

# Physical Chemistry

## Understanding our Chemical World

**Paul Monk**

*Manchester Metropolitan University, UK*



John Wiley & Sons, Ltd



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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

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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 necessarily 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>.

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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 *chlorophyll* and *chlorine*, 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 <sup>a</sup>
Ampère, André	current, electricity	current	<i>amp</i> (unit of current); <i>amperometry</i> ; <i>amperometric</i> ; <i>voltammetry</i>
Coulomb, Charles	charge, electricity	charge passed	<i>coulomb</i> (unit of charge); <i>coulombic</i>
Faraday, Michael	capacitance, electrochemistry	electricity	<i>faraday</i> (molar electronic charge); <i>faradaic</i> ; <i>farad</i> (unit of capacitance)
Voltaire, Allessandro	electricity, potential	potential	<i>volt</i> (unit of potential); <i>voltaic</i> ; <i>voltammetry</i>

<sup>a</sup>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 <sup>2</sup>
Decie(n)s	ten times	ten	decimate (i.e. to kill 1 in 10)	deci (symbol d) factor of 10
Giga(n)s	giant	very large	decimal	decimetre (= metre ÷ 10)
Milli	thousand, thousands	thousand, thousandth	gigantic	giga (symbol G) = factor of 10 <sup>9</sup>
Stratum	bed, couch, coverlet	something beneath	millipede, millennium	milli (symbol m) = factor of 10 <sup>-3</sup>
Sub	under, beneath, directly under	below, less than	stratify (many layered)	strata of rock (in geology)
Super	above, on, over, on top of	above, bigger than	subterfuge, subterranean	substrate (chemistry and physics)
			sub-standard, subset	substrate (i.e. underlying strata)
			superstar, superlative	subscript (in typesetting)
				superscript (in typesetting)

## Words and roots from Greek

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



# List of Symbols

## ***Symbols for variables***

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

$I_o$	intensity of incident light beam	$m$	mass
$I$	ionic strength	$M$	relative molar mass
$I$	ionization energy	$n$	number of moles
$J$	rotational quantum number; rotational quantum number of an excited state	$n$	number of electrons in a redox reaction
$J'$	rotational quantum number of ground state	$n_m$	amount of material in an adsorbed monolayer
$k$	force constant of a bond	$N$	number
$k$	proportionality constant	$p$	pressure
$k$	rate constant	$p_{(i)}$	partial pressure of component $i$
$k'$	pseudo rate constant	$p_{(i)}^\ominus$	vapour pressure of pure $i$
$k_n$	rate constant of an $n$ th-order reaction	$p^\ominus$	standard pressure of $10^5$ Pa
$k_{-n}$	rate constant for the back reaction of an $n$ th-order reaction	$q$	heat energy
$k_{(n)}$	rate constant of the $n$ th process in a multi-step reaction	$Q$	charge
$k_a$	rate constant of adsorption	$Q$	reaction quotient
$k_d$	rate constant of desorption	$r$	separation between ions
$k_H$	Henry's law constant	$r$	radius of a circle or sphere
$K$	equilibrium constant	$r$	bond length
$K$	correction constant of an ion-selective electrode	$r'$	bond length in an optically excited species
$K_a$	acidity constant ('acid dissociation' constant)	$r_o$	equilibrium bond length
$K_{a(n)}$	acidity constant for the $n$ th dissociation reaction	$R$	electrical resistance
$K_b$	basicity constant	$s$	solubility
$K_c$	equilibrium constant formulated in terms of concentration	$s$	stoichiometric ratio
$K_p$	equilibrium constant formulated in terms of pressure	$S$	entropy
$K_s$	equilibrium constant of solubility (sometimes called 'solubility product' or 'solubility constant')	$\Delta S$	change in entropy
$K_w$	autoprotolysis constant of water	$S^\ominus$	standard entropy
$K^\ddagger$	equilibrium constant of forming a transition state 'complex'	$S^\ddagger$	entropy of activation
$l$	length	$t$	time
$m$	gradient of a graph	$t_{\frac{1}{2}}$	half life
		$T$	temperature
		$T$	optical transmittance
		$T_o$	optical transmittance without a sample
		$T_K$	Krafft temperature
		$U$	internal energy
		$\Delta U$	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	$v$	velocity
$V$	volume	$\nu$	frequency (the reciprocal of the period of an event)
$V$	voltage, e.g. of a power pack	$\nu_o$	frequency following transmission (in Raman spectroscopy)
$V$	Coulomb potential energy	$\xi$	extent of reaction
$V_m$	molar volume	$\rho$	density
$w$	work	$\sigma$	electrical conductivity
$x$	controlled variable on the horizontal axis of a graph	$\sigma$	standard deviation
$x$	deviation of a bond from its equilibrium length	$\phi$	electric field strength (electrostatic interaction)
$x_i$	mole fraction of $i$	$\phi$	work function of a metal
$y$	observed variable on the vertical of a graph	$\phi$	primary quantum yield
$z$	charge on ion (so $z^+$ for a cation and $z^-$ for an anion)	$\Phi$	quantum yield of a reaction
$Z$	compressibility	$\chi$	electronegativity
		$\omega$	wavenumber of a vibration (determined as $\omega = \lambda \div c$ )
$\gamma$	activity coefficient	<b>Symbols for constants</b>	
$\gamma_{\pm}$	mean ionic activity coefficient		
$\gamma$	fugacity coefficient	$A$	Debye–Hückel ‘A’ factor
$\gamma$	surface tension	$c$	the speed of light <i>in vacuo</i>
$\delta$	small increment	$c^{\ominus}$	standard concentration
$\partial$	partial differential	$e$	charge on an electron, of value $1.6 \times 10^{-19}$ C
$\Delta$	change in a variable (so $\Delta X = X_{(\text{final form})} - X_{(\text{initial form})}$ )	$f$	mathematical operator (‘function of’)
$\varepsilon$	extinction coefficient (‘molar decadic absorptivity’)	$F$	Faraday constant, of value $96\,485 \text{ C mol}^{-1}$
$\varepsilon_r$	relative permittivity	$k_B$	Boltzmann constant, of value $1.38 \times 10^{-23}$
$\varepsilon_o$	permittivity of free space	$L$	Avogadro constant, of value $6.022 \times 10^{23} \text{ mol}^{-1}$
$\theta$	adsorption isotherm	$N_A$	Avogadro number, of value $6.022 \times 10^{23} \text{ mol}^{-1}$
$\theta$	angle	$g$	acceleration due to gravity, of value $9.81 \text{ m s}^{-2}$
$\kappa$	ionic conductivity	$h$	Planck constant, of value $6.626 \times 10^{-34} \text{ J s}$
$\lambda$	wavelength	$R$	gas constant, of value $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
$\lambda_{(\text{max})}$	the wavelength of a peak in a spectrum		
$\mu$	reduced mass		
$\mu_i$	chemical potential of $i$		
$\mu_i^{\ominus}$	standard chemical potential of $i$		
$\nu$	stoichiometric constant		

**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 <i>never</i> appears on its own)
HOMO	highest occupied molecular orbital
IQ	intelligence quotient
IR	infrared
IUPAC	International Union of Pure and Applied Chemistry

IVF	<i>in vitro</i> 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, – $\log_{10}[\text{variable}]$ , 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	<i>Système Internationale</i>
S <sub>N</sub> 1	unimolecular nucleophilic substitution process
S <sub>N</sub> 2	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 $t = 0$ )
$\infty$	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
$\alpha$	particle emitted during radioactive disintegration of nucleus
$\beta$	particle emitted during radioactive disintegration of nucleus
$\gamma$	high-energy photon (gamma ray)

