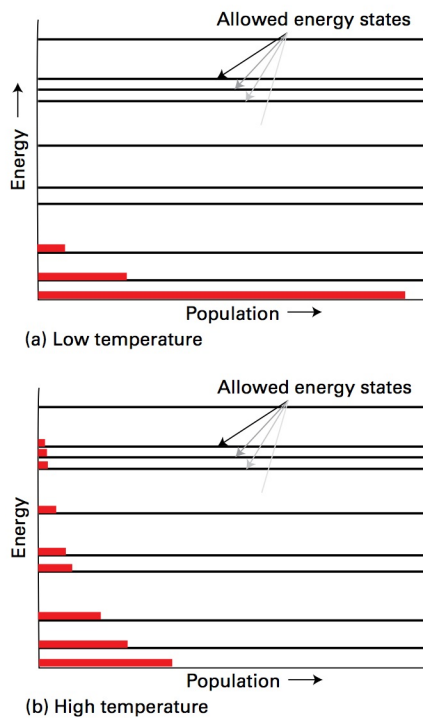
The energy level separations typical of translational, rotational, vibrational, and electronic motion. Only the relative sizes of the energy separations are shown.

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 popula-

tion,  $N_i$ , 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,  $\epsilon_i$ , and the absolute temperature,  $T$ :

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

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.