Physical Chemistry

Understanding our Chemical World

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Jossey-Bass, 989 Market Street, San Francisco, CA 94103-1741, USA

Wiley-VCH Verlag GmbH, Boschstr. 12, D-69469 Weinheim, Germany

John Wiley & Sons Australia Ltd, 33 Park Road, Milton, Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, 2 Clementi Loop #02-01, Jin Xing Distripark, Singapore 129809

John Wiley & Sons Canada Ltd, 22 Worcester Road, Etobicoke, Ontario, Canada M9W 1L1

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Library of Congress Cataloging-in-Publication Data

Monk, Paul M. S.
Physical chemistry : understanding our chemical world / Paul Monk.
p. cm.
Includes bibliographical references and index.
ISBN 0-471-49180-2 (acid-free paper) – ISBN 0-471-49181-0 (pbk. : acid-free paper)
1. Chemistry, Physical and theoretical. I. Title.
QD453.3.M66 2004
541 – dc22
2004004224

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN 0-471-49180-2 hardback
0-471-49181-0 paperback

Typeset in 10.5/12.5pt Times by Laserwords Private Limited, Chennai, India
Printed and bound in Great Britain by Antony Rowe Ltd, Chippenham, Wiltshire
This book is printed on acid-free paper responsibly manufactured from sustainable forestry in which at least two trees are planted for each one used for paper production.

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Preface

This book

Some people make physical chemistry sound more confusing than it really is. One of their best tricks is to define it inaccurately, saying it is 'the physics of chemicals'. This definition is sometimes quite good, since it suggests we look at a chemical system and ascertain how it follows the laws of nature. This is true, but it suggests that chemistry is merely a sub-branch of physics; and the notoriously mathematical nature of physics impels us to avoid this otherwise useful way of looking at physical chemistry.

An alternative and more user-friendly definition tells us that physical chemistry supplies 'the laws of chemistry', and is an addition to the *making* of chemicals. This is a superior lens through which to view our topic because we avoid the bitter aftertaste of pure physics, and start to look more closely at physical chemistry as an *applied* science: we do not look at the topic merely for the sake of looking, but because there are real-life situations requiring a scientific explanation. Nevertheless, most practitioners adopting this approach are still overly mathematical in their treatments, and can make it sound as though the science is fascinating in its own right, but will sometimes condescend to suggest an application of the theory they so clearly relish.

But the definition we will employ here is altogether simpler, and also broader: we merely ask 'why does it happen?' as we focus on the behaviour of each chemical system. Every example we encounter in our everyday walk can be whittled down into small segments of thought, each so simple that a small child can understand. As a famous mystic of the 14th century once said, 'I saw a small hazelnut and I marvelled that everything that exists could be contained within it'. And in a sense she was right: a hazelnut looks brown because of the way light interacts with its outer shell – the topic of spectroscopy (Chapter 9); the hazelnut is hard and solid – the topic of bonding theory (Chapter 2) and phase equilibria (Chapter 5); and the nut is good to eat – we say it is readily metabolized, so we think

Now published as *Revelations of Divine Love*, by Mother Julian of Norwich.

of kinetics (Chapter 8); and the energetics of chemical reactions (Chapters 2–4). The sensations of taste and sight are ultimately detected within the brain as electrical impulses, which we explain from within the rapidly growing field of electrochemistry (Chapter 7). Even the way a nut sticks to our teeth is readily explained by adsorption science (Chapter 10). Truly, the whole of physical chemistry can be encompassed within a few everyday examples.

So the approach taken here is the opposite to that in most other books of physical chemistry: each small section starts with an example from everyday life, i.e. both the world around us and also those elementary observations that a chemist can be certain to have pondered upon while attending a laboratory class. We then work backwards from the experiences of our hands and eyes toward the cause of why our world is the way it is.

Nevertheless, we need to be aware that physical chemistry is not a closed book in the same way of perhaps classical Latin or Greek. Physical chemistry is a growing discipline, and new experimental techniques and ideas are continually improving the data and theories with which our understanding must ultimately derive.

Inevitably, some of the explanations here have been over-simplified because physical chemistry is growing at an alarming rate, and additional sophistications in theory and experiment have yet to be devised. But a more profound reason for caution is in ourselves: it is all too easy, as scientists, to say 'Now I understand!' when in fact we mean that all the facts before us can be answered by the theory. Nevertheless, if the facts were to alter slightly – perhaps we look at another kind of nut – the theory, as far as we presently understand it, would need to change ever so slightly. Our understanding can never be complete.

So, we need a word about humility. It is said, probably too often, that science is not an emotional discipline, nor is there a place for any kind of reflection on the *human* side of its application. This view is deeply mistaken, because scientists limit themselves if they blind themselves to any contradictory evidence when sure they are right. The laws of physical chemistry can only grow when we have the humility to acknowledge how incomplete is our knowledge, and that our explanation might need to change. For this reason, a simple argument is not necessary the right one; but neither is a complicated one. The examples in this book were chosen to show how the world around us manifests *Physical Chemistry*. The explanation of a seemingly simple observation may be fiendishly complicated, but it may be beautifully simple. It must be admitted that the chemical examples are occasionally artificial. The concept of activity, for example, is widely misunderstood, probably because it presupposes knowledge from so many overlapping branches of physical chemistry. The examples chosen to explain it may be quite absurd to many experienced teachers, but, as an aid to simplification, they can be made to work. Occasionally the science has been simplified to the point where some experienced teachers will maintain that it is technically wrong. But we must start from the beginning if we are to be wise, and only then can we progress via the middle ... and physical chemistry is still a rapidly growing subject, so we don't yet know where it will end.

While this book could be read as an almanac of explanations, it provides students in further and higher education with a *unified* approach to physical chemistry. As a teacher of physical chemistry, I have found the approaches and examples here to be effective with students of HND and the early years of BSc and MChem courses. It has been written for students having the basic chemical and mathematical skills generally expected of university entrants, such as rearrangement of elementary algebra and a little calculus. It will augment the skills of other, more advanced, students.

To reiterate, this book supplies no more than an introduction to physical chemistry, and is not an attempt to cover the whole topic. Those students who have learned some physical chemistry are invited to expand their vision by reading more specialized works. The inconsistencies and simplifications wrought by lack of space and style in this text will be readily overcome by copious background reading. A comprehensive bibliography is therefore included at the end of the book. Copies of the figures and bibliography, as well as live links can be found on the book's website at http://www.wileyeurope.com/go/monkphysical.

Acknowledgements

One of the more pleasing aspects of writing a text such as this is the opportunity to thank so many people for their help. It is a genuine pleasure to thank Professor Séamus Higson of Cranfield University, Dr Roger Mortimer of Loughborough University, and Dr Michele Edge, Dr David Johnson, Dr Chris Rego and Dr Brian Wardle from my own department, each of whom read all or part of the manuscript, and whose comments have been so helpful.

A particular 'thank you' to Mrs Eleanor Riches, formerly a high-school teacher, who read the entire manuscript and made many perceptive and helpful comments.

I would like to thank the many students from my department who not only saw much of this material, originally in the form of handouts, but whose comments helped shape the material into its present form.

Please allow me to thank Michael Kaufman of *The Campaign for a Hydrogen Economy* (formerly the *Hydrogen Association of UK and Ireland*) for helpful discussions to clarify the arguments in Chapter 7, and the *Tin Research Council* for their help in constructing some of the arguments early in Chapter 5.

Concerning permission to reproduce figures, I am indebted to *The Royal Society of Chemistry* for Figures 1.8 and 8.26, the *Open University Press* for Figure 7.10, *Elsevier Science* for Figures 4.7 and 10.3, and *John Wiley & Sons* for Figures 7.19, 10.11 and 10.14. Professor Robin Clarke FRS of University College London has graciously allowed the reproduction of Figure 9.28.

Finally, please allow me to thank Dr Andy Slade, Commissioning Editor of Wiley, and the copy and production editors Rachael Ballard and Robert Hambrook. A special thank you, too, to Pete Lewis.

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Etymological introduction

The hero in *The Name of the Rose* is a medieval English monk. He acts as sleuth, and is heard to note at one point in the story how, 'The study of words is the whole of knowledge'. While we might wish he had gone a little further to mention chemicals, we would have to agree that many of our technical words can be traced back to Latin or Greek roots. The remainder of them originate from the principal scientists who pioneered a particular field of study, known as etymology.

"Etymology" means the derivation of a word's meaning.

Etymology is our name for the science of *words*, and describes the sometimes-tortuous route by which we inherit them from our ancestors. In fact, most words change and shift their meaning with the years. A classic example describes how King George III, when first he saw the rebuilt St Paul's Cathedral in London, described it as 'amusing, artificial and awful', by which he meant, respectively, it 'pleased him', was 'an artifice' (i.e. grand) and was 'awesome' (i.e. breathtaking).

Any reader will soon discover the way this text has an unusual etymological emphasis: the etymologies are included in the belief that taking a word apart actually helps us to understand it and related concepts. For example, as soon as we know the Greek for 'green' is *chloros*, we understand better the meanings of the proper nouns *chlor*ophyll and *chlor*ine, both of which are green. Incidentally, *phyll* comes from the Greek for 'leaf', and *ine* indicates a substance.

Again, the etymology of the word *oxygen* incorporates much historical information: *oxys* is the Greek for 'sharp', in the sense of an extreme sensory experience, such as the taste of acidic vinegar, and the ending *gen* comes from *gignesthaw* (pronounced 'gin-es-thaw'), meaning 'to be produced'. The classical roots of 'oxygen' reveal how the French scientists who first made the gas thought they had isolated the distinguishing chemical component of acids.

The following tables are meant to indicate the power of this approach. There are several dozen further examples in the text. The bibliography on p. 533 will enable the interested reader to find more examples.

Words derived from a scientist's name

Scientist	Field of study	Present meaning(s)	Derived words[a]
Ampère, André	current, electricity	current	*amp* (unit of current); *am*perometry; *am*perometric; volt*am*metry
Coulomb, Charles	charge, electricity	charge passed	*coulomb* (unit of charge); *coulomb*ic
Faraday, Michael	capacitance, electrochemistry	electricity	*faraday* (molar electronic charge); *farada*ic; *farad* (unit of capacitance)
Voltaire, Allesandro	electricity, potential	potential	*volt* (unit of potential); *volt*aic; *volt*ammetry

[a] Note that derived words do not start with a capital letter.

Words and roots from Latin

Word or root	Original Latin meaning	Modern meaning	Modern examples	Scientific examples
Centi(n)s	hundred times	hundred	century, cent (= \$/100)	centi (symbol c) = factor of 10^2
Decie(n)s	ten times	ten	decimate (i.e. to kill 1 in 10)	deci (symbol d) factor of 10
			decimal	decimetre (= metre ÷ 10)
Giga(n)s	giant	very large	gigantic	giga (symbol G) = factor of 10^9
Milli	thousand, thousands	thousand, thousandth	millipede, millennium	milli (symbol m) = factor of 10^{-3}
Stratum	bed, couch, coverlet	something beneath	stratify (many layered)	strata of rock (in geology)
				substrate (chemistry and physics)
Sub	under, beneath, directly under	below, less than	subterfuge, subterranean	substrate (i.e. underlying strata)
			sub-standard, subset	subscript (in typesetting)
Super	above, on, over, on top of	above, bigger than	superstar, superlative	superscript (in typesetting)

Words and roots from Greek

Word or root	Original Greek meaning	Modern meaning	Modern examples	Scientific examples
Anode (ανοδος)	ascent	positive electrode	anode	anode, anodic, anodize
Baro (βαρος)	weigh down, heaviness	to do with atmosphere	barometer, barometric	barometer, isobar, bar (unit of pressure)
Cathode (καθοδος)	descent	negative electrode	cathode	cathode, cathodic, cathodize
Cyclo (κυκλος)	circle, circular	cycle, circle	bicycle, cylinder, cyclone	cyclotron, cyclization
Di (δις)	two, twice	to do with two	dihedral dilemma (two options)	to do with two (coordination chemistry) dimer, di-stereoisomer (i.e. one of two images)
Iso (ισο)	level, equality	same	Isomer	e.g. isobutane, isomer
Kilo (κιλος)	lots of, many	factor of a thousand	Kilometre	kilo (symbol k) = factor of 10^3
Mega (μεγα-)	great, large	very large	megabyte	mega (symbol M) = factor of 10^6
Mesos (μεσος)	middle, mid	mid, intermediate	mezzanine (mid floor)	mesophase (i.e. phase between two extremes)
Meta (μετα-)	afterwards	after, beyond	metaphor (i.e. beyond the real meaning)	position beyond ortho on a ring metathesis (i.e. product of mixing)
Meter (μετρητης)	meter	a meter, to meter	gas meter, metrical	barometer (i.e. measures pressure)
Micro (μιχρος)	small	tiny, small	microscope, micrometer	micro (symbolμ) = factor of 10^{-6}
Mono (μονος)	one	one, alone	monorail, monologue monotonous (i.e. on one note)	monomer, e.g. mono-substituted
Ortho (ορθος)	straight	straight, right	orthodox (i.e. to the standard) othopædic (straightening bones)	adjacent position on a ring
Para (παρα-)	near, beyond, contrary	opposite	paranormal (beyond normal) paradox (contrary to standard)	position opposite the primary carbon
Tetra (τετταρεος)	four, four times	to do with four	tetrahedron	to do with four (in coodination chemistry)
Thermo (θερμο)	energy, temperature	Heat	thermos, thermometer	thermos, thermometer

List of Symbols

Symbols for variables

a	Activity
a	van der Waals constant
A	optical absorbance
A	Area
b	van der Waals constant
B'	virial coefficient
c	concentration
c	the intercept on the y-axis of a graph
c	constant of proportionality
C	virial coefficient
C	heat capacity
C_p	heat capacity determined at constant pressure
C_V	heat capacity determined at constant volume
E	energy
E	potential
E_{a}	activation energy
$E_{\mathrm{(ea)}}$	electron affinity
E_{j}	junction potential
$E_{\mathrm{(load)}}$	potential of a battery or cell when passing a current
emf	potential of a cell, determined at zero current
$E_{\mathrm{O,R}}$	electrode potential for the couple $\mathrm{O} + n\mathrm{e}^- = \mathrm{R}$
$E^{\ominus}_{\mathrm{O,R}}$	standard electrode potential for the couple $\mathrm{O} + n\mathrm{e}^- = \mathrm{R}$
$E_{\mathrm{(LHS)}}$	electrode potential of the negative electrode in a cell
$E_{\mathrm{(RHS)}}$	electrode potential of the positive electrode in a cell
f	fugacity
f	frequency
F	force
G	Gibbs function
ΔG	change in Gibbs function
$G^{\ominus}$	standard Gibbs function
$G^{\ddagger}$	Gibbs function of activation
h	height
H	enthalpy
ΔH	change in enthalpy
$H_{\mathrm{(ads)}}$	enthalpy of adsorption
$H^{\ominus}$	standard enthalpy
ΔH_{BE}	bond enthalpy
ΔH_{c}	enthalpy of combustion
ΔH_{f}	enthalpy of formation
$H^{\ddagger}$	enthalpy of activation
I	electrical current
I	intensity of light following absorption

I_{o}	intensity of incident light beam
I	ionic strength
I	ionization energy
J	rotational quantum number; rotational quantum number of an excited state
J'	rotational quantum number of ground state
k	force constant of a bond
k	proportionality constant
k	rate constant
k'	pseudo rate constant
k_n	rate constant of an nth-order reaction
k_{-n}	rate constant for the back reaction of an nth-order reaction
$k_{(n)}$	rate constant of the nth process in a multi-step reaction
k_{a}	rate constant of adsorption
k_{d}	rate constant of desorption
k_{H}	Henry's law constant
K	equilibrium constant
K	correction constant of an ion-selective electrode
K_{a}	acidity constant ('acid dissociation' constant)
$K_{\mathrm{a}(n)}$	acidity constant for the nth dissociation reaction
K_{b}	basicity constant
K_{c}	equilibrium constant formulated in terms of concentration
K_{p}	equilibrium constant formulated in terms of pressure
K_{s}	equilibrium constant of solubility (sometimes called 'solubility product' or 'solubility constant')
K_{w}	autoprotolysis constant of water
$K^{\ddagger}$	equilibrium constant of forming a transition state 'complex'
l	length
m	gradient of a graph
m	mass
M	relative molar mass
n	number of moles
n	number of electrons in a redox reaction
n_{m}	amount of material in an adsorbed monolayer
N	number
p	pressure
$p_{(i)}$	partial pressure of component i
$p^{\ominus}_{(i)}$	vapour pressure of pure i
$p^{\ominus}$	standard pressure of 10^5 Pa
q	heat energy
Q	charge
Q	reaction quotient
r	separation between ions
r	radius of a circle or sphere
r	bond length
r'	bond length in an optically excited species
r_{o}	equilibrium bond length
R	electrical resistance
s	solubility
s	stoichiometric ratio
S	entropy
ΔS	change in entropy
$S^{\ominus}$	standard entropy
$S^{\ddagger}$	entropy of activation
t	time
$t_{\frac{1}{2}}$	half life
T	temperature
T	optical transmittance
T_{o}	optical transmittance without a sample
T_{K}	Krafft temperature
U	internal energy
ΔU	change in internal energy, e.g. during reaction
v	quantum-number of vibration
v'	quantum-number of vibration in an excited-state species

v''	quantum-number of vibration in a ground-state species
V	volume
V	voltage, e.g. of a power pack
V	Coulomb potential energy
V_{m}	molar volume
w	work
x	controlled variable on the horizontal axis of a graph
x	deviation of a bond from its equilibrium length
x_i	mole fraction of *i*
y	observed variable on the vertical of a graph
z	charge on ion (so z^+ for a cation and z^- for an anion)
Z	compressibility

γ	activity coefficient
$\gamma_\pm$	mean ionic activity coefficient
γ	fugacity coefficient
γ	surface tension
δ	small increment
∂	partial differential
Δ	change in a variable (so $\Delta X = X_{\text{(final form)}} - X_{\text{(initial form)}}$)
ε	extinction coefficient ('molar decadic absorptivity')
ε_{r}	relative permittivity
ε_{o}	permittivity of free space
θ	adsorption isotherm
θ	angle
κ	ionic conductivity
λ	wavelength
$\lambda_{\text{(max)}}$	the wavelength of a peak in a spectrum
μ	reduced mass
μ_i	chemical potential of *i*
$\mu_i^{\ominus}$	standard chemical potential of *i*
ν	stoichiometric constant
ν	velocity
ν	frequency (the reciprocal of the period of an event)
ν_{o}	frequency following transmission (in Raman spectroscopy)
ξ	extent of reaction
ρ	density
σ	electrical conductivity
σ	standard deviation
ϕ	electric field strength (electrostatic interaction)
ϕ	work function of a metal
ϕ	primary quantum yield
Φ	quantum yield of a reaction
χ	electronegativity
ω	wavenumber of a vibration (determined as $\omega = \lambda \div c$)

Symbols for constants

A	Debye–Hückel '*A*' factor
c	the speed of light *in vacuo*
$c^{\ominus}$	standard concentration
e	charge on an electron, of value 1.6×10^{-19} C
f	mathematical operator ('function of')
F	Faraday constant, of value $96\,485\ \mathrm{C\,mol^{-1}}$
k_{B}	Boltzmann constant, of value 1.38×10^{-23}
L	Avogadro constant, of value $6.022 \times 10^{23}\ \mathrm{mol^{-1}}$
N_{A}	Avogadro number, of value $6.022 \times 10^{23}\ \mathrm{mol^{-1}}$
g	acceleration due to gravity, of value $9.81\ \mathrm{m\ s^{-2}}$
h	Planck constant, of value 6.626×10^{-34} J s
R	gas constant, of value $8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$

Symbols for units

A	ampère
Å	ångström, length of value 10^{-10} m (non-IUPAC)
bar	standard pressure of 10^5 Pa (non-SI unit)
C	coulomb
°C	centigrade (non-SI)
g	gram
Hz	hertz
J	joule
K	kelvin
kg	kilogram
m	metre
mmHg	millimetre of mercury (non-SI unit of pressure)
mol	mole
N	newton
Pa	pascal
s	second (SI unit)
S	siemen
V	volt
W	watt
yr	year
Ω	ohm

Acronyms and abbreviations

CT	charge transfer
d	differential operator (which *never* appears on its own)
HOMO	highest occupied molecular orbital
IQ	intelligence quotient
IR	infrared
IUPAC	International Union of Pure and Applied Chemistry
IVF	*in vitro* fertilization
LCD	liquid crystal display
LHS	left-hand side
LUMO	lowest unoccupied molecular orbital
MLCT	metal-to-ligand charge transfer
MRI	magnetic resonance imaging
NIR	near-infra red
NMR	nuclear magnetic resonance
O	general oxidized form of a redox couple
p	mathematical operator, $-\log_{10}$[variable], so $\text{pH} = -\log_{10}[\text{H}^+]$
PEM	proton exchange membrane
R	general reduced form of a redox couple
RHS	right-hand side
s.t.p.	standard temperature and pressure
SAQ	self-assessment question
SCE	saturated calomel electrode
SCUBA	self-contained underwater breathing apparatus
SHE	standard hydrogen electrode
SHM	simple harmonic motion
SI	*Système Internationale*
S_N1	unimolecular nucleophilic substitution process
S_N2	bimolecular nucleophilic substitution process
SSCE	silver–silver chloride electrode
TS	transition state
TV	television
UPS	UV-photoelectron spectroscopy
UV	ultraviolet
UV–vis	ultraviolet and visible
XPS	X-ray photoelectron spectroscopy

Standard subscripts (other than those where a word or phrase is spelt in full)

ads	adsorption; adsorbed
aq	aqueous
c	combustion
eq	at equilibrium
f	formation
g	gas
l	liquid
LHS	left-hand side of a cell
m	molar
p	at constant pressure
Pt	platinum (usually, as an electrode)
r	reaction
RHS	right-hand side of cell
s	solid
sat'd	saturated
t	at time t (i.e. after a reaction or process has commenced)
V	at constant volume
0	initially (i.e. at time $t = 0$)
∞	measurement taken after an infinite length of time

Standard superscripts (other than those where a word or phrase is spelt in full)

$\ddagger$	activated quantity
$-$	anion
$+$	cation
$*$	excited state
$\bullet$	radical
$+\bullet$	radical cation
$\ominus$	standard state

Chemicals and materials

A	general anion
Bu	butyl
CFC	chlorofluorocarbon
DMF	*N,N*-dimethylformamide
DMSO	dimethylsulphoxide
DNA	deoxyribonucleic acid
e^-	electron
EDTA	ethylenediamine tetra-acetic acid
HA	general Lowry–Brønsted acid
LPG	liquid petroleum gas
M	general cation
MB	methylene blue
MV	methyl viologen (1,1′-dimethyl-4,4′-bipyridilium)
O	general oxidized form of a redox couple
PC	propylene carbonate
Ph	phenyl substituent
R	general alkyl substituent
R	general reduced form of a redox couple
SDS	sodium dodecyl sulphate
TFA	tetrafluoroacetic acid
α	particle emitted during radioactive disintegration of nucleus
β	particle emitted during radioactive disintegration of nucleus
γ	high-energy photon (gamma ray)