An abstract, artistic photograph of a blue liquid or smoke plume. The plume originates from the top right, where a series of small, clear bubbles are visible at the surface. It then billows and swirls downwards and to the left, creating intricate, organic shapes. The color of the plume varies from a light, airy blue to a deep, dark navy blue, with the darkest areas concentrated in the lower right and the swirling center. The background is a plain, bright white, which makes the blue plume stand out prominently.

# Physical Chemistry

NINTH EDITION

PETER ATKINS ■ JULIO DE PAULA

*This page intentionally left blank*

## General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	$c$	2.997 925 58*	$10^8$	$\text{m s}^{-1}$
Elementary charge	$e$	1.602 176	$10^{-19}$	C
Faraday's constant	$F = N_{\text{A}}e$	9.648 53	$10^4$	$\text{C mol}^{-1}$
Boltzmann's constant	$k$	1.380 65	$10^{-23}$	$\text{J K}^{-1}$
Gas constant	$R = N_{\text{A}}k$	8.314 47		$\text{J K}^{-1} \text{mol}^{-1}$
		8.314 47	$10^{-2}$	$\text{dm}^3 \text{bar K}^{-1} \text{mol}^{-1}$
		8.205 74	$10^{-2}$	$\text{dm}^3 \text{atm K}^{-1} \text{mol}^{-1}$
		6.236 37	10	$\text{dm}^3 \text{Torr K}^{-1} \text{mol}^{-1}$
Planck's constant	$h$	6.626 08	$10^{-34}$	J s
	$\hbar = h/2\pi$	1.054 57	$10^{-34}$	J s
Avogadro's constant	$N_{\text{A}}$	6.022 14	$10^{23}$	$\text{mol}^{-1}$
Atomic mass constant	$m_{\text{u}}$	1.660 54	$10^{-27}$	kg
Mass				
electron	$m_{\text{e}}$	9.109 38	$10^{-31}$	kg
proton	$m_{\text{p}}$	1.672 62	$10^{-27}$	kg
neutron	$m_{\text{n}}$	1.674 93	$10^{-27}$	kg
Vacuum permittivity	$\epsilon_0 = 1/c^2\mu_0$	8.854 19	$10^{-12}$	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
	$4\pi\epsilon_0$	1.112 65	$10^{-10}$	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
Vacuum permeability	$\mu_0$	$4\pi$	$10^{-7}$	$\text{J s}^2 \text{C}^{-2} \text{m}^{-1} (= \text{T}^2 \text{J}^{-1} \text{m}^3)$
Magneton				
Bohr	$\mu_{\text{B}} = e\hbar/2m_{\text{e}}$	9.274 01	$10^{-24}$	$\text{J T}^{-1}$
nuclear	$\mu_{\text{N}} = e\hbar/2m_{\text{p}}$	5.050 78	$10^{-27}$	$\text{J T}^{-1}$
g value	$g_{\text{e}}$	2.002 32		
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar^2/m_{\text{e}}e^2$	5.291 77	$10^{-11}$	m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 35	$10^{-3}$	
	$\alpha^{-1}$	1.370 36	$10^2$	
Second radiation constant	$c_2 = hc/k$	1.438 78	$10^{-2}$	m K
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3c^2$	5.670 51	$10^{-8}$	$\text{W m}^{-2} \text{K}^{-4}$
Rydberg constant	$R = m_{\text{e}}e^4/8h^3c\epsilon_0^2$	1.097 37	$10^5$	$\text{cm}^{-1}$
Standard acceleration of free fall	$g$	9.806 65*		$\text{m s}^{-2}$
Gravitational constant	$G$	6.673	$10^{-11}$	$\text{N m}^2 \text{kg}^{-2}$

\*Exact value

## The Greek alphabet

A, $\alpha$	alpha	H, $\eta$	eta	N, $\nu$	nu	Y, $\upsilon$	upsilon
B, $\beta$	beta	$\Theta, \theta$	theta	$\Xi, \xi$	xi	$\Phi, \phi$	phi
$\Gamma, \gamma$	gamma	I, $\iota$	iota	$\Pi, \pi$	pi	X, $\chi$	chi
$\Delta, \delta$	delta	K, $\kappa$	kappa	P, $\rho$	rho	$\Psi, \psi$	psi
E, $\epsilon$	epsilon	$\Lambda, \lambda$	lambda	$\Sigma, \sigma$	sigma	$\Omega, \omega$	omega
Z, $\zeta$	zeta	M, $\mu$	mu	T, $\tau$	tau		

*This page intentionally left blank*

# **PHYSICAL CHEMISTRY**

*This page intentionally left blank*



# PHYSICAL CHEMISTRY

**Ninth Edition**

**Peter Atkins**

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

**Julio de Paula**

*Professor of Chemistry,  
Lewis and Clark College,  
Portland, Oregon, USA*



W. H. Freeman and Company  
New York

*Physical Chemistry*, Ninth Edition

© 2010 by Peter Atkins and Julio de Paula

All rights reserved

ISBN: 1-4292-1812-6

ISBN-13: 978-1-429-21812-2

Published in Great Britain by Oxford University Press

This edition has been authorized by Oxford University Press for sale in the United States and Canada only and not for export therefrom.

First printing.

W. H. Freeman and Company

41 Madison Avenue

New York, NY 10010

[www.whfreeman.com](http://www.whfreeman.com)



# Preface

---

We have followed our usual tradition in that this new edition of the text is yet another thorough update of the content and its presentation. Our goal is to keep the book flexible to use, accessible to students, broad in scope, and authoritative, without adding bulk. However, it should always be borne in mind that much of the bulk arises from the numerous pedagogical features that we include (such as *Worked examples*, *Checklists of key equations*, and the *Resource section*), not necessarily from density of information.

The text is still divided into three parts, but material has been moved between chapters and the chapters themselves have been reorganized. We continue to respond to the cautious shift in emphasis away from classical thermodynamics by combining several chapters in Part 1 (Equilibrium), bearing in mind that some of the material will already have been covered in earlier courses. For example, material on phase diagrams no longer has its own chapter but is now distributed between Chapters 4 (*Physical transformation of pure substances*) and 5 (*Simple mixtures*). New *Impact* sections highlight the application of principles of thermodynamics to materials science, an area of growing interest to chemists.

In Part 2 (Structure) the chapters have been updated with a discussion of contemporary techniques of materials science—including nanoscience—and spectroscopy. We have also paid more attention to computational chemistry, and have revised the coverage of this topic in Chapter 10.

Part 3 has lost chapters dedicated to kinetics of complex reactions and surface processes, but not the material, which we regard as highly important in a contemporary context. To make the material more readily accessible within the context of courses, descriptions of polymerization, photochemistry, and enzyme- and surface-catalysed reactions are now part of Chapters 21 (*The rates of chemical reactions*) and 22 (*Reaction dynamics*)—already familiar to readers of the text—and a new chapter, Chapter 23, on *Catalysis*.

We have discarded the Appendices of earlier editions. Material on mathematics covered in the appendices is now dispersed through the text in the form of *Mathematical background* sections, which review and expand knowledge of mathematical techniques where they are needed in the text. The review of introductory chemistry and physics, done in earlier editions in appendices, will now be found in a new *Fundamentals* chapter that opens the text, and particular points are developed as *Brief comments* or as part of *Further information* sections throughout the text. By liberating these topics from their appendices and relaxing the style of presentation we believe they are more likely to be used and read.

The vigorous discussion in the physical chemistry community about the choice of a ‘quantum first’ or a ‘thermodynamics first’ approach continues. In response we have paid particular attention to making the organization flexible. The strategic aim of this revision is to make it possible to work through the text in a variety of orders and at the end of this Preface we once again include two suggested paths through the text. For those who require a more thorough-going ‘quantum first’ approach we draw attention to our *Quanta, matter, and change* (with Ron Friedman) which covers similar material to this text in a similar style but, because of the different approach, adopts a different philosophy.

The concern expressed in previous editions about the level of mathematical ability has not evaporated, of course, and we have developed further our strategies for

showing the absolute centrality of mathematics to physical chemistry and to make it accessible. In addition to associating *Mathematical background* sections with appropriate chapters, we continue to give more help with the development of equations, motivate them, justify them, and comment on the steps. We have kept in mind the struggling student, and have tried to provide help at every turn.

We are, of course, alert to the developments in electronic resources and have made a special effort in this edition to encourage the use of the resources on our website (at [www.whfreeman.com/pchem](http://www.whfreeman.com/pchem)). In particular, we think it important to encourage students to use the *Living graphs* on the website (and their considerable extension in the electronic book and *Explorations* CD). To do so, wherever we call out a *Living graph* (by an icon attached to a graph in the text), we include an *interActivity* in the figure legend, suggesting how to explore the consequences of changing parameters.

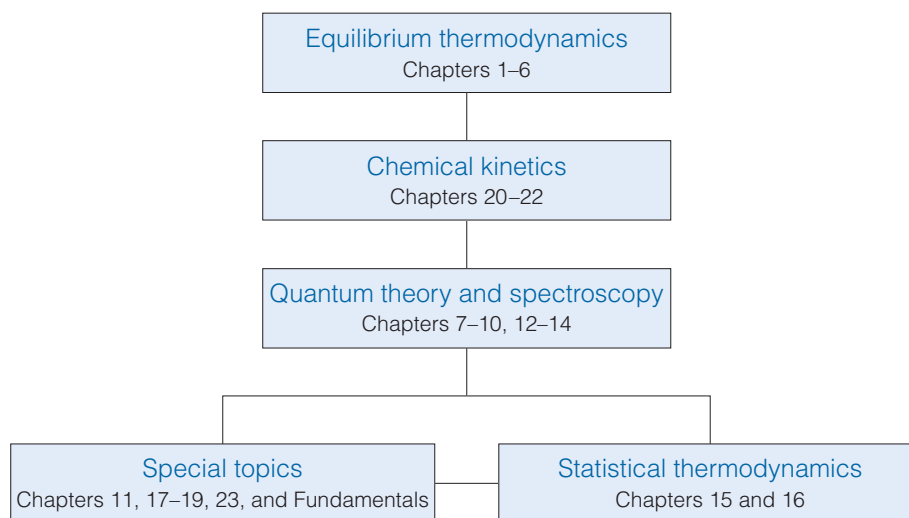
Many other revisions have been designed to make the text more efficient and helpful and the subject more enjoyable. For instance, we have redrawn nearly every one of the 1000 pieces of art in a consistent style. The *Checklists of key equations* at the end of each chapter are a useful distillation of the most important equations from the large number that necessarily appear in the exposition. Another innovation is the collection of *Road maps* in the *Resource section*, which suggest how to select an appropriate expression and trace it back to its roots.

Overall, we have taken this opportunity to refresh the text thoroughly, to integrate applications, to encourage the use of electronic resources, and to make the text even more flexible and up-to-date.

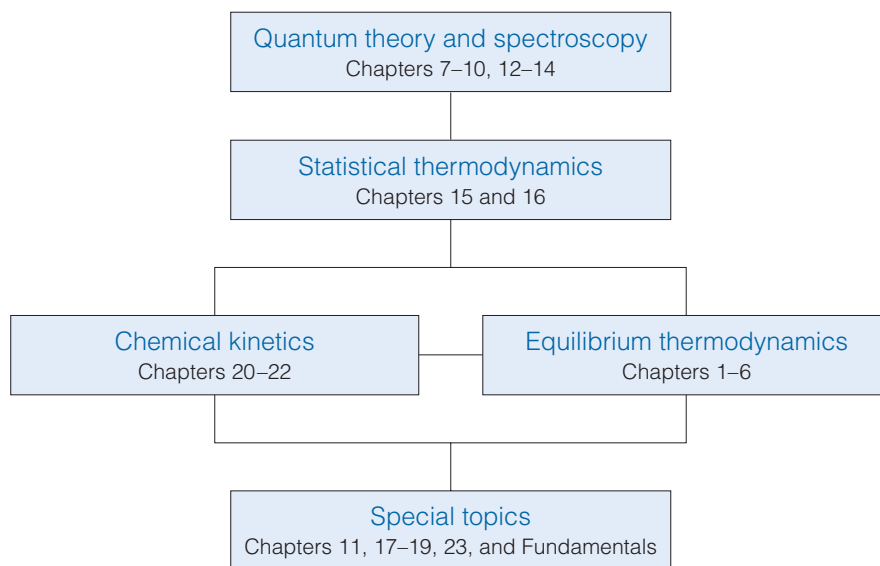
Oxford  
Portland

P.W.A.  
J.de P.

### Traditional approach



### Molecular approach



This text is available as a customizable ebook. This text can also be purchased in two volumes. For more information on these options please see pages xv and xvi.

# About the book

There are numerous features in this edition that are designed to make learning physical chemistry more effective and more enjoyable. One of the problems that make the subject daunting is the sheer amount of information: we have introduced several devices for organizing the material: see *Organizing the information*. We appreciate that mathematics is often troublesome, and therefore have taken care to give help with this enormously important aspect of physical chemistry: see *Mathematics support*. Problem solving—especially, ‘where do I start?’—is often a challenge, and we have done our best to help overcome this first hurdle: see *Problem solving*. Finally, the web is an extraordinary resource, but it is necessary to know where to start, or where to go for a particular piece of information; we have tried to indicate the right direction: see *About the Book Companion Site*. The following paragraphs explain the features in more detail.

## Organizing the information

### Key points

The *Key points* act as a summary of the main take-home message(s) of the section that follows. They alert you to the principal ideas being introduced.

#### 1.1 The states of gases

**Key points** Each substance is described by an equation of state. (a) Pressure, force divided by area, provides a criterion of mechanical equilibrium for systems free to change their volume. (b) Pressure is measured with a barometer. (c) Through the Zeroth Law of thermodynamics, temperature provides a criterion of thermal equilibrium.

The physical state of a sample of a substance, its physical condition, is defined by its physical properties. Two samples of a substance that have the same physical proper-

### Equation and concept tags

The most significant equations and concepts—which we urge you to make a particular effort to remember—are flagged with an annotation, as shown here.

mental fact that each substance is described by an **equation of state**, an equation that interrelates these four variables.

The general form of an equation of state is

$$p = f(T, V, n)$$

General form of  
an equation of state (1.1)

### Justifications

On first reading it might be sufficient simply to appreciate the ‘bottom line’ rather than work through detailed development of a mathematical expression. However, mathematical development is an intrinsic part of physical chemistry, and to achieve full understanding it is important to see how a particular expression is obtained. The *Justifications* let you adjust the level of detail that you require to your current needs, and make it easier to review material.

These relations are called the **Margules equations**.

#### Justification 5.5 The Margules equations

The Gibbs energy of mixing to form a nonideal solution is

$$\Delta_{\text{mix}} G = nRT \{x_A \ln a_A + x_B \ln a_B\}$$

This relation follows from the derivation of eqn 5.16 with activities in place of mole fractions. If each activity is replaced by  $\gamma x$ , this expression becomes

$$\Delta_{\text{mix}} G = nRT \{x_A \ln x_A + x_B \ln x_B + x_A \ln \gamma_A + x_B \ln \gamma_B\}$$

Now we introduce the two expressions in eqn 5.64, and use  $x_A + x_B = 1$ , which gives

$$\begin{aligned} \Delta_{\text{mix}} G &= nRT \{x_A \ln x_A + x_B \ln x_B + \xi x_A x_B^2 + \xi x_B x_A^2\} \\ &= nRT \{x_A \ln x_A + x_B \ln x_B + \xi x_A x_B (x_A + x_B)\} \\ &= nRT \{x_A \ln x_A + x_B \ln x_B + \xi x_A x_B\} \end{aligned}$$

as required by eqn 5.29. Note, moreover, that the activity coefficients behave correctly for dilute solutions:  $\gamma_A \rightarrow 1$  as  $x_B \rightarrow 0$  and  $\gamma_B \rightarrow 1$  as  $x_A \rightarrow 0$ .

At this point we can use the Margules equations to write the activity of A as

## Checklists of key equations

We have summarized the most important equations introduced in each chapter as a checklist. Where appropriate, we describe the conditions under which an equation applies.

Property	Equation	Comment
Chemical potential	$\mu_i = (\partial G/\partial n_i)_{T,p}$	
Fundamental equation of chemical thermodynamics	$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \dots$	$G = n_A \mu_A + n_B \mu_B$
Gibbs–Duhem equation	$\sum_i n_i d\mu_i = 0$	
Chemical potential of a gas	$\mu = \mu^\circ + RT \ln(p/p^\circ)$	Perfect gas
Thermodynamic properties of mixing	$\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B)$ $\Delta_{\text{mix}}S = -nR(x_A \ln x_A + x_B \ln x_B)$ $\Delta_{\text{mix}}H = 0$	Perfect gases and ideal solutions
Raoult's law	$p_A = x_A p_A^\circ$	True for ideal solutions; limiting law as $x_A \rightarrow 1$
Henry's law	$p_A = x_A K_A$	True for ideal-dilute solutions; limiting law as $x_A \rightarrow 0$
van't Hoff equation	$\Pi = [B]RT$	Valid as $[B] \rightarrow 0$
Activity of a solvent	$a_A = p_A/p_A^\circ$	$a_A \rightarrow x_A$ as $x_A \rightarrow 1$
Chemical potential	$\mu_i = \mu_i^\circ + RT \ln a_i$	General form for a species $i$
Conversion to biological standard state	$\mu_i^\circ(\text{H}^+) = \mu_i^\circ(\text{H}^+) - 7RT \ln 10$	
Mean activity coefficient	$\gamma_\pm = (\gamma_+ \gamma_-)^{1/2}$	
Ionic strength	$I = \frac{1}{2} \sum_i z_i^2 (b_i/b^\circ)$	Definition
Debye–Hückel limiting law	$\log \gamma_\pm = - z_+ z_-  A I^{1/2}$	Valid as $I \rightarrow 0$
Margules equation	$\ln \gamma_i = \xi_{ii}^2$	Model regular solution
Lever rule	$n_A I_A = n_B I_B$	

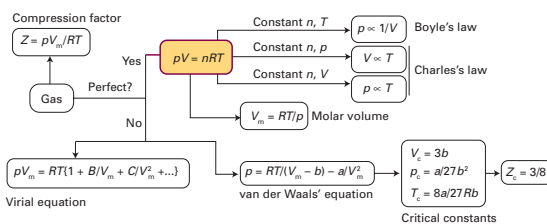
## Road maps

In many cases it is helpful to see the relations between equations. The suite of ‘Road maps’ summarizing these relations are found in the *Resource section* at the end of the text.

### Part 1 Road maps

#### Gas laws (Chapter 1)

##### Gas laws (Chapter 1)



#### The First Law (Chapter 2)

## Impact sections

Where appropriate, we have separated the principles from their applications: the principles are constant and straightforward; the applications come and go as the subject progresses. The *Impact sections* show how the principles developed in the chapter are currently being applied in a variety of modern contexts.

### IMPACT ON NANOSCIENCE

#### 18.1 Quantum dots

Nanoscience is the study of atomic and molecular assemblies with dimensions ranging from 1 nm to about 100 nm and nanotechnology is concerned with the incorporation of such assemblies into devices. The future economic impact of nanotechnology could be very significant. For example, increased demand for very small digital electronic devices has driven the design of ever smaller and more powerful microprocessors. However, there is an upper limit on the density of electronic circuits that can be incorporated into silicon-based chips with current fabrication technologies. As the ability to process data increases with the number of components in a chip, it follows that soon chips and the devices that use them will have to become bigger if processing

## Notes on good practice

Science is a precise activity and its language should be used accurately. We have used this feature to help encourage the use of the language and procedures of science in conformity to international practice (as specified by IUPAC, the International Union of Pure and Applied Chemistry) and to help avoid common mistakes.

**Answer** The number of photons is

$$N = \frac{E}{h\nu} = \frac{P\Delta t}{h(c/\lambda)} = \frac{\lambda P\Delta t}{hc}$$

Substitution of the data gives

$$N = \frac{(5.60 \times 10^{-7} \text{ m}) \times (100 \text{ J s}^{-1}) \times (1.0 \text{ s})}{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})} = 2.8 \times 10^{20}$$

Note that it would take the lamp nearly 40 min to produce 1 mol of these photons.

**Self-test 7.1** How many photons does a monochromatic (single frequency) infrared rangefinder of power 1 mW and wavelength 1000 nm emit in 0.1 s? [ $5 \times 10^{14}$ ]

**A note on good practice** To avoid rounding and other numerical errors, it is best to carry out algebraic calculations first, and to substitute numerical values into a single, final formula. Moreover, an analytical result may be used for other data without having to repeat the entire calculation.

## InterActivities

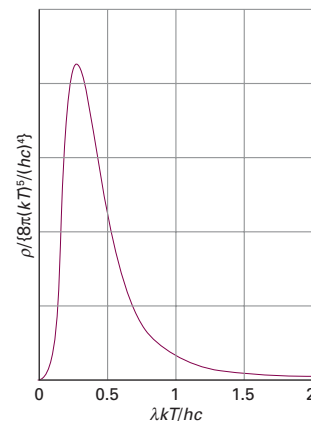
You will find that many of the graphs in the text have an interActivity attached: this is a suggestion about how you can explore the consequences of changing various parameters or of carrying out a more elaborate investigation related to the material in the illustration. In many cases, the activities can be completed by using the online resources of the book's website.

before it is switched on, the lamp is at 20°C (293 K). When it is switched on, it emits nearly white light. •

While Rayleigh's was not, the Rayleigh–Jeans law excites the oscillators of the field at the highest frequencies are excited only at large for the walls to suppress the latter remain unexcited. The energy available from the high frequency energy available.

Louis Dulong and Alexis Berthollet (Section 2.4), of a number of slender experimental monatomic solids are the

classical physics in much the same way. If classical physics predicts that the mean energy of each oscillator is  $kT$  for each direction of displacement, the average energy of each oscillator is  $3kT$  and the distribution of this motion to



**Fig. 7.7** The Planck distribution (eqn 7.8) accounts very well for the experimentally determined distribution of black-body radiation. Planck's quantization hypothesis essentially quenches the contributions of high frequency, short wavelength oscillators. The distribution coincides with the Rayleigh–Jeans distribution at long wavelengths.

**interActivity** Plot the Planck distribution at several temperatures and confirm that eqn 7.8 predicts the behaviour summarized by Fig. 7.3.

Further information

In some cases, we have judged that a derivation is too long, too detailed, or too different in level for it to be included in the text. In these cases, the derivations will be found less obtrusively at the end of the chapter.

Further information

**Further information 7.1 Classical mechanics**

Classical mechanics describes the behaviour of objects in terms of two equations. One expresses the fact that the total energy is constant in the absence of external forces; the other expresses the response of particles to the forces acting on them.

**(a) The trajectory in terms of the energy**

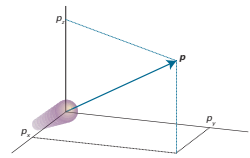
The velocity,  $v$ , of a particle is the rate of change of its position:

$$v = \frac{dr}{dt} \tag{7.44}$$

The velocity is a vector, with both direction and magnitude. (Vectors are discussed in *Mathematical background 5*.) The magnitude of the velocity is the speed,  $v$ . The linear momentum,  $p$ , of a particle of mass  $m$  is related to its velocity,  $v$ , by

$$p = mv \tag{7.45}$$

Like the velocity vector, the linear momentum vector points in the direction of travel of the particle (Fig. 7.31). In terms of the linear



**Fig. 7.31** The linear momentum of a particle is a vector property and points in the direction of motion.

momentum, the total energy—the sum of the kinetic and potential energy—of a particle is

$$E = E_k + V(x) = \frac{p^2}{2m} + V(x) \tag{7.46}$$

Resource section

Long tables of data are helpful for assembling and solving exercises and problems, but can break up the flow of the text. The *Resource section* at the end of the text consists of the *Road maps*, a *Data section* with a lot of useful numerical information, and *Character tables*. Short extracts of the tables in the text itself give an idea of the typical values of the physical quantities being discussed.

van der Waals equation of state

(1.21a)

Equation is often written in

(1.21b)

**Table 1.6\*** van der Waals coefficients

	$a/(\text{atm dm}^6 \text{ mol}^{-2})$	$b/(10^{-2} \text{ dm}^3 \text{ mol}^{-1})$
Ar	1.337	3.20
CO <sub>2</sub>	3.610	4.29
He	0.0341	2.38
Xe	4.137	5.16

\* More values are given in the *Data section*.

Mathematics support

A brief comment

A topic often needs to draw on a mathematical procedure or a concept of physics; a brief comment is a quick reminder of the procedure or concept.

**in magnetic fields**

fields, which remove the degeneracy of the quantized resented on the vector model as vectors precessing at

moment  $\mu$  in a magnetic field  $\mathcal{B}$  is equal to the

$$\tag{14.1}$$

duction and is measured in tesla, T; 1 T = is also occasionally used: 1 T =  $10^4$  G.

**A brief comment**

Scalar products (or ‘dot products’) are explained in *Mathematical background 5* following Chapter 9.

Mathematical background

It is often the case that you need a more full-bodied account of a mathematical concept, either because it is important to understand the procedure more fully or because you need to use a series of tools to develop an equation. The *Mathematical background* sections are located between some chapters, primarily where they are first needed, and include many illustrations of how each concept is used.

**MATHEMATICAL BACKGROUND 5**

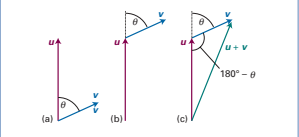
**Vectors**

A vector quantity has both magnitude and direction. The vector shown in Fig. MB5.1 has components on the  $x$ ,  $y$ , and  $z$  axes with magnitudes  $v_x$ ,  $v_y$ , and  $v_z$ , respectively. The vector may be represented as

$$v = v_x i + v_y j + v_z k \tag{MB5.1}$$

where  $i$ ,  $j$ , and  $k$  are unit vectors, vectors of magnitude 1, pointing along the positive directions on the  $x$ -,  $y$ -, and  $z$ -axes. The magnitude of the vector is denoted  $v$  or  $|v|$  and is given by

$$v = (v_x^2 + v_y^2 + v_z^2)^{1/2} \tag{MB5.2}$$



**Fig. MB5.2** (a) The vectors  $u$  and  $v$  make an angle  $\theta$ . (b) To add  $v$  to  $u$ , we first join the tail of  $v$  to the head of  $u$ , making sure that the angle  $\theta$  between the vectors remains unchanged. (c) To finish the process, we draw the resultant vector by joining the tail of  $u$  to the head of  $v$ .

Problem solving

A brief illustration

A brief illustration is a short example of how to use an equation that has just been introduced in the text. In particular, we show how to use data and how to manipulate units correctly.

**• A brief illustration**

The unpaired electron in the ground state of an alkali metal atom has  $l = 0$ , so  $j = \frac{1}{2}$ . Because the orbital angular momentum is zero in this state, the spin-orbit coupling energy is zero (as is confirmed by setting  $j = s$  and  $l = 0$  in eqn 9.42). When the electron is excited to an orbital with  $l = 1$ , it has orbital angular momentum and can give rise to a magnetic field that interacts with its spin. In this configuration the electron can have  $j = \frac{3}{2}$  or  $j = \frac{1}{2}$ , and the energies of these levels are

$$E_{3/2} = \frac{1}{2} hc\tilde{A} \left\{ \frac{3}{2} \times \frac{5}{2} - 1 \times 2 - \frac{1}{2} \times \frac{3}{2} \right\} = \frac{1}{2} hc\tilde{A}$$
$$E_{1/2} = \frac{1}{2} hc\tilde{A} \left\{ \frac{1}{2} \times \frac{3}{2} - 1 \times 2 - \frac{1}{2} \times \frac{3}{2} \right\} = -hc\tilde{A}$$

The corresponding energies are shown in Fig. 9.30. Note that the baricentre (the ‘centre of gravity’) of the levels is unchanged, because there are four states of energy  $\frac{1}{2} hc\tilde{A}$  and two of energy  $-hc\tilde{A}$ . •

## Examples

We present many worked examples throughout the text to show how concepts are used, sometimes in combination with material from elsewhere in the text. Each worked example has a *Method* section suggesting an approach as well as a fully worked out answer.

### Example 9.2 Calculating the mean radius of an orbital

Use hydrogenic orbitals to calculate the mean radius of a 1s orbital.

**Method** The mean radius is the expectation value

$$\langle r \rangle = \int \psi^* r \psi d\tau = \int r |\psi|^2 d\tau$$

We therefore need to evaluate the integral using the wavefunctions given in Table 9.1 and  $d\tau = r^2 dr \sin \theta d\theta d\phi$ . The angular parts of the wavefunction (Table 8.2) are normalized in the sense that

$$\int_0^\pi \int_0^{2\pi} |Y_{l,m_l}|^2 \sin \theta d\theta d\phi = 1$$

The integral over  $r$  required is given in Example 7.4.

**Answer** With the wavefunction written in the form  $\psi = RY$ , the integration is

$$\langle r \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} r R_{n,l}^2 |Y_{l,m_l}|^2 r^2 dr \sin \theta d\theta d\phi = \int_0^\infty r^3 R_{n,l}^2 dr$$

For a 1s orbital

$$R_{1,0} = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$$

Hence

$$\langle r \rangle = \frac{4Z^3}{a_0^3} \int_0^\infty r^3 e^{-2Zr/a_0} dr = \frac{3a_0}{2Z}$$

## Self-tests

Each *Example* has a *Self-test* with the answer provided as a check that the procedure has been mastered. There are also a number of free-standing *Self-tests* that are located where we thought it a good idea to provide a question to check your understanding. Think of *Self-tests* as in-chapter exercises designed to help you monitor your progress.

**Self-test 9.4** Evaluate the mean radius of a 3s orbital by integration. [27a<sub>0</sub>/2Z]

## Discussion questions

The end-of-chapter material starts with a short set of questions that are intended to encourage reflection on the material and to view it in a broader context than is obtained by solving numerical problems.

### Discussion questions

- 9.1 Discuss the origin of the series of lines in the emission spectra of hydrogen. What region of the electromagnetic spectrum is associated with each of the series shown in Fig. 9.1?
- 9.2 Describe the separation of variables procedure as it is applied to simplify the description of a hydrogenic atom free to move through space.
- 9.3 List and describe the significance of the quantum numbers needed to specify the internal state of a hydrogenic atom.
- 9.4 Specify and account for the selection rules for transitions in hydrogenic atoms.
- 9.5 Explain the significance of (a) a boundary surface and (b) the radial distribution function for hydrogenic orbitals.
- 9.6 Outline the electron configurations of many-electron atoms in terms of their location in the periodic table.
- 9.7 Describe and account for the variation of first ionization energies along Period 2 of the periodic table. Would you expect the same variation in Period 3?
- 9.8 Describe the orbital approximation for the wavefunction of a many-electron atom. What are the limitations of the approximation?
- 9.9 Explain the origin of spin-orbit coupling and how it affects the appearance of a spectrum.
- 9.10 Describe the physical origins of linewidths in absorption and emission spectra. Do you expect the same contributions for species in condensed and gas phases?

## Exercises and Problems

The core of testing understanding is the collection of end-of-chapter *Exercises* and *Problems*. The *Exercises* are straightforward numerical tests that give practice with manipulating numerical data. The *Problems* are more searching. They are divided into ‘numerical’, where the emphasis is on the manipulation of data, and ‘theoretical’, where the emphasis is on the manipulation of equations before (in some cases) using numerical data. At the end of the *Problems* are collections of problems that focus on practical applications of various kinds, including the material covered in the *Impact* sections.

### Exercises

- 9.1(a) Determine the shortest and longest wavelength lines in the Lyman series.
- 9.1(b) The Pfund series has  $n_1 = 5$ . Determine the shortest and longest wavelength lines in the Pfund series.
- 9.2(a) Compute the wavelength, frequency, and wavenumber of the  $n = 2 \rightarrow n = 1$  transition in  $\text{He}^+$ .
- 9.2(b) Compute the wavelength, frequency, and wavenumber of the  $n = 5 \rightarrow n = 4$  transition in  $\text{Li}^{2+}$ .
- 9.3(a) When ultraviolet radiation of wavelength 58.4 nm from a helium lamp is directed on to a sample of krypton, electrons are ejected with a speed of  $1.59 \text{ Mm s}^{-1}$ . Calculate the ionization energy of krypton.
- 9.3(b) When ultraviolet radiation of wavelength 58.4 nm from a helium lamp is directed on to a sample of xenon, electrons are ejected with a speed of  $1.79 \text{ Mm s}^{-1}$ . Calculate the ionization energy of xenon.
- 9.12(a) What is the orbital angular momentum of an electron in the orbitals (a) 1s, (b) 3s, (c) 3d? Give the numbers of angular and radial nodes in each case.
- 9.12(b) What is the orbital angular momentum of an electron in the orbitals (a) 4d, (b) 2p, (c) 3p? Give the numbers of angular and radial nodes in each case.
- 9.13(a) Locate the angular nodes and nodal planes of each of the 2p orbitals of a hydrogenic atom of atomic number  $Z$ . To locate the angular nodes, give the angle that the plane makes with the  $z$ -axis.
- 9.13(b) Locate the angular nodes and nodal planes of each of the 3d orbitals of a hydrogenic atom of atomic number  $Z$ . To locate the angular nodes, give the angle that the plane makes with the  $z$ -axis.
- 9.14(a) Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (a)  $2s \rightarrow 1s$ , (b)  $2p \rightarrow 1s$ , (c)  $3d \rightarrow 2p$ ?
- 9.14(b) Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (a)  $2s \rightarrow 1s$ , (b)  $2p \rightarrow 1s$ , (c)  $3d \rightarrow 2p$ ?

### Problems\*

#### Numerical problems

- 9.1 The *Humphreys series* is a group of lines in the spectrum of atomic hydrogen. It begins at 12 368 nm and has been traced to 3281.4 nm. What are the transitions involved? What are the wavelengths of the intermediate transitions?
- 9.2 A series of lines in the spectrum of atomic hydrogen lies at 656.46 nm, 486.27 nm, 434.17 nm, and 410.29 nm. What is the wavelength of the next line in the series? What is the ionization energy of the atom when it is in the lower state of the transition?
- 9.3 The  $\text{Li}^{2+}$  ion is hydrogenic and has a Lyman series at 740 747  $\text{cm}^{-1}$ , 877 924  $\text{cm}^{-1}$ , 925 933  $\text{cm}^{-1}$ , and beyond. Show that the energy levels are of the form  $-hcR/n^2$  and find the value of  $R$  for this ion. Go on to predict the wavenumbers of the two longest-wavelength transitions of the Balmer series of the ion and find the ionization energy of the ion.

the spectrum are therefore expected to be hydrogen-like, the differences arising largely from the mass differences. Predict the wavenumbers of the first three lines of the Balmer series of positronium. What is the binding energy of the ground state of positronium?

9.9 The *Zeeman effect* is the modification of an atomic spectrum by the application of a strong magnetic field. It arises from the interaction between applied magnetic fields and the magnetic moments due to orbital and spin angular momenta (recall the evidence provided for electron spin by the Stern-Gerlach experiment, Section 8.8). To gain some appreciation for the so-called *normal Zeeman effect*, which is observed in transitions involving singlet states, consider a p electron, with  $l = 1$  and  $m_l = 0, \pm 1$ . In the absence of a magnetic field, these three states are degenerate. When a field of magnitude  $\mathcal{B}$  is present, the degeneracy is removed and it is observed that the state with  $m_l = +1$  moves up in energy by  $\mu_B \mathcal{B}$ , the state with  $m_l = 0$  is unchanged, and the state with  $m_l = -1$  moves down in energy by  $\mu_B \mathcal{B}$ , where  $\mu_B = e\hbar/2m_e = 9.274 \times 10^{-24} \text{ J T}^{-1}$  is the Bohr magneton (see Section 13.1). Therefore, a

## Molecular modelling and computational chemistry

Over the past two decades computational chemistry has evolved from a highly specialized tool, available to relatively few researchers, into a powerful and practical alternative to experimentation, accessible to all chemists. The driving force behind this evolution is the remarkable progress in computer

technology. Calculations that previously required hours or days on giant mainframe computers may now be completed in a fraction of time on a personal computer. It is natural and necessary that computational chemistry finds its way into the undergraduate chemistry curriculum as a hands-on experience, just as teaching experimental chemistry requires a laboratory experience. With these developments in the chemistry curriculum in mind, the text's website features a range of computational problems, which are intended to be performed with special software that can handle 'quantum chemical calculations'. Specifically, the problems have been designed with the student edition of Wavefunction's *Spartan* program (*Spartan Student*<sup>TM</sup>) in mind, although they could be completed with any electronic structure

program that allows Hartree-Fock, density functional and MP2 calculations.

It is necessary for students to recognize that calculations are not the same as experiments, and that each 'chemical model' built from calculations has its own strengths and shortcomings. With this caveat in mind, it is important that some of the problems yield results that can be compared directly with experimental data. However, most problems are intended to stand on their own, allowing computational chemistry to serve as an exploratory tool.

Students can visit [www.wavefun.com/cart/spartaned.html](http://www.wavefun.com/cart/spartaned.html) and enter promotional code WHFPCHEM to download the *Spartan Student*<sup>TM</sup> program at a special 20% discount.



# About the Book Companion Site

---

The Book Companion Site to accompany *Physical Chemistry 9e* provides teaching and learning resources to augment the printed book. It is free of charge, and provides additional material for download, much of which can be incorporated into a virtual learning environment.

The Book Companion Site can be accessed by visiting

[www.whfreeman.com/pchem](http://www.whfreeman.com/pchem)

Note that instructor resources are available only to registered adopters of the textbook. To register, simply visit [www.whfreeman.com/pchem](http://www.whfreeman.com/pchem) and follow the appropriate links. You will be given the opportunity to select your own username and password, which will be activated once your adoption has been verified.

Student resources are openly available to all, without registration.

## For students

### Living graphs

A *Living graph* can be used to explore how a property changes as a variety of parameters are changed. To encourage the use of this resource (and the more extensive *Explorations in physical chemistry*; see below), we have included a suggested *interActivity* to many of the illustrations in the text.

### Group theory tables

Comprehensive group theory tables are available for downloading.

## For instructors

### Artwork

An instructor may wish to use the figures from this text in a lecture. Almost all the figures are available in electronic format and can be used for lectures without charge (but not for commercial purposes without specific permission).

### Tables of data

All the tables of data that appear in the chapter text are available and may be used under the same conditions as the figures.

## Other resources

### *Explorations in Physical Chemistry* by Valerie Walters, Julio de Paula, and Peter Atkins

*Explorations in Physical Chemistry* consists of interactive Mathcad® worksheets, interactive Excel® workbooks, and stimulating exercises. They motivate students to simulate physical, chemical, and biochemical phenomena with their personal computers. Students can manipulate over 75 graphics, alter simulation parameters, and solve equations, to gain deeper insight into physical chemistry.

*Explorations in Physical Chemistry* is available as an integrated part of the eBook version of the text (see below). It can also be purchased on line at <http://www.whfreeman.com/explorations>.

### *Physical Chemistry, Ninth Edition* eBook

The eBook, which is a complete online version of the textbook itself, provides a rich learning experience by taking full advantage of the electronic medium. It brings together a range of student resources alongside additional functionality unique to the eBook. The eBook also offers lecturers unparalleled flexibility and customization options. The eBook can be purchased at [www.whfreeman.com/pchem](http://www.whfreeman.com/pchem).

Key features of the eBook include:

- Easy access from any Internet-connected computer via a standard Web browser.
- Quick, intuitive navigation to any section or subsection, as well as any printed book page number.
- Living Graph animations.
- Integration of *Explorations in Physical Chemistry*.
- Text **highlighting**, down to the level of individual phrases.
- A **book marking** feature that allows for quick reference to any page.
- A powerful **Notes** feature that allows students or instructors to add notes to any page.
- A full **index**.
- **Full-text search**, including an option to search the glossary and index.
- Automatic saving of all notes, highlighting, and bookmarks.

Additional features for instructors:

- Custom chapter selection: Instructors can choose the chapters that correspond with their syllabus, and students will get a custom version of the eBook with the selected chapters only.

- Instructor notes: Instructors can choose to create an annotated version of the eBook with their notes on any page. When students in their course log in, they will see the instructor's version.

- Custom content: Instructor notes can include text, web links, and images, allowing instructors to place any content they choose exactly where they want it.

### Physical Chemistry, 9e is available in two volumes!

For maximum flexibility in your physical chemistry course, this text is now offered as a traditional, full text or in two volumes. The chapters from Physical Chemistry, 9e, that appear each volume are as follows:

Volume 1: Thermodynamics and Kinetics (1-4292-3127-0)  
 Chapter 0: Fundamentals  
 Chapter 1: The properties of gases  
 Chapter 2: The First Law  
 Chapter 3: The Second Law  
 Chapter 4: Physical transformations of pure substances  
 Chapter 5: Simple mixtures  
 Chapter 6: Chemical equilibrium  
 Chapter 20: Molecules in motion  
 Chapter 21: The rates of chemical reactions  
 Chapter 22: Reaction dynamics  
 Chapter 23: Catalysis

Volume 2: Quantum Chemistry, Spectroscopy, and Statistical Thermodynamics (1-4292-3126-2)  
 Chapter 7: Quantum theory: introduction and principles  
 Chapter 8: Quantum theory: techniques and applications  
 Chapter 9: Atomic structure and spectra  
 Chapter 10: Molecular structure  
 Chapter 11: Molecular symmetry  
 Chapter 12: Molecular spectroscopy 1: rotational and vibrational spectra  
 Chapter 13: Molecular spectroscopy 2: electronic transitions  
 Chapter 14: Molecular spectroscopy 3: magnetic resonance  
 Chapter 15: Statistical thermodynamics 1: the concepts  
 Chapter 16: Statistical thermodynamics 2: applications

Chapters 17, 18, and 19 are not contained in the two volumes, but can be made available on-line on request.

### Solutions manuals

As with previous editions, Charles Trapp, Carmen Giunta, and Marshall Cady have produced the solutions manuals to accompany this book. A *Student's Solutions Manual* (978-1-4292-3128-2) provides full solutions to the 'b' exercises and the odd-numbered problems. An *Instructor's Solutions Manual* (978-1-4292-5032-0) provides full solutions to the 'a' exercises and the even-numbered problems.

## About the authors

---



Professor Peter Atkins is a fellow of Lincoln College, University of Oxford, and the author of more than sixty 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 a member of IUPAC's Physical and Biophysical Chemistry Division.



Julio de Paula is Professor of Chemistry at Lewis and 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.

# 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 eight editions.

Many people gave their advice based on the eighth edition of the text, and others reviewed the draft chapters for the ninth edition as they emerged. We would like to thank the following colleagues:

Adedoyin Adeyiga, Cheyney University of Pennsylvania

David Andrews, University of East Anglia

Richard Ansell, University of Leeds

Colin Bain, University of Durham

Godfrey Beddard, University of Leeds

Magnus Bergstrom, Royal Institute of Technology, Stockholm, Sweden

Mark Bier, Carnegie Mellon University

Robert Bohn, University of Connecticut

Stefan Bon, University of Warwick

Fernando Bresme, Imperial College, London

Melanie Britton, University of Birmingham

Ten Brinke, Groningen, Netherlands

Ria Broer, Groningen, Netherlands

Alexander Burin, Tulane University

Philip J. Camp, University of Edinburgh

David Cedenio, Illinois State University

Alan Chadwick, University of Kent

Li-Heng Chen, Aquinas College

Aurora Clark, Washington State University

Nigel Clarke, University of Durham

Ron Clarke, University of Sydney

David Cooper, University of Liverpool

Garry Crosson, University of Dayton

John Cullen, University of Manitoba

Rajeev Dabke, Columbus State University

Keith Davidson, University of Lancaster

Guy Dennault, University of Southampton

Caroline Dessent, University of York

Thomas DeVore, James Madison University

Michael Doescher, Benedictine University

Randy Dumont, McMaster University

Karen Edler, University of Bath

Timothy Ehler, Buena Vista University

Andrew Ellis, University of Leicester

Cherice Evans, The City University of New York

Ashleigh Fletcher, University of Newcastle

Jiali Gao, University of Minnesota

Sophya Garashchuk, University of South Carolina in Columbia

Benjamin Gherman, California State University

Peter Griffiths, Cardiff, University of Wales

Nick Greeves, University of Liverpool

Gerard Grobner, University of Umeå, Sweden

Anton Guliaev, San Francisco State University

Arun Gupta, University of Alabama

Leonid Gurevich, Aalborg, Denmark

Georg Harhner, St Andrews University

Ian Hamley, University of Reading

Chris Hardacre, Queens University Belfast

Anthony Harriman, University of Newcastle

Torsten Hegmann, University of Manitoba

Richard Henschman, University of Manchester

Ulf Henriksson, Royal Institute of Technology, Stockholm, Sweden

Harald Høiland, Bergen, Norway

Paul Hodgkinson, University of Durham

Phillip John, Heriot-Watt University

Robert Hillman, University of Leicester

Pat Holt, Bellarmine University

Andrew Horn, University of Manchester

Ben Horrocks, University of Newcastle

Rob A. Jackson, University of Keele

Seogjoo Jang, The City University of New York

Don Jenkins, University of Warwick

Matthew Johnson, Copenhagen, Denmark

Mats Johnsson, Royal Institute of Technology, Stockholm, Sweden

Milton Johnston, University of South Florida

Peter Karadakov, University of York

Dale Keefe, Cape Breton University

Jonathan Kenny, Tufts University

Peter Knowles, Cardiff, University of Wales

Ranjit Koodali, University Of South Dakota

Evguenii Kozliak, University of North Dakota

Krish Krishnan, California State University

Peter Kroll, University of Texas at Arlington

Kari Laasonen, University of Oulu, Finland

Ian Lane, Queens University Belfast

Stanley Latesky, University of the Virgin Islands

Daniel Lawson, University of Michigan

Adam Lee, University of York

Donál Leech, Galway, Ireland

Graham Leggett, University of Sheffield

Dewi Lewis, University College London

Goran Lindblom, University of Umeå, Sweden

Lesley Lloyd, University of Birmingham

John Lombardi, City College of New York

Zan Luthey-Schulten, University of Illinois at Urbana-Champaign

Michael Lyons, Trinity College Dublin

Alexander Lyubartsev, University of Stockholm

Jeffrey Mack, California State University

Paul Madden, University of Edinburgh

Arnold Maliniak, University of Stockholm

Herve Marand, Virginia Tech

Louis Massa, Hunter College  
 Andrew Masters, University of Manchester  
 Joe McDouall, University of Manchester  
 Gordon S. McDougall, University of Edinburgh  
 David McGarvey, University of Keele  
 Anthony Meijer, University of Sheffield  
 Robert Metzger, University of Alabama  
 Sergey Mikhlovsky, University of Brighton  
 Marcelo de Miranda, University of Leeds  
 Gerald Morine, Bemidji State University  
 Damien Murphy, Cardiff, University of Wales  
 David Newman, Bowling Green State University  
 Gareth Parkes, University of Huddersfield  
 Ruben Parra, DePaul University  
 Enrique Peacock-Lopez, Williams College  
 Nils-Ola Persson, Linköping University  
 Barry Pickup, University of Sheffield  
 Ivan Powis, University of Nottingham  
 Will Price, University of Wollongong, New South Wales, Australia  
 Robert Quandt, Illinois State University  
 Chris Rego, University of Leicester  
 Scott Reid, Marquette University  
 Gavin Reid, University of Leeds  
 Steve Roser, University of Bath  
 David Rowley, University College London  
 Alan Ryder, Galway, Ireland  
 Karl Ryder, University of Leicester  
 Stephen Saeur, Copenhagen, Denmark  
 Sven Schroeder, University of Manchester  
 Jeffrey Shepherd, Laurentian University  
 Paul Siders, University of Minnesota Duluth  
 Richard Singer, University of Kingston  
 Carl Soennischsen, The Johannes Gutenberg University of Mainz  
 Jie Song, University of Michigan  
 David Steytler, University of East Anglia  
 Michael Stockenhuber, Nottingham-Trent University

Sven Stolen, University of Oslo  
 Emile Charles Sykes, Tufts University  
 Greg Szulczewski, University of Alabama  
 Annette Taylor, University of Leeds  
 Peter Taylor, University of Warwick  
 Jeremy Titman, University of Nottingham  
 Jeroen Van-Duijneveldt, University of Bristol  
 Joop van Lenthe, University of Utrecht  
 Peter Varnai, University of Sussex  
 Jay Wadhawan, University of Hull  
 Palle Waage Jensen, University of Southern Denmark  
 Darren Walsh, University of Nottingham  
 Kjell Waltersson, Mälardalen University, Sweden  
 Richard Wells, University of Aberdeen  
 Ben Whitaker, University of Leeds  
 Kurt Winkelmann, Florida Institute of Technology  
 Timothy Wright, University of Nottingham  
 Yuanzheng Yue, Aalborg, Denmark  
 David Zax, Cornell University

We would like to thank two colleagues for their special contribution. Kerry Karaktis (Harvey Mudd College) provided many useful suggestions that focused on applications of the material presented in the text. David Smith (University of Bristol) made detailed comments on many of the chapters.

We also thank Claire Eisenhandler and Valerie Walters, who read through the proofs with meticulous attention to detail and caught in private what might have been a public grief. Our warm thanks also go to Charles Trapp, Carmen Giunta, and Marshall Cady who have produced the *Solutions manuals* that accompany this book.

Last, but by no means least, we would also like to thank our two publishers, Oxford University Press and W.H. Freeman & Co., for their constant encouragement, advice, and assistance, and in particular our editors Jonathan Crowe and Jessica Fiorillo. Authors could not wish for a more congenial publishing environment.

*This page intentionally left blank*

# Summary of contents

---

Fundamentals	1
<b>PART 1 Equilibrium</b>	<b>17</b>
1 The properties of gases	19
Mathematical background 1: Differentiation and integration	42
2 The First Law	44
Mathematical background 2: Multivariate calculus	91
3 The Second Law	94
4 Physical transformations of pure substances	135
5 Simple mixtures	156
6 Chemical equilibrium	209
<b>PART 2 Structure</b>	<b>247</b>
7 Quantum theory: introduction and principles	249
Mathematical background 3: Complex numbers	286
8 Quantum theory: techniques and applications	288
Mathematical background 4: Differential equations	322
9 Atomic structure and spectra	324
Mathematical background 5: Vectors	368
10 Molecular structure	371
Mathematical background 6: Matrices	414
11 Molecular symmetry	417
12 Molecular spectroscopy 1: rotational and vibrational spectra	445
13 Molecular spectroscopy 2: electronic transitions	489
14 Molecular spectroscopy 3: magnetic resonance	520
15 Statistical thermodynamics 1: the concepts	564
16 Statistical thermodynamics 2: applications	592
17 Molecular interactions	622
18 Materials 1: macromolecules and self-assembly	659
19 Materials 2: solids	695
Mathematical background 7: Fourier series and Fourier transforms	740
<b>PART 3 Change</b>	<b>743</b>
20 Molecules in motion	745
21 The rates of chemical reactions	782
22 Reaction dynamics	831
23 Catalysis	876
Resource section	909
Answers to exercises and odd-numbered problems	948
Index	959

*This page intentionally left blank*



# Contents

<b>Fundamentals</b>	<b>1</b>	<b>Thermochemistry</b>	<b>65</b>
<b>F.1</b> Atoms	1	<b>2.7</b> Standard enthalpy changes	65
<b>F.2</b> Molecules	2	<b>I2.1</b> Impact on biology: Food and energy reserves	70
<b>F.3</b> Bulk matter	4	<b>2.8</b> Standard enthalpies of formation	71
<b>F.4</b> Energy	6	<b>2.9</b> The temperature dependence of reaction enthalpies	73
<b>F.5</b> The relation between molecular and bulk properties	7	<b>State functions and exact differentials</b>	<b>74</b>
<b>F.6</b> The electromagnetic field	9	<b>2.10</b> Exact and inexact differentials	74
<b>F.7</b> Units	10	<b>2.11</b> Changes in internal energy	75
Exercises	13	<b>2.12</b> The Joule–Thomson effect	79
		Checklist of key equations	83
		Further information 2.1: Adiabatic processes	84
		Further information 2.2: The relation between heat capacities	84
		Discussion questions	85
		Exercises	85
		Problems	88
<b>PART 1 Equilibrium</b>	<b>17</b>	<b>Mathematical background 2: Multivariate calculus</b>	<b>91</b>
<b>1 The properties of gases</b>	<b>19</b>	<b>MB2.1</b> Partial derivatives	91
<b>The perfect gas</b>	<b>19</b>	<b>MB2.2</b> Exact differentials	92
<b>1.1</b> The states of gases	19	<b>3 The Second Law</b>	<b>94</b>
<b>1.2</b> The gas laws	23	<b>The direction of spontaneous change</b>	<b>95</b>
<b>I1.1</b> Impact on environmental science: The gas laws and the weather	28	<b>3.1</b> The dispersal of energy	95
<b>Real gases</b>	<b>29</b>	<b>3.2</b> Entropy	96
<b>1.3</b> Molecular interactions	30	<b>I3.1</b> Impact on engineering: Refrigeration	103
<b>1.4</b> The van der Waals equation	33	<b>3.3</b> Entropy changes accompanying specific processes	104
Checklist of key equations	37	<b>3.4</b> The Third Law of thermodynamics	109
Discussion questions	38	<b>I3.2</b> Impact on materials chemistry: Crystal defects	112
Exercises	38	<b>Concentrating on the system</b>	<b>113</b>
Problems	39	<b>3.5</b> The Helmholtz and Gibbs energies	113
<b>Mathematical background 1: Differentiation and integration</b>	<b>42</b>	<b>3.6</b> Standard molar Gibbs energies	118
<b>2 The First Law</b>	<b>44</b>	<b>Combining the First and Second Laws</b>	<b>121</b>
<b>The basic concepts</b>	<b>44</b>	<b>3.7</b> The fundamental equation	121
<b>2.1</b> Work, heat, and energy	45	<b>3.8</b> Properties of the internal energy	121
<b>2.2</b> The internal energy	47	<b>3.9</b> Properties of the Gibbs energy	124
<b>2.3</b> Expansion work	49	Checklist of key equations	128
<b>2.4</b> Heat transactions	53	Further information 3.1: The Born equation	128
<b>2.5</b> Enthalpy	56	Further information 3.2: The fugacity	129
<b>I2.1</b> Impact on biochemistry and materials science: Differential scanning calorimetry	62		
<b>2.6</b> Adiabatic changes	63		

Discussion questions	130	<b>6 Chemical equilibrium</b>	<b>209</b>
Exercises	131		
Problems	132		
<b>4 Physical transformations of pure substances</b>	<b>135</b>		
<b>Phase diagrams</b>	<b>135</b>	<b>Spontaneous chemical reactions</b>	<b>209</b>
<b>4.1</b> The stabilities of phases	135	<b>6.1</b> The Gibbs energy minimum	210
<b>4.2</b> Phase boundaries	137	<b>16.1</b> Impact on biochemistry: Energy conversion in biological cells	211
<b>4.3</b> Three representative phase diagrams	140	<b>6.2</b> The description of equilibrium	213
<b>14.1</b> Impact on technology: Supercritical fluids	142	<b>The response of equilibria to the conditions</b>	<b>221</b>
<b>Thermodynamic aspects of phase transitions</b>	<b>143</b>	<b>6.3</b> How equilibria respond to changes of pressure	221
<b>4.4</b> The dependence of stability on the conditions	143	<b>6.4</b> The response of equilibria to changes of temperature	223
<b>4.5</b> The location of phase boundaries	146	<b>16.2</b> Impact on technology: Supramolecular chemistry	226
<b>4.6</b> The Ehrenfest classification of phase transitions	149	<b>Equilibrium electrochemistry</b>	<b>227</b>
Checklist of key equations	152	<b>6.5</b> Half-reactions and electrodes	228
Discussion questions	152	<b>6.6</b> Varieties of cells	229
Exercises	153	<b>6.7</b> The cell potential	230
Problems	154	<b>6.8</b> Standard electrode potentials	233
		<b>6.9</b> Applications of standard potentials	235
<b>5 Simple mixtures</b>	<b>156</b>	<b>16.3</b> Impact on technology: Species-selective electrodes	239
<b>The thermodynamic description of mixtures</b>	<b>156</b>	Checklist of key equations	240
<b>5.1</b> Partial molar quantities	157	Discussion questions	241
<b>5.2</b> The thermodynamics of mixing	161	Exercises	241
<b>5.3</b> The chemical potentials of liquids	164	Problems	243
<b>The properties of solutions</b>	<b>167</b>	<b>PART 2 Structure</b>	<b>247</b>
<b>5.4</b> Liquid mixtures	167		
<b>5.5</b> Colligative properties	169	<b>7 Quantum theory: introduction and principles</b>	<b>249</b>
<b>15.1</b> Impact on biology: Osmosis in physiology and biochemistry	175	<b>The origins of quantum mechanics</b>	<b>249</b>
<b>Phase diagrams of binary systems</b>	<b>176</b>	<b>7.1</b> Energy quantization	250
<b>5.6</b> Vapour pressure diagrams	176	<b>7.2</b> Wave–particle duality	255
<b>5.7</b> Temperature–composition diagrams	179	<b>17.1</b> Impact on biology: Electron microscopy	259
<b>5.8</b> Liquid–liquid phase diagrams	181	<b>The dynamics of microscopic systems</b>	<b>260</b>
<b>5.9</b> Liquid–solid phase diagrams	185	<b>7.3</b> The Schrödinger equation	260
<b>15.2</b> Impact on materials science: Liquid crystals	188	<b>7.4</b> The Born interpretation of the wavefunction	262
<b>Activities</b>	<b>190</b>	<b>Quantum mechanical principles</b>	<b>266</b>
<b>5.10</b> The solvent activity	190	<b>7.5</b> The information in a wavefunction	266
<b>5.11</b> The solute activity	191	<b>7.6</b> The uncertainty principle	276
<b>5.12</b> The activities of regular solutions	194	<b>7.7</b> The postulates of quantum mechanics	279
<b>5.13</b> The activities of ions in solution	195	Checklist of key equations	280
Checklist of key equations	198	Further information 7.1: Classical mechanics	280
Further information 5.1: The Debye–Hückel theory of ionic solutions	199	Discussion questions	283
Discussion questions	200	Exercises	283
Exercises	201	Problems	284
Problems	204		

<b>Mathematical background 3: Complex numbers</b>	<b>286</b>	Further information 9.2: The energy of spin–orbit interaction	363
<b>MB3.1</b> Definitions	286	Discussion questions	363
<b>MB3.2</b> Polar representation	286	Exercises	364
<b>MB3.3</b> Operations	287	Problems	365
<b>8 Quantum theory: techniques and applications</b>	<b>288</b>	<b>Mathematical background 5: Vectors</b>	<b>368</b>
<b>Translational motion</b>	<b>288</b>	<b>MB5.1</b> Addition and subtraction	368
<b>8.1</b> A particle in a box	289	<b>MB5.2</b> Multiplication	369
<b>8.2</b> Motion in two and more dimensions	293	<b>MB5.3</b> Differentiation	369
<b>I8.1</b> Impact on nanoscience: Quantum dots	295	<b>10 Molecular structure</b>	<b>371</b>
<b>8.3</b> Tunnelling	297	<b>The Born–Oppenheimer approximation</b>	<b>372</b>
<b>I8.2</b> Impact on nanoscience: Scanning probe microscopy	299	<b>Valence-bond theory</b>	<b>372</b>
<b>Vibrational motion</b>	<b>300</b>	<b>10.1</b> Homonuclear diatomic molecules	372
<b>8.4</b> The energy levels	301	<b>10.2</b> Polyatomic molecules	374
<b>8.5</b> The wavefunctions	302	<b>Molecular orbital theory</b>	<b>378</b>
<b>Rotational motion</b>	<b>306</b>	<b>10.3</b> The hydrogen molecule-ion	378
<b>8.6</b> Rotation in two dimensions: a particle on a ring	306	<b>10.4</b> Homonuclear diatomic molecules	382
<b>8.7</b> Rotation in three dimensions: the particle on a sphere	310	<b>10.5</b> Heteronuclear diatomic molecules	388
<b>8.8</b> Spin	315	<b>I10.1</b> Impact on biochemistry: The biochemical reactivity of O <sub>2</sub> , N <sub>2</sub> , and NO	394
Checklist of key equations	317	<b>Molecular orbitals for polyatomic systems</b>	<b>395</b>
Discussion questions	317	<b>10.6</b> The Hückel approximation	395
Exercises	317	<b>10.7</b> Computational chemistry	401
Problems	319	<b>10.8</b> The prediction of molecular properties	405
<b>Mathematical background 4: Differential equations</b>	<b>322</b>	Checklist of key equations	407
<b>MB4.1</b> The structure of differential equations	322	Further information 10.1: Details of the Hartree–Fock method	408
<b>MB4.2</b> The solution of ordinary differential equations	322	Discussion questions	409
<b>MB4.3</b> The solution of partial differential equations	323	Exercises	409
<b>9 Atomic structure and spectra</b>	<b>324</b>	Problems	410
<b>The structure and spectra of hydrogenic atoms</b>	<b>324</b>	<b>Mathematical background 6: Matrices</b>	<b>414</b>
<b>9.1</b> The structure of hydrogenic atoms	325	<b>MB6.1</b> Definitions	414
<b>9.2</b> Atomic orbitals and their energies	330	<b>MB6.2</b> Matrix addition and multiplication	414
<b>9.3</b> Spectroscopic transitions and selection rules	339	<b>MB6.3</b> Eigenvalue equations	415
<b>The structures of many-electron atoms</b>	<b>340</b>	<b>11 Molecular symmetry</b>	<b>417</b>
<b>9.4</b> The orbital approximation	341	<b>The symmetry elements of objects</b>	<b>417</b>
<b>9.5</b> Self-consistent field orbitals	349	<b>11.1</b> Operations and symmetry elements	418
<b>The spectra of complex atoms</b>	<b>350</b>	<b>11.2</b> The symmetry classification of molecules	420
<b>9.6</b> Linewidths	350	<b>11.3</b> Some immediate consequences of symmetry	425
<b>9.7</b> Quantum defects and ionization limits	352	<b>Applications to molecular orbital theory and spectroscopy</b>	<b>427</b>
<b>9.8</b> Singlet and triplet states	353	<b>11.4</b> Character tables and symmetry labels	427
<b>9.9</b> Spin–orbit coupling	354	<b>11.5</b> Vanishing integrals and orbital overlap	433
<b>9.10</b> Term symbols and selection rules	357	<b>11.6</b> Vanishing integrals and selection rules	439
<b>I9.1</b> Impact on astrophysics: Spectroscopy of stars	361		
Checklist of key equations	362		
Further information 9.1: The separation of motion	362		

Checklist of key equations	441	<b>The fates of electronically excited states</b>	<b>503</b>
Discussion questions	441	<b>13.4</b> Fluorescence and phosphorescence	503
Exercises	441	<b>I13.2</b> Impact on biochemistry: Fluorescence microscopy	507
Problems	442	<b>13.5</b> Dissociation and predissociation	507
		<b>13.6</b> Laser action	508
		Checklist of key equations	512
		Further information 13.1: Examples of practical lasers	513
		Discussion questions	515
		Exercises	515
		Problems	517
<b>12 Molecular spectroscopy 1: rotational and vibrational spectra</b>	<b>445</b>	<b>14 Molecular spectroscopy 3: magnetic resonance</b>	<b>520</b>
<b>General features of molecular spectroscopy</b>	<b>446</b>	<b>The effect of magnetic fields on electrons and nuclei</b>	<b>520</b>
<b>12.1</b> Experimental techniques	446	<b>14.1</b> The energies of electrons in magnetic fields	521
<b>12.2</b> Selection rules and transition moments	447	<b>14.2</b> The energies of nuclei in magnetic fields	522
<b>I12.1</b> Impact on astrophysics: Rotational and vibrational spectroscopy of interstellar species	447	<b>14.3</b> Magnetic resonance spectroscopy	523
<b>Pure rotation spectra</b>	<b>449</b>	<b>Nuclear magnetic resonance</b>	<b>524</b>
<b>12.3</b> Moments of inertia	449	<b>14.4</b> The NMR spectrometer	525
<b>12.4</b> The rotational energy levels	452	<b>14.5</b> The chemical shift	526
<b>12.5</b> Rotational transitions	456	<b>14.6</b> The fine structure	532
<b>12.6</b> Rotational Raman spectra	459	<b>14.7</b> Conformational conversion and exchange processes	539
<b>12.7</b> Nuclear statistics and rotational states	460	<b>Pulse techniques in NMR</b>	<b>540</b>
<b>The vibrations of diatomic molecules</b>	<b>462</b>	<b>14.8</b> The magnetization vector	540
<b>12.8</b> Molecular vibrations	462	<b>14.9</b> Spin relaxation	542
<b>12.9</b> Selection rules	464	<b>I14.1</b> Impact on medicine: Magnetic resonance imaging	546
<b>12.10</b> Anharmonicity	465	<b>14.10</b> Spin decoupling	548
<b>12.11</b> Vibration–rotation spectra	468	<b>14.11</b> The nuclear Overhauser effect	548
<b>12.12</b> Vibrational Raman spectra of diatomic molecules	469	<b>14.12</b> Two-dimensional NMR	550
<b>The vibrations of polyatomic molecules</b>	<b>470</b>	<b>14.13</b> Solid-state NMR	551
<b>12.13</b> Normal modes	471	<b>Electron paramagnetic resonance</b>	<b>553</b>
<b>12.14</b> Infrared absorption spectra of polyatomic molecules	472	<b>14.14</b> The EPR spectrometer	553
<b>I12.2</b> Impact on environmental science: Climate change	473	<b>14.15</b> The g-value	553
<b>12.15</b> Vibrational Raman spectra of polyatomic molecules	475	<b>14.16</b> Hyperfine structure	555
<b>12.16</b> Symmetry aspects of molecular vibrations	476	<b>I14.2</b> Impact on biochemistry and nanoscience: Spin probes	557
Checklist of key equations	479	Checklist of key equations	559
Further information 12.1: Spectrometers	479	Further information 14.1: Fourier transformation of the FID curve	559
Further information 12.2: Selection rules for rotational and vibrational spectroscopy	482	Discussion questions	559
Discussion questions	484	Exercises	560
Exercises	484	Problems	561
Problems	486		
<b>13 Molecular spectroscopy 2: electronic transitions</b>	<b>489</b>	<b>15 Statistical thermodynamics 1: the concepts</b>	<b>564</b>
<b>The characteristics of electronic transitions</b>	<b>489</b>	<b>The distribution of molecular states</b>	<b>565</b>
<b>13.1</b> Measurements of intensity	490	<b>15.1</b> Configurations and weights	565
<b>13.2</b> The electronic spectra of diatomic molecules	491	<b>15.2</b> The molecular partition function	568
<b>13.3</b> The electronic spectra of polyatomic molecules	498		
<b>I13.1</b> Impact on biochemistry: Vision	501		

<b>The internal energy and the entropy</b>	<b>574</b>	<b>17.6</b> Repulsive and total interactions	642
<b>15.3</b> The internal energy	574	<b>I17.2</b> Impact on materials science: Hydrogen storage in molecular clathrates	643
<b>15.4</b> The statistical entropy	576		
<b>I15.1</b> Impact on technology: Reaching very low temperatures	578	<b>Gases and liquids</b>	<b>643</b>
<b>The canonical partition function</b>	<b>579</b>	<b>17.7</b> Molecular interactions in gases	644
<b>15.5</b> The canonical ensemble	579	<b>17.8</b> The liquid–vapour interface	645
<b>15.6</b> The thermodynamic information in the partition function	581	<b>17.9</b> Surface films	649
<b>15.7</b> Independent molecules	582	<b>17.10</b> Condensation	652
Checklist of key equations	585	Checklist of key equations	653
Further information 15.1: The Boltzmann distribution	585	Further information 17.1: The dipole–dipole interaction	654
Further information 15.2: The Boltzmann formula	587	Further information 17.2: The basic principles of molecular beams	654
Discussion questions	588	Discussion questions	655
Exercises	588	Exercises	655
Problems	590	Problems	656
<b>16 Statistical thermodynamics 2: applications</b>	<b>592</b>	<b>18 Materials 1: macromolecules and self-assembly</b>	<b>659</b>
<b>Fundamental relations</b>	<b>592</b>	<b>Structure and dynamics</b>	<b>659</b>
<b>16.1</b> The thermodynamic functions	592	<b>18.1</b> The different levels of structure	660
<b>16.2</b> The molecular partition function	594	<b>18.2</b> Random coils	660
<b>Using statistical thermodynamics</b>	<b>601</b>	<b>18.3</b> The mechanical properties of polymers	665
<b>16.3</b> Mean energies	601	<b>18.4</b> The electrical properties of polymers	667
<b>16.4</b> Heat capacities	602	<b>18.5</b> The structures of biological macromolecules	667
<b>16.5</b> Equations of state	605	<b>Aggregation and self-assembly</b>	<b>671</b>
<b>16.6</b> Molecular interactions in liquids	607	<b>18.6</b> Colloids	671
<b>16.7</b> Residual entropies	609	<b>18.7</b> Micelles and biological membranes	674
<b>16.8</b> Equilibrium constants	610	<b>Determination of size and shape</b>	<b>677</b>
<b>I16.1</b> Impact on biochemistry: The helix–coil transition in polypeptides	615	<b>18.8</b> Mean molar masses	678
Checklist of key equations	616	<b>18.9</b> The techniques	680
Further information 16.1: The rotational partition function of a symmetric rotor	617	Checklist of key equations	688
Discussion questions	618	Further information 18.1: Random and nearly random coils	689
Exercises	618	Discussion questions	690
Problems	619	Exercises	690
<b>17 Molecular interactions</b>	<b>622</b>	Problems	691
<b>Electric properties of molecules</b>	<b>622</b>	<b>19 Materials 2: solids</b>	<b>695</b>
<b>17.1</b> Electric dipole moments	622	<b>Crystallography</b>	<b>695</b>
<b>17.2</b> Polarizabilities	625	<b>19.1</b> Lattices and unit cells	695
<b>17.3</b> Polarization	626	<b>19.2</b> The identification of lattice planes	697
<b>17.4</b> Relative permittivities	628	<b>19.3</b> The investigation of structure	699
<b>Interactions between molecules</b>	<b>631</b>	<b>19.4</b> Neutron and electron diffraction	708
<b>17.5</b> Interactions between dipoles	631	<b>19.5</b> Metallic solids	709
<b>I17.1</b> Impact on medicine: Molecular recognition and drug design	640	<b>19.6</b> Ionic solids	711
		<b>19.7</b> Molecular solids and covalent networks	714
		<b>I19.1</b> Impact on biochemistry: X-ray crystallography of biological macromolecules	715

<b>The properties of solids</b>	<b>717</b>	<b>21 The rates of chemical reactions</b>	<b>782</b>
19.8 Mechanical properties	717	<b>Empirical chemical kinetics</b>	<b>782</b>
19.9 Electrical properties	719	21.1 Experimental techniques	783
I19.2 Impact on nanoscience: Nanowires	723	21.2 The rates of reactions	786
19.10 Optical properties	724	21.3 Integrated rate laws	790
19.11 Magnetic properties	728	21.4 Reactions approaching equilibrium	796
19.12 Superconductors	731	21.5 The temperature dependence of reaction rates	799
Checklist of key equations	733	<b>Accounting for the rate laws</b>	<b>802</b>
Further information 19.1: Solid state lasers and light-emitting diodes	733	21.6 Elementary reactions	802
Discussion questions	734	21.7 Consecutive elementary reactions	803
Exercises	735	<b>Examples of reaction mechanisms</b>	<b>809</b>
Problems	737	21.8 Unimolecular reactions	809
<b>Mathematical background 7: Fourier series and Fourier transforms</b>	<b>740</b>	21.9 Polymerization kinetics	811
MB7.1 Fourier series	740	21.10 Photochemistry	815
MB7.2 Fourier transforms	741	I21.1 Impact on biochemistry: Harvesting of light during plant photosynthesis	822
MB7.3 The convolution theorem	742	Checklist of key equations	825
<b>PART 3 Change</b>	<b>743</b>	Discussion questions	825
<b>20 Molecules in motion</b>	<b>745</b>	Exercises	826
<b>Molecular motion in gases</b>	<b>745</b>	Problems	828
20.1 The kinetic model of gases	746	<b>22 Reaction dynamics</b>	<b>831</b>
I20.1 Impact on astrophysics: The Sun as a ball of perfect gas	752	<b>Reactive encounters</b>	<b>831</b>
20.2 Collisions with walls and surfaces	753	22.1 Collision theory	832
20.3 The rate of effusion	754	22.2 Diffusion-controlled reactions	839
20.4 Transport properties of a perfect gas	755	22.3 The material balance equation	842
<b>Molecular motion in liquids</b>	<b>758</b>	<b>Transition state theory</b>	<b>843</b>
20.5 Experimental results	758	22.4 The Eyring equation	844
20.6 The conductivities of electrolyte solutions	759	22.5 Thermodynamic aspects	848
20.7 The mobilities of ions	760	<b>The dynamics of molecular collisions</b>	<b>851</b>
I20.2 Impact on biochemistry: Ion channels	764	22.6 Reactive collisions	851
<b>Diffusion</b>	<b>766</b>	22.7 Potential energy surfaces	852
20.8 The thermodynamic view	766	22.8 Some results from experiments and calculations	853
20.9 The diffusion equation	770	<b>The dynamics of electron transfer</b>	<b>856</b>
20.10 Diffusion probabilities	772	22.9 Electron transfer in homogeneous systems	857
20.11 The statistical view	773	22.10 Electron transfer processes at electrodes	861
Checklist of key equations	774	I22.1 Impact on technology: Fuel cells	867
Further information 20.1: The transport characteristics of a perfect gas	775	Checklist of key equations	868
Discussion questions	776	Further information 22.1: The Gibbs energy of activation of electron transfer	868
Exercises	777	Further information 22.2: The Butler–Volmer equation	869
Problems	779	Discussion questions	871
		Exercises	871
		Problems	873