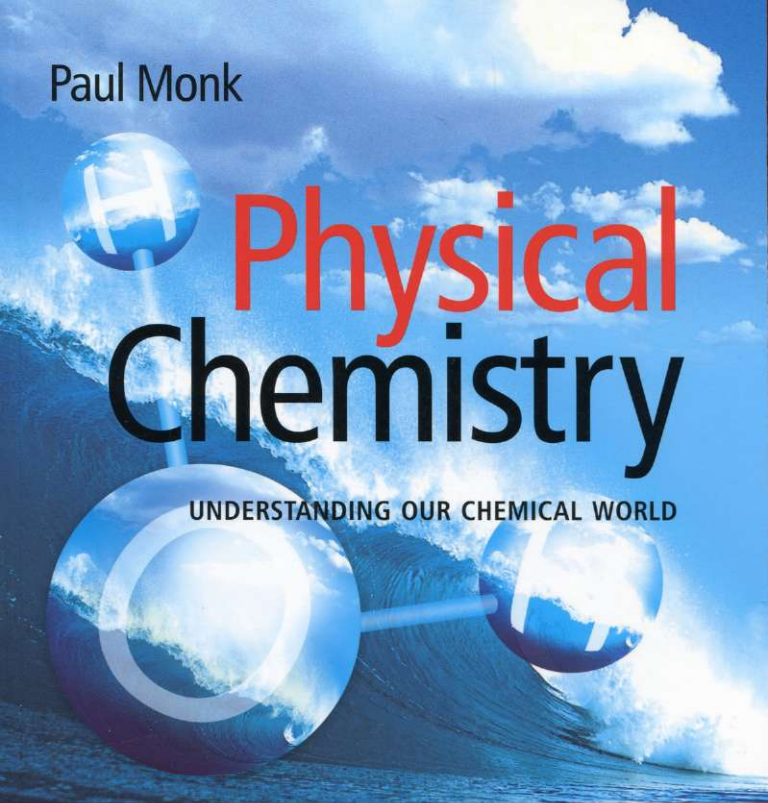


Paul Monk



# Physical Chemistry

UNDERSTANDING OUR CHEMICAL WORLD

 WILEY



# Contents

Preface	xv
Etymological introduction	xix
List of symbols	xxiii
Powers of ten: standard prefixes	xxviii
<b>1 Introduction to physical chemistry</b>	<b>1</b>
1.1 What is physical chemistry: variables, relationships and laws	1
Why do we warm ourselves by a radiator?	1
Why does water get hot in a kettle?	2
Are these two colours complementary?	2
Does my radio get louder if I vary the volume control?	3
Why does the mercury in a barometer go up when the air pressure increases?	5
Why does a radiator feel hot to the touch when 'on', and cold when 'off'?	7
1.2 The practice of thermodynamic measurement	9
What is temperature?	9
How long is a piece of string?	14
How fast is 'greased lightning'?	15
Why is the SI unit of mass the kilogram?	17
Why is 'the material of action so variable'?	18
1.3 Properties of gases and the gas laws	20
Why do we see eddy patterns above a radiator?	20
Why does a hot-air balloon float?	20
How was the absolute zero of temperature determined?	21
Why pressurize the contents of a gas canister?	23
Why does thunder accompany lightning?	25
How does a bubble-jet printer work?	26

What causes pressure?	30
Why is it unwise to incinerate an empty can of air freshener?	32
1.4 Further thoughts on energy	33
Why is the room warm?	33
What do we mean by 'room temperature' ?	34
Why do we get warmed-through in front of a fire, rather than just our skins?	35
<b>2 Introducing interactions and bonds</b>	<b>37</b>
2.1 Physical and molecular interactions	37
What is 'dry ice' ?	37
How is ammonia liquefied?	38
Why does steam condense in a cold bathroom?	39
How does a liquid-crystal display work?	40
Why does dew form on a cool morning?	42
How is the three-dimensional structure maintained within the DNA double helix?	44
How do we make liquid nitrogen?	47
Why is petrol a liquid at room temperature but butane is a gas?	49
2.2 Quantifying the interactions and their influence	50
How does mist form?	50
How do we liquefy petroleum gas?	52
Why is the molar volume of a gas not zero at 0 K?	54
2.3 Creating formal chemical bonds	59
Why is chlorine gas lethal yet sodium chloride is vital for life?	59
Why does a bicycle tyre get hot when inflated?	59
How does a fridge cooler work?	60
Why does steam warm up a cappuccino coffee?	61
Why does land become more fertile after a thunderstorm?	63
Why does a satellite need an inert coating?	64
Why does water have the formula $H_2O$ ?	66
Why is petroleum gel so soft?	67
Why does salt form when sodium and chlorine react?	69
Why heat a neon lamp before it will generate light?	69
Why does lightning conduct through air?	72
Why is argon gas inert?	74
Why is silver iodide yellow?	75
<b>3 Energy and the first law of thermodynamics</b>	<b>77</b>
3.1 Introduction to thermodynamics: internal energy	77
Why does the mouth get cold when eating ice cream?	77
Why is skin scalded by steam?	79
Why do we sweat?	81
Why do we still feel hot while sweating on a humid beach?	83

	Why is the water at the top of a waterfall cooler than the water at its base?	85
	Why is it such hard work pumping up a bicycle tyre?	86
	Why does a sausage become warm when placed in an oven?	87
	Why, when letting down a bicycle tyre, is the expelled air so cold?	88
	Why does a tyre get hot during inflation?	89
	Can a tyre be inflated without a rise in temperature?	89
	How fast does the air in an oven warm up?	90
	Why does water boil more quickly in a kettle than in a pan on a stove?	91
	Why does a match emit heat when lit?	94
	Why does it always take 4 min to boil an egg properly?	95
	Why does a watched pot always take so long to boil?	98
3.2	Enthalpy	99
	How does a whistling kettle work?	99
	How much energy do we require during a distillation?	102
	Why does the enthalpy of melting ice decrease as the temperature decreases?	104
	Why does water take longer to heat in a pressure cooker than in an open pan?	106
	Why does the temperature change during a reaction?	107
	Are diamonds forever?	109
	Why do we burn fuel when cold?	111
	Why does butane burn with a hotter flame than methane?	114
3.3	Indirect measurement of enthalpy	118
	How do we make 'industrial alcohol'?	118
	How does an 'anti-smoking pipe' work?	120
	Why does dissolving a salt in water liberate heat?	123
	Why does our mouth feel cold after eating peppermint?	125
	How does a camper's 'emergency heat stick' work?	127
4	Reaction spontaneity and the direction of thermodynamic change	129
4.1	The direction of physicochemical change: entropy	129
	Why does the colour spread when placing a drop of dye in a saucer of clean water?	129
	When we spill a bowl of sugar, why do the grains go everywhere and cause such a mess?	130
	Why, when one end of the bath is hot and the other cold, do the temperatures equalize?	131
	Why does a room containing oranges acquire their aroma?	133
	Why do damp clothes become dry when hung outside?	134
	Why does crystallization of a solute occur?	137
4.2	The temperature dependence of entropy	139
	Why do dust particles move more quickly by Brownian motion in warm water?	139
	Why does the jam of a jam tart burn more than does the pastry?	139

4.3	Introducing the Gibbs function	144
	Why is burning hydrogen gas in air (to form liquid water) a spontaneous reaction?	144
	How does a reflux condenser work?	144
4.4	The effect of pressure on thermodynamic variables	148
	How much energy is needed?	148
	Why does a vacuum 'suck'?	151
	Why do we sneeze?	152
	How does a laboratory water pump work?	153
4.5	Thermodynamics and the extent of reaction	156
	Why is a 'weak' acid weak?	156
	Why does the pH of the weak acid remain constant?	158
	Why does the voltage of a battery decrease to zero?	159
	Why does the concentration of product stop changing?	162
	Why do chicken eggs have thinner shells in the summer?	165
4.6	The effect of temperature on thermodynamic variables	166
	Why does egg white denature when cooked but remain liquid at room temperature?	166
	At what temperature will the egg start to denature?	170
	Why does recrystallization work?	171
5	Phase equilibria	177
5.1	Energetic introduction to phase equilibria	177
	Why does an ice cube melt in the mouth?	177
	Why does water placed in a freezer become ice?	181
	Why was Napoleon's Russian campaign such a disaster?	182
5.2	Pressure and temperature changes with a single-component system: qualitative discussion	184
	How is the 'Smoke' in horror films made?	184
	How does freeze-drying work?	185
	How does a rotary evaporator work?	188
	How is coffee decaffeinated?	189
5.3	Quantitative effects of pressure and temperature change for a single-component system	192
	Why is ice so slippery?	192
	What is 'black ice'?	193
	Why does deflating the tyres on a car improve its road-holding on ice?	198
	Why does a pressure cooker work?	199
5.4	Phase equilibria involving two-component systems: partition	205
	Why does a fizzy drink lose its fizz and go flat?	205
	How does a separating funnel work?	207
	Why is an ice cube only misty at its centre?	208
	How does recrystallization work?	209
	Why are some eggshells brown and some white?	211

5.5	Phase equilibria and colligative properties	212
	Why does a mixed-melting-point determination work?	212
	How did the Victorians make ice cream?	216
	Why boil vegetables in salted water?	217
	Why does the ice on a path melt when sprinkled with salt?	218
5.6	Phase equilibria involving vapour pressure	221
	Why does petrol sometimes have a strong smell and sometimes not?	221
	How do anaesthetics work?	222
	How do carbon monoxide sensors work?	224
	Why does green petrol smell different from leaded petrol?	224
	Why do some brands of 'green' petrol smell different from others?	225
	Why does a cup of hot coffee yield more steam than above a cup of boiling water at the same temperature?	229
	How are essential oils for aromatherapy extracted from plants?	229

## 6 Acids and Bases 233

6.1	Properties of Lowry-Bronsted acids and bases	233
	Why does vinegar taste sour?	233
	Why is it dangerous to allow water near an electrical appliance, if water is an insulator?	235
	Why is bottled water 'neutral' ?	236
	What is 'acid rain'?	237
	Why does cutting an onion make us cry?	239
	Why does splashing the hands with sodium hydroxide solution make them feel 'soapy'?	239
	Why is aqueous ammonia alkaline?	240
	Why is there no vinegar in crisps of salt and vinegar flavour?	241
	How did soldiers avoid chlorine gas poisoning at the Second Battle of Ypres?	242
	How is sherbet made?	244
	Why do steps made of limestone sometimes feel slippery?	244
	Why is the acid in a car battery more corrosive than vinegar?	245
	Why do equimolar solutions of sulphuric acid and nitric acid have different pHs?	250
	What is the pH of a 'neutral' solution?	251
	What do we mean when we say blood plasma has a 'pH of 7.4'?	251
6.2	'Strong' and 'weak' acids and bases	253
	Why is a nettle sting more painful than a burn from ethanoic acid?	253
	Why is 'carbolic acid' not in fact an acid?	254
	Why does carbonic acid behave as a mono-protic acid?	259
	Why is an organic acid such as trichloroethanoic acid so strong?	260
6.3	Titration analyses	261
	Why does a dock leaf bring relief after a nettle sting?	261
	How do indigestion tablets work?	262

6.4	pH buffers	267
	Why does the pH of blood not alter after eating pickle?	267
	Why are some lakes more acidic than others?	267
	How do we make a 'constant-pH solution' ?	270
6.5	Acid-base indicators	273
	What is 'the litmus test' ?	273
	Why do some hydrangea bushes look red and others blue?	274
	Why does phenolphthalein indicator not turn red until pH 8.2?	276
7	Electrochemistry	279
7.1	Introduction to cells: terminology and background	279
	Why does putting aluminium foil in the mouth cause pain?	279
	Why does an electric cattle prod cause pain?	281
	What is the simplest way to clean a tarnished silver spoon?	282
	How does 'electrolysis' stop hair growth?	283
	Why power a car with a heavy-duty battery yet use a small battery in a watch?	283
	How is coloured ('anodized') aluminium produced?	285
	How do we prevent the corrosion of an oil rig?	286
	What is a battery?	288
	Why do hydrogen fuel cells sometimes 'dry up' ?	289
	Why bother to draw cells?	291
	Why do digital watches lose time in the winter?	293
	Why is a battery's potential not constant?	294
	What is a 'standard cell'?	295
	Why aren't electrodes made from wood?	300
	Why is electricity more dangerous in wet weather?	302
7.2	Introducing half-cells and electrode potentials	303
	Why are the voltages of watch and car batteries different?	303
	How do 'electrochromic' car mirrors work?	305
	Why does a potential form at an electrode?	306
7.3	Activity	308
	Why does the smell of brandy decrease after dissolving table salt in it?	308
	Why does the smell of gravy become less intense after adding salt to it?	308
	Why add alcohol to <i>eau de Cologne</i> ?	309
	Why does the cell <i>emf</i> alter after adding LiCl?	312
	Why does adding NaCl to a cell alter the <i>emf</i> but adding tonic water doesn't?	314
	Why does MgCl <sub>2</sub> cause a greater decrease in perceived concentration than KCl?	315
	Why is calcium better than table salt at stopping soap lathering?	316
	Why does the solubility of AgCl change after adding MgSO <sub>4</sub> ?	318
7.4	Half-cells and the Nernst equation	321
	Why does sodium react with water yet copper doesn't?	321

Why does a torch battery eventually 'go flat' ?	325
Why does $E_{AgCl.A.}$ change after immersing an SSCE in a solution of salt?	326
Why 'earth' a plug?	328
7.5 Concentration cells	333
Why does steel rust fast while iron is more passive?	333
How do pH electrodes work?	336
7.6 Transport phenomena	339
How do nerve cells work?	339
What is a 'salt bridge' ?	342
7.7 Batteries	343
How does an electric eel produce a current?	343
What is the earliest known battery?	345

## 8 Chemical kinetics 349

8.1 Kinetic definitions	349
Why does a 'strong' bleach clean faster than a weaker one does?	349
Why does the bleaching reaction eventually stop?	351
Why does bleach work faster on some greases than on others?	354
Why do copper ions amminate so slowly?	356
How fast is the reaction that depletes the ozone layer?	358
Why is it more difficult to breathe when up a mountain than at ground level?	359
8.2 Qualitative discussion of concentration changes	361
Why does a full tank of petrol allow a car to travel over a constant distance?	361
Why do we add a drop of bromine water to a solution of an alkene?	362
When magnesium dissolves in aqueous acid, why does the amount of fizzing decrease with time?	364
8.3 Quantitative concentration changes: integrated rate equations	368
Why do some photographs develop so slowly?	368
Why do we often refer to a 'half-life' when speaking about radioactivity?	378
How was the Turin Shroud 'carbon dated' ?	382
How old is Otzi the iceman?	385
Why does the metabolism of a hormone not cause a large chemical change in the body?	387
Why do we not see radicals forming in the skin while sunbathing?	388
8.4 Kinetic treatment of complicated reactions	393
Why is arsenic poisonous?	393
Why is the extent of Walden inversion smaller when a secondary alkyl halide reacts than with a primary halide?	394
Why does 'standing' a bottle of wine cause it to smell and taste better?	397
Why fit a catalytic converter to a car exhaust?	399
Why do some people not burn when sunbathing?	400
How do Reactolite <sup>(R)</sup> sunglasses work?	403



8.5	Thermodynamic considerations: activation energy, absolute reaction rates and catalysis	408
	Why prepare a cup of tea with boiling water?	408
	Why store food in a fridge?	408
	Why do the chemical reactions involved in cooking require heating?	409
	Why does a reaction speed up at higher temperature?	411
	Why does the body become hotter when ill, and get 'a temperature' ?	415
	Why are the rates of some reactions insensitive to temperature?	416
	What are catalytic converters?	420
<b>9</b>	<b>Physical chemistry involving light: spectroscopy and photochemistry</b>	<b>423</b>
9.1	Introduction to photochemistry	423
	Why is ink coloured?	423
	Why do neon streetlights glow?	424
	Why do we get hot when lying in the sun?	425
	Why is red wine so red?	426
	Why are some paints red, some blue and others black?	427
	Why can't we see infrared light with our eyes?	429
	How does a dimmer switch work?	433
	Why does UV-b cause sunburn yet UV-a does not?	434
	How does a suntan protect against sunlight?	436
	How does sun cream block sunlight?	439
	Why does tea have a darker colour if brewed for longer?	442
	Why does a glass of apple juice appear darker when viewed against a white card?	442
	Why are some paints darker than others?	444
	What is ink?	445
9.2	Photon absorptions and the effect of wavelength	446
	Why do radical reactions usually require UV light?	446
	Why does photolysis require a powerful lamp?	452
	Why are spectroscopic bands not sharp?	453
	Why does hydrogen look pink in a glow discharge?	455
	Why do surfaces exposed to the sun get so dusty?	457
	Why is microwave radiation invisible to the eye?	458
9.3	Photochemical and spectroscopic selection rules	459
	Why is the permanganate ion so intensely coloured?	459
	Why is chlorophyll green?	461
	Why does adding salt remove a blood stain?	462
	What is gold-free gold paint made of?	462
	What causes the blue colour of sapphire?	463
	Why do we get hot while lying in the sun?	464
	What is an infrared spectrum?	467
	Why does food get hot in a microwave oven?	469
	Are mobile phones a risk to health?	471

9.4	Photophysics: emission and loss processes	472
	How are X-rays made?	472
	Why does metal glow when hot?	473
	How does a light bulb work?	474
	Why is a quartz-halogen bulb so bright?	474
	What is 'limelight' ?	476
	Why do TV screens emit light?	476
	Why do some rotting fish glow in the dark?	478
	How do 'see in the dark' watch hands work?	479
	How do neon lights work?	480
	How does a sodium lamp work?	481
	How do 'fluorescent strip lights' work?	482
9.5	Other optical effects	483
	Why is the mediterranean sea blue?	483
	Do old-master paintings have a 'fingerprint'?	485
10	Adsorption and surfaces, colloids and micelles	487
10.1	Adsorption and definitions	487
	Why is steam formed when ironing a line-dried shirt?	487
	Why does the intensity of a curry stain vary so much?	489
	Why is it difficult to remove a curry stain?	492
	Why is <i>iron</i> the catalyst in the Haber process?	494
	Why is it easier to remove a layer of curry <i>sauce</i> than to remove a curry <i>stain</i> !	496
	How does water condense onto glass?	497
	How does bleach remove a dye stain?	498
	How much beetroot juice does the stain on the plate contain?	499
	Why do we see a 'cloud' of steam when ironing a shirt?	503
10.2	Colloids and interfacial science	504
	Why is milk cloudy?	504
	What is an 'aerosol' spray?	505
	What is 'emulsion paint' ?	506
	Why does oil not mix with water?	508
10.3	Colloid stability	509
	How are cream and butter made?	509
	How is chicken soup 'clarified' by adding eggshells?	510
	How is 'clarified butter' made?	510
	Why does hand cream lose its milky appearance during hand rubbing?	511
	Why does orange juice cause milk to curdle?	512
	How are colloidal particles removed from waste water?	513
10.4	Association colloids: micelles	514
	Why does soapy water sometimes look milky?	514
	What is soap?	517
	Why do soaps dissolve grease?	518

Why is old washing-up water oily when cold but not when hot?	519
Why does soap generate bubbles?	521
Why does detergent form bubbles?	522
Answers to SAQs	525
Bibliography	533
Index	565