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Teacher Guide

Cambridge Pre-U
Chemistry
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Cambridge Advanced

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Introduction

The main purpose of this Teacher Guide is to support teachers in their delivery of the Cambridge Pre-U Chemistry syllabus so that their learners can achieve well and enjoy their learning.

The intention is not to instruct colleagues how to teach, more it is the case of providing resources on topics that teachers may not have taught before, and sharing material so that teachers, especially those new to the profession, will have some indication of the time scale for the teaching of each section and are aware of opportunities for practical work.

The Guide begins with two exemplar teaching orders currently used by schools with experience of teaching Cambridge Pre-U Chemistry, one for teaching by one teacher and the other for teaching shared between two teachers. These are used by these schools as working documents subject to change and are not intended to be prescriptive, but it is hoped that they will give some ideas as to how to approach the teaching of the syllabus and an approximation of the time required for each topic.

The following section gives suggestions for practical work; not only bench chemistry, but other hands-on activities to support learning and links to websites for learners to explore.

The major part of the guide covers the topics in the Cambridge Pre-U syllabus for which resources are not readily available. Four of these are listed in the syllabus as TNTs, Totally New Topics: the van Arkel triangle, functional group level, carbon-13 NMR and orbitals. At the time the syllabus was introduced, none of these had previously appeared in UK syllabuses at this level though carbon-13 NMR has since been introduced to UK A Level.

It should be noted that the chapter on orbitals is chiefly intended as background material for teachers who may be asked questions in class about some of these topics, or who might wish to extend the most mathematically able learners in some of the directions explored in the chapter. As is noted in the syllabus, there is little scope for examining this concept at this level and it is included in the syllabus to allow learners to develop a proper understanding of molecular electronic spectroscopy and for understanding mechanism in further study.

This teacher guide includes website links providing direct access to internet resources. Cambridge International Examinations is not responsible for the accuracy or content of information in these sites. The inclusion of a link to an external website should not be understood to be an endorsement of that website or the site's owners (or their products/services).

Section 1: Suggested teaching orders

1.1 Exemplar teaching order – for one teacher

Year 1

Topic	**Syllabus codes**
Term 1	
Atomic structure Electronic spectroscopy Chemical forces (first half term)	A 1.1 A 4.3 A 1.2
Chemical models and evidence (ongoing)	B 1.7
Energy changes Equilibrium (Le Chatelier's principle, acid models, pH)* Gases and Kinetics* (second half term)	A 1.3 B 1.5 B 1.6
*revisited and extended in Year 2 Practical work should begin in Term 1. Practicals may be out of context with the theory covered. Qualitative and quantitative analysis can be introduced.	
Term 2	
Periodic Table Main group chemistry From non-metals to metals: Group 14 Qualitative and quantitative analysis Preliminaries of organic chemistry	A2.1 A2.2 B2.3 A4.1 A3.1
A3.1(g) and (h) may be covered as you go along in Term 3 instead, in relation to the functional group levels as they are covered. Learners need to be encouraged to read journals and to discuss what of interest they have read. Encourage learners to read ahead with the textbook so that the pace of lessons can be fast. This is good preparation for what they will eventually have to do at university, as well as for interviews and for answering questions on unfamiliar ground.	

Term 3	
Mass spectrometry	A4.2
Addition to C=C and elimination	A3.5 (b)–(e)
Electrophilic addition and Markovnikov's rule	B3.9 (e)–(g)
Functional group level	A3.2 (a)–(f), (h)
Alcohol level	A3.3
Nucleophilic substitution	B3.9 (a)–(d)
Infra-red	A4.4
Green chemistry	A3.6
Organic chemistry lends itself to doing regular practicals in context. Regular weekly tests on naming molecules from the different functional group level could be given as starter activities. Atom economy and green chemistry concepts can be taught as you go along with functional group level rather than being taught in isolation. It is a good idea to teach learners general principles and get them to work things out for themselves, e.g. A3.5 (b). Never underestimate how difficult some find thinking in 3D. To assist all learners with this way of thinking/understanding, regular use of molymods is recommended.	

Year 2

Topic	Syllabus codes
Term 1	
Carbonyl level C=O compared with C=C Carboxylic Acid level Mechanisms* Stereochemistry (first half term)	A3.4 A3.5 (a) B3.7 B3.9 (h)–(i) B3.12
Carbon dioxide level Aromatic chemistry NMR of other spin ½ nuclei Carbon-13 NMR (second half term)	B3.8 B3.10 B4.6 A4.5
*Part of this topic, B3.9 (a)–(g) was covered in Year 1.	
Term 2	
Acidity and basicity Equilibrium Transition elements Free energy and entropy Gases and kinetics Crystal structures	B3.11 B1.5 (g)–(q) B2.4 B1.4 B1.6 (d)–(j) B2.5
The target is to have taught the entire course by the end of this term and completed at least one practical under exam conditions. One or two small sections are not specifically listed, but are covered when the appropriate opportunity arises or during practical work. An example is the conversion of aromatic nitro compounds into amines.	
Term 3	
Revision	

1.2 Exemplar teaching order – for two teachers

Year 1

(Teaching weeks stated are only a guide.)

Term 1				
Teacher A ……………………			**Teacher B …………………**	
Topic	**Syllabus codes**		**Topic**	**Syllabus codes**
Chemical calculations (4 weeks)	A1.0 : (a), (b), (c), (d) A4.1 : (a), (b), (c), (d), (e) A3.6 : (a)		Atomic structure (4 weeks)	A1.0 : (e), (f), (g) A1.1 : (a), (b), (c), (d), (e), (f), (g), (h), (l), (j) A4.3 : (a), (b), (c) B1.7 : (b)
Chemical bonding and structures (4 weeks)	A1.0 : (h), (k) A1.2 : (a), (b), (c), (d), (e), (f), (g), (h), (i), (j), (k), (l) A2.1 : (b), (d)		Energetics (5 weeks)	A1.0 : (i) A1.3 : (a), (b), (c), (d), (e), (f), (g)
Introduction to redox chemistry (2 weeks)	A2.1 : (e) B1.5 : (j)		Introduction to organic chemistry (2 weeks)	A3.1 : (a), (b), (c), (d), (e), (f), (g), (h) A3.2 : (a), (b), (c), (d), (e), (f), (g), (h) B3.12 : (a), (b), (c)

Term 2			
Teacher A ……………….…..		**Teacher B ………………..**	
Topic	**Syllabus codes**	**Topic**	**Syllabus codes**
Introduction to organic chemistry (2 weeks)	A3.1 : (a), (b), (c), (d), (f), (g), (h) A3.2 : (a), (b), (c), (d), (e), (f), (g), (h) B3.12 : (a), (b), (c)	Ideal gas theory (2 week)	B1.6 : (a), (b) B1.7 : (c)
Organic chemistry – alcohol level (2 weeks)	A3.1 : (f) A3.3 : (a), (b), (c), (d) B1.7 : (a) B3.9 : (a), (b), (c), (d)	Periodic table (Period 3) (3 weeks)	A2.1 : (a), (b), (c), (d), (e), (f), (g), (h), (i)
Organic chemistry – carbonyl level (2 weeks)	A3.4 : (a), (b), (c), (d) B3.9 : (h), (i)	Main group chemistry 1 (4 weeks)	A2.2 : (a) A2.2 : (b), (c), (d) A2.2 : (e), (f), (g), (h) A2.2 : (i), (j), (k), (l), (m), (n), (o)
Organic chemistry – alkenes (2 weeks)	A1.2 : (d), (e) A3.5 : (a), (b), (c), (d), (e) B3.9 : (e), (f), (g)		

Term 3			
Teacher A ……………….…..		**Teacher B ………………..**	
Topic	**Syllabus codes**	**Topic**	**Syllabus codes**
Introduction to chemical equilibria (8 weeks)	A1.0 : (j) B1.5 : (a), (c), (d) (K_p and K_{sp} only), (e)	Reaction kinetics (use S_{N1} and S_{N2} as examples) (8 weeks)	A1.0 : (l) B1.6 : (c), (d), (e), (f), (g), (h), (I), (j) A1.3 : (g), (h) B3.9 : (a) B1.7 : (a)

Year 2

Term 1				
Teacher A ……………………..			**Teacher B …………………**	
Topic	**Syllabus codes**		**Topic**	**Syllabus codes**
Free energy and entropy (4 weeks)	B1.4 : (a), (b), (c), (d), (e), (f), (g)		Acid / Base Equilibria (5 weeks)	B1.5 : (b), (d), (e), (f), (g), (h)
Transition elements (General and Complexes) (4 weeks)	B2.4 : (a), (b), (c), (d), (e), (f), (g), (h), (i)		Organic chemistry – *Alkene* (2 weeks)	A1.2 : (d), (e) A3.5 : (a), (b), (c), (d), (e) B3.9 : (e), (f), (g)
Redox equilibria (including transition elements) (4 weeks)	A1.0 : (m) B1.5 : (i), (j), (k), (l), (m), (n), (o), (p), (q) B2.4 : (i), (k), (l)		Organic chemistry – *Aromatic* (3 weeks)	B3.10 : (a), (b), (c), (d)
			Crystal structures (2 weeks)	B2.5 : (a), (b), (c), (d), (e), (f) B1.7 : (d)

Term 2				
Teacher A ……………………			**Teacher B …………………**	
Topic	**Syllabus codes**		**Topic**	**Syllabus codes**
Organic chemistry – analytic techniques (4 weeks)	A4.2 : (a), (b), (c) A4.4 : (a), (b), (c), (d) A4.5 : (a), (b), (c) B4.6 : (a), (b), (c), (d)		Organic chemistry – *revise mechanisms* (1 week) *Stereochemistry : optical isomerism* (the later could be weaved into the following topics rather than stand-alone)	(S_N1, S_N2, curly arrows in general) B3.12 : (d)
Main Group Chemistry II Group 14 (5 weeks)	B2.3 : (a), (b), (c), (d), (e)		Organic chemistry – *Carboxylic acid level* (2 weeks)	A3.1 : (h) B3.7 : (a), (b), (c), (d)
			Organic chemistry – *Carbon dioxide level* (2 weeks)	B3.8 : (a), (b)
			Organic chemistry – acidity / basicity (2 weeks)	B3.11 : (a), (b), (c), (d)
			Green chemistry (1 week)	A3.6 : (a), (b)

Term 3
Revision

Section 2: Suggested experiments and activities

2.1 Introduction

The Cambridge Pre-U Chemistry course should be at least 20% practical work. Practical work is important if each learner is to develop the necessary skills for the Practical exam and the next phase of their education at university. It should be viewed as an enrichment activity to enhance and support the theory teaching and to foster learners' enjoyment of the subject. Teachers should try to remember that when they do a suggested practical it might be the first time the learner has seen a particular experiment and this should be a stimulating experience where questions are to be encouraged. Teachers will be able to select a range of practicals from those suggested as there is not time to do them all. The age of learners, time and budgetary constraints within a school/college will determine which suggested practicals are done as demonstrations and which are carried out as whole class experiments.

2.2 References

Some online references are given for material written specifically for this Cambridge Pre-U Chemistry course and from university chemistry departments. Weblinks have been chosen that have been around and stable for at least five years and which are worth learners investigating.

2.3 Safety

Cambridge International Examinations accepts no responsibility for the safety of these experiments and it is the responsibility of teachers to carry out a full risk assessment for each experiment undertaken. Hazard data sheets should be available from your suppliers. Sources of chemical safety information can be found in **Section 10:** Resources.

Syllabus reference	Suggested practical work / activities
1. Physical chemistry	
A1.1 Atomic structure	
A1.1(c) A1.1(d)	It is possible to buy molymods of the various s, p, and d orbitals which are useful models for appreciating their shapes relative to the Cartesian coordinates. There are no experiments but learners would benefit from investigating the following weblinks: http://winter.group.shef.ac.uk/orbitron/ www.orbitals.com/orb/index.html www.btinternet.com/~chemistry.diagrams/electron_order.htm www.btinternet.com/~chemistry.diagrams/aufbau_animated.htm

Syllabus reference	**Suggested practical work / activities**
A1.2 Chemical forces	
	The gallium spoon is an excellent demonstration to show the unusual property of a low melting point solid metal. Using a teaspoon-mould a gallium spoon is made which can be shown to melt in hot water. www.disappearingspoons.com The metal can be recovered and recycled for further demonstrations.
A1.2(g)	VSEPR theory can be demonstrated by twisting together three different coloured and inflated long thin magician's balloons. The static on the balloons leads to maximum repulsion of the six lobes and the formation of an octahedral shape. By carefully popping one lobe at a time all the shapes from octahedral to linear can be achieved.
A1.2(i)	Deflection of a polar liquid, e.g. propanone, ethanol, water, can be achieved by running these liquids through separate burettes and bringing a freshly rubbed polythene rod close to the stream as it falls into a beaker below. The experiment works best when there is low humidity and if the polythene rods have been thoroughly dried with a hair dryer prior to use.
A1.2(k)	Investigate relative densities by adding ice to ethanol and then ice to water. Perhaps surprisingly, the ice sinks in ethanol. Learners enjoy varying the proportions of water and ethanol until the ice 'floats' in the middle of the liquid in its container. To get a paper clip to float on water place it on top of a thin piece of tissue paper and then lay it carefully on the water's surface. Then sink the tissue paper leaving the floating paper clip. The paper clip can be made to sink by changing the surface tension of the water by addition of a few drops of a washing up liquid/detergent.
A1.2(j)	A model of graphite shows clearly the location of Van der Waals forces between layers. Writing on a piece of paper with pure graphite as a mineral reinforces the theory of layers which can peel away when a force is exerted. An electrical circuit can be completed by placing two electrodes at either end of a thick line drawn with graphite.

Syllabus reference	**Suggested practical work / activities**
A1.3 Energy change	
A1.3(a)	There are many experiments which lend themselves to showing the temperature changes associated with exothermic and endothermic processes. A good exothermic practical is to add water dropwise to conc.H_2SO_4 and record the initial and final temperature. A good endothermic practical is to mix together solid ammonium chloride and solid barium hydroxide and record the initial and final temperature. One trick when doing this experiment as a demonstration is to freeze the beaker onto a block of wet wood. www.practicalchemistry.org/experiments/endothermic-solid-solid-reactions,277,EX.html An endothermic reaction which looks exothermic as the liquid appears to be boiling is the addition of pellets of iron(III) chloride to thionyl chloride in a fume cupboard.
A1.3(b)	Energy changes can be measured using a flame calorimeter. Combust 1 cm^3 of a fuel (ethanol or methanol) in a crucible and use the energy released to heat 50 cm^3 of water in an aluminium can supported above the crucible whilst recording the highest temperature reached. Calculate the temperature change (ΔT). If spirit burners are available they can also be used. Energy changes can also be measured using a simple calorimeter. Mix reactants in a polystyrene cup and calculate ΔT. Reactants which work well are Mg(s) and H_2SO_4, NH_4Cl(s) and H_2O(l), 2.0 mol dm^{-3} NaOH and 2.0 mol dm^{-3} HC*l*. It is helpful to put the polystyrene cup inside a beaker for support and a cardboard lid with a hole cut for the thermometer.
A1.3(c)	Hess's Law experiments allow learners to calculate energy changes for reactions that are difficult to measure experimentally such as the decomposition of limestone. ΔH can be calculated for the reaction between $CaCO_3$ and HC*l*, and the reaction between CaO and HC*l*. Determining ΔH for the hydration of $MgSO_4$ can be achieved by calculating the ΔH value for the reaction between $MgSO_4$ (3.00 g) and water (45 cm^3) and from the ΔH value for the reaction between $MgSO_4.7H_2O$ (6.60 g) and water (45 cm^3).
A1.3(e)	A demonstration of the catalytic oxidation of ammonia. Bubble oxygen gas into conc.NH_3 (aq) and lower in a red hot Pt gauze above the surface. Remove the gauze for a few seconds and return it to the flask where it will re-glow. The experiment can also be done with an indicator, e.g. litmus in the ammonia solution to allow the change in pH to be observed.
A1.3(f)	Decomposition of 20 vol. H_2O_2 can be achieved in a number of ways, e.g. with enzymes found in vegetables (celery, potato, and peas), or using the enzyme catalase, or inorganic catalysts (MnO_2, ZnO or CuO). If a few drops of detergent are added to the test-tubes the height of the froth produced gives a qualitative indication of relative rates of reaction.

Syllabus reference	**Suggested practical work / activities**
	A simple experiment to demonstrate catalysis is a comparison of the reaction of untreated zinc granules in conc.H_2SO_4 with zinc granules treated by dipping them into $CuSO_4$ (aq).
B1.4 Free energy and entropy	
B1.4(b)	20 minutes is needed to demonstrate the reaction between conc.NH_3 and conc. HC*l* in a diffusion tube. Small pieces of cotton wool are dipped into the separate solutions. The cotton wool dipped into conc.NH_3 is pushed into one end of the diffusion tube and stoppered. The cotton wool dipped into conc.HC*l* is pushed into the other end of the diffusion tube and stoppered. The relative rates of diffusion can be related to the position where the white ring of ammonium chloride is formed.
B1.5 Equilibrium	
B1.5(a)	Nitrogen dioxide forms an equilibrium with dinitrogen tetraoxide in a closed system. Generation of red-brown NO_2 is possible by reacting copper turnings with conc.HNO_3. Suck some of the red-brown gas into a syringe. Seal the syringe then compare the colour of the gas when it is dipped into hot water (darker) and ice-cooled water (lighter). The 'blue bottle' experiment where methylene blue changes from blue to colourless and back again with shaking is always a good lesson starter www.practicalchemistry.org/experiments/the-blue-bottle-experiment,269,EX.html
B1.5(b)	Carbonic acid can be made by dissolving dry ice (solid carbon dioxide) in water. Add 2 cm^3 of universal indicator. The indicator goes from orange to yellow as the solution is warmed up.
B1.5(c)	Determination of an equilibrium constant K_c. Esterifications are good as they are kinetically slow. Reactions take placed in sealed glass ampoules at room temperature over several days. The total volume of the chemicals in the ampoules is 10 cm^3, which includes 5 cm^3 of 3.0 $mol\,dm^{-3}$ HC*l*, and different volumes of ethanoic acid, ethanol, ethyl ethanoate and water. Do a titration of an acid vs. alkali, recording the pH in the conical flask after the addition of 1 cm^3 of alkali from the burette and every 0.1 cm^3 around the end point. Learners can then determine K_a from the half-neutralisation points in the titration curves. Ensure the pH probe is fully immersed in solutions and read pH to one decimal place. It is suggested that all solutions (HC*l*, H_3PO_4, CH_3COOH, vs. NaOH or NH_3) have the same concentration of 0.100 $mol\,dm^{-3}$.

Syllabus reference	Suggested practical work / activities
B1.5(f)	Measure the pH of distilled water at different temperature to show how K_w is temperature dependent. Learners often like to make a rack of test-tubes with the colours of the rainbow and compare them to a coloured pH chart from 0–14. This can be achieved by providing them with acids and alkalis and universal indicator. One interesting experiment with data-logging potential is to show how the pH of milk varies over several hours. Typically it plummets after several hours, becoming increasingly acidic once bacteria numbers grow and the lactose is converted into lactic acid. An experiment to help learners overcome the confusion between strong and weak acids is to get them to measure the pH of a selection of strong and weak acids having different concentrations.

Syllabus reference	Suggested practical work / activities
B1.5(g)	Get learners to plot titration curves of strong (HCl, H_2SO_4) and weak acids (CH_3COOH, H_3PO_4) vs. strong ($NaOH$) and weak alkalis (NH_3) by measuring pH at regular intervals. It is important that learners get practice with the colours of the familiar and less familiar indicators, e.g. litmus, methyl orange, bromophenol blue and bromothymol blue in neutral, acidic and alkaline conditions.
B1.5(h)	An acidic buffer can be made by dissolving solid sodium ethanoate to make ethanoic acid. A basic buffer can be made by dissolving ammonium chloride in ammonia solution. Recipes for specific pH value solutions to calibrate pH meters can be found on CLEAPPS Hazcards (see Section 10 Resources). A Faraday's Law experiment is the quantitative electrolysis of $CuSO_4$(aq) for 30 minutes using a current of 0.5 A. In this experiment the masses of the anode and cathode are recorded at the start and the end of the electrolysis. Washing electrodes needs care and can done first with distilled water, and then with propanone which quickly air dries as it is so volatile.
B1.5(k)	One half-cell can be made by dipping a piece of zinc into a 1 mol dm^{-3} solution of $ZnSO_4$ and another half-cell can be made by dipping a piece of copper into a 1 mol dm^{-3} solution of $CuSO_4$. The two half-cells can be connected by a salt bridge. A salt bridge can be made by soaking a strip of filter paper into a saturated solution of KCl or KNO_3. When the two half-cells are connected to a voltmeter the cell e.m.f. can be measured. A half-cell can be measured against a standard hydrogen electrode.
B1.5(o) B1.5(p)	Learners can investigate the effect of standard and non-standard conditions on the cell e.m.f. by using dilute or more concentrated solutions or by changing the temperature.
B1.5(q)	A simulation of a hydrogen fuel cell is the electrolysis of acidified water (dilute H_2SO_4) using platinum electrodes in a Hofmann voltameter. Weblinks of fuel cell diagrams are worth learners investigating, e.g. www.btinternet.com/~chemistry.diagrams/Fuel_cell.htm

Syllabus reference	**Suggested practical work / activities**
B1.6 Gases and kinetics	
B1.6(a)	Demonstrate kinetic theory using diffusion of bromine in a gas jar and by looking at a drop of water containing lycopodium powder on a microscope slide.
B1.6(b)	Boyle's Law: Measure the volume of gas in a syringe with different weights placed on the end of the clamped syringe. When a marshmallow is placed in a round bottomed flask and the air is removed by connecting to a vacuum pump the marshmallow gets much larger. This demonstrates how for a constant mass the volume increases as the pressure is reduced. http://dwb.unl.edu/Chemistry/MicroScale/MScale11.html Charles' Law: Measure the volume of gas in a syringe in a beaker of water at different temperatures. http://dwb.unl.edu/Chemistry/MicroScale/MScale12.html Experiment to determine M_r of CO_2: weigh a dry and stoppered empty volumetric flask, pass $CO_2(g)$ from a cylinder into the flask for 1 minute and re-stopper and reweigh. Weigh the volumetric flask when it is full of water to calculate its true volume. This is possible from the mass of water as it has a density of $1\,\text{g}\,\text{cm}^{-3}$. Record the room temperature and atmospheric pressure. Calculate M_r from mRT/PV.
B1.6(d)	Experiment to calculate E_a for the reaction between $0.020\,\text{mol}\,\text{dm}^{-3}$ of $S_2O_8^{2-}$ ($10\,\text{cm}^3$) and $0.50\,\text{mol}\,\text{dm}^{-3}$ of I^- ($5\,\text{cm}^3$) in the presence of $0.010\,\text{mol}\,\text{dm}^{-3}$ of $S_2O_3^{2-}$ ($5\,\text{cm}^3$) and starch solution ($2.5\,\text{cm}^3$). The time recorded at different temperatures (20 °C, 30 °C, 40 °C, 50 °C) is the time (t) for the blue-black colour to appear. A graph of $\log_e$ (1/t) versus 1/T can be used to calculate E_a.
B1.6(f)	Disappearing cross experiment: The reaction between $0.1\,\text{mol}\,\text{dm}^{-3}$ $Na_2S_2O_3$ and $0.2\,\text{mol}\,\text{dm}^{-3}$ HCl produces yellow sulfur which obscures a cross written on a white tile placed underneath a conical flask. Change the concentration of the individual reactants to see how rate is affected to solve the rate equation. This experiment works well also using a colorimeter. Rate is the reciprocal of the time taken to obscure the cross by the sulfur.

Syllabus reference	**Suggested practical work / activities**
B1.6(h)	Kinetics of iodination of propanone: Propanone (2.0 mol dm^{-3}), iodine (0.020 mol dm^{-3}) and hydrochloric acid (2.0 mol dm^{-3}) follow by colorimetry (reference Expt 9.5 *Advanced Practical Chemistry* p.148 ILPAC, Second Edition, John Murray, ISBN 9780719575075). Kinetics of Harcourt-Esson experiment, i.e. the reaction between hydrogen peroxide and iodide in the presence of acid. Start the stopwatch when 10 cm^3 of KI (0.10 mol dm^{-3}) and 25 cm^3 of H_2SO_4 (0.25 mol dm^{-3}) are poured into a conical flask containing 5 cm^3 of $Na_2S_2O_3$ (0.01 mol dm^{-3}), 5 cm^3 of H_2O_2 (0.10 mol dm^{-3}), water (20 cm^3) and 1 cm^3 of 1% starch solution. The time is recorded when the blue-black colour appears. In one set of experiments keep the total volume of H_2O_2 and water at 25 cm^3 and vary their proportions. This experiment might be more familiar as the iodine clock experiment. www.practicalchemistry.org/experiments/iodine-clock-reaction,55,EX.html or http://dwb.unl.edu/Chemistry/MicroScale/MScale37.html. In another set of experiments keep the total volume of KI and water at 25 cm^3 and vary their proportions. Plot graphs of $\log_{10} 1/t$ vs. $\log_{10} [H_2O_2]$ or $\log_{10} [KI]$.
B1.6(i)	Initial rates method is where the initial rate is calculated from the slope of a graph of volume of gas evolved versus time. Suitable experiments include the reaction between magnesium and different concentrations of HCl, and the decomposition of H_2O_2 having different concentrations (20 vol or 100 vol).
B1.7 Chemical models and evidence	
	No suggestions for this section.

Syllabus reference	**Suggested practical work / activities**
2. Inorganic chemistry	
A2.1 Periodic Table	
A2.1(a)	Shapes of simple molecules, e.g. H_2, O_2, O_3, N_2, Cl_2, P_4, S_8 and H_2O_2 and the types of bonds (single, double and triple) are often best taught through the use of molymods.
A2.1(e)	Reaction of period 3 elements (Na, Mg, S) with oxygen can easily achieved by igniting the element on the end of a combustion spoon which is then placed in a gas jar of oxygen. If white phosphorus is available react it with oxygen in a large flask and a darkened room for the best effect. Place sand in the bottom of a large pyrex or glass flask. Then fill the flask with oxygen and stopper it. Put a small piece of white phosphorus in a crucible and lower it onto the bed of sand. Ignite the phosphorus by touching it with the hot end of a heated glass rod and then seal the flask. Pulling down the blinds or turning off the lights makes for a more spectacular reaction which emits a large amount of bright white light. On cooling add 200 cm^3 of distilled water followed by universal indicator. The red colour indicates the formation of an acid from the non-metallic oxides of phosphorus. The poor reactivity of aluminium is unexpected from its position in the reactivity series. The protective oxide layer of Al_2O_3 can be removed from aluminium by an aqueous solution of mercury(II) chloride. This experiment is described in the inspiring book called Uncle Tungsten by Oliver Sacks www.oliversacks.com/books/uncle-tungsten/ (Chapter 4).
A2.1(f)	Reaction of Period 3 elements with water. React sodium in a small trough on top of an OHP with a few drops of phenolphthalein. Place a 10 cm strip of magnesium ribbon under a funnel in cold water with Blu-Tack® and collect the H_2(g) in an inverted boiling tube over several weeks. A safe method to react magnesium with steam is to hold a piece of ribbon using tongs above a conical flask (protected with a ceramic wool heatproof collar) containing boiling water.
A2.1(g)	'Reaction' of Period 3 oxides (Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5) with water; measure the pH of any resulting solutions. SO_2 can be made by burning sulfur on a combustion spoon and placing it into a gas jar. Adding water and adding universal indicator gives a red acidic solution.
A2.1(h)	Reaction of Period 3 chlorides (NaCl, $MgCl_2$, $AlCl_3$) with water. Measure the pH and test fumes of HCl(g) with moist blue litmus paper.

Syllabus reference	**Suggested practical work / activities**
A2.2 Main group chemistry (except Group 14)	
A2.2(a)	Thermal decomposition of $MgCO_3$ and $CaCO_3$. Heat these carbonates in crucibles to constant mass. Record masses to at least three decimal places.
A2.2(d)	The high solubility of ammonia can be illustrated by demonstration of the ammonia fountain experiment. A dry round bottomed flask (fitted with a glass tube in its neck) is filled with ammonia gas followed by addition of a few drops of litmus. The flask is then inverted and clamped and the glass tube is lowered into a trough of water. Hold a piece of red litmus paper near the neck of a recently unstoppered bottle of ammonia solution. To show the reaction of ammonia with an acid dip a glass rod into conc.HCl and bring it near a bottle of conc.NH_3 which has had its stopper removed. If you want learners to make ammonia they can easily do this by stirring two solids together (NH_4Cl and $Ca(OH)_2$) in a fume cupboard.
A2.2 (f)	The chemistry of hydrogen peroxide is familiar in terms of its decomposition. To follow the rate of this decomposition collect the evolved oxygen gas in a syringe or by downward displacement using different concentrations of H_2O_2 (10, 20, 50, 100 vol) with MnO_2 as the catalyst (see also A1.3(f)). Cleaning of silver coins is possible with hydrogen peroxide as the surface will be coated with silver(I) oxide. http://metaldetectingworld.com/cleaning_coin_p12_peroxide.shtml
A2.2(h)	Test H_2SO_4 for sulfate ion with $BaCl_2$(aq). Leave beaker of conc. H_2SO_4 in a fume cupboard and mark the changing surface level over several months. Make plaster of Paris by adding water to $CaSO_4.0.5H_2O$(s). Dehydration experiments using conc.H_2SO_4. To 20 g of sucrose in a small beaker add 5 cm^3 of water and stir with a glass rod. Continue stirring whilst adding 10 cm^3 of conc.H_2SO_4 until the mixture turns black. An even more impressive dehydration can be achieved by dehydrating 4-nitroacetanilide (10 g) with 10 cm^3 of conc.H_2SO_4 and heating the mixture in a crucible.
A2.2(j)	Test-tube reactions of conc.H_2SO_4 with small amounts of solid Group 1 halides, e.g. $NaCl$, $NaBr$, NaI. Reactions of conc.H_2SO_4 with small pieces of Mg, Zn, Fe and Cu and testing the evolved SO_2(g) with filter paper soaked in orange dichromate paper.
A2.2(m)	Titration of 0.05 $mol\,dm^{-3}$ I_2 solution with 0.10 $mol\,dm^{-3}$ $Na_2S_2O_3$ using 1% starch solution as indicator.

Syllabus reference	Suggested practical work / activities
B2.3 From non-metals to metals: Group 14	
B2.3(a)	A simple conductivity experiment is to place samples of Group 14 elements (carbon as graphite, Si, Ge, Sn and Pb) in turn into a circuit with a lamp to observe which conducts electricity and completes the circuit. Learners would benefit from researching these weblinks when considering the structures of the recently discovered allotropes of carbon: www.creative-science.org.uk/c60model.html www.btinternet.com/~chemistry.diagrams/bucky.htm www.btinternet.com/~chemistry.diagrams/C70.htm
B2.4 Transition elements	
	To illustrate a range of colours shown by transition metals of varying oxidation states get learners to make a series of aqueous solutions in test-tubes, e.g. $FeSO_4$, $CuSO_4$, $Fe_2(SO_4)_3$, $CoCl_2$, $KMnO_4$ and show them a selection of coloured compounds in sample jars, e.g. green ($NiCl_2.6H_2O$), blue $CuSO_4.5H_2O$, $VOSO_4$ (blue), $FeSO_4.7H_2O$ (green), $ZnSO_4.7H_2O$ (white).
B2.4(c)	The structure of the hexadentate ligand EDTA takes time to learn and can be sped up by getting learners to make its structure using molymods.
B2.4(e)	Molymods of geometric isomers, e.g. *cis*-platin and *trans*-platin and optical isomers, e.g. $[CrCl_2(en)_2]^{1+}$ Learners find it helpful to have mirrors available so they can check that mirror images are non-superimposable.
B2.4(g)	A simple experiment to show that different oxidation states for a transition metal have different colours is the reduction of vanadium from 5+ through all its oxidation states to 2+. This can be achieved by dissolving a spatula of ammonium vanadate(V) in $20\,cm^3$ of dil. HCl, followed by the addition of zinc granules and warming the mixture gently in a Bunsen flame.

Syllabus reference	Suggested practical work / activities
	Titrations between 0.1 mol dm^{-3} solutions of $Ni^{2+}(aq)$ or $Cr^{3+}(aq)$ and $[EDTA]^{4-}$ or 1,2-diaminoethane(en) to work out the formula of complexes using a colorimeter. The filter in the colorimeter is chosen as the complementary colour to the complex. Ensure the metal ions and ligands have the same concentrations and mix them in varying proportions keeping the overall volume constant. The test-tube containing the mixture with the maximum or minimum absorbance corresponds to the formula of the complex.
B2.4(h)	To improve learners' laboratory technique why not get them to prepare the greenish coloured complex salt potassium trioxalatoferrate(III)? This can be done by dissolving 3.6 g of iron(II) ethanedioate in water (20 cm^3) and 5.5 g of potassium ethanedioate at a temperature below 50 °C. Add 20 cm^3 of 20 vol. H_2O_2 from a burette in 1 cm^3 portions. Filter and add ethanol (20 cm^3) to the filtrate, cool in an ice-water bath and filter the complex *via* Buchner filtration.
B2.4(i)	Ligand exchanges and colour changes, e.g. Cu^{2+} reacting with these ligands dil. NH_3, conc.NH_3, Cl^-, OH^- and Fe^{3+} with KSCN to form the blood red complex. There are plenty of redox titrations to chose from, for example Fe^{2+}/Fe^{3+} or Cu^+/Cu^{2+} vs. MnO_4^-/Mn^{2+} and Fe^{2+} vs. Cl^- or H_2O_2 or $(CO_2H)_2$. An example of a disproportionation is warming red $Cu_2O(s)$ with conc.H_2SO_4. Take a spatula of red copper(I) oxide, add conc.H_2SO_4 and warm in a test-tube for a few minutes. Blue Cu^{2+} and copper metal will be evident.
B2.5 Crystal structures	
B2.5(a)	There are no experiments directly involving crystals but learners would benefit from investigating the following weblinks. http://chemistry.about.com/od/growingcrystals/ht/purplecystal.htm www-teach.ch.cam.ac.uk/links/3Dindex.html Learners will get ideas of efficient and inefficient packing and the two major crystal types (hexagonal close packing and cubic close packing) by being given polystyrene balls and Blu-Tack® or glue. Print off the nett on the following weblink www.btinternet.com/~chemistry.diagrams/crystals_unit_cells.htm Photocopy enough netts so that each learner has eight. Colour in the circles, semicircles and part circles on the nett. Make eight cubes from the netts so that each fraction of an atom/ion's contribution to each cube (unit cell) can be worked out.

Syllabus reference	**Suggested practical work / activities**
3. Organic chemistry	
A3.1 Preliminaries	
A3.1(c)	There are no experiments but learners would benefit from visiting this weblink each month. www.chm.bris.ac.uk/motm/motm.htm
A3.1(d)	Making simple organic molecules with molymods will allow learners to appreciate the realistic zig-zag, explore functional group isomers (aldehydes/ketones, alcohols/ethers, esters/carboxylic acids), geometric isomers (*cis* and *trans*), optical isomers (with four different groups attached to a tetrahedral carbon atom).
A3.2 Functional group level	
A3.2(a)	Reaction of 5 cm^3 of cyclohexane with 2 cm^3 of bromine water under a UV lamp. Reaction of 5 cm^3 of cyclohexene with 2 cm^3 of bromine water.
A3.2(c)	Preparation of cyclohexene by the dehydration of cyclohexanol (20 cm^3) using conc.H_3PO_4 (8 cm^3) as the dehydrating agent. Collect the fraction that distils <95 °C. Treat the distillate with a saturated solution of $NaCl$ (4 cm^3). Separate the two layers and dry the upper layer with $CaCl_2$ and filter. The product can be tested for unsaturation with bromine water.
A3.2(d)	Make use of molymods to illustrate the concept of primary, secondary and tertiary with molymods of alcohols, amines, and halogenoalkanes. Natural product extractions are possible in school laboratories, e.g. steam distillation of limonene from orange/lemon peel or extraction of eugenol from cloves. www.westfield.ma.edu/cmasi/organic_lab/organic1_lab/isolation_of_eugenol.pdf
A3.3 Lower functional group level reactions – Alcohol level	
A3.3(a)	Hydrolysis of liquid halogenoalkanes can be carried out on in a water-bath at 50 °C. Just 5 drops of each halogenoalkane is added to a mixture of ethanol (1 cm^3) and silver nitrate (1 cm^3) in a test-tube clamped in the water-bath. Rate = 1/time for the precipitate to appear (see also A4.1(d)).
A3.3(b)	1°, 2° and 3° alcohols can be distinguished at room temperature using the Lucas test, where 2 cm^3 of alcohol are added to 1 cm^3 of conc.HCl and 1 cm^3 of $ZnCl_2$(aq). 3° alcohols rapidly give a cloudy mixture and 2° alcohols give a cloudy mixture after five minutes. Bromoethane can be prepared by reacting ethanol (6 cm^3) with conc.H_2SO_4 (6 cm^3) and 6 g of solid sodium bromide. This method results in the *in situ* generation of HBr(g). The fraction that distils between 38–40 °C is collected by distilling into a test-tube held in an ice-bath. To purify the product add 4 cm^3 of saturated $NaHCO_3$(aq) to the distillate. Using a separating funnel the organic layer is separated from the aqueous layer and then dried with anhydrous $MgSO_4$.

Syllabus reference	**Suggested practical work / activities**
A3.4 Lower functional group level reactions – Carbonyl level	
A3.4(a)	A suggested introduction to the carbonyl level is giving learners a selection of carbonyl compounds to smell. Aldehyde examples include vanillin, benzaldehyde, and cinnamaldehyde. Ketone examples include caraway seeds (S-carvone) and spearmint (R-carvone) and nail varnish remover (propanone).
A3.4(c)	A very quick practical is making use of sodium bisulfite ($NaHSO_3$) to purify simple aldehydes such as ethanal. Addition of a saturated bisulfite solution to ethanal leads to white crystals which can be filtered. Hydrolysis of the addition product using dilute $\mathrm{HC}l$ (aq) will return the aldehyde. Tollens' reagent (silver mirror test) is made by adding 1 drop of dilute NaOH(aq) to 2 cm^3 of $AgNO_3$(aq) and adding ~10 drops of dilute NH_3(aq) until the brown ppt. of Ag_2O just dissolves. To get a positive test (silver mirror) add 1 cm^3 of aldehyde to the Tollens' reagent. Adding a spatula of glucose to Tollens' reagent gives consistently good silver mirrors. A recipe for a giant silver mirror useful for demonstration purposes can be found by investigating this weblink www.rsc.org/images/mirror_tcm18–188809.pdf
A3.4(d)	To dry (remove water) from a solvent such as diethyl ether which may be needed for some reactions, e.g. when using $\mathrm{LiA}l\mathrm{H}_4$ or in preparing Grignard reagents, add small pieces of sodium or sodium wire extruded through a hole.
A3.5 Addition and elimination reactions	
A3.5(b)	Decolorisation of alkenes by bromine water, e.g. cyclohexene, butter, margarine, by simply shaking the unsaturated chemical in a stoppered test-tube.
A3.5(c)	It is possible to make polystyrene from styrene using a peroxide initiator. www.terrificscience.org/lessonpdfs/PolymerLab13.pdf
A3.5(d)	Dehydration of an ethanol soaked in mineral wool using $\mathrm{A}l_2\mathrm{O}_3$ catalyst. Collect the ethene produced under water and test with bromine water. Another alcohol that can be dehydrated is 2-methylpropan-2-ol at 170 °C by refluxing with conc. H_2SO_4.
A3.6 Green chemistry	
	No suggestions.

Syllabus reference	**Suggested practical work / activities**
B3.7 Higher functional group level reactions – Carboxylic Acid level	
B3.7(a)	The detection of the carboxylic acid group in aqueous solutions of ethanoic, propanoic and benzoic acid is achieved by adding either Na_2CO_3(aq) or $NaHCO_3$ (aq). Both reactions lead to the release of a colourless gas (CO_2) which when bubbled into limewater turns it cloudy. It is a simple matter to compare the relative rates of reaction of a weak acid (CH_3COOH) and a strong acid (HCl) having identical concentrations by reacting 0.1 mol dm^{-3} solutions with 2 cm pieces of magnesium ribbon. Hydrolysis of 2 cm^3 of ethanoyl chloride or benzoyl chloride by addition of 2 cm^3 of water leads to the evolution of white fumes of HCl(g) which can be tested for with moist blue litmus paper.
B3.7(b)	Another carboxylic acid practical is the hydrolysis of oil of wintergreen (methyl salicylate). 0.003 mol of the ester is refluxed with 40 cm^3 of 2.0 mol dm^{-3} hydrochloric acid for 15 minutes. Once the precipitate has disappeared the reaction mixture is filtered and then fractionally distilled. To precipitate the salicylic acid add 20 cm^3 of 2.0 mol dm^{-3} hydrochloric acid. The aspirin is collected by Buchner filtration and washed with a small quantity of distilled water. To find out which alcohols and carboxylic acids are needed to make fruity esters learners should investigate this weblink www.chm.bris.ac.uk/motm/ethylacetate/smells.htm One simple method is to mix 1 cm^3 of alcohol and 1 cm^3 of carboxylic acid in a test-tube with a few drops of the catalyst conc.H_2SO_4 and warm the reaction mixture gently in a test-tube for several minutes.
B3.7(c)	The nylon rope trick is a good example of a condensation polymerisation. The method involves adding 20 cm^3 of a 5% solution of hexanedioyl chloride in lotoxane (a 'green' solvent) to a 5% aqueous solution of 1,6-diaminohexane (20 cm^3). Using a pair of tweezers at the interface of the two immiscible liquids it is possible to pull out a thread of nylon and with practice several metres of polymer can be wrapped around a glass rod. It is possible to buy two ingredients which, when mixed, result in the formation of polyurethane foam. In a recyclable plastic cup mix 10 cm^3 of solution A and 10 cm^3 of solution B. Useful weblinks include: http://video.google.com/videoplay?docid=-6367640639873461283# and www.cfsnet.co.uk/acatalog/CFS_Catalogue__2_Part_Polyurethane_Foam_Liquid_415.html

Syllabus reference	**Suggested practical work / activities**
B3.8 Higher functional group level reactions – Carbon dioxide level	
B3.8(a)	There are no experiments but learners would benefit from investigating the following weblinks: www.demochem.de/chembox_urease-e.htm www.seriaz.org/downloads/4-caffiene.pdf
B3.9 Mechanisms	
B3.9(e)	There are no experiments but learners would benefit from investigating the following weblinks: www.btinternet.com/~chemistry.diagrams/Animations.htm www.rod.beavon.clara.net/slides.htm
B3.10 Aromatic chemistry	
B3.10(a) B3.10(b)	A safer nitration is the nitration of the aromatic ester methylbenzoate. Dissolve the ester in equimolar mixtures of conc.HNO_3 and conc.H_2SO_4. Heat the mixture to 50 °C for 30 minutes. Then pour the mixture onto iced water and filter using Buchner filtration. Recrystallise the nitromethylbenzoate from a minimum volume of warm ethanol.
B3.10(c)	Reaction of 1 cm^3 of toluene, 1 cm^3 of aqueous phenol solution and 1 cm^3 of aniline with bromine water. Compare the rate of formation of the resultant white precipitate.
	To test for phenol dissolve 10 mg in warm water. Addition of $FeCl_3$(aq) will result in a purple complex.
	Preparation of aspirin by reacting 5 g of 2-hydroxybenzoic acid with 7.0 cm^3 of ethanoic anhydride in a conical flask. Add 3 drops of conc.H_2SO_4 and swirl, then warm for 15 minutes at 50-60 °C stirring with a thermometer. Cool and add cold water (70 cm^3) and filter. Recrystallise the aspirin by dissolving in warm ethanol (15 cm^3) and pouring onto cold water.
B3.11 Acidity and basicity	
B3.11(a)	In a boiling tube react 4 mm^3 of sodium with 20 cm^3 of ethanol in the presence of a few drops of a suitable indicator.
B3.11(b)	Prepare aqueous solutions of acidic and basic compounds and record their pH values, e.g. phenol, benzoic acid, ethanol, methylamine, ethylamine, aniline and ethanoic acid. Record the pH of chloroethanoic, dichloroethanoic and trichloroethanoic acid having the same concentrations and compare to ethanoic acid.

Syllabus reference	**Suggested practical work / activities**
B3.12 Stereochemistry	
B3.12(b)	Dissolve 1 g of sucrose in 20 cm^3 of distilled water and record its optical rotation in a polarimeter. To the sucrose solution add 2 cm^3 of 2.0 $mol\,dm^{-3}$ HCl and record this new mixture's optical rotation every five minutes until it remains constant.

Syllabus reference	Suggested practical work / activities
4. Analysis	
A4.1 Qualitative and quantitative analysis	
A4.1(a)	This section covers all the qualitative tests found in the *Data Booklet* for the course. A lot of the tests can be carried out whilst teaching other parts of the course and where opportunities arise they are referenced to the appropriate section of the syllabus. Tests for cations (Al^{3+}, Fe^{3+} (B2.4(i)), Cr^{3+}, Ba^{2+} (A2.2(j)), Cu^{2+}, Fe^{2+} (B2.4(l)), Pb^{2+} (B2.3), Mn^{2+} & Zn^{2+} (B2.4) and NH_4^+) Tests for anions (SO_4^{2-} (A2.4(h)), CO_3^{2-}, SO_3^{2-}, NO_3^-, NO_2^-, Cl^-, Br^-, I^-, gases (NH_3, CO_2, H_2, Cl_2 (A2.1(h)), SO_2 (A2.1(a)), O_2, HCl) and organic functional groups, e.g. alcohol (A3.3) (and distinguish between 1°, 2° and 3°), halogenoalkane, carboxylic acid, aldehyde, ketone, phenol and alkene.
A4.1(b)	Calculate the empirical formula of MgO by heating 2.43 g of magnesium in a crucible with a lid. Take care not to lose too much smoke as you lift the crucible's lid to let in more air for reaction.
A4.1(c)	***Volumetric analysis:*** *Redox titrations* (mostly using indicators), e.g. Fe^{2+} vs. MnO_4^- (B2.4i), I_2 vs. $S_2O_3^{2-}$, Fe^{2+} vs. H_2O_2. *Thermometric titrations* (A1.3(c)), where changes in temperature are measured, e.g. neutralisation of NaOH (aq) by adding 5 cm^3 portions of HCl(aq) carried out in a polystyrene cup. *Potentiometric titrations*, where changes in conductivity are measured, e.g. Fe^{2+} vs. Ce where changes in conductivity are measured.
A4.1(d)	*Gravimetric analysis* for example thermal decompositions by heating carbonates to constant mass, e.g. $MgCO_3$, $CaCO_3$, $NaHCO_3$, Na_2CO_3; or by removing water of crystallisation of hydrates, e.g. $Na_2CO_3.10H_2O$, $CaSO_4.2H_2O$, $FeSO_4.7H_2O$, $MgSO_4.7H_2O$ or $BeCl_2.2H_2O$. *Precipitation reactions* for example mixing solutions of $AgNO_3$ and KCl or HCl, or $BaCl_2$ and H_2SO_4 (A2.2(h)).

Syllabus reference	**Suggested practical work / activities**
A4.2 Mass spectrometry	
A4.2(a)	There are no experiments but learners would benefit from investigating the following weblinks: www.btinternet.com/~chemistry.diagrams/mass_spec6.swf www.btinternet.com/~chemistry.diagrams/electron_impact.htm http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi www.btinternet.com/~chemistry.diagrams/Spectroscopy–1a.doc
A4.3 Electronic spectroscopy	
A4.3(a)	Weblinks that learners would benefit from investigating are: www.btinternet.com/~chemistry.diagrams/element_discharge.htm www.avogadro.co.uk/light/bohr/spectra.htm www.chemguide.co.uk/inorganic/group1/flametests.html www.btinternet.com/~chemistry.diagrams/Bohr_hydrogen_transitions.htm www.btinternet.com/~chemistry.diagrams/hydrogen_energy_states.htm www.btinternet.com/~chemistry.diagrams/Hspec_animation2.swf
A4.3(c)	*Flame tests:* Make a small loop on the end of a nichrome or platinum wire. Dip the wire into conc.HC*l* and use the moisture to stick small amounts of compounds onto the loop, e.g. chlorides of Li, Na, K, Ca, Ba, Cu and Pb. Hold the loop in the hottest part of a Bunsen flame and note the flame colour. If a hand-held spectroscope is available look at the coloured flame through it, or alternatively look at elements in discharge tubes. If your school has a darkroom make use of it for these experiments. Hold the back of a CD up to a light to see spectral lines which show mercury is present in fluorescent strip lighting.

Syllabus reference	**Suggested practical work / activities**
A4.4 Infra-red	
A4.4(a)	Web links that learners would benefit from investigating are: www.btinternet.com/~chemistry.diagrams/aspirin.htm www.le.ac.uk/spectraschool/ www.chem.ed.ac.uk/bunsen_learner/ir.html To model what happens to the resonance frequency of different bonds in IR spectroscopy stick different sized polystyrene balls on one end of a series of springs. If your school does not have easy access to a local university or its own IR spectrometer then there is "*Spectroscopy in a suitcase*" outreach provided by the Royal Society of Chemistry www.rsc.org/education/hestem/sias.asp
A4.5 Carbon-13 NMR	
A4.5(a)	There are no experiments but learners would benefit from investigating the following weblinks: www.btinternet.com/~chemistry.diagrams/C13nmrshifts.htm www.chemguide.co.uk/analysis/nmr/backgroundc13.html http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi
A4.6 NMR of other spin ½ nuclei	
A4.6(a)	There are no experiments but learners would benefit from investigating the following web links: www.cis.rit.edu/htbooks/mri/ www.rod.beavon.clara.net/nmr2.htm www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/nmr/nmr1.htm www.goldennumber.net/pascal.htm www.knockhardy.org.uk/sci_htm_files/nmr1.pdf www.rod.beavon.clara.net/spectra.htm

Section 3: The van Arkel triangle

3.1 Introduction

3.1.1 History

The van Arkel triangle has not had a prominent place in British chemical education. It has, however, been more popular in continental Europe and the United States.

It is a scheme in which the three idealised forms of chemical bonding – covalent, ionic and metallic – are related to one another. Its development had to wait until all three modes of chemical bonding were established.

The first of these bonding theories to be developed was ionic bonding, which was first pioneered by Helmholtz in 1881, who was inspired by Faraday's laws of electrolysis. Following much important work in the first three decades of the twentieth century by J J Thompson, Lewis, Born, Landé, Fajans and many others, the Dutch chemists van Arkel and de Boer published a definite description of ionic bonding in *Chemical Bonding as an Electrostatic Phenomenon* in 1929.

The theory of covalent bonding began its development in the first decade of the twentieth century with the work of the Germans, Stark and Kauffmann, as well as J J Thompson, William Ramsay and others. The seminal paper on covalent bonding came from Lewis in 1916.

Metallic bonding has a much less glorious history in the chemical literature. Chemists have long been put off by the non-stoichiometric intermetallic compounds and alloys, which often defy simple electron-counting rules. It has mainly therefore been solid-state physicists and metallurgists who have made the most impressive advances in metallic bonding theory. Lewis, in 1913, was the first chemist to recognise metallic bonding as a model to sit alongside the ionic and covalent models in chemical bonding theory.

The use of a triangle to describe the relationship between the three main types of bonding did not strictly begin with van Arkel. The German, Grimm, produced the first in 1928, before the concept of electronegativity was even developed. The electronegativity scale was first introduced by Pauling in 1932. The triangle, with the appearance that we associate with it today, was first published by van Arkel in his text book *Molecules and Crystals* in 1941. Van Arkel's triangle only considered intermediate bonding along the edges. In 1947 his colleague Ketelaar went on to consider compounds placed in the body of the triangle.

Van Arkel's and Ketelaar's triangles were only made strictly quantitative in 1980 by Bill Jensen of the University of Cincinnati. He has investigated the appearance of the triangle using types of electronegativity scale other than Pauling's and considered the limitations of the triangle in predicting the structure and properties of compounds.

3.1.2 Theory

The van Arkel triangle pertains only to binary compounds and elements whose atoms can bond together. It arises from a plot of the difference of the electronegativity values of the two elements in the compound (y-axis) against the average of the electronegativity values (x-axis). The electronegativity values are used without any regard for the stoichiometry of the binary compound.

In the van Arkel triangle the x-axis therefore describes the degree of localisation of the bonding electrons. At the left-hand extreme of the x-axis lies the most electropositive element, caesium. (Francium is probably not more electropositive than caesium as it has been shown to have a higher first ionisation energy than caesium – due to relativistic effects.) At this metallic extreme the valence electrons are delocalised. At the right-hand extreme of the *x*-axis lies the most electronegative element, fluorine. (The light noble gases are not at this extreme as they do not bond with themselves, or indeed anything else.) At this covalent extreme, the valence electrons are absolutely localised within the F–F bond.

In the van Arkel triangle the *y*-axis therefore describes the degree of asymmetry of the bonding electrons between the two bonding atoms. At the bottom of the triangle, where $y = 0$, which is where the elements are found, there can be no asymmetry in the electron distribution across the bond. At the top of the triangle, where there is the greatest asymmetry of the electron distribution in the bond, there is the extreme of ionic bonding. The compound at this apex is therefore caesium fluoride, which has the greatest difference in the electronegativity values of its constituent elements.

A quantified van Arkel diagram can be found in the Journal of Chemical Education, volume 72, page 395 (1995) at http://pubs.acs.org/doi/pdf/10.1021/ed072p395 The label ***i*** on the y-axis is used by Jensen to denote the ionicity parameter (the difference in electronegativity values); the label ***C*** on the x-axis stands for the covalency parameter (the average electronegativity value).

When plotting the point corresponding to some compound, one can simply plot the intersection of two lines – each starting with a constituent element on the *x*-axis. The line from the left-hand element runs parallel to the left-hand edge pointing towards the ionic vertex, and the line from the right-hand element parallel to the right-hand edge. It follows then that all the compounds of an element lie on one of two lines that intersect at the element on the *x*-axis. These lines run parallel with the two edges leading to the ionic vertex. On the left-hand branch there are the compounds of which the element in question is the more electronegative; on the right-hand branch the element is the less electronegative of the pair. The compounds of caesium and of fluorine are exceptional in this regard, lying at the extremes of the base of the triangle; their compounds only lie on the line connecting them to the ionic vertex.

The great advantage of the van Arkel triangle is that the three principal models of chemical bonding are seen to be part of a single scheme in which they are all related and indeed have equal weighting. If offers a quantitative appreciation of intermediate bonding, and also demonstrates that intermediate bonding is not limited to polar-covalent / polarised ionic. Furthermore, it is based on the already familiar topic of electronegativity.

The simplest application of the van Arkel triangle is to anticipate – based on electronegativity values – the type of bonding in some unfamiliar compound. This is straightforward in cases where a plot places a compound near to one of the bonding extremes. However, in more borderline cases there is a danger of the assignment of bonding type being the result of a circular process, where bonding type is arbitrarily defined by electronegativity values. The main point about the van Arkel triangle is that it provides a clear picture of the fact that bonding type is not black and white, but rather a continuous scale between idealised extremes.

One subtle but important point about the van Arkel triangle is that its reflection of bonding type cannot be assumed to provide reliable information about structure. This is because structure depends on other factors besides electronegativity values – principally stoichiometry and electronic configuration. A similar problem is apparent when considering elements such as carbon, tin and phosphorus. These elements have allotropes of very different structures and electrical properties, yet of course the allotropes of an element will all have the same electronegativity value. A further shortcoming of the triangle is observed when multiple oxidation states are possible in a binary compound, for example lead chloride. In this case the tetravalent compound has appreciable covalent character while the bivalent analogue is essentially ionic.

It is, however, possible to find systematic predictors of structure in the van Arkel triangle if the compounds being considered are limited to those with a fixed stoichiometry and electronic configuration. This has been demonstrated by Bill Jensen.

There has been some discussion in the literature about semiconductor regions in the van Arkel triangle. Some authors have proposed a small triangle sitting on the base line of the main triangle. However, semiconductivity is also seen along the metallic–ionic edge of the triangle. Owing to the problems of definition as to what constitutes a semiconductor, Bill Jensen performed a simple probe–buzzer–battery conductivity detector on a range of compounds and found a region within a distance of the metallic corner that showed appreciable conductivity (see *Journal of Chemical Education*, volume 72 page 398 (1995) at http://pubs.acs.org/doi/pdf/10.1021/ed072p395). It can be assumed that a semiconducting region will be found around the edge of this conductivity region.

The shaded in area in Jenson's diagram contains compounds that showed detectable conductivity in the simple test referred to above. Compounds outside this region did not show detectable conductivity in this test.

A range of electronegativity scales has been applied to the constructing of van Arkel triangles. Allen has proposed that his scale produces the most realistic placement of compounds according to their properties. Jensen has found that the variation between the different electronegativity scales is not significant. He used the little-known Martynov Batsanov scale which uses the average of the successive ionisation energies of the valence electrons of an atom. Allen's scale uses the average orbital energy of the valence electron orbitals, which he calls the configuration energy.

3.1.3 Bibliography

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3.2 Teaching strategy

The van Arkel triangle has the principal purposes of illuminating the idea of intermediate bonding, and showing the connection between ionic, covalent and metallic bonding.

One possible place to put it in the curriculum would be after teaching electronegativity. The electronegativity concept is only commonly used to explain the existence of dipoles, which indicate a form of intermediate bonding, though this angle may not always be pursued at the time. Therefore the van Arkel triangle should make for a substantial and meaningful application of the electronegativity concept and relate it to the dipoles seen in heteronuclear covalent bonds. The three basic bonding models will have been met by learners in their pre–16 chemistry course. This strategy will serve to revise and reinforce their understanding of the basic modes of bonding within a different framework.

Given the template van Arkel triangle provided overleaf, teachers can easily set straightforward exercises to plot binary compounds and to make predictions about bonding type and electrical properties. Piloting this topic showed that learners do require some practice of this plotting. We also found that teachers will need to emphasise that the electronegativity values used must not be modified to take into account stoichiometry.

This topic also lends itself well to extension work. Groups could consider the more subtle points discussed in the theory section, and investigate the basis of the different types of electronegativity scale (which ties in with thermodynamics (Pauling), effective nuclear charge (Allred-Rochow), ionisation energy (Mulliken, Allen and Martynov Batsanov) and atomic radius (Sanderson)).

3.3 Classroom materials

The van Arkel triangle

- It is only for binary compounds (between only two elements) and elements.
- The *x*-axis gives a measure of how localised the electrons are on their atoms. On the left-hand side the electrons are delocalised and the element is a metal. On the right-hand side the electrons are localised and the element is a covalently bonded non-metal.
- The *y*-axis gives a measure of how equally the electrons are shared between the two elements. When $y = 0$ (i.e. on the *x*-axis) the two atoms bonded are the same and so the electrons in the bond are equally shared between them. At high values of *y*, towards the top of the triangle, there is a big difference in electronegativity and so the electrons are very unequally shared: the electrons are pulled towards the most electronegative element. This is what leads to ionic bonding.
- The three types of bonding can all be rationalised in terms of electronegativity values:

  Small similar values = metallic

  Large similar values = covalent

  Very different values = ionic

How to plot a compound on a van Arkel triangle

Method one

- Take the average of the electronegativity values of the two elements. This is the *x* value.
- Work out the difference between the two electronegativity values. This is the *y* value.
- Ignore the stoichiometry of the compound, i.e. the numbers in the formula.

Method two

- Find the two elements that constitute the compound on the *x*-axis.
- Draw lines from these elements that are parallel to the sides of the triangle. The line from the left-hand element is parallel to the left-hand side; the line from the right-hand is parallel to the right-hand side.
- Where these lines intersect is the place to plot the compound in the triangle.

Intermediate bonding

- At the corners of the van Arkel triangle are the idealised cases of bonding. We can consider caesium to be pure metallic, fluorine as pure covalent, and caesium fluoride as pure ionic. However, most compounds are not right at the corners.
- The van Arkel triangle shows that many combinations of elements produce a type of bonding that is intermediate between the three idealised models. Silicon lies between metallic and covalent. Hydrogen fluoride lies between covalent and ionic. Caesium hydride lies between ionic and metallic. Mercury(II) bromide is near the centre of the triangle and so is intermediate between all three types of bonding.

Electrical properties

- Metallic compounds conduct electricity. Covalent and ionic compounds do not. We can therefore predict whether or not a compound will conduct electricity or not if it is near one of the corners of the van Arkel triangle.
- Compounds which conduct electricity can be found in a segment of the triangle around the metallic corner. Compounds near to the borderline of this segment are likely to be semiconductors.

3.4 Sample question

Electronegativity and bonding

(a) Define electronegativity.

(b) Explain why elements with low electronegativities can conduct electricity.

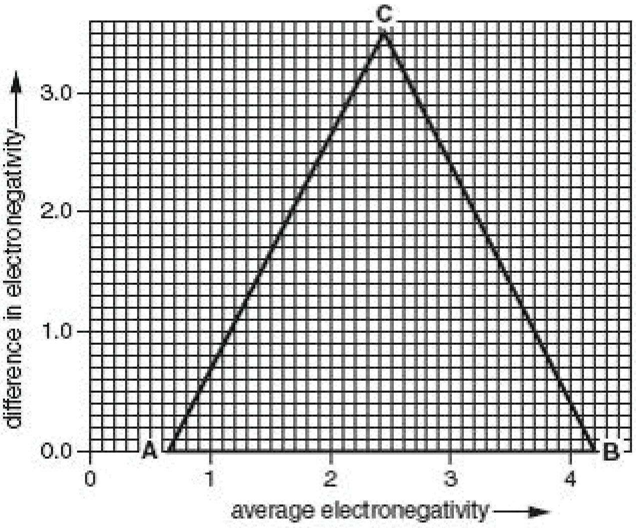
(c) Ionic bonding results from the transfer of one or more electrons from one atom to another. Explain in terms of electronegativities why this transfer takes place.

(d) Where might a compound that is described as polar covalent be found in the van Arkel triangle?

(e) Plot the following compounds on the van Arkel template using the electronegativity values provided.

- Li_2O
- NO
- A*l*N
- A*l*Li

Element	Electronegativity
Li	0.91
N	3.07
O	3.61
A*l*	1.61



(f) For each of the four compounds in the previous part, decide which of the following words best describes the bonding. Write the name of the compound beneath the word describing its bonding.

Ionic	**Covalent**	**Metallic**	**Intermediate**

[4]

(g) Suggest for each of the four compounds which of the following words is most likely to describe its electrical conductivity. Write the name of the compound beneath the word describing the conductivity.

Conductor	**Semiconductor**	**Insulator**

[4]

Answers

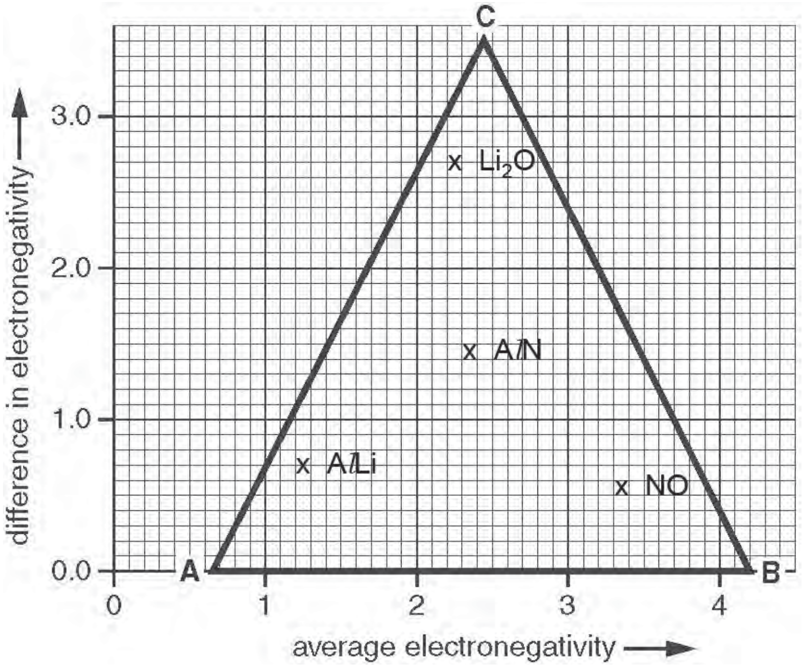
(a) Electronegativity is a measure of the ability of (the core of) an atom to attract (1) the valence OR bonding electrons toward itself. (1) [2]

(b) Electrical conductivity arises because the atoms' valence electrons are only weakly held (1) and so can delocalise throughout the structure [2]

(c) One atoms is significantly more electronegative than the other (1)
One or more electrons are pulled off the less electronegative atom (1)
and add to the more electronegative atom (1) [3]

(d) Polar covalent compound are found on or close to the middle of the ionic-covalent edge [1]

(e) Points must be plotted correctly to within half a square's length in the diagram.



One mark for each correctly plotted point. [4]

	Ionic	**Covalent**	**Metallic**	**Intermediate**	
(f)	Li$_2$O (1)	NO (1)	AlLi (1)	AlN (1)	[4]

	Conductor	**Semiconductor**	**Insulator**	
(g)	AlLi (1)	AlN (1)	NO (1) Li$_2$O (1)	[4]

Section 4: Functional group level

4.1 Introduction

To some learners, organic chemistry can seem like a collection of unconnected chemical reactions transforming one functional group to another which just have to be memorised, along with all the conditions and other details.

Of course there are many facets in the interpretation and prediction of organic transformations; we need to consider where the most reactive centres are in a molecule, likely mechanisms and stereochemistry. However, a very useful organising principle when considering reacting carbon atoms in molecules is the one of so-called "functional group level".

The functional group level classifies a single carbon atom in a molecule – typically the one carrying the functional group – depending on the number of bonds it has to an atom or atoms of greater electronegativity than itself. Due to the valency of carbon this number must clearly be an integer in the range 0 to 4. The different levels are named after the simplest possible oxygen-containing functional groups in that level. Some examples are in the table below.

Name of functional group level	No. bonds to electronegative atoms	Examples
Hydrocarbon	0	Alkanes, alkenes, alkynes, Grignard reagents
Alcohol	1	Alcohols, alkyl halides, amines, thiols, ethers, peroxides
Carbonyl	2	Aldehydes, ketones, imines, acetals, hemiacetals, ketals, hemiketals, hydrates
Carboxylic acid	3	Carboxylic acids, esters, amides, nitriles, acid anhydrides, acid chlorides, ortho esters
Carbon dioxide	4	Carbon dioxide, carbonic acid, urea, carbonate esters, guanidine, carbon disulfide, carbon oxysulfide

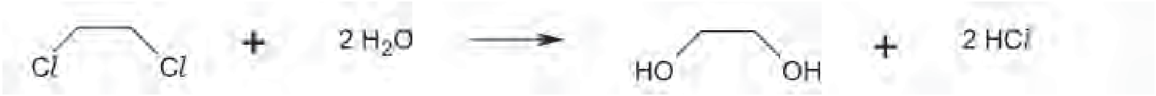
Indeed, categorising the carbon atom from any molecule into this scheme is just a trivial case of bond counting. We will see many examples of this in the coming pages.

4.2 Hydrolysis

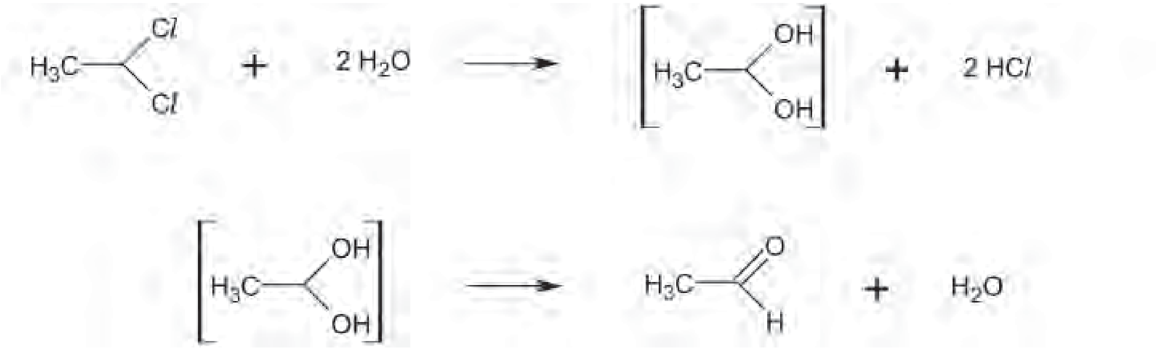
One of the most useful features of the functional group level model is the simple rule that hydrolysis of any functional group carbon leads to no change in the functional group level and the transformation of that carbon's functional group to the title functional group of that level.

This is easily visualised by considering the hydrolysis reaction to be that all bonds to more electronegative atoms are replaced by bonds to –OH. However, when more than one –OH group is bonded to a carbon there is a strong entropic driving force for a molecule of water to be eliminated.

Comparison between the hydrolysis of *vic*- and *gem*-dihalides is instructive here. *Vic*-dihalides have a halogen atom bonded to two adjacent carbon atoms; gem-dihalides have two halogen atoms bonded to the same carbon atoms.



The *vic*-dihalide gives a diol. Both carbon atoms on the dihalides are in the alcohol functional group as they are both bonded to one electronegative atom, chlorine. Each carbon atom hydrolyses to give the title functional group of that level, namely the alcohol functional group.



In the case of the *gem*-dihalide the functional group carbon is in the carbonyl functional group as it has two bonds to electronegative atoms. We imagine these groups to be replaced by –OH groups to give us the compound in brackets. However, this compound is unstable because there is more than one –OH group bonded to a single carbon. This unstable intermediate is shown eliminating a molecule of water in the second step, yielding the final product, ethanal, a carbonyl compound.

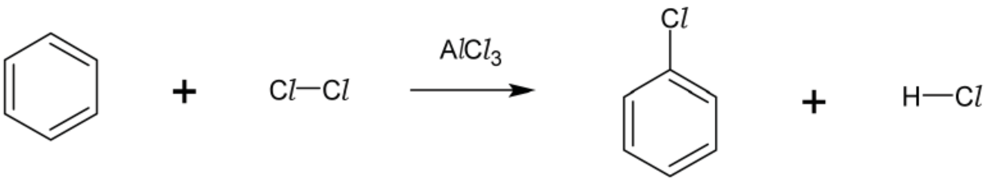
4.3 Classifying functional group interconversions

When a substitution reaction involves the exchange of one electronegative atom bonded to a carbon with another, there is no change in functional group level. This is usually the case with substitution reactions. A typical example would be the hydrolysis of a halogenoalkane:

$$RCH_2Br + H\text{–}OH \rightarrow RCH_2OH + HBr$$

in which the reacting carbon on the bromoalkane remains in the alcohol functional group level during the reaction.

When a reaction causes a carbon to go up in functional group level – in other words when the carbon has more bonds to electronegative atoms in the product molecule than it had in the reactant molecule – then there will have been an oxidation process, and an oxidising agent must have been present. For example, in the chlorination of benzene,



the reacting carbon which forms a bond with a chlorine atom is oxidised up from the hydrocarbon level to the alcohol level.

Similarly when a carbon atom goes down in oxidation level a reduction must have taken place, and a reducing agent must have been present. For example, in the reaction between a nitrile and lithium aluminium hydride, $LiAlH_4$,

$$R{-}C{\equiv}N \xrightarrow{LiAlH_4} R{-}CH_2NH_2$$

the nitrile carbon is lowered from the carboxylic acid functional group level (three bonds to electronegative nitrogen) to the alcohol level (just one such bond).

There are some functional group interconversions that deserve particular mention to clarify the concept.

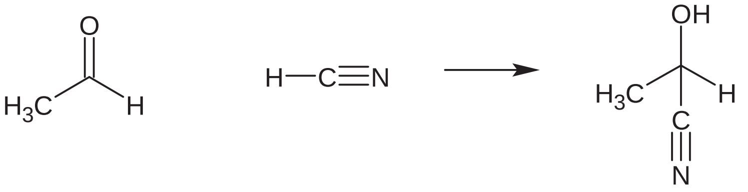
1. Reactions involving cyanide ions

Reactions in which an electronegative atom is substituted for a cyanide group, for example:

$RCH_2Br + NaCN \rightarrow RCH_2CN + NaBr$

involve a formal lowering of the functional group level of the CH_2 carbon from the alcohol level to the hydrocarbon level. Of course another carbon atom has been introduced into the molecule. This cyanide carbon is in the carboxylic acid functional group level as the carbon has three bonds to a more electronegative atom (nitrogen).

A similar drop in functional group level is observed when hydrogen cyanide undergoes nucleophilic addition to a carbonyl compound,



except in this case the functional group level of the reacting carbon in the carbonyl compound goes from the carbonyl level to the alcohol level, as there is now only one bond to an electronegative atom (oxygen) in the product molecule.

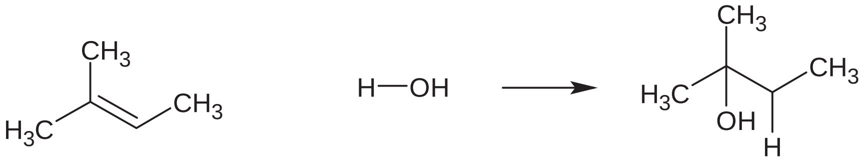
2. Addition to alkene addition

Addition reactions are slightly different from the reactions seen so far as two functional group carbons (the carbons of the C=C bond) react at once. There is no rule of thumb; the changes in functional group level of each of the C=C carbons depend on what is being added to them. For example, in the hydrogenation reaction

$$H_2C{=}CH_2 + H{-}H \rightarrow H_3C{-}CH_3$$

there is no change in any of the carbons' functional group levels, since hydrogen is not an electronegative atom.

However, in the case of a hydration reaction, such as



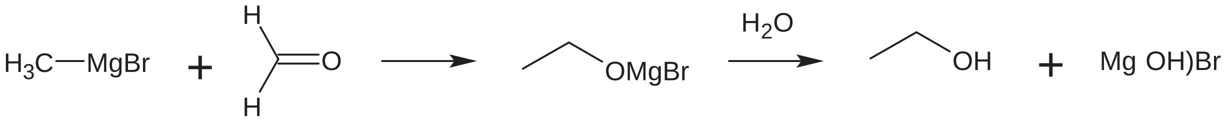
one of the carbon atom's functional group level (the more substituted carbon, which bonds to the oxygen) has increased from the hydrocarbon level to the alcohol level, whereas the other carbon has remained in the hydrocarbon level since it hasn't formed a bond with an electronegative atom (only hydrogen).

In the case of addition of bromine, however, both carbon atoms in the C=C bond go up in oxidation level from the hydrocarbon level to the alcohol level, as they both have a bond to an electronegative atom (bromine) in the product 1,2-dibromoethane.

$$H_2C{=}CH_2 + Br{-}Br \rightarrow BrCH_2{-}CH_2Br$$

3. Grignard reactions

Grignard reactions lead to carbon-carbon bond formation. The Grignard carbon remains in the same hydrocarbon level as it isn't bonded to any electronegative atoms in either the Grignard reagent or the product of the reaction. The carbon atom that is attacked by the Grignard reagent will go down in functional group level by one level. For example, in the reaction between a Grignard reagent and methanal,

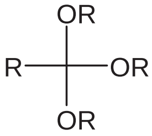


the methanal carbon goes from the carbonyl level to the alcohol level. The Grignard carbon remains in the hydrocarbon level as a methyl group.

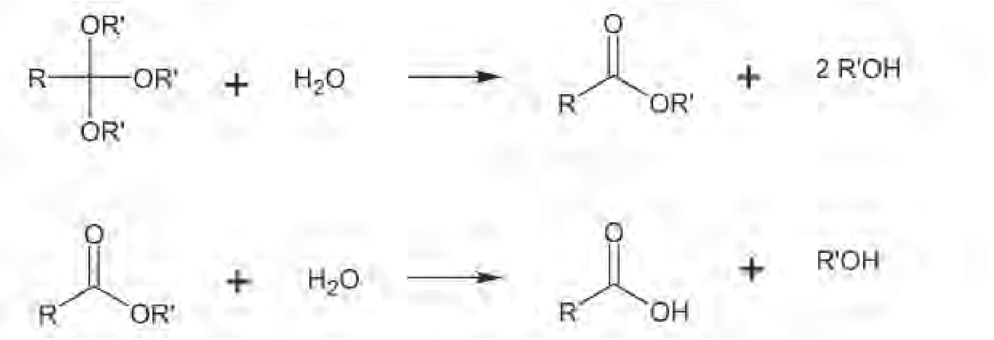
4.4 Dealing with unfamiliar functional groups

Even with unfamiliar functional groups it is easy to work out the functional group level for the functional group carbon atom; just count the number of bonds to a more electronegative element. It is also easy to predict the product of the hydrolysis of that functional group; it is just the title functional group for that particular functional group level.

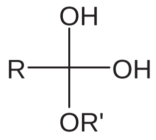
For example, let us consider ortho esters. The general structure of an ortho ester is shown below.



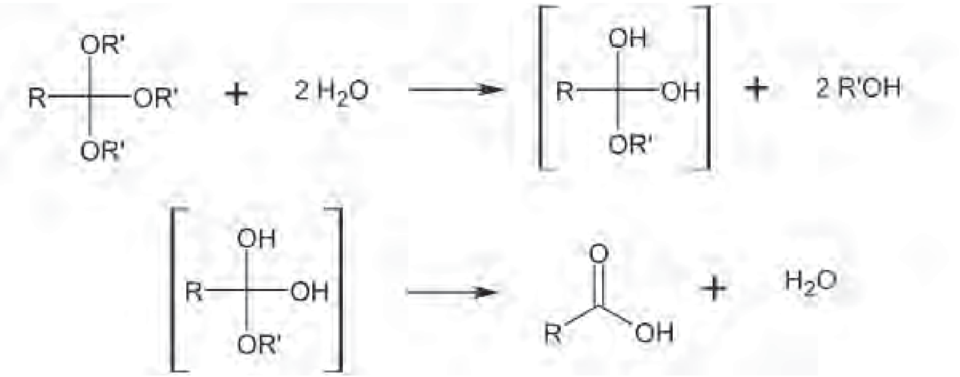
Inspection of the functional group carbon in the above ortho ester reveals that it has three bonds to electronegative oxygen atoms. It is therefore in the carboxylic acid level. Hydrolysis of ortho esters should therefore yield carboxylic acids. This is indeed the case, in a two-step reaction going via an ester:



The first of the reactions above is consistent with the ideas discussed in the hydrolysis section. Initially, two of the –OR' groups are replaced by –OH groups, producing the intermediate



which, having two –OH groups bonded to the same carbon, is unstable and eliminates water to produce the ester. So the first hydrolysis reaction above can itself be considered to proceed in two steps:



The two steps above sum to give the equation for the first hydrolysis reaction.

4.5 Teaching strategies

Some teachers may wish learners to be presented with functional group interconversions in the traditional fashion, and only to consider the functional group level approach later on as a means of unifying the organic chemistry covered.

At the beginning of a Cambridge Pre-U course, learners will be aware of some functional group interconversions from their previous chemistry course, and so should in fact be ready to meet the functional group level concept level early on – after all, it is a very simple construct. In fact, learners' pre-existing organic chemical knowledge could be neatly revised while framing it in the functional group level approach.

4.6 Sample questions

1 Ethanamide is a simple example of an amide.

(a) Draw the structure of ethanamide showing the geometry of the molecule. [2]

(b) What is the functional group level of the amide group?

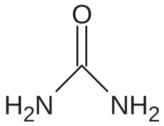
.... [1]

Amides may be hydrolysed by reaction with dilute acid to give a carboxylic acid.

(c) Write an equation for the hydrolysis of ethanamide.

.... [2]

Urea, shown below, might be thought of as a diamide, although in fact its chemistry is quite distinctive.



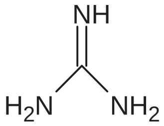
(d) What is the functional group level of the carbon atom in urea?

.... [1]

(e) Write an equation for the hydrolysis of urea.

.... [2]

The structure of guanidine is shown below.



(f) What is the functional group level of the carbon atom in guanidine?

.... [1]

(g) What are the products of hydrolysis of guanidine?

.... [2]

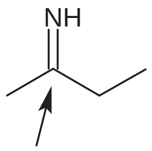
[Total: 11]

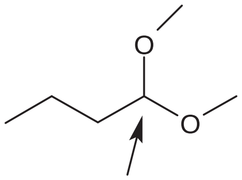
2 The structures below may look unfamiliar. Use your knowledge of functional group levels to work out the following for each.

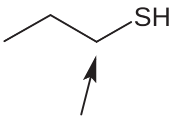
(a) the functional group level of the carbon atom indicated by the arrow [8]

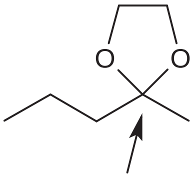
(b) the product of hydrolysis of the species [8]

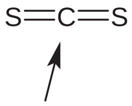
(c) the chemical equation for the hydrolysis [8]

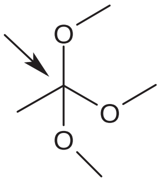








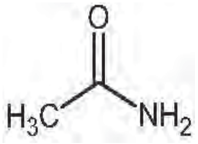




[Total: 24]

Answers

1 **(a)** Bond angles of approximately 120° around the central carbon (1)
Correct molecule (1)



[2]

(b) FGL 3 or carboxylic acid level [1]

(c) $CH_3CONH_2 + H_2O + H^+ \rightarrow CH_3COOH + NH_4^+$
1 mark only if H^+ omitted and products are CH_3COOH and NH_3 [2]

(d) FGL 4 or carbon dioxide level [1]

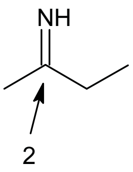
(e) $CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3$
1 mark for correct products, 1 mark for balancing [2]

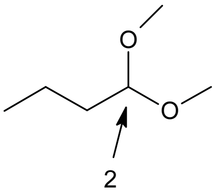
(f) FGL 4 or carbon dioxide level [1]

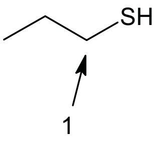
(g) CO_2 (1)
NH_3 (1) [2]

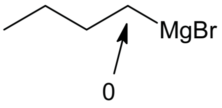
[Total: 11]

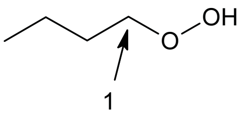
2 **(a)** 1 mark for each correct assignment

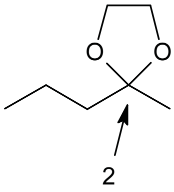


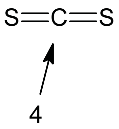


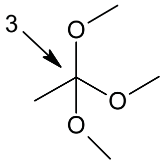






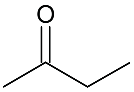


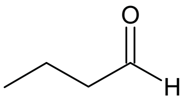


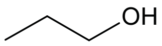


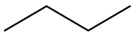
[8]

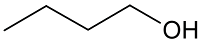
(b) 1 mark for each correct principal product

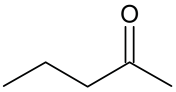


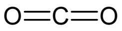


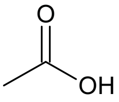












[8]

(c) 1 mark for each correct equation from left to right for each row in turn.

$C_4H_9N + H_2O \rightarrow C_4H_8O + NH_3$

$C_6H_{14}O_2 + H_2O \rightarrow C_4H_8O + 2CH_4O$

$C_3H_8S + H_2O \rightarrow C_3H_8O + H_2S$

$C_4H_9MgBr + H_2O \rightarrow C_4H_{10} + Mg(OH)Br$

$C_4H_{10}O_2 + H_2O \rightarrow C_4H_{10}O + H_2O_2$

$C_7H_{14}O_2 + H_2O \rightarrow C_5H_{10}O + C_2H_6O_2$

$CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S$

$C_5H_{12}O_3 + 2H_2O \rightarrow C_2H_4O_2 + 3CH_4O$ **[8]**

[Total: 24]

Section 5: Carbon-13 NMR

5.1 Introduction

Carbon-13 NMR has enough in common with proton NMR for it to be used to illustrate NMR in general. For example, its chemical scale is referenced to the same compound, tetramethylsilane; both nuclei have a spin quantum number of ½ and are ubiquitous in organic molecules; both techniques are routine in chemical laboratories. Carbon-13 NMR offers two distinct advantages over proton NMR:

- Spin-spin coupling is not observed in spectra. With a natural abundance of about 1%, $^{13}C–^{13}C$ coupling can go unnoticed in spectra. $^{13}C–^{1}H$ coupling is routinely eliminated from spectra by broadband proton decoupling. Note that a consequence of this decoupling is that peak intensities are not proportional to the number of nuclei in a given environment.
- The chemical shift scale with carbon-13 is simpler and more intuitive than the proton scale. The general pattern of resonances shown in the chart on the next page is easily remembered.

An important point is that when a carbon atom has more than one of the features on the chart (e.g. it has a C-C bond and a C=O bond) then its resonance appears in the range with the highest chemical shift values.

The absence of spin-spin coupling means that carbon-13 spectra will be simpler in appearance than proton spectra. They therefore lend themselves to the study of larger and more complex molecules. With larger molecules there are more likely to be interesting symmetry considerations manifesting themselves in spectra. It is therefore an ideal context for considering molecular symmetry.

5.2 Teaching strategy

Spectral problem-solving is most easily mastered through practice. A series of spectra can be taken from the National Institute of Advanced Industrial Science and Technology of Japan at http://riodb01.ibase.aist.go.jp/sdbs/.

Learners need to concentrate on two aspects of the spectra:

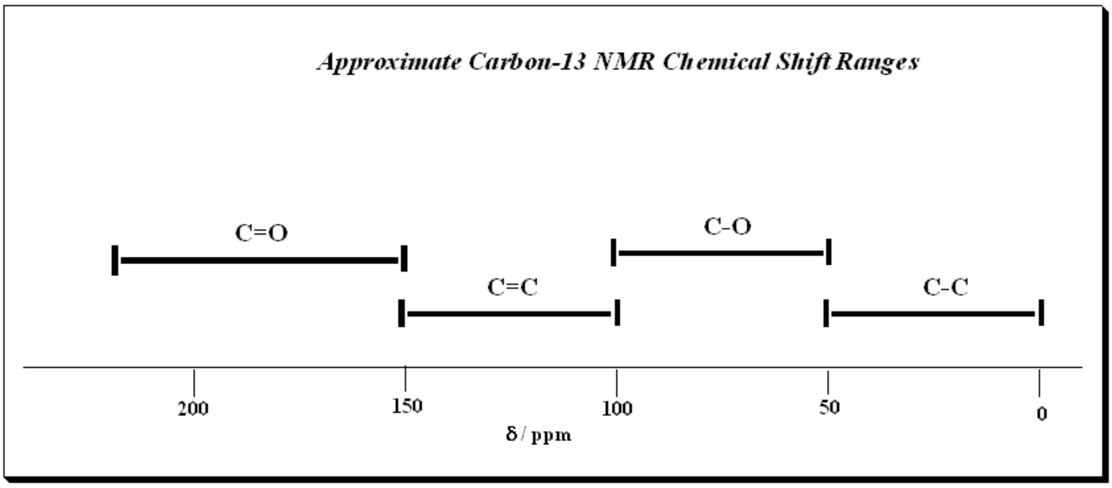
- The types of carbon atom in the molecule (following the chart on the next page).
- The number of different chemical environments of carbon in the molecule (and the region of the spectrum that pertains to each one). In order to appreciate when chemical environments are the same, learners must be able to recognise symmetry relationships where they apply, and that rotation of carbon-carbon single bonds is fast on the NMR time scale.

Learners should, as far as possible, assign all the peaks in the spectra and explain how the number of peaks is consistent with the symmetry of the molecule.

Initially learners could be given the full assignment and asked to justify the assignment. Then learners could be given the molecular structure and asked to assign as far as possible each of the carbons in the molecule to a peak in the spectrum. The most able could be given just the spectrum and asked to propose a molecule that is consistent with it.

Learners should also be able to predict the number of peaks in each of the four regions of the spectrum for a given molecule.

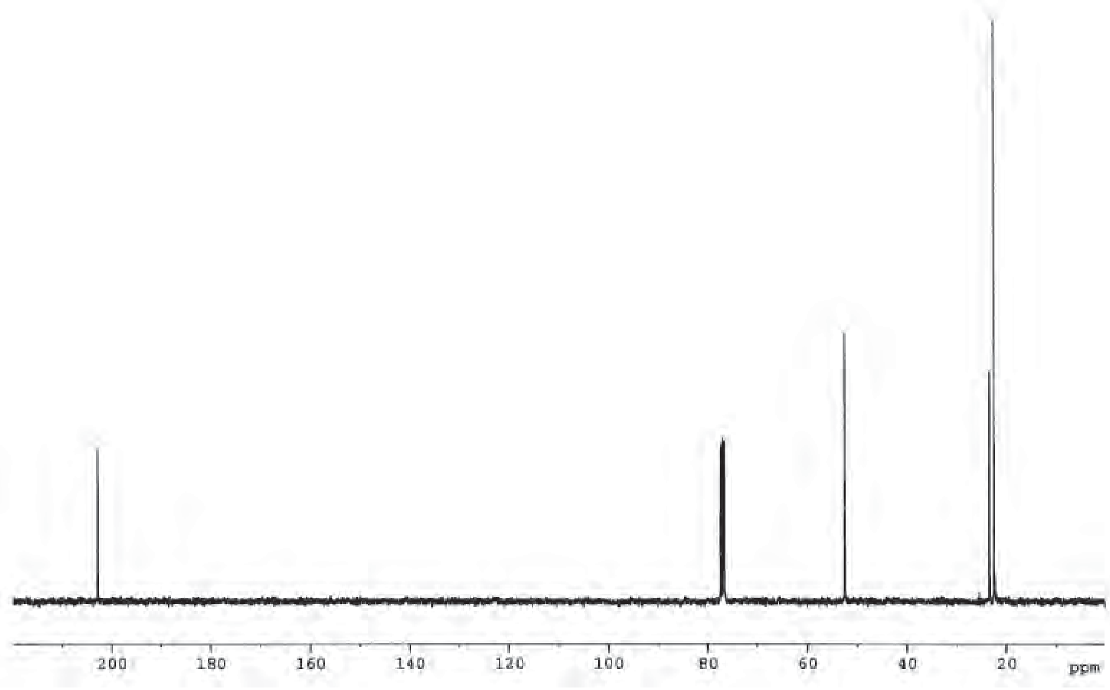
Handout on approximate carbon-13 chemical shift ranges. (Adapted from *Chemistry*, Dr Michael A Thompson, Keytomes, 2009, ISBN 978098071004)

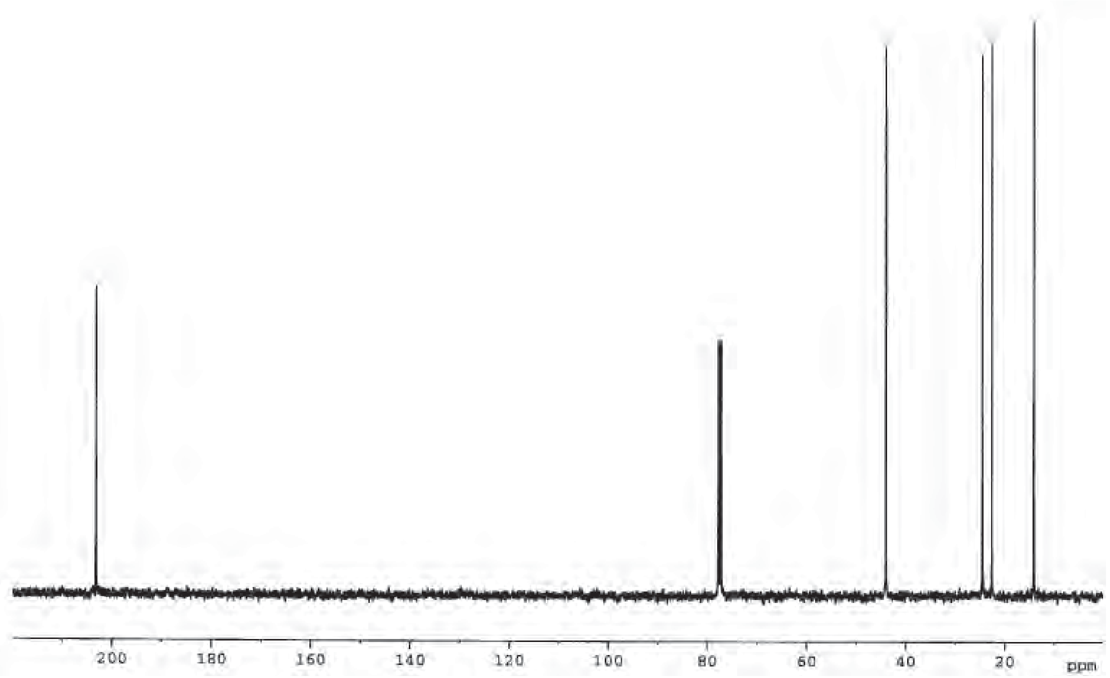


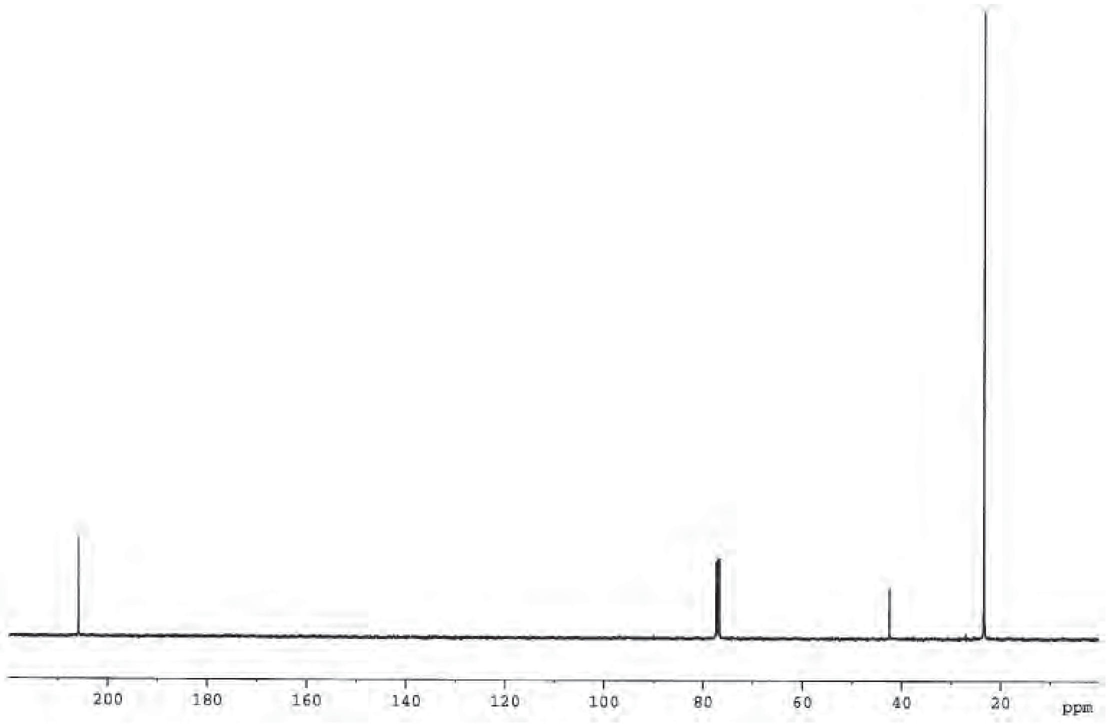
5.3 Sample question

The carbon-13 spectra below are of isomers of $C_5H_{10}O$. The three molecules are:

- Pentan-2-one
- Dimethylpropanal
- 3-Methylbutanal







Assign each molecule to one of the spectra, explaining your reasoning. Note that in each of the spectra there is a peak at 78 ppm that corresponds to the solvent, chloroform.

Answer

Top spectrum is 3-methylbutanal. The two methyl groups are equivalent, leaving four carbon signals. They are all in the 0-50 ppm region except the carbonyl carbon just past 200 ppm.

Middle spectrum is pentan-2-one. All five carbons are non-equivalent, so there are five peaks. Four are in the 0-50 ppm region except the carbonyl carbon just past 200 ppm.

Bottom spectrum is dimethylpropanal. The three methyl groups are equivalent, leaving three carbon signals. Again, the carbonyl carbon appears a little over 200 ppm and the remaining carbon signals are in the 0-50 ppm region.

Section 6: Orbitals

6.1 Introduction

In the author's experience of teaching sixth-form Chemistry, the topic of orbitals is challenging for learners, across the ability range. The abstract and counter-intuitive elements are difficult enough for learners to grasp as it is, while the apparent contradiction with what was learnt at (I)GCSE level can draw protest. Demands for justification and explanation can be tricky to field. Of course such enquiries lead inevitably to quantum mechanics.

The purposes of this section are several.

- To provide guidance to teachers on useful approaches to teaching this area. Some of the material in this chapter is worth conveying directly to all learners; some could be useful extension material; parts could be useful reference for teachers to be able to draw upon if certain questions arise in discussion. Each subsection begins with advice about how the material may be employed and how much is required by the syllabus.
- To explain the origin of atomic orbitals from first principles, and extend the treatment to bonding and anti-bonding molecular orbitals. This should give teachers greater confidence discussing orbitals.
- To treat the subject rigorously while remaining comprehensible at the level of a bright sixth former with knowledge of Cambridge Pre-U or Cambridge International A Level Further Maths. Nothing in this chapter will be beyond the capacity of the brightest learners, and much will be within grasp of any interested Cambridge Pre-U Chemistry learner.
- To provide figures that illustrate the subject matter exactly, rather than using the artists' impressions that are seen in many text books at this level.
- To correct common misconceptions at this level about orbitals.

It must, however, be stressed that a great deal of this chapter is background material and teachers should not be put off by the volume or depth of content, but rather be selective as to the level of content they require to suit their learners. The Cambridge Pre-U syllabus requires learners to 'understand that electrons occupy orbitals in molecules as well as atoms; understand that putting electrons into a bonding orbital leads to the nuclei being held together (i.e. bonded) whereas putting electrons into an anti-bonding orbital weakens bonding by pulling the nuclei apart from one another as these orbitals lie outside the internuclear region.' As stated in the syllabus, an appreciation that these vacant orbitals exist is vital for a proper understanding of molecular electronic spectroscopy and for understanding mechanism in further study. A sample question from a past paper has been included to illustrate one way in which this topic may be examined.

6.2 What are orbitals and why are they necessary?

Most learners begin their sixth-form chemical studies thinking of electrons orbiting a nucleus like planets orbit the sun, i.e. with classical mechanics. How do orbitals and subshells fit into this picture? This is an ideal time to discuss what is meant by a model, how they can be useful up to point, but may need refining under different circumstances. In this context it might also be worth pointing out that even the Schrödinger equation isn't the last word since it does not take into account the effects of special relativity (the Dirac equation does this) and more besides.

Cambridge Pre-U learners should certainly be familiar with the concept of wave-particle duality covered in section 6.2.1 and the definition of an orbital described in section 6.2.6. Learners also studying maths and physics could be given extension work by considering the wave functions in greater detail, as explained in sections 6.2.2 and 6.2.3. The remaining sections, 6.2.4, 6.2.5 and 6.2.7 would probably only be worth using as extension material for learners who are confident at the level of Further Maths.

6.2.1 Wave-particle duality

At the root of it all is wave-particle duality, which is an experimental fact: electrons can impart momentum in collisions as particles do, and they can be diffracted and produce interference patterns as waves do. Cambridge Pre-U learners need to know that electrons in atoms are described by a wave function, and so this in itself implies the wave nature of the electron. Whether electrons behave as waves or particles depends on the experiment. For our purposes we are taking electrons in atoms to behave as standing waves. By analogy, a plucked guitar string holds a standing wave. We can imagine the string to be a one-dimensional object. The two-dimensional analogue might be the flat surface of a drum being struck. The three-dimensional analogue might be a rubber ball vibrating around its own centre. Electron wave functions have three spatial dimensions. Learners are familiar with standing waves and so this will be a useful analogy.

Paul Dirac argued in his classic monograph on quantum mechanics (see the first section in [1][1]) that wave-particle duality could be justified on philosophical grounds. Considering the experimental fact that matter is not continuous but composed of fundamental particles, it follows that there must be some degree of indeterminacy at the level of these particles, since any observation made of a fundamental particle must involve disturbing it (with a photon, for example). In describing an electron as a wave we have introduced the required indeterminacy in the simultaneous measurement of its position and momentum.

6.2.2 Wave functions

Learners who have seen the equations of simple waves in physics and maths may be interested or relieved that electron wave functions may be approached (initially, at least) from the same direction. More mathematically able learners could be extended to consider the complex exponential form of the wave functions.

The Greek letter psi, ψ, is normally used to represent the wave function of an electron. A general formula for the amplitude at a given point on the x-axis of a wave travelling from right to left is

$$\psi = A\sin(\omega t + \phi) \qquad (1)$$

where A is the amplitude of the wave at the given point, ω is the angular frequency, t is time elapsed and ϕ is the phase of the wave in radians at $t = 0$. The angular frequency is defined as

$$\omega = 2\pi f \qquad (2)$$

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[1] all references in square brackets are to the Bibliography at the end of Section 6.

where f is the frequency in Hertz (s^{-1}). ωt is therefore 2π times the number of wavelengths that passed the point in time t. It is therefore the phase of the wave in radians at time t when $\phi = 0$. A general formula for a stationary wave on the x-axis is

$$\psi = A\sin(kx + \phi) \tag{3}$$

where ϕ is the phase of the wave in radians at $x = 0$ and k is the wavenumber. Wavenumber is defined as

$$k = \frac{2\pi}{\lambda} \tag{4}$$

where λ is the wavelength. This means that kx is 2π times the number of multiples of the wavelength along the x-axis. k is therefore the spatial equivalent of the angular frequency, meaning that kx is a spatial equivalent of angular phase, and is also measured in radians. We can combine equations (1) and (3) to describe a wave in terms of both space and time coordinates,

$$\psi = A\sin(kx + \omega t + \phi) \tag{5}$$

where ϕ is the phase of the wave in radians at $x = 0$ and $t = 0$.

We could also have written equation (5) with a cosine function if we had adjusted the value of ϕ by $\pi/2$. Since there are multiple phases in the argument of the trig function it becomes mathematically convenient to express the wave function as a complex exponential function, which is related to trig functions through de Moivre's equation,

$$e^{i\phi} = \cos\phi + i\sin\phi \tag{6}$$

where $i = \sqrt{-1}$. The complex exponential form is useful because the expression can be written as the product of complex exponentials of the component phases

$$Ae^{i(\phi_1 + \phi_2 + \phi_3)} = Ae^{i\phi_1}e^{i\phi_2}e^{i\phi_3} \tag{7}$$

It might seem unsettling to have the complex i appearing in a wave function, but there are mathematical tricks to make these complex exponentials real. For example,

$$Ae^{i\phi} + Ae^{-i\phi} = 2A\cos\phi \tag{8}$$

since $\cos\phi = \cos(-\phi)$, but $\sin\phi = -\sin(-\phi)$. The properties of complex exponentials and their use in describing oscillating functions are explained in [2].

6.2.3 Schrödinger and his equation

When Schrödinger first constructed a wave function to describe a fundamental particle he wrote it in terms of variables that might be measured: position, momentum, energy and time. He combined these with the Planck constant, h, since this was a measure of the smallest packets or quanta of energy that could be measured, as illustrated by the well-known equation relating the energy, E, of a photon of light to its frequency, f,

$$E = hf \tag{9}$$

Equation (9) shows that Planck's constant has units of J s. These are the same units as momentum × distance and also energy × time. Learners will all be familiar with this equation. Those with some ability in maths might be able to appreciate a generic wave function, comparable to equation (5) but expressed in the form of a complex exponential is

$$\psi = A\exp\left\{2\pi i\left(\frac{px - Et}{h} + \phi\right)\right\} \tag{10}$$

There is a negative sign in front of the Et term as the wave is defined as travelling in the positive direction. (In equations (1) and (5) the wave is travelling in the negative direction.)

Schrödinger's famous equation is an eigenvalue equation. Such equations take the general form

$$\hat{O}\psi = \lambda\psi \tag{11}$$

where $\hat{O}$ is an operator (as indicated by the hat symbol). An operator is something that acts on a function to produce another function. In an eigenvalue equation, when the operator acts on the function, called an eigenfunction, it returns the same function multiplied by a constant, λ, known as the eigenvalue. Schrödinger constructed operators that generated eigenvalues that correspond to physical observables. Most learners won't have met eigenvalue equations, but will understand the concept, given some explanation. For example, if an operator is the second derivative with respect to x then the function $A\sin 2x$ will be an eigenfunction, giving the eigenvalue –4.

The operator for momentum along the x-axis, $\hat{p}_x$, is $\frac{\mathrm{h}}{2\pi i}\times\frac{\partial}{\partial x}$.The partial differential operator $\frac{\partial}{\partial x}$ denotes differentiating with respect to x while keeping other variables constant. Applying this operator to the generic wave function, $\hat{p}_x\psi$, returns the momentum, p, as the eigenvalue

$$\begin{aligned}\hat{p}_x\psi &= \frac{h}{2\pi i}\times\frac{\partial\psi}{\partial x}\\ &= \frac{h}{2\pi i}\times\frac{\partial}{\partial x}\left\{A\exp\left(2\pi i\left(\frac{px-Et}{h}+\quad\right)\right)\right\}\\ &= pA\exp\left(2\pi i\left(\frac{px-Et}{h}+\quad\right)\right) = p\psi\end{aligned} \tag{12}$$

This is known as the position representation, as it is the position variable being operated on. The operator for position in this representation is trivially $\times x$.

These operators for momentum and position are used to construct the Schrödinger equation in the following sections. This field is known as wave mechanics.

6.2.4 Properties of eigenvalue equations

These equations have certain properties from which chemists can take advantage. In fact, many of the standard operations in quantum chemistry, such as normalising wave functions, creating bonding and antibonding combinations, and constructing hybrid orbitals, depend on the following properties.

- An eigenfunction may be multiplied by any constant and it remains an eigenfunction that produces the same eigenvalue from the operator.
- A linear combination, i.e. a sum, of eigenfunctions is also an eigenfunction of the operator. In this sense eigenfunctions add up rather like vectors and so wave functinos are often called eigenvectors. Using the arbitrary constants from the previous point, our eigenvectors can effectively all be normalised to the same length.
- A certain class of operator is particularly useful for quantum chemistry, namely Hermitian operators. When operating on a linear combination of n eigenvectors an $n\times n$ matrix is required. Such a matrix is Hermitian if it is self-adjoint. A self-adjoint matrix is equal to its conjugate transpose, which is formed by reflecting all the matrix elements in the leading diagonal and taking the complex conjugate of each element that has been reflected. The reason Hermitian operators are so useful is that their eigenvalues are always real, a requirement for physical observables.
- Another property of Hermitian operators is that their eigenvectors are all mutually orthogonal. Two vectors are orthogonal when their scalar, i.e. dot, product is zero. The analogous procedure with wave functions is to integrate the product of two wave functions over all space. This fact provides much simplification to quantum chemical calculations.

The properties of Hermitian operators are derived and discussed in detail in [3] and [4].

6.2.5 The meaning of the wave function

Quantum mechanics – dynamics on the smallest scales – raises many perplexing questions. One is on the physical meaning of the wave function itself (a question asked by many learners being introduced to orbitals). As Dirac wrote (in the first part of [1]), it is "important to remember that science is concerned only with observable things". The wave function itself is not observable, so one might question the validity of employing it. However, predictions of observable quantities made using wave functions have been confirmed experimentally countless times. Despite the philosophical problems with quantum mechanics it is arguably science's most tested and successful theory.

For an eigenvalue to relate to a physical observable, it must be a real number. Wave functions are typically complex but can be made real by multiplication by their complex conjugate, denoted ψ^*, which is the wave function with the sign of the imaginary component reversed. Most learners will be familiar with complex numbers, and will be able to appreciate this by writing a general complex function as ($a + ib$), where a and b are real:

$$(a + ib)(a - ib) = a^2 - i^2 b^2 = a^2 + b^2 \tag{13}$$

which is real. Hence a wave function only, in general, corresponds to an observable quantity when it is multiplied by its complex conjugate. Such a quantity is a mathematical function, typically of three spatial coordinates. The arbitrary constant that belongs to each wave function is chosen such that the function $\psi^* \psi$, integrated over all space gives 1. Thus, when the wave function $\psi^* \psi$ is integrated over a range of spatial coordinates, the resulting value is the probability of the electron being found in that volume. The wave nature of the electron implies that the position of the electron at any given instant is uncertain, and so only probabilities of position can be obtained with the wave function.

6.2.6 The definition of an orbital

This is another question that learners persist in asking. Strictly, orbitals are the three-dimensional probability density functions, $\psi^* \psi$, that describe the location of an electron in that state. As we shall see in section 6.3.5, the radial functions decay asymptotically to zero as r increases. If we want to describe an orbital with a three-dimensional shape we have to decide what proportion of the function to show. Typically 90% of the probability density function is used, i.e. r is limited to the value such that 90% of the volume of the function (which, since it is defined as a probability, has a total value of 1) is shown. The boundary of this function is known as an isosurface since the wave function has a common value at all points on this surface.

Models and pictures of orbitals commonly involve lobes of different colour. These represent the phase or sign of the wave function in the different lobes. This sign has no significance in isolated atoms since once the wave function is multiplied by its complex conjugate this phase information is lost. It is significant, however, when orbitals on different atoms combine to make chemical bonds: there will be cancellation where orbitals lobes of opposite sign overlap, for example. This point will be considered further in section 6.4.

6.2.7 Dirac notation

For learners who are extended in quantum matters, this notation can save a lot of writing. Multiplication of a wave function by its complex conjugation and integration over all space is such a common operation in quantum chemistry that Dirac developed a short-hand notation used by all in the field. The integral of $\psi^* \psi$ over all space is abbreviated as

$$\langle \psi | \psi \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^*(x, y, z)\psi(x, y, z)\, dx\, dy\, dz \tag{14}$$

where $\langle\psi|$ is known as the bra vector, and $|\psi\rangle$ as the ket vector. The bra vector is a complex conjugate. Expressions involving operators can also be expressed with this notation. For example, equation (11) is written as

$$O|\psi\rangle = \lambda|\psi\rangle \tag{15}$$

It is only when the bra vector is included that an integration over all space is implied.

6.3 Orbitals in the hydrogen atom

The main benefit of this section to Cambridge Pre-U learners will be the figures depicting the 3D analytical functions describing the shapes of different types of orbital, and the radial wave function descriptions of the orbitals, and the contour maps that combine the information from the angular and radial wave functions. For the average Cambridge Pre-U learner, any exposure to the mathematical background could be simply to reinforce the point that the orbital shapes are mathematical functions that can be explained and derived from first principles of angular momentum and energy. Only the strongest further mathematicians are likely to have the interest and grounding to work through all the maths, but at least it is there for those who need persuading that there are mathematical foundations to orbitals.

6.3.1 Spherical polar coordinates

In the hydrogen atom, it is easiest to consider the nucleus to be at the centre of our coordinate system. Given the spherical symmetry of an isolated hydrogen atom, it is most practical to use spherical polar coordinates. Learners will have met polar coordinates and some will be familiar with spherical polars too.

6. These are illustrated in Fig. 6.1.

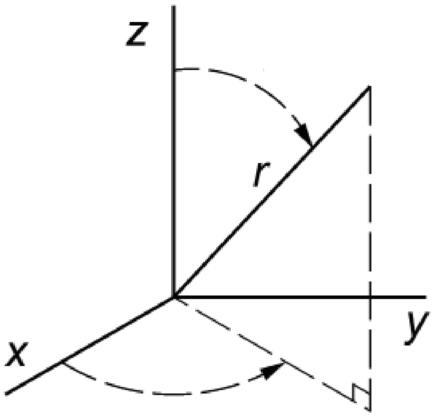


Fig. 6.1 The spherical polar coordinate system

r is the radial distance, which is always positive. The angles θ and φ are a little like latitude and longitude when considering locations on the globe (except they are measured in degrees and latitude is measured from the equator). In spherical polar coordinates θ is known as the colatitude and lies in the range 0 to π radians; φ is known as the azimuth angle and lies in the range 0 to 2π radians. They are related to Cartesian coordinates as follows:

$$r = \sqrt{x^2 + y^2 + z^2} \tag{16a}$$

$$\theta = \arccos\left(z/\sqrt{x^2 + y^2 + z^2}\right) \tag{16b}$$

$$\varphi = \arctan(y/x) \tag{16c}$$

The inverse relations are:

$$x = r\sin\theta\cos\varphi \tag{17a}$$

`

$$y = r\sin\theta\sin\varphi \tag{17b}$$

$$z = r\sin\theta \tag{17c}$$

A great advantage of using spherical polar coordinates to describe the hydrogen electron is that the wave function can factorise into a radial part, i.e. depending only on r, and an angular part, depending only on θ and φ which simplifies calculations.

6.3.2 Degrees of freedom and quantum numbers

Since the earliest spectroscopic experiments in the nineteenth century it has been evident that atoms absorb and emit energy in discrete amounts. (The first equation to describe the energy gaps in hydrogen atoms using what was effectively a quantum number was devised by the German schoolmaster J. J. Balmer in 1885.) This caused terrible problems for classical mechanics, which could not explain the results adequately.

Solving the Schrödinger equation and deriving quantum numbers, even for simple model systems, can be hard work mathematically for the uninitiated. However, this can be avoided, and much useful ground covered, by employing some simple analogies using standing waves to illustrate the origin of quantum numbers. Let us consider the standing wave on a plucked guitar string. The standing wave may only have certain wavelengths due to the constraint that the string is fixed at each end. In wave mechanics such a constraint is known as a boundary condition. The lowest energy, or fundamental, note is when the length of the string is half a wavelength, i.e. the only points on the string where the amplitude is fixed at zero are at the ends. These zero points are known as nodes. Higher energy standing waves have shorter wavelength. The next-highest energy wave, the first harmonic, has half the wavelength of the fundamental, so that a whole wavelength is held by the string and there is a third node half way along the string. In music, these harmonic differences are the octaves. The harmonic to higher energy has one third the wavelength of the fundamental. It turns out that the energy of the allowed standing waves is a function of $n - 1$, where n is the number of nodes on the string. ($n - 1$ is used so the fundamental takes a value of 1 and harmonics are multiples of this.) n here is analogous to a quantum number and its origin lies in the boundary condition imposed on the standing wave.

In the plucked guitar string example, there is only degree of freedom in the vibration as the string may be considered to be one-dimensional. A two-dimensional analogy would be a square drum in the xy plane. When the membrane is struck, its vibrations have two degrees of freedom as the membrane can be considered two-dimensional. (The x- and y-axes are independent in that they are mutually perpendicular, or orthogonal.) This leads to two quantum numbers, n_x and n_y, say, where n_x is the number of nodes on the x-axis of the drum while n_y refers to the y-axis. Each quantum number relates to a boundary condition: the fact that the amplitude at the ends of the drum on each axis are fixed at zero. The energy of these standing waves would, analogously, be a function of $(n_x - 1)(n_y - 1)$. The three-dimensional analogue, a vibrating cube, is harder to visualise, but we could extend the analysis to conclude that it has three degrees of freedom, that its vibrations are associated with three quantum numbers, n_x, n_y and n_z, and that the energy of its standing waves is a function of $(n_x - 1)(n_y - 1)(n_z - 1)$.

Analogies involving circular motion will bear a closer resemblance to the hydrogen atom. What about standing waves on a circular loop of wire? A circle may be thought to have no boundary but there is, in fact, a boundary condition. In order for a wave on the circular loop to be a standing wave, its amplitude at an angle φ from some reference point must be equal to its amplitude at the angle $\varphi + 2\pi$. While we may consider a circle in the xy plane to be two-dimensional, if we describe it with spherical polar coordinates from the centre of the circle r and θ are constant, leaving only a single coordinate, φ. So the circle is one-dimensional with one degree of freedom, and there is one boundary condition for standing waves. We could describe the standing wave with a single quantum number, say *m*, that is the number of nodes of the standing wave on the loop. Being a circular standing wave, successive harmonics have two more nodes rather than one. It turns out that the energy of these circular standing waves is a function of *m*/2. This is a more natural quantum number than the number of nodes since angular momentum quantum numbers naturally go up in integer steps. By analogy with the harmonics on the one-dimensional string and equation (6), the general wave function for standing waves on a circular wire is

$$\psi = N_\varphi e^{im\varphi} \tag{18}$$

where N_φ is the arbitrary constant in front of any eigenfunction and *m* is now defined as half the number of nodes on the standing wave.

The two-dimensional analogy of a circular standing wave is a vibrating elastic sphere. In spherical polar coordinates measured from the centre of the sphere *r* is constant, leaving θ and φ as the two degrees of freedom, each with their own boundary conditions, $\psi(r,\theta,\varphi) = \psi(r,\theta + 2\pi,\varphi)$ and $\psi(r,\theta,\varphi) = \psi(r,\theta,\varphi + 2\pi)$) There are two resulting quantum numbers, *m* relating to φ and l relating to θ. The nodes relating to l will be discussed further in section 6.3.4.

The three-dimensional circular standing wave gives the solutions for the hydrogen electron. With *r*, θ and φ all variable there are three degrees of freedom, three boundary conditions and three quantum numbers. The boundary condition for *r* is that it must decay to zero at infinity – otherwise the electron would not be localised on the atom. The quantum number associated with *r* is called *n* as there are certain parallels with the case of the vibrating string.

6.3.3 Angular momentum

Learners studying physics may be interested in the important role that angular momentum plays in orbitals, and how the uncertainty principle affects angular momentum in quantum systems.

We saw in section 6.2.3 that there is an operator for determining the momentum of an electron using an eigenvalue equation. This was a linear momentum, $m\mathbf{v}$ which is a vector since velocity ($\mathbf{v}$) is a vector. A more relevant quantity for circular motion is the angular momentum, $\boldsymbol{l}$, also a vector, which is defined as the cross product $\mathbf{r} \times \mathbf{p}$. If a particle is moving in a circle, the vector describing its angular momentum points perpendicular to the plane of the circle. Rather than defining the kinetic energy as $\frac{1}{2}mv^2 = p^2/2m$ we use the rotational kinetic energy $\frac{1}{2}I\omega^2 = l^2/2I$ where I is the moment of inertia of the electron and ω is the magnitude of the angular velocity (which is the magnitude of the velocity divided by the radius of the circle). There are, however, three degrees of freedom to angular momentum, $l_x = xp_x$, $l_y = yp_y$, and $l_z = zp_z$.

The quantum mechanics of angular momentum is a complicated subject because Heisenberg's uncertainty principle (which is a manifestation of the indeterminacy of certain quantities being measured simultaneously) forbids all three components of angular momentum being known simultaneously. Only one component of angular momentum can be known exactly which, by convention, is l_z. It is, however, permissible to know simultaneously l_z and the square magnitude of the total angular momentum, $l^2 = l_x^2 + l_y^2 + l_z^2$. This result can be derived from the angular momentum operators [3]. Since there are only two simultaneously observable orbital angular momenta for an electron, these are the quantities described by the two angular quantum numbers, l and *m*. (The definition of *m* used by chemists is equivalent to the *m*/2 mentioned in section 6.3.2 in the context of nodes.) l relates to the magnitude of the orbital angular momentum of the electron in that state and so is always positive. It increases in integer steps, with its minimum permissible value being 0. *m* relates to the orientation of the angular momentum vector – specifically its projection on the *z*-axis. It also varies in integer steps, as discussed in section 6.3.2. It is not surprising, then, that the permissible range of *m* is $-l, -l + 1, \ldots, 0, 1, \ldots, l - 1, l$. It follows that for each value of l there are $2l + 1$ possible values of *m*.

6.3.4 Angular wave functions of the hydrogen electron

Many learners will at least be curious to see what the mathematical functions are that describe the orbital shapes. They are described in this subsection; their exact 3D rendering given in figures 2, 3 and 4 and the analytical wave functions are given table 2. The derivation of the orbitals' cartesian labels are given in equations (17) and (21). Learners will need to be able to able to reproduce the approximate shapes of the orbitals with the relevant label.

Using the quantum theory of angular momentum it is possible to find simultaneous eigenfunctions of the operators for l_z and l^2 [3]. Following the arguments in sections 6.2.2 and 6.3.2, it is not surprising to find that the wave function involving φ, with its link to the one-dimensional circular motion and the m quantum number is the same as equation (18). The normalisation constant in front of each of the exponentials (see section 6.2.5) is

$$N_\varphi = \frac{1}{\sqrt{2\pi}} \tag{19}$$

The normalisation of this function is as follows. The complex conjugate of $N_\varphi e^{im\varphi}$ is $N_\varphi e^{-im\varphi}$. The product of these two functions is simply N_φ^2 since $e^{im\varphi} e^{-im\varphi} = e^0 = 1$. N_φ is chosen so that the integral of $\psi^* \psi$ with respect to φ between 0 and 2π (which is all space for φ) gives 1. Since N_φ is just a number it is taken out of the integral:

$$N_\varphi^2 \int_0^{2\pi} d\varphi = 1 \tag{20}$$

The integral comes to 2π so N_φ must equal $1/\sqrt{2\pi}$.

Much algebra is required to derive the functions of θ that are simultaneous eigenfunctions of l_z and l^2 [3]. They are the associated Legendre functions, which actually depend on m as well as l. They are all real and given the symbol P_l^m; they are collected in Table 6.1 with the arbitrary constants, N_θ required to normalise them [5], as discussed in section 6.2.5. The product of $P_l^m(\theta)$ and $\psi_m(\varphi)$ are the spherical harmonic functions, $Y_{lm}(\theta, \varphi)$, which describe the oscillations of an elastic sphere. There is more than one phase convention with these functions; here we follow those of Pauling [5].

The angular functions give the characteristic shapes of atomic orbitals. The l quantum number relates to the type of subshell, which are usually referred to by letter, as shown in Table 6.2.

P_l^m	N_θ	$P_l^m(\theta)$
P_0^0	$\sqrt{2}/2$	1
P_1^0	$\sqrt{6}/2$	$\cos\theta$
$P_1^{\pm 1}$	$\sqrt{3}/2$	$\sin\theta$
P_2^0	$\sqrt{10}/4$	$(3\cos^2\theta - 1)$
$P_2^{\pm 1}$	$\sqrt{15}/2$	$\sin\theta\cos\theta$
$P_2^{\pm 2}$	$\sqrt{15}/4$	$\sin^2\theta$

Table 6.1 The associated Legendre functions, P_l^m, up to $l = 2$ with their normalisation constants, N_θ [5].

For non-zero *m* the $\psi(\varphi)$ are imaginary. These are made real by taking linear combinations, as shown in equation (8). It is a property of eigenfunctions (discussed in section 6.2.4) that linear combinations are still solutions to the same eigenvalue equation. Similarly, subtracting the complex conjugate function is acceptable since the resulting orbital is wholly imaginary. When this is multiplied by its complex conjugate to obtain the probability density function the result is wholly real and positive. The real orbital functions together with their chemical labels are collected in Table 6.2.

Orbital	N_θ	$\psi(\theta)$	**Linear -comb.**	N_φ	$\psi(\varphi)$
s	$\sqrt{2}/2$	1	n/a	$1/\sqrt{2\pi}$	1
p_x	$\sqrt{3}/2$	$\sin\theta$	$\|1>+\|-1>$	$1/\sqrt{\pi}$	$\cos\varphi$
p_y	$\sqrt{3}/2$	$\sin\theta$	$\|1>-\|-1>$	$1/\sqrt{\pi}$	$\sin\varphi$
p_z	$\sqrt{6}/2$	$\cos\theta$	n/a	$1/\sqrt{2\pi}$	1
d_{xz}	$\sqrt{15}/2$	$\sin\theta\cos\theta$	$\|1>+\|-1>$	$1/\sqrt{\pi}$	$\cos\varphi$
d_{yz}	$\sqrt{15}/2$	$\sin\theta\cos\theta$	$\|1>-\|-1>$	$1/\sqrt{\pi}$	$\sin\varphi$
$d_{x^2-y^2}$	$\sqrt{15}/4$	$\sin^2\theta$	$\|2>+\|-2>$	$1/\sqrt{\pi}$	$\cos 2\varphi$
d_{xy}	$\sqrt{15}/4$	$\sin^2\theta$	$\|2>-\|-2>$	$1/\sqrt{\pi}$	$\sin 2\varphi$
d_{z^2}	$\sqrt{10}/4$	$(3\cos^2\theta-1)$	n/a	$1/\sqrt{2\pi}$	1

Table 6.2 The orbital angular wave functions in real form for s, p and d orbitals with their normalisation constants, N_φ and the linear combinations of the $e^{im\varphi}$ functions required [5].

The cartesian labels for the real forms of the p and d orbitals can be obtained by converting the $\psi(\theta, \varphi)$ to $\psi(x, y, z)$ using equations (17). We need some trig identities to establish the cartesian labels for the d orbitals that involve double-angle trig functions. These are collected in equations (21).

$$\sin^2\theta\cos 2\varphi = \sin^2\theta\cos^2\varphi - \sin^2\theta\sin^2\varphi = x^2 - y^2 \tag{21a}$$

$$\sin^2\theta\sin 2\varphi = 2\sin\theta\cos\varphi\sin\theta\sin\varphi = 2xy \tag{21b}$$

$$3\cos^2\theta - 1 = 3z^2 - (x^2 + y^2 + z^2) = 3z^2 - r^2 \tag{21c}$$

Figs 6.2, 6.3 and 6.4 show the exact forms of the probability density functions for the angular wave functions of the s, p and d orbitals, respectively. They appear to be three-dimensional plots, but are only two-dimensional in terms of spherical polar coordinates, since they are just functions of θ and φ. The nodes in these angular functions are planes. The number of nodal planes is equal to l, i.e. no nodal plane for s orbitals, one for p orbitals (the *yz* plane for the p_x orbital, etc.) and two for d orbitals (the *xz* and *yz* planes for the d_{xy} orbital, etc.). In the case of d_{z^2} the two nodal planes are conical, one above and one below the *xy* plane. When $m = 0$, $e^{im\varphi} = 1$ and so in these cases the angular function is just the appropriately normalised associated Legendre function.

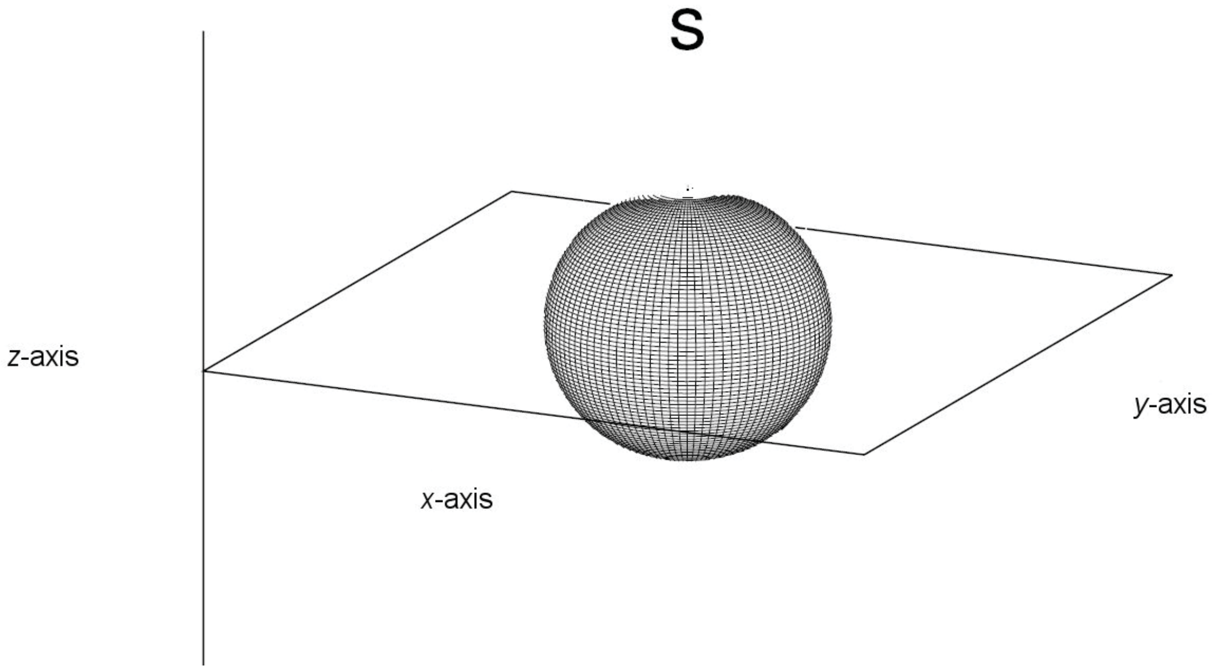


Fig. 6.2 The angular probability density function for the H atom s orbital

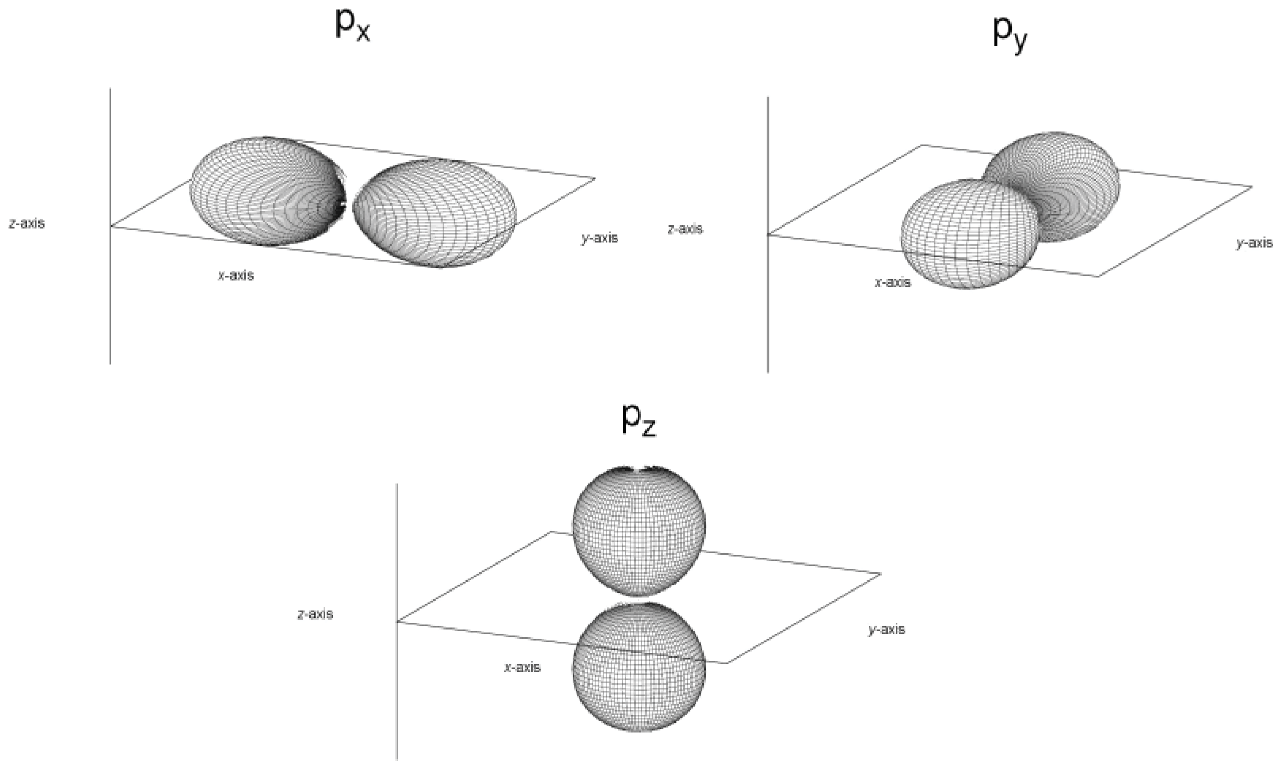


Fig. 6.3 The angular probability density functions for the H atom p orbitals

6.3.5 Radial wave functions of the hydrogen electron

Learners often encounter radial wave functions or probability density functions in the context of subshells shielding one another, or the probabilistic nature of the electron, and may ask questions relating to the radial functions.

We consider now the Schrödinger equation for the hydrogen electron. As mentioned in section 6.2.3 it is an eigenvalue equation. The operator is known as the Hamiltonian, given the symbol $\hat{H}$, and is the operator for total energy, i.e. kinetic energy + potential energy. It therefore returns the total energy of the electron as its eigenvalue. Using the quantum operator for momentum and for distance we can translate the classical expression for total energy,

$$E = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) - \frac{Ze^2}{4\pi\varepsilon_0\sqrt{x^2 + y^2 + z^2}} \tag{22}$$

into a wave mechanical equation. In equation (22) the second energy term is the potential energy of the electron. It is the Coulombic potential energy and is negative because of the attraction between the electron and the hydrogen nucleus. e is the fundamental charge and ε_0 is the permitivity of free space. Z is the number of protons in the nucleus. This is useful because ions He^+ and Li^{2+} are hydrogen-like in that they only have one electron.

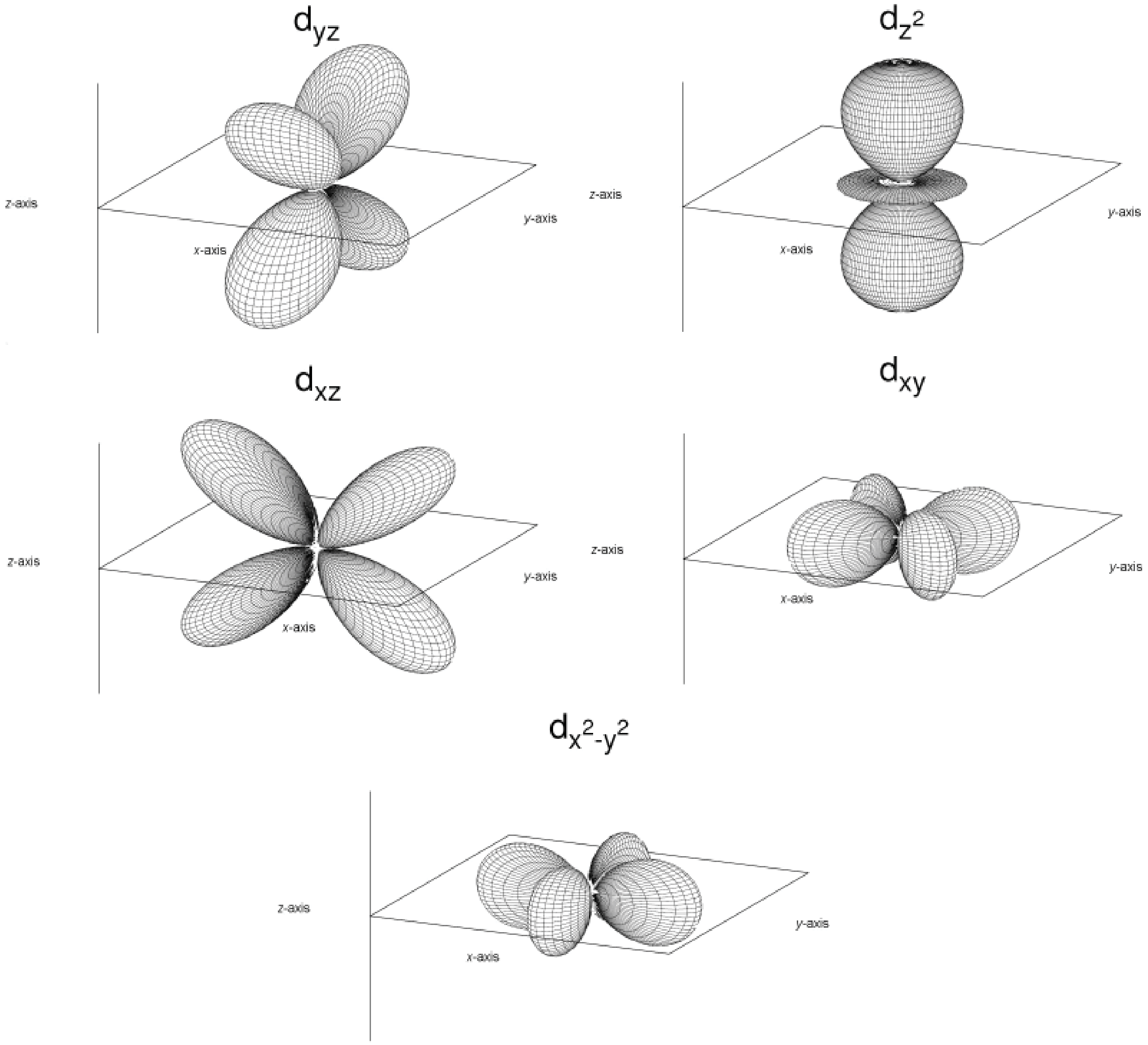


Fig. 6.4 The angular probability density functions for the H atom d orbitals

As explained in section 6.3.1 it is most convenient to express the wave function in spherical polar coordinates. The Hamiltonian operator will therefore need to be transformed so that it acts on spherical polar coordinates. This is achieved for functions using equations (17) but is more complicated for the differential operators required for the momentum operator for which the theory of partial derivatives is required.

It is a long and difficult process to construct the Schrödinger equation for the hydrogen electron in spherical polar coordinates and to find the radial eigenfunction solutions. Interested readers should consult one of the advanced texts in the Bibliography ([3], [4] and [5]).

The crucial point in the algebra of finding the radial eigenfunctions is setting the boundary condition that the radial function should decay to zero as r approaches infinity. As with the examples in section 6.3.2 the boundary condition leads to a quantum number, which is the principal (shell) quantum number n, which can take values 1, 2, 3,. . . . The full analysis [3] yields the following expression for n:

$$n = \frac{\mu Z e^2}{\hbar}\sqrt{\frac{K}{-2E}} \qquad (23)$$

where E is the total energy of the electron, which is defined to be negative (zero at the ionisation limit). It can also be shown that for a given value of n, l may take values in the range 0, 1, . . . , $n-1$ [3]. In equation (23), $\hbar$ is $h/2\pi$. Planck's constant, h, is usually divided by 2π in the context of rotational motion, as this division converts frequencies in Hertz to angular frequencies in radians per second (radians are required for the calculus involving trig functions). μ is the reduced mass of the electron, which takes into account the fact that the electron and nucleus both rotate around a common centre of mass (rather than the nucleus being at the centre of the rotation of the electron).

$$\mu = \frac{m_e \times m_N}{m_e + m_N} \qquad (24)$$

where m_e is the mass of the electron and m_N is the mass of the nucleus. μ provides only a slight correction to the mass of the electron since its mass is so small compared to the mass of the nucleus. K is shorthand for the constants in the Coulomb expression:

$$K = \frac{1}{4\pi \;\; _0} \qquad (25)$$

The radial eigenfunctions turn out to be the associated Laguerre functions, which depend on the quantum numbers n and l, and therefore pertain to each subshell. They are shown in Table 6.3 with their normalisation constants, N_r.

Subshell	N_r	$\psi(r)$
1s	1	$(Z/a_0)^{3/2}.2e^{-\rho r/2}$
2s	$1/(2\sqrt{2})$	$(Z/a_0)^{3/2}.(2-\rho r)e^{-\rho r/2}$
2p	$1/(2\sqrt{6})$	$(Z/a_0)^{3/2}.\rho r e^{-\rho r/2}$
3s	$1/(9\sqrt{3})$	$(Z/a_0)^{3/2}.(6-6\rho r+\rho^2 r^2)e^{-\rho r/2}$
3p	$1/(9\sqrt{6})$	$(Z/a_0)^{3/2}.(4-\rho r)\rho r e^{-\rho r/2}$
3d	$1/(9\sqrt{30})$	$(Z/a_0)^{3/2}.\rho^2 r^2 e^{-\rho r/2}$

Table 6.3 The radial wave functions for the subshells of the first three shells, with their normalisation constants, N_r [5]

In Table 6.3, a_0 is the Bohr radius, about 52.9 pm (1 pm = 10^{-12} m), which is the most probable distance of the electron from the nucleus in hydrogen. It can be expressed as a series of constants (see section 6.3.6).

$$a_0 = \frac{\hbar^2}{\mu e^2 K} \qquad (26)$$

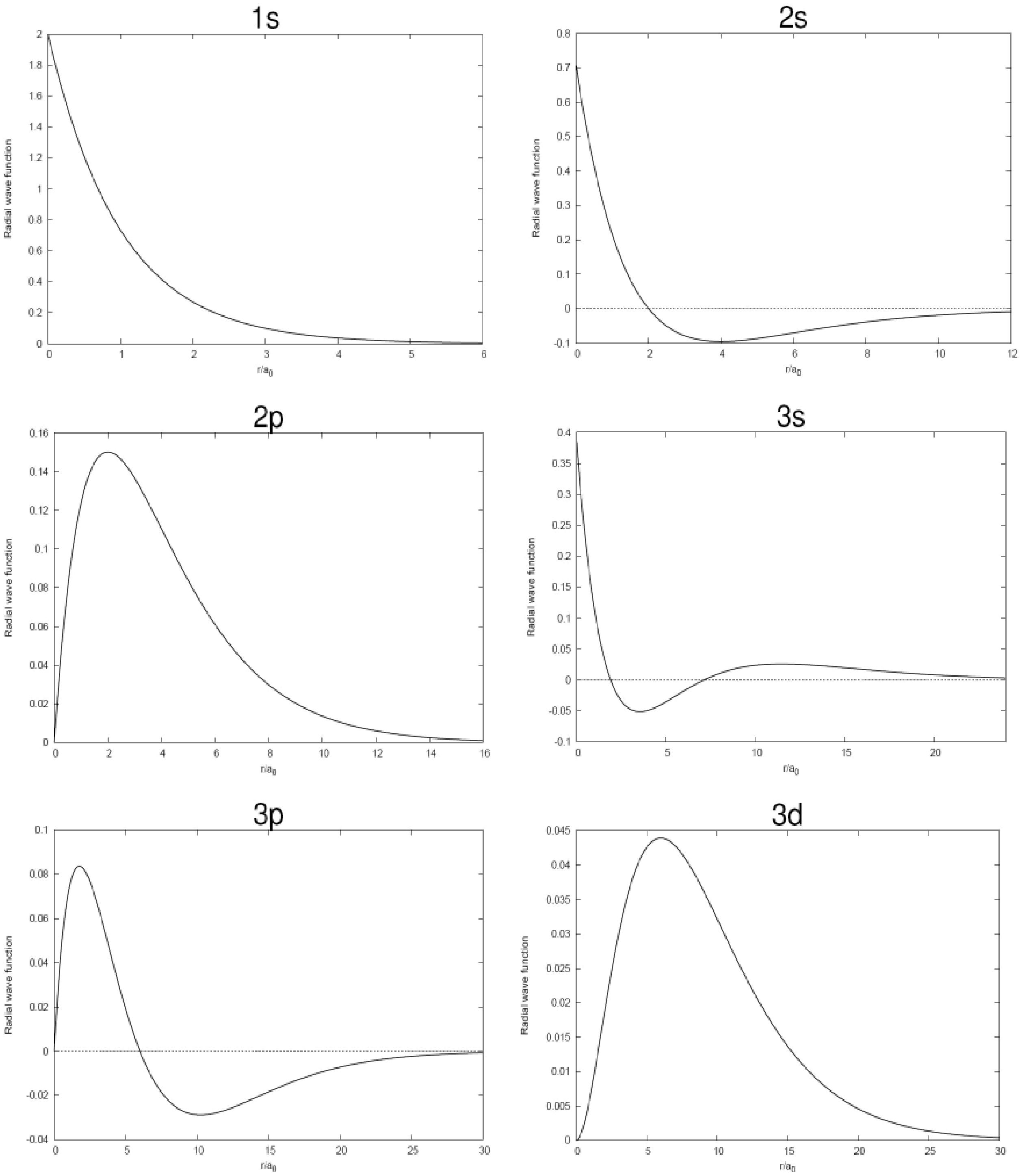
The value usually assigned to a_0 strictly only pertains to hydrogen as when there are more protons in the nucleus the reduced mass of the electron will be slightly different. From the definition of K in equation (25) and the Coulomb energy expression, the base units of K are $\mathrm{kg\,m^3\,s^{-2}\,C^{-2}}$. Given that the base units of h are $\mathrm{kg\,m^2\,s^{-1}}$, one can appreciate that equation (26) is dimensionally correct. The constant ρ that appears in the radial wave functions is a collection of constants that has dimensions of reciprocal distance.

$$\rho = \frac{2Z}{na_0} \tag{27}$$

Looking at the form of the radial eigenfunctions in Table 6.3, bearing in mind that ρ has units of inverse distance, the eigenfunctions all have dimensions of $(\text{distance})^{-3/2}$. This is required for them to be normalised since the integral over all space of the square modulus of the wave function must equal 1. The integration over all space is the equivalent of summing over all spherical shells from $r = 0$ to ∞. Since the surface area of a sphere is given by $4\pi r^2$,

$$4\pi = \int_0^\infty \quad (r)^2 r^2 \, dr = 1 \tag{28}$$

The square of the wave function multiplied by r^2 gives a function of inverse distance which, integrated over r, leads to a pure number, which is what is required for a probability. The normalised radial wave functions for the subshells of the first three shells are plotted in Fig. 6.5.


1s

2s

2p

3s

3p

3d

Fig. 6.5 Radial wave functions for the H atoms orbitals of the first three shells

A common way to visualise radial wave functions is the radial density function (RDF). The RDF describes the probability of finding an electron a distance r from the nucleus, i.e. in the shell $4\pi r^2 \delta r$. Following equation (28) the RDF is defined as $4\pi r^2 \psi(r)^2$, which integrates over all r to give 1. The radial density functions for the subshells of the first three shells are plotted in Fig. 6.6.

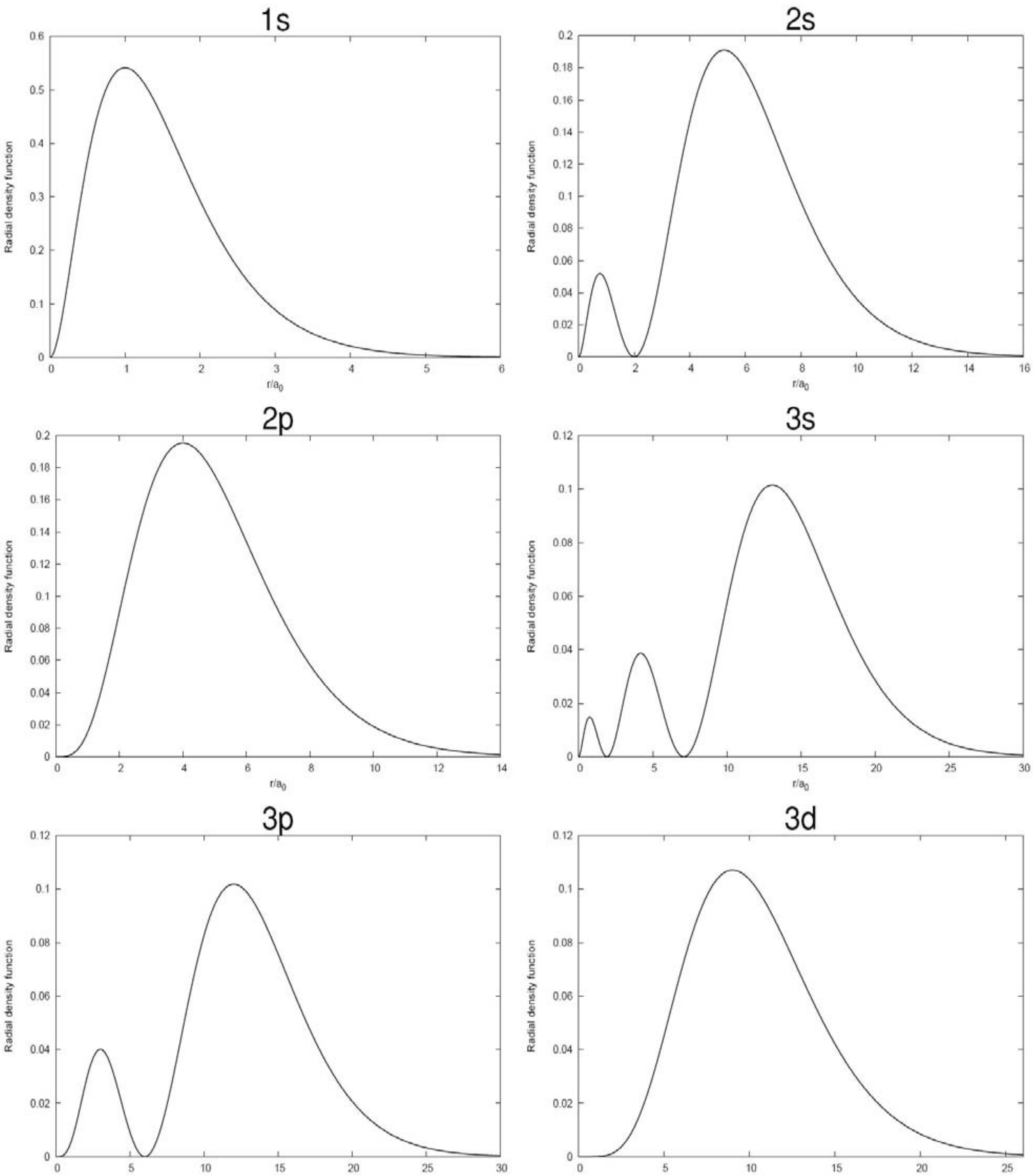


Fig. 6.6 Radial density functions for H atom subshells of the first three shells

Inspection of Figs 6.5 and 6.6 shows that the number of nodes shown by the radial density function, excluding $r = 0$ and ∞, is given by $n - l - 1$. These radial nodes are distinct from the angular nodes discussed in Section 6.3.4. The radial and angular nodes are both visible in the probability density map of the *xy* plane for the 2s and $3d_{xy}$ orbitals in Fig. 6.7. The 2s orbital just has one radial node at the bottom of the spike. The $3d_{xy}$ orbital has no radial node but two angular nodal planes (*xz* and *yz* planes). Careful inspection of the 2*s* orbital probability density contour map in the *xy* plane of Fig. 6.8 reveals a radial node at about $r = 2$ Bohr radii. The contour map for the $3p_x$ reveals both an angular and a radial node. The angular nodal plane is the *yz* plane, and the radial node is at about $r = 5$ Bohr radii.

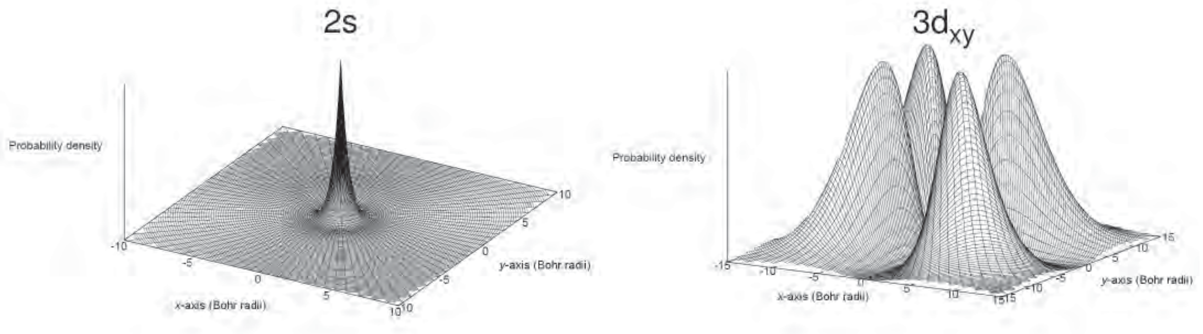
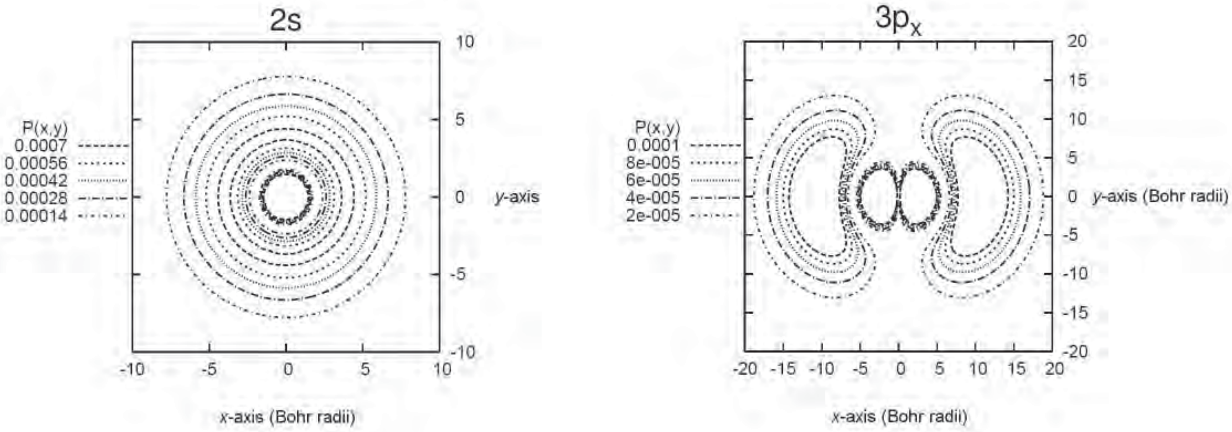


Fig. 6.7 Probability density for the H atom 2s and 3d$_{xy}$ orbitals in the *xy* plane



θ

Fig. 6.8 Probability density contour maps for the H atom 2s and 3p$_x$ orbitals in the *xy* plane

6.3.6 The Bohr radius

A remarkable fact about the expression for the Bohr radius in equation (26) is that it can be derived in a simple classical calculation. If we picture an electron orbiting a proton such that the electrostatic force of attraction is equal to the centripetal force, then:

$$\frac{\overset{\varphi}{e^2} K}{r^2} = \frac{\mu v^2}{r} \qquad (29)$$

We then quantise angular momentum, using a quantum number, *n*, and $\hbar$

$$\mu v r = n\hbar \qquad (30)$$

By equating equations (29) and (30), eliminating *v* and setting *n* to 1, we arrive at equation (26). This raises the question of why the solution for *r* is the most probable distance rather than the average distance. The answer is justified by Louis de Broglie in his discussion of least action (action has the units of momentum × distance, like $\hbar$) in part 5 of the first chapter of his classic book [6].

6.3.7 Orbital energies in the hydrogen atom

It is evident from the line spectrum of hydrogen that the energy of an electron in a hydrogen atom depends only on the quantum number, n. Rearrangement of the expression for n (equation (23)) gives the energy of the electron as a function of the quantum number n.

$$E_n = \frac{\mu^2 Z^2 e^4 K}{2\hbar^2 n^2} = -\frac{Z^2 e^2 K}{2n^2 a_0} \tag{31}$$

The energy of the electron is defined to be negative since it is trapped in the attractive potential well of the nuclear attraction. This equation may be simplified using the Rydberg constant,

$$E_n = -\frac{Z^2 R}{n^2} \tag{32}$$

where R is the Rydberg constant with dimensions of energy. It takes a value of 13.6 eV or 2.18×10^{-18} J.

It is interesting to note that the total energy of the electron in a one-electron atom depends only on the quantum number n, not the subshell quantum number l. Given knowledge of the Aufbau principle, learners often ask why the hydrogen electron's energy doesn't depend on l; it is justified by equation (34). This raises some questions. Is the kinetic : potential energy ratio the same for electrons in the same shell but different subshells? Electrons with a greater l value have greater angular momentum (since l is the quantum number for the magnitude of the orbital angular momentum) so they must possess greater rotational kinetic energy.

We can find the average value of observable quantities that are inherently probabilistic by working out their expectation values. In general the expectation value, $\langle \lambda \rangle$, of an observable quantity, λ, with the quantum operator $\hat{O}$ is given by

$$\langle \lambda \rangle = \langle \psi | O | \psi \rangle \tag{33}$$

The potential energy operator is $1/r$ multiplied by a constant. A very useful result is the expectation value for the operator $1/r$ when applied to the associated Laguerre functions, i.e. $\psi(r)$ [4].

$$\left\langle \frac{1}{r} \right\rangle = \left\langle \psi(r) \middle| \frac{1}{r} \middle| \psi(r) \right\rangle = \frac{Z}{a_0 n^2} \tag{34}$$

The significance of this result is that the potential energy of an electron in a one-electron atom depends only on the shell quantum number n, not the angular momentum (subshell) quantum number l. A very general result known as the virial theorem, which applies to classical as well as quantum systems, imposes that the kinetic energy, T, and the potential energy, V, for system of conservative forces, i.e. one where energy isn't exchanged with the environment, are related. In the case of Coulombic attraction, the relation is

$$\langle T \rangle = -\frac{1}{2} \langle T \rangle \tag{35}$$

So if the potential energy of the hydrogen electron is independent of the l quantum number then the same must be true of the kinetic energy. Since the angular momentum of the hydrogen electron does depend on l, then electrons with higher l must have greater rotational kinetic energy. Therefore they must have lower linear kinetic energy so that their total kinetic energy is constant.

Another useful result is the expectation value $\langle r \rangle$ for the hydrogen electron. Its value for the associated Laguerre functions is [4].

$$\langle r \rangle = \frac{n^2 a_0}{Z} \left\{ 1 + \frac{1}{2} \left(1 - \frac{l(l+1)}{n^2} \right) \right\} \tag{36}$$

which shows that $\langle r \rangle$ decreases as l increases. This is evident from inspection of the radial density functions in Fig. 6.6. While s orbitals have the greatest $\langle r \rangle$ in a given shell one can appreciate how the $1/r$ is equal to other subshells since there is greater probability density for s electrons close to the nucleus due to larger number of radial nodes.

6.4 Orbitals in molecules

Learners should know that the chemical bonds that hold together atomic nuclei in molecules are shared electrons between the nuclei: the electron-nuclear electrostatic forces of attraction bind the nuclei together. Electrons are shared in bonds as a result of the overlap and interaction between atomic orbitals on the two bonding atoms. Before going any further it is necessary to state the approximations involved with these atomic orbitals in multi-electron atoms.

Learners should be able to understand sections 6.4.2 and 6.4.3 on the linear combination of atomic orbitals and bonding and anitbonding sigma and pi orbitals. Section 6.4.1 on shielding provides the opportunity for some fairly gentle extension material after the qualitative consideration of shielding required to understand trends in ionisation energies. Hybridisation, dealt with in sections 6.4.4 and 6.4.5, is not on the Cambridge Pre-U syllabus, but many teachers at sixth form level like to teach this topic anyway, and so these materials provide a quantitative basis for this sort of extension material. The mathematics presented here is easily visualised with vectors in three-dimensional space, and so is easier to get across than much of the more abstract quantum maths.

6.4.1 The orbital approximation and Slater's Rules

The orbitals derived for hydrogen atoms are exact solutions of the Schrödinger equation. There are no known exact solutions for the Schrödinger equation for multi-electron atoms due to the complication of electron-electron repulsion. Instead they are approximated to the hydrogen orbitals, with the atomic number, Z, being taken into account. However, we also need to take into account the shielding from the nuclear charge that outer electrons experience from inner electrons (and electrons in the same shell). A set of empirical rules was established by Slater to find the shielding contribution, σ, from each other electron in the atom. The sum of these shielding contributions gives the overall shielding factor S which, when subtracted from Z, gives the Z_{eff} experienced by the electron.

Slater's Rules
(1) $\sigma = 0$ for electrons of higher n.
(2) $\sigma = 0.35$ for electrons of the same n (0.30 for 1s)
(3) $\sigma = 0.85$ for s and p electrons with n one less
(4) $\sigma = 1.00$ for d and p electrons with n one less
(5) $\sigma = 1.00$ for electrons with n two or more less

6.4.2 The linear combination of atomic orbitals (LCAO)

The overlap of atomic orbitals is normally considered pictorially, with lobes of the same phase reinforcing each other to form a bonding molecular orbital and those of different phase cancelling, leaving an antibonding molecular orbital. In the antibonding orbital most of the electron density is on the other side of each nucleus, so that the electrostatic repulsion between the atoms is maximised. When such a state is occupied, it may result in the two atoms becoming completely disconnected.

In this pictorial approach to LCAO theory, the relative orientation of the phases of the lobes determines whether interactions are bonding or antibonding. This is somewhat problematic for the overlap of two 1s orbitals, say, where the phase is only positive in both orbitals. However, following the properties of eigenfunctions (section 6.2.4) we know that we can choose any value for the constant in front of the eigenfunction, with it remaining a valid solution to the eigenvalue (Schrödinger) equation. The sign is therefore unrestricted so we can assign phases to orbital wave functions. In this way, one of two overlapping s orbitals can be given a negative phase arbitrarily, allowing for an antibonding combination. All of the possible phase combinations of orbitals need to be considered when constructing a molecular orbital diagram.

Fig. 6.9 shows a sketch of the molecular orbital diagram for N_2. The relative energy levels of the valence atomic orbitals are shown on the right and left, with the molecular orbitals shown in order of energy up the middle. The most important interactions are shown between atomic orbitals of the same type. Since it is a homonuclear diatomic, the like orbitals will have identical energy, which maximises the interaction between them. Antibonding orbitals are denoted with an asterisk. The bond order of the molecule is equal to the number of fully occupied bonding orbitals minus the number of fully occupied antibonding orbitals.

It is helpful to consider standing waves here too. In a bonding interaction the overlap of the orbitals extends the length of the orbital. This means that the resulting standing wave will have a longer wavelength and therefore a lower energy. The opposite applies to antibonding interactions. The bonding orbitals may be considered to be the result of constructuve interference between wave functions causing an increase in amplitude, while antibonding orbitals result from destructive interference. This picture is easily understood by learners who will have met constructive and destructive interference in physics, and adds further weight to the idea of electrons as waves.

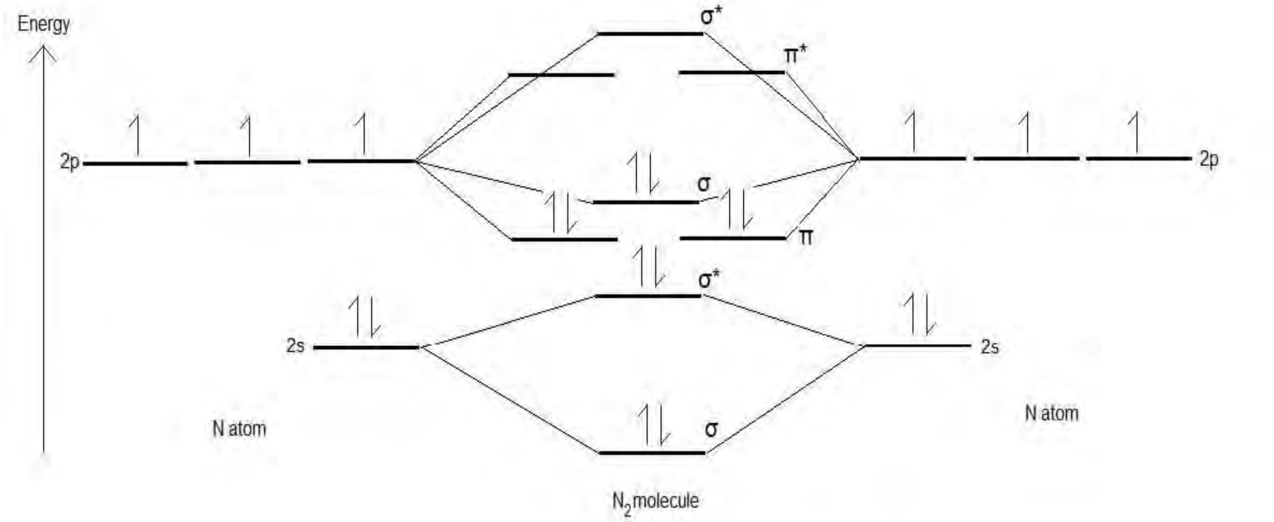


Fig. 6.9 Sketch of the molecular orbital diagram for N_2

6.4.3 Sigma and pi bonding and antibonding orbitals

In Fig. 6.9 we see that the 2p orbitals on each N atom overlap in two different ways, giving molecular orbitals carrying σ or π labels. These labels relate to the geometry of the overlap involved. Single chemical bonds always involve sigma overlap, which is when the lobes of the two orbital are aligned head-on so that they meet directly between the two nuclei associated with the two orbitals. Pi overlap is when the orbitals overlap while they are sideways-on, i.e. the overlapping lobes are not pointing at each other. The regions of overlap therefore do not lie on the internuclear axis: they are between the nuclei but displaced from the internuclear axis. Pi bonds are found in multiple bonds, in addition to one sigma bond. Learners will need to be able to represent these different types of overlap and know the difference between sigma and pi interactions.

Normally the head-on sigma alignment allows for greater overlap between orbitals. This leads to a larger interaction and a greater energy gap between the resulting bonding and antibonding orbitals. One way of breaking a chemical bond is to promote an electron from the bonding orbital to the antibonding one. The more energy required to do this, the stronger the bond is considered to be. Sigma bonds are therefore generally stronger than pi bonds. Pi bonds, however, are made stronger by delocalisation since extending the orbital lengthens the standing wave, increasing its wavelength and lowering its energy relative to its antibonding orbital.

In Fig. 6.9 the energies of the molecular orbitals from the overlap of the 2p electrons do not seem consistent with this approach: given the absence of pi delocalisation, one would expect the sigma bonding orbital to be lower in energy than the pi bonding one. The picture has been distorted by an effect known as s-p mixing. It was a simplification to assume that orbitals on one atom only combine with orbitals of the same type on the other atoms. In the full treatment the combinations of orbitals are determined by their symmetry label on the basis of the overall molecule's symmetry. Since the 2s and $2p_z$ orbitals have the same symmetry label in this homonuclear diatomic they can interact, which causes the sigma bonding orbital from the 2p overlap to increase in energy above the pi bonding orbitals. It is a smaller effect than the $2p_z$-$2p_z$ sigma overlap since the 2s and $2p_z$ atomic orbitals are at different energies.

In Fig. 6.10 the radial function of the 1s orbital of two hydrogen atoms a distance of 1.4 Bohr radii apart are added together and squared to give the probability density of the bonding orbital, and subtracted and squared to give the probability density of the antibonding orbital. This is the distance between H atoms in an H_2 molecule. The probability density of the molecular orbitals along the internuclear axis shows that most of the electron density is between the nuclei, consistent with section 6.4.2. Note that in the antibonding orbital there is a nodal plane perpendicular to the internuclear axis midway between the hydrogen nuclei.

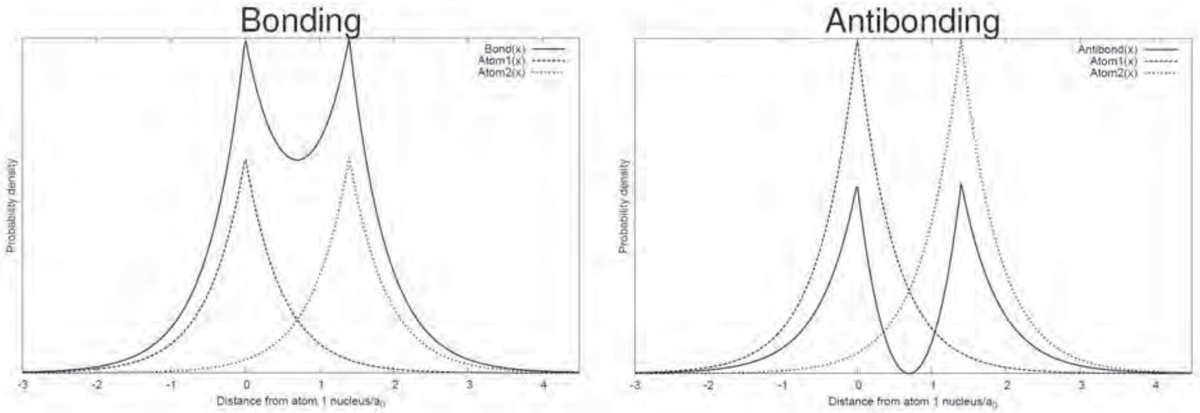


Fig. 6.10 Sigma bonding and antibonding LCAOs of 1s orbitals in the H_2 molecule: probability density along the internuclear axis

Fig. 6.11 shows the probability density of the molecular orbital in the *xy* plane using contour lines. It makes clear the nodal plane in the antibonding orbital.

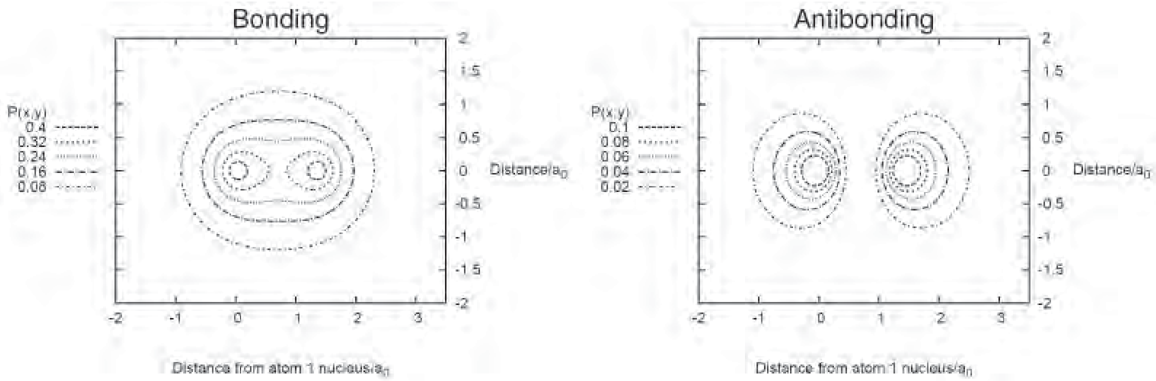


Fig. 6.11 Sigma bonding and antibonding LCAOs of 1s orbitals in the H_2 molecule: probability density contour maps in the *xy* plane

Figs 6.12 and 6.13 show the molecular orbital probability densities for sigma overlap between p orbitals in two carbon atoms a distance of 2.5 Bohr radii apart. This is the distance between two carbon atoms in an ethene molecule. The sigma bonding of carbon atoms actually involves hybridised orbitals (see section 6.4.4); the figure is intended to illustrate the general principle of molecular orbitals from the overlap of atomic orbitals that have two lobes. Again, there is a nodal plane perpendicular to the nuclear axis midway between the nuclei in the antibonding orbital.

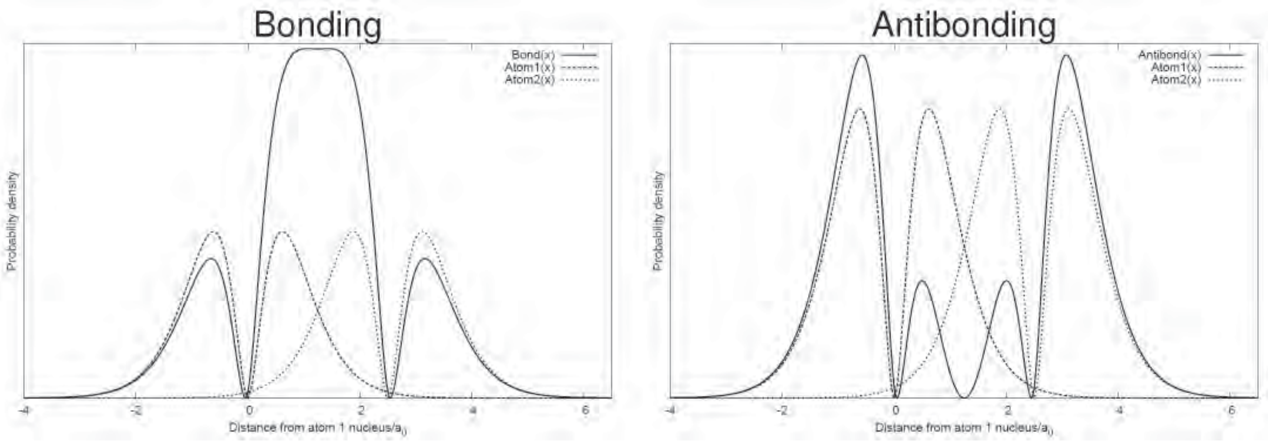


Fig. 6.12 Sigma bonding and antibonding LCAOs of $2p_x$ orbitals: probability density along the internuclear axis

Wave functions for carbon atoms are hydrogen-like but with *Z* corrected for the extra protons in the nucleus and the shielding by other electrons. Following Slater's rules in section 6.4.1, Z_{eff} for the carbon 2p electron is 6 – 2.75 = 3.25.

Fig. 6.14 shows the molecular orbital probability densities for pi overlap between p orbitals in two carbon atoms a distance of 2.5 Bohr radii apart. As in all molecular orbitals from pi overlap, there is a nodal plane in the plane of the molecule. In the antibonding orbital there is a further nodal plane perpendicular to the internuclear axis, as is seen in the sigma antibonds.

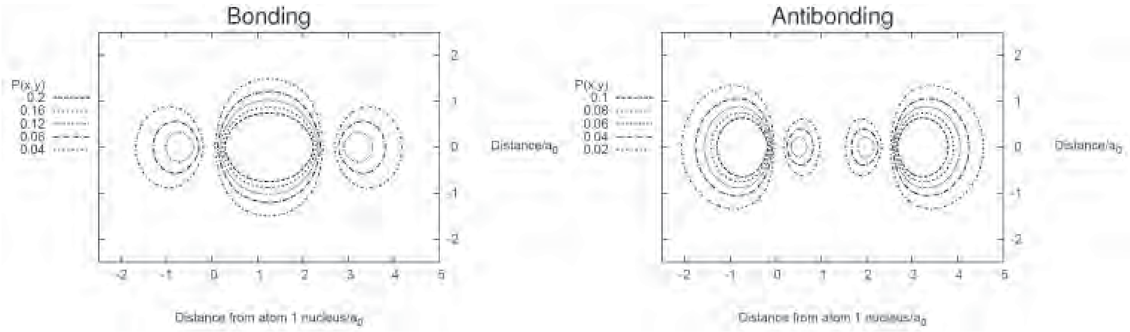


Fig. 6.13 Sigma bonding and antibonding LCAOs of $2p_x$ orbitals:
probability density contour maps in the *xy* plane

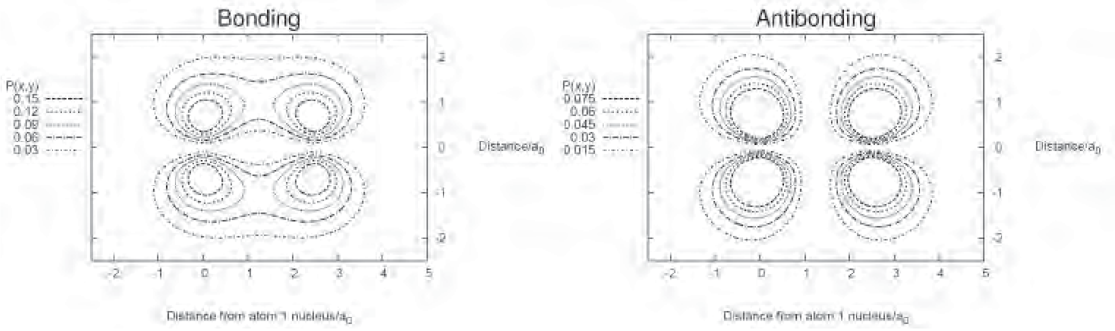


Fig. 6.14 Pi bonding and antibonding LCAOs of $2p_y$ orbitals:
probability density contour maps in the *xy* plane

6.4.4 Hybridised atomic orbitals

While hybridisation isn't explicitly in the Cambridge Pre-U Chemistry syllabus, many teachers find it such a useful concept when teaching organic chemistry that they teach it nevertheless. This may lead to questions of how their construction may be justified and what their wave functions look like. Their wave functions are given in Table 6.4 and probability density contour maps of sp^2 orbitals are given in Fig. 6.16.

The bond angles in differently hybridised molecules can be predicted using Valence Shell Electron Pair Repulsion theory, and have been determined experimentally by x-ray diffraction (109° in methane, 120° in BF_3, etc.). These bond angles are not consistent with the 90° bond angles between p orbitals. The angles are justified by the concept of orbital hybridisation, popular with organic chemists in particular. s and p orbitals are considered to "mix" to give these hybrids. What is this mixing?

We saw in section 6.2.4 that we can take linear combinations of the eigenfunctions with arbitrary constants in front of each eigenfunction, and the result is still a solution of the eigenvalue equation. Following the comparison of the addition of eigenfunctions to the addition of vectors in section 6.2.4, we can consider the p orbitals as vectors along their given axis. Given that the eigenfunctions are all normalised, we can assume that the p orbital vectors are all the same length.

The hybridisation of a carbon atom involves the linear combination of the s orbital with $(3 – n)$ p orbitals where n is the number of pi bonds on the carbon atom (which may not exceed two).

In the case of sp^3 hybridisation, four bonds around carbon point to the corners of a tetrahedron. If we consider the carbon nucleus to be at the centre of a cube, then the bonds would point to four corners of the cube that are mutually diagonally opposite each other on each face. Considering the p orbitals to be vectors whose length is equal to half the length of an edge of the cube, we can construct the four hybrid orbitals as:

$$\mathrm{sp}^3(1) = N_\mathrm{s}\mathrm{s} + N_\mathrm{p}\mathrm{p}_x + N_\mathrm{p}\mathrm{p}_y + N_\mathrm{p}\mathrm{p}_z \quad (37a)$$

$$\mathrm{sp}^3(2) = N_\mathrm{s}\mathrm{s} + N_\mathrm{p}\mathrm{p}_x - N_\mathrm{p}\mathrm{p}_y - N_\mathrm{p}\mathrm{p}_z \quad (37b)$$

$$\mathrm{sp}^3(3) = N_\mathrm{s}\mathrm{s} - N_\mathrm{p}\mathrm{p}_x + N_\mathrm{p}\mathrm{p}_y - N_\mathrm{p}\mathrm{p}_z \quad (37c)$$

$$\mathrm{sp}^3(4) = N_\mathrm{s}\mathrm{s} - N_\mathrm{p}\mathrm{p}_x - N_\mathrm{p}\mathrm{p}_y + N_\mathrm{p}\mathrm{p}_z \quad (37d)$$

where the N represent normalisation constants. Since the x, y and z axes are equivalent in a tetrahedron, the normalisation constants in front of each p orbital are assumed to be equal. As well as being normalised, the hybrid orbitals should also be orthogonal to each other. To be orthogonal, the scalar (dot) product of any two of the sp^3 hybrids should come to zero. Any cross terms in the multiplication come to zero since the atomic orbitals are all defined to be orthogonal with one another. The dot product of any two different sp^3 hybrids gives the same expression from which the normalisation constants may be found:

$$< \mathrm{sp}^3 \mid \mathrm{sp}^{3'} > = 0 = N_\mathrm{s} < \mathrm{s}|\mathrm{s} > - N_\mathrm{p}^2 < \mathrm{p} \mid \mathrm{p} > \quad (38)$$

Since the atomic orbitals are normalised, all the integrals come to 1, leaving $N_\mathrm{s}^2 = N_\mathrm{p}^2$. Normalisation of all the hybrids leads to the common expression, $N_\mathrm{s}^2 + 3N_\mathrm{p}^2 = 1$. These equations can be solved simultaneously, yielding $N_s = N_p = 1/2$. With the normalisation constants all equal to $\frac{1}{\sqrt{n}}$, where n is the number of normalised atomic orbitals in the linear combination, the hybrid orbital is evidently properly normalised. It is also evident that the s orbital makes up 1/4 of the probability density of the orbital, which is its fraction of the 4-orbital hybrid. The three p orbitals are equally weighted in the wave function as they are symmetrically equivalent in a tetrahedral environment.

Following the results from the previous paragraph, it is obvious that two sp hybrid orbitals, pointing along the z-axis will have wave functions $|sp\rangle = \frac{1}{\sqrt{2}}(|s\rangle \pm |pz\rangle)$, which are clearly normalised and orthogonal with one another.

The wave functions for the sp^2 hybrid orbitals are not quite so obvious. Following the arguments relating to sp^3 orbitals, the normalisation constant for the s orbital component will be $\frac{1}{\sqrt{3}}$. The sum of the squares of the normalisation constants for the p orbitals in each hybrid must therefore come to 2/3. We define the three sp^2 orbitals to be in the xy plane such that one is pointing along the positive x-axis, as shown in Fig. 6.15. The hybrid orbital pointing along the x-axis will only have the p_x orbital combined with the s orbital. We can therefore immediately deduce that the normalisation constant in front of the p_x orbital in that hybrid is $\sqrt{2/3}$. In the other two sp^2 hybrid orbitals the normalisation constant in front of the p_x orbital must be negative and, due to the angles between the hybrids, will have the factor $\cos 60° = 1/2$. The normalisation constant in front of the p_y orbital will be positive in one of these hybrids and negative in the other. The angles dictate that a factor of $\cos 30° = \sqrt{3/2}$ appears with the p_y orbitals. Squaring and summing these trigonometric factors gives 1. As they account for two p orbitals, the squares of these factors should sum to 2. This is achieved by multiplying these trigonometric factors by $\sqrt{2}$. Multiplying the trigonometric factors by the overall normalisation factor of $\frac{1}{\sqrt{3}}$ will therefore give the correct overall normalisation constants, which are collected in Table 6.4. The reader is left to check that they are normalised and orthogonal.

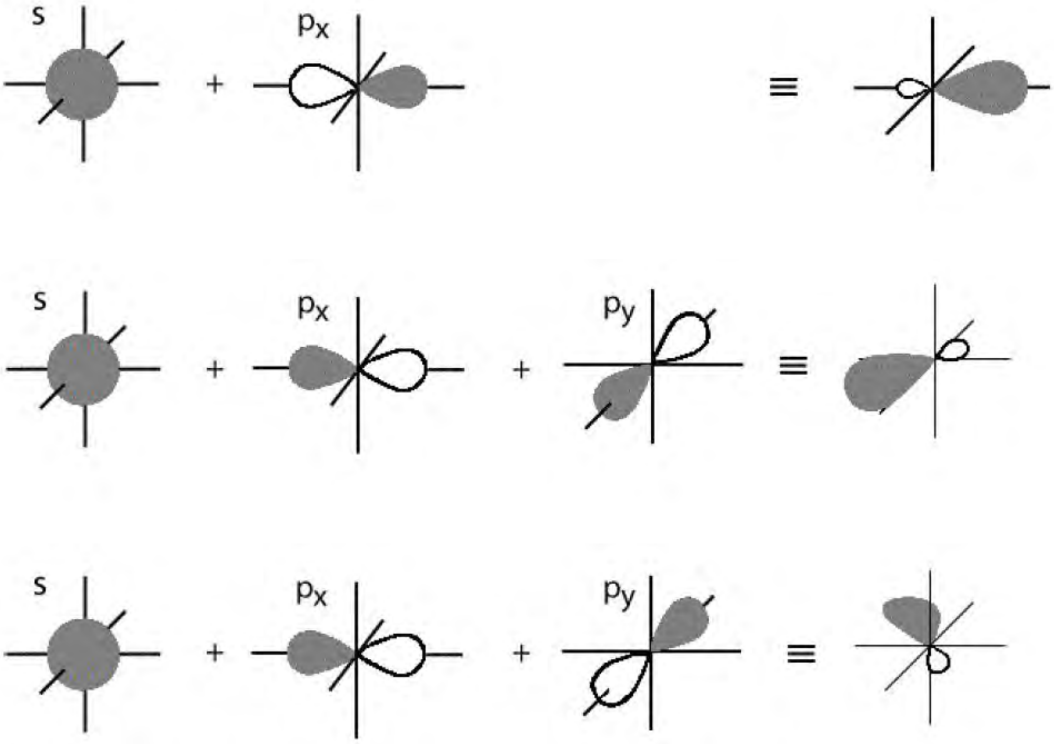


Fig. 6.15 Sketches showing linear combinations of s and p that form the sp^2 hybrids

The geometry of the linear combinations for the sp^2 hybrid orbitals is shown in Fig. 6.15, which is a standard way of depicting the orbitals, with the shaded lobes having a positive phase. It is assumed that the s orbital has a positive phase, but this is not the case for 2s orbitals, where its radial node means that the exterior of the orbital (which will be overlapping with other orbitals) has a negative phase. Given that second-row elements most commonly exemplify these hybrid orbitals, the normalisation constant for the s orbital will have to be made negative so that the combinations of atomic orbitals follow the scheme in Fig. 6.15.

Fig. 6.16 shows the probablility density functions in the *xy* plane using contour lines for the three sp^2 orbitals in a carbon atom using the linear combinations of atomic orbitals given in Table 6.4.

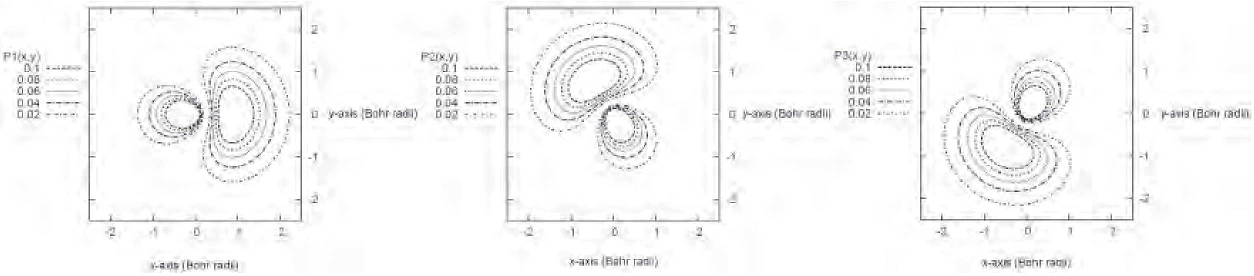


Fig. 6.16 The three sp^2 hybrid orbitals:
probability density contour maps in the *xy* plane

Hybrid orbital	Wave function
$sp^3(1)$	$(1/2)(-s + p_x + p_y + p_z)$
$sp^3(2)$	$(1/2)(-s + p_x - p_y - p_z)$
$sp^3(3)$	$(1/2)(-s - p_x + p_y - p_z)$
$sp^3(4)$	$(1/2)(-s - p_x - p_y + p_z)$
$sp^2(1)$	$(1/\sqrt{3})(-s + \sqrt{2}\,p_x)$
$sp^2(2)$	$(1/\sqrt{3})(-s - (1/\sqrt{2})p_x + \sqrt{3/2}\,p_y)$
$sp^2(3)$	$(1/\sqrt{3})(-s - (1/\sqrt{2})p_x - \sqrt{3/2}\,p_y)$
$sp(1)$	$(1/\sqrt{2})(-s + p_z)$
$sp(2)$	$(1/\sqrt{2})(-s - p_z)$

Table 6.4 The wave functions of all the sp^n orbitals for second-row elements

6.4.5 Hybridised bonding and antibonding orbitals

BF_3 is a classic example of a molecule with an sp^2 hybridised central atom, and is met by all learners when studying VSEPR theory. Using the rule in section 6.4.4 one would expect the fluorine atoms to be sp^3 hybridised. However they may be considered to be sp^2 hybridised since there is also some pi bonding between a lone pair in a p orbital on each fluorine and the vacant p orbital on boron [7] – see Bibliography. The average B–F bond energy in BF_3 is greater than any known single bond, at 646 kJ mol^{-1}; the B–F bond length is also surprisingly short [7] – see Bibliography, shorter than the C–F bond despite the smaller atomic radius of carbon.

Fig. 6.17 shows the bonding and antibonding molecular orbitals in BF_3 from overlap of the sp^2 hybrid orbitals on boron and fluorine. The plot uses contour lines to visualise the probability density in the plane of the molecule. Electron density from the inner electrons on B and F, and from the pi interactions between boron and fluorine are not shown.

In the full molecular orbital treatment of a polyatomic molecule, all the atomic orbitals on all the atoms in the molecule need to be taken together, with their group theoretical label to determine which orbitals can interact. The overlap of hybridised orbitals is therefore a simplification, but very often a useful one to gain a reasonable general impression of the bonding.

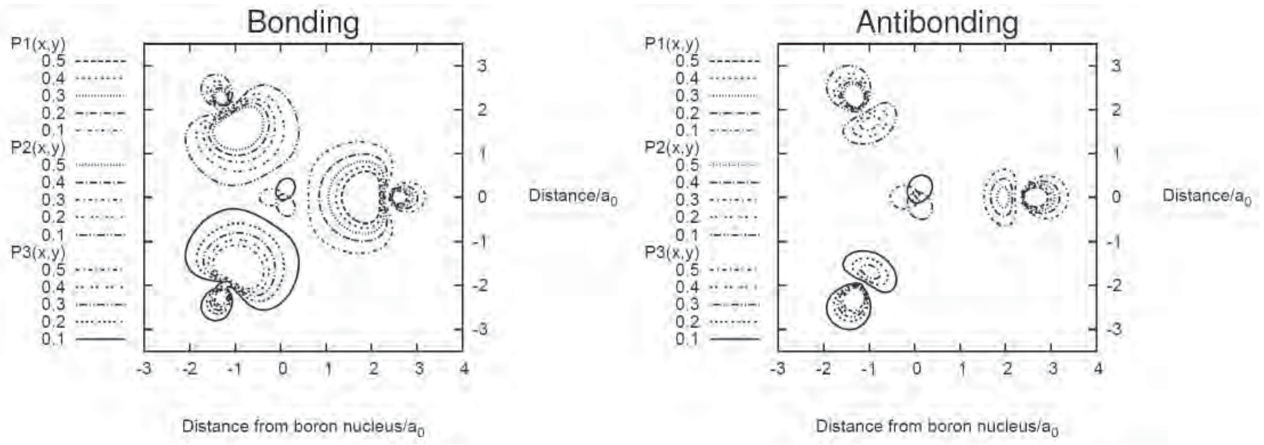


Fig. 6.17 The three sigma bonds and the three sigma antibonds of BF_3 formed from overlap of sp^2 hybrid orbitals on boron and fluorine: probability density contour maps in the *xy* plane

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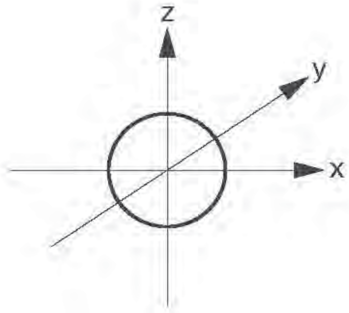
6.5 Sample questions

1 **(a)** **(i)** Sketches of the shapes of the atomic orbitals from the s, p and d subshells are shown below, in random order. Label **each** orbital using labels such as p_x, d_{xy}, etc.



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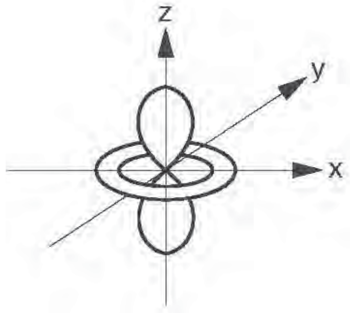

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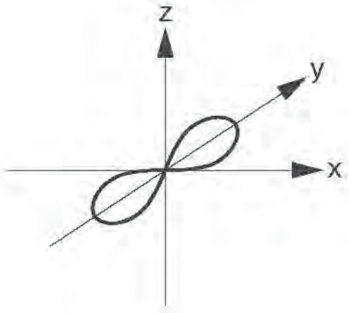

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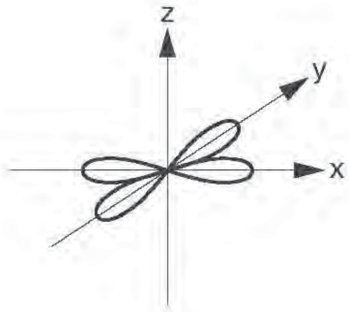

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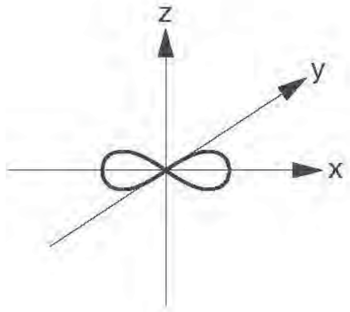

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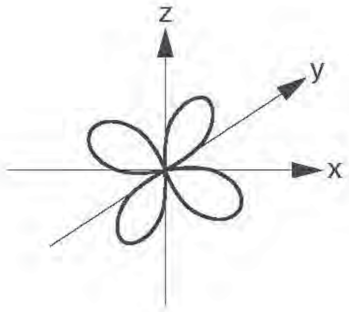

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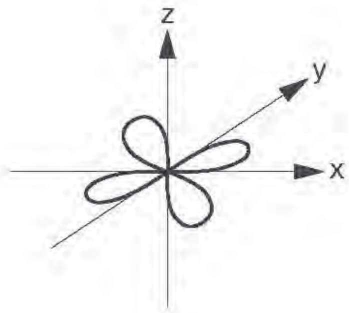

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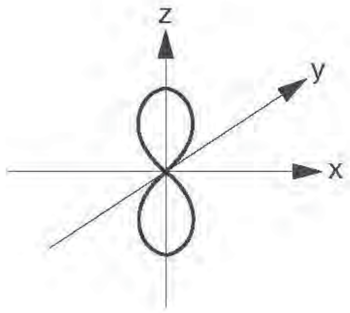

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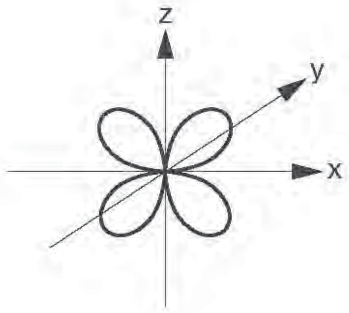


....

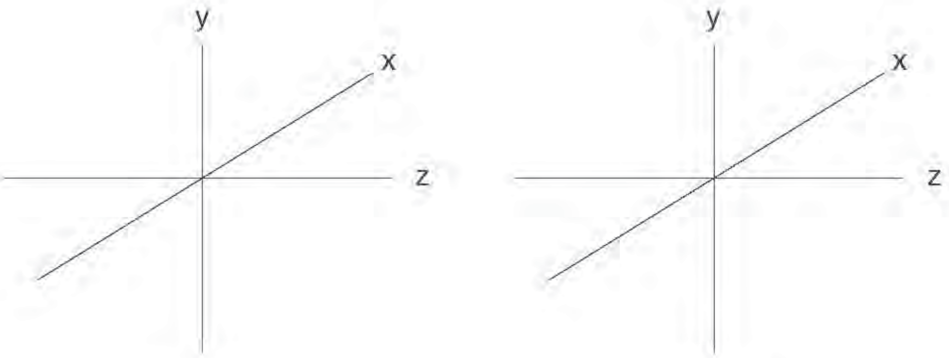
[5]

(ii) There are two elements in the first row of the d block whose gaseous atoms have all their 3d orbitals fully occupied. Name the two elements.

.... and .... [2]

(b) When the atomic orbitals from two atoms overlap a chemical bond may result. The p orbitals can overlap to form sigma (σ) or pi (π) bonds. When two atoms overlap the *z*-axis is used to define the internuclear axis.

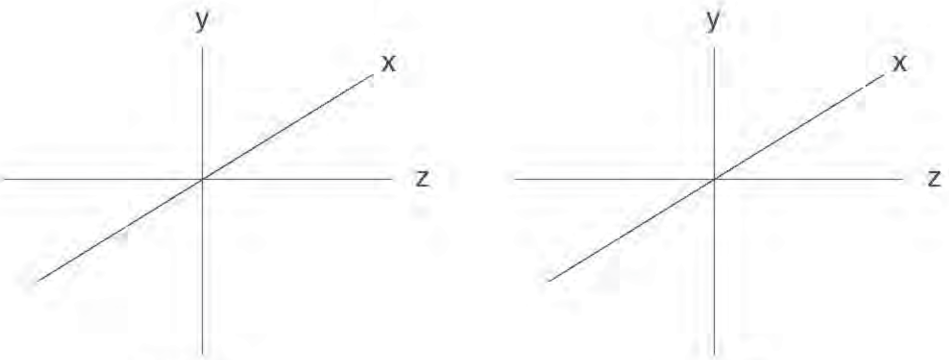
(i) On the diagram below draw two p orbitals (one orbital on each atom) that could overlap to produce a sigma (σ) bond.



atom 1 atom 2

[1]

(ii) On the diagram below draw two p orbitals (one orbital on each atom) that could overlap to produce a **single** pi (π) bond.



atom 1 atom 2

[1]

2 Which statement about bond formation is **not** correct?

A A triple bond consists of one σ bond and two π bonds.

B A π bond restricts rotation about the σ bond axis.

C Bonds formed from atomic s orbitals are always σ bonds.

D End-to-end orbital overlap results in a bond with electron density above and below the bond axis.

3 When the N_2^+ ion is formed from N_2 a σ bonding electron is removed.

Which statement is correct?

A The bond order decreases so N_2^+ has a stronger, shorter bond than N_2.

B The bond order decreases so N_2^+ has a weaker, longer bond than N_2.

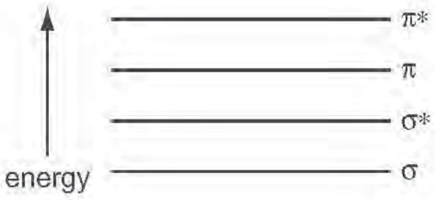
C The bond order increases so N_2^+ has a stronger, shorter bond than N_2.

D The bond order increases so N_2^+ has a weaker, longer bond than N_2.

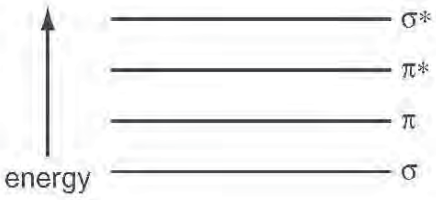
4 The carbon atoms in ethene are bonded through σ and π bonds. When atomic orbitals overlap they form bonding (σ and π) and antibonding (σ* and π*) orbitals.

What is the correct order of energies of the σ and π orbitals in an ethene molecule?

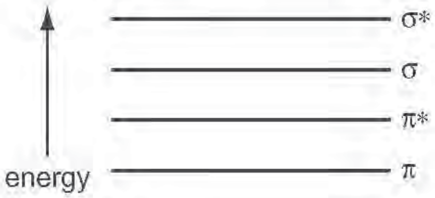
A



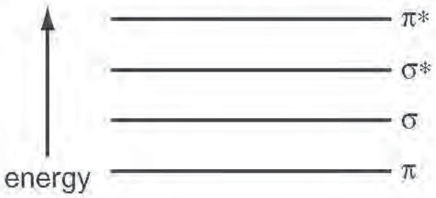
B



C



D



Answers

1 **(a)** **(i)**

s	d_{z^2}	p_y
$d_{x^2-y^2}$ (allow $d_{y^2-x^2}$)	p_x	d_{yz} (allow d_{yz})
d_{xy} (allow d_{yx})	p_z	d_{xz} (allow d_{zx})

The first three marks are for correctly identifying the orbitals with the relevant subshell: 1 for the s, 1 for identifying the three p, and 1 for the five d orbitals. These marks are awarded regardless of the orbital subscripts offered.

1 mark is awarded for the correct subscripts on the p orbitals. This mark can only be awarded if the correct orbitals were identified as p orbitals.

1 mark is awarded for the correct subscripts on the d orbitals. This mark can only be awarded if the correct orbitals were identified as d orbitals.

(ii) Copper (1)
Zinc (1)
Do not penalise a symbol if used instead of a name. [2]

(b) **(i)** A p_z orbital drawn on each atom (both needed for the mark) [1]

(ii) Either a p_x or a p_y orbital drawn on each atom (both needed and both of the same type for the mark) [1]

2 **D**

3 **B**

4 **B**

Section 7: A microscopic approach to entropy

7.1 The thermodynamic approach

7.1.1 Internal energy and enthalpy

When energy is added to a body, its *internal energy* U increases by an amount ΔU. The energy added may be either as heat or work and this is summarised in the equation $\Delta U = q + w$, where q is the energy added as heat and w the energy added as work. This equation assumes that the energy has been added at constant volume but if it is added at constant pressure some additional work may be absorbed in expansion, which requires $p\Delta V$ of work. Under these conditions the added heat or work changes a quantity called the *enthalpy* H of the body. If we compare the equations $\Delta U = q + w$ (constant volume) with $\Delta H = q + w$ (constant pressure), we have $\Delta H = \Delta U + p\Delta V$. As chemical reactions are usually done at atmospheric pressure, ΔH is more commonly used than ΔU. In practice ΔU and ΔH have similar values even when there are large changes in volume because the reaction involves a change in the number of moles of gas. For example for the reaction

$$CH_4(g) = C(s) + 2H_2(g)$$

$\Delta U = +72.3$ kJ mol^{-1} and $\Delta H = +74.8$ kJ mol^{-1}. The difference between these two values is $p\Delta V$, the work required to expand one mole of gas at 1 atmosphere and 298 K. The energy required to bring about this expansion is most easily calculated using the ideal gas equation $pV = nRT$. As p, R and T are constants, $p\Delta V = \Delta nRT = +1 \times 8.31 \times 298 = +2.5$ kJ mol^{-1}.

7.1.2 Heat and entropy

Heating involves the passage of random kinetic energy, while doing work (for example by compressing a gas or by passing an electric current) involves the passage of ordered energy. As entropy is a measure of the degree of disorder of a system, it increases whenever random kinetic energy is added to a body; on the other hand the addition of ordered energy in the form of work will leave the entropy unchanged. So to look at entropy changes, we must first consider what happens to various systems when energy added to them in the form of heat. The following examples illustrate some of the different effects.

An inert gas

If energy is added to an inert gas, it is absorbed by the individual atoms of the gas. As long as the energy is not in packets large enough to excite the electrons in the atoms, the energy appears as translational kinetic energy of the atoms and the temperature of the gas increases.

A polyatomic gas

The absorbed energy can now appear as translational kinetic energy, rotational kinetic energy and as increased vibrational energy of the bonds. Vibrational energy has two components, kinetic energy when the atoms are moving and potential energy when the atoms are momentarily at rest while at their maximum or minimum distance apart. Vibrational energy is absorbed in bigger packets than rotational energy, while energy absorbed as translation is absorbed in packets so small that they appear to be continuous. This means that that most of the energy is absorbed as translational kinetic energy and the temperature of the gas increases.

A crystalline solid

The only type of motion in a crystalline solid such as sodium chloride is vibration and any energy absorbed increases the vibration of the individual ions. As vibration energy is partly kinetic energy, the temperature of the solid increases.

A solid at its melting point

When a solid melts, some of the intermolecular forces are broken. Usually this results in expansion as solid changes to a liquid (water being the obvious exception). Complex changes take place at the molecular level during this melting process as a liquid is composed of solid-like aggregates that are randomly mixed and can move freely over each other. The net result is that the potential energy of the system has increased because some bonds have been broken, while the overall kinetic energy has stayed the same. The energy is absorbed as *latent* heat, a name that indicates that the energy is *hidden* as there is no increase in temperature.

A liquid evaporating

A similar situation occurs when a liquid evaporates. The remaining intermolecular forces are broken so that there is a large increase in potential energy, accompanied by a large increase in volume. The nature of the forces that are broken depends on the material; for a liquid inert gas, they will all be London dispersion forces, while for an ionic liquid they will be the simple electrostatic forces between the ions.

The increase in entropy ΔS of the system depends on the temperature of the system. At high temperatures the system contains a lot of random kinetic energy and the addition of small extra amount has little effect on the total disorder. At low temperatures the amount of random kinetic energy is small and any increase has a big effect on the disorder. A popular analogy, used by Peter Atkins in his books on thermodynamics, is that a sneeze in a quiet room (ordered, low temperature) is very distracting, while in a busy noisy street (disordered, high temperature) the sneeze passes unnoticed. This dependence on temperature is shown by the equation $\Delta S = q/T$, which relates the increase of entropy ΔS to the amount of heat energy absorbed q when it is transferred to a system at temperature T. This temperature is on the absolute (Kelvin) scale of temperature; on this scale the maximum increase in entropy is at very low temperatures when the system is highly ordered and the minimum at high temperatures when the system is already very disordered.

7.1.3 Some entropy changes

Heat flowing from a hot to a cold body

If a body at temperature T_2 is placed in contact with another at a lower temperature T_1, a quantity of heat q flows from the hot body to the cold. The gain in entropy of the cold body is q/T_1 and the loss in entropy of hot body is q/T_2. As $T_2 > T_1$, there is an overall gain in entropy. This is quite general; processes that take place *spontaneously* (that is can take place on their own accord) are always accompanied by an overall increase in entropy. Under special circumstances it is possible for the change to take place *reversibly* when the overall entropy change is zero. This must be the case for a reversible change which can go either way. If a reversible change has an entropy increase in one direction it would have an entropy decrease in the other (which is impossible); the only way to avoid an entropy decrease in one direction is to have the entropy changes in both direction equal to zero. This entropy condition is called the *Second Law of Thermodynamics* and may be expressed in the form $\Delta S \geq 0$.

A solid melting at its melting point

At 273 K, ice melts and becomes water. In doing so it absorbs 6000 J mol^{-1} so there is an entropy decrease of 6000/273 = 22.0 J mol^{-1} K^{-1} (note the units). This entropy decrease arises from the amount of heat absorbed from the *surroundings* and must be balanced by an entropy increase of at least the same amount if the process is to be spontaneous. The entropy increase comes from the *system* and arises because water is far more disordered than ice. We can measure this entropy increase ΔS_{system} by using the equation

$$\Delta S_{\text{total}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$$

At 273 K, the system is in equilibrium so that $\Delta S_{\text{total}} = 0$. Thus

$$0 = -6000/273 + \Delta S_{\text{system}}$$

and ΔS_{system} = +22.0 J mol^{-1} K^{-1}. In chemistry we pay attention to changes in the system, rather than to changes in the surroundings and ΔS_{system} is often written just ΔS. This can cause confusion when it has a negative value as it appears to violate the Second Law of Thermodynamics, but we must remember that any entropy decrease in the system must be balanced (or overcome) by an entropy increase of the surroundings; this is a common situation in chemistry for it implies that the reaction is exothermic.

If the temperature is slightly above 273 K, $\Delta S_{\text{surroundings}} < \Delta S_{\text{system}}$ and under these conditions $\Delta S_{\text{total}} > 0$ and all the ice turns to water. A similar argument shows that below 273 K, $\Delta S_{\text{total}} > 0$ for the reverse process (water to ice).

7.1.4 Liquid to vapour

In the presence of air, a liquid can be in equilibrium with its vapour at a range of temperatures, but there is only one temperature at which its vapour pressure is one atmosphere (namely at its boiling point T_b). At this temperature there are entropy changes similar to those at the melting point of a solid. For most liquids, at their boiling points, their change in disorder when they change to the vapour is very similar, which implies that ΔS_b has a fixed value. This entropy change is equal to the latent enthalpy change of boiling ΔH_b divided by the boiling point T_b; experimentally it has been shown that this has a value of ~88 J mol^{-1} K^{-1}. This constant value of ΔS_b is known as Trouton's Rule and is a useful way of estimating molar latent enthalpy changes. However, some liquids, such as water, have values of ΔS_b much larger than 88 J mol^{-1} K^{-1} which indicates that the liquid at its boiling point is more ordered than usual, probably because of hydrogen bonding.

7.1.5 Entropy and heat capacity

If a substance is heated from T to $T + \delta T$, it absorbs an amount of heat $C_p\delta T$, where C_p is the molar heat capacity of the substance (the amount of heat needed to raise the temperature of one mole of the substance one Kelvin). The entropy change associated with this absorption of heat is $C_p\delta T/T$. If the temperature change is from T_1 to T_2, the overall entropy change is given by

$$\Delta S = \int_{T_1}^{T_2} C_p\delta T/T.$$

If we know how C_p varies with temperature we can plot a graph of C_p/T against T and the entropy change can then be found by measuring the area of the graph between T_1 and T_2. Experiment (and theory) shows that C_p approaches zero as T approaches zero (Fig. 7.1). This does not necessarily mean that C_p/T also approaches zero as T approaches zero, but measurements at very low temperatures suggest that this is the case (Fig. 7.2). This is the basis of the Third Law of Thermodynamics, which states that 'the entropy of a pure, crystalline substance is zero at absolute zero'. Thus S, unlike U and H, has an absolute value.

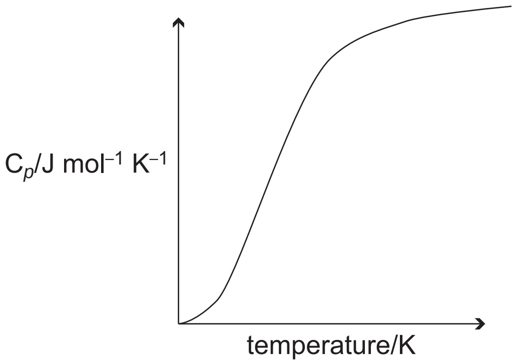


Fig. 7.1. Variation of C_p with temperature.

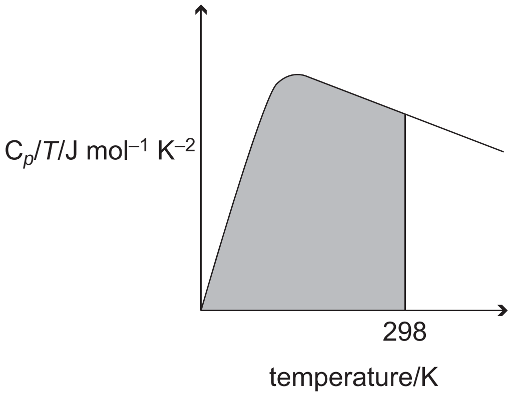


Fig. 7.2 Variation of C_p/T with temperature. The area under the graph gives the value of the absolute entropy of the substance $S^\ominus$

As shown by Fig. 7.1, the value of C_p at high temperatures becomes nearly constant. Under these conditions, we can calculate the entropy change when a substance is heated from T_1 to T_2. If C_p is constant, we can evaluate the integral in the expression

$$\Delta S = \int_{T_1}^{T_2} C_p \delta T/T$$

and this leads to $\Delta S = C_p \ln T_2/T_1$.

7.1.6 Molar heat capacities and absolute entropies of solids.

Table 7.1 lists some values of molar heat capacities and absolute entropies under standard conditions $S^\ominus_{298}$.

Substance	Cp/mol^{-1} K^{-1}	$S^\ominus_{298}$/J mol^{-1} K^{-1}
Diamond	6.2	2.4
Pb	26	65
LiF	42	36
CsI	52	126
$BaCl_2$	75	126
$CaCO_3$	82	93
Naphthalene, $C_{10}H_8$	166	167

Table 7.1 Molar heat capacities and absolute entropies of some solids at 298 K

In a solid, heat is absorbed in the form of increased vibrational energy. If the atoms in the solid vibrate slowly, the energy is easily absorbed as energy levels are close together (remember $E = hf$). This is the case with heavy atoms, weakly attracted to each other. The reverse is true for light atoms, strongly attracted to each other. Thus lead can absorb heat easily and its heat capacity and entropy are large, while the reverse is the case for diamond and its heat capacity and entropy are low. The same effect is shown by LiF (light ions attracted strongly to each other) and $CsCl$ (heavy ions less strongly attracted). A mole of each of these two ionic substances have two moles of particles that can vibrate so that in order to compare one solid substance with another we ought to look at the values per mole of particles, rather than per mole of substance. We should note that per mole of atoms, the values of C_p for Pb, CsI and $BaCl_2$ are very similar and we shall come back to this point later on. The entropy of crystalline $CaCO_3$ is much larger as it contains 5 moles of particles which can vibrate; the vibrations will be of two types; those between the Ca^{2+} ions and CO_3^{2-} ions and those between the Ca and O atoms in the CO_3^{2-} ion. The complexity of this situation makes it difficult to calculate its actual value, but the value suggests that the average bond vibration is intermediate between that for diamond and that for lead. The situation in naphthalene is even more complicated as it has vibrations within the naphthalene molecule and much weaker vibrations between the naphthalene molecules.

7.1.7 Absolute entropies of liquids

The absolute entropy of a liquid is made up of three parts; the entropy of the solid up to its melting point, the entropy change at its melting point and the entropy change of the liquid to 298 K. These individual terms can be measured so that absolute entropies of liquids can be found (Table 7.2).

Substance	**$S^{\ominus}_{298}$/J mol^{-1} K^{-1}**
Pentane	261.2
Hexane	295.9
Heptane	328.5
Octane	361.1
Nonane	393.7
Decane	425.9
2-Methylpentane	290.6
2-Methylhexane	323.3
2-Methylheptane	356.4
Methanol	127.2
Ethanol	159.9
Propan-1-ol	192.8
Propan-2-ol	180.6

Table 7.2 Absolute entropies of some liquids

While it is difficult to calculate values of absolute entropies for individual liquids, some trends are easy to see; for example absolute entropies become larger in a regular fashion as we ascend a homologous series. Another trend is that straight chain molecules have higher entropies than their branched chain isomers as the straight chain form can adopt more different molecule configurations. This is more easily understood when the statistical (rather than the heat) approach to thermodynamics is used. Statistics also enables us to calculate absolute entropies of gases.

7.2 The statistical approach

7.2.1 The Boltzmann equation

The interpretation of entropy as a measure of disorder in a system suggests that it should be related to how probable the state is. As an ordered state has fewer ways of being arranged than a disordered state, it should have a lower probability and a smaller entropy.

The connection between entropy and probability is given by the Boltzmann equation $S = R/N \ln W$, where W is the number of ways the microstates of the system can be arranged, R is the gas constant and N the Avogadro constant. (A microstate is a distinct way in which a particle can be made distinguishable from another, either because it is in a different position or because it has a different amount of energy.)

There is much evidence to support this equation and we will look at some of it.

1. At the absolute zero, all the atoms in a crystal are fixed in position and are in their lowest energy state; this means there is only one arrangement of the microstates. As $\ln 1 = 0$, this leads to the Third Law of Thermodynamics, namely that the entropy of a pure crystalline substance is zero at absolute zero.
2. If we go from a state with entropy S_1 that has W_1 arrangements to a state S_2 that has W_2 arrangements, the entropy change is $S_2 - S_1$ but the probabilities of these arrangements change by the factor W_2/W_1. This suggests that there should be a logarithmic relationship between S and W.
3. If we expand a gas reversibly against a piston at constant pressure p from volume V_1 to volume V_2, the work done is given by the expression
$$W = \int_{V_1}^{V_2} p\mathrm{d}V.$$
4. If at the same time as the expansion takes place the temperature is kept constant by allowing a quantity of heat q to flow into the system we can, using the gas equation, make the substitution $p = RT/V$ and then
$$W = RT \int_{V_1}^{V_2} \mathrm{d}V/V = RT \ln V_2/V_1.$$
5. The absorption of this quantity of heat q is accompanied by an entropy *decrease* of q/T. In order that the overall entropy change is zero (the expansion is under reversible conditions), the expansion of the gas will have an equivalent entropy *increase* of $R \ln V_2/V_1$.

We can show that the equation $S = R/N \ln W$ leads to a similar result. If we consider gas contained in a volume V_1 that expands to a volume V_2, each molecule is now more likely to be in the whole volume V_2 rather than in the smaller volume V_1; that is it has a V_2/V_1 chance of being found in the bigger container. For N molecules, all initially in volume V_1, the chance they will be spread out into the larger volume V_2 is $(V_2/V_1)^N$. The entropy change associated with this expansion is $R/N \ln(V_2/V_1)^N = R \ln V_2/V_1$. (This argument ignores that fact that gas molecules have a range of molecular speeds. A more rigorous derivation, which makes allowance for the distribution of molecular speeds, can be done and leads to the same result.)

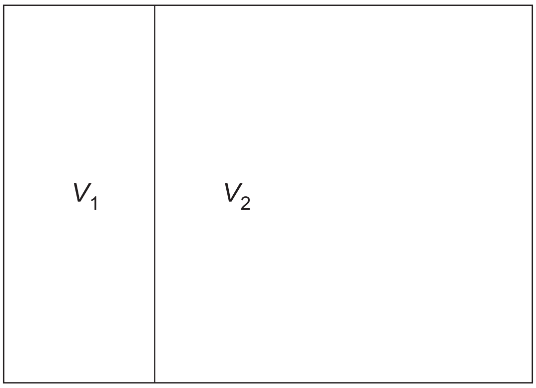


Fig. 7.3 A box of volume V_2 contains a partition enclosing a volume V_1.
When the partition is removed, a molecule originally in V_1 has a V_2/V_1 chance of being found anywhere in the box. For N molecules, all originally in V_1, the chance that they are spread throughout V_2 is $(V_2/V_1)^N$

The mathematics of using the Boltzmann formula is complicated as we are dealing with a very large number of molecules distributed among an even larger number of microstates. In practice, the very large number of particles means we can use approximations in the statistical calculations, which yield extremely accurate results. We can, for example, work out the distribution of energy among molecules and can calculate absolute entropies for a variety of solids and gases. For simple solids, such as metals, it is possible to calculate the variation of C_p with temperature by using equations derived by Einstein and Debye; this then enables us to calculate their absolute entropies without having to use a graphical method. Theory predicts that for substances with low vibration frequencies (for example Pb, CsI and $BaCl_2$) C_p per mole of particles is $3R$ (24.9 J mol^{-1} K^{-1}) at room temperature (Table 1). As the values are slightly higher than this, there must be some additional disorder in the lattice to account for the difference.

It is also possible to calculate absolute entropies of gases. The value for a monoatomic gas depends solely on its relative molecular mass M_r and it can be shown that $S^\ominus = 108.7 + 12.5 \ln M_r$. Calculations for other gases are more complicated as they require information about bond lengths and vibrational frequencies. The values for some gases at 298 K are shown in Table 7.3.

Gas	M_r	$S^\ominus_{298}$/J mol^{-1} K^{-1}
He	4.0	126.0
Ne	20.2	146.2
Ar	39.9	154.7
HF	20.0	173.7
HCl	36.5	186.8
HBr	80.9	198.6
HI	127.9	206.5
H_2O	18.0	188.7
NH_3	17.0	192.3
CH_4	16.0	186.2
C_4H_{10}	58.1	310.1

Table 7.3 Absolute entropies for some gases

7.2.2 Calculations using absolute entropies

When doing calculations using ΔH or ΔG, we ignore the values for the elements as they are zero (by definition). Entropies, however, have absolute values and so the values for the elements has to be included in the calculation. For example in the reaction

$$\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{C}l_2\mathrm{(g)} \rightarrow \mathrm{NaC}l\,\mathrm{(s)}$$

$\Delta H^\ominus = \Delta_f H^\ominus(\mathrm{NaC}l) - \Delta_f H^\ominus(\mathrm{Na}) - \Delta_f H^\ominus(\tfrac{1}{2}\mathrm{C}l_2)$

$= -411.2 \quad - 0 \quad - 0 \quad = -411.2\ \mathrm{kJ\ mol^{-1}}$.

Similarly the value of $\Delta G^\ominus = -384.2 - 0 - 0 = -384.2\ \mathrm{kJ\ mol^{-1}}$.

The value of $\Delta S^\ominus$, however, must include the values for Na(s) and $\tfrac{1}{2}\mathrm{C}l_2$(g); thus for

$$\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{C}l_2\mathrm{(g)} \rightarrow \mathrm{NaC}l\,\mathrm{(s)}$$

$\Delta S^\ominus = S^\ominus(\mathrm{NaC}l) - S^\ominus(\mathrm{Na}) - S^\ominus(\tfrac{1}{2}\mathrm{C}l_2)$

$72.1 \quad - 51.2 \quad - 111.5 \quad = -90.6\ \mathrm{J\ mol^{-1}\ K^{-1}}$.

At 298 K, $-T\Delta S^\ominus = +90.6 \times 298/1000 = +27.0\ \mathrm{kJ\ mol^{-1}}$, the difference between the values of $\Delta G^\ominus$ and $\Delta H^\ominus$.

(Note that the absolute entropy of $\tfrac{1}{2}\mathrm{C}l_2$(g) is larger than that of Cl (g) as $\tfrac{1}{2}\mathrm{C}l_2$(g) includes a contribution from the rotational and vibrational energy associated with bond.

7.3 Equilibrium constants and $\Delta G^\ominus$

The criterion for a spontaneous reaction is that ΔG is negative; this is equivalent to an overall entropy increase in the system and the surroundings. The equation $\Delta G^\ominus = -RT\ln K$, which relates $\Delta G^\ominus$ to the equilibrium constant K appears to be violate the principle of spontaneity as it predicts that some equilibrium reactions proceed to a certain extent, even when $\Delta G^\ominus$ is positive. A positive value of $\Delta G^\ominus$ means that the equilibrium constant of the reaction is less than one and the position of equilibrium is towards the reactant side, rather than the product side, of the equation.

There is only one temperature when water and ice are in equilibrium, namely 273 K. If water is cooled below 273 K it sometimes stays liquid as ‘supercooled’ water. Thermodynamically it should spontaneously change into ice as has been discussed earlier (the total entropy change is positive), but it may stay in this metastable state because there is no nucleus to promote the formation of ice. Scratching the sides of the container or adding a crystal of ice will make the supercooled water change into ice. This releases heat, so that unless this heat is removed the temperature will rise until 273 K is reached when the ice and water are equilibrium. But if the temperature is maintained below 273 K, all the water changes to ice, there is no equilibrium position. Remember that $\Delta G^\ominus$ is the free energy change accompanying the conversion of one mole of reactants completely into one mole of products. As the ice and water form two separate phases which do not mix together, the ΔG graph against composition graph is a straight line with a minimum at the ice end (Fig. 7.4).

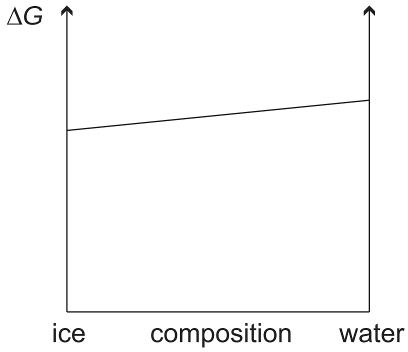


Fig. 7.4 The Δ*G* against composition graph for ice and water at <273 K

The situation is different if the products and reactants can mix together. When they mix, there is an additional entropy of mixing term which leads to a minimum in the composition graph. Mixing of reactants and products can be considered as an expansion of the reactants into the volume of the mixture and a similar expansion of the products into the mixture. If we mix together 0.5 mole of gas A with 0.5 mole of gas B, the entropy of mixing will be ½ ln2 (for gas A) + ½ ln2 (for gas B) = (0.69 J mol^{-1} K^{-1}). If we have two thirds of a mole of gas A mixed with one third of a mol of gas B, the entropy of mixing is 2/3 ln3/2 (for gas A) + 1/3 ln3 (for gas B) = 0.27 + 0.37 = 0.64 J mol–1 K^{-1} (slightly smaller than the 0.5/0.5 case).

If we consider how Δ*G*, at 298 K, for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

changes with composition, there is a minimum at about 20% conversion. Although $\Delta G^\ominus$ for the reaction is positive (+4.8 kJ mol–1), there is a minimum in the Δ*G*/composition graph because of the entropy of mixing. This is shown in Fig. 7.5 by the dotted line.

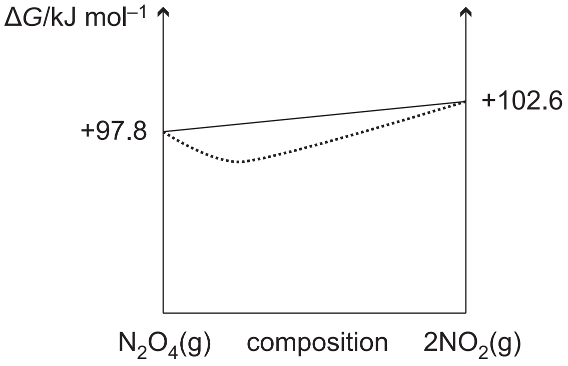


Fig. 7.5 Δ*G* against composition for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Without mixing it would be a straight line. With mixing there is a minimum in the curve even though $\Delta G^\ominus$ is positive.

In practice if $\Delta G^\ominus$ is more negative than –10 kJ mol^{-1}, the minimum is near 100% conversion and we may regard the reaction as having gone to completion. On the other hand, if $G^\ominus$ is more positive than +10 kJ mol^{-1}, the minimum is near 0% conversion and we may regard the reaction as not having taken place at all.

7.4 Summary

The enthalpy of a system may be increased either by adding energy as heat q or as work w. This heat or work comes from the surroundings; the total amount of energy is unchanged (First Law of Thermodynamics). As heat is random kinetic energy, the addition of heat increases the disorder of the system; this increase in disorder is shown as an increase in entropy ΔS.

When a quantity of heat q is added to a system, ΔS increases by q/T, where T is the temperature in kelvin. This heat comes from the surroundings leading to an entropy decrease; if the temperature of the surroundings is maintained at the same temperature T, the overall change in entropy, ΔS_{total}, is zero. In order that the heat can flow irreversibly, the temperature of the surroundings must be higher than that of the system; under these conditions the overall entropy change is positive. In general $\Delta S_{\text{total}} \geq 0$ (Second Law of Thermodynamics).

Any change in the chemical structure of a system will be accompanied by an entropy change ΔS_{system} (often abbreviated to ΔS). Some examples when ΔS increases are: solid turning to liquid, liquid turning to gas and increase in number of gas molecules.

The entropy of a substance can be found by measuring its heat capacity C_p over a wide range of temperatures. The entropy is then found by measuring the area under the C_p/T against T graph. Experiment shows that, near absolute zero, the heat capacity of a pure crystalline substance approaches zero (Third law of Thermodynamics). This means that the absolute entropy of a substance $S^{\ominus}$ can be found.

Absolute entropies enable us to calculate the Gibbs free energy ΔG from ΔH values, using the equation $\Delta G = \Delta H - T\Delta S$. While free energies and enthalpies of elements are zero (by definition), this is not the case for absolute entropies; they must, therefore, be included in the calculation even when elements are involved in the reaction.

As entropy is a measure of disorder it can be related to the number of microstates W of the system. Microstates are the different ways in which the particles of the system can be arranged and the distribution of different packets of energy among these arrangements. The entropy is connected to the number of microstates by the Boltzmann equation $S = R/N\ln W$.

The Boltzman equation enables us to calculate absolute entropies of simple substances. The increase in entropy when gases (or liquids) are mixed can also be found.

If a system has two separate phases (e.g. ice and water) then the position of minimum free energy is either 100% ice (<273 K) or 100% water (>273 K). If the system has substances that mix together, the minimum in the free energy against composition graph lies in an intermediate position, which is therefore the position of equilibrium. If $\Delta G^{\ominus}$ is more negative than -10 kJ mol^{-1}, the minimum is near 100% conversion; if $G^{\ominus}$ is more positive than $+10$ kJ mol^{-1}, the minimum is near 0% conversion. The $G^{\ominus}$ position is related to the equilibrium constant K by the equation $G^{\ominus} = RT\ln K$.

7.5 Sample question

1 The elements of Group 14 can all form monoxides and dioxides. The stabilities of the monoxides, with respect to disproportionation into the element and the dioxide, vary. The equations for the disproportionation reactions are given in Table 3.1 together with some thermodynamic data for the reactions.

Table 3.1

disproportionation equation	$\Delta_r S^\ominus$ (298 K) / J K^{-1} mol^{-1}	$\Delta_r H^\ominus$ (298 K) / kJ mol^{-1}	$\Delta_r G^\ominus$ (298 K) / kJ mol^{-1}
$2CO(g) \rightarrow C(s) + CO_2(g)$	–175.9	–172.5	–120.1
$2SiO(g) \rightarrow Si(s) + SiO_2(s)$	–362.9	–711.5	–603.4
$2GeO(s) \rightarrow Ge(s) + GeO_2(s)$		–126.8	
$2SnO(s) \rightarrow Sn(s) + SnO_2(s)$	–9.200	–9.100	–6.360
$2PbO(s) \rightarrow Pb(s) + PbO_2(s)$	–4.000	+157.2	+158.4

(a) Explain why the entropy change for the disproportionation of

(i) SiO is so much bigger than for CO,

....

....

....[2]

(ii) PbO is so close to zero.

....

....

....[2]

(b) Table 3.2 gives the standard molar entropies for germanium and its oxides.

Table 3.2

name	standard molar entropy at 298 K, $S^{\ominus}(298\,K)$ / J K^{-1} mol^{-1}
germanium, $Ge(s)$	31.1
germanium monoxide, $GeO(s)$	50.0
germanium dioxide, $GeO_2(s)$	55.3

(i) Calculate the standard entropy change, $\Delta_r S^{\ominus}(298\,K)$, for the disproportionation of germanium monoxide.

.... [2]

(ii) Calculate the standard free energy change, $\Delta_r G^{\ominus}(298\,K)$, for the same reaction.

.... [2]

(c) Use data from Table 3.1 to calculate

(i) the value of the equilibrium constant, K_p, for the disproportionation of carbon monoxide, CO.

.... [2]

(ii) the temperature above which the disproportionation of carbon monoxide ceases to be favourable.

.... [2]

(d) Explain why carbon monoxide does not spontaneously disproportionate at room temperature.

....

....[1]

[Total: 13]

Answers

1 **(a)** **(i)** for CO change is from 2 moles of gas to 1 mole gas and 1 mole solid
whereas for SiO change is from 2 moles of gas to 2 moles of solid owtte (1)
decrease in <u>disorder</u> / <u>randomness</u> is greater with SiO (1)
[2]

(ii) 2 moles of solid produce 2 moles of solid owtte (1)
very little change in disorder (1) [2]

(b) **(i)** $\Delta_r S = \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}} = (31.1 + 55.3) - (2 \times 50)$ (1)
$= -13.4$ (J K^{-1} mol^{-1}) (1) [2]

(ii) $\Delta_r G^{\ominus} = \Delta H - \text{T}\Delta S = -126.8 - (298 \times -3.4 / 1000)$ (1)
$= -122.8$ (kJ mol^{-1}) (1) [2]
(-22800 J mol^{-1})

(c) **(i)** $\Delta_r G^{\ominus} = -\text{RT}\ln K_p$ so $\ln \text{K}_p = \Delta_r G^{\ominus} / -\text{RT}$
$= -120.1 \times 10^{-3} / (-8.31 \times 298) = 48.50$ (1) [2]
so $K_p = 1.15 \times 10^{21}$ (1)

(ii) $\Delta_r G^{\ominus} = 0 = \Delta H - \text{T}\Delta S$ so $\Delta H = \text{T}\Delta S$ and $\text{T} = \Delta H/\Delta S$ (1) [2]
$= -172500/-175.9 = 980.7$ K (1)

(d) activation energy / kinetic barrier too high [1]

Total: [13]

Section 8: Crystal structures

Supporting interactive 3D images of crystal structures and more advanced material may be found at
www-teach.ch.cam.ac.uk/links/3Dindex.html

8.1 Introduction

Chemists are inspired by beauty and have long been fascinated by crystals, including snowflakes, minerals and gemstones.

The first attempt to relate the external shape of a crystal to its structure at the molecular level was made in a study of snowflakes by Johannes Kepler, in 1611. He related the six-fold symmetry of the snowflake to the hexagon formed when packing equally-sized balls into a densely packed layer. This work was extended by Robert Hooke who realised that balls could stack to form the different shapes that crystals were observed to adopt.

One of the triumphs of twentieth century science was the development by Max von Laue and Lawrence Bragg of the theory and practice of X-ray diffraction and how, from these experiments, crystal structures could be determined. One of the first X-ray diffraction photographs, taken in 1912 of zinc blende (ZnS), can be seen in *The Basics of Crystallography and Diffraction* by Christopher Hammond, OUP. This finally demonstrated the existence of internal atomic regularity in crystals and its relationship to external symmetry.

The technique was made most famous 40 years later by Rosalind Franklin and Raymond Gosling whose X-ray photograph of DNA in May 1952 led to the elucidation of the double helix structure of DNA by Francis Crick and James Watson in 1953. Their X-ray photograph of DNA is published in the 25 April issue of *Nature*, volume 171, p 737, 1953.

8.2 Close-packing

The simplest place to start with crystal structures is how to pack together as tightly as possible lots of atoms of the same size. We assume atoms to be spherical in shape, which keeps the problem simple. So it is rather like packing oranges into a box. First, if we consider balls sitting on a plane in a single layer we find that the most neighbours that a sphere can be touching simultaneously is six, as was suggested by Kepler in 1611 (see earlier). This can easily be appreciated by considering pennies in contact on the surface of a table.

With all the circles/balls being of equal sides the centres of all the objects form a grid of equilateral triangles sharing their edges with their neighbours. Given that the internal angle in an equilateral triangle is 60° one can see the origin of the hexagonal symmetry. The close packing of spheres in a plane is shown in Fig. 8.1.

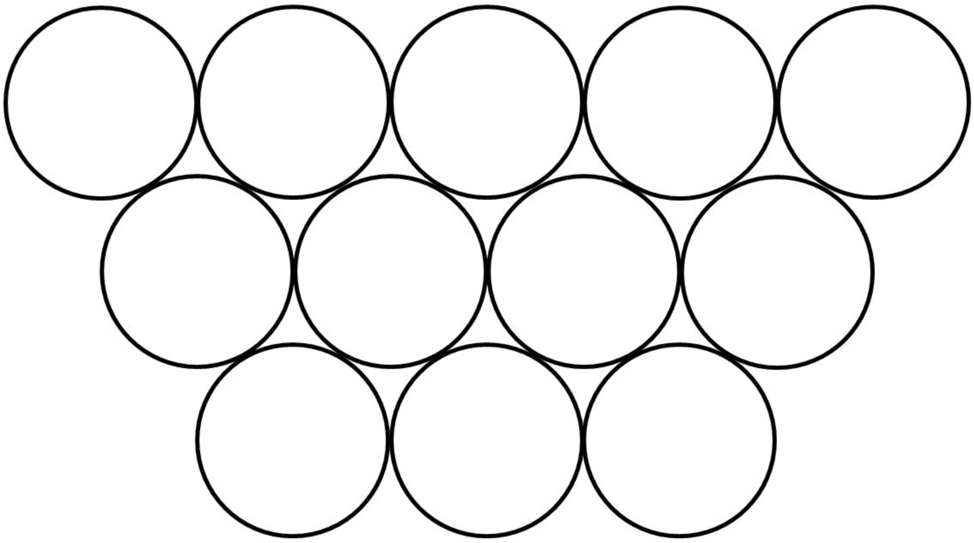


Fig. 8.1 The close-packing of spherical balls (or circles) in a plane. By considering one of the two central balls it is evident that there are six neighbours in contact in a hexagonal arrangement.

The above diagram shows close-packing in two dimensions. The next problem is to consider the third dimension. The most efficient way to pack together layers of these atoms is for one plane to nestle into the gaps in the plane below. By looking along a row of circles above you can see that there are twice as many gaps between them as there are circles. When placing a plane of atoms on top of a close-packed layer there is only space for half of these gaps to have an atom right on top of it. In this way the gaps can be considered to be of two types, as shown below.

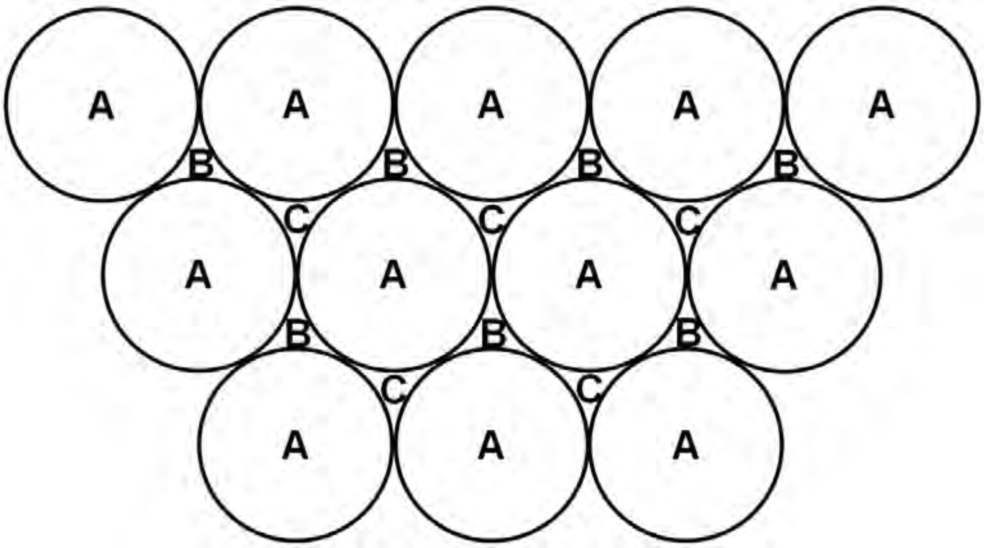


Fig. 8.2 A close-packed layer of atoms, showing two types of hole in the layer, labelled 'B' and 'C'.
[Image adapted from *The Basics of Crystallography and Diffraction* by Christopher Hammond, OUP.]

So a plane of close-packed atoms from above could sit on the holes labelled ‘B’ or the holes labelled ‘C’ but not both at once. Clearly the two different possibilities for the second plane are equivalent. However, when considering where to place a third plane of atoms, there really is a choice. If the second plane of atoms were to sit on the ‘B’ holes then the atoms in the third plane could either rest directly above the atoms in the first plane (in the ‘A’ position) or they could reside above the ‘C’ holes. These two possibilities are both equally efficient at filling space as the ‘B’ and ‘C’ holes are the same (as is evident from Fig. 8.1). They are not, however, equivalent from the point of view of symmetry. But since both of the above methods of stacking planes of close-packed atoms are equally efficient, both are seen in nature – in metallic crystals. The two types are described separately below.

8.2.1 Hexagonal close-packing

The type where atoms only occupy the ‘A’ and ‘B’ positions in an alternating sequence is known as ‘AB’ packing or hexagonal close-packing, relating to the hexagonal symmetry discussed earlier. This arrangement is illustrated in the Fig. 8.3 below. The atoms are shown at half actual radii, ie not actually in contact, to make the structure easier to interpret. While all of the atoms are identical, the atoms in alternating (‘B’) layers are shown in green to make the packing arrangement clear. Magnesium is an example of a metal that adopts this structure.

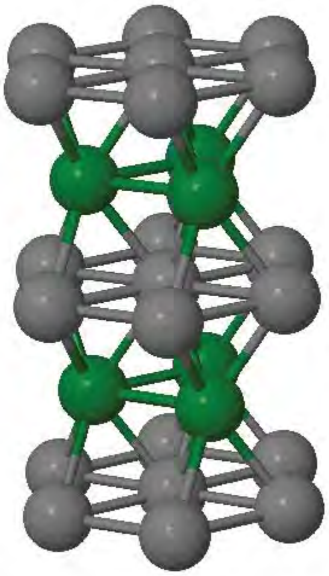


Fig. 8.3 The ‘AB’ close-packing arrangement of hexagonal close-packing. The ‘B’ layers are shown in green, even though all the atoms in the structure are actually identical. The bonds in the figure connect atoms that are in contact in the structure.

Considering the central grey atom in Fig. 8.3 it is evident that an atom in a hexagonal close-packed lattice will be in contact with 12 neighbours: six in the hexagonal arrangement in the plane, and three in an equilateral triangle arrangement in the plane above and the plane below. The number of nearest neighbours with which an atom is in contact is known as the coordination number.

8.2.2 Cubic close-packing

The type where atoms occupy the 'A', 'B' and 'C' positions in that sequence is known as 'ABC' packing, or cubic close-packing. It is not particularly obvious at first that there is cubic symmetry in 'ABC' packing; we shall explore this in the next section. This arrangement is illustrated in the figure below. Again, the atoms are shown not actually in contact to make the structure easier to see. Similarly, despite the colour coding of the 'A', 'B' and 'C' layers all of the atoms are identical. Copper is an example of a metal that adopts this structure.

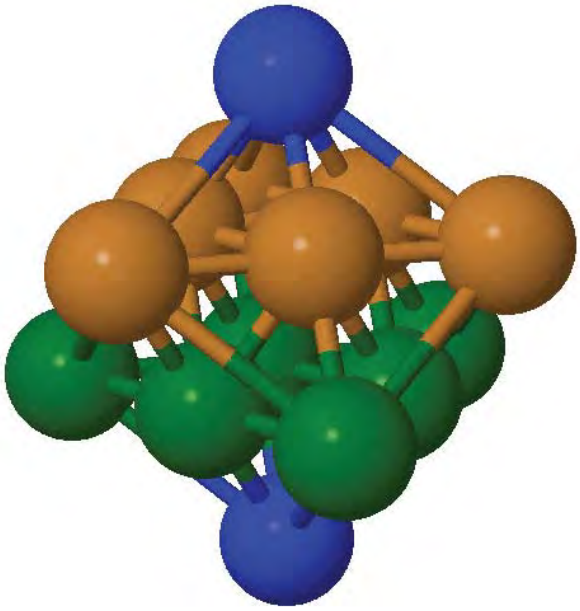


Fig. 8.4 The 'ABC' close-packing arrangement of cubic close-packing. The 'A', 'B' and 'C' layers are colour coded, even though all the atoms in the structure are actually identical. The bonds in the figure connect atoms that are in contact in the structure.

In cubic close-packing there is also a coordination number of twelve. This is not surprising in view of the equal efficiency of the lattices in filling space. The arrangement is similar to the one in the hexagonal close-packing case, except that triangles of atoms in contact in the layers above and below are at a different orientation to each other (rotated by 60°).

8.3 The unit cell

In a high quality crystal the structure is highly ordered and repeats itself countless times. The most convenient way to discuss the structure is to consider the smallest repeating unit of the structure that contains all the symmetry of the crystal. This is known as the unit cell. A crystal can be built up by stacking lots of unit cells together side-by-side. The only unit cells we shall consider here are those of cubic symmetry as these are the geometrically the most straightforward and the easiest to visualise.

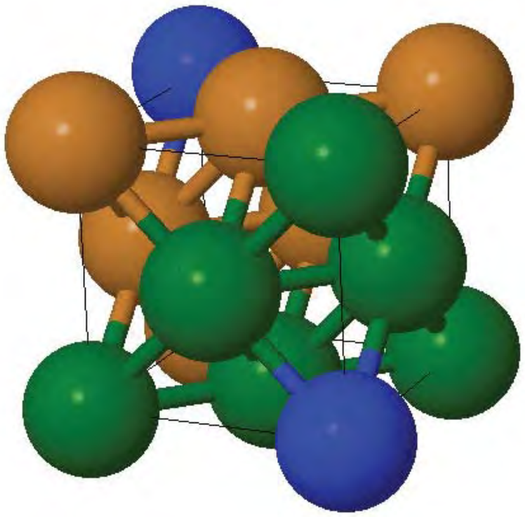


Fig. 8.5 The cubic close-packed unit cell, with colour-coded close-packed layers. The black wireframe depicts the cubic region that repeats itself in the structure. The coloured bonds in the figure connect atoms that are in contact in the structure.

In the last section it was pointed out that the 'ABC' type of close-packing has cubic symmetry. Indeed the unit cell that describes the structure is cubic, and is shown in Fig. 8.5. Again, the atoms are shown not actually in contact and the close-packed layers are colour coded. The unit cell cube is superimposed in black. The lines of the cube do not represent bonds but rather the region of space that repeats itself in the lattice. Note that the atoms below are just rotated in space compared to the earlier depiction of the cubic close-packed lattice.

Within the unit cell in Fig. 8.5 we see atoms in one of two types of position. Atoms are either sitting on the corner of the cube or else they are in the centre of one of the faces. The eight corners and six faces are all associated with an atom. Each atom in a corner position is actually shared between the eight adjacent cubes that meet at that corner. These eight cubes are equivalent and so one eighth of a corner atom is within the unit cell. As there are eight corners on a cube, this leads to a total cell occupancy of 1 for the corner atoms. Each atom at the centre of a face is shared with one other cube and so one half of a face-centre atom is within the unit cell. As there are six faces on a cube, there is a cell occupancy of 3 for the face-centre atoms. The total cell occupancy for the cubic close-packed unit cell is therefore 4, despite the fact that 14 atoms are visible in Fig. 8.5.

8.4 Compounds

The picture is more complicated in compounds because, with more than one element involved, there is more than one size of atom. The lattices for compounds that we encounter are commonly ionic (or considered to be ionic) and so the atoms involved will be referred to as ions from now on. A convenient way of considering the problem is for one ion to fit into the gaps of a lattice formed by the oppositely charged ion. Such an arrangement maximises the contact between oppositely charged ions, providing attractive forces, and minimises the contact between similarly charged ions, minimising the repulsive forces. In this way ionic compounds achieve the highest possible lattice energy and therefore the maximum possible energetic stability.

So we need to consider the gaps in a lattice of ions. One way of imagining the gaps, or holes, in a lattice is to refer back to Fig. 8.2. Let us imagine that there is a second layer of ions above the ‘A’ layer (of the same type as the ‘A’ layer ions) that are all sitting on the ‘B’ gaps. In this picture we can find two types of hole in the lattice.

8.4.1 Tetrahedral holes

In Fig. 8.6, below each ion in the ‘B’ layer there is a small hole. The centre of this hole is slightly above the level of the centres of the ‘A’ ions. Such a hole is surrounded by four neighbours – three ‘A’ ions arranged as an equilateral triangle just beneath and a ‘B’ ion immediately above. Because those ‘A’ and ‘B’ ions are all an equal distance from each other, their centres are at the corners of a tetrahedron, and so the hole is known as a tetrahedral hole.

An ion residing in such a hole will therefore have four nearest-neighbour ions of the other type. Since every ion in a close-packed lattice can be considered to be in a plane and fitting into a hole on the plane on either side, then every ion has a tetrahedral hole associated with it on either side. Therefore there are twice as many tetrahedral holes in a close-packed lattice as there are ions. An ion occupying a tetrahedral hole is shown in the figure below.

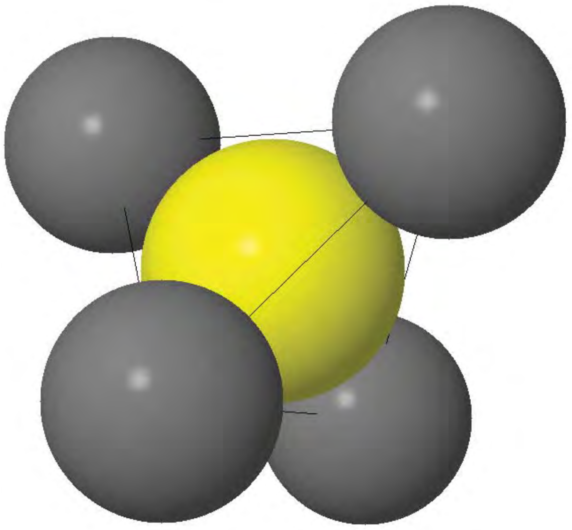


Fig. 8.6 Non-metal ion (shown in yellow) occupying the tetrahedral hole between four metal ions (shown in grey). The metal ions are nominally close-packed though in fact are not in contact due to the size of the non-metal ion. The black wireframe connects the centres of the four metal ions, illustrating the tetrahedral symmetry of the hole.

Let’s assume that the grey ions are metal cations and the yellow ion is a non-metal anion. Three of the four metal cations can be considered to be in one close-packed layer with the fourth one in the adjacent layer. The non-metal ion is occupying the tetrahedral hole just above the layer with the three metal ions. Since the non-metal ion is larger than the hole itself it has forced the metal ions apart. Ions fitting into such holes are in fact larger than the holes for this reason: since the metal ions are of like charges, and like charges repel, the added size of the non-metal ion compared to the hole reduces the electrostatic repulsion between the metal ions.

8.4.2 Octahedral holes

Going back to Fig. 8.2 again, assuming that there are ions in the ‘A’ and ‘B’ positions, we can also identify octahedral holes in the lattice. In this case the octahedral holes are the holes labelled ‘C’. These are not quite so easy to see. The centre of the hole is half way between the ‘A’ and ‘B’ planes. Beneath it there is an equilateral triangle of ‘A’ ions and above it is an equilateral triangle of ‘B’ ions. The triangles have different orientations: one rotated 60° relative to the other. However, the corners of two such triangles connect together to form a regular octahedron. An ion inside an octahedral hole of counter-ions is shown in Fig. 8.7.

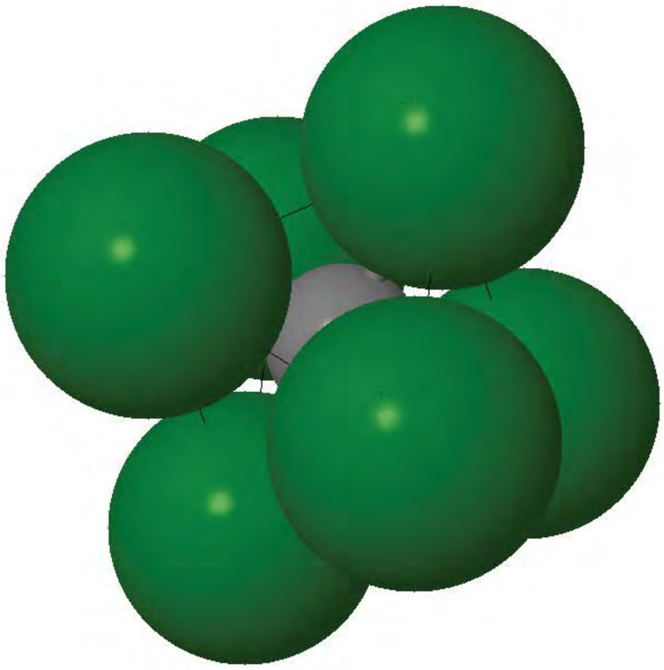


Fig. 8.7 Metal ion (shown in grey) occupying the octahedral hole between six non-metal ions (shown in green). The non-metal ions are nominally close-packed though in fact are not in contact due to the size of the non-metal ion. The black wireframe connects the centres of the six non-metal ions, illustrating the octahedral symmetry of the hole.

In Fig. 8.7 above it is apparent how the octahedral hole relates to close-packed layers. Consider the three non-metal ions above and to the left of the central metal ion to be in one close-packed layer and the three bottom-right ions to be of the adjacent close-packed layer of non-metal ions. Each group of three ions forms an equilateral triangle rotated 60° relative to the other.

An ion residing in such a hole will therefore have six nearest-neighbour ions of the other type. Referring back to Fig. 8.2, since every ‘C’ hole in this model is an octahedral hole, and since inspection along rows of ions reveals that there is an equal number of ‘C’ holes compared to ions in a row, then there is the same number of octahedral holes in a close-packed lattice as there are ions.

Now that we have considered occupying tetrahedral and octahedral holes in close-packed lattices with counter-ions to form ionic compounds, we can go on to consider a couple of classic examples.

8.4.3 Sodium chloride, NaCl

In the sodium chloride lattice there is a 1:1 ratio (stoichiometry) between the two types of ion. The lattice can be considered as a close-packed arrangement of one type of ion with the other type of ion occupying all the octahedral holes in the lattice. This is consistent with the ratio of octahedral holes to ions arrived at earlier. The structure is illustrated in Fig. 8.8.

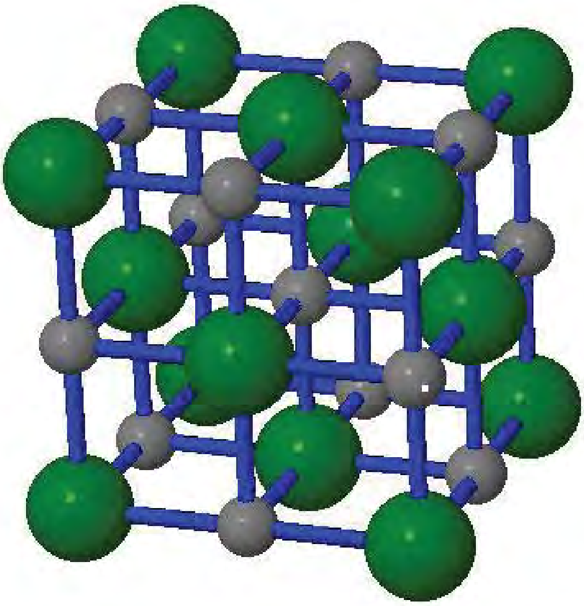


Fig. 8.8 The unit cell of the sodium chloride lattice. The green ions are chloride ions and the grey ions are sodium ions. In this view the close-packed layers of the chloride ions are clearly visible. The bonds connect the ions that are in contact in the structure.

The symmetry of the above structure is very high. Indeed the sodium and chloride ions are in fact in equivalent lattices: the lattice can equally be considered as a close-packed lattice of sodium ions with chloride ions in all the octahedral holes. By considering a unit cell displaced by half of a cell length, a similar cell emerges but with the two types of ion having exchanged position in the cell.

By considering the central sodium ion in the unit cell it is apparent that the ions are sitting in octahedral holes: it has six nearest neighbours chloride ions which are arranged along the plus and minus directions of the *x*, *y* and *z* axes, assuming they are drawn along the bonds connecting the ion to the neighbours with which it is in contact. This is made clear in Fig. 8.9.

It is unfortunate that only one ion in the unit cell for Na*Cl* has all six of its nearest neighbours visible in the cell. However, when considering another of the sodium ions, which are all half-way along the edges of the unit cell cube, four of its nearest-neighbour chloride ions are visible in the cell. These ions can be found along the *x*, *y* and *z* axes (as defined in the last paragraph) and with a bit of imagination it can be seen that the other two nearest neighbours will lie in adjacent unit cells, and that therefore all the sodium ions are in octahedral holes.

Similarly, consideration of the chloride ions in the unit cell, which are at the corner and face-centre positions, reveals that they are all in octahedral holes of sodium ions. In the case of the corner chlorides, only three of the nearest-neighbour sodium ions are visible in the unit cell, but these are along the *x*, *y* and *z* axes; it is obvious by symmetry that there are three other nearest neighbours in adjacent unit cells, forming an octahedral arrangement. In the case of the face-centre chlorides, five of the nearest-neighbour sodium ions are visible in the unit; it is clear that the sixth neighbouring sodium ion is in the adjacent unit cell, forming an octahedral arrangement.

Now that we have established that both sets of ions are in octahedral holes we can confirm that both ions are 6-coordinate, i.e. they each have six nearest neighbours. The fact that both ions have the same coordination number is consistent with their 1:1 stoichiometry in the compound.

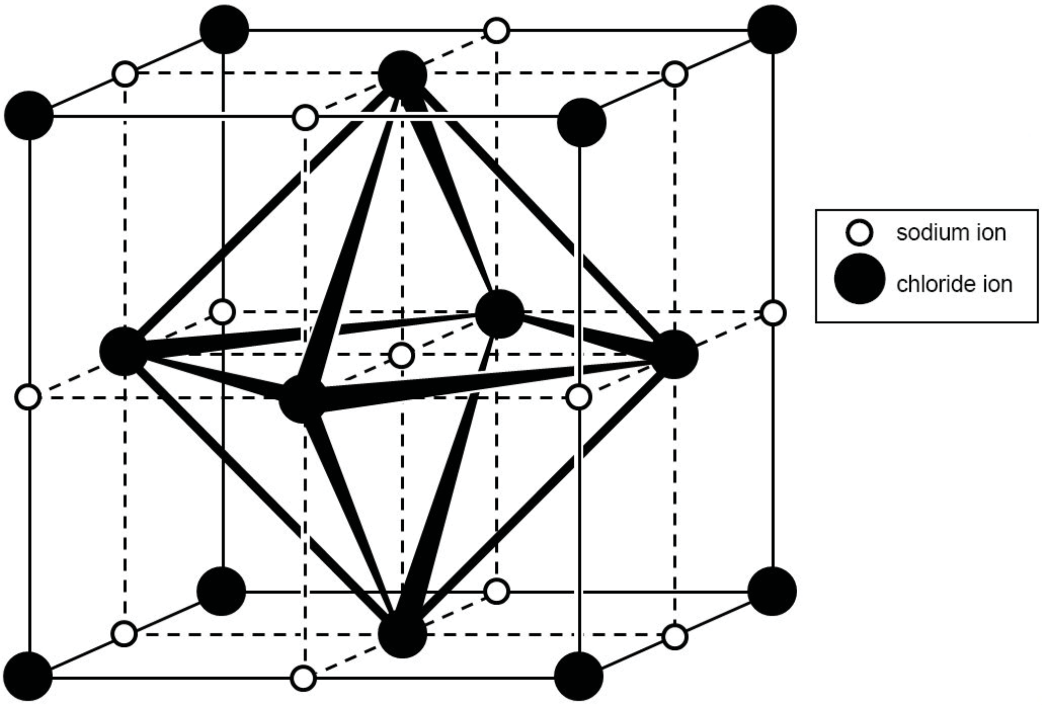


Fig. 8.9 The unit cell for $\mathrm{NaC}l$ showing the octahedral coordination around the central ion. [Image adapted from *The Basics of Crystallography and Diffraction* by Christopher Hammond, OUP.]

It is good practice to consider the cell occupancy of each type of ion. The chloride ions in Fig. 8.8 occupy the cubic-close-packed positions and so, according to the discussion in the section 8.3, have a cell occupancy of 4 (from the calculation $(8 \times 1/8) + (6 \times 1/2)$). As for the sodium ions, they occupy the body-centre of the cube and the edge-centre positions. The edge-centre ions are shared by four unit cells, and since the cubes are equivalent, each ion has an occupancy of 1/4. Since a cube has 12 edges, the total cell occupancy of sodium ions is $(12 \times 1/4) + 1 = 4$. The sodium and chloride ions therefore have the same cell occupancy of 4, which is consistent with their 1:1 stoichiometry in the compound.

8.4.4 Fluorite, CaF_2

In the fluorite (calcium fluoride) lattice there is a 1:2 stoichiometry between the two types of ion. The lattice can be considered as a close-packed arrangement of calcium ions with the fluoride ions occupying all the tetrahedral holes in the lattice. This is consistent with the ratio of tetrahedral holes to ions arrived at earlier. The structure is illustrated in Fig. 8.10.

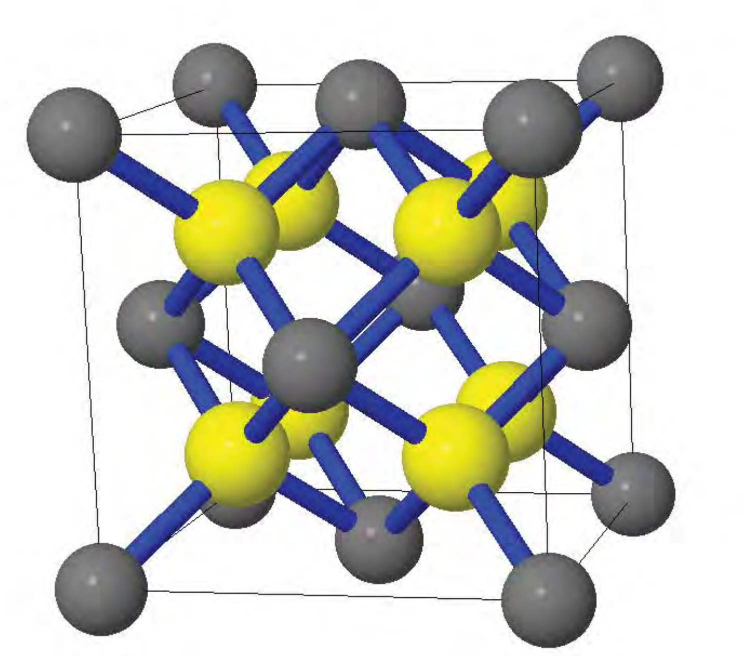


Fig. 8.10 The unit cell of the fluorite (CaF_2) lattice. The grey ions are calcium ions and the yellow ions are fluoride ions. The blue bonds connect the ions that are in contact in the structure. The black wireframe depicts the cubic region that repeats itself in the structure.

Inspection of the yellow fluoride ions shows that they have four nearest neighbours (the blue bonds indicate which ions in the structure are in contact with them). It may not be obvious that these four neighbours are in a tetrahedral arrangement; this symmetry can be confirmed by thinking of the unit cell divided up into eight equal cubes, or octants. The cell length of the octant is half that of the unit cell. In three dimensions the octant has a volume of (1/2)3 = 1/8 of the unit cell. In each of these octants, four of the eight corners have calcium ions at the corners, as shown in Fig. 8.11. By symmetry the fluoride ion must be at the centre of the cube: since it is in contact with all four calcium ions, the distances between the fluoride ion and the calcium ions must be the same.

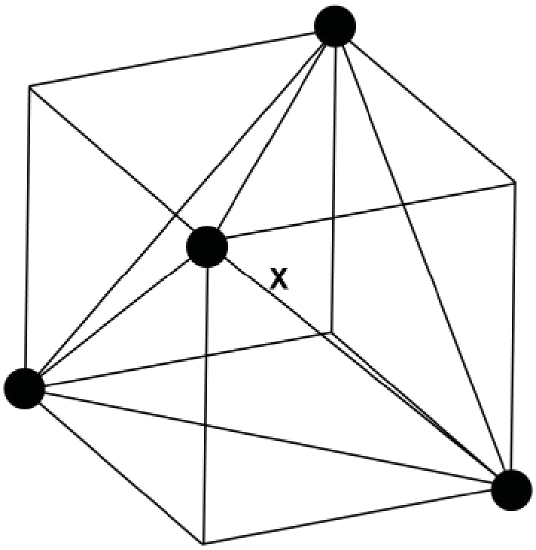


Fig. 8.11 The tetrahedral hole within an octant of the fluorite unit cell. **X** marks the centre of the hole and the centre of the octant. The arrangement of the four calcium ions at the alternating corners of a cube gives a tetrahedral arrangement: the distances between all four calcium ions are equal, by symmetry, which defines the tetrahedron.

A tetrahedral hole shown within the fluorite unit cell is given in Fig. 8.12.

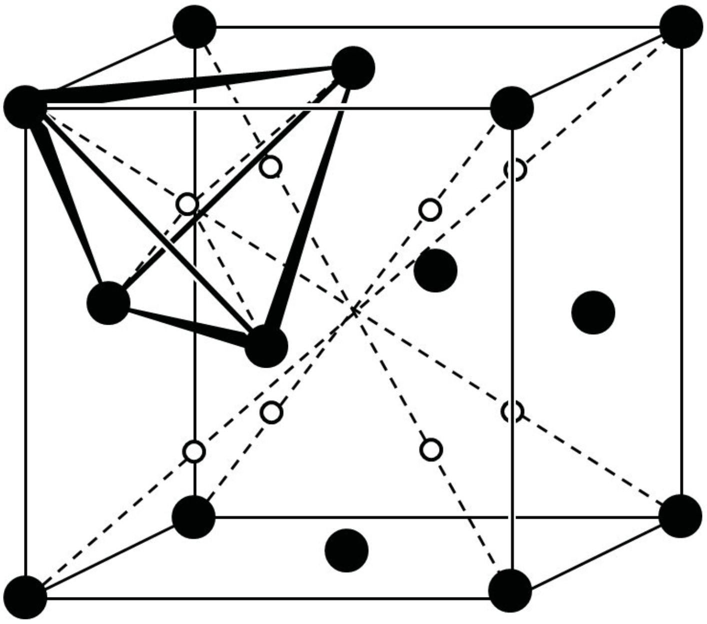


Fig. 8.12 The unit cell for CaF_2 showing the tetrahedral coordination around one of the fluoride ions. [Image adapted from *The Basics of Crystallography and Diffraction* by Christopher Hammond, OUP.]

Since every corner calcium ion is in contact with a fluoride ion in the unit cell, and since each corner calcium ion is shared between eight unit cells, it follows that the corner calcium ions have eight nearest neighbour fluoride ions, and therefore a coordination number of eight.

In Fig. 8.12 above, it is apparent, by symmetry, that the calcium ion at the centre of the top face of the unit cell has four fluoride nearest neighbours in the unit cell – one in each of the four top octants. Since every face-centre calcium ion is shared between two unit cells, then by symmetry each of these face-centre calcium ions, like the corner calcium ions, has a coordination number of eight.

In summary, the fluoride ions have a coordination number of 4 and the calcium ions have a coordination number of 8. This is consistent with the 2:1 stoichiometry of the compound. [You may also be able to see that the calcium ions occupy cubic holes, half of which are occupied.]

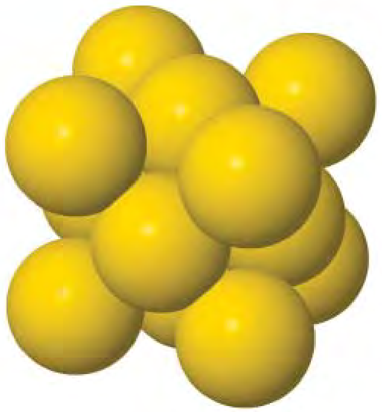
It is good practice to consider the cell occupancy of each type of ion. The calcium ions occupy the cubic-close-packed positions and so, according to the discussion in the Unit Cell section, have a cell occupancy of 4 (from the calculation (8 × 1/8) + (6 × 1/2)). As for the fluoride ions, they are all within the body of the cube and so have a cell occupancy of 8. This 1:2 ratio of cell occupancy is consistent with their 1:2 stoichiometry in the compound.

8.5 Sample questions

1. This question is about gold nanoparticles

UK scientists have found a way to target cancer with gold (*Photochemical and Photobiological Sciences*, 2006).

Gold crystallises in the arrangement shown below.



The above structure is known as a *unit cell*. Running perpendicular to the body-diagonals in the unit cell are the close-packed layers. These are shown with colour-coding in the representation below.

An anti-cancer drug is bound to the gold nanoparticle. The drug-nanoparticle complex is attracted to cancer cells. In the presence of light, the cancer drug excites oxygen molecules to a reactive form known as 'singlet oxygen', which causes apoptosis ('cell suicide') of the cancer cells.

(a) Gold is unusual in being made up of a single isotope, Au^{197}. Write down the number of protons, neutrons and electrons in an atom of Au^{197}. [A periodic table is available in the *Data Booklet*.] [2]

(b) If a gold nanoparticle contains a million gold atoms, calculate its mass. [Hint: you will need Avogadro's number, which is in the *Data Booklet*.] [1]

(c) Given that the radius of a gold atom is 0.135 nm (1 nm = 10–9 m), calculate the number of gold atoms in a gold nanoparticle that has dimensions 10 nm × 10 nm × 10 nm. Assume that 74% of the volume of the nanoparticle is taken up by spherical gold atoms. (The other 26% of the volume is the spaces between the atoms.) The volume of a sphere is $\frac{4}{3}\pi r^2$ where r is the radius. [Hint: calculate the volume of the nanoparticle occupied by gold atoms, and the volume of one gold atom.] [3]

(d) What is the name of the particular type of structure adopted by gold crystals? [1]

(e) Given that atoms are located at the corners of the unit cell and in the centre of the faces, calculate the total number of atoms within the cell. [Hint: remember that the corners of the unit cell are in the *centres* of the atoms, so not all the atom is actually inside the cell. [1]

(f) Within the bulk of a gold nanoparticle how many neighbouring atoms are in contact with a gold atom? [1]

(g) In the figure above, the close-packed layers are colour-coded. There is more than one direction in which the close-packed layer planes can be shown to be propagating. Given that the close-packed planes are perpendicular to a body-diagonal axis in the cube [a body-diagonal axis passes through two corners and the centre of the cube] deduce in how many different directions the close-packed layers can be drawn. [1]

[Total: 10]

2 In most metals the atoms pack in one of three possible ways. One of these is called *body-centred cubic (bcc)*, in which there is 32% empty space between the atoms. In the other two common metal structures there is only 26% empty space, so these structures are described as *close-packed*.

(a) Give the coordination number of a metal atom in a *close-packed* metal structure.

.... [1]

(b) Complete the table to give the names and layer structures of the two close-packed metal structures.

name	layer structure

[4]

(c) Explain the differences between the lattice structures of sodium chloride, $NaCl$, and calcium fluoride, CaF_2, by completing the following sentences.

(i) $NaCl$ can be considered to consist of a close-packed structure of sodium ions with chloride ions occupying the .... holes. [1]

(ii) CaF_2 can be considered to consist of a close-packed lattice of .... ions with .... ions occupying the .... holes. [2]

[Total: 8]

Answers

1 **(a)** No. protons = $Z = 79$ (1)
No. neutrons = 197 – 79 = 118 (1)
[2]

(b) Mass of 1 gold atom = 197 g mol^{-1} / 6.02×10^{23} mol^{-1} = 3.27×10^{-22} g
Mass of 1 million gold atoms = 3.27×10^{-16} g
[1]

(c) Volume of nanoparticle occupied by Au atoms = $0.74 \times (10\ \text{nm})^3 = 740\ \text{nm}^3$ (1)
Volume of 1 gold atom = $4/3 \times \pi(0.135\ \text{nm})^3 = 0.0103\ \text{nm}^3$ (1)
Number of Au atoms in nanoparticle = $740\ \text{nm}^3 / 0.0103\ \text{nm}^3 = 71800$ (3 sf) (1)
[3]

(d) Cubic close packed
Allow face-centred cubic
[1]

(e) 4 (from 8 corners @ 1/8 and 6 face-centres @ 1/2) [1]

(f) 12 (six in the close-packed layer and three from the layers above and below) [1]

(g) 4 (as the cube has 4 body-diagonals, each connecting two diagonally-opposite vertices) [1]

[Total: 10]

2 **(a)** 12 [1]

(b) HCP (1) = ABA(B) (1)
FCC/CCP (1) = ABC(ABC) (1)
[4]

(c) **(i)** octahedral [1]

(ii) calcium; fluoride/fluorine (1)
tetrahedral (1)
[2]

[Total: 8]

Section 9: Time-of-flight mass spectrometry (TOF-MS)

9.1 Introduction

Mass spectrometry is a technique used to separate, and to measure the (relative) masses of ions produced in the gas phase under high-vacuum conditions. Both the time-of-flight (TOF) mass spectrometer and the conventional magnetic-deflection mass spectrometer involve the same four processes: ionisation, acceleration, analysis and detection; and both require very high vacuum conditions for their accurate operation. Their main difference lies in the way that the beam of ions is separated and analysed.

In the TOF mass spectrometer separation is achieved by allowing the ions to pass through an electric field-free zone between their acceleration and their detection. If the ions have all been given the same kinetic energy by the accelerating voltage, their velocities, and hence the time it takes them to traverse the field-free zone, will differ according to their masses. The heavier ions will move more slowly, so will take longer to reach the detector.

$$t = \frac{d}{\sqrt{2eE}}\sqrt{m/z} \qquad [1]$$

where t = time; d = length of field-free zone; e = fundamental electronic charge; E = accelerating potential; m = mass of ion; z = charge on ion.

[The Appendix to this section shows a derivation of this equation.]
[Activity: learners could be asked to derive this themselves]

9.2 The features of the instrument

The physical design of the TOF mass spectrometer, and in principle its electronic circuitry, are both more simple than that of a conventional mass spectrometer.

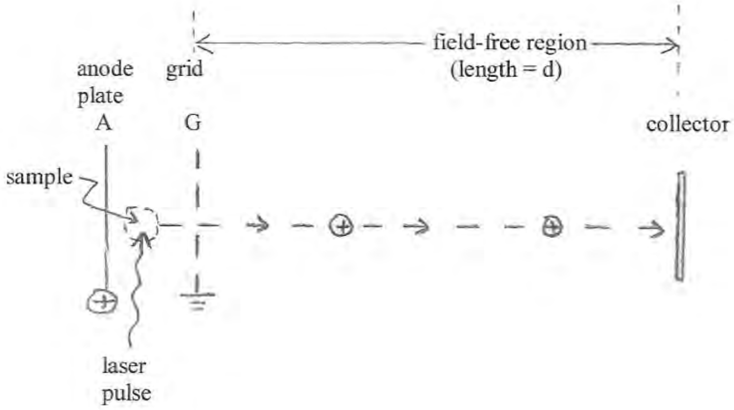


Fig. 9.1 A linear TOF mass spectrometer

Accurate TOF mass spectrometry is highly reliant on the accurate measurement of time, so progress in TOF spectrometry had to wait for the development of sensitive time-to-digital converters. New techniques of ionisation have also been developed, since in several types of spectrometer the instantaneous time of ionisation needs to be known with relation to the time of detection. Laser pulses are often used to effect ionisation.

9.2.1 Some rough dimensions and values

Using equation [1], we can calculate the time of flight for a typical molecule-ion.

In many TOF mass spectrometers, the path length, *d*, of the field-free zone is about 1.5 m and the accelerating voltage is often about 5000 V. Let us assume the molar mass of the sample to be about 500 a.m.u. Taking $e = 1.6 \times 10^{-19}$ C and $m_H = 1.67 \times 10^{-27}$ kg (mass of hydrogen atom), and assuming a singly-charged molecular ion ($z = 1$), we can calculate *t* as follows:

$$t = [1.5/\sqrt{(2 \times 1.6022 \times 10^{-19} \times 5000)}\,] \times \sqrt{(500 \times 1.6736 \times 10^{-27})} = \mathbf{3.428 \times 10^{-5}}\ \text{s}$$

The corresponding time for an ion of mass 499 (i.e. 1 a.m.u. lower) is $\mathbf{3.425 \times 10^{-5}}$ s, so if we need the spectrometer to distinguish between these two ions, the electronic circuitry must be capable of measuring to an accuracy of 0.003×10^{-5}, i.e. 3×10^{-8} s.
*[**Q:** learners could be asked to calculate the time for m/e = 499 and hence work out the sensitivity required]*

9.2.2 The advantages of the TOF mass spectrometer over a conventional instrument

- Its cost is often less than that of a conventional instrument.
- Only small amounts of sample are needed to obtain the mass spectrum: fractions of a femtogram (1×10^{-15} g) or even attogram (1×10^{-18} g) quantities can be used.
- Theoretically, the mass range that can be analysed is virtually unlimited, so the technique has found great use in analysing large biological macromolecules with high M_r.
- It is much lighter than a conventional instrument, and can be constructed to be much smaller too, so it is ideally suited for use in spacecraft and interplanetary probes.

9.3 The spectrometer described in greater detail

9.3.1 How the ions are formed

The standard methods of ion formation (electron impact and chemical ionisation) are covered in many texts and so are not detailed here. Novel methods of ionisation have been developed for use with TOF machines, both because the time of ionisation often needs to be known accurately, but also because the substances to be analysed can be fairly unstable biological molecules. Two of them will be described here:

a. Electrospray ionisation

In this technique a solution of the sample is ejected through a small-diameter tip of a capillary tube. The tip is kept at a high positive potential of a few thousand volts. While the solution passes through the tip, electrons are removed from it and a spray of positively-charged droplets emerges. As the solvent evaporates, the droplets become smaller and smaller, and their surface charge density increases until the electrostatic repulsion between touching ionic charges causes a 'coulombic explosion' to occur, forming even smaller droplets. Eventually, all the solvent molecules will have evaporated, leaving ionised molecules of the sample in the gas phase.

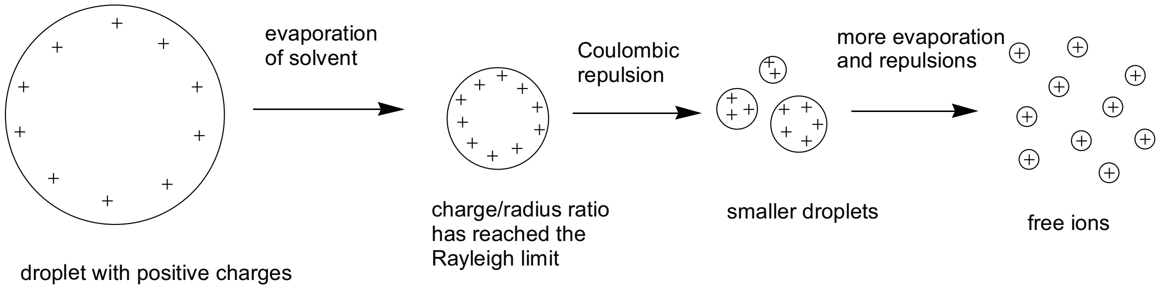


Fig. 9.2 The break-up of an electrospray

b. Matrix-assisted laser desorption ionisation (MALDI)

In this technique the sample and the matrix compound are co-dissolved in a solvent (the ratio is often about 1:1000 by mass). Spreading the solution onto a solid stainless steel plate and allowing the solvent to evaporate produces a solid crystalline matrix containing a small proportion of the sample. When the surface of the matrix is exposed to a short pulse of laser light (tuned to the wavelength of maximum absorbance of the matrix molecule), positively-charged ions of the sample are produced (along with many neutral molecules, which are readily removed via the vacuum pump). The ions are often radical-cations (formed by the loss of an electron from a lone pair on the sample molecule) or protonated molecular ions (formed by H^+ being transferred from an ionised matrix molecule to the sample molecule). The compounds used as the matrix need to have various properties. They need to absorb strongly at the wavelength range of the laser (lasers cannot be tuned over too large a range); they need to be inert with respect to the sample; they need to be fairly involatile; but they need to be fairly soluble in the same solvents that dissolve the substrate (often water). Three common ones are nicotinic acid, 2,5-dihydroxybenzoic acid and 3,5-dimethoxy-4-hydroxycinnamic acid.

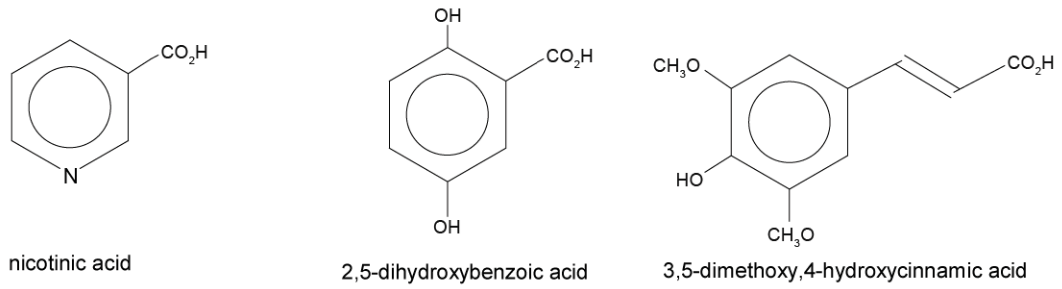


Fig. 9.3 Some compounds used as matrices

Ions derived from the matrix compound will also appear in the mass spectrum, but these are easily identified. Also, ions derived from the sample are usually of much higher M_r than those derived from the matrix compound, so little interference results. (See http://spectroscopymag.findpharma.com/spectroscopy/Mass+Spectroscopy/Time-of-Flight-Mass-Spectrometry-for-Proteomics-Re/ArticleStandard/Article/detail/161412)

9.3.2 The acceleration process

Once formed, the ions are accelerated by applying a positive potential (5 – 15 kV) to the anode plate A (Fig. 9.1), relative to grid G. This potential repels the positive ions and they pass through the grid G into the field-free region.

As mentioned before, it is important that the exact time at which the ions enter the field-free region is known. There are two ways of achieving this:

- The accelerating voltage is applied continuously, and the 'clock' is started at the exact time that the pulsed laser responsible for ionisation is turned on.
- In the 'delayed extraction' method, the sample is ionised and the resulting small plasma cloud is then allowed to equilibrate and expand for a small time (a fraction of a microsecond). A pulse of accelerating voltage is then applied, at the same time as the 'clock' is started.

The second method allows a better focusing of the ion beam, and is the one usually used with the MALDI method of ionisation.

9.3.3 The analyser

In the simple 'linear' TOF spectrometer, the analyser is merely a length of tube, evacuated to a very low pressure, through which the ions travel towards the detector at the right hand end (see Fig. 9.1). However, the line-resolution of the linear TOF spectrometer is not very high. Ions of the same mass can arrive at the detector at slightly different times, for three possible reasons.

- The ions may not all have been formed at exactly the same time – some may have been formed a few nanoseconds after others. Errors due to this temporal spread can be eliminated by the 'delayed extraction' method of acceleration, wherein ALL ions are accelerated at the same time, no matter when then were formed.
- The ions may not all start at the same place – some may be on the left of the source, near the accelerating plate A, whilst others may start near the grid G. Once the accelerating potential is applied, although those to the left will have a greater length to travel to the detector, they will however experience the accelerating potential for a greater time, and so will pass through the grid G at a faster speed than those ions that started near to grid G.
- The ions may not all have exactly the same kinetic energy as each other. For ions of the same mass number, this means that some will be travelling at a faster speed than others. Once formed, the positive ions in the plasma will repel each other. Some ions will be moving toward the left, whilst others will be moving towards the right. The former will not pick up as much speed as the latter when the accelerating potential is applied.

9.3.4 The reflectron

Ions with the same mass number travelling at different speeds can still arrive at the detector at the same time if a reflectron is used. This is a series of positively charged plates that repel the ion beam, and “reflect” it back towards the detector, which is placed slightly to one side of the un-reflected ion beam. (see Fig. 9.5). Ions that are travelling faster will penetrate the field within the reflectron more, before they are turned back. Their path-length from grid G to the detector will therefore be longer than the path-length of ions that are moving more slowly. The instrument geometry and the reflectron potentials can be adjusted so that all ions of the same mass number will eventually reach the detector at the same time.

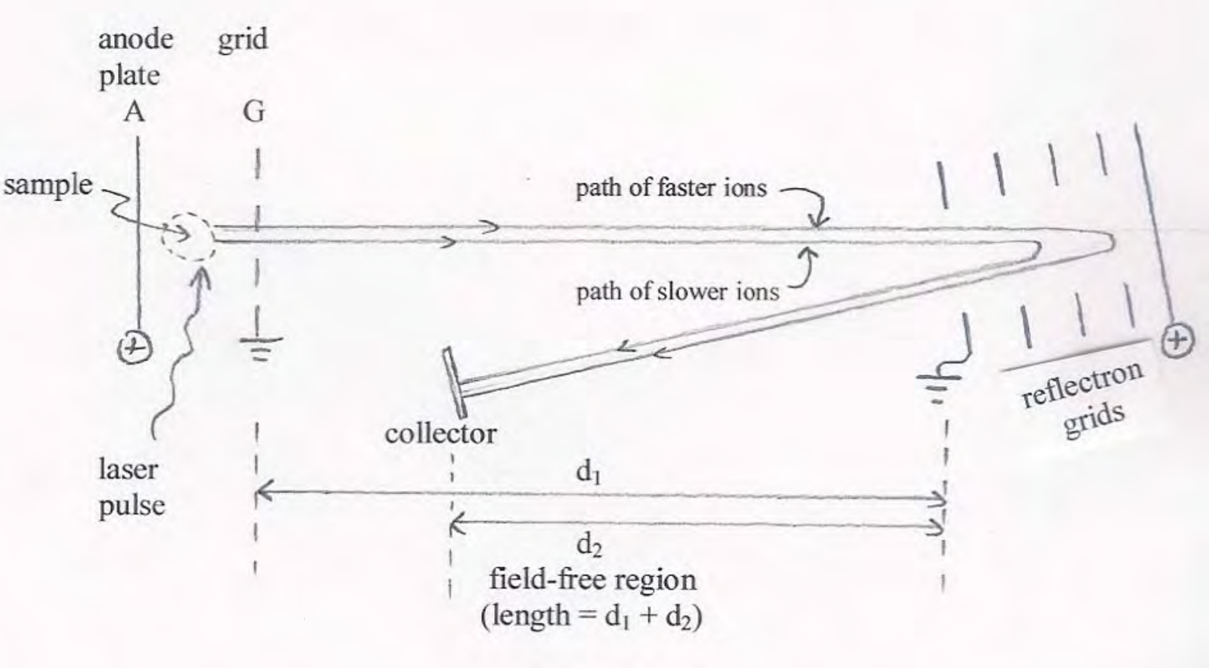


Fig. 9.4 A reflectron-TOF mass spectrometer

See figure 2 at www.abrf.org/ABRFNews/1997/June1997/jun97lennon.html this shows the greatly increased resolution obtained by using a reflectron: the 1 in 600 resolution of the linear instrument has been increased to 1 in 3400.

9.3.5 The detector

This is usually a microchannel plate coupled to a time-to-digital converter (essential a counting device that measures the time elapsed since the acceleration of the ion beam). The specification of one such detector is as follows (www.rmjordan.com/mcpdetector.html). “Designed to handle the fast ion pulses provided by our linear and reflectron Time Of Flight Mass Spectrometers, the MCP Microchannel Plate Detector has a 50 ohm coaxial output and provides high gain (1×10^6 to 1×10^7) with sub-nanosecond rise times.”

9.4 Applications of TOF mass spectrometry

9.4.1 The analysis of biological macromolecules

Making use of its ability to deal with ions of high *m/z* values, TOF-MS has not only been used to identify chemically large M_r compounds in biological samples, but also to deduce the structures of small protein fragments by the technique of 'ladder' sequencing. This is illustrated in figure 5 at www.abrf.org/ABRFNews/1997/June1997/jun97lennon.html which shows the spectra obtained from a series of partial hydrolyses of the adrenocorticotropic hormone (ACTH) fragment 18-39 by carboxypeptidase-Y (CPY) at various concentrations. The bottom spectrum is that of the ACTH fragment with no CPY added, and the other spectra are of hydrolysates derived from mixtures ocontaining increasing [CPY]. The amino acid sequence can be read off by noting the difference in *m/z* values of adjacent peaks.

Interpretation of the spectra in figure 5 at www.abrf.org/ABRFNews/1997/June1997/jun97lennon.html allows the sequence of the first 11 amino acids from the -CO_2H end of the peptide to be determined. Further exposure to CPY would cause more hydrolysis, and allow the sequence of the other 11 amino acids of the fragment to be determined. *[Activity: learners could be asked to work out the sequence of the first 11 amino acids.]*

9.4.2 Space exploration

"Although unmanned probes sent to sample the atmospheres of other planets and moons in the solar system have usually employed quadrupole mass spectrometers, small lightweight TOF spectrometers are being developed to enable in-craft analysis of astronauts' biomarkers, to monitor their health on long space voyages. The following passage describes work carried out for NASA by Johns Hopkins University (www.nsbri.org/Research/Projects/viewsummary.epl?pid=108).

"At present, identification of each biomarker requires a separate protocol. Many of these procedures are complicated and the identification of each biomarker requires a separate protocol and associated laboratory equipment. To carry all of this equipment and chemicals on a spacecraft would require a complex clinical laboratory, and it would occupy much of the astronaut's time. What is needed is a small, efficient, broadband medical diagnostic instrument to rapidly identify important biomarkers for human space exploration."

"The Miniature Time-Of-Flight Mass Spectrometer Project in the Technology Development Team is developing a small, high resolution, time-of-flight mass spectrometer (TOFMS) to quantitatively measure biomarkers for human space exploration. Virtues of the JHU/APL TOFMS technologies reside in the promise for a small (less than one cubic ft), lightweight (less than 5 kg), low-power (less than 50 watts), rugged device that can be used continuously with advanced signal processing diagnostics. To date, we have demonstrated mass capability resolution from under 100 to beyond 10,000 atomic mass units (amu) in a very small, low-power prototype for biological analysis. Further, the electronic nature of the TOFMS output makes it ideal for rapid telemetry to Earth for in-depth analysis by ground support teams."
[Activity: learners could be asked to carry out internet searches to describe more applications of TOF-MS, different ionisation techniques, and also to present short papers on how the detector works, or the physics of the reflectron.]

9.5 Appendix: The theory of mass spectrometry

In both the conventional magnetic-deflection mass spectrometer and the TOF mass spectrometer, the ions are separated according to their mass-to-charge ratio, m/z. Once formed, the ions, having an electrical charge of q coulombs, are accelerated by an electrical potential of E volts. Being in the gas phase and free of any constraints, the potential energy they have gained, qE, is converted into kinetic energy, $\frac{1}{2}mv^2$ (m = mass of ion; v = velocity).

$$qE = \tfrac{1}{2} mv^2$$

9.5.1 The physics of the conventional magnetic-deflection spectrometer

(This is included mainly for completeness, and by way of a comparison with the equations for the TOF instrument.)

The conventional mass spectrometer uses the fact that a beam of ions moving with a velocity v will experience a sideways force as it traverses a magnetic field, given by the equation

$$\text{force} = Bqv$$

As this force acts at right angles to its direction of motion, the ion will follow a circular path, the normal acceleration being v_2/r, and the force being given by the equation

$$\text{force} = mv^2/r$$

Combining the three equations [1] – [3] gives the required relationship between ***m/z***, the field ***B*** and the radius of the circular path, ***r***.

$$Bqv = mv^2/r \quad \Rightarrow \quad B^2q^2v^2 = m^2v^4/r^2 \quad \Rightarrow \quad B^2r^2v^2 = (m^2v^2/q^2)(v^2)$$

$$\Rightarrow \quad B^2r^2 = 2(m/q^2)(\tfrac{1}{2}mv^2) \quad \Rightarrow \quad B^2r^2 = 2(m/q^2)\, qE \quad \Rightarrow \quad (m/q) = B^2r^2/2E$$

Replacing the charge ***q*** by ***ze***, where ***z*** is the charge on the ion in units of ***e***, the fundamental electron charge, we have the relationship

$$m/z = B^2r^2e/2E$$

Thus, if ***E*** and ***B*** are constant, ions with different ***m/z*** ratios will follow paths with different radii ***r***, or (as is more usually the case in a conventional mass spectrometer) ions with different ***m/z*** ratios will require different a magnetic field strength ***B*** to keep constant the radius of their path through to the detector.

9.5.2 The physics of the Time-of-Flight mass spectrometer

There is no magnetic field in the TOF spectrometer. Instead, once the ions have been accelerated, the time they take to traverse a field-free region from the accelerator grid to the detector is measured. This time will depend on their velocity as follows:

$$v = d/t \quad \text{or} \quad t = d/v$$

where ***d*** is the length of the field-free region, and ***v*** is the velocity of the ions.

Combining this with equation [1], we have

$$qE = \tfrac{1}{2}\, mv^2 \quad \Rightarrow \quad qE = \tfrac{1}{2}\, md^2/t^2 \quad \Rightarrow \quad m/q = 2E\, t^2/d^2$$

Replacing the charge ***q*** by ***ze***, where ***z*** is the charge on the ion in units of ***e***, the fundamental electron charge, we have the relationship

$$m/z \; = \; 2eEt^2/d^2$$

Thus, if ***E*** and ***d*** are constant, ions with larger ***m/z*** ratios will take longer to reach the detector. Rearranging this equation to make ***t*** the subject produces equation [1] at the beginning of this chapter.

9.6 Sample questions

1 **(a)** Outline one method of removing an electron to form ions in a TOF mass spectrometer. [3]

(b) Suggest **three** reasons why ions of the same mass and charge can arrive at the detector of a TOF mass spectrometer at slightly different times. [3]

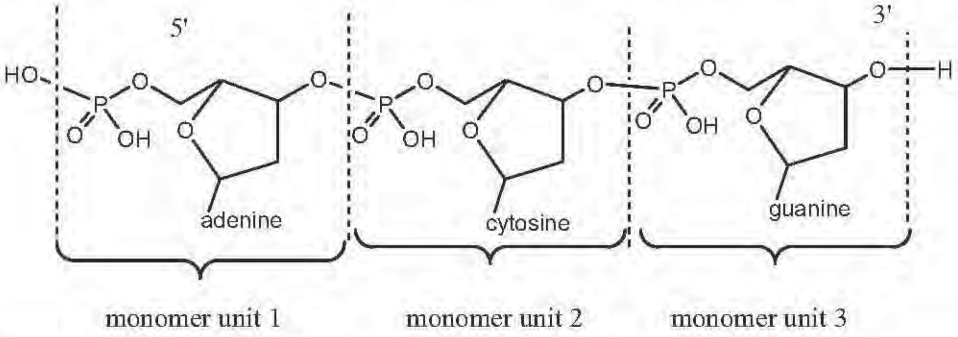
[Total: 6]

2 DNA fragments can be analysed in a TOF mass spectrometer.

A single strand of DNA consists of a deoxyribose-phosphate diester polymer chain. Each deoxyribose unit has one of four organic bases attached to it: adenine, cytosine, guanine or thymine.

At one end of the chain the last phosphate terminates with an OH group, whilst at the other end of the chain, the last deoxyribose has a free OH group.

For example, the trimer in which the bases are adenine, cytosine and guanine has the following structure.



Each monomer unit (phosphate+deoxyribose+base) is specified by a single letter corresponding to its base, so the above trimer could be written as HO-**A**-**C**-**G**-H. The M_r values of the four possible monomer units are as follows.

monomer unit code	M_r
A	313
C	289
G	329
T	304

The M_r of the above trimer is therefore 17 (OH) + 313 (**A**) + 289 (**C**) + 329 (**G**) + 1 (H) = 949

To analyse a DNA fragment, it is first subjected to partial enzymic hydrolysis. A commonly used enzyme is snake venom phosphodiesterase. This "chops off" repeat units starting from the 3' end of the chain (the right hand side of the chain shown above), one at a time.

(a) If the trimer above is exposed to snake venom phosphodiesterase for only a short period of time, a mixture of monomers, dimers and trimers is formed.

When the MALDI-TOF mass spectrum of the mixture is taken, it is found to contain three main peaks, one of which has an m/z value of 619.

(i) Predict the m/z values of the two other peaks in the mass spectrum and explain your answers.

[3]

(ii) How does the mass spectrum prove that the trimer is HO-**A**-**C**-**G**-H and **not** HO-**A**-**G**-**C**-H or HO-**G**-**C**-**A**-H?

[2]

(b) The mass spectrum of the mixture obtained by a similar partial hydrolysis of a 10-base length of DNA has peaks at the following m/z values.

m/z
923
1227
1556
1885
2189
2478
2791
3104

Deduce the sequence of the seven bases at the 3' end of the chain, and the identities of the three bases that are contained in the trimer residue at the 5' end. You must show your working.

[5]

[Total: 10]

Answers

1 **(a)** Electrospray ionisation, any three from:
Solution of sample injected through a tip kept at several thousand volts produces positively charged droplets (1)
As solvent evaporates in vacuum, drops become very small; (1)
Surface change density increases and a coulombic explosion occurs (1)
Eventually all solvent evaporates and ionised molecules are left (1)

OR
Electron impact, any three from:
Sample vapourised (1)
High energy electrons emitted (1)
Collide with sample (1)
Cause ejection of one or more electrons resulting in positively charged ions (1)

[3]

(b) Ions may not be formed at the same time (1)
Ions might not start from the same place - so some have further to travel (1)
Ions might not have the same kinetic energy (1)

[3]

[Total: 6]

2 **(a)** **(i)** Peak at 948 (1)
Due to the whole trimer minus H^+ (1)
Peak at 330, due to HO-**A** (1)

[3]

(ii) If middle base had been **G**, the middle peak would have been at m/z 659, not 619 (1)
If left hand base had been **G**, the lowest m/z peak would have been at m/z 346, not 330 (1)

[2]

(b) The first thing to do is to take each m/z value away from its successor, and then by comparison with the table of residue values given, identify the residue lost at each stage.

m/z	difference	residue
923		
1227	304	**T**
1556	329	**G**
1885	329	**G**
2189	304	**T**
2478	289	**C**
2791	313	**A**
3104	313	**A**

Give one mark for a demonstration of correct method i.e. calculating difference (1)
Give two marks for all seven residues correct, one mark for 6 correct, or zero marks for <6 correct. (2)

The 3-base trimer at the 5' end has m/z = 923, corresponding to 17 + 289 + 313 + 304,
i.e. **C**, **A** and **T** (in any order)
One mark for deduction of 17 for OH (1)
One mark for correct three bases identified (1)

[5]

[Total: 10]

Section 10: Resources

10.1 Recommended resources for the theory syllabus

Recommended textbooks include:
Chemistry for Advanced Level by P Cann and P Hughes, published by Hodder Murray (ISBN 9780719586026)

*Chemistry** by Dr. M A Thompson, published by Keytomes (ISBN 9780980711004)

*written to accompany this syllabus

For very useful and comprehensive resource packs:
Philip Allan Teacher Resource Packs: www.philipallan.co.uk. Chemistry AS/A level titles are:

Calculations, Structure and Bonding by H Hammond (ISBN 9780860032267)

Equilibria, Acids and Bases by R King (ISBN 9780860032243)

Organic Chemistry 1 by E Sie (ISBN 9780860032221)

Organic Chemistry 2 by E Sie (ISBN 9780860032236)

The Periodic Table by R King (ISBN 9780860032250)

Thermodynamics and Kinetics by H Hammond (ISBN 9780860032274)

For using IT in chemistry teaching:
Using ICT to enhance Teaching and Learning in Chemistry by S Lewis, published by the Royal Society of Chemistry (ISBN 0854043837)

Additional material can be found on Teacher Support at http://teachers.cie.org.uk

10.2 Recommended resources for practical work

ILPAC Advanced Practical Chemistry (second edition) by A Thompson, published by Hodder Murray (ISBN 0719575079)

Microscale Chemistry by J Skinner, published by the Royal Society of Chemistry (ISBN 1870343492)

Classic Chemistry Experiments by K Hutchings, published by the Royal Society of Chemistry (ISBN 0854049193)

Classic Chemical Demonstrations by T Lister, published by the Royal Society of Chemistry (ISBN 1870343387)

The Chemistry Video Consortium at the Southampton University Chemistry Department (www.focusbiz.co.uk/chemistry/) has much excellent practical material on video.

A number of websites offer ideas for and advice on practical investigations. These include http://my.rsc.org/chemnet/resources_

10.3 Safety and regulations

Responsibility for safety matters rests with centres. Attention is drawn to the following resources.

Control of Substances Hazardous to Health Regulations (COSHH) 2002,
www.opsi.gov.uk/SI/si2002/20022677.htm; a brief guide may be found at
www.hse.gov.uk/pubns/indg136.pdf

Safeguards in the School Laboratory, ASE, 11th Edition, 2006
CLEAPSS Laboratory Handbook (available to CLEAPSS members only)
CLEAPSS Hazcards (available to CLEAPSS members only)

www.ase.org.uk/resources/health-and-safety-resources/
www.ncbe.reading.ac.uk/NCBE/SAFETY/menu.html

CLEAPSS is an advisory service providing support in practical science and technology, primarily for UK schools. www.cleapss.org.uk/secondary

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