

ATKINS' **PHYSICAL CHEMISTRY**

Eighth Edition

Peter Atkins

*Professor of Chemistry,
University of Oxford,
and Fellow of Lincoln College, Oxford*

Julio de Paula

*Professor and Dean of the College of Arts and Sciences,
Lewis and Clark College,
Portland, Oregon*

OXFORD
UNIVERSITY PRESS

OXFORD

UNIVERSITY PRESS

Great Clarendon Street, Oxford OX2 6DP

Oxford University Press is a department of the University of Oxford.

It furthers the University's objective of excellence in research, scholarship
and education by publishing worldwide in

Oxford New York

Auckland Cape Town Dar es Salaam Hong Kong Karachi
Kuala Lumpur Madrid Melbourne Mexico City Nairobi
New Delhi Shanghai Taipei Toronto

With offices in

Argentina Austria Brazil Chile Czech Republic France Greece
Guatemala Hungary Italy Japan Poland Portugal Singapore
South Korea Switzerland Thailand Turkey Ukraine Vietnam

Oxford is a registered trade mark of Oxford University Press
in the UK and in certain other countries

Published in the United States and Canada
by W. H. Freeman and Company

© Peter Atkins 1978, 1982, 1986, 1990, 1994, 1998
and © Peter Atkins & Julio de Paula 2002, 2006

The moral rights of the authors have been asserted
Database right Oxford University Press (maker)

First published 2006

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

You must not circulate this book in any other binding or cover
and you must impose the same condition on any acquirer

British Library Cataloguing in Publication Data
Data available

Library of Congress Cataloging in Publication Data
Data available

Typeset by Graphicraft Limited, Hong Kong
Printed in Italy
on acid-free paper by Lito Terrazzi s.r.l.

ISBN 9780198700722 ISBN 0198700725

1 3 5 7 9 10 8 6 4 2

D 5174 i



2006 10

Contents

PART 1 Equilibrium	1	Discussion questions	70
		Exercises	70
		Problems	73
1 The properties of gases	3	3 The Second Law	76
The perfect gas	3	The direction of spontaneous change	77
1.1 The states of gases	3	3.1 The dispersal of energy	77
1.2 The gas laws	7	3.2 Entropy	78
11.1 Impact on environmental science: The gas laws and the weather	11	13.1 Impact on engineering: Refrigeration	85
Real gases	14	3.3 Entropy changes accompanying specific processes	87
1.3 Molecular interactions	14	3.4 The Third Law of thermodynamics	92
1.4 The van der Waals equation	17	Concentrating on the system	94
1.5 The principle of corresponding states	21	3.5 The Helmholtz and Gibbs energies	95
Checklist of key ideas	23	3.6 Standard reaction Gibbs energies	100
Further reading	23	Combining the First and Second Laws	102
Discussion questions	23	3.7 The fundamental equation	102
Exercises	24	3.8 Properties of the internal energy	103
Problems	25	3.9 Properties of the Gibbs energy	105
		Checklist of key ideas	109
2 The First Law	28	Further reading	110
The basic concepts	28	Further information 3.1: The Born equation	110
2.1 Work, heat, and energy	29	Further information 3.2: Real gases: the fugacity	111
2.2 The internal energy	30	Discussion questions	112
2.3 Expansion work	33	Exercises	113
2.4 Heat transactions	37	Problems	114
2.5 Enthalpy	40	4 Physical transformations of pure substances	117
12.1 Impact on biochemistry and materials science: Differential scanning calorimetry	46	Phase diagrams	117
2.6 Adiabatic changes	47	4.1 The stabilities of phases	117
Thermochemistry	49	4.2 Phase boundaries	118
2.7 Standard enthalpy changes	49	14.1 Impact on engineering and technology: Supercritical fluids	119
12.2 Impact on biology: Food and energy reserves	52	4.3 Three typical phase diagrams	120
2.8 Standard enthalpies of formation	54	Phase stability and phase transitions	122
2.9 The temperature-dependence of reaction enthalpies	56	4.4 The thermodynamic criterion of equilibrium	122
State functions and exact differentials	57	4.5 The dependence of stability on the conditions	122
2.10 Exact and inexact differentials	57	4.6 The location of phase boundaries	126
2.11 Changes in internal energy	59	4.7 The Ehrenfest classification of phase transitions	129
2.12 The Joule–Thomson effect	63	Checklist of key ideas	131
Checklist of key ideas	67	Further reading	132
Further reading	68	Discussion questions	132
Further information 2.1: Adiabatic processes	69		
Further information 2.2: The relation between heat capacities	69		

Exercises	132	7 Chemical equilibrium	200
Problems	133		
5 Simple mixtures	136		
The thermodynamic description of mixtures	136	Spontaneous chemical reactions	200
5.1 Partial molar quantities	136	7.1 The Gibbs energy minimum	200
5.2 The thermodynamics of mixing	141	7.2 The description of equilibrium	202
5.3 The chemical potentials of liquids	143	The response of equilibria to the conditions	210
15.1 Impact on biology: Gas solubility and breathing	147	7.3 How equilibria respond to pressure	210
The properties of solutions	148	7.4 The response of equilibria to temperature	211
5.4 Liquid mixtures	148	17.1 Impact on engineering: The extraction of metals from their oxides	215
5.5 Colligative properties	150	Equilibrium electrochemistry	216
15.2 Impact on biology: Osmosis in physiology and biochemistry	156	7.5 Half-reactions and electrodes	216
Activities	158	7.6 Varieties of cells	217
5.6 The solvent activity	158	7.7 The electromotive force	218
5.7 The solute activity	159	7.8 Standard potentials	222
5.8 The activities of regular solutions	162	7.9 Applications of standard potentials	224
5.9 The activities of ions in solution	163	17.2 Impact on biochemistry: Energy conversion in biological cells	225
Checklist of key ideas	166	Checklist of key ideas	233
Further reading	167	Further reading	234
Further information 5.1: The Debye–Hückel theory of ionic solutions	167	Discussion questions	234
Discussion questions	169	Exercises	235
Exercises	169	Problems	236
Problems	171		
6 Phase diagrams	174	PART 2 Structure	241
Phases, components, and degrees of freedom	174	8 Quantum theory: introduction and principles	243
6.1 Definitions	174	The origins of quantum mechanics	243
6.2 The phase rule	176	8.1 The failures of classical physics	244
Two-component systems	179	8.2 Wave–particle duality	249
6.3 Vapour pressure diagrams	179	18.1 Impact on biology: Electron microscopy	253
6.4 Temperature–composition diagrams	182	The dynamics of microscopic systems	254
6.5 Liquid–liquid phase diagrams	185	8.3 The Schrödinger equation	254
6.6 Liquid–solid phase diagrams	189	8.4 The Born interpretation of the wavefunction	256
16.1 Impact on materials science: Liquid crystals	191	Quantum mechanical principles	260
16.2 Impact on materials science: Ultrapurity and controlled impurity	192	8.5 The information in a wavefunction	260
Checklist of key ideas	193	8.6 The uncertainty principle	269
Further reading	194	8.7 The postulates of quantum mechanics	272
Discussion questions	194	Checklist of key ideas	273
Exercises	195	Further reading	273
Problems	197	Discussion questions	274
		Exercises	274
		Problems	275

9 Quantum theory: techniques and applications	277	11 Molecular structure	362
Translational motion	277	The Born–Oppenheimer approximation	362
9.1 A particle in a box	278	Valence-bond theory	363
9.2 Motion in two and more dimensions	283	11.1 Homonuclear diatomic molecules	363
9.3 Tunnelling	286	11.2 Polyatomic molecules	365
19.1 Impact on nanoscience: Scanning probe microscopy	288	Molecular orbital theory	368
Vibrational motion	290	11.3 The hydrogen molecule-ion	368
9.4 The energy levels	291	11.4 Homonuclear diatomic molecules	373
9.5 The wavefunctions	292	11.5 Heteronuclear diatomic molecules	379
Rotational motion	297	11.1.1 Impact on biochemistry: The biochemical reactivity of O ₂ , N ₂ , and NO	385
9.6 Rotation in two dimensions: a particle on a ring	297	Molecular orbitals for polyatomic systems	386
9.7 Rotation in three dimensions: the particle on a sphere	301	11.6 The Hückel approximation	387
19.2 Impact on nanoscience: Quantum dots	306	11.7 Computational chemistry	392
9.8 Spin	308	11.8 The prediction of molecular properties	396
Techniques of approximation	310	Checklist of key ideas	398
9.9 Time-independent perturbation theory	310	Further reading	399
9.10 Time-dependent perturbation theory	311	Discussion questions	399
Checklist of key ideas	312	Exercises	399
Further reading	313	Problems	400
Further information 9.1: Dirac notation	313	12 Molecular symmetry	404
Further information 9.2: Perturbation theory	313	The symmetry elements of objects	404
Discussion questions	316	12.1 Operations and symmetry elements	405
Exercises	316	12.2 The symmetry classification of molecules	406
Problems	317	12.3 Some immediate consequences of symmetry	411
10 Atomic structure and atomic spectra	320	Applications to molecular orbital theory and spectroscopy	413
The structure and spectra of hydrogenic atoms	320	12.4 Character tables and symmetry labels	413
10.1 The structure of hydrogenic atoms	321	12.5 Vanishing integrals and orbital overlap	419
10.2 Atomic orbitals and their energies	326	12.6 Vanishing integrals and selection rules	423
10.3 Spectroscopic transitions and selection rules	335	Checklist of key ideas	425
The structures of many-electron atoms	336	Further reading	426
10.4 The orbital approximation	336	Discussion questions	426
10.5 Self-consistent field orbitals	344	Exercises	426
The spectra of complex atoms	345	Problems	427
110.1 Impact on astrophysics: Spectroscopy of stars	346	13 Molecular spectroscopy 1: rotational and vibrational spectra	430
10.6 Quantum defects and ionization limits	346	General features of spectroscopy	431
10.7 Singlet and triplet states	347	13.1 Experimental techniques	431
10.8 Spin–orbit coupling	348	13.2 The intensities of spectral lines	432
10.9 Term symbols and selection rules	352	13.3 Linewidths	436
Checklist of key ideas	356	113.1 Impact on astrophysics: Rotational and vibrational spectroscopy of interstellar space	438
Further reading	357		
Further information 10.1: The separation of motion	357		
Discussion questions	358		
Exercises	358		
Problems	359		

Pure rotation spectra	441	Discussion questions	508
13.4 Moments of inertia	441	Exercises	509
13.5 The rotational energy levels	443	Problems	510
13.6 Rotational transitions	446		
13.7 Rotational Raman spectra	449		
13.8 Nuclear statistics and rotational states	450		
The vibrations of diatomic molecules	452	The effect of magnetic fields on electrons and nuclei	513
13.9 Molecular vibrations	452	15.1 The energies of electrons in magnetic fields	513
13.10 Selection rules	454	15.2 The energies of nuclei in magnetic fields	515
13.11 Anharmonicity	455	15.3 Magnetic resonance spectroscopy	516
13.12 Vibration–rotation spectra	457		
13.13 Vibrational Raman spectra of diatomic molecules	459	Nuclear magnetic resonance	517
The vibrations of polyatomic molecules	460	15.4 The NMR spectrometer	517
13.14 Normal modes	460	15.5 The chemical shift	518
13.15 Infrared absorption spectra of polyatomic molecules	461	15.6 The fine structure	524
I13.2 Impact on environmental science: Global warming	462	15.7 Conformational conversion and exchange processes	532
13.16 Vibrational Raman spectra of polyatomic molecules	464	Pulse techniques in NMR	533
I13.3 Impact on biochemistry: Vibrational microscopy	466	15.8 The magnetization vector	533
13.17 Symmetry aspects of molecular vibrations	466	15.9 Spin relaxation	536
Checklist of key ideas	469	I15.1 Impact on medicine: Magnetic resonance imaging	540
Further reading	470	15.10 Spin decoupling	541
Further information 13.1: Spectrometers	470	15.11 The nuclear Overhauser effect	542
Further information 13.2: Selection rules for rotational and vibrational spectroscopy	473	15.12 Two-dimensional NMR	544
Discussion questions	476	15.13 Solid-state NMR	548
Exercises	476	Electron paramagnetic resonance	549
Problems	478	15.14 The EPR spectrometer	549
		15.15 The <i>g</i> -value	550
		15.16 Hyperfine structure	551
		I15.2 Impact on biochemistry: Spin probes	553
		Checklist of key ideas	554
		Further reading	555
		Further information 15.1: Fourier transformation of the FID curve	555
		Discussion questions	556
		Exercises	556
		Problems	557
14 Molecular spectroscopy 2: electronic transitions	481		
The characteristics of electronic transitions	481	16 Statistical thermodynamics 1: the concepts	560
14.1 The electronic spectra of diatomic molecules	482	The distribution of molecular states	561
14.2 The electronic spectra of polyatomic molecules	487	16.1 Configurations and weights	561
I14.1 Impact on biochemistry: Vision	490	16.2 The molecular partition function	564
The fates of electronically excited states	492	I16.1 Impact on biochemistry: The helix–coil transition in polypeptides	571
14.3 Fluorescence and phosphorescence	492	The internal energy and the entropy	573
I14.2 Impact on biochemistry: Fluorescence microscopy	494	16.3 The internal energy	573
14.4 Dissociation and predissociation	495	16.4 The statistical entropy	575
Lasers	496		
14.5 General principles of laser action	496		
14.6 Applications of lasers in chemistry	500		
Checklist of key ideas	505		
Further reading	506		
Further information 14.1: Examples of practical lasers	506		

The canonical partition function	577	Checklist of key ideas	646
16.5 The canonical ensemble	577	Further reading	646
16.6 The thermodynamic information in the partition function	578	Further information 18.1: The dipole–dipole interaction	646
16.7 Independent molecules	579	Further information 18.2: The basic principles of molecular beams	647
Checklist of key ideas	581	Discussion questions	648
Further reading	582	Exercises	648
Further information 16.1: The Boltzmann distribution	582	Problems	649
Further information 16.2: The Boltzmann formula	583		
Further information 16.3: Temperatures below zero	584		
Discussion questions	585		
Exercises	586		
Problems	586		
17 Statistical thermodynamics 2: applications	589	19 Materials 1: macromolecules and aggregates	652
<hr/>		<hr/>	
Fundamental relations	589	Determination of size and shape	652
17.1 The thermodynamic functions	589	19.1 Mean molar masses	653
17.2 The molecular partition function	591	19.2 Mass spectrometry	655
 		19.3 Laser light scattering	657
Using statistical thermodynamics	599	19.4 Ultracentrifugation	660
17.3 Mean energies	599	19.5 Electrophoresis	663
17.4 Heat capacities	601	119.1 Impact on biochemistry: Gel electrophoresis in genomics and proteomics	664
17.5 Equations of state	604	19.6 Viscosity	665
17.6 Molecular interactions in liquids	606	 	
17.7 Residual entropies	609	Structure and dynamics	667
17.8 Equilibrium constants	610	19.7 The different levels of structure	667
Checklist of key ideas	615	19.8 Random coils	668
Further reading	615	19.9 The structure and stability of synthetic polymers	673
Discussion questions	617	119.2 Impact on technology: Conducting polymers	674
Exercises	617	19.10 The structure of proteins	675
Problems	618	19.11 The structure of nucleic acids	679
		19.12 The stability of proteins and nucleic acids	681
		Self-assembly	681
18 Molecular interactions	620	19.13 Colloids	682
<hr/>		19.14 Micelles and biological membranes	685
Electric properties of molecules	620	19.15 Surface films	687
18.1 Electric dipole moments	620	119.3 Impact on nanoscience: Nanofabrication with self-assembled monolayers	690
18.2 Polarizabilities	624	Checklist of key ideas	690
18.3 Relative permittivities	627	Further reading	691
 		Further information 19.1: The Rayleigh ratio	691
Interactions between molecules	629	Discussion questions	692
18.4 Interactions between dipoles	629	Exercises	692
18.5 Repulsive and total interactions	637	Problems	693
118.1 Impact on medicine: Molecular recognition and drug design	638	 	
 		20 Materials 2: the solid state	697
Gases and liquids	640	<hr/>	
18.6 Molecular interactions in gases	640	Crystal lattices	697
18.7 The liquid–vapour interface	641	20.1 Lattices and unit cells	697
18.8 Condensation	645	20.2 The identification of lattice planes	700
		20.3 The investigation of structure	702
		120.1 Impact on biochemistry: X-ray crystallography of biological macromolecules	711
		20.4 Neutron and electron diffraction	713

Crystal structure	715	22 The rates of chemical reactions	791
20.5 Metallic solids	715	Empirical chemical kinetics	791
20.6 Ionic solids	717	22.1 Experimental techniques	792
20.7 Molecular solids and covalent networks	720	22.2 The rates of reactions	794
The properties of solids	721	22.3 Integrated rate laws	798
20.8 Mechanical properties	721	22.4 Reactions approaching equilibrium	804
20.9 Electrical properties	723	22.5 The temperature dependence of reaction rates	807
I20.2 Impact on nanoscience: Nanowires	728	Accounting for the rate laws	809
20.10 Optical properties	728	22.6 Elementary reactions	809
20.11 Magnetic properties	733	22.7 Consecutive elementary reactions	811
20.12 Superconductors	736	I22.1 Impact on biochemistry: The kinetics of the helix–coil transition in polypeptides	818
Checklist of key ideas	738	22.8 Unimolecular reactions	820
Further reading	739	Checklist of key ideas	823
Discussion questions	739	Further reading	823
Exercises	740	Further information 22.1: The RRK model of unimolecular reactions	824
Problems	741	Discussion questions	825
		Exercises	825
		Problems	826
PART 3 Change	745		
21 Molecules in motion	747	23 The kinetics of complex reactions	830
Molecular motion in gases	747	Chain reactions	830
21.1 The kinetic model of gases	748	23.1 The rate laws of chain reactions	830
I21.1 Impact on astrophysics: The Sun as a ball of perfect gas	754	23.2 Explosions	833
21.2 Collision with walls and surfaces	755	Polymerization kinetics	835
21.3 The rate of effusion	756	23.3 Stepwise polymerization	835
21.4 Transport properties of a perfect gas	757	23.4 Chain polymerization	836
Molecular motion in liquids	761	Homogeneous catalysis	839
21.5 Experimental results	761	23.5 Features of homogeneous catalysis	839
21.6 The conductivities of electrolyte solutions	761	23.6 Enzymes	840
21.7 The mobilities of ions	764	Photochemistry	845
21.8 Conductivities and ion–ion interactions	769	23.7 Kinetics of photophysical and photochemical processes	845
I21.2 Impact on biochemistry: Ion channels and ion pumps	770	I23.1 Impact on environmental science: The chemistry of stratospheric ozone	853
Diffusion	772	I23.2 Impact on biochemistry: Harvesting of light during plant photosynthesis	856
21.9 The thermodynamic view	772	23.8 Complex photochemical processes	858
21.10 The diffusion equation	776	I23.3 Impact on medicine: Photodynamic therapy	860
I21.3 Impact on biochemistry: Transport of non- electrolytes across biological membranes	779	Checklist of key ideas	861
21.11 Diffusion probabilities	780	Further reading	862
21.12 The statistical view	781	Further information 23.1: The Förster theory of resonance energy transfer	862
Checklist of key ideas	783	Discussion questions	863
Further reading	783	Exercises	863
Further information 21.1: The transport characteristics of a perfect gas	784	Problems	864
Discussion questions	785		
Exercises	786		
Problems	788		

24 Molecular reaction dynamics	869	25.12 Working galvanic cells	945
Reactive encounters	869	I25.3 Impact on technology: Fuel cells	947
24.1 Collision theory	870	25.13 Corrosion	948
24.2 Diffusion-controlled reactions	876	I25.4 Impact on technology: Protecting materials against corrosion	949
24.3 The material balance equation	879	Checklist of key ideas	951
Transition state theory	880	Further reading	951
24.4 The Eyring equation	880	Further information 25.1: The relation between electrode potential and the Galvani potential	952
24.5 Thermodynamic aspects	883	Discussion questions	952
The dynamics of molecular collisions	885	Exercises	953
24.6 Reactive collisions	886	Problems	955
24.7 Potential energy surfaces	887	Appendix 1 Quantities, units, and notational conventions	959
24.8 Some results from experiments and calculations	888	Names of quantities	959
24.9 The investigation of reaction dynamics with ultrafast laser techniques	892	Units	960
Electron transfer in homogeneous systems	894	Notational conventions	961
24.10 The rates of electron transfer processes	894	Further reading	962
24.11 Theory of electron transfer processes	896	Appendix 2 Mathematical techniques	963
24.12 Experimental results	898	Basic procedures	963
I24.1 Impact on biochemistry: Electron transfer in and between proteins	900	A2.1 Logarithms and exponentials	963
Checklist of key ideas	902	A2.2 Complex numbers and complex functions	963
Further reading	903	A2.3 Vectors	964
Further information 24.1: The Gibbs energy of activation of electron transfer and the Marcus cross-relation	903	Calculus	965
Discussion questions	904	A2.4 Differentiation and integration	965
Exercises	904	A2.5 Power series and Taylor expansions	967
Problems	905	A2.6 Partial derivatives	968
25 Processes at solid surfaces	909	A2.7 Functionals and functional derivatives	969
The growth and structure of solid surfaces	909	A2.8 Undetermined multipliers	969
25.1 Surface growth	910	A2.9 Differential equations	971
25.2 Surface composition	911	Statistics and probability	973
The extent of adsorption	916	A2.10 Random selections	973
25.3 Physisorption and chemisorption	916	A2.11 Some results of probability theory	974
25.4 Adsorption isotherms	917	Matrix algebra	975
25.5 The rates of surface processes	922	A2.12 Matrix addition and multiplication	975
I25.1 Impact on biochemistry: Biosensor analysis	925	A2.13 Simultaneous equations	976
Heterogeneous catalysis	926	A2.14 Eigenvalue equations	977
25.6 Mechanisms of heterogeneous catalysis	927	Further reading	978
25.7 Catalytic activity at surfaces	928	Appendix 3 Essential concepts of physics	979
I25.2 Impact on technology: Catalysis in the chemical industry	929	Energy	979
Processes at electrodes	932	A3.1 Kinetic and potential energy	979
25.8 The electrode–solution interface	932	A3.2 Energy units	979
25.9 The rate of charge transfer	934		
25.10 Voltammetry	940		
25.11 Electrolysis	944		

Classical mechanics	980	Electrostatics	985
A3.3 The trajectory in terms of the energy	980	A3.11 The Coulomb interaction	986
A3.4 Newton's second law	980	A3.12 The Coulomb potential	986
A3.5 Rotational motion	981	A3.13 The strength of the electric field	986
A3.6 The harmonic oscillator	982	A3.14 Electric current and power	987
Waves	983	Further reading	987
A3.7 The electromagnetic field	983	Data section	988
A3.8 Features of electromagnetic radiation	983	Answers to 'b' exercises	1028
A3.9 Refraction	984	Answers to selected problems	1034
A3.10 Optical activity	985	Index	1040