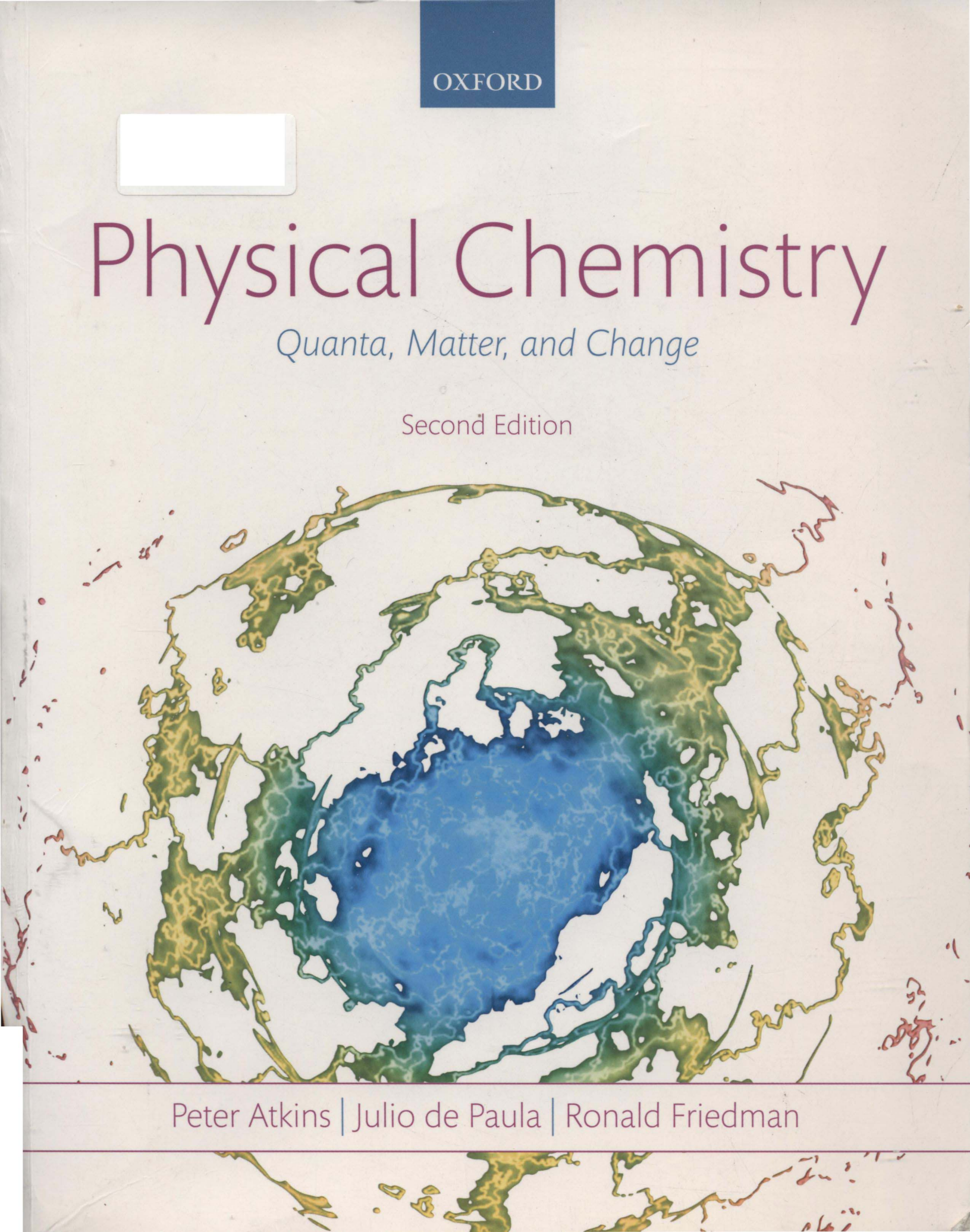# Physical Chemistry

Quanta, Matter, and Change

Second Edition

Peter Atkins | Julio de Paula | Ronald Friedman

PHYSICAL CHEMISTRY

Quanta, Matter, and Change

Second edition

Peter Atkins

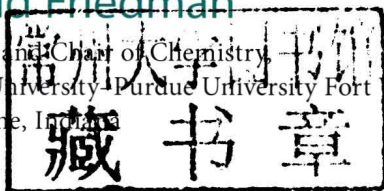Fellow of Lincoln College, Oxford

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FUNDAMENTAL CONSTANTS

Constant	Symbol	Value	Power of 10	Units
Speed of light	c	2.997 924 58*	10^8	$m\ s^{-1}$
Elementary charge	e	1.602 176 565	10^{-19}	C
Planck's constant	h	6.626 069 57	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 571 726	10^{-34}	J s
Boltzmann's constant	k	1.380 6488	10^{-23}	$J\ K^{-1}$
Avogadro's constant	N_A	6.022 141 29	10^{23}	mol^{-1}
Gas constant	$R = N_A k$	8.314 4621		$J\ K^{-1}\ mol^{-1}$
Faraday's constant	$F = N_A e$	9.648 533 65	10^4	$C\ mol^{-1}$
Mass				
electron	m_e	9.109 382 91	10^{-31}	kg
proton	m_p	1.672 621 777	10^{-27}	kg
neutron	m_n	1.674 927 351	10^{-27}	kg
atomic mass constant	m_u	1.660 538 921	10^{-27}	kg
Vacuum permeability	μ_0	4π*	10^{-7}	$J\ s^2\ C^{-2}\ m^{-1}$
Vacuum permittivity	$\varepsilon_0 = 1/\mu_0 c^2$	8.854 187 817	10^{-12}	$J^{-1}\ C^2\ m^{-1}$
	$4\pi\varepsilon_0$	1.112 650 056	10^{-10}	$J^{-1}\ C^2\ m^{-1}$
Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 009 68	10^{-24}	$J\ T^{-1}$
Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.050 783 53	10^{-27}	$J\ T^{-1}$
Proton magnetic moment	μ_p	1.410 606 743	10^{-26}	$J\ T^{-1}$
g-Value of electron	g_e	2.002 319 304		
Magnetogyric ratio				
electron	$\gamma_e = -g_e e/2m_e$	−1.001 159 652	10^{10}	$C\ kg^{-1}$
proton	$\gamma_p = 2\mu_p/\hbar$	2.675 222 004	10^8	$C\ kg^{-1}$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/e^2 m_e$	5.291 772 109	10^{-11}	m
Rydberg constant	$\tilde{R}_\infty = m_e e^4/8h^3 c\varepsilon_0^2$	1.097 373 157	10^5	cm^{-1}
	$hc\tilde{R}_\infty/e$	13.605 692 53		eV
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 352 5698	10^{-3}	
	α^{-1}	1.370 359 990 74	10^2	
Second radiation constant	$c_2 = hc/k$	1.438 777 0	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3 c^2$	5.670 373	10^{-8}	$W\ m^{-2}\ K^{-4}$
Standard acceleration of free fall	g	9.806 65*		$m\ s^{-2}$
Gravitational constant	G	6.673 84	10^{-11}	$N\ m^2\ kg^{-2}$

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

ABOUT THE BOOK

This new edition follows the approach of the first edition in so far as it puts quantum theory in the forefront of the development, but we have transformed the presentation. Instead of the chapters of conventional texts, we have presented the material as a series of short *Topics* arranged into thematic groups we call *Focuses*. Our aim is to present reader and instructor with maximum flexibility. Although we had in mind a particular sequence when writing the book, we acknowledge that instructors might have different ideas. The division into many Topics will allow the instructor to tailor the text within the time constraints of the course as omissions will be much easier to make. The student should also find the Topics easier to assimilate and review. No longer is it necessary to take a linear path through chapters. Instead, students and instructors can match the choice of Topics to their learning objectives. Indeed, we have carefully avoided language that suggests the Topics have been read in the order they appear in the book.

We did consider avoiding any implication of structure, but came to the view that because the Topics do fall into thematic groups it would be sensible to acknowledge that fact. Moreover, we wanted the student, if not the instructor, to appreciate the intellectual coherence of the subject and to understand the context of each Topic. Each Focus therefore begins with a brief discussion of how its Topics cover a shared theme and how that theme links to others in the book. This contextual relationship is also captured by the 'Road Map' that lies at the head of each Focus. These maps also indicate not only how the Topics relate to each other but how certain Topics can be discarded and how each one draws on and feeds into other Focus groups. We wanted to convey the intellectual structure of the subject without imposing our will on its order of presentation.

We have focused on helping students master this sometimes daunting material. Thus, each Topic opens with three questions a student typically asks: 'Why do you need to know this material?', 'What is the key idea?', and 'What do you need to know already?'. The answers to the third question point to other Topics that we consider appropriate to have studied or at least to refer to as background to the current Topic.

This edition has more *Examples*, which require readers to collect and organize their thoughts about how to proceed, and more *Brief illustrations*, which show how to use an equation in a straightforward way. Both have *Self-tests* to enable the reader to assess their grasp of the material. In response to requests from students and reviewers, we have added more steps to many of the derivations of equations and solutions of Examples and have added hints about how to go from one expression to the next. Furthermore, we bring to this edition a new feature: *The chemist's toolkit*, which offers quick and immediate help on a concept from mathematics or physics. The *Mathematical background* sections provide more support and appear where we judge they are most needed. We have structured the end-of-Focus *Discussion questions*, *Exercises*, and *Problems* to match the grouping of the Topics, but have added Topic- and Focus-crossing *Integrated activities* to emphasize that no Topic is an island. We have added new material throughout the text and have incorporated as Topics sections that were previously 'Further information' sections.

Teaching and learning are being transformed by technology, and this edition of the text incorporates several web-based resources that enhance learning: they are identified in the *How to use this book* section that follows this preface.

We hope that you will enjoy using this text as much as we have enjoyed writing it. As ever, we hope that you will contact us with your suggestions for its continued improvement.

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RSF

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USING THE BOOK

For the second edition of *Physical Chemistry: Quanta, Matter, and Change* we have tailored the text even more closely to meet the needs of students. First, it has been radically re-organized to improve its accessibility, clarity, and flexibility. Second, in addition to the variety of learning features already present in the first edition, we have significantly enhanced the mathematics support by adding new Chemist's toolkit boxes, equation annotations and labels, and checklists of key equations at the end of each Topic.

Organizing the information

➤ Innovative new structure

Instead of being organized into chapters, the material is presented as 97 short Topics grouped into 20 Focus sections. The 'Roadmaps' at the beginning of each Focus group show you the connections between the different Topics. Then each Topic opens with a comment on why it is important, a statement of the key idea, and a short summary of the background needed.

FOCUS 1 ON Foundations

Topic 1	Topic 2	Topic 3	The entire text
Matter	Energy	Waves	
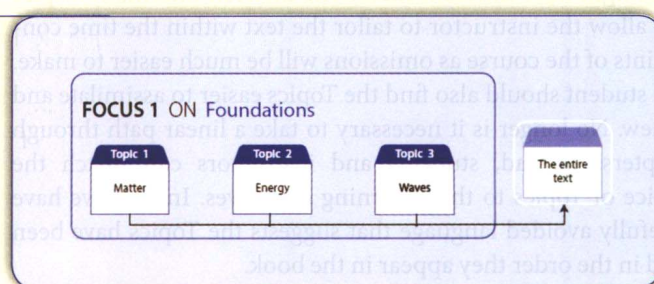
➤ Notes on good practice

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

A note on good practice Be careful to distinguish atomic or molecular mass (the mass of a single atom or molecule; units kg) from molar mass (the mass per mole of atoms or molecules; units kg mol^{-1}). *Relative* molecular masses of atoms and molecules, $M_r = m/m_u$, where m is the mass of the atom or molecule and m_u is the atomic mass constant (see inside front cover), are still widely called 'atomic weights' and 'molecular weights' even though they are dimensionless quantities and not weights (the gravitational force exerted on an object).

➤ Resource section

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

PART 1 Common integrals

Algebraic functions

A.1 $\int x^n dx = \frac{x^{n+1}}{n+1} + \text{constant}, \ n \neq -1$

A.2 $\int \frac{1}{x} dx = \ln x + \text{constant}$

Exponential functions

E.1 $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}, \quad n! = n(n-1)\dots1; \ 0! \equiv 1$

E.2 $\int_0^\infty \frac{x^3 e^x}{(e^x - 1)^2} dx = \frac{\pi^4}{15}$

Gaussian functions

G.1 $\int_0^\infty e^{-ax^2} dx = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$

G.2 $\int_0^\infty x e^{-ax^2} dx = \frac{1}{2a}$

G.3 $\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}$

G.4 $\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2}$

T.2 $\int \sin^2 ax \, dx = \frac{1}{2}x - \frac{\sin 2ax}{4a} + \text{constant}$

T.3 $\int \sin^3 ax \, dx = -\frac{(\sin^2 ax + 2)\cos ax}{3a} + \text{constant}$

T.4 $\int \sin^4 ax \, dx = \frac{3x}{8} - \frac{3}{8a}\sin ax \cos ax - \frac{1}{4a}\sin^3 ax \cos ax + \text{constant}$

T.5 $\int \sin ax \sin bx \, dx = \frac{\sin(a-b)x}{2(a-b)} - \frac{\sin(a+b)x}{2(a+b)} + \text{constant}, \ a^2 \neq b^2$

T.6 $\int_0^L \sin nax \sin^2 ax \, dx = -\frac{1}{2a}\left\{\frac{1}{n} - \frac{1}{2(n+2)} - \frac{1}{2(n-2)}\right\} \times [(-1)^n - 1]$

T.7 $\int \sin ax \cos ax \, dx = \frac{1}{2a}\sin^2 ax + \text{constant}$

T.8 $\int \sin bx \cos ax \, dx = -\frac{\cos(a-b)x}{2(a-b)} - \frac{\cos(a+b)x}{2(a+b)} + \text{constant}, \ a^2 \neq b^2$

T.9 $\int x \sin ax \sin bx \, dx = -\frac{d}{da}\int \sin bx \cos ax \, dx$

➤ Checklist of concepts

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

Checklist of concepts

☐ 1. In the **nuclear model** of an atom negatively charged electrons occupy atomic orbitals which are arranged in shells around a positively charged nucleus.

☐ 2. The **periodic table** highlights similarities in electronic configurations of atoms, which in turn lead to similarities in their physical and chemical properties.

☐ 3. **Covalent compounds** consist of discrete molecules in which atoms are linked by covalent bonds.

☐ 4. **Ionic compounds** consist of cations and anions in a crystalline array.

☐ 5. **Lewis structures** are useful models of the pattern of bonding in molecules.

☐ 6. The **valence-shell electron pair repulsion theory** (VSEPR theory) is used to predict the three-dimensional shapes of molecules from their Lewis structures.

☐ 7. The electrons in **polar covalent bonds** are shared unequally between the bonded nuclei.

☐ 8. The **physical states** of bulk matter are solid, liquid, or gas.

☐ 9. The state of a sample of bulk matter is defined by specifying its properties, such as mass, volume, amount, pressure, and temperature.

☐ 10. The **perfect gas equation** is a relation between the pressure, volume, amount, and temperature of an idealized gas.

☐ 11. A **limiting law** is a law that becomes increasingly valid in a particular limit.

Presenting the mathematics

➤ Justifications

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

Justification 6.1 The hermiticity of the linear momentum operator

Our task is to show that

$$\int_{-\infty}^{\infty} f^* \hat{p} g \, dx = \left\{ \int_{-\infty}^{\infty} g^* \hat{p} f \, dx \right\}^*$$

with $\hat{p}$ given in eqn 6.4b. To do so, we use 'integration by parts', the relation

$$\int u \frac{dv}{dx} dx = uv - \int v \frac{du}{dx} dx$$

with $u = f^*$ and $v = g$. In the present case we write

➤ Chemist's toolkits

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

The chemist's toolkit 10.1 Hyperbolic functions

The hyperbolic cosine (cosh) and hyperbolic sine (sinh) functions are defined as

$$\cosh x = (e^x + e^{-x})/2 \quad \sinh x = (e^x - e^{-x})/2$$

These functions, which are illustrated in Sketch 10.1 and available in most mathematical software packages, are related by

$$\cosh^2 x - \sinh^2 x = 1$$

At $x = 0$, $\cosh x = 1$ and $\sinh x = 0$. The cosh function is even, $\cosh(-x) = \cosh x$, whereas the sinh function is odd, $\sinh(-x) = -\sinh x$. In the limits of $x \to \pm\infty$,
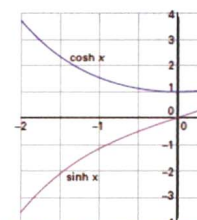
➤ Mathematical backgrounds

There are eight Mathematical background sections dispersed throughout the text. They cover in detail the main mathematical concepts that you need to understand in order to be able to master physical chemistry. Each one is located at the end of the Focus where it is first needed.

Mathematical background 1 Differentiation and integration

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

MB1.1 Differentiation: definitions

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

$$\frac{df}{dx} = \lim_{\delta x \to 0} \frac{f(x + \delta x) - f(x)}{\delta x} \quad \text{Definition} \quad \text{First derivative} \quad \text{(MB1.1)}$$

As shown in Fig. MB1.1, the derivative can be interpreted as the slope of the tangent to the graph of $f(x)$. A positive first derivative indicates that the function slopes upwards (as x increases), and a negative first derivative indicates the opposite. It is sometimes convenient to denote the first derivative as $f'(x)$. The second derivative, d^2f/dx^2, of a function is the derivative of the first derivative (here denoted f''):

$$\frac{d^2f}{dx^2} = \lim_{\delta x \to 0} \frac{f'(x + \delta x) - f'(x)}{\delta x} \quad \text{Definition} \quad \text{Second derivative} \quad \text{(MB1.2)}$$

It is sometimes convenient to denote the second derivative f''. As shown in Fig. MB1.1, the second derivative of a function can be interpreted as an indication of the sharpness of

the curvature of the function. A positive second derivative indicates that the function is ∪ shaped, and a negative second derivative indicates that it is ∩ shaped.

The derivatives of some common functions are as follows:

$$\frac{d}{dx} x^n = n x^{n-1} \quad \text{(MB1.3a)}$$

$$\frac{d}{dx} e^{ax} = a e^{ax} \quad \text{(MB1.3b)}$$

$$\frac{d}{dx} \sin ax = a \cos ax \quad \frac{d}{dx} \cos ax = -a \sin ax \quad \text{(MB1.3c)}$$

$$\frac{d}{dx} \ln ax = \frac{1}{x} \quad \text{(MB1.3d)}$$

When a function depends on more than one variable, we need the concept of a **partial derivative**, $\partial f/\partial x$. Note the change from d to ∂: partial derivatives are dealt with at length in *Mathematical background 8*; all we need know at this stage is that they signify that all variables other than the stated variable are regarded as constant when evaluating the derivative.

Brief illustration MB1.1 Partial derivatives

Suppose we are told that f is a function of two variables, and specifically $f = 4x^2 y^3$. Then, to evaluate the partial derivative of f with respect to x, we regard y as a constant (just like the 4), and obtain

$$\frac{\partial f}{\partial x} = \frac{\partial}{\partial x}(4x^2 y^3) = 4y^3 \frac{\partial}{\partial x} x^2 = 8xy^3$$

➤ Annotated equations and equation labels

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

$$\int_{-\infty}^{\infty} (\psi')^* \psi' dx = 1 \tag{5.1}$$

A wavefunction that satisfies condition (5.1) is said to be **normalized** (strictly, normalized to 1). In terms of the original wavefunction this equation becomes

$$N^2 \int_{-\infty}^{\infty} \psi^* \psi dx = 1$$

It follows that the **normalization constant** N is given by

$$N = \frac{1}{\left(\int_{-\infty}^{\infty} \psi^* \psi dx\right)^{1/2}} \qquad \text{Definition} \quad \boxed{\text{Normalization constant}} \tag{5.2}$$

Almost all wavefunctions go to zero at sufficiently great distances so there is rarely any difficulty with the evaluation of the integral in eqn 5.2. Wavefunctions for which the integral exists (in the sense of having a finite value) are said to be 'square-integrable'.

From now on, unless we state otherwise, we always use wavefunctions that have been normalized to 1. That is, from now on we assume that ψ already includes a factor which ensures that (in one dimension)

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1 \qquad \text{One dimension} \quad \boxed{\text{Normalization condition}} \tag{5.3a}$$

In three dimensions, the wavefunction is normalized if

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^* \psi dx dy dz = 1 \qquad \text{Three dimensions} \quad \boxed{\text{Normalization condition}} \tag{5.3b}$$

➤ Checklists of equations

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

Checklist of equations

Property	Equation	Comment	Equation number
Velocity	$v = dr/dt$	Definition	2.1
Linear momentum	$p = mv$	Definition	2.2
Angular momentum	$l = I\omega, I = mr^2$	Point particle	2.3–4
Force	$F = ma = dp/dt$	Definition	2.5
Torque	$T = dl/dt$	Definition	2.6
Work	$dw = -F ds$	Definition	2.7
Kinetic energy	$E_k = \frac{1}{2}mv^2$	Definition	2.8
Potential energy	$F_x = -dV/dx$	One dimension	2.10
Coulomb potential energy	$V(r) = Q_1 Q_2/(4\pi\varepsilon_0 r)$	Vacuum	2.14
Coulomb potential	$\phi = Q_2/4\pi\varepsilon_0 r$	Vacuum	2.16
Electric field strength	$E = -d\phi/dx$	One dimension	2.18
Electrical power	$P = I\Delta\phi$		2.19

Setting up and solving problems

➤ Brief illustrations

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

Brief illustration 1.1 Octet expansion

Octet expansion is also encountered in species that do not necessarily require it, but which, if it is permitted, may acquire a lower energy. Thus, of the structures (1a) and (1b) of the SO_4^{2-} ion, the second has a lower energy than the first. The actual structure of the ion is a resonance hybrid of both structures (together with analogous structures with double bonds in different locations), but the latter structure makes the dominant contribution.

1a   1b
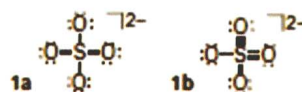
➤ Worked examples

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

Example 1.1 Using the perfect gas equation

Calculate the pressure in kilopascals exerted by 1.25 g of nitrogen gas in a flask of volume 250 cm³ at 20 °C.

Method To use eqn 1.5, we need to know the amount of molecules (in moles) in the sample, which we can obtain from the mass and the molar mass (by using eqn 1.3) and to convert the temperature to the Kelvin scale (by using eqn 1.4).

Answer The amount of N_2 molecules (of molar mass 28.02 g mol^{-1}) present is

$$n(N_2) = \frac{m}{M(N_2)} = \frac{1.25\,g}{28.02\,g\,mol^{-1}} = \frac{1.25}{28.02}\,mol$$

The temperature of the sample is

➤ Discussion questions

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

➤ Exercises and problems

Exercises and problems are also provided at the end of every Focus and organized by Topic. They prompt you to test your understanding of the Topics in that Focus group. Exercises are designed as relatively straightforward numerical tests whereas the problems are more challenging. The Integrated activities, which are problems that cross several Topics, also appear at the end of each Focus.

➤ Integrated activities

At the end of most Focus sections, you will find questions designed to help you use your knowledge creatively in a variety of ways. Some of the questions refer to the Living graphs on the Online Resource Centre, which you will find helpful for answering them.

➤ Solutions manuals

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

The *Student's Solutions Manual* (ISBN 9780198701286) provides full solutions to the 'a' exercises and to the odd-numbered problems.

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

ONLINE RESOURCE CENTRE

The Online Resource Centre to accompany *Physical Chemistry: Quanta, Matter, and Change*, second edition provides a number of useful teaching and learning resources for students and lecturers.
The site can be accessed at:

http://www.oxfordtextbooks.com/orc/qchem2e/

Lecturer resources are available only to registered adopters of the textbook. To register, simply visit

http://www.oxfordtextbooks.com/orc/qchem2e/
and follow the appropriate links.

Student resources are openly available to all, without registration.

@ Materials on the online resource centre include:

Online Impact sections

Impact sections place the subject of physical chemistry in context by showing how it has been applied in a variety of modern contexts. New for this edition, the Impacts are linked from the text by QR codes. Alternatively, visit the URL displayed next to the QR code.

Group theory tables

Comprehensive group theory tables are available to download.

Web links

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

Instructor's Solutions Manual

Lecturers can download the *Instructor's Solutions Manual* in PDF format. This provides full solutions to the 'b' exercises and to the even-numbered problems in the book.

Figures and tables from the book

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

Molecular modelling problems

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

Living graphs

These interactive graphs can be used to explore how a property changes as various parameters are changed. Living graphs are sometimes referred to in the Integrated activities section of a Focus group.

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BRIEF CONTENTS

FULL CONTENTS