

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 1

Science in context

This section touches upon the development of the atomic theory through the ages. But until the latter part of the last century most people thought that the idea of tiny machines made up of a few atoms was science fiction. With the advent of nanotechnology, these ideas are becoming a step closer.

Tiny clusters of atoms are useful for catalysts because they have a much larger surface area and so the catalysis can be much quicker (link with reaction rate at IGCSE level). In recent years, chemists have been designing 'tailor made' catalysts, especially zeolites (a type of silicate with AlO_4 units replacing some of the SiO_4 units), of precise dimensions with tiny pores in which the surface area is increased dramatically. These can also be modified to bond other catalyst particles such as platinum and allow a vast increase in the catalytic surface area.

Nanoclusters of atoms can be made on a cold surface simply by evaporating a metal for example and then letting it condense onto the cold surface. Students may realise that the substance which is being condensed needs to be spread out so that the particles can separate. This can be done by evaporating a metal for example, in a stream of inert gas such as helium. The gas dilutes the metal and so makes it more likely that small groups of atoms can cluster together when they condense on the cold surface.

Encourage students to think about things in everyday life that have already been scaled down, e.g. hint about mobile phones. Scientists already have the means to move clusters of atoms around on specially prepared surfaces. Tiny switches and wires can be made from groups of atoms. Tiny magnets and electronic devices could be made. Microscopic molecular cages could be used to deliver cancer drugs to specific places in the body.

Clusters of atoms or small molecules could be used to 'cage' radioactive atoms such as radon. A lower dose of radioactivity is therefore used rather than a (directed) beam of more intense radioactivity which may damage surrounding cells. The caged molecules could be conveyed to the cancer cells by attaching an antibody to the outside of the molecule. This would result in a more targeted treatment. Disadvantages may be that the body reacts to the unusual molecule in the bloodstream and unwelcome side-effects may be felt. If antibodies are not attached or become detached or become denatured then the caged molecules have no target in the body. So the radioactivity may harm healthy cells.

Students are asked to suggest more ideas for nanomachines. These could include nanomagnets, nanoswitches, nanorobots and nanomotors.

Self-assessment questions

- 1
 - a i Protons are deflected towards the plate / move towards the plate; because unlike charges are attracted to each other.
 - ii Neutrons are not deflected; because neutrons have no charge / zero charge / are uncharged.
 - b Electrons; because of the charged particles it has the least mass / has a lower mass than the proton.
- 2

vanadium-51: electrons = 23,
neutrons = 28

Strontium-88: electrons = 38,
neutrons = 54

phosphorus-31: electrons = 15,
neutrons = 16

- 3 a $^{81}_{35}\text{Br}$
 b $^{44}_{20}\text{Ca}$
 c $^{58}_{26}\text{Fe}$
 d $^{110}_{46}\text{Pd}$
- 4 a 18
 b 10
 c 10
 d 28
- 5 C (number of electrons in each atom)
- 6 a electrons 36; protons 35; neutrons 46
 b electrons 55; protons 58; neutrons 78

Exam-style questions

- 1 a i protons = 5 [1]
 ii neutrons = 6 [1]
 iii electrons = 5 [1]
 b Isotopes are atoms of the same element with different nucleon numbers / mass numbers / different numbers of neutrons. [1]
 c i $\text{mass} = \frac{1}{1836}$ [1]
 charge = -1 [1]
 ii mass = 1 [1]
 charge = zero [1]
 iii mass = 1 [1]
 charge = +1 [1]
 [Total: 10]
- 2 a i $^{91}_{40}\text{Zr}$ [1]
 ii 51 [1]
 b 70 [1]
 c i It is deflected / bends away from the anode (or positive plate), or towards the cathode (or negative plate), or downwards. [1]
 ii Proton has positive charge, and like charges repel / opposite charges attract. [1]
 d no deflection / go straight through; [1]
 neutrons have no charge [1]
 [Total: 7]
- 3 a positively charged nucleus; [1]
 containing protons and neutrons; [1]
 electrons outside the nucleus in energy levels; [1]
 protons are positively charged with relative charge of +1 and relative mass of 1; [1]
 neutrons are neutral with relative charge of zero and relative mass of 1; [1]
 electrons are negative with relative charge of -1 and relative mass of $\frac{1}{1836}$
 [allow $\frac{1}{2000}$ or negligible] [1]
 b atomic number = number of protons (in the nucleus); [1]
 nucleon number = number of protons + number of neutrons [1]
 c Mg = 12 protons, 12 electrons, 12 neutrons [1]
 Al = 13 protons, 13 electrons, 14 neutrons [1]
 d number of positively charged protons = number of negatively charged electrons [1]
 e it would not be oxygen / it would be another element / oxygen can only have 8 protons [1]
 f The mass of an electron is negligible. [1]
 [Total: 13]
- 4 a Isotopes are atoms of the same element with different nucleon numbers / mass numbers / different numbers of neutrons. [1]
 b both have 92 protons; [1]
 both have 92 electrons [1]
 c uranium-235 has 143 neutrons; [1]
 uranium-238 has 146 neutrons [1]
 d 90 [1]
 [Total: 6]
- 5 a number of protons = 17 and 17 [1]
 number of electrons = 17 and 17 [1]
 number of neutrons in chlorine-35 = 18; in chlorine-37 = 20 [1]
 b the chlorine-35 isotope is more abundant; [1]
 the weighted average is nearer 35 than 37 [1]



- c** **i** it has more protons than electrons [1]
- ii** it has 17 protons and 18 electrons /
it has 1 more electron than protons [2]
- [it has more electrons than
protons for 1 mark]

[Total: 8]



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Chapter 2

Science in context

Students may realise that the electrons will collide with the gas molecules. The gas molecules in the air scatter the electrons so that a beam of electrons moving in the same direction is not easily obtained. Very low pressure or a vacuum is needed to make sure that there are no collisions.

The material used as a specimen must be dry and stable at low pressures. This is because any water present will interact with the electron beam and prevent the electrons penetrating further into the material and increase the scattering of the electrons.

The greater detail 'seen' by the electron microscope means that you may be able to see detailed structures and surface features of materials such as steel or stone, wood or biological structures such as skin and plant surfaces. The structure of different types of cell, including diseased cells, may be seen and this might give useful information about the nature of disease. The greater magnification and greater penetrating power of electrons compared with light means that even tiny cracks (stress fractures) can be seen within the material and not just on the surface of the material. The presence of a number of small cracks within a particular area may suggest that the material may be undergoing stress. This could indicate that larger cracks may develop leading to a failure of the material altogether. Irregularities in the surface of the structure can also be studied.

There is a limit below which it is difficult to get a good image using a light microscope. Most light microscopes have a magnification of about $\times 1000$. Using a beam of high speed electrons instead of light allows magnifications of $\times 1000\,000$ to $\times 50\,000\,000$.

There are several types of electron microscope. The original form is the transmission electron

microscope (TEM). An electron beam is produced by a heated tungsten filament cathode. The electron beam is then accelerated by an anode with a high positive voltage with respect to the cathode. The electron beam is then focused by electromagnetic lenses onto the specimen and transmitted through the specimen that is in part transparent to electrons and in part scatters or reflects them. When it emerges from the specimen, the electron beam carries information about the structure of the specimen. This is magnified by the electromagnetic image-forming lens (objective lens) of the microscope. The images formed in a TEM depend on the electrons passing through the specimen to give high resolution images of the internal structure. The specimen must be very thin (less than 10^{-7} m thick). Some of the electrons are also reflected (scattered) directly and others (secondary lower energy electrons) are scattered by interaction with the specimen.

X-rays are also formed when the electrons strike inner shell electrons in atoms in the specimen. These collisions give the atoms enough energy to ionise. Once the inner shell electrons are removed, electrons from higher energy orbitals drop down to lower energy levels and emit excess energy as photons. The energies of the photons are characteristic of the elements from which they have been formed. The X-rays produced have energies that are characteristic of the elements contained in the specimen. This can lead to the identification of elements with atomic numbers 5 to 92 and also give their position in the sample. A scanning electron microscope (SEM) is usually used for this analysis.

Another type of electron microscopy is high-resolution transmission electron microscopy (HRTEM) and this can be used to determine the positions of atoms within materials.

Self-assessment questions

- 1** a 2, 8, 6
b 2, 8, 2
c 2, 7
d 2, 8, 8, 1
e 2, 4
- 2** a i $\text{Ca(g)} \rightarrow \text{Ca}^+(\text{g}) + \text{e}^-$
ii $\text{K}^{2+}(\text{g}) \rightarrow \text{K}^{3+}(\text{g}) + \text{e}^-$
iii $\text{Li}^+(\text{g}) \rightarrow \text{Li}^{2+}(\text{g}) + \text{e}^-$
iv $\text{S}^{4+}(\text{g}) \rightarrow \text{S}^{5+}(\text{g}) + \text{e}^-$
b The charge on the ion is greater when the third electron is removed than when the second is removed. So, it is more difficult to remove the third electron as there is a greater attractive force between the outer electrons and the nucleus.
- 3** a i The large change between the third and fourth ionisation energies suggests that the first three electrons are easier to remove because they are further away from the nucleus and are shielded by the inner electrons from the full nuclear charge. The fourth electron is much more difficult to remove because it is closer to the nucleus and there is no (or little) shielding.
ii Three electrons are easily removed, so are on the outside (in the second shell) and two are very difficult to remove (in the first shell).
b Gradual rise in IE for first 3 electrons. Large rise between IE_3 and IE_4 . Gradual rise in IE for next 8 electrons. Large rise between IE_{11} and IE_{12} . Gradual rise in IE for next 2 electrons.
- 4** a Group 14. There is a large increase in value of IE between the removal of the fourth and fifth electrons.
b Small rise in IE for first 2 electrons. Large rise between IE_2 and IE_3 . (Gradual rise in IE for next electrons)
- 5** a s, p, d
b $s = 2, p = 6, d = 10$
- 6** a $1s^2 2s^2 2p^6 3s^2 3p^4$
b $1s^2 2s^2 2p^5$
c $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
- 7** a $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
b $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
c $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$
- 8** a i p block
ii Group 17
iii iodine
b d block
- 9** B (3p-type and 2 s-type)
- 10** a $1s^2 2s^2 2p^6$
b $1s^2 2s^2 2p^6$
c $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
d $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
e $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
- 11** a For the negative ions, the outer electrons are in the 3rd energy level since the 3rd energy level has been filled when negative ions are formed. For the positive ions, the outer electrons are in the 2nd energy level because electrons in the 3rd energy level have been removed when the ions are formed. The outer electrons in the negative ions are further from the nucleus than the outer electrons in the positive ions and there is more shielding so the ionic radius is greater.
- b**
-
- | Atomic number | Ion | Ionic radius / nm |
|---------------|------------------|-------------------|
| 11 | Na^+ | 0.10 |
| 12 | Mg^{2+} | 0.07 |
| 13 | Al^{3+} | 0.05 |
| 14 | Si^{4+} | 0.04 |
| 15 | P^{3-} | 0.21 |
| 16 | S^{2-} | 0.19 |
| 17 | Cl^- | 0.18 |
- 12** a i From sodium to silicon, the nuclear charge increases. The distance between the nucleus and the outer electron remains

reasonably constant. The shielding by inner shells remains reasonably constant. Ionisation energy increases to match increase in attraction from the nucleus with an increased nuclear charge.

ii The distance between the nucleus and the outer electrons increases from Mg to Al. The shielding by inner shells increases. These two factors outweigh the increased nuclear charge.

b The distance between the nucleus and the outer electron increases from F to I. The shielding by inner shells increases. These two factors outweigh the increased nuclear charge.

13 Diagram D

Exam-style questions

- 1 a The energy needed to remove one electron [1]
from each atom in a mole of gaseous atoms [1]
to form a mole of gaseous $1+$ ions. [1]
- b The first three electrons are easy to remove, so these are in the outer shell / energy level; [1]
large increase in ionisation energy between third and fourth electrons removed; [1]
so fourth electron in next shell towards nucleus; [1]
fourth to eleventh electrons in same shell as only gradual increase in ionisation energy; [1]
large increase in ionisation energy between 11th and 12th electrons removed; [1]
so 12th and 13th electrons in shell close to nucleus. [1]
- c $\text{Al}^+(\text{g}) \rightarrow \text{Al}^{2+}(\text{g}) + \text{e}^-$ [2]
[1 mark for balancing, 1 mark for state symbols]
- d $1s^2 2s^2 2p^6$ [1]
- [Total: 12]

- 2 a Increase in number of protons / increased nuclear charge; [1]
electrons added go into the same outer shell / quantum level; [1]
so same amount of shielding; [1]
greater force of attraction across period between (positive) nucleus and (negative) electrons. [1]
- b Outermost electron of aluminium is in p subshell; [1]
outermost electrons of magnesium in s subshell (of same quantum level as p); [1]
outermost electron of aluminium in subshell with higher energy (or further from nucleus) / outermost electron of magnesium in lower energy sublevel (or nearer the nucleus / more shielding of p electron); [1]
greater force of attraction between nucleus and s electron than p electron (or reverse argument). [1]
- c $1s^2 2s^2 2p^6 3s^2 3p^6$ [1]
- d i sub-shells shown in correct order, i.e. 2s, 2p, 3s, 3p [1]
ii two electrons as arrows in each box for 2s, 2p and 3s orbitals; [1]
electrons shown as arrows in opposite direction in 2s, 2p and 3s orbitals; [1]
one electron as arrow in each of the 3p orbitals with arrows pointing in same direction [1]
- e value less than 494 (ignore lack of units) [1]
- [Total: 14]
- 3 a Region of space outside the nucleus where there is a likelihood of finding an electron / two electrons. [1]
- b i sphere / circle drawn; [1]
ii correct shape of p orbital (hourglass / propeller shape) with two lobes [1]
- c i d block [1]
ii 10 [1]
- d i $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$ [1]
ii 4p [1]
- [Total: 7]

- 4 a** C; [1]
 there is big decrease in ionisation energy between B and C; [1]
 the outer electron in C is in the next quantum shell. [1]
- b** D [1]
- c** Increase in number of protons / increased nuclear charge; [1]
 electrons added go into the same outer shell / quantum level; [1]
 so same amount of shielding; [1]
 greater force of attraction across period between (positive) nucleus and (negative) electrons. [1]
- d** above 1250 [1]
 but below 2050 [1]
- e** The first seven electrons removed are in the outermost energy level / quantum level; [1]
 there is a big jump in energy required when the eighth electron is removed; [1]
 the eighth and ninth electrons are in the next energy level (nearer the nucleus). [1]
- [Total: 13]**
- 5 a i** The energy needed to remove one electron [1]
 from each atom in a mole of gaseous atoms [1]
 to form a mole of gaseous 1+ ions. [1]
- ii** The energy required to remove one electron [1]
 from each ion in a mole of gaseous 2+ ions [1]
 to form a mole of gaseous 3+ ions. [1]
- b i** $\text{Mg(g)} \rightarrow \text{Mg}^+(\text{g}) + \text{e}^-$ [2]
 [1 mark for balancing, 1 mark for state symbols]
- ii** $\text{Mg}^{2+}(\text{g}) \rightarrow \text{Mg}^{3+}(\text{g}) + \text{e}^-$ [2]
 [1 mark for balancing, 1 mark for state symbols]
- c i** 4th ionisation energy of magnesium [1]
- ii** 6th ionisation energy of aluminium [1]
- [Total: 12]**
- 6 a** They are in the outermost energy level / subshell; [1]
 greatest shielding by inner electrons; [1]
 least attractive force from nucleus on the outer electrons. [1]
- b** Third electron is in the next main energy level / principal quantum shell further in; [1]
 closer to the nucleus; [1]
 less shielding (by inner shells of electrons). [1]
- c** There are 2 electrons in the outermost energy level / quantum shell; [1]
 the next 8 electrons are in the energy level quantum shell further in; [1]
 there are 2 electrons in the innermost energy level / quantum shell. [1]
- d** $\text{Mg}^{4+}(\text{g}) \rightarrow \text{Mg}^{5+}(\text{g}) + \text{e}^-$ [2]
 [1 mark for balancing, 1 mark for state symbols]
- [Total: 11]**
- 7 a** A is in Group 14. [1]
 B is in Group 2. [1]
 C is in Group 1. [1]
 D is in Group 14. [1]
 E is in Group 13. [1]
- b** There is a big increase in ionisation energy from the 3rd to the 4th electron removed. [1]
- c** Correctly labelled axes; [1]
 gradual increase in IE for the first 5 electrons removed; [1]
 sudden increase in IE between the 5th and 6th electrons removed; [1]
 gradual increase between 6th and 13th electrons removed; [1]
 sudden increase in IE between the 13th and 14th electrons removed; [1]
 gradual increase between the 14th and 15th electrons removed. [1]
- [Total: 12]**

- 8 a** The energy needed to remove one electron [1]
from each atom in a mole of gaseous atoms; [1]
to form a mole of gaseous $1+$ ions. [1]
- b** Correctly labelled axes; [1]
gradual increase in IE for the first 7 electrons removed; [1]
sudden increase in IE between the 7th and 8th electrons removed; [1]
gradual increase in IE between electrons 8th and 15th electrons removed; [1]
sudden increase in IE between the 15th and 16th electrons removed; [1]
gradual increase between the 16th and 17th electrons removed. [1]
- c** The first 7 electrons are easiest to remove, as they are in the outermost energy level; [1]
the steady increase shows that each electron is attracted more strongly by a more positive ion. [1]
There is a big jump in energy required from the 7th to the 8th electrons; [1]
this is because the 8th electron is in the next energy level; [1]
which is closer to the nucleus and the electrons in it are less shielded. [1]
There is a large jump from the 15th to the 16th electrons because the 16th electron is in a new energy level. [1]
- [Total: 15]**

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Chapter 3

Science in context

Opencast mining, where material is excavated from an open pit, is one of the most common forms of mining for minerals. Learners should be able to make a list of pollution and other factors involved in opencast mining from their previous courses. These could include:

- Exposure to harmful dust from quarrying: Rocks contain mixtures of many compounds; when crushed, dust from rocks could expose asbestos-like minerals, dust containing poisonous metal compounds, e.g. cadmium and mercury compounds, and even radioactive material. These are harmful to the lungs and can cause lung cancer on even quite short exposures. Tiny particles can be absorbed into lung tissue, causing problems like pneumoconiosis and silicosis.
- Pollution of rivers by washing rocks: Mining of materials often involves washing the rock with water to remove muddy or sandy material that is not required. These rock slurries, which are mixtures of crushed rock and liquid, often produce washings which contain toxic substances especially heavy metals (lead, cadmium, mercury). These can leak into bedrock and into rivers if not properly contained. Once in the rivers, poisonous materials can kill fish and water plants. The most extreme examples of these slurries come from iron ore mines in Brazil, where huge areas of land are polluted by large amounts of reddish brown waste which destroy habitats and pollute rivers. The contaminated water can pollute the region surrounding the mine and for large areas beyond.
- Increasing sediments in nearby rivers: Many mines use hydraulic pumps and suction dredges. These remove topsoil so that plants are less likely to grow and make it difficult for vegetation to recover.
- Deforestation due to mining: This leads to the loss of biomass and contributes to the effects of erosion by wind or water because plant roots stabilise the topsoil.
- Use of fossil fuels / pollution due to lorries and equipment used for mining: Mining, like many heavy industries, is dependent on fossil fuels, which generate the energy needed to operate a mine. The emissions from this equipment, such as particulates and nitrogen oxides, are harmful for health (lung complaints, heart attacks for nitrogen dioxide and cancer and other conditions similar to silicosis for particulates). The use of large amounts of fossil fuels in mining operations adds greenhouse gases, especially carbon dioxide, to the atmosphere.
- Loss of habitat of species of plants and animals: Mining causes damage to the landscape in an area much larger than the mining site itself. It can lead to the death of flora and fauna, and erosion of land and habitat. The effects of this damage can continue years after a mine has shut down.
- Students may also suggest other issues such as noise, the quarry being an eyesore, more traffic on the roads. Note, however, that mines can provide work for local people. However, many mines are in areas which are well away from habitation so many of these concerns are not globally important.

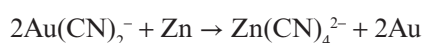
Gold often occurs native (as the element) in small amounts in rocky or muddy deposits and becomes concentrated in streams and rivers. Over time, these deposits have hardened into rock. Opencast mining for ores or native metals such as gold and silver is particularly damaging to the environment because the metal is only available in small concentrations. This increases the amount

of waste rock and slurry which is excavated. It is commercially viable to extract gold from gold ores. In some cases cyanide is used to extract metals from oxidized ores and the resulting rock slurries produced have caused significant wildlife mortality, including the deaths of nearly 8000 animals between 1980 and 1989 at cyanide-extraction ponds in the United States.

The ore is ground to a fine slurry in sodium cyanide solution and air is blown through for about 50 hours. The purpose of the cyanide process is to remove contaminating materials from the gold.



The gold is precipitated by adding zinc powder.



Heating sulfide concentrates in air will produce sulfur dioxide by oxidation of the sulfides. Sulfur dioxide contributes to acid rain. In addition sulfides are poisonous, especially hydrogen sulfide which is a gas.

Why should materials be mixed in the correct amounts?

- The reaction may not go to completion if the wrong amounts are mixed. In order to make the reaction go to completion, one of the reactants may need to be in excess.
- If the reactant in excess is harmful, there must be some way of removing it so that it does not harm humans or the environment.
- If not added in the correct amounts, energy may be wasted and other unwanted reactions may occur.

The advantages of using bacteria are:

- heating the ore is not necessary thus saving fuel and reducing carbon dioxide emissions
- less oxygen is used
- the products are made water soluble more easily
- a greater percentage of the gold is extracted
- the process is carried out on the site rather than away from the site.

The major disadvantage is:

- bacteria have to be grown in large amounts. This may be time consuming and in industry time is important.

Note that poisonous cyanide is still used.

- The bacterium used is the heat-loving bacterium *Sulfolobus acidocalderius*, which is found in hot sulfur springs. The bacterium catalyses two processes:
 - It uses atmospheric oxygen to oxidise sulfide minerals
 - It helps to make the products of oxidation water-soluble.

Self-assessment questions

- 111.1
 - 159.6
 - 132.1
 - 256.3
- $^{76}_{32}\text{Ge}$

$$\frac{(20.6 \times 70) + (27.4 \times 72) + (7.7 \times 73) + (36.7 \times 74) + (7.6 \times 75)}{100}$$

$$= 72.7$$
- 31
 - CH_3O^+
 - CH_3^+
 - CH_3CO^+
 - COOH^+
 - CH_3COOH^+ (the molecular ion)
- 6
- $M = \text{CH}_2\ ^{79}\text{Br}^{79}\text{Br}^+$
 $[M + 2] = \text{CH}_2\ ^{79}\text{Br}^{81}\text{Br}^+$
 $[M + 4] = \text{CH}_2\ ^{81}\text{Br}^{81}\text{Br}^+$
 - 64 (from $\text{C}_2\text{H}_5\ ^{35}\text{Cl}^+$) and 66 (from $\text{C}_2\text{H}_5\ ^{37}\text{Cl}^+$), relative abundances 3 : 1
 - two peaks beyond the M^+ ion: one at m/e of 188 (twice as abundant as the M^+ ion) and one at 190 (with the same abundance as the M^+ ion)
- 0.33 mol
 - 0.25 mol
 - 0.25 mol
 - $$\text{mol Cl} = \frac{7.10}{35.5} = 0.200 \text{ mol}$$

$$0.20 \times 6.02 \times 10^{23}$$

$$= 1.20 \times 10^{23} \text{ (to 3 significant figures)}$$

7 a 880g

b 5.3 g

c 449.0 g

8 a $46.0 \text{ g Na} \rightarrow 78.0 \text{ g Na}_2\text{O}_2$
so $4.6 \text{ g Na} \rightarrow 7.8 \text{ g Na}_2\text{O}_2$

b $150.7 \text{ g SnO}_2 \rightarrow 24 \text{ g C}$
so $14.0 \text{ g SnO}_2 \rightarrow 2.23 \text{ g C}$

9 $\frac{56.2}{28.1} = 2 \text{ mol Si}$

$\frac{284.0}{71.0} = 4 \text{ mol Cl}_2$

$\frac{340.2}{170.1} = 2 \text{ mol SiCl}_4$

so ratio of Si : Cl₂ : SiCl₄ = 1 : 2 : 1

$\text{Si} + 2\text{Cl}_2 \rightarrow \text{SiCl}_4$

10 $100 \times \frac{24}{46} = 52.2\%$ (to 3 significant figures)

11 a NH₂

b C₄H₉

c CH

d NH₃

Carbon	Hydrogen
$\frac{90}{12.0}$	$\frac{10}{1.0}$
= 7.5	= 10

simplest ratio is 3C to 4H

empirical formula is C₃H₄

13 Compound A:

$\text{C}_3\text{H}_5 = (3 \times 12.0) + (5 \times 1.0) = 41.0$;

$\frac{82}{41.0} = 2$, so molecular formula is C₆H₁₀

Compound B:

$\text{CCl}_3 = 12.0 + (3 \times 35.5) = 118.5$;

$\frac{237}{118.5} = 2$, so molecular formula is C₂Cl₆

Compound C:

$\text{CH}_2 = 12.0 + (2 \times 1.0) = 14.0$; $\frac{112}{14.0} = 8$,

so molecular formula is C₈H₁₆

14 a i Mg(NO₃)₂

ii CaSO₄

iii NaI

iv HBr

v Na₂S

b i sodium phosphate

ii ammonium sulfate

iii aluminium chloride

iv calcium nitrate

15 a $\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$

b $2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$

c $2\text{C}_6\text{H}_{14} + 19\text{O}_2 \rightarrow 12\text{CO}_2 + 14\text{H}_2\text{O}$

16 a $\text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow$
 $\text{CaCl}_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

b $\text{ZnSO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow$
 $\text{Zn(OH)}_2(\text{s}) + \text{Na}_2\text{SO}_4(\text{aq})$

17 b $\text{Fe}_2\text{O}_3(\text{g}) + 3\text{CO}(\text{g}) \rightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$

18 a $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$

b $\text{Br}_2(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Br}^-(\text{aq}) + \text{I}_2(\text{aq})$

19 a $\text{Cu}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Cu(OH)}_2(\text{s})$

b $\text{Pb}^{2+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow \text{PbI}_2(\text{s})$

20 a i $\frac{2}{40} \times \frac{1000}{50} = 1.0 \text{ mol dm}^{-3}$

ii $\frac{12}{60.0} \times \frac{1000}{250} = 0.80 \text{ mol dm}^{-3}$

b i $0.2 \times \frac{40}{1000} = 8 \times 10^{-3} \text{ mol}$

ii $0.01 \times \frac{50}{1000} = 5 \times 10^{-4} \text{ mol}$

21 a number of moles of HCl = $0.100 \times \frac{15.00}{1000}$
= $1.5 \times 10^{-3} \text{ mol}$

number of moles of Sr(OH)₂ = $\frac{1.5 \times 10^{-3}}{2}$
= $7.50 \times 10^{-4} \text{ mol}$

concentration of Sr(OH)₂ = $7.50 \times 10^{-4} \times \frac{1000}{25}$
= $3.00 \times 10^{-2} \text{ mol dm}^{-3}$

b number of moles of NaOH

= $0.400 \times \frac{20}{1000}$

= $8.00 \times 10^{-3} \text{ mol}$

number of moles of H₂SO₄ = $\frac{8.00 \times 10^{-3}}{2}$

= $4.00 \times 10^{-3} \text{ mol}$

concentration of H₂SO₄

= $4.00 \times 10^{-3} \times \frac{1000}{25.25}$

= $1.58 \times 10^{-1} \text{ mol dm}^{-3}$ (to 3 significant figures)

22 a $0.0600 \times \frac{20}{1000} = 1.20 \times 10^{-3} \text{ mol}$

b $0.100 \times \frac{24.00}{1000} = 2.40 \times 10^{-3} \text{ mol}$

c 1 mol metal hydroxide : 2 mol hydrochloric acid



23 A (the solution has a total of 2 moles of ions)

24 a $\frac{26.4}{44.0} = 0.60 \text{ mol}$

$0.60 \times 24 = 14.4 \text{ dm}^3$

b number of moles of He = $\frac{120}{24000}$

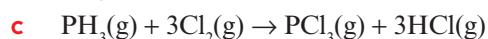
$= 5.0 \times 10^{-3} \text{ mol}$

mass = $4.0 \times 5.0 \times 10^{-3}$

$= 2.0 \times 10^{-2} \text{ g}$

25 a 3 moles

b PH_3 (ratio of volumes = ratio of moles)



26 B (24.0 dm^3)

Exam-style questions

1 a i The weighted average mass of the atom of an element compared with the unified atomic mass unit. [1]

ii $\frac{(18.7 \times 10) + (81.3 \times 11)}{100} = 10.8$ [2]

[1 mark for showing masses \times % abundance or 1 error carried forwards from this]

b 2 [1]

c i 184.2 [1]

ii Fe has several isotopes. [1]

[Total: 6]

2 a i 262.5 [1]

ii Salt which has water of crystallisation in its structure [1]

b $^{180}_{72}\text{Hf}$ [1]

c i $^{90}_{40}\text{Zr}$ [1]

$(51.5 \times 90) + (11.2 \times 91) + (17.1 \times 92)$

ii $\frac{+ (17.4 \times 94) + (2.8 \times 96)}{100}$ [2]

[1 mark for showing masses \times % abundance or 1 error carried forwards from this]

iii The average mass of an atom of a particular isotope compared with the unified atomic mass unit. [1]

d moles of $\text{SnO}_2 = \frac{15.2}{150.7} = 0.10086 \text{ mol}$

moles of C = $\frac{2.41}{12} = 0.2008 \text{ mol}$ [1]

for exact reaction moles C required = $0.10086 \times 2 = 0.2017 \text{ mol}$

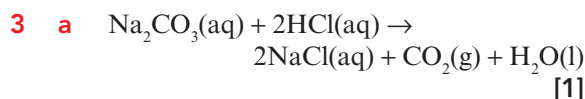
0.2017 mol less than 0.2498 mol (the amount required) so SnO_2 in excess [1]

e moles of $\text{ZrCl}_4 = \frac{58.30}{233.2} = 0.250 \text{ mol}$

moles of Zr = $\frac{20.52}{91.2} = 0.225 \text{ mol}$ [1]

% yield = $\frac{0.225}{0.250} \times 100 = 90.0\%$ [1]

[Total: 11]



b molar mass of sodium carbonate calculated correctly = 106 [1]

moles sodium carbonate

$= \frac{4.15}{106} = 0.039 \text{ mol}$ [1]

moles HCl = $2 \times 0.039 = 0.078 \text{ mol}$ [1]

c The amount of substance that has the same number of specified particles / atoms / molecules, etc. as there are atoms in exactly 12 g of the carbon-12 isotope (or similar wording). [1]

d i moles sodium carbonate = $\frac{25.0}{1000} \times 0.0200 = 5.0 \times 10^{-4} \text{ mol}$ [1]

ii moles HCl = $2 \times 5.0 \times 10^{-4} = 1.0 \times 10^{-3} \text{ mol}$ [1]

concentration of HCl =

$1.0 \times 10^{-3} \times \frac{1000}{12.50} = 0.080 \text{ mol dm}^{-3}$ [1]

e 0.2 mol [1]

f $0.2 \times 24 = 4.8 \text{ dm}^3$ [1]

[Total: 10]

4 a $C = \frac{80}{12}, H = \frac{20}{1.0}$ [1]

$C = 6.67; H = 20$

divide by lowest

$C = \frac{6.67}{6.67} = 1; H = \frac{20}{6.67} = 3$ [1]

empirical formula is CH_3 [1]

b empirical formula mass = 15

$15 \times n = 30; n = 2$, so molecular formula is C_2H_6 [1]

c Any three explanatory statements for 3 marks from:

volume of gas proportional to number of moles;

mole ratio is 50 : 300 : 200

so 1 mol hydrocarbon : 6 mol oxygen : 4 mol carbon dioxide.

As 4 moles of carbon dioxide from 1 mole of hydrocarbon, hydrocarbon has 4 carbon atoms.

4 carbon atoms will react with 4 moles of oxygen molecules, leaving 2 moles of oxygen molecules (4 moles of oxygen atoms) to react with the hydrogen;

so 4 moles of water formed, meaning 8 hydrogen atoms in hydrocarbon. [1]

And final deduced equation:
 $C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O$ [1]

d moles propane = $\frac{600}{24000} = 0.025$ mol [1]

mass = $0.025 \times 44.0 = 1.1$ g [1]

[Total: 10]



[1 mark for correct formulae; 1 mark for balancing]

b 1 mole of $TiCl_4$ gives 1 mole of Ti
 $189.9 \text{ g } TiCl_4 \rightarrow 47.9 \text{ g Ti}$ [1]

$1.0 \text{ g } TiCl_4 \rightarrow \frac{47.9}{189.9} \text{ g Ti}$

$380 \text{ g } TiCl_4 \rightarrow 380 \times \frac{47.9}{189.9} \text{ g Ti} = 95.9 \text{ g Ti}$ [1]

c 4 moles of Na gives 1 mole of Ti
 $4 \times 23.0 \text{ g Na} \rightarrow 47.9 \text{ g Ti}$ [1]

$1.0 \text{ g Na} \rightarrow \frac{47.9}{4 \times 23.0} \text{ g Ti}$

$46.0 \text{ g Na} \rightarrow 46 \times \frac{47.9}{4 \times 23.0} \text{ g Ti} = 24.0 \text{ g Ti}$ [1]

[Total: 6]

6 a i 0.0150 dm^3 [1]

ii 0.0200 dm^3 [1]

b $0.0200 \times 0.0500 = 0.00100 \text{ mol}$ [1]

c 0.00100 mol [1]

$\frac{0.00100}{0.0150} = 0.0667 \text{ mol dm}^{-3}$ [1]

[Total: 5]

7 a $80.0 \text{ (g mol}^{-1}\text{)}$ [1]

b $\frac{0.800}{80.0}$ [1]

$= 0.0100 \text{ mol}$ [1]

c moles nitrogen(IV) oxide = 0.0100 [1]

volume = $0.0100 \times 24.0 = 0.24 \text{ dm}^3$
 $= 240 \text{ cm}^3$ [1]

[Total: 5]

8 a i moles of $HCl = \frac{1.20}{24.0} = 0.0500 \text{ mol}$ [1]

ii concentration =
 $\frac{\text{moles}}{\text{volume in dm}^3} = \frac{0.0500}{0.100}$ [1]

$= 0.500 \text{ mol dm}^{-3}$ [1]

b i $0.500 \times \frac{25.0}{1000}$ [1]

$= 0.0125 \text{ mol}$ [1]

ii moles $NaOH$ = moles of HCl
 $= 0.0125 \text{ mol}$ [1]

volume = $\frac{\text{moles}}{\text{concentration}}$
 $= \frac{0.0125}{0.200} = 0.0625 \text{ dm}^3$ [1]

[Total: 7]

9 a moles of $Cl_2 = \frac{4.80}{24.0} = 0.200 \text{ mol}$ [1]

b moles of $NaOCl$ = moles of $Cl_2 = 0.200 \text{ mol}$ [1]

mass of $NaOCl = 74.5 \times 0.200 = 14.9 \text{ g}$ [1]

c moles of NaOH = $2 \times$ moles of chlorine = 0.400 mol [1]

volume of NaOH = $\frac{0.400}{2.00} = 0.200 \text{ dm}^3$ [1]

d $\text{Cl}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + \text{OCl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$ [1]

[Total: 6]

10 a 1 mole of CaO gives 1 mole of CaCl_2
56.1 g CaO \rightarrow 111.1 g CaCl_2 [1]

28.05 g CaO $\rightarrow 111.1 \times \frac{28.05}{56.1} \text{ g}$
 $\text{CaCl}_2 = 55.5 \text{ g CaCl}_2$ [1]

b 1 mole of CaO reacts with 2 moles of HCl
56.1 g CaO reacts with 73.0 g HCl [1]

28.05 g CaO reacts with $73.0 \times \frac{28.05}{56.1} = 36.5 \text{ g HCl}$ [1]

c mass of water is $\frac{28.05}{56.1} \times 18.0 = 9.0 \text{ g}$ [1]

[Total: 5]

11 a $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$ [2]
[1 mark for reactants and products;
1 mark for state symbols]

b $\text{NH}_3 = 17.0 \text{ g mol}^{-1}$ [1]

$\text{HCl} = 36.5 \text{ g mol}^{-1}$ [1]

$\text{NH}_4\text{Cl} = 53.5 \text{ g mol}^{-1}$ [1]

c $\frac{10.7}{53.5} \text{ g NH}_4\text{Cl} = 10.7 = 0.2 \text{ mol}$ [1]

moles of NH_3 and of HCl = 0.2 mol [1]

$0.2 \times 24.0 = 4.8 \text{ dm}^3$ of NH_3 and HCl [1]

[Total: 8]

12 a i CH_3^+ [1]

ii C_2H_5^+ [1]

iii C_3H_7^+ [1]

iv $\text{C}_4\text{H}_{10}^+$ [1]

b use of formula $\frac{100}{1.1} \times \frac{\text{abundance of } [\text{M}+1]^+ \text{ ion}}{\text{abundance of } \text{M}^+ \text{ ion}}$ [1]

12 carbon atoms [1]

c Heavier isotope of chlorine present / ^{37}Cl present [1]

d Ratio of bromine isotopes is equal / equal amount of R^{79}Br^+ and R^{81}Br^+ [1]

Not chlorine because chlorine isotopes are in 3:1 ratio of lighter to heavier isotopes / chlorine isotopes are in 3:1 ratio of R^{35}Cl^+ to R^{37}Cl^+ [1]

So peak of R^{37}Cl^+ is on-third as high as peak of R^{35}Cl^+ [1]

[Total: 10]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 4

Science in context

Floating a paper clip on water is a simple exercise that has links to both Biology and Physics. You may wish to organise learners into groups which include those taking Biology and Physics as well as Chemistry. Some learners may need hints to help them answer the questions but there is sufficient information at the beginning of the passage to help them.

Suggested hints could include:

- pressure = force divided by area
- spongy surfaces absorb water
- what happens when you add cooking oil to vinegar?
- hairs on feet/legs could trap air

Skating insects have wide feet because a larger surface area means there is less downward pressure on the water surface for the same mass. The lower the pressure on the water surface, the less likely it is that the feet of the insects will go through the surface.

Learners might suggest oils of various types, e.g. cooking oil.

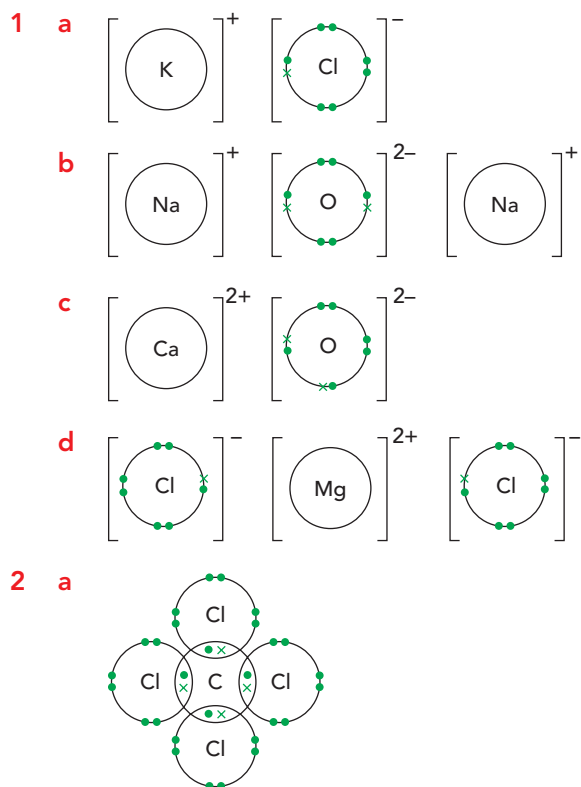
A soft layer such as paper will absorb water and so drag the insect into the water.

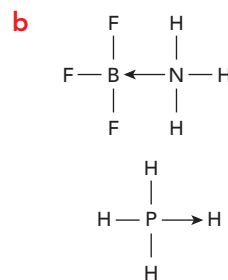
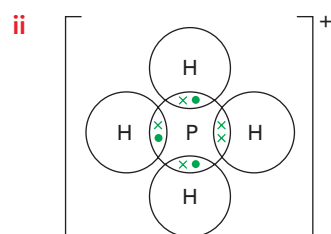
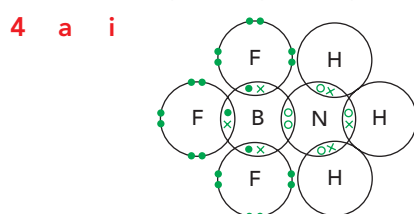
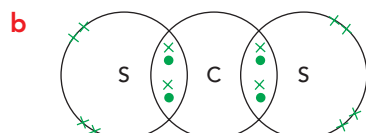
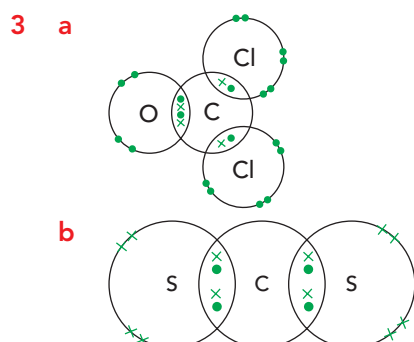
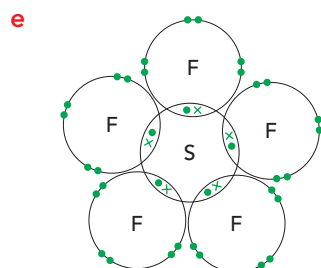
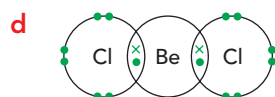
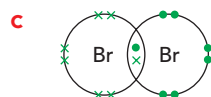
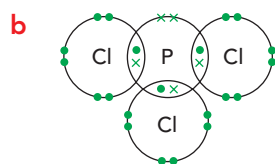
For the insect design, learners could draw their perfect insect and present it to the class. This could be done as a group activity. Things that they might incorporate could include:

- very light mass so the force per unit area on the surface of the water is minimised
- long legs and narrow body so the downforce is spread over a wider area
- legs which are flexible (have very good joints) so that the weight is evenly distributed
- hard surface on feet and legs so water is not absorbed

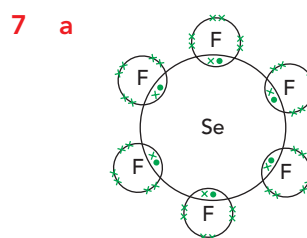
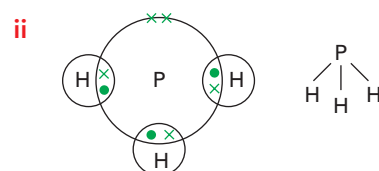
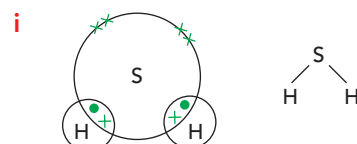
- smooth surface on bottom of feet so insects can slide easily (but see also the next suggestion)
- hairs on feet/legs to trap bubbles of air if the legs go below the surface (to buoy them up again)
- grooved feet to trap air, which will increase buoyancy
- they may also suggest that an oily surface on the feet will help reduce attractions between the water and the surface of the insect's body.

Self-assessment questions

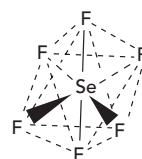


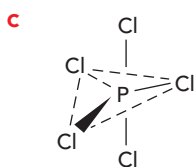


- 5 a** The longer the bond length, the weaker the bond.
- b** Going down the halogen group, the atoms are bigger; the attractive force between the bonding electrons and the nucleus gets smaller; so less energy is needed to break the bond.
- c** Allow between 0.09 and 0.11 nm.
- 6 a**
- i** tetrahedral
 - ii** linear
 - iii** triangular pyramidal / trigonal pyramidal
- b** When you have completed each dot-and-cross diagram, look for another molecule with the same number of lone pairs, and bond pairs. The shapes, and bond angles, of the H_2S and the PH_3 molecules can be predicted if you think like this.



b octahedron





8 c (about 109.5°)

9 a Metallic bonding is between metal ions in a sea of delocalised electrons. In aluminium there are more delocalised electrons and the ions have a higher charge compared with sodium. There is a greater force of attraction between the electrons and the ions in aluminium, so it requires more energy to overcome these forces of attraction, leading to a higher melting point.

b Copper provides better heat transfer because it conducts better than stainless steel. Flow of delocalised electrons is greater in copper than in stainless steel / electrons are held more strongly by iron ions in steel. For a saucepan, you want higher thermal conductivity at the base, so copper is used at the base.

c Electric current in metals is due to a flow of delocalised electrons. Three electrons are released when aluminium ion is formed but only one when sodium ion is formed. There is a higher density of delocalised electrons in aluminium than in sodium.

10 a Cl_2 : non-polar; electronegativity values are the same.

b HF : polar; fluorine more electronegative than hydrogen.

c SCl_2 : polar; chlorine more electronegative than sulfur and the V-shape of the molecules means that the electron density is asymmetric / centres of positive and negative charge do not coincide.

d CH_3Cl : polar; chlorine more electronegative than hydrogen so very small dipoles on $\text{C}-\text{H}$ bonds can't cancel out the dipoles on the $\text{C}-\text{Cl}$ bond. Electron density is asymmetric / centres of positive and negative charge do not coincide).

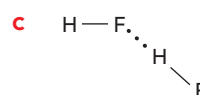
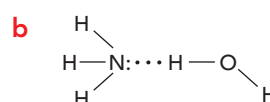
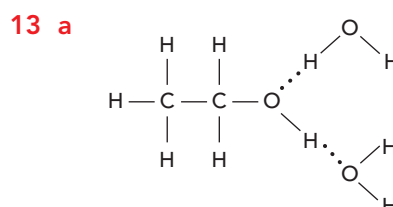
e CBr_4 : non polar; equal dipoles on each $\text{C}-\text{Br}$ bond and these cancel each other out because the molecule is symmetrical.

11 a i The trend is for higher boiling points going down Group 17.

ii Bigger molecules (more protons) have more electrons. Id-id attractive forces are larger with increasing number of electrons. So the id-id forces are greater as the halogen molecules increase in size.

b The trend is for higher boiling points with increasing length of alkane molecules. Longer and bigger molecules have more electrons. There are more contact points with longer molecules. Id-id attractive forces are larger with increasing number of contact points as well as with increasing number of electrons. So the id-id forces are greater as molecules get longer.

12 Bromine is a non-polar molecule so only has id-id forces as intermolecular forces. Iodine monochloride has a permanent dipole, as chlorine is more electronegative than iodine. The permanent dipole-dipole force makes for a greater attraction between iodine monochloride molecules compared with the van der Waals' forces between bromine molecules. So it requires relatively more energy to overcome these dipole-dipole forces.



14 a Increased number of electrons from HCl to HI ; so increased id-id forces between the molecules.

b F atom is very electronegative; hydrogen bond formed between fluorine atom of one $\text{H}-\text{F}$ molecule and an H atom on a neighbouring molecule; hydrogen bonds are stronger than id-id forces.

15 a The trend is for higher boiling points with increasing size of Group 15 hydride molecules. Bigger molecules have more electrons, id-id attractive forces are larger with increasing number of electrons. So the id-id forces are greater as the hydrides of Group 15 increase in size.

b Atoms of nitrogen are more electronegative than hydrogen. Hydrogen bonding occurs in ammonia, as there is hydrogen attached to a very electronegative atom (nitrogen), and a very electronegative atom (nitrogen) with a lone pair of electrons on a neighbouring atom. Hydrogen bonds are stronger than dipole-dipole bonds or id-id forces present in phosphine. So it takes more energy to break the intermolecular forces in ammonia and the boiling point is correspondingly higher.

16 D

17 a Aluminium oxide is ionic. There are strong electrostatic forces between the metal ions and the delocalised electrons in the metal structure. So, it requires a lot of energy to break these forces. This can only be done at high temperature. Aluminium chloride has a simple molecular structure. The attractive forces between molecules are weak. So, it only requires a small amount of energy to break these intermolecular forces.

b Electrical conduction in ionic compounds is due to the movement of ions. In the solid the ions are not free to move because of the strong electrostatic forces keeping them together in the ionic lattice. So, solid magnesium chloride does not conduct. Molten magnesium chloride conducts because its ions are free to move.

c Iron conducts electricity because it has a metallic structure of ions in a sea of mobile delocalised electrons. The movement of the mobile electrons is an electric current. Iron chloride does not conduct because the ions are not free to move because of the strong electrostatic forces keeping them together in the ionic lattice. In addition there are no free delocalised electrons to conduct electricity.

d Water molecules are polar so they can form bonds with the sodium and sulfate

ions in the solid. The bonds formed allow the water molecules to go into solution. Sulfur is a non-polar solid. It cannot form bonds with water molecules and so cannot go into solution.

e Propanol can form hydrogen bonds with water because both water and propanol have a hydrogen atom attached to a very electronegative (oxygen) atom. Propane does not dissolve in water because it is non-polar.

f Hydrogen chloride reacts with water to form hydrogen ions and chloride ions, and these ions allow the solution to conduct electricity.

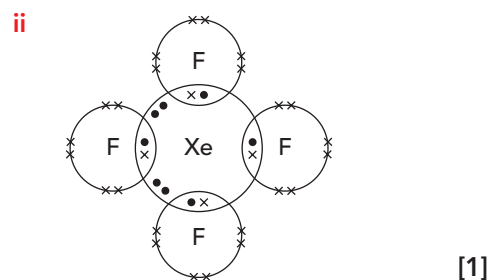
Exam-style questions

1 a Ask yourself first, is the structure giant or simple? If the structure is simple, ask yourself, are the intermolecular forces van der Waals' forces, polar forces or hydrogen bonds? If you don't know the significance of these two questions, discuss them with your teacher.

Number of electrons rises from helium to xenon; [1]

increasing id-id forces with increasing number of electrons. [1]

b i Bond formed by sharing a pair of electrons. [1]



iii (Square) Planar; [1]

lone pairs repel each other more than lone pair-bond pairs; [1]

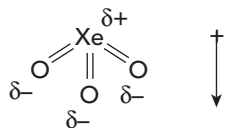
lone pairs get away as far as possible from each other to minimise repulsions. [1]

[incorrect structure with lone pairs adjacent, 2 marks]

c i Lone pair-bond pair repulsion more than bond pair-bond pair repulsion; [1]

so closes up $\text{O}=\text{Xe}=\text{O}$ bond angle
/ oxygens pushed out of planar
position / tetrahedral arrangement
of electron pairs distorted. [1]

ii

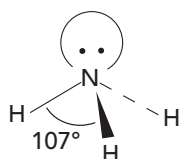


Need to show partial charges
correct on at least one
 $\text{Xe}=\text{O}$ bond; [1]

direction of overall dipole
correct. [1]

[Total: 11]

2 a i



Correct structure of ammonia,
i.e. N attached to 3 H atoms; [1]

correct 3-dimensional structure
of ammonia; [1]

lone pair of electrons shown. [1]

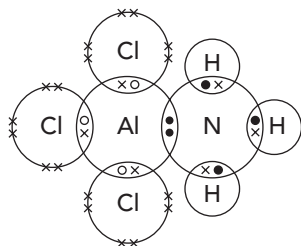
ii 107° [1]

b Nitrogen is more electronegative
than H; [1]

asymmetric distribution of electrons /
centre of positive and negative charge
does not coincide. [1]

c i One atom donates both electrons /
an electron pair to the bond. [1]

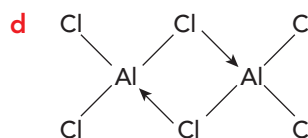
ii



Electron arrangement of
ammonia correct; [1]

electron arrangement of
aluminium chloride correct; [1]

both electrons in the co-ordinate
bond come from the ammonia. [1]



Bridge structure correct; [1]

co-ordinate bonds with both arrows
in correct direction. [1]

[Total: 12]

3 a The ability of a bonded atom to draw
the pair of electrons in a covalent bond
... towards itself. [1]b i $\text{H}^{\delta+}-\text{I}^{\delta-}$ [1]ii $\text{F}^{\delta-}-\text{I}^{\delta+}$ [1]iii $\text{C}^{\delta+}-\text{Cl}^{\delta-}$ [1]

[3 correct for 2 marks; 2 correct
for 1 mark; 0 or 1 correct for 0 marks]

c i The difference in the
electronegativity is 0.5 [1]

This is a relatively small difference /
less than 1.0 difference so the
molecule is covalent [1]

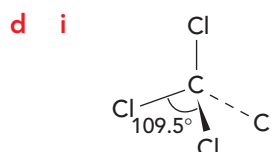
ii planar; [1]

trigonal [1]

iii Lone pairs repel each other more
than lone pair-bond pairs; [1]

lone pairs get away as far as
possible from each other to
minimise repulsions. [1]

iv 120° [1]



Correct arrangement of Cl and C
atoms; [1]

correct 3-dimensional structure. [1]

ii Electron clouds (or charge)
symmetrical / dipoles cancel each
other out. [1]

[Total: 15]

4 a Metal cations; [1]

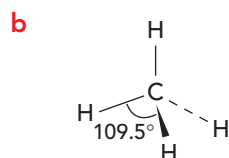
in sea of electrons / delocalised
electrons; [1]

strong electrostatic force between the
delocalised electrons and the ions. [1]

- b** Some of the electrons are delocalised / not associated with any one atom; [1]
Some of the electrons are able to move. [1]
- c** Strong electrostatic forces between ions and delocalised electrons; [1]
a lot of energy required to overcome these attractions/ forces. [1]
- d** Potassium larger ion than lithium ion; [1]
potassium has lower charge density; [1]
electrons more easily lost from potassium; [1]
more electrons to act as charge carriers / conduct electricity in potassium. [1]

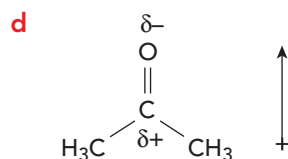
[Total: 11]

- 5 a** Methane is a non-polar molecule; [1]
only weak attractive forces between methane molecules. [1]



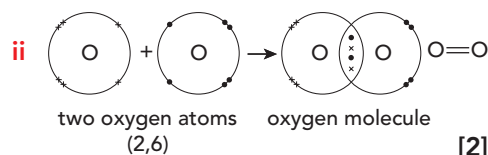
- Molecule with correct bonding; [1]
correct 3-dimensional shape of methane; [1]
bond angle 109.5° (allow 109°). [1]

- c** Perfumes need to be volatile / easily vaporised for people to smell; [1]
only structures which are simple molecules have low boiling points. [1]



- Correct diagram; [1]
correct dipole shown; [1]
 δ^+ end of dipole attracted to negative charge on rod. [1]

[Total: 10]

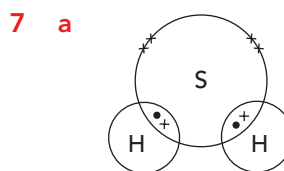


[2]

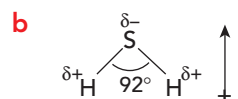
[1 mark for each correct structure]

- b** Sodium iodide is soluble and iodine is insoluble; [1]
sodium iodide has ions that can form bonds with water molecules; [1]
iodine is non-polar / molecules can't disrupt hydrogen bonded structure of water. [1]
- c** In molten sodium iodide the ions can move (to carry the charge); [1]
iodine has no ions or mobile electrons to carry the charge. [1]
- d** Sodium iodide is ionic; [1]
great force of attraction between ions and mobile electrons; [1]
needs a lot of energy to overcome these strong forces of attraction; [1]
iodine is a small molecule; [1]
forces between molecules weak. [1]
- e** The difference in the electronegativity is 1.6 [1]
This is a relatively large difference / more than 1.0 difference so the molecule is ionic [1]

[Total: 14]



[2]

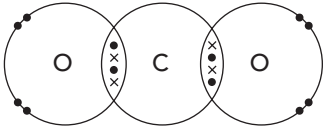


- V-shaped molecule; [1]

- i** bond angle $90-102^\circ$ (actual value is 92°); [1]
ii partial charges correct; [1]
iii direction of dipole correct. [1]

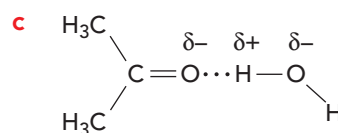
- c i** H_2Se has larger molecule with more electrons; [1]
increased id-id forces in H_2Se . [1]
- ii** Oxygen very electronegative; [1]
water can form hydrogen bonds [1]
between H of one molecule and O of another molecule; [1]
hydrogen sulfide has pd-pd forces / no hydrogen bonds; [1]
hydrogen bonding stronger than other intermolecular forces. [1]

[Total: 13]

- 8 a** Regular arrangement of ions; [1]
electrons dispersed between the ions. [1]
- b** Magnesium chloride is ionic; [1]
great force of attraction between ions and mobile electrons; [1]
needs a lot of energy to overcome these strong forces of attraction; [1]
bromine is a small molecule; [1]
forces between molecules weak. [1]
- c** Sodium has delocalised electrons, which are free to move; [1]
in solid sodium chloride the ions are not free to move (and there are no mobile electrons). [1]
- d i**  [1]
- ii** linear [1]
- iii** Only bonding pairs of electrons on carbon / no lone pairs on carbon; [1]
electron pairs get as far away as possible from each other. [1]
- e** Electrons in atoms in constant movement; [1]
temporary electron density in one part of atom/molecule greater than in another; [1]
temporary dipole formed; [1]
induces dipole on neighbouring atom/molecule; [1]
dipoles attract each other. [1]

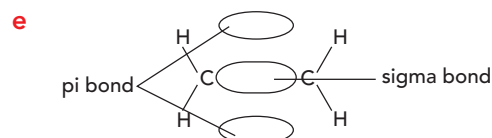
[Total: 18]

- 9 a i** In ice, water molecules in fixed position / in lattice; [1]
caused by hydrogen bonds being in fixed positions; [1]
in liquid, structure is irregular / water molecules can be closer together. [1]
- ii** Any two of:
(relatively) high melting point (or boiling point);
high surface tension;
(relatively) high viscosity. [2]
- b** One atom with hydrogen with covalent bond to very electronegative atom; [1]
another electronegative atom with lone pair in adjacent molecule. [1]



Bond shown between oxygen of propanone and hydrogen of water; [1]
hydrogen bond shown as dots, and $\text{O} \cdots \text{H}-\text{O}$ bond angle of about 180° . [1]

- d** σ bond (sigma bond) from overlap of atomic orbital 'end-on' / linearly; [1]
 π bond (pi bond) formed from sideways overlap of p orbitals / orbitals other than s orbitals. [1]



Sigma bond shown between the two carbon atoms and labelled; [1]
electron clouds of pi bond shown above and below the plane of the ring; [1]
both cloud charges of the pi bond labelled as belonging to the pi bond. [1]

[Total: 15]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 5

Science in context

Liquid crystal displays are commonplace nowadays but the phenomenon of the 'metaphase' was discovered a long time ago (1888 by the Austrian botanist Friedrich Reinitzer). The molecules in liquid crystals are rod-shaped and have an uneven electron distribution. At certain temperatures, this causes the molecules to line up in the same overall direction. The intermolecular forces between the molecules are strong enough to keep the molecules in vague line with each other but not strong enough to keep them firmly in one place.

Learners do not need to know details of polarised light and how it is formed. It is sufficient to tell them that a ray of light vibrates in all directions (planes) but when passed through a sheet of polaroid, it vibrates in only one plane. This light is called plane-polarised light. Some substances can change the direction in which the plane-polarised light travels. Some substances rotate the plane-polarised light to the left and other rotate it to the right. These substances are called optical isomers (see Chapter 30). In the diagram (Figure 5.2) the piece of polaroid which causes the light to vibrate in one plane is called the polariser. If we put a second piece of polaroid at right angles to the first, no light comes through. But if the substance in between the polaroids rotates plane-polarised light by 90° the light is seen again.

The first practical liquid crystal display was developed in 1970. A thin layer of liquid crystal is placed between two glass plates coated with a mixture of indium oxide and tin oxide. The upper plate is treated chemically to make the rod-shaped molecules line up in one direction and the bottom plate is treated chemically to make the rod-shaped molecules line up at right angles to this. This has the effect of making the molecules arrange themselves into a helical form. This form rotates plane-polarised light by 90° and so light comes

through the bottom plate. This is the 'off' state. The on state (dark) is formed by the molecules arranging themselves vertically when an electric field is applied. The plane of polarised light is not rotated.

Learners are asked to compare the metaphase with a liquid and solid. There is no clear answer to the question as to whether it is a different phase:

- there is some structure and the molecules are not arranged randomly as in a liquid (so could be more like a solid)
- there is limited movement of the molecules (so more like a solid)
- goes cloudy (so more like solid dispersed through a liquid)
- there is no definite arrangement as in a solid (so could be more like a liquid)
- there is some movement of the molecules (so more like a liquid)
- goes cloudy (so more like oil dispersed in water or like milk, which are liquids)

Learners may decide in the end that the metaphase is a liquid (it has some structure but even water has considerable structure due to hydrogen bonding).

The second question addresses the issue of looking at screens (either computer or mobile phone screens) for extended periods. You could do a straw poll to determine how long the class on average looks at screens. The flow of information through these devices is undoubtedly useful but may also have drawback through too much use. The following issues could be discussed in groups.

- For example, more hours sitting at a computer or mobile phone means fewer hours of being physically active.
- Looking at a screen at night can stimulate the brain and make it difficult to fall asleep.

- There are various conditions that result from looking at a computer or smartphone screen. One is computer vision syndrome, which results from staring at a screen for long periods of time. This can lead to dry eyes or itching through lack of blinking. Another problem is caused by the glare of the screen, which can make some people feel uncomfortable, especially people with cataracts. Eyestrain can also be a problem.
- The longer you spend looking at a screen, the less time you have for social contacts and discussing issues (as you are doing now!). Some may argue that you can have wider social contacts over the internet!

You could widen the discussion to include questions related to the use of mobile phones during mealtimes / at restaurants / at the theatre / in trains.

Finish up by posing the question: Why do so many chief executives of IT companies turn off completely when they go home and so avoid modern technology?

Self-assessment questions

- Particles in a solid are close together / touching. When a solid changes to a liquid the particles move slightly further apart but many are still touching. In a solid the particles are only vibrating. As the temperature is raised, the particles vibrate more until they can move from place to place by sliding over other particles.
 - Particles in a liquid are close together and many are still touching. As the temperature is raised they move faster then escape to form a gas, in which the particles are much further apart. The particles in a liquid are moving slowly over each other but in a gas they move more rapidly.
- Helium and neon atoms are non-polar so the only forces between them are van der Waals' forces. There are very few electrons in each atom so the van der Waals' forces here are particularly weak.
- 518 K
 - 228 K
 - $15 \times 10^3 = 15\,000$ Pa
- At high temperatures the molecules are moving very fast. They have a lot of kinetic energy. The particles hit the walls of the tube with a considerable force. If the temperature is too high the force of the particle hitting the wall may be great enough to break the tube.
- A gas whose volume varies in proportion to the kelvin temperature and in inverse proportion to the pressure.
 - Real gases deviate from the ideal gas at high pressures and low temperatures. This is because, under these conditions, the molecules are close enough for intermolecular forces of attraction to pull the molecules towards one another. The volume of the molecules must also be taken into account.
- $54\text{ }^{\circ}\text{C} = 54 + 273 = 327\text{ K}$;
 $250\text{ kPa} = 250\,000\text{ Pa}$
 $\text{moles of methane} = \frac{272}{16} = 17\text{ mol}$
rearrange the gas equation:
 $pV = nRT$ so $V = \frac{nRT}{p}$

$$V = \frac{17 \times 8.31 \times 327}{250\,000}$$

$$V = 0.185\text{ m}^3 \text{ (to 3 significant figures)}$$
 - $10\text{ dm}^3 = 10/1000\text{ m}^3 = 0.01\text{ m}^3$
 $120\text{ kPa} = 120\,000\text{ Pa}$
rearrange the gas equation:
 $pV = nRT$ so $T = \frac{pV}{nR}$

$$T = \frac{120\,000 \times 0.01}{0.25 \times 8.31}$$

$$T = 578\text{ K (to 3 significant figures)}$$
- $100\text{ }^{\circ}\text{C} = 100 + 273 = 373\text{ K}$
 $23\text{ cm}^3 = 2.3 \times 10^{-5}\text{ m}^3$
rearrange the gas equation:
 $pV = \frac{mRT}{M_r}$ so $M_r = \frac{mRT}{pV}$

$$M_r = \frac{0.08 \times 8.31 \times 373}{(1.02 \times 10^5) \times (2.3 \times 10^{-5})} = 105.7$$

$$M_r = 106 \text{ (to 3 significant figures)}$$
- A
- At first, bromine molecules escape from the surface of the liquid to become vapour. The colour of the vapour above the liquid

becomes darker. As more and more molecules escape, the molecules in the vapour become closer together. Eventually the molecules with lower kinetic energy will not be able to overcome the attractive forces of neighbouring molecules. Some of the molecules in the vapour begin to condense, these bromine molecules return to the liquid. Eventually, bromine molecules return to the liquid at the same rate as bromine molecules escape to the vapour. A position of equilibrium is reached. The colour of the vapour above the liquid remains constant.

- 10 a** Many metals are strong because of the strong forces of attraction between the ions and the delocalised electrons. Ionic solids are brittle because when a force is applied along the planes of ions in the lattice, the ions come to occupy new positions in which ions with the same charge are opposite each other. The repulsion between many ions of the same charge weakens the forces keeping the ions together and the layers break apart.
- b** In pure copper or pure tin, the layers of metal atoms / ions can slide over each other when a force is applied. New bonds are formed due to the force of attraction between the metal ions and the delocalised electrons. In the alloy, the different sized atoms cause the lattice structure to be disrupted. So the layers of metal ions do not slide over each other as easily.
- 11 a** Although aluminium is not as good an electrical conductor as copper, pure copper is too dense and cannot support its own weight in the air. Aluminium has low

density, also but has low tensile strength. So steel, which has high tensile strength, is used to support the aluminium.

- b** Aluminium is less dense than steel. So the engine block has a lower mass and less energy is used by the car. The lower strength of aluminium compared with steel is not a problem for this application.
- c** Iron is strong because of the strong metallic bonding between the ions and the mobile electrons in the metallic lattice. Sulfur breaks easily because it has a simple molecular structure. Intermolecular forces / id-id forces between sulfur molecules are weak and easily broken.
- 12** Start your answer by describing the structure and bonding.
- a** Silicon(IV) oxide has a giant covalent structure. It has a high melting point because of the strong covalent bonding throughout the whole structure. A high temperature is needed to break these strong bonds and separate the atoms.
- b** Silicon(IV) oxide does not conduct electricity because all the electrons are used in bonding. So there are no free electrons available to carry the electric current.
- c** Silicon(IV) oxide is a crystalline solid because the atoms are in a regular tetrahedral arrangement (or, the atoms are in a lattice structure.)
- d** Silicon(IV) oxide is hard because it is difficult to break the three-dimensional network of strong covalent bonds by simply scratching the surface.

13

	Giant ionic	Giant molecular	Metallic	Simple molecular
Two examples	e.g. sodium chloride, magnesium oxide	e.g. graphite, silicon(IV) oxide	e.g. copper, iron	e.g. bromine, carbon dioxide
Particles present	ions	atoms	positive ions in sea of electrons	small molecules
Forces keeping particles together	electrostatic attraction between oppositely charged ions	electrons in covalent bonds between atoms	delocalised sea of electrons attracts positive ions	weak intermolecular forces between molecules (but covalent bonds within the molecules)
Physical state at room temperature	solid	solid	solid	solid, liquid or gas

	Giant ionic	Giant molecular	Metallic	Simple molecular
Melting points and boiling points	high	very high	moderately high to high	low
Hardness	hard, brittle	very hard	hard, malleable	soft
Electrical conductivity	conduct when molten or in aqueous solution	non-conductors (except graphite)	conduct when solid or molten	non-conductors
Solubility in water	most are soluble	insoluble	insoluble but some react	usually insoluble but soluble if polar enough to form hydrogen bonds with water

14 D

15 a Buckminsterfullerene is molecular. There are id-id forces between the molecules. So not much energy is required to overcome these weak intermolecular forces.

b Some of the p electrons are not used in bonding in graphene. These electron clouds join up and form extended delocalised rings above and below the plane of the graphene. The mobile electrons move when a voltage is applied.

c There are only weak forces between the buckminsterfullerene molecules. So it requires only a small amount of force to overcome these weak intermolecular / id-id forces.

Exam-style questions

1 a two examples of a giant ionic structure, e.g. sodium chloride, magnesium oxide [2]
[1 mark each]

two examples of a simple molecular structure, e.g. carbon dioxide, bromine [2]
[1 mark each]

b Ionic structure is brittle because force applied along layers displaces the ions; [1]

ions of like charge come near each other; [1]

repulsion between like charged ions disrupts bonding. [1]

Metals are malleable because force applied along layers causes layers of atoms/ions to slide; [1]

there are still / there are new forces of attraction [1]

between the ions and the delocalised electrons. [1]

c Giant molecular structures have strong covalent bonds; [1]

throughout / network of bonds; [1]

takes a lot of energy to break these (strong) bonds. [1]

Simple molecular structures have weak forces / bonds [1]

between molecules / intermolecular forces; [1]

requires only a small amount of energy to overcome these forces. [1]

d In graphite, each carbon atom is bonded to three others; [1]

fourth outer electron on each carbon atom is free / delocalised; [1]

moving electrons are a flow of current / can carry current. [1]

In diamond all electrons involved in covalent bond formation; [1]

no moving electrons to carry current. [1]

[Total: 21]

2 a Carbon dioxide has a simple molecular structure; [1]

intermolecular forces or id-id forces are weak. [1]

b Silicon(IV) oxide has a giant covalent / giant molecular structure; [1]

all bonds [1]

are strong. [1]

c Both compounds are covalent; [1]

no mobile electrons (to carry the current). [1]

[Total: 8]

3 a A gas in which the volume is proportional to the (kelvin) temperature / inversely proportional to pressure. [1]

b high pressure; [1]

low temperature; [1]

molecules close together [1]

Significant intermolecular forces between molecules / volumes of molecules must be taken into account. [1]

c i weak forces between atoms; [1]

easy to break interatomic forces [1]

ii no mobile / free electrons [allow: not an ion] [1]

d Change temperature to correct units:

$$-20\text{ }^{\circ}\text{C} = -20 + 273 = 253\text{ K} \quad [1]$$

$$\text{moles of He} = \frac{0.5 \times 1000}{4} = 125\text{ mol} \quad [1]$$

$$\text{gas equation: } pV = nRT$$

rearrange gas equation correctly:

$$V = \frac{nRT}{p} \quad [1]$$

$$V = \frac{125 \times 8.31 \times 253}{50000} \quad [1]$$

$$V = 5.256\text{ m}^3 = 5.26\text{ m}^3 \text{ (to 3 significant figures)} \quad [1]$$

[Total: 13]

4 a A regular arrangement of ions or atoms [1]
in three dimensions. [1]

b Bromine has only id-id forces [1]

which are weak. [1]

Water has hydrogen bonding; [1]

hydrogen bonding (in water) is stronger than id-id forces / hydrogen bonding is the strongest type of intermolecular force. [1]

c Molecules in liquid kept together / close to each other because of weak attractive / intermolecular forces; [1]

molecules in liquid gain kinetic energy; [1]

this energy is sufficient to overcome attractive forces; [1]

molecules are free enough / have enough energy to move about independently / are far apart. [1]

d Change temperature to correct units:

$$98\text{ }^{\circ}\text{C} = 98 + 273 = 371\text{ K} \quad [1]$$

change volume to correct units:

$$80\text{ cm}^3 = 8.0 \times 10^{-5}\text{ m}^3 \quad [1]$$

$$\text{gas equation: } pV = \frac{mRT}{M_r}$$

rearrange gas equation correctly:

$$M_r = \frac{mRT}{pV} \quad [1]$$

$$M_r = \frac{0.2 \times 8.31 \times 371}{(1.1 \times 10^5) \times (8.0 \times 10^{-5})}$$

$$= 70.06$$

$$= 70 \text{ (to 2 significant figures)} \quad [1]$$

[Total: 15]

5 a i giant ionic [1]

ii poor [1]

iii poor [1]

iv simple molecular [1]

v giant covalent / giant molecular [1]

vi good [1]

vii poor [1]

b A is ionic so has high melting point because of strong electrostatic attractions; [1]

between oppositely charged [1]

ions. [1]

Solid has low electrical conductivity; [1]

ions can't move from place to place; [1]

in liquid the ions are able to move from place to place. [1]

c B is simple molecular so has low melting point because of weak van der Waals' forces [1]

between molecules; [1]

only small amount of energy needed to overcome these forces. [1]

Low electrical conductivity because has covalent bonding; [1]

none of the electrons able to move. [1]

[Total: 18]

6 a Ions in lattice / regularly arranged; [1]
in sea of delocalised electrons. [1]

b Layers of metal ions; [1]

slide when force applied; [1]

6

- d** B: weak forces / id-id forces
between tubes; [1]
tubes slide over each other (when force
applied). [1]
C: covalent bonds / cross links [1]
between the tubes; [1]
tubes can't slide over each other
(when force applied). [1]
[Total: 16]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 6

Science in context

This is a very wide ranging discussion about climate change and what individuals can do to reduce their carbon footprint. In reality, it is very difficult because most of us have limits as to what we are prepared to concede. For example, do you want to give up that trip to somewhere nice because you are worried about the emissions from aircraft or cars? Do you want to ban all steam train enthusiasts? Encourage learners to start with a list that is personal to them and their local community. The list given below relating to the first question is not exhaustive.

- Walk or cycle instead of using the car: This avoids putting extra CO_2 into the atmosphere from combustion in car engines.
- Use public transport or car share: This reduces CO_2 emissions per person.
- Drive an electric car rather than a petrol or diesel car: Electric cars emit no CO_2 themselves. Unfortunately, at present they are likely to use electricity generated from fossil fuels. If they are recharged with electricity from a renewable energy source there is no carbon footprint.
- Drive sensibly: Properly inflated tyres, unnecessary acceleration and not leaving the engine running in traffic jams, etc. all reduce the amount of CO_2 emitted.
- Reduce air travel: If you have to fly take longer holidays but fewer of them.
- Solar panels to generate electricity or hot water: Reduces the amount of electricity used that is generated from fossil fuels.
- Heat pumps / ground pumps: Reduce carbon emissions by taking heat from the environment. (Heat energy is taken in from the air or ground to evaporate a refrigerant. The refrigerant is then compressed, which increases the temperature. The refrigerant gas transfers heat into the central heating system. This causes the refrigerant to condense back into a liquid. The cooled refrigerant passes through the expansion valve, which decreases the pressure. This decreases the temperature further and the cycle starts again.) Heat pumps do require electricity but the amount of electricity used is small.
- Home insulation: Stops heat escaping so that you do not use more energy than necessary
- Lower use of air conditioning systems: These are often left running unnecessarily.
- Use thermostats sensibly / use smart technology: Remote control of thermostats can turn off the heating system when you are not at home.
- Turn off lighting: Turn off lights you're not using and when you leave the room. Office blocks lit up fully at night are a particular problem. Replace outdated light bulbs with LED lamps.
- Appliances (vacuum cleaners, refrigerators etc): Choose an energy-efficient one when buying a new appliance.
- Food: Eat more locally produced foods. This may save on production and transport costs which are still largely based on the consumption of fossil fuels. Grow your own vegetables!
- Reuse and recycle: In many countries over 25% of the energy used goes into the extraction of resources, manufacturing, transport, and final disposal of consumer goods and food, including packaging. If you recycle items you no longer use or buy used products you can reduce the amount of fossil fuels used.

After discussing what can be done by the individual, more general issues of reducing the amount of fossil fuels burned can be discussed. These could include.

- Use alternative energy sources: Wind, solar, geothermal, hydroelectric power and suitable biomass energy projects.
- Stop deforestation / plant more trees. Deforestation occurs because of the increased hunger for land for mining or agriculture or just for human habitation. Deforestation is a major contributor to climate change because it reduces the number of plants which absorb carbon dioxide in photosynthesis. Trees are a particularly good 'sink' for absorbing carbon dioxide.

Governments are often reluctant to take steps to combat climate change because:

- It is easier and cheaper to continue with coal or gas fired power stations than to build solar farms, wind farms etc. (However, many of these are now built by private companies.)
- A country may have many natural resources and large supplies of coal and many people may lose their jobs when these industries are closed down. (But this could be offset by new jobs in 'green' energy.)
- Politicians in developing countries feel that it is unfair that developed countries have had the benefits of using fossil fuels to develop their economies but they are then being denied the benefits of continuing development by using a cheaper source of energy.
- Some politicians may still not believe in climate change or the extent to which it will affect the planet. (Since there are alternative theories relating to sunspot activity etc.)
- Inertia: Planning for large scale changes in energy policy and the practical aspects of implementing it are so large that a government may feel that it needs a much longer time (decades) to prepare for any changes.
- Other priorities: There may be more urgent needs e.g. housing, food, welfare (building hospitals etc.) and the general population sees these as a more immediate threat.
- Time scale: Some politicians do not see climate change as an immediate threat because it has not affected their country.

- Influence of pressure groups: People who do not want wind turbines or solar farms close to their homes may put pressure on politicians.

Self-assessment questions

1 a exothermic

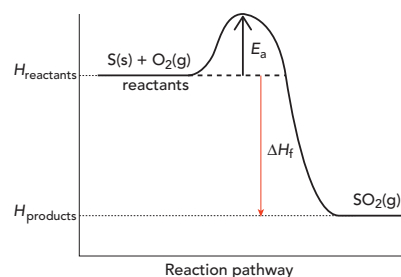
b exothermic

c endothermic

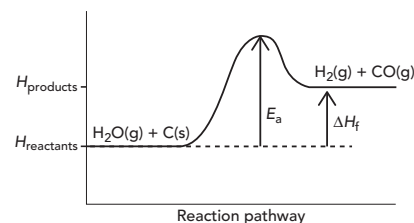
d exothermic

e endothermic

2 a



b



3 a ΔH_r^\ominus

b $\Delta H_f^\ominus [\text{CO}_2(\text{g})]$ or $\Delta H_c^\ominus [\text{C}(\text{graphite})]$

c ΔH_r^\ominus

d $\Delta H_f^\ominus [\text{H}_2\text{O}(\text{l})]$ or $\Delta H_c^\ominus [\text{H}_2(\text{g})]$

4 a 9718.5 J (9720 J to 3 significant figures)

b 250.8 J / 251 J

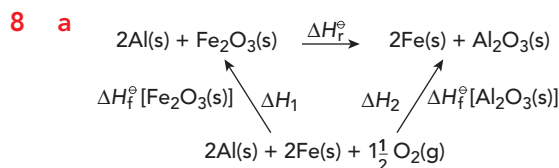
c 6270 J

5 One mole of sulfuric acid reacts with two moles of sodium hydroxide to form two moles of water. The definition of standard enthalpy change of neutralisation relates only to one mole of water formed. So the enthalpy change for sulfuric acid is twice this.

6 Time taken for sodium to dissolve / energy loss to thermometer or air or calorimeter; assumption that the specific thermal capacity of the solution is the same as that of water.

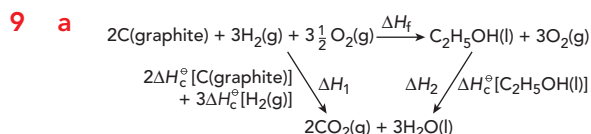
7 In the experiment there may be: heat losses to the surroundings from the flame and into the calorimeter, thermometer and air;

incomplete combustion of the ethanol;
evaporation of ethanol so that not all the
weight loss is due to burning.



b

$$\begin{aligned}
 \Delta H_r + \Delta H_1 &= \Delta H_2 \\
 \Delta H_r + (-824.2) &= -1675.7 \\
 \Delta H_r &= -851.5 \text{ kJ mol}^{-1}
 \end{aligned}$$



b

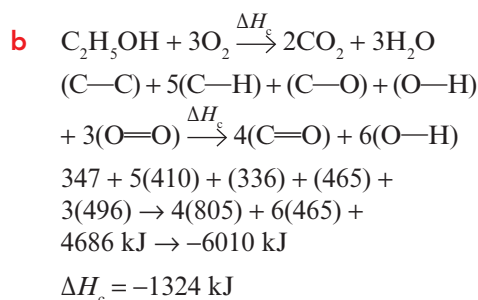
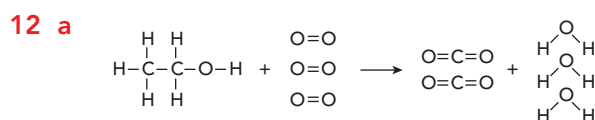
$$\begin{aligned}
 \Delta H_r + \Delta H_2 &= \Delta H_1 \\
 \Delta H_r + (-1367.3) &= 2(-393.5) + 3(-285.8) \\
 \Delta H_r &= -277.1 \text{ kJ mol}^{-1}
 \end{aligned}$$

10 D $\Delta H_r = 3\Delta H_f[\text{MgO(s)}] - \Delta H_f[\text{Fe}_2\text{O}_3\text{(s)}]$

11 $\Delta H_r = +1663.5 \text{ kJ mol}^{-1}$

There are 4 C—H bonds in methane so the
average C—H bond energy is

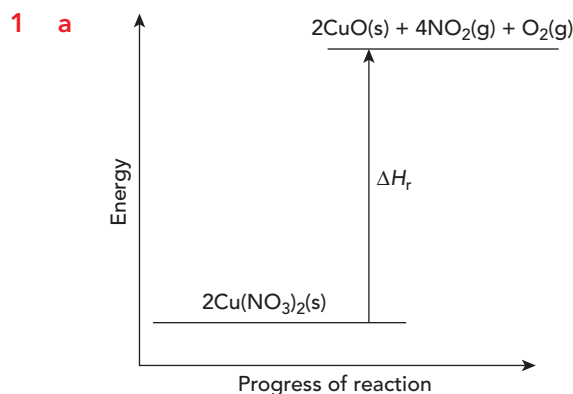
$$\frac{1663.5}{4} = +415.9 \text{ kJ mol}^{-1}$$



c Bond energies used are average bonds
energies. Bond energies are based on data
from gaseous reactants and products
whereas experimental combustion results
for ethanol are for ethanol liquid.

13 B

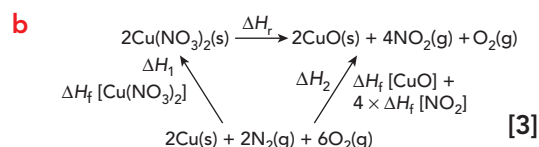
Exam-style questions



Copper(II) nitrate on left and products
on right with arrow showing energy
going upwards; [1]

copper(II) nitrate below products; [1]

arrow in upwards direction from
copper nitrate to products with ΔH
written near the arrow. [1]



c $\Delta H_r + \Delta H_1 = \Delta H_2$ [1]

$$\Delta H_r + 2(-302.9) = 2(-157.3) + 4(+33.2) \quad [1]$$

$$\begin{aligned}
 \Delta H_r + (-605.8) &= -181.8, \\
 \text{so } \Delta H_r &= (+)424 \text{ kJ mol}^{-1} \quad [1]
 \end{aligned}$$

d i energy released
= $100 \times 4.18 \times 2.9 = 1212.2 \text{ J}$ [1]

1212.2 J for 25 g so for 1 mol

$$= 1212.2 \times \frac{249.7}{25.0} \quad [1]$$

$$= (-)12\,107.5 \text{ J} / 12.1 \text{ kJ to 3} \quad [1]$$

significant figures

ii Time taken for copper sulfate
to dissolve / energy loss to
thermometer or air or calorimeter [1]
so temperature recorded lower
than expected / energy loss to
surroundings and therefore energy
released is less. [1]

Or

assumption that the specific thermal
capacity of the solution is the same as
that of water; [1]

the thermal capacity is likely to be slightly higher so the value calculated for the energy released is too low. [1]

[Total: 14]

- 2 a $\text{CH}_3\text{COCH}_3(\text{l}) + 4\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O}$
 $2(\text{C}-\text{C}) + 6(\text{C}-\text{H}) + (\text{C}=\text{O}) + 4(\text{O}=\text{O}) \rightarrow 6(\text{C}=\text{O}) + 6(\text{O}-\text{H})$ [1]
 $2(347) + 6(413) + (805) + 4(496) \rightarrow 6(805) + 6(465)$ [1]
 $+5961$ for bond breaking; -7620 for bond making; realisation that bond breaking is + and bond making is; [1]
 answer = -1659 kJ [1]

- b Any two of:
 the same type of bonds are in different environments;
 example, e.g. $\text{C}=\text{O}$ bonds in carbon dioxide and propanone;
 average bond energies are generalised / obtained from a number of different bonds of the same type. [2]

- c Bond energies calculated by using enthalpy changes of gaseous compound to gaseous atoms; [1]
 enthalpy changes of combustion done experimentally using liquid (propanone). [1]
 [energy needed to evaporate the propanone for 2 marks]

- d i Enthalpy change when 1 mol of a compound [1]
 is formed from its constituent elements in their standard states [1]
 under standard conditions. [1]

- ii $3\text{C}(\text{graphite}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_3\text{H}_6\text{O}(\text{l})$ [2]
 [1 mark for correct equation; 1 mark for correct state symbols]

- iii Carbon does not react directly with hydrogen under standard conditions. [1]

[Total: 14]

- 3 a $\frac{2.40}{24000} = 0.01$ mol [1]
 b heat change = $-100 \times 4.18 \times 33.5$ [1]
 $= 14\,003 \text{ J} = 14.0 \text{ kJ}$ (to 3 significant figures) [1]

c $\Delta H_c = \frac{-14.0}{0.01}$ [1]

$= -1400 \text{ kJ mol}^{-1}$ [1]

d $\Delta H_c^\ominus = 2(-394) + 3(-286)$ [1]

$= (-85)$ [1]

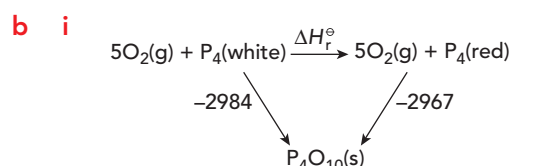
$= -1561$ [1]

kJ mol^{-1} [1]

- e incomplete combustion; heat losses through sides of calorimeter, etc. [1]

[Total: 11]

- 4 a The energy change when 1 mole [1]
 is completely combusted in excess oxygen [1]
 under standard conditions. [1]



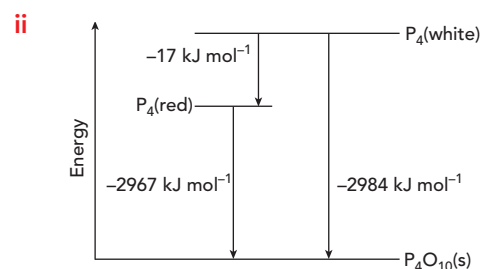
for correct cycle [1]

for arrows [1]

for correct values on arrows [1]

Using Hess's law, $\Delta H_r^\ominus - 2967 = -2984$ [1]

$\Delta H_r^\ominus - 2984 + 2967 = -17 \text{ kJ mol}^{-1}$ [1]



$\text{P}_4(\text{red})$ below $\text{P}_4(\text{white})$ [1]

for arrows from both down to P_4O_{10} [1]

for energy label [1]

[Total: 11]

- 5 a Enthalpy change when 1 mol of a compound [1]
 is formed from its constituent elements in their standard states [1]
 under standard conditions. [1]

- b** $\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$ is the equation for ΔH_r^\ominus [1]
 $\Delta H_c^\ominus = \text{sum of } \Delta H_r^\ominus \text{ of reactants} - \text{sum of } \Delta H_r^\ominus \text{ of products}$ [1]
 $= 2(-286) - 394 - (-891)$ [1]
 $= -572 - 394 + 891$ [1]
 $= -75 \text{ kJ mol}^{-1}$ [1]

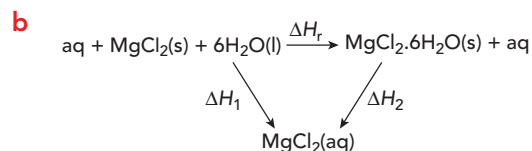
- c** $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
 $4(\text{C}-\text{H}) \quad 2(\text{O}=\text{O}) \quad 2(\text{C}=\text{O}) \quad 4(\text{O}-\text{H})$ [1]
 $4 \times 412 \quad 2 \times 496 \quad 2 \times 805 \quad 4 \times 463$ [1]
 $\Delta H_c^\ominus = 1648 + 992 - 1610 - 1852$ [1]
 $= -822 \text{ kJ mol}^{-1}$ [1]

[Total: 11]

- 6 a** The average energy needed to break 1 mole of bonds in the gaseous state. [1]
b Bond enthalpies of $\text{H}_2 + \text{I}_2 = 436 + 151 = +587 \text{ kJ mol}^{-1}$ [1]
 Bond enthalpies of $2\text{HI} = 2 \times 299 = +598 \text{ kJ mol}^{-1}$ [1]
 Enthalpy change $= 587 - 598 = -11 \text{ kJ mol}^{-1}$ [1]
c H_2 and I_2 on left and 2HI on right and energy label going upwards; [1]
 H_2 and I_2 below 2HI ; [1]
 arrow going downwards showing ΔH_r^\ominus [1]

[Total: 8]

- 7 a** Enthalpy change when reactants converted to products [1]
 in the amounts shown in the equation [1]
 under standard conditions. [1]



- 1 mark each for the three reactions with the arrows in the correct order/directions; [3]
 for ΔH values in correct places [1]

[Total: 7]

- 8 a** $250 \times 4.18 \times 23.0$ [1]
 $= 24\,000 \text{ J (to 3 significant figures)}$ [1]
b $M_r = 32.0$ [1]
 $\frac{2.9}{32.0} = 0.0906 \text{ moles}$ [1]
c $\frac{24\,000}{0.0906} = 265\,000 \text{ J mol}^{-1}$ or $(265 \text{ kJ mol}^{-1})$ [2]
d heat loss; [1]
 incomplete combustion; [1]
 conditions not standard [1]

[Total: 9]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 7

Science in context

This activity introduces learners to the redox reaction taking place in photochromic lenses. Introduce the activity by discussing the harmful effects of ultraviolet radiation in sunlight on the eyes. Learners may ask about the different types of UV radiation.

Ultraviolet (UV) radiation can be classified as:

- **UVA:** These have a lower energy than UVB and UVC rays. But UVA rays can reach the lens and retina inside the eye.
- **UVB:** These have more energy than UVA rays. These rays can reach the Earth's surface but are partly filtered out by the ozone layer.
- **UVC:** These are the highest-energy UV rays and most harmful to your eyes. However, the ozone layer absorbs nearly all UVC rays.

Harmful effects of UV radiation on the eyes include:

- Formation of cataracts in the eye and macular degeneration (vision becomes blurred because part of the retina becomes thin). This is linked to UVA exposure.
- UVB rays may cause growths on the eye surface which results in corneal problems as well as distorted vision.
- High exposure to UVB rays can cause photokeratitis (inflammation of the cornea). This can result in temporary loss of vision for 1 to 2 days.

To protect the eyes from harmful solar radiation, sunglasses should block 100 percent of UV rays. Frames which cover the sides of the eyes (wraparound frames) give the best protection because they limit how much stray sunlight reaches your eyes from above and to the side of the lenses.

Note that risk of UV exposure can be quite high even on cloud-covered days.

The advantages of photochromic lenses are:

- They darken according to the amount of light. With ordinary sunglasses, if the sun goes in, everything will appear very dark.
- They darken fairly rapidly so your eyes are not exposed to UV radiation for too long.
- You can use these glasses as ordinary glasses indoors or outside.
- They offer continuous UV protection. You are less likely to forget your sunglasses when you go out.
- They can save you money. You may not need to buy prescription eyeglasses and prescription sunglasses as well.

The disadvantages of photochromic lenses are:

- In cold places / weather, the darkening may be more than expected so your vision may not be as good as with normal sunglasses.
- In hot places / weather, the darkening may be less than expected so not all the UV light may be blocked.
- When you come in from bright sunlight to a darker place it takes time for the lenses go light again.
- They take up to a minute to darken so your eyes are exposed to UV radiation for a while. This problem does not arise if you put on ordinary sunglasses immediately.
- They don't darken as well inside cars because the glass in many windcreens has some UV protection. This prevents the photochromic lenses from darkening.

Self-assessment questions

- 1 a i H_2
 ii CO
 iii Mg
 b i I_2O_5
 ii SO_2
 iii CH_2CH_2
- 2 a i $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$ reduction
 $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$ oxidation
 ii $2\text{Mg} \rightarrow 2\text{Mg}^{2+} + 4\text{e}^-$ (or
 $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$) oxidation
 $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$ reduction
 iii $4\text{Fe} \rightarrow 4\text{Fe}^{3+} + 12\text{e}^-$ (or
 $\text{Fe} \rightarrow \text{Fe}^{3+} + 3\text{e}^-$) oxidation
 $3\text{O}_2 + 12\text{e}^- \rightarrow 6\text{O}^{2-}$ (or
 $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$) reduction
 b $2\text{IO}_3^- + 5\text{Zn} + 12\text{H}^+ \rightarrow \text{I}_2 + 5\text{Zn}^{2+} + 6\text{H}_2\text{O}$
- 3 a +5
 b +6
 c -2
 d +3
 e -3
 f +3
 g +4
- 4 a i 0 to -1 = -1 (reduction)
 ii -3 to 0 = +3 (oxidation)
 iii +3 to +5 = +2 (oxidation)
 b i Oxidising agent is Br_2 ; reducing agent is I^-
 ii Reducing agent is As_2O_3 ; oxidising agent is I_2
- 5 a sodium sulfate(IV)
 b sodium sulfate(VI)
 c iron(II) nitrate(V) or iron(II) nitrate
 d iron(III) nitrate(V) or iron(III) nitrate
 e iron(II) sulfate(VI) or iron(II) sulfate
 f copper(I) oxide
 g sulfuric(IV) acid
 h manganese(VII) oxide

- 6 a NaClO
 b Fe_2O_3
 c KNO_2
 d PCl_3
- 7 a $\text{H}_2\text{SO}_4 + 6\text{HI} \rightarrow \text{S} + 3\text{I}_2 + 4\text{H}_2\text{O}$
 b $2\text{HBr} + \text{H}_2\text{SO}_4 \rightarrow \text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$
 c $2\text{V}^{3+} + \text{I}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{VO}^{2+} + 2\text{I}^- + 4\text{H}^+$
- 8 B

Exam-style questions

- 1 a $\text{N}_2 = 0$; $\text{NH}_3 = -3$; $\text{NO} = +2$;
 $\text{NO}_2 = +4$; $\text{HNO}_3 = +5$ [5]
 [1 mark each]
 b Stage 1 is reduction because of decrease in oxidation number; [1]
 stages 2–4 are all oxidation because of increase in oxidation number. [1]
 c nitrogen(IV) oxide [1]
 d P (element) has oxidation number of 0 and P in H_3PO_4 has oxidation number of +5; [1]
 P has been oxidised as oxidation number increases; [1]
 N has oxidation number of +5 in HNO_3 and +4 in NO_2 ; [1]
 N has been reduced as decreases in oxidation number; [1]
 oxidation and reduction occur together, so redox. [1]
 e Nitric acid increases oxidation number of P / nitric acid gains electrons / nitric acid has been reduced. [1]

[Total: 14]

- 2 a i 0 [1]
 ii +2 [1]
 b i +1 [1]
 ii 0 [1]
 c i $\text{Ca} \rightarrow \text{Ca}^{2+} + 2\text{e}^-$ [1]
 ii $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$ [1]
 d equation c ii ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$) because electrons are being gained / oxidation number of hydrogen is decreasing [1]

- e** $\text{Ca} + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{H}_2$ [1]
f Water is acting as an oxidising agent, because it causes the oxidation of calcium, or because hydrogen from water is reduced. [1]

[Total: 9]

- 3 a i** +4 [1]
ii +6 [1]
b i 0 [1]
ii -1 [1]

- c** SO_2 because it decreases the oxidation number of the bromine / it loses electrons / the sulfur increases its oxidation state. [1]

- d i** +2 [1]
ii -1 [1]

- e** $\text{SO}_2 + \text{Br}_2 + 2\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{Br}^- + 4\text{H}^+$
 1 mark for correct stoichiometry of $\text{SO}_2 + \text{Br}_2 \rightarrow \text{SO}_4^{2-} + 2\text{Br}^-$ [1]
 1 mark for correct balance of atoms and ions [1]

[Total: 9]

- 4 a** One reactant is oxidised by loss of electrons; [1]
 electrons are gained by another reactant; [1]
 this happens at the same time / reduction and oxidation occur together. [1]

- b i** $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$ [1]
ii $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ [1]
iii -1 [1]

- c** $2\text{Al} + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 3\text{H}_2$ [1]

[Total: 7]

- 5 a i** +2 [1]
ii $+2\frac{1}{2}$ [1]

- b** Iodine atoms gain electrons. [1]

- c i** manganese(IV) oxide [1]
ii +6 [1]

- iii** I^- ions because they increase in oxidation number (from -1 to 0). [1]

- iv** MnO_2 because it has caused I^- to be oxidised / has lost oxygen / has lost electrons / the oxidation number of the Mn has decreased. [1]

[Total: 7]

- 6 a i** +5 [1]
ii -1 [1]

- b** The oxidation number of bromine has decreased (from +5 to -1); [1]
 the oxidation number of oxygen has increased (from -2 to 0); [1]
 oxidation and reduction have occurred together. [1]

- c** potassium bromate(V) [1]

- d i** -6 [1]

- ii** N in hydrazine = -2 and N in N_2 = 0; [1]
 for each nitrogen atom oxidation number change is +2. [1]

- iii** Oxidation number changes must balance; [1]

- $3 \times (2 \times +2)$ for nitrogen atoms = +12 [1]

- $2 \times (-6)$ for bromine atoms = -12 [1]

[Total: 12]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 8

Science in context

This activity introduces learners to the ways that industrial chemical processes develop over time to make them more efficient and less polluting. The production of ammonia is a case in point. One of the most important factors in 'improving' a process is to make it more energy efficient. This reduces the volume of pollutant gases present in the atmosphere (link with Science in context in Chapter 6). Other more energy efficient / less polluting industrial processes include the use of bacteria (see Science in context Chapter 3) and finding alternative processes such as producing zinc by electrolysis rather than using a blast furnace. Copper can be produced by growing bacteria on low grade copper ore. The solid copper is obtained from the copper ions produced by displacement from the solution with zinc or by electrolysis.

Ideas for greener manufacturing processes could include:

- Find a method which is more energy efficient, preferably methods which can take place at room temperature and pressure (use of enzymes / bacteria). The higher the temperature and the higher the pressure, the more energy is used.
- Atom economy: design methods to maximise the use of the reactants so that no unwanted waste products are formed in the reaction, e.g. try and find a method that produces a single product with no side reactions
- Try to find a method that produces waste that is less hazardous.
- Use chemicals which are less hazardous: If pollution does occur, the risks to the environment are minimised, e.g. try to use methods that do not involve use of cyanide (see Science in context Chapter 3 for the use of cyanide).

- Use safer solvents. Solvents are used as a medium in which to carry out the reaction and are also used as separating agents (link with partition coefficients in Chapter 21).
- Use of catalysts to lower the energy requirement for the reaction. The development of better and more efficient catalysts is important (link to Science in context Chapter 1 using molecular clusters).
- Design products so they break down easily in the environment to materials which don't produce harmful gases, e.g. polymers based on plant or animal material. (Mention of some 'biodegradable plastics' forming microscopic particles which are harmful to wildlife.)
- Reduce use of 'fillers' in products which bulk out or have other properties, e.g. make plastics more or less flexible. Reduce potentially harmful dyes and inks.
- Redesign processes so that chemicals used for temporary modification of chemicals in a process (to stop unwanted reactions) are not used. These add to additional waste.
- Monitor the whole manufacturing process constantly to be able to shut down the process if any poisonous substances are released.
- Safety procedures to prevent accidents, either from hazardous chemicals themselves or to minimise the dangers from fires, high pressure explosions etc.
- Devise processes which reuse or recycle waste material and make these into useful products which can themselves be recycled.

The second question touches upon the bad press that chemists have sometime had for polluting the environment. From time to time, there have been incidents in which chemicals have leaked from factories or there have been explosions polluting the air with toxic materials. However, nowadays, the (responsible) chemical industries do

make safety and the environment a priority. The following areas could be discussed:

- Public demand: In a society where there is an increasing demand for material things, once a new material or drug has been discovered, it is impossible to 'undiscover it'. Plastics are a case in point, where unless there is legislation many people still continue to use the material despite the fact that there is plenty of information in the media about the negative effects on the environment. The public will still be demanding cars. The steel or aluminium needed for their construction requires the ores to be mined and the metal to be extracted, with both processes being environmentally damaging.
- The quest for knowledge cannot be stopped. Most research chemists nowadays will always try to develop methods which are safe. It is how we put discoveries to use which is the critical thing.
- The press and stories on the internet may put a negative slant on chemists and chemical companies whenever there is a problem, before any investigation has been carried out.
- It is the chemical companies rather than the chemists themselves which are responsible for management issues in relation to safety factors.
- Business leaders and shareholders may have a large say in how chemical companies are run rather than the chemists themselves. Greed for more profits may be a driving factor in forcing management to 'cut corners' in terms of safety or pay less attention to environmental impacts.
- Mining for ores in remote areas may be unregulated. This can lead to deforestation, loss of habitat and pollution of rivers many kilometres away from the source. Some mining companies are simply a supply chain for the chemical companies rather than being involved in the extraction of metals from the ore.

Self-assessment questions

- 1 a According to the reaction equation, HI decomposes to form equal numbers of moles of hydrogen and iodine.
- b The gas in the vessel starts off colourless and then becomes more and

more purple (as more iodine vapour is formed from the decomposition of hydrogen iodide). Eventually the depth of colour does not change (when equilibrium has been reached).

- c For every mol of I_2 formed, 2 moles of iodine are decomposed. To form 0.68 mol of I_2 , $2 \times 0.68 = 1.36$ mol of HI must decompose. We started with 10 mol of HI so mol of HI present = $10 - 1.36 = 8.64$ mol.
- 2 a i There is no loss of matter.
- ii rate of movement of Na^+ and Cl^- ions from solution to solid = rate of movement from solid to solution
- b Initially more bromine molecules evaporate than return to the liquid. So the concentration of the bromine in the vapour increases and the colour deepens. At equilibrium the concentration of bromine in the vapour is constant. The depth of colour remains the same. This is because the rate of movement of bromine molecules from gas to liquid = rate of movement from liquid to gas.
- 3 a i moves to left / more ethanoic acid and ethanol formed; reaction moves in direction to oppose the effect of added ethyl ethanoate; so ethyl ethanoate decreases in concentration
- ii moves to left / more ethanoic acid and ethanol formed; reaction moves in direction to oppose the removal of ethanol; so more ethanol (and ethanoic acid) formed from ethyl ethanoate and water
- b i moves to right / more Ce^{3+} and Fe^{3+} formed; reaction moves in direction to oppose the effect of added Fe^{2+} ; so Ce^{4+} and Fe^{2+} decrease in concentration
- ii no effect – the water dilutes all the ions equally – there is no change in the ratio of reactants to products
- 4 a i equilibrium shifts to the left as fewer gas molecules on left
- ii equilibrium shifts to the left as no gas molecules on left but CO_2 on right

- b** equilibrium shifts to the right as greater number of gas molecules on the right
- 5 a** equilibrium shifts to the right as endothermic reaction favours the products
- b** endothermic as the forward reaction is favoured by an increase in temperature

6 a $K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$; units are $\text{dm}^6 \text{mol}^{-2}$

b $K_c = \frac{[\text{H}_2\text{O}]^2[\text{Cl}_2]}{[\text{HCl}]^4[\text{O}_2]}$; units are $\text{dm}^3 \text{mol}^{-1}$



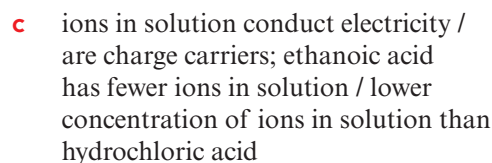
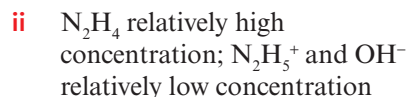
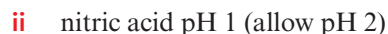
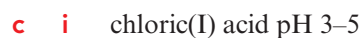
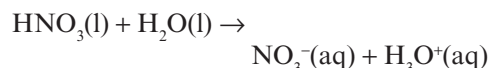
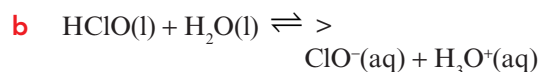
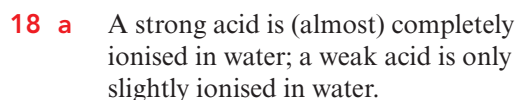
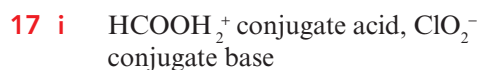
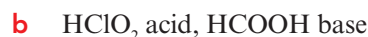
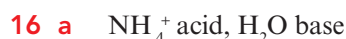
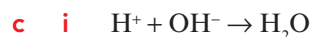
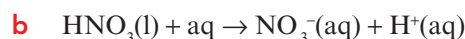
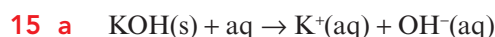
initial concentrations	10.00	10.00	0	0
equilibrium concentrations	$10.00 - 9.47 = 0.53$	$10.00 - 9.47 = 0.53$	9.47	9.47

$$K_c = \frac{(9.47)^2}{(0.53)^2} = 319$$

- 8** C (0.1–1.5n)
- 9 a** reaction is exothermic – so increase in temperature shifts the equilibrium in the direction of the reactants – so K_c decreases
- b** position of equilibrium shifts to the right / favours product; oxygen combines with NO to form more NO_2 until K_c returns to original value
- 10** partial pressure of NO
 $= (10.00 \times 10^4) - (4.85 \times 10^4 + 4.85 \times 10^4)$
 $= 0.30 \times 10^4 \text{ Pa} / 3 \times 10^3 \text{ Pa}$
- 11 a** Pa
b Pa^{-2}
c no units
- 12 a** total pressure at start = total pressure at equilibrium
 $(7.27 \times 10^6) + (4.22 \times 10^6)$
 $= 3.41 + 7.72 + p_{\text{I}_2}$
 partial pressure of iodine = $0.36 \times 10^6 \text{ Pa}$
- b** $K_p = \frac{(7.72 \times 10^6)^2}{(3.41 \times 10^6) \times (0.36 \times 10^6)}$
 $= 48.5$ (no units)

13 A

- 14 a** reaction is exothermic; so the back reaction is favoured with increase in temperature; position of equilibrium is moved away from ammonia synthesis by increase in temperature
- b** with increase in pressure, reaction goes in direction of fewer moles of gas; which is the forward reaction; so more ammonia formed
- c** removal of ammonia shifts equilibrium in direction of forward reaction; this is in favour of increased ammonia production
- d** the ammonia is stored at very low temperatures, and there is no catalyst present with the stored ammonia; any decomposition reaction is far too slow to matter



- d** hydrogen ions react with magnesium; ethanoic acid has fewer ions in solution / lower concentration of ions in solution than hydrochloric acid, therefore lower rate of reaction.

20 a The slope of the graph is steep between pH 3.5 and 10.5. Any indicator with a colour change range between these values is suitable: bromocresol green, methyl red, bromothymol blue or phenolphthalein. Methyl yellow, methyl orange and bromophenol blue would not be first choice indicators. Although the mid-point of their colour range is just within the range of the steep slope, their full range is outside the lower limit of 3.5.

- b** Methyl violet, methyl yellow and alizarin yellow have mid-points in their colour ranges at pH values that do not correspond with the steepest point of the pH / volume curve.

- 21 a i** Nitric acid is a strong acid and aqueous ammonia is a weak base. The steepest part of the pH curve is in the region of 7.5 to 3.5. So any indicator that has its colour change range within this region would be suitable, e.g. methyl red or bromothymol blue
- ii** Sulfuric acid is a strong acid and sodium hydroxide is a strong base. The steepest part of the pH curve is in the region of 10.5 to 3.5. So any indicator that has its colour change range within this region would be suitable, e.g. methyl red, bromothymol blue, phenolphthalein.
- iii** Butanoic acid is a weak acid and potassium hydroxide is a strong base. The steepest part of the pH curve is in the region of 11 to 7.5. So any indicator that has its colour change range within this region would be suitable, e.g. phenolphthalein.
- b** The titration of a strong acid with a weak base has a steep pH change only in acidic regions and not alkaline regions, for example, between pH 3 and pH 9. Phenolphthalein has a midpoint in its colour range above

pH 9. This is a pH value that does not correspond with the steepest part of the pH–volume curve.

22 D

Exam-style questions

- 1 a** Forward and backward reactions; [1]
happening at equal rates. [1]
- b i** goes to right [1]
ii goes to right [1]
iii no effect [1]
iv goes to left [1]
- c** If a system at equilibrium is disturbed [1]
the reaction goes in the direction to minimise the disturbance / oppose the change. [1]
- d** Reaction moves to right; [1]
some of the hydrogen must be removed [1]
to reduce the concentration of added hydrogen; [1]
more hydrogen reacts with CO_2 to form more H_2O and CO ; [1]
until value of K_c restored / to keep K_c constant. [1]

[Total: 13]

- 2 a** Pressure that one gas exerts / pressure of individual gas [1]
in a mixture of gases. [1]
- b** $13.5 \times 10^6 \text{ Pa} = 1.35 \times 10^7 \text{ Pa}$ [1]
- c** $K_p = \frac{p_{\text{HI}}^2}{p_{\text{H}_2} \times p_{\text{I}_2}}$ [1]
- d** $K_p = \frac{(10.2 \times 10^6)^2}{(2.33 \times 10^6) \times (0.925 \times 10^6)} = 48.3$
(no units) [1]
- e i** Reaction goes to left; [1]
increase in temperature increases the energy of the surroundings; [1]
reaction goes in the direction that opposes the increase in energy; [1]
reaction goes in the direction in which energy is absorbed; [1]
endothermic reaction favoured. [1]
- ii** Reaction moves to left; [1]
some more iodine needed [1]

to increase the concentration of iodine removed; [1]
 more hydrogen iodide decomposes; [1]
 until value of K_p restored / to keep K_p constant. [1]

[Total: 15]

3 a A = 0.08 mol [1]
 B = 0.18 mol [1]

b [A] = 0.04 mol dm⁻³ [1]
 [B] = 0.09 mol dm⁻³ [1]
 [C] = 0.02 mol dm⁻³ [1]

c i $K_c = \frac{[C]^2}{[A][B]}$ [1]

ii $K_c = \frac{(0.02)^2}{(0.04) \times (0.09)} = 0.11$ [1]
 (no units) [1]

[Total: 8]

4 a amount of hydrogen starts at 1.00 mol; [1]
 amount of hydrogen decreases [1]
 during the time interval in which number of moles of hydrogen iodide are increasing; [1]
 levels off; [1]
 at 0.25 mol [1]

b 0.25 mol [1]
 (0.5 mol I₂ reacts for every mole of HI formed. So 0.75 mol I₂ reacted. Therefore mol I₂ at equilibrium = 1.00 – 0.75 mol.)

c i $K_c = \frac{[HI]^2}{[H_2][I_2]}$ [1]

ii $K_c = \frac{(0.75)^2}{(0.25) \times (0.25)} = 9.00$ [1]
 (no units) [1]

[Total: 9]

5 a Any three of:
 closed system;
 reactants and products at constant concentration / macroscopic properties constant;
 equilibrium is dynamic / products are forming reactants at same time as reactants are forming products;
 rate of forward reaction = rate of backward reaction [3]

b i $K_c = \frac{[NO_2]^2}{[N_2O_4]}$ [1]

ii $[N_2O_4] = \frac{1-0.2}{1} = 0.8 \text{ mol dm}^{-3}$ [1]

$[NO_2] = \frac{0.4}{1} = 0.4 \text{ mol dm}^{-3}$ [1]

$K_c = \frac{(0.4)^2}{(0.8)} = 0.2$ [1]

mol dm⁻³ [1]

c i Increasing pressure has no effect on K_c ; [1]
 increasing pressure increases the number of moles of NO₂ so that K_c remains constant. [1]

ii Increasing temperature increases K_c ; [1]
 reaction is endothermic so higher yield at higher temperature. [1]

[Total: 12]

6 a ethanoic acid = 0.8 mol dm⁻³ [1]

ethanol = 0.8 mol dm⁻³ [1]

b ethanoic acid = 0.24 mol dm⁻³ [1]

ethanol = 0.24 mol dm⁻³ [1]

c ethyl ethanoate = 0.56 mol dm⁻³ [1]

water = 0.56 mol dm⁻³ [1]

d i $K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$ [1]

ii $K_c = \frac{(0.56) \times (0.56)}{(0.24) \times (0.24)} = 5.44$ [1]

iii all the concentration terms in the equilibrium expression cancel [1]

e no change [1]

f less ethyl ethanoate; [1]

position of equilibrium shifted to the left [1]

[Total: 12]

7 a i oxonium / hydronium / hydroxonium [1]

ii equation 1: HCl is the acid and H₂O the base [1]

equation 2: NH₃ is the base and H₂O the acid [1]

iii Amphoteric means can act as an acid or base / as proton donor or acceptor; [1]

in equation 1, water accepts a proton from HCl; [1]

therefore water is a base; [1]

in equation 2, water donates a proton to NH_3 ; [1]

therefore water is an acid. [1]

b H_2Cl^+ is the conjugate acid of HCl , and I^- is the conjugate base of HI . [2]

c i Strong acid is (almost) completely ionised in water; [1]

weak acid is only slightly ionised in water. [1]

ii accept between pH 2 and 4 [1]

iii $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons$ [2]

[1 mark for correct products and reactants; 1 mark for equilibrium sign]

[Total: 15]

8 a 32.0 mol nitrogen [1]

96.0 mol hydrogen [1]

b 8.00 moles nitrogen + 24.0 moles hydrogen \rightarrow 16 moles ammonia [1]

c $K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$ [1]

d $K_c = \frac{(16)^2}{(32)(96)^3} = 9.04 \times 10^{-16}$ [1]

$\text{dm}^6 \text{ mol}^{-2}$ [1]

e no change [1]

f decreases [1]

[Total: 8]

9 a $K_p = \frac{P_{\text{C}_2\text{H}_5\text{OH}}}{P_{\text{C}_2\text{H}_4} \times P_{\text{H}_2\text{O}}}$ [1]

b Pa^{-1} [1]

c i $[7.00 - (4.20 + 1.50)] \times 10^6 = 1.30 \times 10^6 \text{ Pa}$ [1]

ii $K_p = \frac{(1.30 \times 10^6)}{(1.50 \times 10^6) \times (4.20 \times 10^6)} = 0.206 \times 10^{-6} = 2.06 \times 10^{-7} (\text{Pa}^{-1})$ [1]

d Substances cannot enter or leave a closed system. [1]

e More gas molecules on the left; so position of equilibrium shifts left; increasing pressure until K_p restored. [1]

f As temperature increases, % of ethene converted decreases; [1]

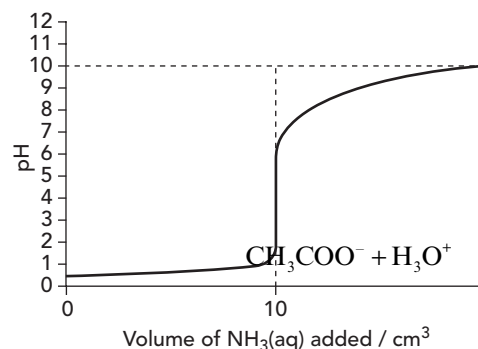
backward reaction favoured by increase in temperature; [1]

backward reaction favoured if forward reaction is exothermic [1]

so sign of enthalpy change is negative. [1]

[Total: 12]

10 a



initial pH less than 1 (as strong acid pH of 0.7); [1]

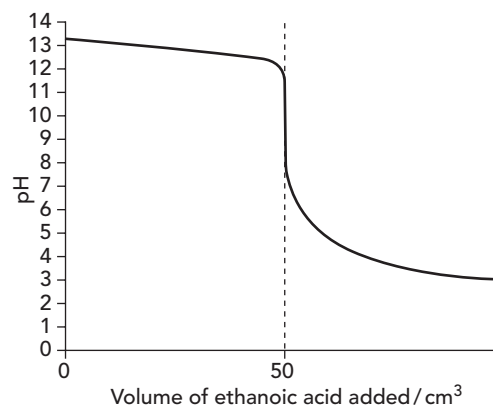
Vertical line at 10 cm^3 to show maximum pH change when the volume of ammonia is near the equivalence point; [1]

line tails off to about pH 10 as ammonia is a weak base. [1]

b Methyl orange will change colour at a point corresponding to the maximum pH change at neutralisation; [1]

phenolphthalein changes colour between pH 8 and 10, which does not correspond to the steepest slope of the graph (it would change colour after neutralisation, and it would change very slowly). [1]

c



initial pH at about 13.3 (as strong base); [1]

vertical line at 50 cm^3 to show maximum pH change when the

volume of ethanoic acid is near the equivalence point (the ethanoic acid is half the concentration of the sodium hydroxide); [1]

line tails off to about pH 3 as ethanoic acid is a weak acid. [1]

- d Phenolphthalein will change colour at a point corresponding to the maximum pH change at neutralisation; [1]

methyl orange changes colour between pH 3 and 4.5, which does not correspond to the steepest slope of the graph (it would change colour after neutralisation, and it would change very slowly). [1]

- e Bromocresol green is suitable for the HCl/NH₃ titration; [1]

as its pK_a value is within the range 4–6 (so its colour will change at the end-point); [1]

neither indicator is suitable for the ethanoic acid/sodium hydroxide titration; [1]

as neither pK_a value is within the range 8–10, where the steepest pH change occurs. [1]

[Total: 14]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 9

Science in context

This activity introduces rate of reaction in terms of slow or fast reactions and widens the idea of rate to slow and fast biological processes. Slow and fast are relative terms but the idea that very slow reactions take a few days or more to complete and very fast ones are complete in a second or less could be a guide. It might be useful to arrange the groups so that there are learners taking biology in each group to help discuss the first question.

Foods which go bad quickly are usually those which have some water in them which then allows bacteria and fungi to grow. Although these appear to be slow reactions because it takes time to release sufficient enzymes into the growth medium to decompose it, enzyme-catalysed reactions are usually rapid and once decomposition of the food has started, rapid growth of the bacteria or fungus occurs. Foods which have some sugar in them are also likely to spoil quickly because the sugar serves as a good growth medium for bacteria and fungi. Some fresh foods may also have minute amounts of bacteria or fungal spores in them which 'spoil' them quickly. Fresh berries such as raspberries and fresh vegetables get fungal growths very rapidly and fresh fruits also 'spoil' easily. Tomatoes, peaches, mushrooms, cooked grains and yoghurt are also foods which readily go bad even in the refrigerator.

Methods of stopping food go bad are:

- Refrigeration: decreasing the rate of enzyme-catalysed reactions
- Freezing: has similar effect as refrigeration but affects the texture of many foods.
- Addition of preservatives: These slow bacteria or fungal growth. Examples are sulfur dioxide, sulfites (added to fruits and wine), sorbic acid (added to cheese), sodium nitrite (added to

preserved meats) and sodium nitrate (added to meat). Preservatives such as sodium nitrite, however, have been linked to 'blue baby syndrome' and they can also react at high temperatures with proteins to form harmful nitrosoamines.

- Pickling: Placing in vinegar. Many bacteria and fungi do not grow well if the pH is too acidic.
- Curing and drying: Dry food is less likely to go bad because bacteria and fungi require moisture. Curing often involves addition of salt. Salty conditions help dry the food. Many bacteria and fungi do not grow well in salty conditions.
- Canning: Storing foods in cans after cooking prevents air from entering. Most bacteria and fungi 'spoil' food need oxygen from the air for respiration.

Some animals lower their body temperature in cold seasons to conserve energy when there is little or no food available. This lowers the rate of the chemical reactions going on in the body so less energy is used. Hibernation may last days or months. Animals that hibernate include hedgehogs and ground squirrels.

Some reaction which are very fast include explosive reactions, e.g. the effect of a lighted splint on hydrogen gas and reactions involving ions. Learners should be able to make a list of ionic reactions which appear almost instantaneous, e.g. the addition of sodium hydroxide to iron(II) ions or the neutralisation of an alkali by the immediate addition of excess acid. Photolytic reactions, e.g. the conversion of chlorine molecules to chlorine atoms in the presence of ultraviolet light, often occur in picoseconds (link with activity in Chapter 22).

Slow reactions include rusting, hardening of resins, fermentation reactions and biological reactions such as decomposition of wood.

Self-assessment questions

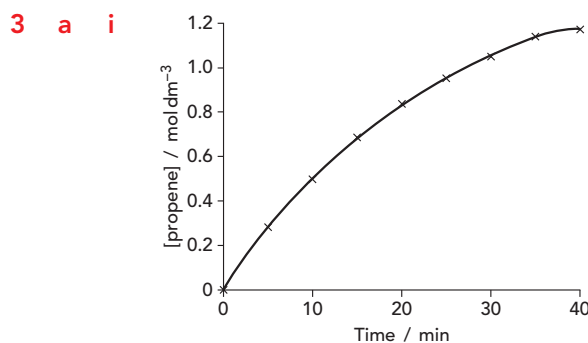
- 1 a** $0.254 \text{ g I}_2 = 0.254 / (2 \times 127)$
 $= 1.00 \times 10^{-3} \text{ mol}$; this is the change in number of moles in 1 hour;
 volume = 1 dm^3 , so the change in concentration is $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ in 1 hour.
 As 1 hour = 3600 seconds:
 rate = $1.00 \times 10^{-3} / 3600 \text{ s mol dm}^{-3} \text{ s}^{-1}$
 $= 2.78 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$
- b** $0.0440 \text{ g CH}_3\text{COOC}_2\text{H}_5 = 0.0440 / 88.0$
 $= 5.00 \times 10^{-4} \text{ mol}$; this is the change in number of moles in 1 hour;
 volume = 400 cm^3 so the change in concentration is:
 $5.00 \times 10^{-4} \times 1000 / 400$
 $= 1.25 \times 10^{-3} \text{ mol dm}^{-3}$ in 1 min
 As 1 hour = 60 minutes:
 rate = $1.25 \times 10^{-3} / 60 \text{ s mol dm}^{-3} \text{ s}^{-1}$
 $= 2.08 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$
- 2 a i** *Either:* Measure the decrease in electrical conductivity. As the reaction proceeds the iodide and hydrogen ions (which are charge carriers in aqueous solution) are converted to molecules (which do not carry charge).
Or: Measure the increase in colour of the solution by colorimetry. The reactants are colourless but the iodine produced is brown. *Or:* Sample the solution and titrate the sample with sodium thiosulfate.
- ii** Titrate small samples with standard strong alkali using a suitable acid-base indicator. As the reaction proceeds, the amount of methanoic acid formed increases.

iii Measure the volume of oxygen gas produced. This increases with time.

iv *Either:* Measure the decrease in electrical conductivity. As the reaction proceeds the bromate, bromide and hydrogen ions (which are charge carriers in aqueous solution) are converted to molecules (which do not carry charge).

Or: Measure the increase in colour of the solution by colorimetry. The reactants are colourless but the bromine produced is reddish-brown.

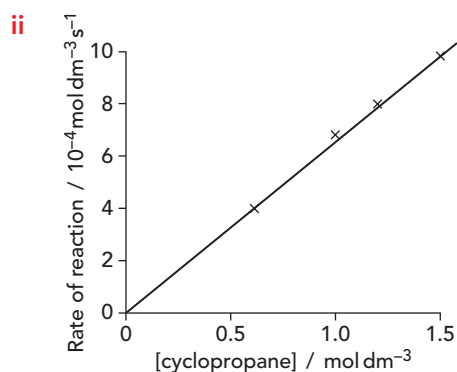
b Change in temperature changes the reaction rate markedly. Increase in temperature increases the value of the rate constant.



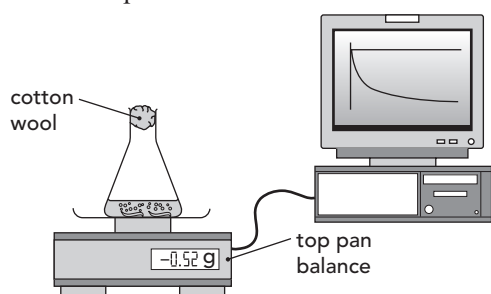
ii $6.68 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

b initial rate = $9.98 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
 at 0.3 mol dm^{-3} : rate = $8.00 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
 at 0.9 mol dm^{-3} : rate = $4.00 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

c i when [propene] = 0.00 [cyclopropane] = $1.50 - 0.0 = 1.50 \text{ mol dm}^{-3}$
 when [propene] = 0.30 [cyclopropane] = $1.50 - 0.30 = 1.20 \text{ mol dm}^{-3}$
 when [propene] = 0.50 [cyclopropane] = $1.50 - 0.50 = 1.00 \text{ mol dm}^{-3}$
 when [propene] = 0.90 [cyclopropane] = $1.50 - 0.90 = 0.60 \text{ mol dm}^{-3}$



4 a For example:



- b i the minimum energy required for a reaction to occur when reactant particles collide
- ii a substance that speeds up a reaction by providing an alternative route with a lower activation energy; a catalyst also remains chemically unchanged at the end of the reaction
- c option **B** – increasing the proportion of particles with energy greater than the activation energy
- d Increasing the surface area will expose more particles to attack by reactant particles, resulting in more frequent collisions, thereby increasing the rate of reaction.

5 a option **B** – 10 cm^3 of 1.0 mol dm^{-3}

- b The more concentrated the acid, the greater the number of hydrogen ions dissolved in a given volume of solution, resulting in an increased frequency in collisions between the hydrogen ions in solution and the

carbonate ions in the marble chips. The volume of acid will not affect the initial rate of the reaction.

6 C

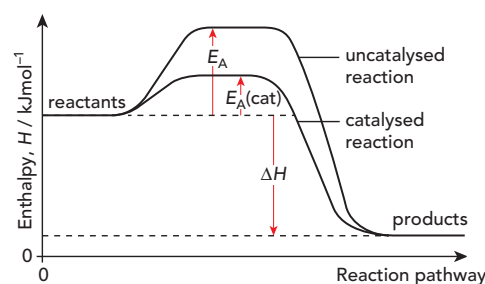
7 a The Boltzmann distribution is a frequency graph showing the numbers of particles with different energies in a sample at a given temperature.

- b At the higher temperature the particles have more energy and are moving around more quickly. This increases the rate of the reaction for two reasons: it increases the frequency of collisions and it increases the chances of successful / effective collisions occurring as the proportion of particles exceeding the activation energy increases. The second factor is more important.

8 D

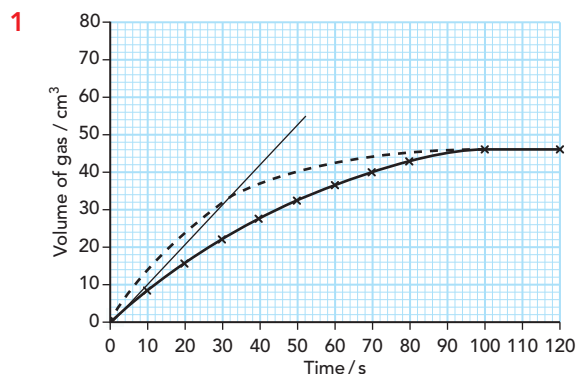
- 9 a i It is heterogeneous because the reactants (which are gases) are in a different phase to the catalyst (which is a solid).
- ii A catalyst lowers the activation energy of the reaction so, although it does not affect the distribution of energies of reactant molecules, there is a greater number of molecules in the sample with energy equal or greater than the activation energy needed to react.

b For example:



(or the equivalent energy profile diagram for an exothermic reaction)

Exam-style questions



- a Correct labelling of axes with units [1]
plotting points correctly [1]
curve of best fit drawn [1]

- b initial gradient drawn as tangent to 0-0 [1]
rise/ run drawn as triangle [1]
 $52/50 = 1.04 \text{ cm}^3 \text{ s}^{-1}$ (allow error carried forward from incorrect gradient) [1]

- c rate decreases with time [1]
the gradient of the curve gets shallower [1]

- d Draw a tangent to the curve at 40 s [1]
calculate the rise / run [1]

- e $\text{moles CaCO}_3 = \frac{0.1875}{100.1} = 1.873 \times 10^{-3} \text{ mol}$ [1]
 $\text{moles HCl} = \frac{40}{1000} \times 0.100$
 $= 4 \times 10^{-3} \text{ mol}$ [1]

Using the 1:2 stoichiometry in the equation for HCl to be in excess moles needs to be $2 \times \text{moles CaCO}_3$ [1]

$1.873 \times 10^{-3} \text{ mol (CaCO}_3\text{)}$ is less than $2 \times 10^{-3} \text{ mol HCl} / 1.873 \times 2 \text{ mol (CaCO}_3\text{)}$ is less than $4 \times 10^{-3} \text{ mol HCl}$ so CaCO_3 is limiting [1]

- f Dashed line on graph shows what is expected. Initial gradient steeper [1]
line levels off at same final volume [1]

[Total: 16]

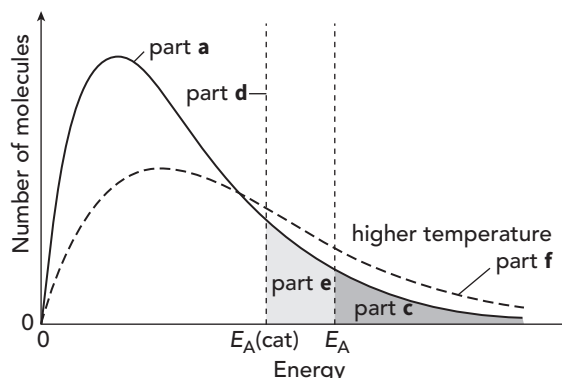
- 2 a more particles per cm^3 / particles closer together; [1]
so more frequent collisions [1]

- b more particles per cm^3 / particles closer together / more frequent collisions [1]
c more surface area exposed to reaction; [1]
therefore more frequent collisions [1]
d The higher the temperature, the greater the average kinetic energy of the particles. [1]
This leads to more frequent collisions. [1]
More of the reactant particles possess the activation energy. [1]
The frequency of successful / effective collisions increases. [1]

[Total: 9]

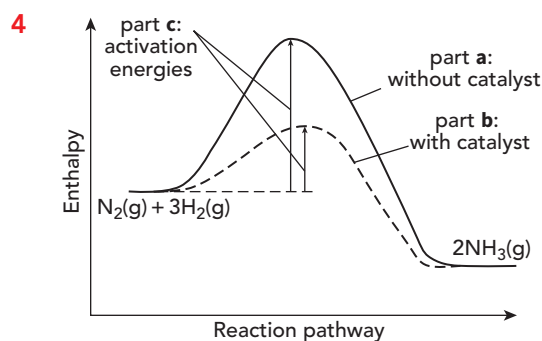
- 3 When sketching graphs like these, it is important to attend to all the details, as follows:

- Part a: the line starts at the origin, it rises to a curved peak then descends towards the bottom axis, but doesn't touch it or cut it. The line is not symmetrical. The label on the left-hand axis is 'number of molecules' or 'number of molecules with energy E ', not 'number of molecules with energy E_A '.
- Part c: the Boltzmann distribution is most relevant for a slow reaction, i.e. one with a high value of E_A , so put your E_A well over to the right.
- Part f: your second curve should also start at the origin. It should rise at a more shallow angle to the original curve. Its peak should be lower and to the right of the peak of the original curve. It should cross the original curve then stay above the original curve as it descends.



- a** x -axis = energy [1]
 y -axis = number of molecules [1]
 graph line rises from (0, 0) to peak [1]
 tails off but doesn't reach x -axis [1]
- b** The minimum energy [1]
 for a collision to be effective. [1]
- c** E_A shown as vertical line; [1]
 area under graph to the right of E_A line is shaded [1]
- d** labelled vertical line to the left of the original E_A line [1]
- e** area under graph to the right of $E_A(\text{cat})$ line is shaded [1]
- f** Graph line starts at (0, 0), has lower slope and peak than original line so its peak is moved to the right; [1]
 tails off above original line. [1]

[Total: 12]



- a** reactant line and product line linked by 'up and over' curve with product line lower than reactant line [1]
- b** as part a, but height of 'up and over' curve is lower [1]
- c** Activation energy shown as vertical distance from reactant line to top of curve. [1]

[Total: 3]

- 5** It may help with this question to draw an energy profile diagram first.

- a** $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ [3]
 [1 mark for correct formulae; 1 mark for balancing; 1 mark for state symbols]
- b** $E_A = +335 - 92 = +243 \text{ kJ mol}^{-1}$ [3]
 [1 mark for use of these quantities; 1 mark for subtracting 92 from 335; 1 mark for correct answer with units]
- c** It will lower the activation energy. [1]

[Total: 7]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 10

Science in context

This activity shows how the idea of periodicity of chemical properties developed over a period of time and how scientists build upon the ideas of other scientists. A brief time line is given below:

- 1801–1810: John Dalton developed an atomic theory (perhaps partly based on ideas of other scientists). This included the ideas that:
 - Elements are made of extremely small particles (atoms).
 - Atoms of the same element have the same size, mass and other properties.
 - Atoms cannot be subdivided.
 - Atoms of different elements combine in simple whole-number ratios to form compounds.
 - In chemical reactions atoms are rearranged.
- 1817–1829: Johann Döbereiner was the first to group similar elements together and link them with atomic weights (atomic masses). E.g. calcium, strontium and barium have similar properties and strontium has an atomic 'weight' which is the mean of the atomic 'weight' of calcium and barium.
- 1860: Cannizzaro and Stas developed accurate ways of determining atomic 'weights'.
- 1860s: de Chancourtois tried to correlate chemical properties with atomic 'weights'. He plotted atomic 'weights' on a 45° spiral on the surface of an upright cylinder. One turn round the cylinder was 16 atomic 'weight' units.
- 1863–1866: John Newlands arranged the elements in 'octaves' and noted that elements with similar properties were separated by intervals of 8 elements.
- 1860s: Lothar Meyer plotted atomic volume against atomic number and found a periodic variation in the properties of the elements.
- 1869: Mendeleev published his first Periodic Table as a list in 6 columns, the first column H and Li, the second column Be, B, C, N, O, F and Na and the third from Mg to In. The rest of the columns were rather muddled.
- 1872: Mendeleev published his revised Periodic Table in 7 groups which has similarities to our modern Periodic Table.

At the end of the main text, there is a question about the element of atomic number 117. Tennesine is a Group 17 element. It is named with the suffix *-ine* for consistency with the names of the other halogens. Only a few atoms of this radioactive element have ever been noted and these decay very rapidly.

Some points arising from the discussion questions may include:

- Learners should be aware of the order of metals in the reactivity series from their previous courses. Lead and copper are low in the reactivity series and so were relatively easy to extract by heating with charcoal (carbon). Copper is also found native in small amounts. Sodium and potassium are high in the reactivity series and so cannot be extracted with carbon (unless the temperature is extremely high). Reactive metals are extracted by electrolysis. Learners should realise that although the concept of electricity had been known for many centuries, the production of a steady electric current was not possible until the much later. The process of electrolysis only invented in the early 1800s.
- The noble gases are inert and so were not isolated until 1890s. Although Cavendish

had isolated a mixture of inert gases from the air in 1784, this was not followed up until accurate balances for weighing were developed when a small difference was noted between the density of nitrogen prepared from chemical sources (1.2505 g dm^{-3}) and nitrogen prepared from the air (1.2572 g dm^{-3}). Isolation also depended on the separation by liquefaction of air, which did not take place until 1883, and, even then, scientists were not expecting anything other than nitrogen and oxygen to be separated.

Radioactive elements decay rapidly into other substances, eventually to lead, so it was difficult to study these elements because many were not stable for more than a few minutes or seconds.

The last section of the activity introduces the role of women scientists in the discovery of some elements in the last century. This could serve as a starting point for a discussion about why there are fewer women in science and what can be done to address this. Although women are well represented in Medicine, they are less so in Chemistry and Physics research. Only one-third of researchers in North America are women. Well known cases of discrimination are: Marie Curie (did not at first get full credit for her work in radioactivity since she worked with husband Pierre) and Rosalind Franklin (her role in the elucidation of the structure of DNA was belittled at the time).

The following points could be discussed but care is needed: Fixed views related to kinship, heredity, religious factors and conscious bias may cause difficulties with the discussion. The following could be discussed:

- Historical bias: Women responsible for child rearing and household jobs.
- Institutional bias: Science has been traditionally seen as a man's world.
- Unconscious bias: Accepting that things must change but not prepared to facilitate the changes for no particular reason: 'Doesn't feel right'.
- Education: In many places women did / do not have the same educational opportunities or some subjects are seen as more 'male orientated'.
- Peer pressure / Group pressure: Especially in the past, the presence of male-dominated groups (clubs / societies) tended / tends to reinforce stereotypes.
- Workplace structures not in place: Minimal or no opportunities for childcare at workplace.
- Advancement opportunities: If women take time out for childcare, they may make slower progression through pay grades / positions of responsibility even though they are of equal competence.

Self-assessment questions

- 1
 - a bromine
 - b If they are put in atomic mass order, tellurium (Te) and iodine (I) do not line up with similar elements in the same groups. Mendeleev reversed their order.
 - c The s-block elements all have electronic configurations with the outermost electrons in an 's' subshell (s^1 in Group 1 or s^2 in Group 2). The Group 17 elements have electronic configurations with the outermost electrons in a 'p' subshell (they are all p^5).
- 2
 - a A lithium atom is larger than a fluorine atom. A fluorine atom has six more electrons than a lithium atom and these occupy the same principal quantum shell as lithium's single outer electron. This means that the shielding effect is approximately the same in both atoms but the nuclear charge of a fluorine atom (9+) is greater than that of lithium (3+), which pulls fluorine's outermost electrons closer to the nucleus than lithium's.
 - b A lithium atom is larger than a Li^+ ion. The positively charged Li^+ ion has lost its outer shell electron (effectively removing the second principal quantum shell) from the Li atom, so Li^+ ions are much smaller than Li atoms.
 - c An oxygen atom is smaller than an O^{2-} ion. The O^{2-} ion has gained two extra electrons in the third principal quantum shell while keeping the same nuclear charge. The third shell in an oxygen atom contains six electrons, which repel each other. In an O^{2-} ion the third shell contains eight electrons, so there is more repulsion, increasing the radius. Therefore O^{2-} ions are larger than O atoms.
 - d A nitride ion, N^{3-} , is larger than a fluoride ion, F^- . An N^{3-} ion has a smaller positive nuclear charge (7+) than an F^- ion (9+).

As the outermost electrons are in the same principal quantum shell in both anions, they are not held as tightly in a N^{3-} ion, making it larger than an F^- ion.

- 3 a** Sulfur has a simple molecular structure with relatively weak van der Waals' forces between its S_8 molecules, whereas silicon has a giant molecular structure with a giant lattice of silicon atoms bonded throughout its structure by strong covalent bonds. Therefore it takes a lot less energy to overcome the van der Waals' forces between sulfur molecules than it does to break the covalent bonds between silicon atoms.
- b** S_8 molecules contain more electrons than Cl_2 molecules, so there are greater van der Waals' forces between S_8 molecules than there are between Cl_2 molecules.
- c i** Magnesium has free delocalised electrons, which can carry electrical charge through its giant metallic structure. Phosphorus has a simple molecular structure; each molecule has no overall electrical charge and the electrons are unable to move from molecule to molecule.
- ii** Each magnesium atom donates two electrons into the 'sea' of delocalised electrons, whereas each sodium atom only donates one electron, making more electrons available to carry the charge through the metal in magnesium.
- 4 a** In general, the first ionisation energies increase across Period 3.
- b** Although aluminium has a greater nuclear charge than magnesium, the outer electron lost in its first ionisation is removed from a 3p orbital, which is slightly further away from the nucleus than the 3s orbital from which magnesium loses its first electron. Therefore the first electron removed is not held as strongly in aluminium compared with magnesium.
- c** Although sulfur has a greater nuclear charge than phosphorus, the first electron it loses comes from a 3p orbital that is occupied by a pair of electrons, whereas phosphorus loses its first electron from a singly occupied 3p orbital. It is the mutual repulsion between the 3p electron

pair in sulfur that makes it slightly easier to remove than the first electron from phosphorus.

- d** A value lower than 966 kJ mol^{-1} but higher than 800 kJ mol^{-1} (actual value is 941 kJ mol^{-1}).
- 5 B**
- 6 a i** $4\text{Li(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{Li}_2\text{O(s)}$
- ii** $2\text{Li(s)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{LiCl(s)}$
- b i** $\text{Ca(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2\text{(aq)} + \text{H}_2\text{(g)}$
- ii** Calcium hydroxide is more soluble in water than magnesium hydroxide, so more hydroxide ions per unit volume are in the solution formed from calcium.
- 7 a i** covalent bonding and giant molecular structure (or giant covalent structure)
- ii** $\text{GeO}_2\text{(s)} + 2\text{NaOH(aq)} \rightarrow \text{Na}_2\text{GeO}_3\text{(aq)} + \text{H}_2\text{O(l)}$
- iii** no reaction / remains unchanged / does not dissolve
- b i** $\text{K}_2\text{O(s)} + \text{H}_2\text{O(l)} \rightarrow 2\text{KOH(aq)}$
- ii** $\text{K}_2\text{O(s)} + 2\text{HNO}_3\text{(aq)} \rightarrow 2\text{KNO}_3\text{(aq)} + \text{H}_2\text{O(l)}$
- iii** ionic bonding and giant ionic structure
- 8 C**
- 9 a i** Group 15
- ii** hydrolysis
- iii** hydrogen chloride gas
- b** Group 1

Exam-style questions

- 1 a** When the property is plotted against atomic number [1]
it shows a pattern that is repeated in other periods. [1]
- b i** first ionisation energy [1]
This question is about ionisation energies. Learn the list of possible explanations for different ionisation energies:
- different nuclear charge
 - electron in a different shell (so distance is not the same)

- electron in a different subshell (so distance is not the same)
 • different amount of shielding
 • spin-pair repulsion.
- ii** Moving across a period the outermost electron shell fills up but no new shells are added; [1]
 at the same time the nuclear charge increases. [1]
 Therefore the attractive force on each electron in the outer shell increases; [1]
 making it harder to remove an electron. [1]
- [Total: 7]**
- 2 a** It shows a repeating pattern going across each period. [1]
- b i** Silicon is a giant covalent structure; [1]
 all the bonds are strong covalent bonds. [1]
 Phosphorus is a simple molecular substance; [1]
 molecules held together by weak intermolecular forces (van der Waals' forces). [1]
- ii** The structure and bonding in sodium and aluminium is giant metallic; [1]
 the charge on the metal ions in aluminium is greater than that in sodium. [1]
 Each aluminium atom donates three electrons into the 'sea' of delocalised electrons, whereas each sodium only donates one electron; [1]
 therefore, in aluminium there is more attraction between the positive ions and delocalised electrons; [1]
 therefore, more energy is needed to separate the ions and melt aluminium. [1]
- [Total: 10]**
- 3 a i** It decreases across the period. [1]
- ii** Moving across a period, the outermost electron shell fills up but no new shells are occupied; [1]
 at the same time the nuclear charge increases; [1]
 therefore the attractive force on each electron in the outer shell increases; [1]
 thus the electrons are pulled in, decreasing the atomic radius. [1]
- b i** It increases down the group. [1]
- ii** As the group is descended, electron shells are added to the structure. [1]
- [Total: 7]**
- 4 a i** neutral [1]

$$\text{NaCl(s)} \xrightarrow{\text{Water}} \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$$
 [1]
- ii** acidic [1]

$$\text{SO}_3(\text{g}) + \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{SO}_4(\text{aq})$$
 [1]
- iii** basic / alkaline [1]

$$\text{Na}_2\text{O(s)} + \text{H}_2\text{O(l)} \rightarrow 2\text{NaOH(aq)}$$
 [1]
- iv** acidic [1]

$$\text{PCl}_5(\text{l}) + 4\text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{PO}_4(\text{aq}) + 5\text{HCl(g or (aq))}$$
 [1]
- b i**
$$\text{Mg(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Mg(OH)}_2(\text{aq}) + \text{H}_2(\text{g})$$
 [1]
- ii** 10–12 [1]
 weakly alkaline as the magnesium hydroxide is only sparingly soluble [1]
- c i**
$$\text{PCl}_3(\text{l}) + 3\text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{PO}_3(\text{aq}) + 3\text{HCl(g or (aq))}$$
 [1]
- ii** 1–3 [1]
- iii** white fumes given off [1]
- [Total: 14]**

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 11

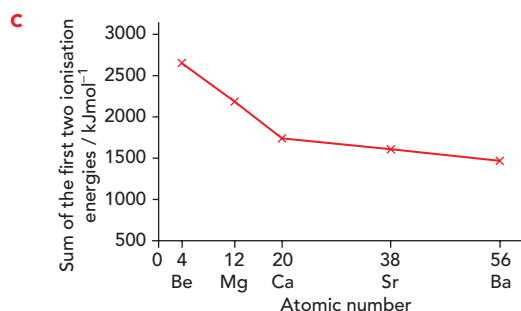
Science in context

- 1 Learners could raise the following environmental impacts:
- scar on landscape made by limestone quarry
 - loss of habitats for wildlife due to quarrying
 - noise pollution of explosions when mining limestone
 - dust in atmosphere (from extraction of the rock and its subsequent manufacture into cement powder)
 - atmospheric pollution from diggers and lorries transporting the limestone and its products.
- 2 $\text{Ca}(\text{OH})_2(\text{aq}) + 2\text{HNO}_3(\text{aq}) \rightarrow \text{Ca}(\text{NO}_3)_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
- 3 Points raised should include:
- concrete is the most common building material in the world and the consequences of not using it for housing, transport (roads and bridges) would be huge
 - having the correct pH of soil is essential for crops grown world-wide – so the importance is in feeding populations.

- d i about 700 °C (below 714 °C)
 ii about 4.5 g cm⁻³ (above 3.5 g cm⁻³)
 iii 2.18–2.19 nm
- 2 a i B
 ii $\text{Ca} \rightarrow \text{Ca}^{2+} + 2\text{e}^-$
 iii The oxidation number increases by 2 / changes from 0 to 2. The calcium atom has been oxidised, as it loses 2 electrons when it becomes the calcium ion.

b

Group 2 element	Sum of first two ionisation energies / kJ mol ⁻¹
beryllium (Be)	2660
magnesium (Mg)	2186
calcium (Ca)	1740
strontium (Sr)	1608
barium (Ba)	1468



Self-assessment questions

- 1 a The melting points generally decrease down the group.
magnesium
- b A new (principle quantum) shell of electrons is occupied with each new period.
- c i 2+
 ii smaller, as the outer (principle quantum) shell has been removed
- d The 'sum of the first two ionisation energies' decreases so it takes less energy to remove the two outer shell electrons; so this would mean that the 2+ ions are easier to form; and so the elements get more reactive going down the group.

- 3 a i $2\text{Sr(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{SrO(s)}$
 ii $\text{SrO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Sr(OH)}_2\text{(aq)}$
 b i $\text{Ba(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Ba(OH)}_2\text{(aq)} + \text{H}_2\text{(g)}$
 ii pH 11–14
 c i Ra^{2+}
 ii RaO ; Ra(OH)_2
 iii 450–480 kJ mol⁻¹
 iv more reactive than Ba
 v higher pH than $\text{Ca(OH)}_2\text{(aq)}$
 vi less soluble than SrSO_4
 vii $\text{RaO(s)} + 2\text{HCl(aq)} \rightarrow \text{RaCl}_2\text{(aq)} + \text{H}_2\text{O(l)}$

viii A white precipitate forming

- d 1.5×10^{-3} moles of Ca(OH)_2 dissolve in 100 cm³

Therefore in 1 cm³ of solution there will be

$$\frac{1.5 \times 10^{-3}}{100} \text{ moles dissolved}$$

So in 50 cm³ there will be

$$\frac{1.5 \times 10^{-3}}{100} \times 50 \text{ moles dissolved}$$

$$\text{Multiplying } \frac{1.5 \times 10^{-3}}{100} \times 50 \text{ moles of}$$

Ca(OH)_2 by its relative formula mass, i.e. $40.1 + (16.0 + 1.0) \times 2$, will give the mass of calcium hydroxide dissolved in 50 cm³:

$$\left[\frac{(1.5 \times 10^{-3})}{100} \times 50 \right] \times 74.1 \text{ g}$$

$$= 5.6 \times 10^{-2} \text{ g (or 0.056 g)}$$

- 4 a i MgCO_3
 ii Because the charge on the magnesium ion is 2+, not 1+; the charge on the compound magnesium carbonate is neutral when the magnesium ion and carbonate ions combine in the ratio 1 : 1, as the carbonate ions each carry a 2- charge which is balanced out by the 2+ charges on the magnesium ions; hence the correct formula MgCO_3 .

- b $\text{BaCO}_3\text{(s)} + 2\text{HNO}_3\text{(aq)} \rightarrow \text{Ba(NO}_3)_2\text{(aq)} + \text{H}_2\text{O(l)} + \text{CO}_2\text{(g)}$
 c i calcium carbonate
 ii magnesium nitrate
 d i $\text{SrCO}_3\text{(s)} \xrightarrow{\text{heat}} \text{SrO(s)} + \text{CO}_2\text{(g)}$
 ii $2\text{Ba(NO}_3)_2\text{(s)} \xrightarrow{\text{heat}} 2\text{BaO(s)} + 4\text{NO}_2\text{(g)} + \text{O}_2\text{(g)}$

Exam-style questions

- 1 A [1]

- 2 a $1s^2 2s^2$ [2]

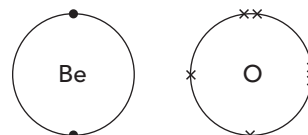
- b $2\text{Be} + \text{O}_2 \rightarrow 2\text{BeO}$ [2]

[1 mark for correct symbols and formulae; 1 mark for balancing]

- $2\text{Ra} + \text{O}_2 \rightarrow 2\text{RaO}$ [2]

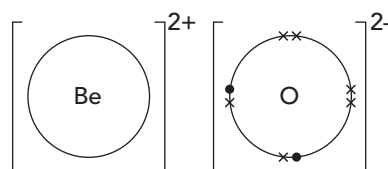
[1 mark for correct symbols and formulae; 1 mark for balancing]

- c before bonding: [2]



[1 mark for Be; 1 mark for O]

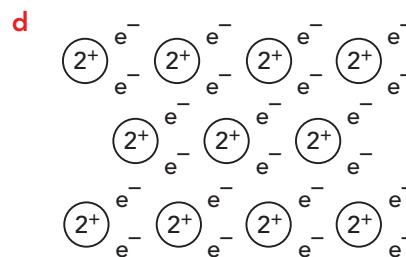
after bonding:



no electrons in the outer shell of Be^{2+} [1]

8 electrons in the outer shell of O^{2-} [1]

the two dots distinguished from the crosses in O^{2-} [1]



for layers of positive ions [1]

for 2^+ ions [1]

for e^- present between ions [1]

- e** In radium, the charge density on the positive ions is less than in beryllium; [1]
the attraction between the electrons and the positively charged ions is less. [1]
The metallic bond in beryllium is stronger than in radium and therefore a higher temperature is needed to melt it. [1]
[Total: 18]
- 3 a i** Ca(OH)_2 [1]
ii It neutralises acids; [1]
so lowers acidity of soil. [1]
- b** Barium hydroxide is more soluble (in water) than calcium hydroxide [1]
so produces a higher concentration of hydroxide ions in solution ($\text{OH}^-(\text{aq})$). [1]
[Total: 5]
- 4** Guidance: if the oxidation number of an element increases, it is oxidised in the reaction. If the oxidation number of an element decreases, it is reduced in the reaction. Note: if the oxidation number of an element increases and decreases, it disproportionates in the reaction (see Chapter 12).
- a** Sr is oxidised, Cl is reduced [1]
oxidation numbers:
reactants: Sr 0; Cl 0 [1]
products: Sr +2; Cl -1 [1]
- b** Sr is oxidised, H is reduced [1]
oxidation numbers:
reactants: Sr 0; H +1 [1]
products: Sr +2; H 0 [1]
- c** Mg is oxidised, C is reduced [1]
oxidation numbers:
reactants: Mg 0; C +4 [1]
products: Mg +2; C 0 [1]
[Total: 9]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 12

Science in context

This activity should make learners aware that the development of new compounds by chemists can be used in ways that benefit or harm humankind.

- If time, learners can research the uses of the halogens in greater detail to further inform their opinions.
- The learners can work in small groups for an initial discussion – the small group as opposed to the whole class discussion ensures that more learners can make an active contribution to the debate.
- Then each small group can appoint a spokesperson to feedback a report of their group's conclusions to the whole class.

Self-assessment questions

- The volatility of the halogens decreases down Group 17.
 - Fluorine is a gas; chlorine is a gas; bromine is a liquid; iodine is a solid.
 - The atomic radii increase down the group because one more (principle quantum) shell of electrons is occupied as each new period is started.
 - solid
 - black / dark grey
 - about 0.15 nm
- Chlorine atoms have a stronger attraction for an incoming electron entering its outer (principle quantum) shell than a bromine atom has; so it forms its 1^- ion more easily and is more reactive. This is because chlorine's outer shell is nearer to the attractive force of the nucleus, and an electron entering its outer shell will

also experience less shielding than bromine from the attraction of the positive nuclear charge. These two factors outweigh bromine's higher nuclear charge.

- $\text{Cl}_2(\text{aq}) + 2\text{KI}(\text{aq}) \rightarrow 2\text{KCl}(\text{aq}) + \text{I}_2(\text{aq})$
 - $\text{Cl}_2(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Cl}^-(\text{aq}) + \text{I}_2(\text{aq})$
 - purple / violet

- $\text{H}_2(\text{g}) + \text{At}_2(\text{g}) \rightleftharpoons 2\text{HAt}(\text{g})$
 - slow reaction
 - HAt decomposes easily on heating

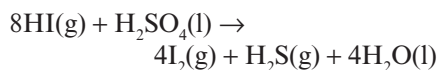
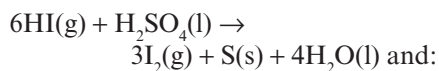
- Oxidation is loss of electrons. Chlorine atoms have a smaller atomic radius than bromine atoms. Therefore, an incoming electron will experience a stronger force of attraction from the nuclear charge of a chlorine atom, which is also less shielded by complete inner (principle quantum) shells of electrons.

- Dissolve the compound in dilute nitric acid and add silver nitrate solution. A cream precipitate should form; this is insoluble in dilute ammonia solution but will dissolve in concentrated ammonia solution.

- purple vapour given off, yellow solid produced
 - $$\text{KI}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{KHSO}_4(\text{s}) + \text{HI}(\text{g})$$

followed by oxidation of HI(g):

$$2\text{HI}(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{I}_2(\text{g}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \text{ and:}$$



- c** D, iodide. This is because the outer (principle quantum) shell electrons in an iodide ion are furthest from the attractive positive charge of the nucleus and are shielded by more complete inner shells of electrons than the other ions. These factors must overcome the attraction of the larger positive charge on the nucleus of an iodide ion for its outer shell electrons, as the iodide ion reacts most readily as a reducing agent.

Exam-style questions

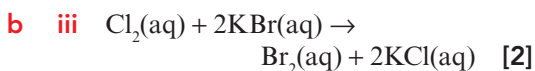
- 1 a** C [1]
b C [1]

[Total: 2]

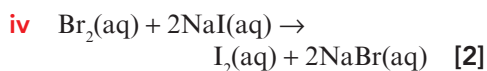
- 2 a** Br₂ [1]
b chlorine before bromine; [1]
 bromine before iodine [1]
c Iodine has the strongest intermolecular forces / van der Waals' forces; [1]
 because it has most electrons / biggest molecules. [1]

[Total: 5]

- 3 a i** no reaction [1]
ii no reaction [1]
iii reaction [1]
iv reaction [1]



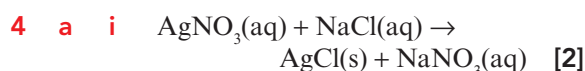
[1 mark for correct formulae; 1 mark for balancing]



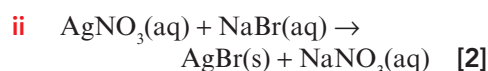
[1 mark for correct formulae; 1 mark for balancing]

- c** displacement / redox [1]
d strength as oxidising agent / reactivity is in order Cl > Br > I [1]
e e.g. for iii: chlorine is reduced; [1]
 bromide ions are oxidised [1]
f e.g. for iii: $\text{Cl}_2\text{(aq)} + 2\text{Br}^-\text{(aq)} \rightarrow \text{Br}_2\text{(aq)} + 2\text{Cl}^-\text{(aq)}$ [1]
g Chlorine has a higher tendency to gain electrons; [1]
 as Cl atoms have smaller radius. [1]

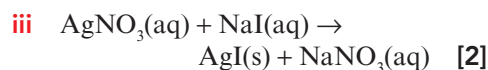
[Total: 15]



[1 mark for correct state symbols;
 1 mark for correct equation]



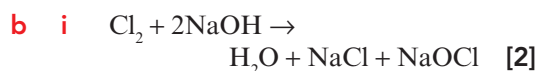
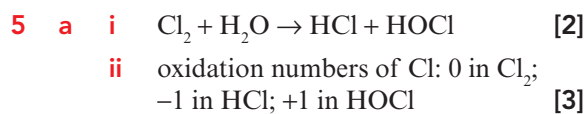
[1 mark for correct state symbols;
 1 mark for correct equation]



[1 mark for correct state symbols;
 1 mark for correct equation]

- b** precipitation: [1]
i white [1]
ii pale cream [1]
iii yellow [1]
c only AgCl would dissolve [1]
d AgCl and AgBr would dissolve [1]

[Total: 12]



[Total: 12]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 13

Science in context

This discussion should bring out the vital importance of manufactured fertilisers to feed the world's ever-growing population.

The suggestions to reduce the risk of eutrophication should include:

- education for farmers in using the correct amount of fertiliser for an area of crops so excess fertiliser is not used and subsequently leached out of the soil into waterways and groundwater.
- apply fertilisers at the most efficient time of year for uptake by crops
- maximise use of organic fertilisers.

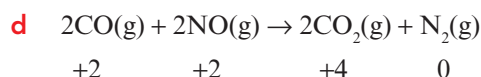
Self-assessment questions

- 1 a Nitrogen, N_2 , is such an unreactive gas because of the high bond energy needed to break its triple bond and start a reaction.
- b D
- c C
- Discussion of changing oxidation numbers of nitrogen in the 3-step complete oxidation, in which N is oxidised in each successive step by sharing increasing numbers of electrons with a more electronegative element (oxygen), changing its oxidation number (state) from zero to +5 in the whole process.
- 2 a NH_4^+
- b Both ammonia and the ammonium ion have four pairs of electrons around the N atom, with ammonia adopting a triangular pyramidal shape, with its three H atoms, compared with the

ammonium ion's tetrahedral shape, with its four H atoms.

The H—N—H bond angles are less in ammonia, about 107° , compared with the perfect tetrahedral angles of 109.5° in the ammonium ion. This is because of higher charge density of ammonia's lone pair of electrons on the central nitrogen atom. The lone pair has a greater repulsive force than bonding pairs of electrons, effectively squeezing the hydrogen atoms in ammonia closer together.

- c $NH_3(aq) + HNO_3(aq) \rightarrow NH_4NO_3(aq)$
- d i $(NH_4)_2SO_4(s) + 2NaOH(s) \rightarrow Na_2SO_4(s) + 2H_2O(l) + 2NH_3(g)$
- ii Because ammonium ions / NH_4^+ act as an acid (proton, H^+ , donor) and hydroxide ions / OH^- ions act as a base (proton, H^+ , acceptor).
- 3 a i e.g. lightning (during a thunderstorm)
- ii Car exhausts / power stations
- b i because PAN is not given off directly when a fuel is burned, but is produced in reactions of the primary pollutants in the atmosphere.
- ii photochemical smog
- iii sunlight / ultraviolet light
- c $SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$
- Then NO_2 is regenerated because NO reacts with oxygen in the air:
- $$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$$
- NO_2 can then go on to oxidise more sulfur dioxide, and so on, acting as a catalyst for the oxidation of SO_2 to SO_3 .



The oxidation number of oxygen is –2 throughout.

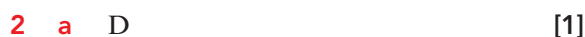
Carbon is oxidised as it changes from carbon monoxide (ox. no. +2) to carbon dioxide (in which its ox. no. has increased to +4).

Nitrogen in NO (ox. no. +2) is reduced to nitrogen gas (in which its ox. no. has been reduced to 0).

Exam-style questions

- 1 a** NH_3 [1]
b $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ [1]
c The ammonia molecule accepts a proton / H^+ ion [1]
 $\text{NH}_3\text{(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_4^+\text{(aq)} + \text{OH}^-\text{(aq)}$ [1]
d i NH_4^+ [1]
 ii tetrahedral [1]
 iii 109.5° [1]
e i NH_4Cl [1]
 ii NH_4NO_3 [1]
 iii $(\text{NH}_4)_2\text{SO}_4$ [1]
f i solids [1]
 ii $2\text{NH}_4\text{Cl} + \text{Ca(OH)}_2 \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O} + 2\text{NH}_3$ [1]
 iii A [1]
 iv Damp red litmus paper will turn blue [1]

[Total: 14]



c Nitrogen will have the higher 1st ionisation energy [1]

because electrons in its outer shell (outer principle quantum shell) are nearer to the attractive force of the nucleus, [1]

and will be shielded by fewer inner shell electrons, [1]

than the electrons in phosphorus, despite the larger positive nuclear charge of phosphorus [1]

d Phosphine has four pairs of electrons around its P atom, [1]

so these will achieve maximum separation in a tetrahedral shape around the central atom. So with its three H atoms, the molecule will adopt a triangular pyramidal shape. [1]

The H—P—H bond angles are less in phosphine (about 108°) compared with the perfect tetrahedral angle of 109.5° in the ammonium ion. [1]

This is because of higher charge density of ammonia's lone pair of electrons on the central nitrogen atom. The lone pair has a greater repulsive force than the three bonding pairs of electrons, effectively squeezing the hydrogen atoms in phosphine closer together. [1]

e i 3– [1]

ii Argon [1]

iii Giant ionic [1]

[Total: 13]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 14

Science in context

Learners can usefully work in pairs on this introductory activity. Preferably organise the pairs so that each pair has a learner who is studying Biology.

- The fact the intermolecular forces increase with the size of the molecules can be referred (see Chapter 4, Chemical bonding). The melting and boiling points of molecules generally increase as the size of molecules increases.
- Take the opportunity to revisit and describe the different types of intermolecular forces that can operate between organic molecules e.g. induced dipole–induced dipole (dispersion) forces, dipole–dipole forces, and hydrogen bonding.
- The small glucose molecules are soluble, so they can be transported in the blood. Very large molecules are insoluble and so don't cause osmosis issues. Starch is used for energy storage. Cellulose in plants provides structure to the plant and is also an essential source of roughage in our diet.

Self-assessment questions

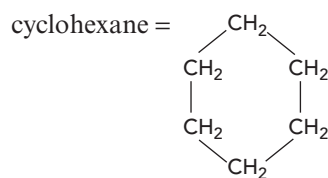
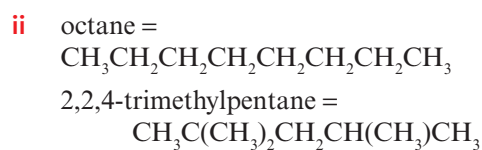
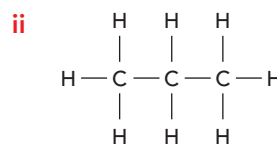
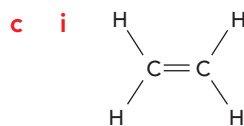
- 1 a i Find out the ratio of moles:

$$\begin{aligned} & \text{C : H} \\ & \frac{72}{12} : \frac{0.18}{1.0} \\ & = 0.06 : 0.18 \end{aligned}$$

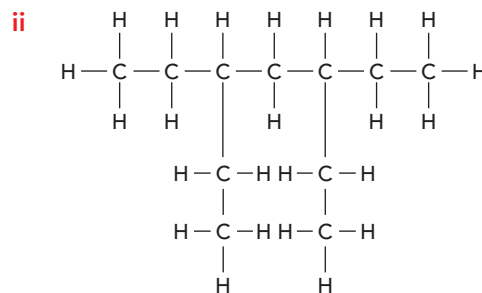
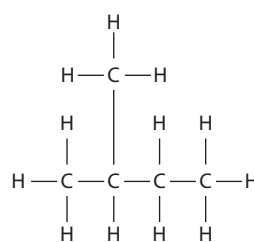
Simplest whole number ratio is:

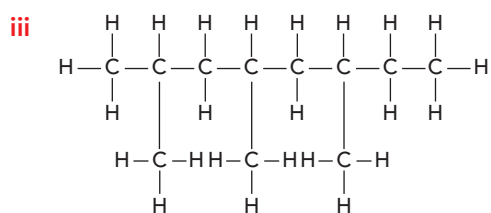
$$1 : 3$$

so empirical formula is CH_3

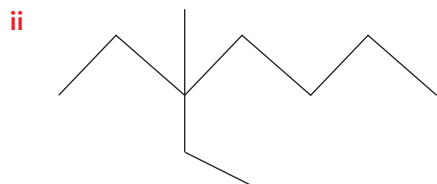


2 a i

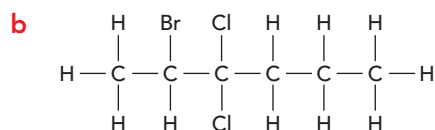
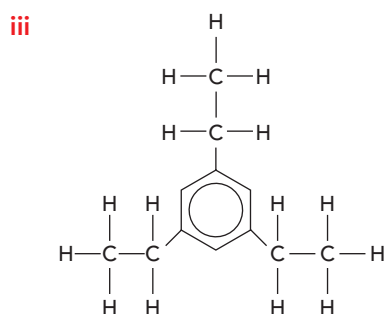
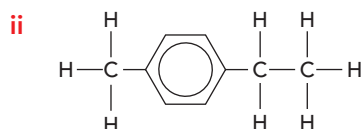
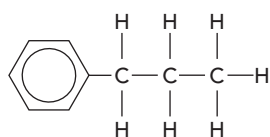




b i 3-ethyl-3-methylheptane

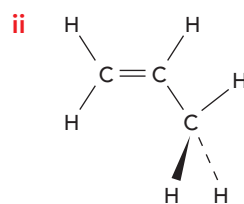
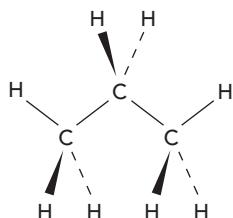


3 a i



c C

4 a i

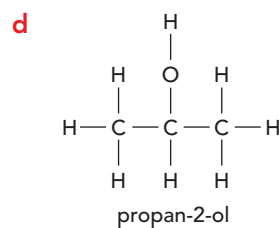
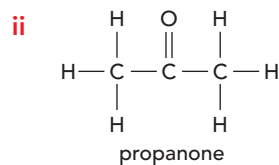
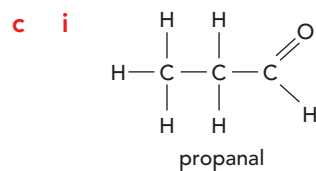
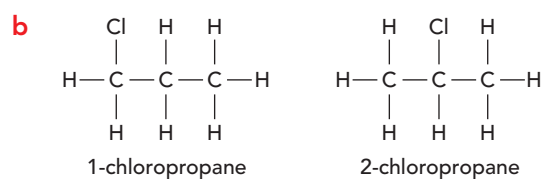


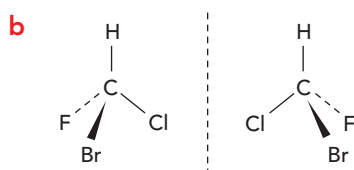
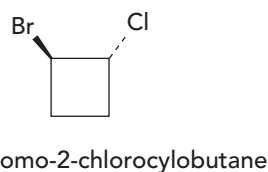
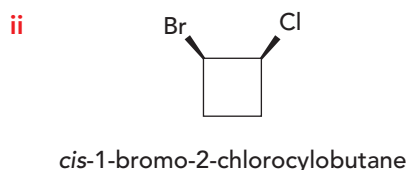
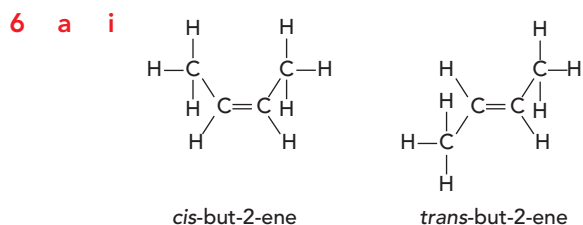
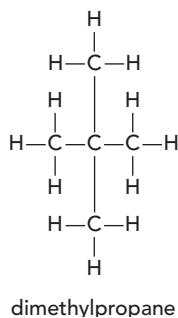
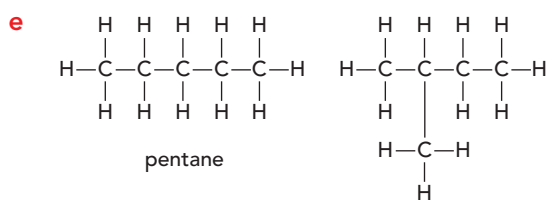
iii $\text{H}-\text{C}\equiv\text{C}-\text{H}$

b i D

ii $\text{A} = \text{sp}$, $\text{B} = \text{sp}^2$, $\text{C} = \text{sp}^3$

5 a 1,2-dibromopropane,
1,3-dibromopropane,
1,1-dibromopropane,
2,2-dibromopropane



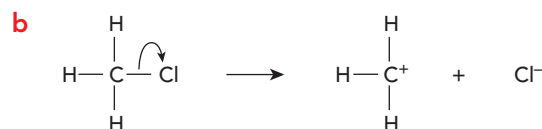
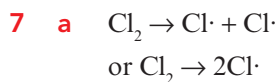


c i B

ii Chiral centre in bold -
 $(\text{CH}_3)_2\text{C}=\text{CHC}^*\text{HClCH}_3$

d methylcyclohexane has no chiral centres, and 2-methylcyclohexanone has one chiral centre. (Label the C atom in the ring bonded to the methyl group in 2-methylcyclohexanone).

e D, 8 chiral centres



c OH^-

d OH^- has lone pairs of electrons on its oxygen atom whereas H_2 and H^+ have no available lone pairs of electrons.

e H^+

f H^+ can accept a pair of electrons, whereas H_2 and OH^- cannot.

g Option B, because in this tertiary carbocation there are three alkyl groups, each tending to donate electrons to the positively charged carbon atom, reducing its charge density and making the ion energetically more stable than the primary (option C) or secondary (option A) carbocations.

8 a hydrolysis

b reduction

c elimination

d addition

e (free-radical) substitution

Exam-style questions

1 B [1]

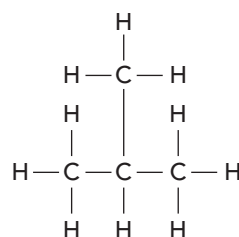
2 C [1]

3 a i Alkanes [1]

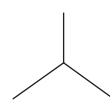
ii C_4H_{10} [1]

iii C_2H_5 [1]

iv [1]



v [1]



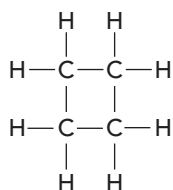
b i C [1]

ii 109.5° [1]

c i Alkenes [1]

ii D [1]

d i [1]



ii CH_2 [1]

[Total: 13]

4 a i carbon ($A_r = 12.0$): 85.7 g of C per 100 g of compound

$$\frac{85.7}{12.0} = 7.14 \text{ mol of C per 100 g of compound} \quad [1]$$

hydrogen ($A_r = 1.0$): 14.3 g of H per 100 g of compound

$$\frac{14.3}{1.0} = 14.3 \text{ mol of H per 100 g of compound} \quad [1]$$

$$\text{ratio} \frac{\text{number of atoms of H}}{\text{number of atoms of C}} = \frac{14.3}{7.14} = 2 \quad [1]$$

empirical formula = CH_2 [1]

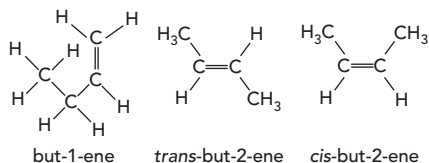
ii Relative molecular mass of empirical formula,
 $\text{CH}_2 = 12 + 2 = 14$

Relative molecular mass of unknown molecule = 56

So the number of units of the

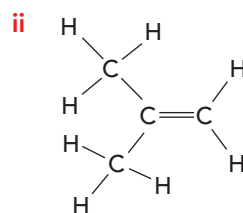
empirical formula is $\frac{56}{14} = 4$
So the molecular formula is $(\text{CH}_2) \times 4 = \text{C}_4\text{H}_8$ [1]

b i



[1 mark for each structure] [3]

[1 mark for each name] [3]



2-methylpropene

[1 mark for the structure, 1 mark for the name] [2]

[Total: 13]

5 a i 600 g of $\text{C}_2\text{H}_6 = \frac{600}{30} \text{ mol} = 20 \text{ mol}$ [1]

ii 20 mol [1]

iii 148.5 g of $\text{C}_2\text{H}_4\text{Cl}_2$
 $= \frac{148.5}{99} \text{ mol} = 1.5 \text{ mol}$ [1]

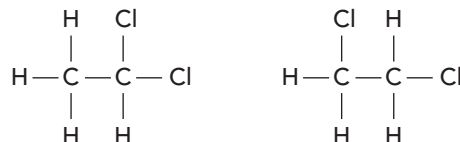
iv $\text{yield} = \frac{1.5}{20} \times 100\% = 7.5\%$ [1]

b 140 g of $\text{C}_2\text{H}_4 = \frac{140}{28} \text{ mol} = 5 \text{ mol}$ [1]

396 g of $\text{C}_2\text{H}_4\text{Cl}_2 = \frac{396}{99} \text{ mol} = 4 \text{ mol}$ [1]

$\text{yield} = \frac{4}{5} \times 100\% = 80\%$ [1]

c



1,1-dichloroethane 1,2-dichloroethane

[1 mark for each correct displayed formula; 1 mark for each correct name] [4]

d i **B** I is substitution [1]

ii **D** II is addition [1]

[Total: 13]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 15

Science in context

The main points discussed should include:

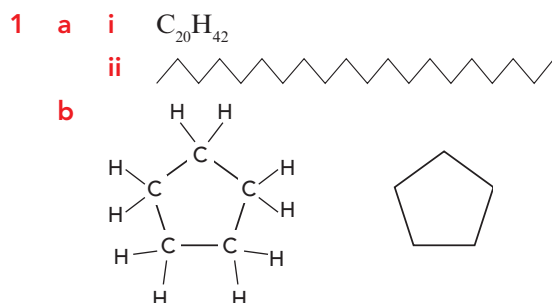
Difficulties, such as:

- limited range of electric cars before electric cells need recharging
- limited availability of recharging points
- will not solve pollution problems causing climate change, i.e. the release of carbon dioxide into the atmosphere, if the source of electricity for recharging comes from power stations run on fossil fuels
- reduced performance (although the technology is improving all the time, hence the introduction of high-speed electric racing cars)
- changing public opinion away from petrol and diesel cars.

Benefits, such as:

- less atmospheric pollution from electric cars
- hence reducing health problems caused by nitrogen oxides, carbon monoxide and unburnt hydrocarbon
- solves the problem of diminishing supplies of crude oil which is processed to provide petrol and diesel for internal combustion engines
- quieter than traditional vehicles.

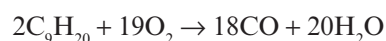
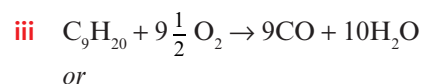
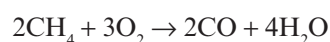
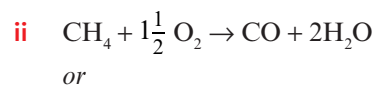
Self-assessment questions



d Two from: cyclopentane is a cyclic molecule, whereas pentane is a straight-chain molecule; pentane molecules have two more hydrogen atoms than those of cyclopentane; pentane molecules have two CH_3 groups, whereas cyclopentane molecules have only CH_2 groups.

2 a no change

b The non-polar alkane would not react with the charged ions in sodium hydroxide solution (nor with the polar water molecules).



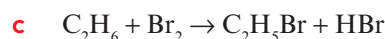
d i carbon monoxide and unburnt hydrocarbons

ii nitrogen oxides

iii carbon dioxide; enhanced greenhouse effect / global warming

3 a sunlight / ultraviolet light

b (free-radical) substitution



d A mixture of bromo-substituted ethane compounds are formed, not pure bromoethane, so it would need to be separated from the mixture.

e i initiation, propagation and termination

ii $\text{Br}_2 \rightarrow 2\text{Br}\cdot$

iii homolytic bond breaking

4 a ethene

b $\text{C}_{18}\text{H}_{36}$

c decane \rightarrow hexane + but-1-ene

d $\text{C}_9\text{H}_{20} \rightarrow \text{C}_7\text{H}_{16} + \text{C}_2\text{H}_4$

e Alkanes are non-polar so do not get attacked by electrophiles or nucleophiles. Alkenes are more reactive because they are attacked by electrophiles. Electrophiles are attracted to the area of high electron density around the alkenes' double bond / $\text{C}=\text{C}$ bond, accepting a pair of electrons from the double bond and forming a new bond.

5 a Platinum / nickel catalyst (finely divided), heat (140°C)

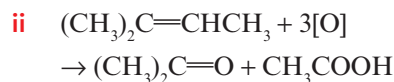
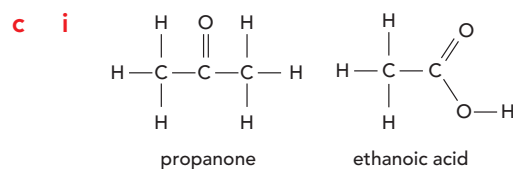
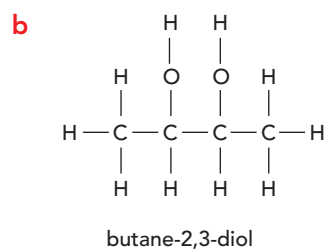
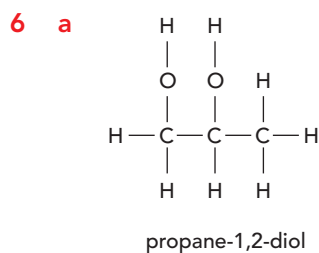
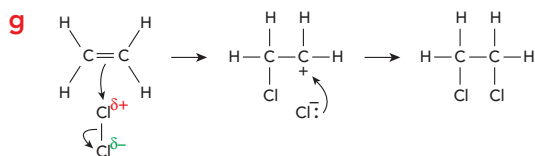
b 1,2-dichloropropane

c Steam and ethene, in the presence of concentrated phosphoric acid catalyst, are reacted at a high temperature and a high pressure.

d chloroethane

e a species that accepts a pair of electrons

f When a chlorine molecule approaches an ethene molecule, the area of high electron density around the $\text{C}=\text{C}$ bond tends to repel the bonding pair of electrons in the $\text{Cl}-\text{Cl}$ bond away from the nearer Cl atom. This makes the nearer Cl atom slightly positive and the further Cl atom slightly negative. The chlorine atom with the partial positive charge is deficient in electrons and is now ready to accept an electron pair from the $\text{C}=\text{C}$ bond.

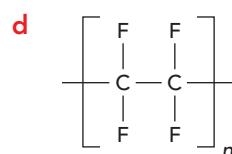


7 B

8 a poly(tetrafluoroethene)

b addition polymerisation

c $n\text{C}_2\text{F}_4 \rightarrow -[\text{C}_2\text{F}_4]_n-$
 where n = a very large number



e The poly(alkene)s could be burnt in power stations to generate electricity instead of using coal-, oil- or gas-fired power stations.

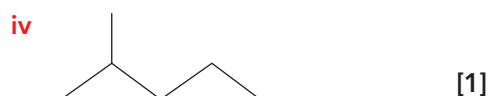
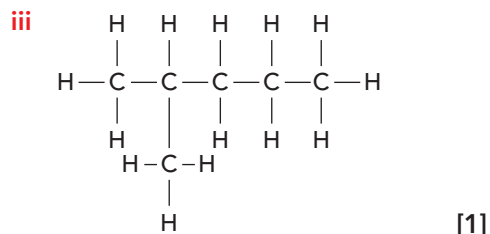
f Carbon dioxide would be produced by burning poly(alkene)s (although not as much as is produced by a coal-fired power station).

g carbon monoxide

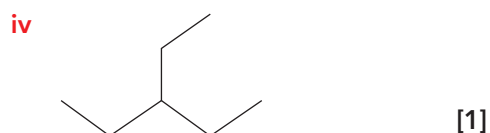
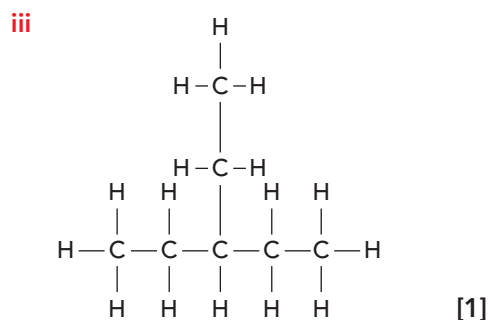
h but-1-ene

Exam-style questions

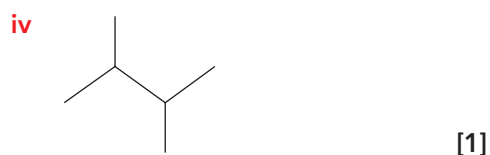
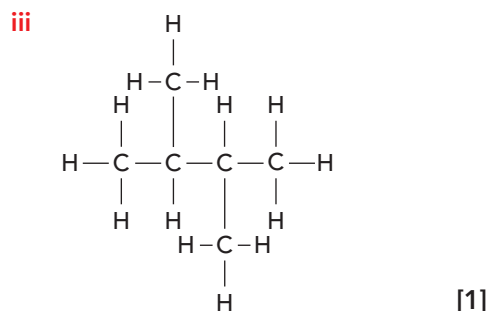
1 a 2-methylpentane:

i C_6H_{14} [1]ii $CH_3CH(CH_3)CH_2CH_2CH_3$ [1]

3-ethylpentane:

i C_7H_{16} [1]ii $CH_3CH_2CH(CH_2CH_3)CH_2CH_3$ [1]

2,3-dimethylbutane:

i C_6H_{14} [1]ii $CH_3CH(CH_3)CH(CH_3)_2$ [1]b C_nH_{2n+2} [1]

c 2-methylpentane and 2,3-dimethylbutane; structural isomerism [1]

d Compounds with the same molecular formula but different structural formulae (or displayed formulae). [1]

e 2,4-dimethylpentane [1]

[Total: 18]

2 a No double bonds / only single bonds; compound of C and H only. [1]

b Non-polar nature / lack of polarity of C—H bond. [1]

c i $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ [2]
[1 mark for correct formulae;
1 mark for balancing]

ii $C_2H_6 + 3\frac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$
or
 $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$ [2]
[1 mark for correct formulae;
1 mark for balancing]

[Total: 8]

3 a free-radical substitution [1]

b $CH_4 + Br_2 \rightarrow CH_3Br + HBr$ [2]
[1 mark for correct formulae;
1 mark for balancing]

c homolytic fission [1]

d UV/sunlight [1]
to break Br—Br bond [1]e i $Br_2 \rightarrow 2Br\cdot$ [2]
[1 mark for correct formulae;
1 mark for showing free radical correctly]

ii $Br\cdot + CH_4 \rightarrow CH_3\cdot + HBr$
or
 $CH_3\cdot + Br_2 \rightarrow CH_3Br + Br\cdot$ [2]
[1 mark for correct formulae;
1 mark for showing free radicals correctly]



or



[1 mark for correct formulae;
1 mark for showing free radicals correctly]

[Total: 12]

4 a $M_r = 30.0$ [1]

$\frac{1.50}{30.0}$ is 0.0500 mol [1]

b $M_r = 64.5$ [1]

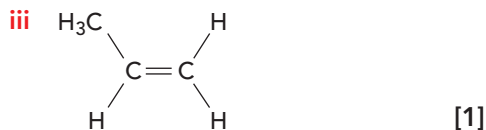
$\frac{1.29}{64.5}$ is 0.0200 mol [1]

c $\frac{0.0200}{0.0500}$ [1]
= 40.0 % [1]

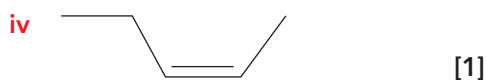
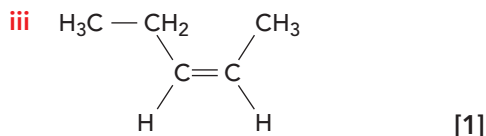
d $0.05 \times 0.6 \times 64.5$ [1]
= 1.94 g [1]

[Total: 8]

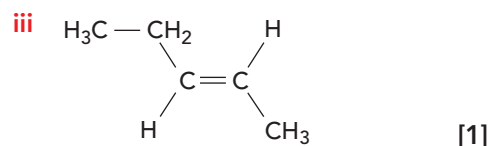
5 a propene:



cis-pent-2-ene:

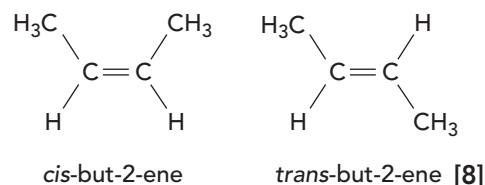
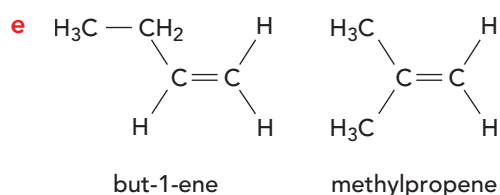


trans-pent-2-ene:

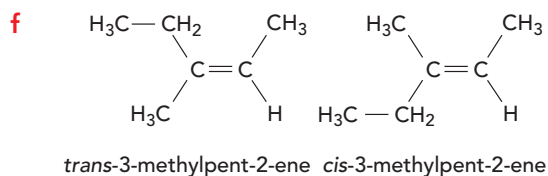


c *cis*-pent-2-ene and *trans*-pent-2-ene [1]

d Because there is restricted rotation about the $\text{C}=\text{C}$ double bond / due to the presence of a π (pi) bond which would need to be broken. [1]



[1 mark for each structure; 1 mark for each name]



[1 mark for each correct isomer;
1 mark for *cis* / *trans* labelled correctly] [3]

[Total: 27]

6 a having one or more double bonds [1]

b As well as a σ bond [1]
there is a π bond caused by overlapping p orbitals. [1]

c planar; [1]
all bond angles about 120° [1]

d A functional group gives particular chemical properties. [1]
 $\text{C}=\text{C}$ double bond [1]

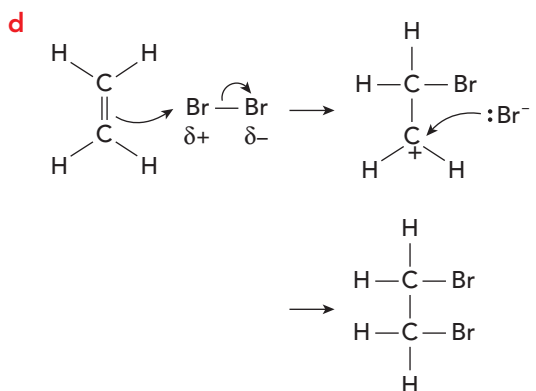
e Add bromine water; [1]
alkenes decolorise it. [1]

[Total: 9]

7 a electrophilic addition [1]

b $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$ [2]

c heterolytic fission [1]



for instantaneous dipole on bromine molecule [1]

for curly arrow from double bond [1]

for bond breaking in bromine molecule [1]

for bond forming from bromide ion [1]

for structure of product [1]

e Br_2 [1]

An electrophile is an electron-pair acceptor. [1]

[Total: 11]

8 a $M_r = 28.0$ [1]

2.80 g is $\frac{2.80}{28.0}$ mol = 0.100 mol [1]

b $M_r = 99.0$ [1]

8.91 g is $\frac{8.91}{99.0}$ mol = 0.0900 mol [1]

c $\frac{0.0900}{0.100}$ [1]

= 90.0% [1]

d 80.0% of 0.100 mol is 0.0800 mol [1]

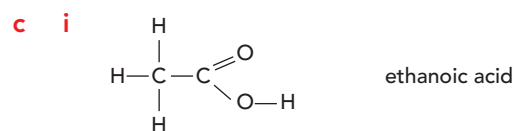
0.0800 mol is 0.0800×99.0 g = 7.92 g [1]

[Total: 8]

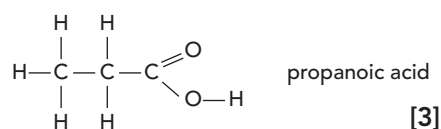
9 a i It breaks the $C=C$ bonds and oxidises the product molecules to give a mixture of oxidation products (carboxylic acids, ketones and carbon dioxide). [2]

ii Chemists can identify the oxidation products and deduce the position of the $C=C$ bond in an alkene. [1]

b but-1-ene (as there must be two hydrogen atoms on one of the $C=C$ carbon atoms for CO_2 to be produced, corresponding to $CH_2=CHCH_2CH_3$) [1]



and



ii $C_5H_{10} + 4[O] \rightarrow CH_3COOH + CH_3CH_2COOH$ [1]

[Total: 8]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 16

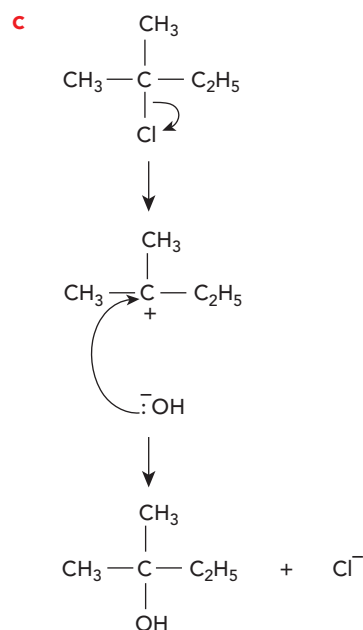
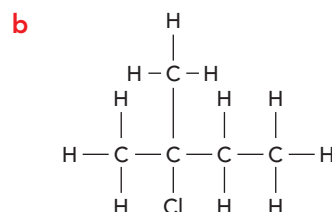
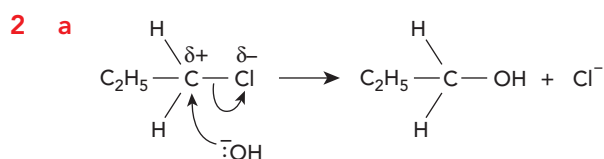
Science in context

Discuss as a group how the information about the use of halogenoalkanes demonstrates how some scientific developments can have both good and bad effects on society and the environment.

- Having read the Science in Context passage, ask learners to shut their Coursebook. Then conduct a quick activity asking individual learners to give a specific example of a beneficial use of halogenoalkanes or a problematic use, until the class runs out of suggestions.
- You might then ask for a class vote, show of hands, on whether the halogenoalkanes have benefitted or hindered human progress in the last century.

Self-assessment questions

- propene and chlorine
 - OH^- ions are negatively charged so are attracted more strongly than neutral water molecules to the partially positively charged carbon atoms in halogenoalkanes.
 - The hydrolysis of halogenoalkanes produces halide ions; the rate of their formation can be monitored by using silver nitrate solution. The silver halide precipitates make the reaction mixture cloudy. The ionic equations for the formation of the precipitates are:
 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
 $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$
 $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$
 - Both ammonia and amines contain a nitrogen atom with a lone pair of electrons that is available to donate.
 - tripropylamine $(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{N}$



- $\text{CH}_3\text{CHBrCH}_3 + \text{NaOH}(\text{ethanol}) \rightarrow \text{CH}_2 = \text{CHCH}_3 + \text{H}_2\text{O} + \text{NaBr}$
 - propene
 - $\text{BrCH}_2\text{CH}_2\text{CH}_3 + \text{NaOH}(\text{ethanol}) \rightarrow \text{CH}_2 = \text{CHCH}_3 + \text{H}_2\text{O} + \text{NaBr}$
(1-bromopropane)

Exam-style questions

1 D [1]

2 D [1]

3 B [1]

4 A [1]

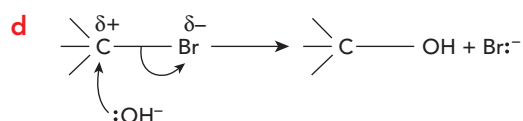
5 a A = aqueous sodium hydroxide (solution) [1]

B = ethanolic sodium hydroxide [1]

b Reaction is faster with 1-iodobutane [1]

as C—I bond is weaker than C—Br bond so is broken more easily. [1]

c nucleophilic substitution [1]

for curly arrow from lone pair of OH⁻ [1]

for curly arrow from C—Br bond to bromine [1]

for products [1]

Make sure that one curly arrow in this mechanism starts from a lone pair or negative charge on the hydroxide ion and points to the electron-deficient carbon atom in the alcohol and that the other starts on the C—Br bond and points to the Br atom.

e i 2-methylpropan-2-ol [1]

ii With 2-bromo-2-methylpropane the C—Br breaks to form a carbocation, which is then attacked by the hydroxide ion; [1]

whereas in 1-bromobutane the C—Br bond starts breaking as the new C—OH bond is forming. [1]

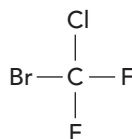
f elimination [1]

g *cis*-but-2-ene [1]*trans*-but-2-ene [1]

([1] for but-2-ene)

[Total: 14]

6 a [1]



b 1, 1, 1, 2-tetrafluoroethane [1]

[Total: 2]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 17

Science in context

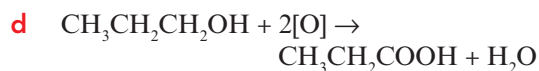
Give the small groups 10 minutes to come up with ideas on helping biofuels achieve 100% carbon neutrality.

Then collect feedback from each group at a time until ideas are exhausted. For example, look for ways in which the use of fossil fuels can be reduced in the process of making chemical fertilisers to grow the sugar cane/beet needed to obtain bio-ethanol, and the use of electric vehicles in harvesting and distributing the bio-ethanol.

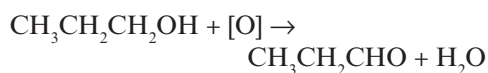
Self-assessment questions

- 1 a i The strongly electronegative oxygen atom in the —OH group has two lone pairs and carries a partial negative charge, and the less electronegative hydrogen atom carries a partial positive charge. Therefore the oxygen atom in ethanol molecules will attract hydrogen atoms in neighbouring molecules, forming hydrogen bonds.
 - ii When mixed with water, the partially positive hydrogen atoms in H_2O are strongly attracted to the partially negative oxygen atom in ethanol molecules, forming hydrogen bonds.
 - b Hexan-1-ol has a longer non-polar hydrocarbon chain than ethanol, which disrupts hydrogen bonding between water and the alcohol.
 - c $\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\text{CH}_3$ – a tertiary alcohol
 - d i alcohol has at least one alkyl (electron-donating) group whereas water only has hydrogen atoms.
 - ii C, a tertiary alcohol
- 2 a i propene, steam, heat
 - ii cold, dilute sulfuric acid (acidified), potassium manganate(VII) solution
 - b i $\text{C}_3\text{H}_7\text{OH} + 4\frac{1}{2}\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$
 - ii $\text{C}_4\text{H}_9\text{OH} + 6\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O}$
 - c i $\text{CH}_3\text{CH}_2\text{OH} + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O}$
 - ii Ethanol, sodium bromide and concentrated sulfuric acid are heated under reflux.
 - iii nucleophilic substitution
- 3 a bubbles of gas given off from the lithium, which gets smaller and smaller until it disappears
 - b lithium propoxide and hydrogen
 - c the fizzing would be more vigorous
- 4 a i butyl ethanoate
 - ii ethyl hexanoate
 - iii pentyl methanoate
 - b i $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
 - ii $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$
 - iii $\text{HCOOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
- 5 a
$$\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O}$$
 - b propene
- 6 a Propan-1-ol should be heated gently with a solution of potassium dichromate(VI) acidified with dilute sulfuric acid; the propanal should be distilled off immediately.
 - b $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O}$

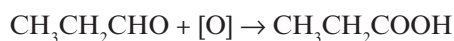
c Propan-1-ol should be refluxed with excess potassium dichromate(VI) acidified with dilute sulfuric acid; the propanoic acid should be distilled off after at least 15 minutes of refluxing.



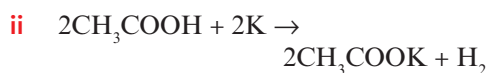
or



followed by



7 a reflux with dilute HCl



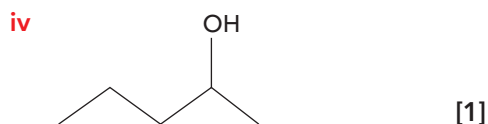
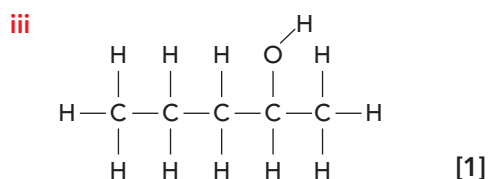
c lithium tetrahydridoaluminate, LiAlH_4 , in dry ether at room temperature

Exam-style questions

1 D [1]

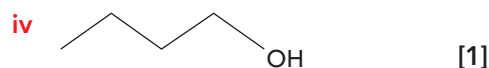
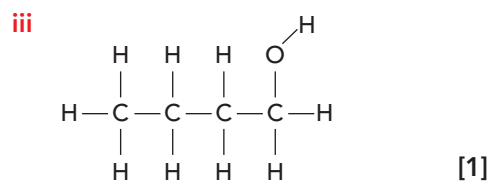
2 B [1]

3 a pentan-2-ol:



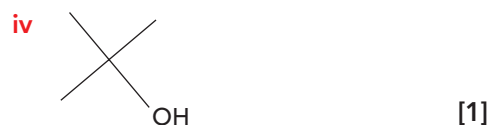
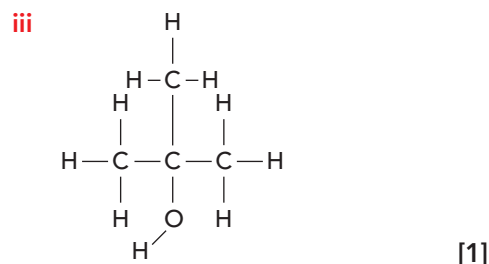
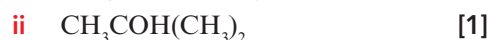
v secondary [1]

butan-1-ol:



v primary [1]

2-methylpropan-2-ol:



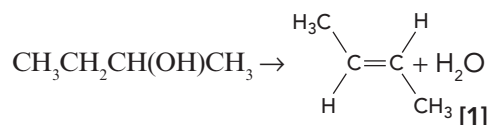
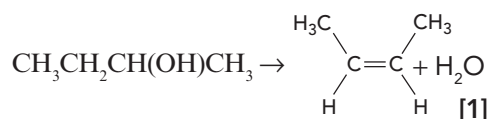
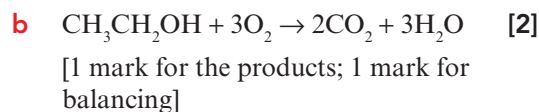
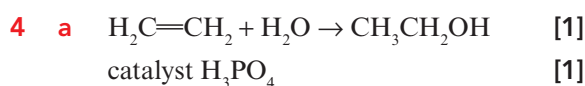
v tertiary [1]



c butan-1-ol and 2-methylpropan-2-ol; structural isomers [1]

d 2-methylbutan-2-ol [1]

[Total: 19]





catalyst concentrated sulfuric(VI) acid; [1]

esterification; [1]

products ethyl ethanoate and water [1]

[Total: 11]



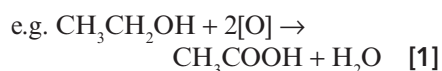
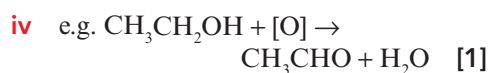
b i displayed formula with —CHO
 (aldehyde group); [1]

displayed formula with —COOH
 group [1]

ii Gives aldehyde after mild heat
 and distilling immediately; [1]
 gives carboxylic acid after
 refluxing with excess oxidising
 agent. [1]

iii aldehydes; [1]

carboxylic acids [1]



c i displayed formula with $>\text{C}=\text{O}$
 group (ketone) [2]

ii ketones [1]



d No H atom on C atom that is bonded
 to the —OH functional group. [1]

[Total: 14]

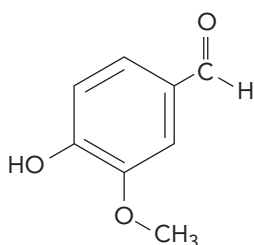
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Coursebook answers

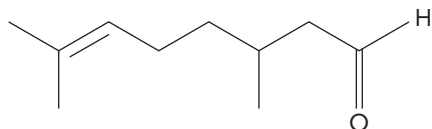
Chapter 18

Science in context

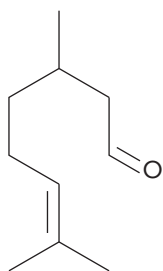
- Aldehyde in vanilla
Name: 4-hydroxy-3-methoxybenzaldehyde



- Aldehydes always at the end of a carbon chain, and the carbonyl carbon always has one hydrogen atom bonded to it. Ketones have two alkyl and/or aryl groups bonded to the carbonyl carbon, so the -C=O group never appears at the end of a carbon chain.
- Citronellal

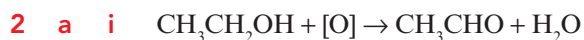
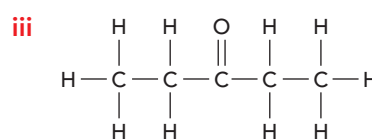
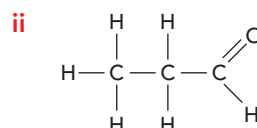
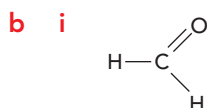


or



Self-assessment questions

- 1 a i hexanal
ii octan-2-one

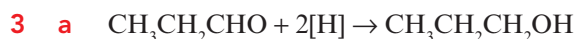


- ii Add a solution of potassium dichromate(VI), acidified with dilute sulfuric acid, one drop at a time to warm ethanol in a flask. Distil off and collect the ethanal as it forms.



- ii The reaction mixture turns from orange to green.

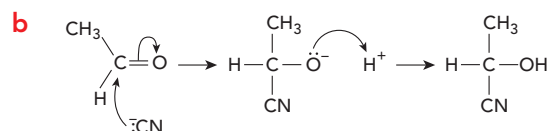
iii A



b pentan-3-ol

4 a i 2-hydroxypropanenitrile

ii 2-hydroxymethylpropanenitrile



5 a A deep orange precipitate is formed.

b i The unknown compound could be butanal or propanone.

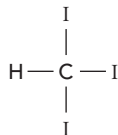
ii butanal

iii Butanal can be oxidised by the silver ions in warm Tollens' reagent, to form butanoate ions. In the process the silver ions are reduced to silver atoms, which form a silver mirror effect on the inside surface of the reaction vessel. However, butanone cannot be oxidised easily so no change is observed when it is warmed with Tollens' reagent – the mixture remains colourless.

c $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$

d $\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$

6 a i tri-iodomethane



ii step 1: CH_3COCl_3 ;
step 2: $\text{CH}_3\text{COO}^-\text{Na}^+ + \text{CHI}_3$

b The ethanol is first oxidised by the alkaline iodine solution to give ethanal, CH_3CHO . Ethanal has a methyl group adjacent to the carbonyl carbon so will give a positive tri-iodomethane test. In step 1 of the test we get tri-iodoethanal. Then in step 2 we get tri-iodomethane and sodium methanoate.

c Options A, D and E will give a yellow precipitate of tri-iodomethane.

7 a IR spectrum A is butanone and B is butan-2-ol.

b A is butanone because of a strong, sharp absorption at 1710 cm^{-1} , characteristic of the $\text{C}=\text{O}$ in the ketone; whereas B shows a strong broad absorption at $3200\text{--}3500\text{ cm}^{-1}$, characteristic of the $\text{O}-\text{H}$ in an alcohol.

Exam-style questions

- 1 a i propanone [1]
ii propan-1-ol [1]
iii ethanal [1]
iv propan-2-ol [1]
v butanone [1]
vi propanal [1]

b from part a, ii and iv are alcohols; i, iii, v and vi are carbonyl compounds [1]

c from part a, iii and vi are aldehydes; i and v are ketones [1]

d i start with ii to make vi; start with iv to make i [4]

ii $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O}$ [1]

potassium dichromate(VI) solution, acidified with dilute sulfuric acid, warm and distil immediately [1]

$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + [\text{O}] \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2\text{O}$ [1]

potassium dichromate(VI) solution, acidified with dilute sulfuric acid, reflux [1]

e i compound iii from part a [1]

ii NaBH_4 / sodium tetrahydridoborate(III) [1]

iii $\text{CH}_3\text{CHO} + 2[\text{H}] \rightarrow \text{CH}_3\text{CH}_2\text{OH}$ [1]

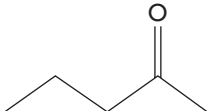
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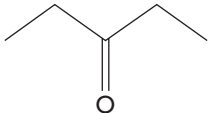
2 a 2,4-dinitrophenylhydrazine (2,4-DNPH) solution [1]

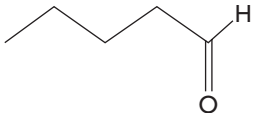
b orange precipitate [1]

c The original aldehyde or ketone could be identified. [1]

[Total: 3]

3 a i  [1]

ii  [1]

iii  [1]

b Pentan-3-one gives no change. [1]

Pentanal gives a silver mirror; [1]

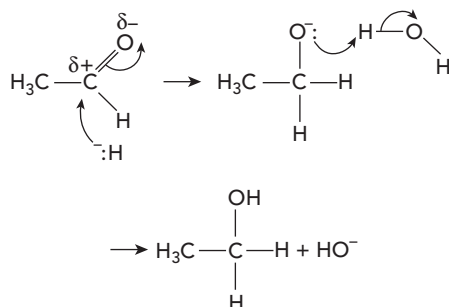
product pentanoic acid; [1]

this is an oxidation. [1]

[Total: 7]

4 a NaBH_4 [1]

b



nucleophilic addition [1]

for dipole [1]

for curly arrow from lone pair on hydride ion (H^-) to electron-deficient carbon [1]

for structure of intermediate [1]

for curly arrow from lone pair on negative oxygen onto hydrogen (δ^+) on water [1]

for curly arrow onto OH [1]

for final products [1]

[Total: 8]

5 a

	Carbon	Hydrogen	Oxygen
Mass of element	66.7 g	11.1 g	22.2 g
Number of moles	$\frac{66.7}{12.0} = 5.56$	$\frac{11.1}{1.0} = 11.1$	$\frac{22.2}{16.0} = 1.39$
Relative number of atoms	$\frac{5.56}{1.39} = 4$	$\frac{11.1}{1.39} = 8$	$\frac{1.39}{1.39} = 1$

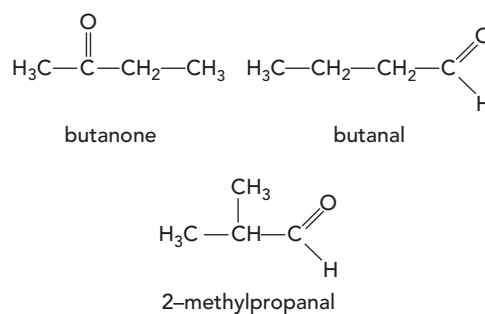
1 mark for number of moles of C, H, O;

1 mark for relative number of atoms [2]

empirical formula = $\text{C}_4\text{H}_8\text{O}$ [1]

b empirical formula mass = 72, so molecular formula is $\text{C}_4\text{H}_8\text{O}$ [1]

c



1 mark for each isomer [3]

d Test with Tollens' reagent: formation of silver mirror indicates aldehyde; no silver mirror indicates ketone. [1]

Add 2,4-dinitrophenylhydrazine; [1]

filter precipitate and purify by recrystallisation; [1]

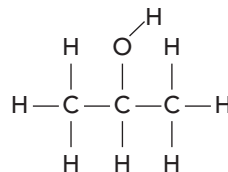
find melting point of precipitate [1]

and compare with literature to find the identity. [1]

[Total: 12]

6 a tri-iodomethane [1]

b [1]



c propanone [1]

d i butan-1-ol, butan-2-ol, methylpropan-1-ol, methylpropan-2-ol [1]

ii butan-1-ol is primary, butan-2-ol is secondary, methylpropan-1-ol is primary, methylpropan-2-ol is tertiary [1]

iii only butan-2-ol [1]

[Total: 6]

7 a Spectrum C [1]

b Any three for 3 marks from: [3]

Spectrum A has the O—H peak at $2500\text{--}3300\text{ cm}^{-1}$ characteristic of carboxylic acids.

Spectrum B has the O—H peak at $3230\text{--}3550\text{ cm}^{-1}$ characteristic of alcohols.

Spectrum C has the C=O peak at $1680\text{--}1750\text{ cm}^{-1}$ characteristic of an aldehyde.

The aldehyde peak in C is sharp (because of no hydrogen bonding in aldehydes).

The broad peaks in A and B are characteristic of the hydrogen bonded carboxylic acids and alcohols.

[Total: 4]

- 8 a E.g. add concentrated hydrochloric acid to the ethene to form chloroethane. [1]

Then add excess ammonia solution to the chloroethane to form ethylamine. [1]

- b E.g. Add steam [1]
in presence of conc. phosphoric acid catalyst [1]

to make ethanol. Then oxidise the ethanol with acidified (dil. sulfuric acid) + potassium dichromate solution [1]

dropwise, warm and distill off the ethanal formed. [1]

- c E.g. add concentrated hydrochloric acid to the ethene to form chloroethane. [1]

Then heat [1]

with KCN (potassium cyanide to form propanenitrile. [1]

Finally add dilute hydrochloric acid (or dilute sodium hydroxide, followed by dilute acid) to form the propanoic acid. [1]

[Total: 10]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 19

Science in context

Since a hydrogen atom has only one electron, its electron density is very low compared with heavier atoms such as carbon and oxygen. The X-rays are absorbed better by heavier, denser atoms. The position of the hydrogen atoms can, however, be inferred from the electron density contours of the atoms to which they are attached by slight 'bulges' in the contours.

It is relatively easy to obtain pure samples of salts such as sodium chloride or zinc sulfide by standard chemical techniques such as crystallisation.

It took longer to produce pure samples of protein or DNA because:

- These molecules had to be separated from other molecules in cells. In the case of proteins the separation had to be from many other proteins of similar structure. Only small quantities of materials were initially available.
- Biological molecules such as proteins are easily degraded or hydrolysed by enzymes present in the cell, so suitable methods have to be found to prevent this.
- Suitable separation techniques had to be developed, e.g. ion exchange chromatography, in order to separate proteins. This took many years.
- Methods had to be developed to crystallise proteins and DNA.
- The analysis of the X-ray diffraction photographs takes longer because the molecules are much more complex and the interpretation of the results was also much more complex. No computers were available to speed up the analysis of the results.

Learners may not have much knowledge of the timeline of the first purification of samples of substances such as sodium chloride, penicillin, proteins and DNA and the relative complexity

of these molecules. You may have to help them by showing them the structures and asking them where the substances are found. A hint could also be given that many molecular structures can also be crystallised and this includes proteins and DNA. One of the first molecular structures to be crystallised was urea.

Learners may ask for further information about X-ray crystallography. Some simplified information is given here. Learners should be told that the mathematical analysis is extremely complex and beyond even first year university maths courses.

In 1912 the German physicist Max von Laue suggested that crystals can act as a diffraction grating. He produced a diffraction pattern from hydrated copper(II) sulfate. William Henry Bragg and his son William Lawrence Bragg developed the X-ray diffraction technique further and determined the structure of zinc sulfide (cubic). They went on to determine the structures of many other simple ionic compounds. One of the most famous developers of the technique was Dorothy Hodgkin, who was able to crystallise complex molecules such as insulin and use the technique to determine the exact three dimensional structure of the molecule. There is an opportunity here to further develop the idea of women in Science (see also the discussion in Chapter 10).

Taking the water wave analogy as a starting point, a crystal acts as a series of slits that act as sources of circular (or, more precisely, spherical) waves. These waves interfere with each other, either cancelling each other out or reinforcing each other to produce bigger waves (in phase).

The absorption and emission of X-rays from crystals follows the same mathematical pattern as the reflection of light from parallel planes. In this case, the 'reflection' is from the layers of ions or atoms. The Braggs showed that the angle of reflection of X-rays was related to the distance between the two layers of ions/atoms.

$$2d \sin \theta = n\lambda$$

where n is a number, λ is the wavelength of the radiation and d is the distance between the layers.

In practice, the crystal is placed on a turntable and rotated gradually. When the 'reflected' X-rays are in phase, a flash of light is seen which is recorded on a photographic plate or a radiation counter. The process is repeated with the crystal at a different angle.

Self-assessment questions

- 1 a standard temperature = 298 K,
standard pressure = 1.01×10^5 Pa / 101 kPa

- b i $\text{Mg}^{2+}(\text{g}) + \text{O}^{2-}(\text{g}) \rightarrow \text{MgO}(\text{s})$
ii $\text{K}^+(\text{g}) + \text{Br}^-(\text{g}) \rightarrow \text{KBr}(\text{s})$
iii $2\text{Na}^+(\text{g}) + \text{S}^{2-}(\text{g}) \rightarrow \text{Na}_2\text{S}(\text{s})$

- 2 a The bond energy for chlorine is the enthalpy change $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$. The enthalpy change of atomisation is $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$. So the enthalpy change of atomisation is $+244/2 = +122 \text{ kJ mol}^{-1}$.

- b i $\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{O}(\text{g})$
ii $\text{Ba}(\text{s}) \rightarrow \text{Ba}(\text{g})$
iii $\frac{1}{2}\text{Br}_2(\text{l}) \rightarrow \text{Br}(\text{g})$

- c 0 kJ mol^{-1}

Because helium exists naturally as single gaseous atoms, no change is involved in the process $\text{He}(\text{g}) \rightarrow \text{He}(\text{g})$.

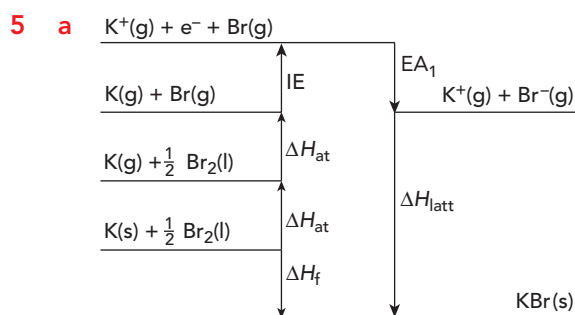
- 3 a There must be an input of energy to overcome the repulsive forces between the (negative) electron and the negative ion.

- b $+440 \text{ kJ mol}^{-1}$

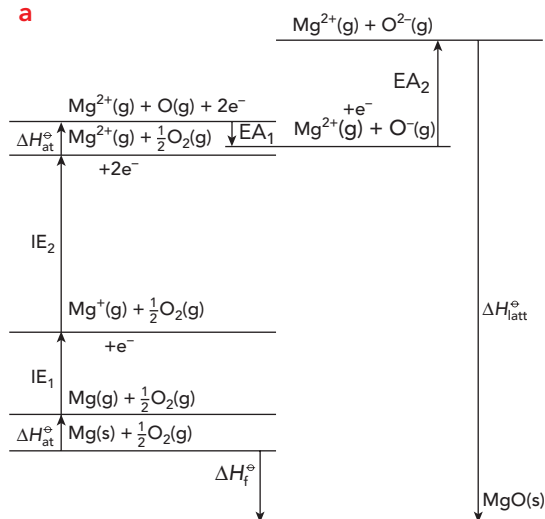
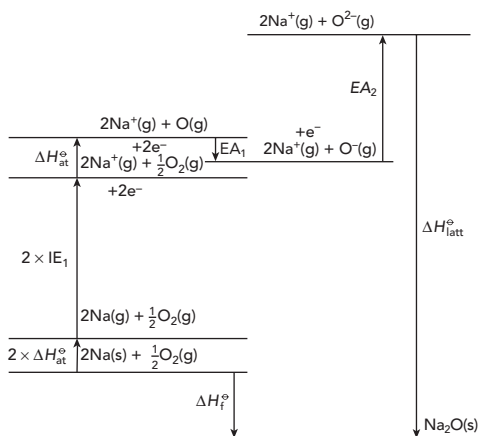
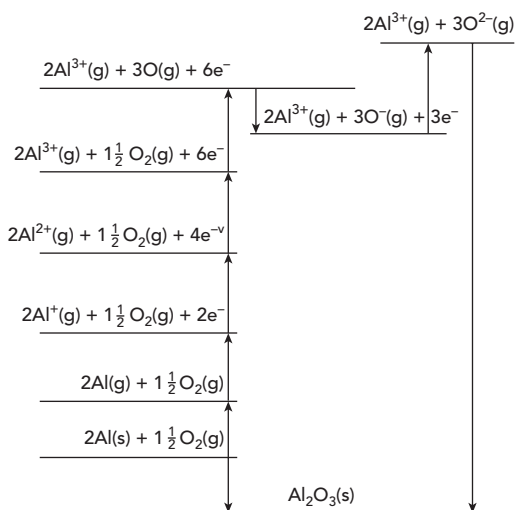
- c i $\text{I}(\text{g}) + \text{e}^- \rightarrow \text{I}^-(\text{g})$
ii $\text{S}^-(\text{g}) + \text{e}^- \rightarrow \text{S}^{2-}(\text{g})$

- d Down the Group there are more shells (outer electrons are further away from the nucleus) so attractive forces between the incoming electrons and nucleus decreases. In addition there is greater shielding with more electron shells. This helps reduce the attraction between the nuclear charge and the incoming electrons.

- 4 a i $\text{Cs}(\text{g}) \rightarrow \text{Cs}^+(\text{g}) + \text{e}^-$
ii $\text{Al}^{2+}(\text{g}) \rightarrow \text{Al}^{3+}(\text{g}) + \text{e}^-$
iii $\text{Ca}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s})$
iv $\text{Fe}(\text{s}) + 1\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{FeCl}_3(\text{s})$
- b $\Delta H_{\text{latt}}^\ominus = \Delta H_{\text{f}}^\ominus - \{\Delta H_{\text{at}}^\ominus[\text{Na}] + \text{IE}_1[\text{Na}] + \Delta H_{\text{at}}^\ominus[\frac{1}{2}\text{Cl}_2(\text{g})] + \text{EA}_1[\text{Cl}]\}$
- $$\Delta H_{\text{latt}}^\ominus = (-411) - \{(+107) + (+496) + (+122) + (-348)\}$$
- $$= +377 \text{ kJ mol}^{-1}$$
- $$\Delta H_{\text{latt}}^\ominus = (-411) - (+377) = -788 \text{ kJ mol}^{-1}$$



- b i enthalpy change of atomisation of iodine
ii first electron affinity of nitrogen
iii enthalpy change of formation of strontium chloride
iv lattice energy of cadmium chloride

6 a**b****7 a**

$$\Delta H_{\text{latt}}^{\ominus} = \Delta H_{\text{f}}^{\ominus} - \{2\Delta H_{\text{at}}^{\ominus}[\text{Al}] + 2\text{IE}_{1+2+3}^{\ominus}[\text{Al}] + 3\Delta H_{\text{at}}^{\ominus}[\frac{1}{2}\text{O}_2(\text{g})] + 3\text{EA}_{1+2}^{\ominus}[\text{O}]\}$$

$$\Delta H_{\text{latt}}^{\ominus} = (-1676) - \{2 \times (+326) + 2 \times (+577 + 1820 + 2740) + 3$$

$$\times (+249) + 3 \times (-141) + 3 \times (+798)\}$$

$$= +13\,644 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{latt}}^{\ominus} = (-1676) - (+13\,644)$$

$$= -15\,320 \text{ kJ mol}^{-1}$$

8 a i BaO**ii** MgI₂**iii** CaO**b** RbCl < LiF < MgO

Lattice energy gets more exothermic the greater the charge on the ions, so MgO > LiF and RbCl.

Lattice energy gets more exothermic the smaller the ions, so LiF > RbCl.

9 a For magnesium oxide $Q_1 \times Q_2$ is 4, for lithium fluoride $Q_1 \times Q_2$ is 1. Because ionic radii are (almost) unchanged, r^2 will be very similar. The force between the particles, which is proportional to $\frac{Q_1 \times Q_2}{r^2}$, will be four times greater for

MgO than it is for LiF, accounting for the greater lattice energy.

b The ionic charges are the same so $Q_1 \times Q_2$ is 1 for both compounds. However, r , the separation of the centres of the ions, is much greater for KBr than it is for LiF. Therefore $\frac{Q_1 \times Q_2}{r^2}$ is much greater for LiF than it is for KBr, so the attractive force between the particles is greater for LiF than it is for KBr, accounting for the greater lattice energy.

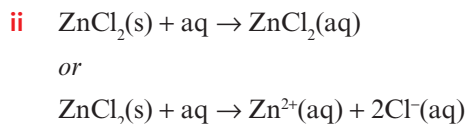
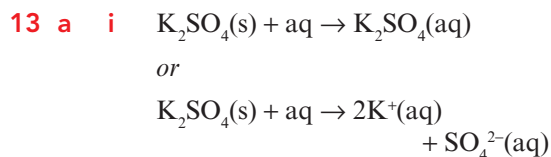
10 D

11 a The charge is spread out over a smaller volume so the charge density is higher.

b Li⁺ because it has the smallest ionic radius and therefore has the highest charge density.

c I⁻ because it has the largest ionic radius.

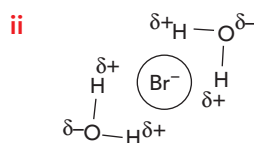
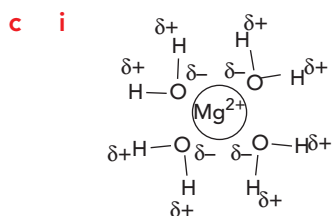
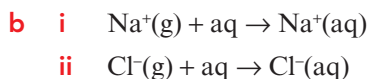
12 The nitrate ion is an ion with a large ionic radius so is easily polarised by a small highly charged cation. Mg²⁺ has a smaller ionic radius than Ba²⁺. Magnesium ions are better polarisers of nitrate ions than barium ions. The greater the polarisation, the lower the thermal stability (the more likely the nitrate is to decompose).



- b** Sodium chloride and sodium bromide are soluble in water (because they have values of $\Delta H_{\text{sol}}^\ominus$ that are negative or slightly positive). Silver chloride and silver bromide are insoluble (because they have large positive values of $\Delta H_{\text{sol}}^\ominus$). The data suggest that silver bromide is less soluble than silver chloride because its value of $\Delta H_{\text{sol}}^\ominus$ is more endothermic. The data suggest that sodium chloride is less soluble than sodium

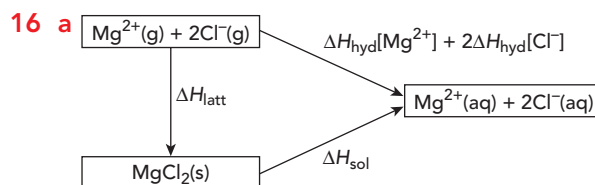
bromide because its value of $\Delta H_{\text{sol}}^\ominus$ is slightly positive, whereas the $\Delta H_{\text{sol}}^\ominus$ of silver bromide is slightly negative.

- 14 a** Bond formation is always exothermic. Ion–dipole bonds are being formed between the gaseous ions and the water molecules.

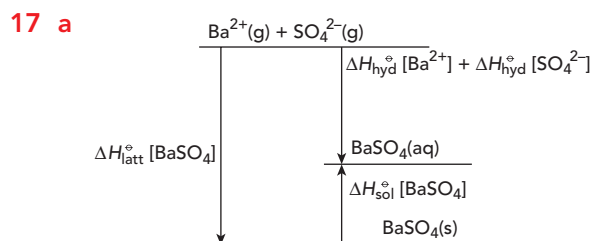


- d** Magnesium has a 2+ ion but potassium has only a 1+ ion. The magnesium ion also has a smaller radius than the potassium ion. So the magnesium ion has a greater charge density than a potassium ion. The greater the charge density, the greater the attractive force between the ion and the polar water molecules and the greater the value of $\Delta H_{\text{hyd}}^\ominus$.

- 15 a** the enthalpy change of solution of KBr
b the enthalpy change of hydration of K^+
c the lattice enthalpy of KBr
d the enthalpy change of hydration of Br^-



b $\Delta H_{\text{latt}}^\ominus + \Delta H_{\text{sol}}^\ominus = \Delta H_{\text{hyd}}^\ominus [\text{Mg}^{2+}] + 2\Delta H_{\text{hyd}}^\ominus [\text{Cl}^-]$
 so $\Delta H_{\text{hyd}}^\ominus [\text{Mg}^{2+}] = \Delta H_{\text{sol}}^\ominus + \Delta H_{\text{latt}}^\ominus - 2\Delta H_{\text{hyd}}^\ominus [\text{Cl}^-]$
 $\Delta H_{\text{hyd}}^\ominus [\text{Mg}^{2+}] = (-2592) + (-55) - 2 \times (-364)$
 $= -2592 + 673$
 $\Delta H_{\text{hyd}}^\ominus [\text{Mg}^{2+}] = -1919 \text{ kJ mol}^{-1}$

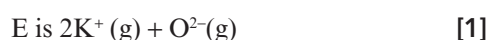
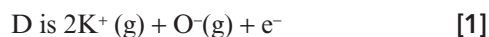
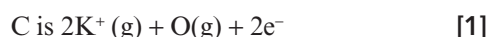
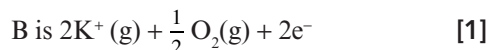
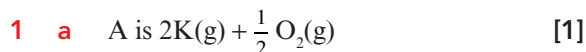


- b** The lattice energy and enthalpy change of hydration of magnesium sulfate are more exothermic than those of barium sulfate, but the difference is more marked for the enthalpy change of hydration than for lattice energy. It is the enthalpy change of hydration of the cations that plays the greatest part in determining the value of $\Delta H_{\text{sol}}^\ominus$.

Because magnesium has a smaller ion than barium, the enthalpy change of hydration is more exothermic than for barium.

Overall, the enthalpy change of solution is less endothermic for magnesium sulfate than for barium sulfate. This means that magnesium sulfate is more soluble because the value of $\Delta H_{\text{sol}}^\ominus$ is less endothermic (than for barium sulfate).

Exam-style questions



b
$$\Delta H_{\text{latt}}^{\ominus} = \Delta H_{\text{f}}^{\ominus} - \left\{ 2\Delta H_{\text{at}}^{\ominus}[\text{K}] + 2\text{IE}_1[\text{K}] + 2\text{IE}_1[\text{K}] + 2\Delta H_{\text{at}}^{\ominus}\left[\frac{1}{2}\text{O}_2(\text{g})\right] + \text{EA}[\text{O}] + \text{EA}_2[\text{O}] \right\}$$
 [1]

$$\Delta H_{\text{latt}}^{\ominus} = (-361) - \{ 2 \times (+89) + 2 \times (+418) + (+249) + (-141) + (+798) \}$$

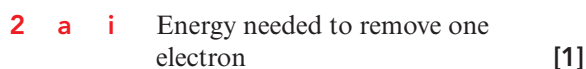
$$\Delta H_{\text{latt}}^{\ominus} = (-361) - (+1920) = -2281 \text{ kJ mol}^{-1}$$
 [1]

- c Lattice energy of sodium oxide greater / more exothermic; [1]
 sodium ion smaller / greater charge density than potassium ion; [1]
 oxide ion smaller / greater charge density than sulfide ion; [1]
 lattice energy more exothermic the smaller the ion / higher charge density on the ions. [1]

[allow reverse arguments]

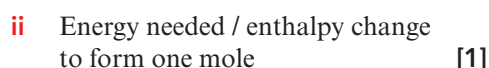
- d Requires input of energy to bring two negative charges together / needs energy to overcome repulsion between the electron and the O^- ion. [1]

[Total: 12]

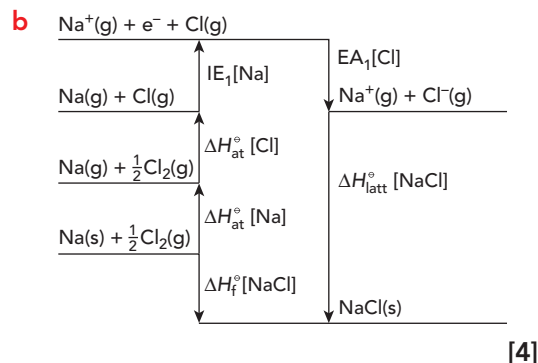


from each atom in a mole of gaseous atoms [1]

to form one mole of gaseous ions. [1]



of gaseous atoms from the element in its standard state. [1]



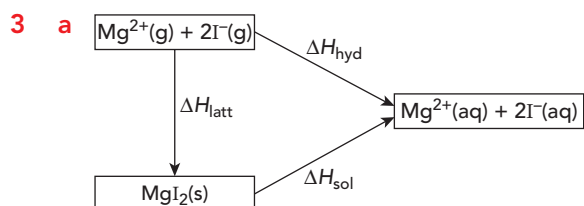
[deduct 1 mark per error]

- c A sodium ion has a lower charge density / larger ionic radius than a lithium ion; [1]

lattice energy is more exothermic the smaller the ion / larger the charge density. [1]

[accept reverse arguments]

[Total: 11]



symbols correct [1 mark for each box correct]; [3]

arrows in the correct direction; [1]

correct ΔH^{\ominus} symbols by correct arrows [1]

- b i Enthalpy change when one mole of gaseous ions completely dissolve in a very large amount of water. [1]

ii
$$\Delta H_{\text{sol}}^{\ominus} = \Delta H_{\text{hyd}}^{\ominus}[\text{Mg}^{2+}] + 2 \times \Delta H_{\text{hyd}}^{\ominus}[\text{I}^-] - \Delta H_{\text{latt}}^{\ominus}$$
 [2]

$$\Delta H_{\text{sol}}^{\ominus} = (-1920) + 2 \times (-314) - (-2327)$$

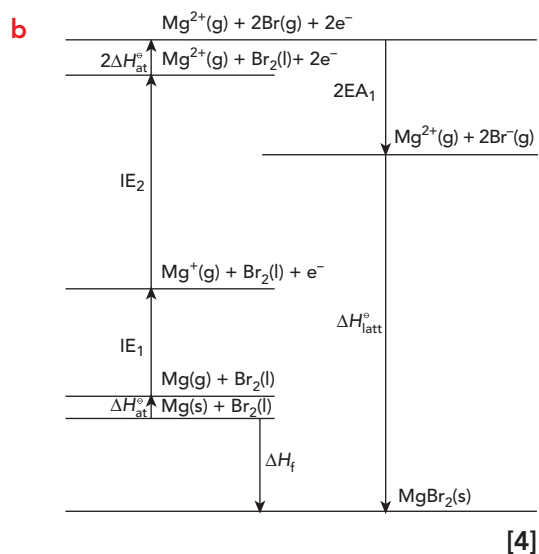
$$\Delta H_{\text{sol}}^{\ominus} = -221 \text{ kJ mol}^{-1}$$
 [1]

- c dipoles on water molecules; [1]
 correct orientation of water molecules [1]

- d greater charge density on magnesium; [1]
greater attraction [1]
between ion and dipoles on water [1]

[Total: 15]

- 4 a i Energy change when one mole of an ionic compound [1]
forms from its constituent gaseous ions. [1]
ii Energy needed to form one mole [1]
of gaseous $2+$ ions [1]
from gaseous $1+$ ions. [1]



[deduct 1 mark per error]

- c $\Delta H_{\text{latt}}^{\ominus} = \Delta H_{\text{f}}^{\ominus}$ [1]

$$- \left\{ \begin{aligned} &\Delta H_{\text{at}}^{\ominus} [\text{Mg}] + \text{IE}_1 [\text{Mg}] \\ &+ \text{IE}_2 [\text{Mg}] + 2\Delta H_{\text{at}}^{\ominus} \left[\frac{1}{2} \text{Br}_2 (\text{g}) + 2\text{EA}_1 [\text{Br}] \right] \end{aligned} \right\}$$

$$\Delta H_{\text{latt}}^{\ominus} = (-524) - \{ (+150) + (+736) + (+1450) + 2 \times (+112) + 2 \times (-325) \}$$

$$\Delta H_{\text{latt}}^{\ominus} = (-524) - (+1910) = -2434 \text{ kJ mol}^{-1}$$
 [1]

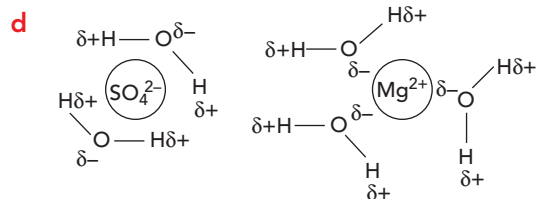
[Total: 11]

- 5 a i NaCl will have the higher lattice energy; it has smaller ions / greater charge density; [1]
the smaller the ion the higher the lattice energy. [1]

- ii SrS will have the higher lattice energy; it has ions with $2+$ and $2-$ charge; [1]
the greater the charge on the ion the higher the lattice energy. [1]
b i deformation of shape / electron cloud [1]
of an anion by a cation. [1]
ii Magnesium ion has greater charge than sodium ion; [1]
magnesium is a smaller ion than sodium ion. [1]
iii Barium ion has larger radius than magnesium ion; [1]
barium ion polarises (large) carbonate ion less well than magnesium ion; [1]
the smaller the polarisation, the greater the thermal stability. [1]
[allow reverse argument for magnesium]

[Total: 11]

- 6 a i Enthalpy change when one mole of solute [1]
dissolves completely in water. [1]
ii Enthalpy change when one mole of aqueous ions [1]
is formed from one mole of gaseous ions. [1]
b i $\text{NaCl}(\text{s}) + \text{aq} \rightarrow \text{NaCl}(\text{aq})$
allow: $\text{NaCl}(\text{s}) + \text{aq} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
left-hand side of equation correct [1]
right-hand side of equation correct [1]
ii $\text{Cl}^-(\text{g}) + \text{aq} \rightarrow \text{Cl}^-(\text{aq})$
left-hand side of equation correct [1]
right-hand side of equation correct [1]
c A is lattice energy / lattice enthalpy [1]
B is enthalpy change of hydration / $\Delta H_{\text{hyd}}^{\ominus}$ [1]
C is enthalpy change of solution / $\Delta H_{\text{sol}}^{\ominus}$ [1]



correct dipole on water molecules; [1]

correct orientation of water molecules around SO_4^{2-} ions; [1]

correct orientation of water molecules around Mg^{2+} ions [1]

e Any five of the following, for 1 mark each;

- the lattice energy and enthalpy change of hydration of magnesium sulfate are more exothermic than those of calcium sulfate;
- the difference in enthalpy changes is more marked for the enthalpy change of hydration than for lattice energy;
- it is the enthalpy change of hydration of the cation that plays the greatest part in determining the value of $\Delta H_{\text{sol}}^{\ominus}$;
- Mg^{2+} has a smaller radius than Ca^{2+} ;
- so the enthalpy change of hydration is more exothermic for magnesium (than calcium);
- the enthalpy change of solution is less endothermic for magnesium sulfate (than for calcium sulfate);
- magnesium sulfate is more soluble because value of $\Delta H_{\text{sol}}^{\ominus}$ is less endothermic (than for calcium sulfate). [5]

[allow reverse arguments]

[Total: 19]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 20

Science in context

This introductory section reintroduces learners to the responsibilities of chemical companies and other manufacturing companies for safeguarding the environment. This builds on the idea of green chemistry introduced in Chapter 8 and the extraction of gold using cyanide in Chapter 3. Cadmium ions are found most often on the sites of old gas works, ironworks or other metal processing works.

The electrochemical process can also be modified to remove uncharged material such as toxic organic compounds by a process called electro-osmosis whereby water can move from anode to cathode and take some of the poisonous organic material with it.

- The electrochemical process is simple and takes place on the site. It does not require removal of large amounts of soil for processing by ion exchange or other methods of chemical treatment. Treatment by removing large amounts of soil is expensive and uses a lot of fuel. There is also additional pollution due to vehicles transporting the soil.

The economics of the electrochemical process depends on the availability of cheap electricity. Removing poisonous ions from even a small area of ground the size of a football pitch requires not only a large number of electrodes but also significant electrical power. If the land is to be used again for housing, the cost of cleaning the land has to be compared with the value of the reclaimed land. The process has not yet been developed enough to treat large areas rapidly.

- Cyanide ions inhibit the electron transport chain in respiration, specifically the electron transport molecule cytochrome oxidase. The redox reactions in the

electron transport chain of respiration stop working, leading to rapid death. Cyanide also inhibits the Fe^{3+} form of the blood pigment heme a3 because it forms a complex ion with the Fe^{3+} , but the effects are less pronounced than the effect of carbon monoxide on the Fe^{2+} form.

Nitrates from fertilisers run off from fields into rivers and cause eutrophication. The process is: Nitrates cause excessive growth of algae which cover the surface and cut off light. Bacteria grow on the dead algae and use up the oxygen in the water. Aquatic organisms die and the river becomes lifeless and often smelly due to decomposition reactions. Nitrates may also have an effect on farm animals (increased rate of respiration and heart rate) and babies where the blood turns a bluish colour. This is partly due to nitrates being converted to more harmful nitrites. There have also been reports that a high nitrate concentration in water leads to problems for pregnant women. The link, however, has not been fully proved. The fact that nitrates may cause harm is reflected by the fact that the permitted level of nitrates in drinking water in some countries is quite low.

- It is very expensive to clear the site. Unless the site has a value greater than the value taken to clear it, it is unlikely that anyone would want to share the expense of removing the poisonous material. Some 'brown field' sites are in places which are not very near existing habitation and so it is less likely that they will be developed. In the past, many manufacturing companies did not consider the effects of the pollutants they emitted on the environment and disposed of waste materials as they wished. Nowadays in some countries, laws have been enacted

to limit the amounts of pollutants that can be discharged into the air, into the ground or into rivers. The number of 'brown field' sites may not increase exponentially as some people fear because of changing attitudes to safety and responsibilities by the chemical and other industries. There is an increasing number of 'responsible' manufacturing companies throughout the world and a greater awareness by the general public of the harmful effects of pollutants. However, if a company stops trading because of lack of money or gets into financial difficulties, problems may arise regarding the cleaning of the ground around the factory.

Self-assessment questions

1 a i Cu^{2+} (in CuCl_2)

ii Fe

iii Cu^{2+} (in CuCl_2)

iv Fe

b i Br_2

ii Cu

iii Br_2

iv Cu

c i PbO_2

ii SO_2

iii PbO_2

iv SO_2

(In part c lead goes from an oxidation state of +4 in PbO_2 to +2 in PbSO_4 ; it gains electrons. S goes from an oxidation state of +4 in SO_2 to +6 on PbSO_4 ; it loses electrons.)

2 a $2\text{I}^- + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$

b $2\text{Cl}^- + \text{MnO}_2 + 4\text{H}^+ \rightarrow \text{Cl}_2 + \text{Mn}^{2+} + 2\text{H}_2\text{O}$

c $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$

3 a The conduction is due to the movement of ions. The ions must be able to move to the electrodes before electrolysis can occur.

b It conducts electricity; this is due to the delocalised electrons, which can move throughout the layers of graphite. It has a high melting point so does not melt under the high temperatures in the electrolytic cell; this is due to its giant molecular structure of strong covalent bonds.

4 a Cations are positively charged. The cathode is negatively charged. Opposite charges attract.

b i $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$

Lead ions are reduced because electrons are gained.

Reduction always occurs at the cathode.

ii $-1 \text{ to } 0 = +1$

5 $Q = It$ (charge = current \times time in seconds)

charge = $1.80 \times 45.0 \times 60 = 4860 \text{ C}$

For $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$

1 mol of silver (108 g) is deposited by 96 500 C

so 4860 C deposits $\frac{4860}{96500} \times 108 = 5.44 \text{ g}$

6 $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

2 moles of electrons are required to produce 1 mole of hydrogen gas

so $2 \times 96\,500 \text{ C} = 193\,000 \text{ C}$ are required to produce 1 mol of hydrogen gas

$Q = It$ (charge = current \times time in seconds)

charge = $1.40 \times 15.0 \times 60 = 1260 \text{ C}$

1 mol hydrogen gas occupies 24 dm^3 at r.t.p.

so volume of hydrogen gas produced

$= \frac{1260}{193000} \times 24$

$= 0.157 \text{ dm}^3$

7 When aqueous sodium sulfate is electrolysed, oxygen is produced at the anode from OH^- ions.

$4\text{OH}^-(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$

4 moles of electrons are released per mole of O_2 formed

$= 4F = 4 \times 96\,500 = 386\,000 \text{ C mol}^{-1}$

$Q = It = 0.70 \times 55 \times 60 = 2310 \text{ C}$

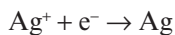
386 000 C produces 1 mol $\text{O}_2 = 24 \text{ dm}^3 \text{ O}_2$

so 2310 C produces $\frac{2310}{386000} \times 24.0$

$= 0.144 \text{ dm}^3 \text{ O}_2$ at r.t.p.

- 8 Quantity of charge passed to deposit 0.45 g of silver $Q = It = 0.15 \times 45 \times 60 = 405 \text{ C}$

The equation for the electrolysis shows that 1 mole of electrons is needed to produce 1 mole of silver:



To deposit 1 mol of silver (108 g) requires

$$\frac{108}{0.45} \times 405 \text{ C} = 97\,200 \text{ C}$$

- 9 $L = \frac{\text{charge on one mole of electrons (F)}}{\text{charge on one electron}}$

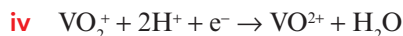
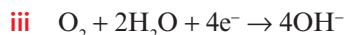
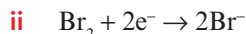
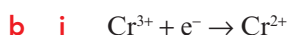
$$L = \frac{96485}{1.6022 \times 10^{-19}}$$

$$= 6.0220 \times 10^{23} \text{ mol}^{-1} \text{ (to 5 significant figures)}$$

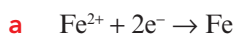
- 10 a Zn



- 11 a Ag^+ would ions react with Cl^- ions in the ZnCl_2 and form a precipitate of silver chloride.



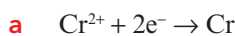
- 12 For the $\text{Fe}^{2+} / \text{Fe}$ half cell



b -0.44 V



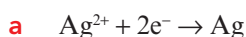
For the $\text{Cr}^{2+} / \text{Cr}$ half cell



b -0.91 V



For the Ag^+ / Ag half cell



b $+0.80 \text{ V}$

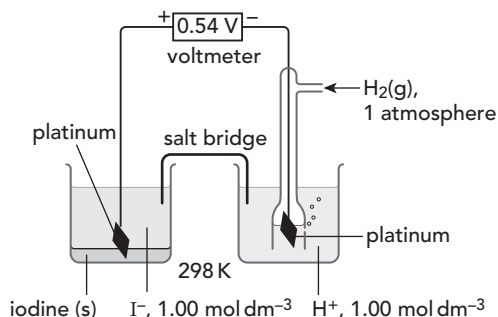


In all three cells the temperature must be 298 K and the standard hydrogen electrodes with H^+ concentration 1.00 mol dm^{-3} , hydrogen gas pressure 1 atm (101 kPa), and electrical contact made by platinum (coated with platinum black).



b $+0.51 \text{ V}$

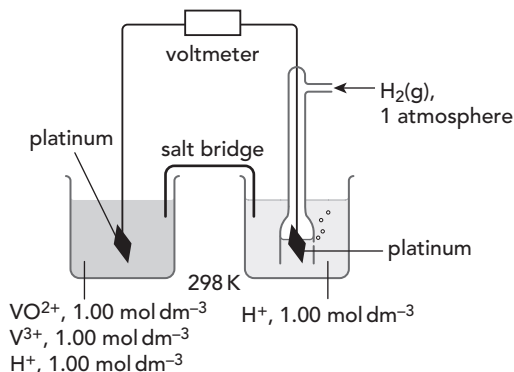
14



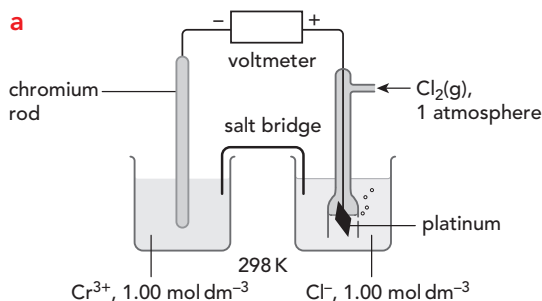
15 $+1.52 \text{ V}$

- 16 Platinum is an inert electrode. It does not take part in reactions.

17



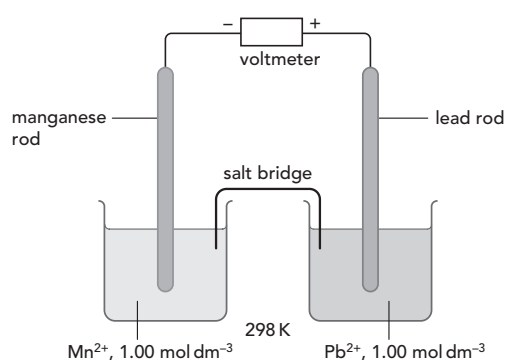
18 a



b $1.36 - (-0.74) = +2.10 \text{ V}$



19 a



- b** $(-0.13) - (-1.18) = 1.05 \text{ V}$
- c** $\text{Pb}^{2+} / \text{Pb}$ half-cell
- 20 a** F_2 / F^- is the + pole and $\text{Mn}^{2+} / \text{Mn}$ is the - pole so electron flow is $\text{Mn}^{2+} / \text{Mn}$ to F_2 / F^-
- b** I_2 / I^- is the + pole and $\text{Sn}^{4+} / \text{Sn}^{2+}$ is the - pole so electron flow is $\text{Sn}^{4+} / \text{Sn}^{2+}$ to I_2 / I^-
- c** $\text{Cr}_2\text{O}_7^{2-} / 2\text{Cr}^{3+}$ is the + pole and $\text{Cu}^{2+} / \text{Cu}$ is the - pole so electron flow is $\text{Cu}^{2+} / \text{Cu}$ to $\text{Cr}_2\text{O}_7^{2-} / 2\text{Cr}^{3+}$
- d** $\text{Ni}^{2+} / \text{Ni}$ is the - pole and $\text{Fe}^{3+} / \text{Fe}$ is the + pole so electron flow is $\text{Ni}^{2+} / \text{Ni}$ to $\text{Fe}^{3+} / \text{Fe}$
- 21 a** yes
 $5\text{Cl}^- + \text{MnO}_4^- + 8\text{H}^+ \rightarrow 2\frac{1}{2}\text{Cl}_2 + \text{Mn}^{2+} + 4\text{H}_2\text{O}$
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$
 has a more positive E^\ominus value so will proceed in the forward direction. The reaction $\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$ proceeds in the reverse direction.
- b** no
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$
 has a less positive E^\ominus value so cannot proceed in the forward direction while $\text{F}_2 + 2\text{e}^- \rightleftharpoons 2\text{F}^-$ proceeds in the back direction.
- c** yes
 $\text{V}^{2+} + \text{H}^+ \rightarrow \text{V}^{3+} + \frac{1}{2}\text{H}_2$
 $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$ has a more positive E^\ominus value so will proceed in the forward direction. The reaction $\text{V}^{3+} + \text{e}^- \rightleftharpoons \text{V}^{2+}$ proceeds in the reverse direction.
- d** no
 $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$ has a less positive E^\ominus value so cannot proceed in the forward direction while $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$ proceeds in the forward direction.
- 22 a** E^\ominus value must be more positive than +0.76 so Br_2 , Cl_2 , F_2 etc will do this.
- b** E^\ominus value must be more positive than +1.07 V so Cl_2 / acidified $\text{Cr}_2\text{O}_7^{2-} / \text{F}_2$ / acidified MnO_4^- / acidified O_2 will do this.
- c** E^\ominus value must be less positive than +0.17 V. Any of the species on the right-hand side that have a half-equation showing a negative value or less positive value than +0.17 V will do this.
- d** E^\ominus value must be more positive than +1.36 V so F_2 , PbO_2 , or acidified MnO_4^- for example will do this.
- 23 a** voltage = $1.52 - 1.36 = +0.16 \text{ V}$, so yes
- b** voltage = $1.52 - 2.87 = -1.35 \text{ V}$, so no
- c** voltage = $0.00 - (-0.26) = 0.26 \text{ V}$, so yes
- d** voltage = $0.00 - 0.77 = -0.77 \text{ V}$, so no
- 24 a** The E^\ominus value for $\frac{1}{2}\text{Br}_2 + \text{e}^- \rightleftharpoons \text{Br}^-$ has a more positive E^\ominus value than $\frac{1}{2}\text{I}_2 + \text{e}^- \rightleftharpoons \text{I}^-$ so $\frac{1}{2}\text{Br}_2 + \text{e}^- \rightleftharpoons \text{Br}^-$ accepts electrons more readily and will proceed in the forward direction while $\frac{1}{2}\text{I}_2 + \text{e}^- \rightleftharpoons \text{I}^-$ proceeds in the reverse direction.
- b** The E^\ominus value for $\frac{1}{2}\text{Br}_2 + \text{e}^- \rightleftharpoons \text{Br}^-$ has a less positive E^\ominus value than $\frac{1}{2}\text{Cl}_2 + \text{e}^- \rightleftharpoons \text{Cl}^-$ so $\frac{1}{2}\text{Br}_2 + \text{e}^- \rightleftharpoons \text{Br}^-$ accepts electrons less readily and cannot proceed in a forward direction while $\frac{1}{2}\text{Cl}_2 + \text{e}^- \rightleftharpoons \text{Cl}^-$ proceeds in the reverse direction. So bromine will not oxidise chloride ions to chlorine.
- 25 a** Cr^{2+}
- b** Ag
- 26 a** i E^\ominus value more than 1.33 V
 ii E^\ominus value less than 1.33 V
 iii E^\ominus value less than 1.33 V
- b** i stronger oxidising agent
 ii weaker oxidising agent
 iii weaker oxidising agent
- c** high concentration of $\text{Cr}_2\text{O}_7^{2-}$, high concentration of H^+ , low concentration of Cr^{3+}
- d** Increasing the concentration of reactants moves the equilibrium to the right in order to reduce these concentrations. E^\ominus goes up (becomes more positive) and the $\text{Cr}_2\text{O}_7^{2-} / \text{H}^+$ solution becomes a stronger oxidising agent.

27 a $E = E^\ominus + \frac{0.059}{z} \log_{10} [\text{Ni}^{2+}(\text{aq})]$

$$E = -0.25 + \frac{0.059}{2} \log_{10} (1.5)$$

$$E = -0.25 + 0.005(19) = -0.24 \text{ V}$$

b $E = E^\ominus + \frac{0.059}{z} \log_{10} [\text{Ag}^+(\text{aq})]$

$$E = +0.80 + \frac{0.059}{1} \log_{10} (0.0002)$$

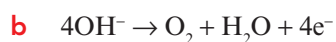
$$E = +0.80 + (-0.22) = +0.58 \text{ V}$$

28 B (+0.62 V)

29 Add a catalyst; increase the temperature; increase the concentration of dissolved reactants; increase the pressure of gaseous reactants; increase the surface area of solid reactants / solid catalyst.

30 E^\ominus values relate to standard conditions, but lab / industry conditions are not usually standard. However, if the E^\ominus values differ by more than 0.30 V, predictions based on E^\ominus values are usually correct. The rate of reaction may be very slow even though E^\ominus values indicate that a reaction is feasible.

31 a Hydrogen is below sodium in the discharge series. The H^+ / H_2 system has a more positive E^\ominus value than the Na^+ / Na system so hydrogen ions accept electrons more readily than sodium ions.

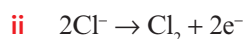


32 a anode: iodine; cathode: aluminium

b anode: chlorine; cathode: hydrogen

c anode: bromine; cathode: hydrogen

d anode: oxygen; cathode: zinc



b A mixture of oxygen and chlorine may be formed. The proportion of oxygen will increase as the solution becomes more dilute. In a concentrated solution of HCl, the chloride ions fall below OH^- ions in the discharge series because they are present in such high concentrations. Oxygen, rather than chlorine, is formed at the anode in very dilute solutions because the relatively lower concentration of Cl^- ions allows OH^- ions to fall below Cl^- ions in the discharge series.

Exam-style questions

1 a voltmeter; [1]

high resistance [1]

b i salt bridge; [1]

maintains an ionic balance in the two half-cells; [1]

completes the circuit [1]

ii filter paper [1]

soaked in (saturated) potassium nitrate [1]

c 1.00 mol dm⁻³ solution [1]

of Zn^{2+} ions / zinc sulfate / other soluble zinc salt [1]

d platinum electrode; [1]

surface allows electron transfer from one species to another; [1]

ensures electrical contact [1]

e all solutions at 1.00 mol dm⁻³; [1]

all gases at 101 kPa pressure; [1]

temperature 298 K [1]

[Total: 15]

2 a $\Delta E^\ominus_{\text{cell}} = +0.80 - (+0.34)$ [1]

$= +0.46 \text{ V}$ [1]

b $2\text{Ag}^+ + \text{Cu} \rightarrow 2\text{Ag} + \text{Cu}^{2+}$ [2]

[1 mark for correct reactants and products; 1 mark for balancing]

c i Cu, because it loses electrons [1]

ii Ag^+ , because it gains electrons [1]

iii Electrons flow through the external circuit to the silver electrode; [1]

electrons flow from negative pole to positive pole / negative pole better at releasing electrons (to external circuit). [1]

d The cell voltage becomes more positive; [1]

diluting the solution for the $\text{Cu}^{2+} / \text{Cu}$ half-cell makes the value of E for this half-cell less positive (accept suitable quoted values, e.g. +0.30 V); [1]

so difference between voltages of the half-cells increases. [1]

[Total: 11]

- 3 a** (The standard electrode potential of a half-cell is) the voltage of the half-cell [1]
relative to a hydrogen electrode [1]
under standard conditions. [1]
- b** standard hydrogen electrode as one of the half-cells; [1]
salt bridge and voltmeter; [1]
other half-cell is platinum electrode in 1.00 mol dm⁻³ Cl⁻ ions, e.g. NaCl; [1]
chlorine gas passed into solution at 1 atmosphere pressure; [1]
temperature 298 K [1]
- c** $\frac{1}{2} \text{Cl}_2 + \text{e}^- \rightarrow \text{Cl}^-$ or $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$ [1]
- d i** $E_{\text{cell}}^{\ominus} = +1.36 - (+0.54) = 0.82 \text{ V}$ [1]
ii $\text{Cl}_2 + 2\text{I}^- \rightarrow 2\text{Cl}^- + \text{I}_2$ or $\frac{1}{2} \text{Cl}_2 + \text{I}^- \rightarrow \text{Cl}^- + \frac{1}{2} \text{I}_2$ [2]
[1 mark for correct reactants and products; 1 mark for balancing]
[Total: 12]
- 4 a i** H⁺ ions for the reaction are supplied by the acid. [1]
ii The half-cell reaction has a large positive standard electrode potential; [1]
MnO₄⁻ ions accepts electrons / can be reduced from oxidation state +7 to +2. [1]
- b i** The standard electrode potential of the half-cell reaction for the iodine / iodide acid reaction is less positive than that for the MnO₄⁻ / Mn²⁺ half-cell; [1]
the iodine / iodide half-cell has a greater tendency to supply electrons; [1]
the iodine / iodide equilibrium loses electrons and moves to the left
 $\text{I}_2 + 2\text{e}^- \rightleftharpoons \text{I}^-$ (or $\frac{1}{2} \text{I}_2 + \text{e}^- \rightleftharpoons \text{I}^-$) [1]
the MnO₄⁻ / Mn²⁺ equilibrium gains electrons
 $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$ [1]
electrons flow from iodide ions to reduce the MnO₄⁻. [1]
ii $2\text{MnO}_4^-(\text{aq}) + 10\text{I}^-(\text{aq}) + 16\text{H}^+(\text{aq}) \rightleftharpoons 2\text{Mn}^{2+}(\text{aq}) + 5\text{I}_2(\text{aq}) + 8\text{H}_2\text{O}(\text{l})$ [2]
[1 mark for correct reactants and products; 1 mark for balancing]
[Total: 10]
- 5 a** $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$ or $\frac{1}{2} \text{Br}_2 + \text{e}^- \rightarrow \text{Br}^-$ [1]
 $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$ or $\frac{1}{2} \text{I}_2 + \text{e}^- \rightarrow \text{I}^-$ [1]
b salt bridge and voltmeter; [1]
Br₂ / Br⁻ half-cell with 1.00 mol dm⁻³ Br⁻ ions, e.g. NaBr; [1]
chlorine gas passed into solution at 1 atmosphere pressure; [1]
I₂ / I⁻ half-cell with 1.00 mol dm⁻³ I⁻ ions and aqueous iodine, e.g. KI; [1]
Pt electrode in both half cells; [1]
Pt electrode in contact with Br(l) as well as Br⁻ (aq); [1]
temperature of 298 K [1]
c Cell reaction for overall equation is + so reaction occurs as shown in the equation, favouring the products; [1]
for $E_{\text{cell}}^{\ominus}$ to be positive the equilibrium $\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$ must have a more positive value (than $\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$); [1]
so $\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$ has greater tendency to accept electrons (and goes in the forward direction); [1]
 $\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$ has a greater tendency to lose electrons (and goes in the backward direction). [1]
d Ni [1]
 $\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni}$ has a more negative E^{\ominus} value than $\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$; [1]
Ni has a greater tendency to lose electrons than I⁻; [1]
so $\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$ goes in the forward direction and Ni / Ni²⁺ in the reverse direction. [1]
[Total: 17]
- 6 a** The voltage of the half-cell [1]
relative to a hydrogen electrode [1]
under standard conditions. [1]

- b i** Fe^{3+} [1]
ii Zn [1]
c i $+0.77 - (+0.34) = +0.43 \text{ V}$ [1]
ii from the $\text{Cu}^{2+} / \text{Cu}$ half-cell to the $\text{Fe}^{3+} / \text{Fe}^{2+}$ half-cell; [1]
 electrons flow from negative pole to positive pole / negative pole better at releasing electrons (to the external circuit) [1]
iii $2\text{Fe}^{3+} + \text{Cu} \rightarrow 2\text{Fe}^{2+} + \text{Cu}^{2+}$ [2]
 [1 mark for correct reactants and products; 1 mark for balancing]
d i E value become more positive. [1]
ii Value of E_{cell} becomes less positive. [1]
iii The value of E_{cell} / the difference in values of the two half-equations is greater than 0.30 V. [1]
[Total: 13]
- 7 a** charge = $1.04 \times 6.00 \times 60 = 374.4 \text{ C}$ [1]
b $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
 2 moles of electrons are required to liberate 1 mole of H_2 [1]
 so $2 \times 96\,500 \text{ C} = 193\,000 \text{ C}$ required [1]
c i $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ [1]
ii charge ($Q = It$) = $0.300 \times 40 \times 60 = 720 \text{ C}$ [1]
 charge required to deposit 1 mole of $\text{Cu} = 720 \times \frac{63.5}{0.240} = 190\,500 \text{ C}$ [1]
 but 2 moles of electrons needed to deposit 1 mole of Cu so charge on a mole of electrons $F = \frac{190\,500}{2}$
 $F = 95\,250 \text{ C mol}^{-1}$ [1]
iii $L = \frac{\text{charge on a mole of electrons}}{\text{charge on one electron}}$ [1]
 $\frac{95\,250}{1.60 \times 10^{-19}} = 5.95 \times 10^{23} \text{ mol}^{-1}$ [1]
[Total: 9]
- 8 a i** Silver is below hydrogen in the discharge series / the ΔE^\ominus value of $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$ is more positive than that of $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$; [1]
 silver ions are better at accepting electrons than are H^+ ions' [1]
ii $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ [1]
- b i** $4\text{OH}^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + 4\text{e}^-$ [1]
ii Oxidation because loss of electrons / oxidation number of O decreases from -2 in OH^- to 0 in O_2 . [1]
c Water is slightly ionised to form OH^- and H^+ ions; [1]
 OH^- ions are removed to form oxygen; [1]
 leaving excess H^+ ions, which are responsible for the acidity. [1]
d charge = $0.180 \times 35 \times 60 = 378 \text{ C}$ [1]
 $96\,500 \text{ C}$ deposits 1 mol Ag / 1 mole electrons forms 1 mole silver ions; [1]
 mass of silver deposited = $\frac{378}{96\,500} \times 108 = 0.42 \text{ g}$ (to 2 significant figures) [1]
[Total: 11]
- 9 a** $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$ oxidation [1]
 $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$ reduction [1]
b i Use $\frac{[\text{Fe}^{3+}(\text{aq})]}{[\text{Fe}^{2+}(\text{aq})]}$ [1]
 correct substitution of values
 $E = +0.77 + 0.059 \log \frac{(0.1)}{(0.02)}$ [1]
 correct answer $+0.81 \text{ V}$ [1]
ii The ratio of the concentration of the oxidised and reduced forms = 1; [1]
 $\log_{10}(1)$ is zero so $0.059 \log 1$ is zero. [1]
c correct substitution of values
 $E = +0.80 + 0.059 \log (0.05)$ [1]
 correct answer $+0.72 \text{ V}$ [1]
d $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{e}^- = -0.72 \text{ V}$
 $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) = +0.81 \text{ V}$
 reversed sign of half-equation showing oxidation; [1]
 adding the two voltages $+0.81 \text{ V} - 0.72 \text{ V}$; [1]
 sign positive $+0.9 \text{ V}$ so reaction will occur; [1]
 explanation in terms of best oxidant and best reductant, e.g. under these conditions $\text{Fe}^{2+}(\text{aq})$ is the better reducing agent and $\text{Ag}^+(\text{aq})$ is the better oxidising agent [1]
[Total: 13]

10 a H^+ ; OH^- ; Na^+ ; Cl^- ; [2]

[all 4 correct = 2 marks; 2 or 3 correct = 1 mark, 0 or 1 correct = 0 marks]

b i $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ [1]

ii $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ [1]

c Cl^- ions lose electrons [1]

d Cl^- and H^+ ions removed; [1]

leaves (Na^+ and) OH^- ions in solution; [1]
 OH^- ions are responsible for alkaline character. [1]

e i -1 [1]

ii +5 [1]

f sodium chlorate(V) [1]

[Total: 11]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 21

Science in context

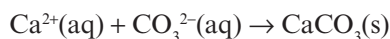
Learners are asked to suggest the problems of hard water. They may come up with the following suggestions. A few prompts may be necessary if they cannot think of anything.

- Waste of soap. Hard water needs much more soap before it forms a lather. So its cleaning power is reduced because it forms a scum. The scum is calcium salts of the long-chained carboxylic acids such as calcium stearate.
- Solid calcium carbonate ('scale' or 'fur') found in kettles, water pipes and boilers for making hot water does not conduct heat so it wastes energy because more energy is needed to boil water in a kettle or boiler. In boilers and hot water pipes the scale can block the boiler tubes and reduces the flow of hot water. In extreme cases the pressure of the steam in the boiler could build up so much that the boiler explodes.
- Scum marks on clothes. Soap and hard water form a scum. This makes dirty marks when washing clothes in the presence of hard water. Modern washing powders sometimes contain chemicals which reduce this by 'sequestering' the calcium ions. Nylon and silk are especially effected by scum.

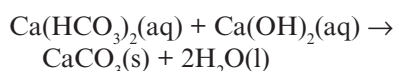
Learners are asked to find out about other methods of softening water.

- Distillation. This removes all hardness because the solids remain in the distillation flask and the water that comes over as a distillate is pure.
- Boiling removes temporary hardness (due to calcium hydrogencarbonate) but not permanent hardness (due to calcium sulfate).

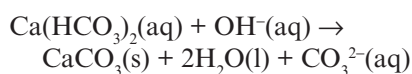
- Adding washing soda (sodium carbonate) changes soluble calcium and magnesium salts to insoluble carbonates.



- Slaked lime (calcium hydroxide) is used to soften water in reservoirs. It only removes temporary hardness.



- Aqueous ammonia (which contains hydroxide ions) removes only temporary hardness.



The resin is regenerated by pouring a concentrated aqueous solution of sodium chloride through it. The high concentration of sodium ions shifts the equilibrium to the left so that the calcium ions are released.

Learners may also ask about how water becomes hard in the first place and about the two types of hardness (temporary and permanent).

Carbon dioxide in the air dissolves in rainwater to form a weak acidic solution containing H^+ and HCO_3^- ions. When this rainwater passes through rocks containing calcium or magnesium carbonates, soluble hydrogencarbonates are formed. This is temporary hard water because the hardness can be removed by boiling. When rainwater passes through rocks containing calcium sulfate or magnesium sulfate, a small amount of these compounds dissolve. The hardness in this water cannot be removed by boiling. This is permanently hard water.

Self-assessment questions

- 1 a i HCOOH_2^+ conjugate acid, ClO_2^- conjugate base
 ii H_3O^+ conjugate acid, HS^- conjugate base
 b CH_3NH_2 conjugate base, CH_3NH_3^+ conjugate acid
- 2 a pH 3.5 (using $\text{pH} = -\log[\text{H}^+]$)
 b pH 2.0
 c pH 7.4
 d pH 11.3
 e pH 9.1
- 3 a $1.26 \times 10^{-3} \text{ mol dm}^{-3}$ (using $[\text{H}^+] = 10^{-\text{pH}}$)
 b $2.00 \times 10^{-4} \text{ mol dm}^{-3}$
 c $6.31 \times 10^{-12} \text{ mol dm}^{-3}$
 d $3.98 \times 10^{-6} \text{ mol dm}^{-3}$
 e $1.26 \times 10^{-13} \text{ mol dm}^{-3}$
- 4 a pH = 0 (the acid is completely ionised so $[\text{HNO}_3] = [\text{H}^+]$)
 b pH = 0.30 (the acid is completely ionised)
 c The aqueous solution contains 3.00 g of hydrogen chloride per dm^3 . To find the pH we need the hydrogen ion concentration in mol dm^{-3} . The relative formula mass of HCl is 36.5 (1.0 + 35.5).
 So concentration of hydrogen ions = $\frac{3.00}{36.5}$
 $= 0.0822 \text{ mol dm}^{-3}$
 HCl is completely ionised so $[\text{H}^+] = 0.0822 \text{ mol dm}^{-3}$
 $\text{pH} = -\log[\text{H}^+] = -\log_{10}(0.0822) = 1.09$
 d KOH dissociates completely in solution. So 0.00100 mol of KOH produces 0.00100 mol of OH^- ions.
 Using $K_w = [\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$
 $[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.00100}$
 $[\text{H}^+] = 1.00 \times 10^{-11} \text{ mol dm}^{-3}$
 $\text{pH} = 11.0$
 e We first have to convert grams of NaOH to moles dm^{-3} of NaOH.
 $M_r[\text{NaOH}] = 40.0$
 so moles NaOH = $\frac{0.200}{40}$
 $= 5.00 \times 10^{-3} \text{ mol dm}^{-3}$

As NaOH dissociates completely in solution the concentration of hydroxide ions is the same as the concentration of sodium hydroxide – $5.00 \times 10^{-3} \text{ mol dm}^{-3}$

Using $K_w = [\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{5.00 \times 10^{-3}}$$

$$[\text{H}^+] = 2.00 \times 10^{-12} \text{ mol dm}^{-3}$$

$$\text{pH} = 11.7$$

- 5 a i $K_a = \frac{[\text{H}^+(\text{aq})][\text{C}_6\text{H}_5\text{COO}^-(\text{aq})]}{[\text{C}_6\text{H}_5\text{COOH}(\text{aq})]}$
 ii $K_a = \frac{[\text{H}^+(\text{aq})][\text{CO}_3^{2-}(\text{aq})]}{[\text{HCO}_3^-(\text{aq})]}$
 iii $K_a = \frac{[\text{H}^+(\text{aq})][\text{NH}_3(\text{aq})]}{[\text{NH}_4^+(\text{aq})]}$
 b i acid = $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ base = $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$
 ii acid = HNO_2 base = NO_2^-
 iii acid = $\text{CO}_2 + \text{H}_2\text{O}$ base = HCO_3^-
 iv acid = HSiO_3^- base = SiO_3^{2-}

(a hydrogen ion has been removed to form the base, which is conjugate to the acid)

- 6 a In each case we first find the hydrogen ion concentration, then use the general equilibrium expression

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

and since $[\text{H}^+] = [\text{A}^-]$ we can write this as

$$K_a = \frac{[\text{H}^+]^2}{[\text{HA}]}$$

- i $[\text{H}^+] = 5.01 \times 10^{-5} \text{ mol dm}^{-3}$
 so $K_a = \frac{(5.01 \times 10^{-5})^2}{0.02}$
 $= 1.26 \times 10^{-7} \text{ mol dm}^{-3}$
 ii $[\text{H}^+] = 7.94 \times 10^{-4} \text{ mol dm}^{-3}$
 so $K_a = \frac{(7.94 \times 10^{-4})^2}{0.05}$
 $= 1.26 \times 10^{-5} \text{ mol dm}^{-3}$
 iii $[\text{H}^+] = 7.94 \times 10^{-5} \text{ mol dm}^{-3}$
 so $K_a = \frac{(7.94 \times 10^{-5})^2}{0.100}$
 $= 6.31 \times 10^{-8} \text{ mol dm}^{-3}$

b In each case $pK_a = -\log_{10} K_a$

i $-\log_{10} 1.26 \times 10^{-7} = 6.90$

ii $-\log_{10} 1.26 \times 10^{-5} = 4.90$

iii $-\log_{10} 6.31 \times 10^{-8} = 7.20$

7 a $K_a = \frac{[H^+]^2}{[\text{benzoic acid}]}$

so $[H^+]^2 = K_a \times [\text{benzoic acid}]$
 $= (6.3 \times 10^{-5}) \times (0.020)$

so $[H^+] = \sqrt{(6.3 \times 10^{-5}) \times (0.020)}$
 $= 1.12 \times 10^{-3} \text{ mol dm}^{-3}$

$pH = -\log_{10} (1.12 \times 10^{-3}) = 2.95$

b $K_a = \frac{[H^+]^2}{[Al(H_2O)_6^{3+}(aq)]}$

so $[H^+]^2 = K_a \times [Al(H_2O)_6^{3+}(aq)]$
 $= (1.0 \times 10^{-5}) \times (0.010)$

so $[H^+] = \sqrt{(1.0 \times 10^{-5}) \times (0.010)}$
 $= 3.16 \times 10^{-4} \text{ mol dm}^{-3}$

$pH = -\log_{10} (3.16 \times 10^{-4}) = 3.5$

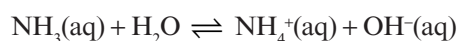
c $K_a = \frac{[H^+]^2}{[\text{methanoic acid}]}$

so $[H^+]^2 = K_a \times [\text{methanoic acid}]$
 $= (1.6 \times 10^{-4}) \times (0.10)$

so $[H^+] = \sqrt{(1.6 \times 10^{-4}) \times (0.10)}$
 $= 4.0 \times 10^{-3} \text{ mol dm}^{-3}$

$pH = -\log_{10} (4.0 \times 10^{-3}) = 2.4$

8 a The equilibrium mixture is:



i When hydrochloric acid is added, the additional H^+ ions combine with the OH^- ions in the equilibrium mixture (forming water). The position of equilibrium shifts to the right. Because there are relatively high concentrations of ammonia (base) and ammonium ions (conjugate acid) present compared with the concentration of added H^+ ions, the pH does not change very much.

ii When sodium hydroxide is added, the additional OH^- ions shift the position of equilibrium to the left. More ammonia and water are formed. Because there are relatively high concentrations

of ammonia and ammonium ions present compared with the concentration of added OH^- ions, the pH does not change very much.

b Ammonia is a weak base. The equilibrium lies well over to the left. So there are not enough NH_4^+ ions in the equilibrium mixture to remove added OH^- ions.

9 a i The equilibrium expression for this weak acid in the presence of its conjugate base is:

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

Rearrange the equilibrium expression to make $[H^+]$ the subject:

$$[H^+] = K_a \times \frac{[HCOOH]}{[HCOO^-]}$$

$$[H^+] = 1.6 \times 10^{-4} \times \frac{(0.0500)}{(0.100)}$$

$$= 8.00 \times 10^{-5} \text{ mol dm}^{-3}$$

$$pH = -\log_{10} [H^+]$$

$$= -\log_{10} (8.00 \times 10^{-5}) = 4.10$$

ii Using the same method as in part **i**:

$$[H^+] = 6.3 \times 10^{-5} \times \frac{(0.0100)}{(0.0400)}$$

$$= 1.58 \times 10^{-5} \text{ mol dm}^{-3}$$

$$pH = -\log_{10} [H^+]$$

$$= -\log_{10} (1.58 \times 10^{-5}) = 4.80$$

b Here we have to rearrange the equilibrium expression to make the conjugate base (sodium ethanoate) the subject.

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$[CH_3COO^-] = K_a \times \frac{[CH_3COOH]}{[H^+]}$$

$$pH = 4.90 = -\log_{10} [H^+]$$

$$\text{so } [H^+] = 1.26 \times 10^{-5} \text{ mol dm}^{-3}$$

Inserting the values:

$$[CH_3COO^-] = 1.74 \times 10^{-5} \times \frac{0.100}{1.26 \times 10^{-5}}$$

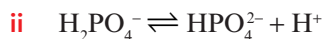
$$[CH_3COO^-] = 0.138 \text{ mol dm}^{-3}$$

$$\text{number of moles} = \text{concentration} \times \text{volume in dm}^3$$

$$= 0.138 \times 1.00 = 0.138 \text{ mol}$$

10 D

11 a i The acid will have one more proton than the base that is conjugate with it. So the acid is H_2PO_4^- and the base is HPO_4^{2-}



b The addition of hydrogen ions shifts the position of equilibrium to the left. Pr^- (the deprotonated form of the protein) combines with the extra hydrogen ions to form HPr (the protonated form of the protein) until equilibrium is re-established. If there are still fairly high concentrations of proteins present then the pH will not change very much.

12 a i $K_{\text{sp}} = [\text{Fe}^{2+}] [\text{OH}^-]^2$

ii $K_{\text{sp}} = [\text{Fe}^{3+}]^2 [\text{S}^{2-}]^3$

iii $K_{\text{sp}} = [\text{Al}^{3+}] [\text{OH}^-]^3$

b i $\text{mol dm}^{-3} \times (\text{mol dm}^{-3})^2 = \text{mol}^3 \text{ dm}^{-9}$

ii $(\text{mol dm}^{-3})^2 \times (\text{mol dm}^{-3})^3 = \text{mol}^5 \text{ dm}^{-15}$

iii $\text{mol dm}^{-3} \times (\text{mol dm}^{-3})^3 = \text{mol}^4 \text{ dm}^{-12}$

13 a i The concentrations of Cd^{2+} and S^{2-} ions are both $1.46 \times 10^{-11} \text{ mol dm}^{-3}$

$$K_{\text{sp}} = [\text{Cd}^{2+}] [\text{S}^{2-}]$$

Inserting the values:

$$K_{\text{sp}} = (1.46 \times 10^{-11}) \times (1.46 \times 10^{-11}) \\ = 2.13 \times 10^{-22} \text{ mol}^2 \text{ dm}^{-6}$$

ii We first have to calculate the concentration of the ions in mol dm^{-3} .

$$M_{\text{r}}(\text{CaF}_2) = 40.1 + (2 \times 19.0) = 78.1$$

$$\text{concentration in mol dm}^{-3} = \frac{0.0168}{78.1} \\ = 2.15 \times 10^{-4} \text{ mol dm}^{-3}$$

For every formula unit CaF_2 that dissolves, 1 Ca^{2+} ion and 2 F^- ions are formed.

$$\text{So } [\text{Ca}^{2+}] = 2.15 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{F}^-] = 2 \times (2.15 \times 10^{-4}) \text{ mol dm}^{-3} \\ = 4.30 \times 10^{-4} \text{ mol dm}^{-3}$$

$$K_{\text{sp}} = [\text{Ca}^{2+}] [\text{F}^-]^2$$

Inserting the values:

$$K_{\text{sp}} = (2.15 \times 10^{-4}) \times (4.30 \times 10^{-4})^2 \\ = 3.98 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$$

b $K_{\text{sp}} = [\text{Zn}^{2+}] [\text{S}^{2-}]$

As the concentration of Zn^{2+} and S^{2-} ions are the same, we can write the equilibrium expression:

$$K_{\text{sp}} = [\text{Zn}^{2+}]^2$$

$$1.6 \times 10^{-23} = [\text{Zn}^{2+}]^2$$

$$\text{so } [\text{Zn}^{2+}] = \sqrt{1.6 \times 10^{-23}} \\ = 4.0 \times 10^{-12} \text{ mol dm}^{-3}$$

(This is also the solubility of zinc sulfide, as one formula unit of ZnS contains one Zn^{2+} ion.)

c The equilibrium equation is:



If the solubility of Ag_2CO_3 is $y \text{ mol dm}^{-3}$, then

$[\text{Ag}^+] = 2y$ (because there are two silver ions in each formula unit of Ag_2CO_3) and

$[\text{CO}_3^{2-}] = y$ (because there is one carbonate ion in each formula unit of Ag_2CO_3).

The equilibrium expression is:

$$K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CO}_3^{2-}]$$

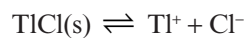
$$\text{so } 6.3 \times 10^{-12} = [\text{Ag}^+]^2 [\text{CO}_3^{2-}]$$

Substituting the values for y :

$$6.3 \times 10^{-12} = (2y)^2(y) = 2y \times 2y \times y = 4y^3$$

$$\text{so } y = \sqrt[3]{\frac{6.3 \times 10^{-12}}{4}} \\ = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$$

14 a This can be explained by the common ion effect. The equilibrium equation and the expression for the solubility product are:



$$K_{\text{sp}} = [\text{Tl}^+] [\text{Cl}^-]$$

When we add hydrochloric acid the chloride ion is common to both hydrochloric acid and thallium chloride; the added chloride ions shift the position of equilibrium to the left so thallium chloride is precipitated because the solubility product $[\text{Tl}^+] \times [\text{Cl}^-]$ is exceeded.

- b i** Equal volumes of each solution are combined. So each solution has diluted the other by 2.

So the concentration of each

$$\text{solution is } \frac{0.0010}{2}$$

$$= 5.0 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{So } [\text{Ca}^{2+}] = [\text{SO}_4^{2-}] =$$

$$5 \times 10^{-4} \text{ mol dm}^{-3}$$

- ii** A precipitate will form if the solubility product of calcium sulfate is exceeded. The equilibrium expression for the solubility product of calcium sulfate is:

$$K_{\text{sp}} = [\text{Ca}^{2+}] [\text{SO}_4^{2-}]$$

$$= 2.0 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$$

Substituting the values:

$$[\text{Ca}^{2+}] [\text{SO}_4^{2-}] = (5.0 \times 10^{-4}) \times (5.0 \times 10^{-4}) \\ = 2.5 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$$

This value is below the value of the solubility product for calcium sulfate. So no precipitate will form.

15 A

$$\text{16 a } [\text{BDA}(\text{H}_2\text{O})] = 0.032 \times \frac{1000}{50} = 0.64$$

$$\text{b } [\text{BDA}(\text{ether})] = (0.034 - 0.032) \times \frac{1000}{20} = 0.1$$

$$\text{c } K_{\text{pc}} = \frac{\text{BDA}(\text{H}_2\text{O})}{\text{BDA}(\text{ether})} = \frac{0.64}{0.1} = 6.4$$

Exam-style questions

$$\text{1 a i } \text{pH} = -\log_{10} [\text{H}^+] \quad [1]$$

$$\text{ii } K_{\text{w}} = [\text{H}^+] [\text{OH}^-] \quad [1]$$

$$\text{iii } K_{\text{a}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad [1]$$

$$\text{b } [\text{H}^+] = 0.00400 \text{ mol dm}^{-3} \quad [1]$$

$$\text{pH} = -\log_{10}(0.00400) = 2.40 \quad [1]$$

$$\text{c } K_{\text{a}} = 1.51 \times 10^{-5} = \frac{[\text{H}^+]^2}{0.00400} \quad [1]$$

$$\text{so } [\text{H}^+] = \sqrt{(1.51 \times 10^{-5}) \times (0.00400)} \\ = 2.45 \times 10^{-4} \text{ mol dm}^{-3} \quad [1]$$

$$\text{pH} = -\log_{10}(2.45 \times 10^{-4}) = 3.61 \quad [1]$$

$$\text{d } [\text{NaOH}] = \frac{\text{number of moles}}{\text{volume in dm}^3} \\ = \frac{0.25}{2.00} = 0.125 \text{ mol dm}^{-3} \quad [1]$$

$$K_{\text{w}} = [\text{H}^+] [\text{OH}^-] \\ = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

$$[\text{H}^+] = \frac{K_{\text{w}}}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.125} \quad [1] \\ = 8.00 \times 10^{-14} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}(8.00 \times 10^{-14}) = 13.1 \quad [1]$$

[Total: 11]

- 2 a** Rearrange the equilibrium expression to make $[\text{H}^+]$ the subject:

$$[\text{H}^+] = K_{\text{a}} \times \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \quad [1]$$

$$[\text{H}^+] = 1.74 \times 10^{-5} \times \frac{0.100}{0.100} \\ = 1.74 \times 10^{-5} \text{ mol dm}^{-3} \quad [1]$$

$$\text{pH} = -\log_{10} [\text{H}^+] \\ = -\log_{10}(1.74 \times 10^{-5}) = 4.76 \quad [1]$$

- b** Here we have to rearrange the equilibrium expression to make the conjugate base (sodium ethanoate) the subject:

$$K_{\text{a}} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{CH}_3\text{COO}^-] = K_{\text{a}} \times \frac{[\text{CH}_3\text{COOH}]}{[\text{H}^+]}$$

Convert pH 5.40 to $[\text{H}^+]$:

$$\text{pH} = -\log_{10} [\text{H}^+] \text{ so } [\text{H}^+] \\ = 3.98 \times 10^{-6} \text{ mol dm}^{-3} \quad [1]$$

Use equilibrium expression:

$$[\text{CH}_3\text{COO}^-] = K_{\text{a}} \times \frac{[\text{CH}_3\text{COOH}]}{[\text{H}^+]} \quad [1]$$

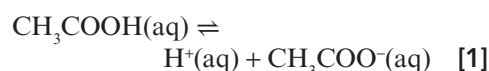
$$[\text{CH}_3\text{COO}^-] = 1.74 \times 10^{-5} \times \frac{0.0100}{3.98 \times 10^{-6}} \quad [1]$$

$$[\text{CH}_3\text{COO}^-] = 0.0437 \text{ mol dm}^{-3} \quad [1]$$

number of moles = concentration \times volume in dm^3

$$= 0.0437 \times 2 = 0.0874 \text{ mol} \quad [1]$$

- c** The buffer solution contains a conjugate pair of weak acid and conjugate base.



The added acid combines with the ethanoate ions to form un-ionised ethanoic acid / the equilibrium shifts to the left on adding more hydrogen ions (from the hydrochloric acid). [1]

The changes in the concentrations of un-ionised acid and conjugate base will be small, so the pH will not change significantly. [1]

[Total: 11]

- 3 a i Product of the ionic concentrations in a saturated solution; [1]

with each concentration raised to the power of the relative concentrations of the ions. [1]

($K_{sp} = [C^{x+}]^x [A^{y-}]^y$ for 2 marks)

- ii The decrease in the solubility of a dissolved salt [1]

by adding a solution of a compound that has an ion in common with the dissolved salt. [1]

- b i $K_{sp} = [Cu^+] [Br^-]$

As the concentrations of Cu^+ and Br^- ions are the same, we can write the equilibrium expression:

$$K_{sp} = [Cu^+]^2$$

$$3.2 \times 10^{-8} = [Cu^+]^2$$

$$\text{so } [Cu^+] = \sqrt{3.2 \times 10^{-8}}$$

$$= 1.8 \times 10^{-4} \text{ mol dm}^{-3} \quad [1]$$

(This is also the solubility of copper(I) bromide, because one formula unit of CuBr contains one Cu^+ ion.)

- ii $K_{sp} = [Cu^+] [Br^-]$

The bromide ion concentration is $0.0100 \text{ mol dm}^{-3}$ (neglecting the Br^- from the CuBr)

$$\text{so } 3.2 \times 10^{-8} = [Cu^+] \times (0.0100)$$

$$[Cu^+] = 3.2 \times 10^{-6} \text{ mol dm}^{-3} \quad [1]$$

- iii The addition of the common ion Br^- [1]

has shifted the equilibrium to the left (so copper(I) bromide precipitates). [1]

[Total: 9]

4 a $\text{concentration} = \frac{\text{moles}}{\text{volume (dm}^3\text{)}}$

$$6.00 \text{ g of ethanoic acid} = \frac{6.00}{60.0}$$

$$= 0.100 \text{ mol} \quad [1]$$

$$\text{concentration} = \frac{0.100}{0.200} = 0.500 \text{ mol dm}^{-3} \quad [1]$$

b $6.00 \text{ g of sodium ethanoate} = \frac{12.3}{82.0}$

$$= 0.150 \text{ mol} \quad [1]$$

$$\text{concentration} = \frac{0.150}{0.200} = 0.750 \text{ mol dm}^{-3} \quad [1]$$

c $[H^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]}$

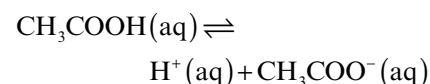
$$[H^+] = 1.74 \times 10^{-5} \times \frac{0.500}{0.750}$$

$$= 1.16 \times 10^{-5} \text{ mol dm}^{-3} \quad [1]$$

$$\text{pH} = -\log_{10}[H^+] = -\log_{10}(1.16 \times 10^{-5})$$

$$= 4.94 \quad [1]$$

- d In the equilibrium

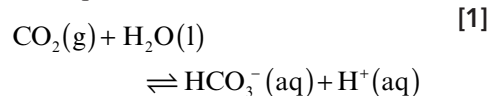


added H^+ ions are removed because they react with ethanoate ions to form un-ionised ethanoic acid molecules; [1]

added OH^- ions are removed because they react with H^+ ions to form water molecules and the equilibrium shifts to the right to form more ethanoate ions; [1]

there are still relatively high amounts of un-ionised ethanoic acid and ethanoate ions in the solution, so the pH does not change very much. [1]

- e The equilibrium is



Excess H^+ ions combine with HCO_3^- ions and the position of equilibrium moves to the left; [1]

excess OH^- ions are neutralised by H^+ ions and the equilibrium moves to the right to restore $[H^+]$ and minimise change in pH. [1]

[Total: 12]

5 a $K_{sp} = [\text{Cu}^+]^2 [\text{S}^{2-}]$ [1]

b $M_r(\text{Cu}_2\text{S}) = (2 \times 63.5) + 32.1 = 159.1$
 concentration in mol dm^{-3}
 $\text{moles} = \frac{(1.91 \times 10^{-12})}{159.1}$
 concentration = $1.20 \times 10^{-14} \text{ mol dm}^{-3}$ [1]

For every formula unit of Cu_2S that dissolves, 2 Cu^+ ions and 1 S^{2-} ion are formed;

$[\text{S}^{2-}] = 1.20 \times 10^{-14} \text{ mol dm}^{-3}$
 $[\text{Cu}^+] = 2 \times (1.20 \times 10^{-14}) \text{ mol dm}^{-3}$
 $= 2.40 \times 10^{-14} \text{ mol dm}^{-3}$ [1]

$K_{sp} = [\text{Cu}^+]^2 [\text{S}^{2-}]$ [1]

Inserting the values:

$K_{sp} = (2.40 \times 10^{-14})^2 \times (1.20 \times 10^{-14})$
 $= 6.91 \times 10^{-42} \text{ mol}^3 \text{ dm}^{-9}$ [2]

[1 mark for value; 1 mark for correct units]

c Copper(II) chromate will be precipitated / a precipitate will be observed; [1]

the product of the ions in solution exceeds the solubility product of copper(II) chromate /
 $[\text{Cu}^{2+}] [\text{CrO}_4^{2-}] > K_{sp}$ [1]

because of the common ion effect / copper(II) ions are present in both compounds. [1]

[Total: 9]

6 a Hydrochloric acid is a strong acid so
 $[\text{HCl}] = [\text{H}^+]$

$\text{pH} = -\log_{10} (0.25) = 0.60$ [1]

b $K_w = [\text{H}^+] [\text{OH}^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$
 (as $[\text{H}^+] = [\text{OH}^-]$, $K_w (1.00 \times 10^{-14}) = [\text{H}^+]^2$)

so $[\text{H}^+] = 2.00 \times 10^{-13} \text{ mol dm}^{-3}$ [1]

$\text{pH} = 12.7$ [1]

c i HI is the acid and HCl is the base [1]

(1) proton donated from HI to HCl to form H_2Cl^+ [1]

ii H_2Cl^+ is conjugate acid of HCl and I^- is conjugate base of HI [1]

d First convert pH to $[\text{H}^+]$:

$[\text{H}^+] = 10^{-3.1} = 7.94 \times 10^{-4} \text{ mol dm}^{-3}$ [1]

as $[\text{H}^+] = [\text{C}_2\text{H}_3\text{COO}^-]$

$K_a = \frac{[\text{H}^+]^2}{[\text{HA}]}$ or $K_a = \frac{[\text{H}^+]^2}{[\text{C}_2\text{H}_3\text{COOH}]}$ [1]

Entering the values:

$K_a = \frac{(7.94 \times 10^{-4})^2}{(0.0500)}$ [1]

$= 1.26 \times 10^{-5} \text{ mol dm}^{-3}$ [1]

[Total: 10]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 22

Science in context

Laser is an acronym for **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation. Learners may ask how a laser works. You cannot be expected to go into great detail because this is complex physics rather than chemistry. Lasers produce a highly focused beam of radiation of a single wavelength in which the vibrations of the light are in phase with one another.

The stages in producing laser radiation are:

- 1 Atoms or molecules are ‘pumped up’ to an excited state using a light source (use an analogy with excited electrons).
 - 2 A few of the excited species (atoms or molecules) lose photons (elementary particles with zero mass which move at speed of light).
 - 3 Each photon reacts with other excited species and stimulates them to emit a photon of the same wavelength.
 - 4 The photons travel in the same direction and are in phase (the vibrations of the waves are in step with each other).
- Learners should know the term absorption from their work on infrared spectra. They may not realise that the reconversion of iodine atoms into iodine molecules is the shape of a decay curve but a hint could be given that it is similar to the curve obtained when monitoring the loss in mass of the reaction mixture when hydrochloric acid reacts with calcium carbonate.
 - The laser technology was new and with any new method there are worries about the effectiveness of the method including its reliability, accuracy and precision. The fact that the experimenters were working in picoseconds means that any

small errors in timings would influence the results. Up to then chemists had assumed that the solvent just slowed the rate of reaction because the solvent just got in the way (reducing the frequency of collisions). The idea of a defined solvent cage around the molecules was controversial and there was no real evidence for it even from these experiments.

Although the idea of solvent cages had been suggested in the 1930s few took much notice of it because no suitable experimental methods were available. Solvents complicate matters when trying to understand how molecules react with each other. Nowadays, the idea of solvent cages has gained more acceptance. Solvent cages stop molecules from breaking up by forming a ‘cage’ around them but smaller fragments can escape the solvent cage, therefore making them recombine more slowly.

- This activity can stimulate arguments about the relationship between the different sciences. In reality, all the sciences are dependent on each other and distinctions between them are often blurred. There are physical chemists, biophysicists, computer analysts: a whole range of scientists having different backgrounds. Because many of the ideas in modern chemistry are complex, development in the subject often requires co-operation between different disciplines and often different institutions.

Although it is obvious that developments in physical chemistry depend on new instrumentation, learners should see that co-operation between the different branches of science is essential. In the development of X-ray diffraction (Chapter 19), mathematicians have played an essential part in developing methods for coping with the

complex calculations required. Physicists have developed techniques such as the laser and spectroscopic techniques which were originally of minor interest but have been taken up and developed by others for a wide range of uses. Sometimes it is chemists or biologists who have seen a possible use for an instrument and have worked together with physicists to develop it, e.g. lasers for specific purposes. A huge variety of lasers are available today, using gases, solutions, inorganic crystals to emit radiation of over a whole range of wavelengths. Chemists studying rates of reaction for biochemical processes often need the help of mathematicians to develop complex rate equations.

Self-assessment questions

- 1 a rate = $k[\text{cyclopropane}]$
 b rate = $k[\text{HI}]^2$
 c rate = $k[\text{C}_{12}\text{H}_{22}\text{O}_{11}][\text{H}^+]$
 d rate = $k[\text{HgCl}_2][\text{K}_2\text{C}_2\text{O}_4]^2$
 e rate = $k[\text{CH}_3\text{COCH}_3][\text{H}^+]$
- 2 a rate = $k[\text{cyclopropane}]$
 i 1st order with respect to cyclopropane
 ii 1st order overall
 b rate = $k[\text{HI}]^2$
 i 2nd order with respect to HI
 ii 2nd order overall
 c rate = $k[\text{C}_{12}\text{H}_{22}\text{O}_{11}][\text{H}^+]$
 i 1st order with respect to $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ and 1st order with respect to H^+
 ii 2nd order overall
 d rate = $k[\text{HgCl}_2][\text{K}_2\text{C}_2\text{O}_4]^2$
 i 1st order with respect to HgCl_2 and 2nd order with respect to $\text{K}_2\text{C}_2\text{O}_4$
 ii 3rd order overall
 e rate = $k[\text{CH}_3\text{COCH}_3][\text{H}^+]$
 i 1st order with respect to CH_3COCH_3 and H^+ , 0 order with respect to I_2
 ii 2nd order overall

- 3 a rearrange the equation in terms of k :

$$k = \frac{\text{rate}}{[\text{NO}_2]^2}$$

substitute the units:

$$k = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}$$

cancel mol dm^{-3} :

$$k = \frac{\cancel{\text{mol dm}^{-3}} \text{ s}^{-1}}{(\cancel{\text{mol dm}^{-3}}) \times (\text{mol dm}^{-3})}$$

units of $k = \text{s}^{-1} \text{ mol}^{-1} \text{ dm}^3 = \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

- b rearrange the equation in terms of k :

$$k = \frac{\text{rate}}{[\text{NO}_3]^0}$$

substitute the units: $k = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{1}$

units of $k = \text{mol dm}^{-3} \text{ s}^{-1}$

- c rearrange the equation in terms of k :

$$k = \frac{\text{rate}}{[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2}$$

substitute the units:

$$k = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})^2}$$

cancel mol dm^{-3} :

$$k = \frac{\cancel{\text{mol dm}^{-3}} \text{ s}^{-1}}{(\cancel{\text{mol dm}^{-3}}) \times (\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})^2}$$

units of $k = \text{s}^{-1} \text{ mol}^{-3} \text{ dm}^9 = \text{dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$

- d rearrange the equation in terms of k :

$$k = \frac{\text{rate}}{[\text{cyclopropane}]}$$

substitute the units: $k = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})}$

cancel mol dm^{-3} : $k = \frac{\cancel{\text{mol dm}^{-3}} \text{ s}^{-1}}{(\cancel{\text{mol dm}^{-3}})}$

units of $k = \text{s}^{-1}$

- 4 a 2nd order reaction, so upward curve (see red line in Figure 22.4)
- b zero order reaction, so horizontal straight line
- c 1st order reaction, so straight line through (0,0) showing direct proportionality (see blue line in Figure 22.4)

5 a shallow curve (see blue line in Figure 22.4)

b straight line in constant decline (see black line in Figure 22.4)

c steep curve, which then levels out (see red line in Figure 22.4)

6 a By measuring the increase in pressure with time in a closed system where the reaction is taking place or by measuring the volume of nitrogen gas given off with time using a gas syringe.

b Graph is a smooth downward curve levelling off gradually so seems to be first order with respect to benzenediazonium chloride.

c 1st half-life (from $0.58 \times 10^{-4} \text{ mol dm}^{-3}$ to $0.29 \times 10^{-4} \text{ mol dm}^{-3}$) = 470 s

2nd half-life (from $0.29 \times 10^{-4} \text{ mol dm}^{-3}$ to $0.145 \times 10^{-4} \text{ mol dm}^{-3}$) = 450 s

d 1st order reaction because successive half-lives are more or less the same (within experimental error).

7 a $\text{rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$

$$\text{so } k = \frac{\text{rate}}{[\text{H}_2\text{O}_2][\text{I}^-]}$$

for experiment 2: rate

$$= \frac{5.30 \times 10^{-6}}{(0.0300) \times (0.0100)}$$

$$= 0.0177 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for experiment 3: rate

$$= \frac{1.75 \times 10^{-6}}{(0.0050) \times (0.0200)}$$

$$= 0.0175 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

b $k = \frac{0.693}{480} = 1.44 \times 10^{-3} \text{ s}^{-1}$

c $t_{\frac{1}{2}} = \frac{0.693}{k}$; $k = 9.63 \times 10^{-5} \text{ s}^{-1}$

$$\text{so } t_{\frac{1}{2}} = \frac{0.693}{9.63 \times 10^{-5}} = 7200$$

(to 3 significant figures)

8 The temperature must remain constant throughout the experiment. The experiment should be designed to study the effect of changing the concentration of only one reactant at a time. The best approach is to ensure a large excess of methanol. The concentration of methanol is then assumed to be constant, as it is much higher than that of the hydrochloric acid, so we can monitor the concentration of HCl.

This allows the order of reaction with respect to HCl to be deduced.

9 a There is only one molecule in the rate equation so the reaction is 1st order.

b $\text{rate} = k[\text{NO}_2]$

$$\text{so } k = \frac{\text{rate}}{[\text{NO}_2]}$$

$$k = \frac{3.15 \times 10^{-5}}{3.00}$$

$$= 1.05 \times 10^{-5} \text{ s}^{-1}$$

(Did you spot the ' 10^{-5} ' in the heading of column 2?)

10 a $\text{rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+][\text{I}_2]^0$
 $= k[\text{CH}_3\text{COCH}_3][\text{H}^+]$

b Rearranging the rate equation then substituting the data:

$$k = \frac{\text{rate}}{[\text{CH}_3\text{COCH}_3][\text{H}^+]}$$

$$k = \frac{10.9 \times 10^{-6}}{(0.5 \times 10^{-3}) \times (1.25)}$$

$$= 1.74 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

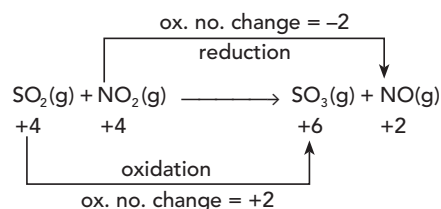
11 The rate-determining step is the slow step. This involves the reaction of H_2O_2 with I^- ions. These are the only two species that appear in the rate equation. The hydrogen ions do not appear in the rate equation because they are involved in a fast step, which takes place after the rate-determining step.

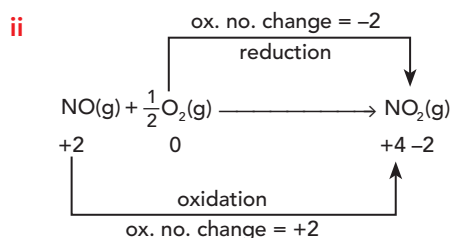
12 D

13 a ii Mn^{3+} and Mn^{2+} and

iii Ce^{4+} and Ce^{3+} ; these are the only pairs that have E^\ominus values between those of the $\text{S}_2\text{O}_8^{2-} / \text{SO}_4^{2-}$ and I^- / I_2 pairs.

b i



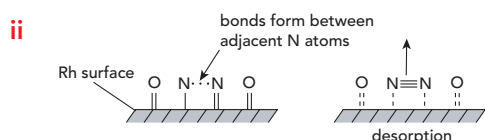
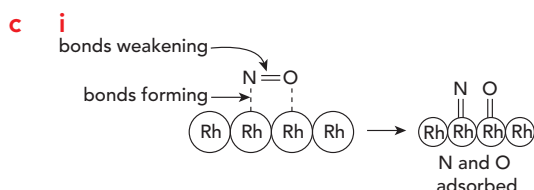


14 a the releasing of product molecules from the surface of a catalyst

b The ethene and hydrogen are adsorbed onto the surface of the nickel. In this process weak bonds are formed between the ethene and the surface of the nickel and between the hydrogen and the surface of the nickel.

The bonds between the hydrogen atoms are weakened and the pi-bond of the ethene is also weakened. Adsorbed hydrogen atoms close to the adsorbed ethene then react to form ethane.

The bonds between the ethane and the surface of the nickel weaken and the ethane moves away from the surface of the catalyst.



Exam-style questions

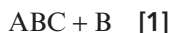
- 1 a correct axes, suitably labelled; [1]
points plotted correctly; [1]
curve of best fit drawn [1]
- b half-life method used; [1]
three successive half-lives shown to be similar [1]
- c tangents drawn correctly at each of the three concentrations (if 2 marks not scored, 1 mark for drawing one tangent correctly); [2]
rates calculated from gradients [1]

- d graph plotted of rate against concentration; [1]
points plotted correctly; [1]
line of best fit drawn [1]
- e it is a straight line; [1]
through 0,0 [1]
[it shows direct proportionality gains 2 marks]

[Total: 13]

- 2 a i the power / index [1]
to which the concentration of a particular reactant is raised in the rate equation [1]
- ii To find the order of reaction with respect to A, use experiments 1, 2 and 3; [1]
doubling [A] has no (significant) effect on the rate; [1]
so reaction is zero order with respect to A. [1]
- To find the order of reaction with respect to B, use experiments 4, 5 and 6; [1]
doubling [B] increases rate by factor of 4; [1]
so reaction is 2nd order with respect to B. [1]
- To find the order of reaction with respect to C, use experiments 7, 8 and 9; [1]
doubling [C] doubles the rate; [1]
so reaction is 1st order with respect to C. [1]
- b i rate = $k[B]^2[C]$ [1]
- ii 3 [1]
- iii rearranging the rate equation:
 $k = \frac{\text{rate}}{[B]^2[C]}$ [1]
correct value:
 $= \frac{0.00073}{(0.300)^2(1.00)} = 8.1 \times 10^{-3}$ [1]
units are $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$ [1]
- c e.g. the first step involves the collision of two molecules of B and one of C, forming B₂C; [1]
this is the slow / rate-determining step; [1]

the fast step involves A colliding with the intermediate; $B_2C + A \rightarrow$



[Total: 19]

3 a zero order [1]

b 2nd order [1]

c i time taken for the concentration of a reactant to fall to half its original value [1]

ii it remains constant [1]

d graph plotted so that [propanone] halves every 10 s (1 mark for each point plotted correctly):

20 s \rightarrow 2 mmol dm⁻³ [1]

30 s \rightarrow 1 mmol dm⁻³ [1]

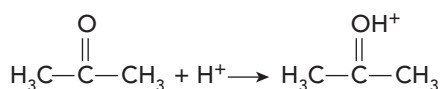
40 s \rightarrow 0.5 mmol dm⁻³ [1]

50 s \rightarrow 0.25 mmol dm⁻³ [1]

e the slowest step; [1]

its rate limits the overall rate of reaction [1]

f [3]



[1 mark for each reactant; 1 mark for the product]

[Total: 13]

4 a a substance that speeds up a chemical reaction / changes the reaction rate; [1]

but is chemically unchanged at the end of the reaction [1]

b i correct axes, suitably labelled; [1]
points correctly plotted; [1]

curve of best fit drawn [1]

ii half-life = 1.5 min; [1]

correct working shown on graph [1]

iii tangent drawn to curve at $t = 2$ min; [1]

$$\text{gradient of tangent} = \frac{-1.18}{4.1} \quad [1]$$

$$= -0.287 \quad [1]$$

$$\text{rate} = 0.287 \text{ mol dm}^{-3} \text{ min}^{-1} \quad [1]$$

c i half-life is constant; [1]

reaction is first order; [1]

$$\text{rate} = k[\text{H}_2\text{O}_2] \quad [1]$$

$$\text{ii } k = \frac{\text{rate}}{[\text{H}_2\text{O}_2]} \quad [1]$$

$$= \frac{0.287}{0.61} = 0.470 \quad [1]$$

units are min⁻¹ [1]

$$\text{iii rate} = k[\text{H}_2\text{O}_2] = 0.470 \times 2 = 0.940 \quad [1]$$

units are mol dm⁻³ min⁻¹ [1]

[Total: 19]

5 a correct axes, suitably labelled; [1]

points correctly plotted; [1]

curve of best fit drawn [1]

b 1st order; [1]

rate of reaction is directly proportional to peroxodisulfate concentration [1]

$$\text{c rate} = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-] \quad [1]$$

d i homogeneous (catalysis); [1]

the catalysts and reactants are in the same phase / are all in the aqueous phase [1]

ii In equation 1, both ions are negative / have the same charge; [1]

so tend to repel each other. [1]

In equations 2 and 3, the ions are oppositely charged / one is positive and the other negative; [1]

so are more likely to attract each other. [1]

[Total: 12]

6 a correct axes, suitably labelled; [1]

points correctly plotted; [1]

line of best fit drawn [1]

b The gradient and therefore the rate is constant, even though the concentration of iodine is changing. [1]

c No – there must be a slow step which doesn't involve iodine. [1]

d The balanced equation tells us about number of molecules of reactants consumed and products produced [1]

and their formulae; [1]

the rate equation tells us how many of each reactant molecules [1]

are present in the slowest / rate-determining step. [1]

[Total: 10]

- 7 a i** (Catalysis in which) the catalyst is in a different phase [1]
from the reactants / rest of the reaction mixture. [1]
- ii** Reactant molecules adsorbed onto the surface (of the catalyst); [1]
bonds within the reactant molecules weakened / broken; [1]
new bonds formed with adjacent atoms to form products; [1]
products desorbed from catalyst surface. [1]
- b** $2\text{NO}_2 \rightarrow \text{NO} + \text{NO}_3$ slow [1]
 $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$ fast [1]
[allow other reactions with suitable intermediate]
- c i** NO : order is 2nd order; [1]
when concentration of NO increased 3-fold, rate of reaction increases 9-fold / by $(3)^2$; [1]
 O_2 : order is 1st order; [1]
when concentration of oxygen increased by $4/3$, rate of reaction is also increased by $4/3$ (or similar argument). [1]
- ii** $\text{rate} = k[\text{O}_2][\text{NO}_2]^2$ [1]
- iii** $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$ [1]
- [Total: 14]**
- 8 a** Any two suitable methods (1 mark for method and 1 mark for explanation); for example:
- Electrical conductivity; [1]
because ions are present in the reactants but not in the products. [1]
- Titration of small **samples** with standard alkali; [1]
because the concentration of hydrogen ions falls during the reaction. [1]
- [not titration with standard alkali without qualification, as this suggests that the whole reaction mixture is being titrated]
- b i** BrO_3^- : order is 1st order; [1]
compare experiments 2 and 3; doubling the concentration doubles the rate; [1]
 Br^- : order is 1st order; [1]
compare experiments 2 and 4; doubling the concentration doubles the rate; [1]
 H^+ : order is 2nd order; [1]
compares experiments 1 and 2; doubling the concentration increases the rate 4-fold / $(2)^2$. [1]
- ii** $\text{rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$ [1]
- iii** $\text{dm}^9 \text{mol}^{-3} \text{s}^{-1}$ [1]
- c** Increase in temperature increases value of rate constant [1]
The maximum of Boltzmann distribution curve shifts to the right when temperature increases [1]
Greater proportion of particles have energy greater than the activation energy [1]
The rate constant is proportional to the fraction of molecules with energy equal to or greater than the activation energy. [1]
- [Total: 16]**

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 23

Science in context

Students are introduced to entropy via the Second Law of Thermodynamics. Entropy changes do not account fully for the essential features of rubber because loosely held molecules should slide past each other and untangle as well as uncoiling when a pulling force is applied. Polymers such as rubber (elastomers) seem to have a 'molecular memory' which enables them to return to their original arrangement. The reason for this elastic recovery is that the coiled chains in unstretched rubber are looped round each other so they are more or less knotted together in some places. This effect is greatly enhanced in synthetic elastomers by replacing the 'knots' with cross links. These permanently anchor the chain at various points. The best elastomers have only a small amount of cross linking so that they can successfully combine large movement of parts of the chain whilst not interfering with the cross-linked parts.

Students are then asked to think of some environmental issues relating to rubber production. They should be reminded of some of the similar issues mentioned in Chapters 3, 6 and 16.

These include:

- pollution of waterways by run-off of pollutants from the large quantities of water used in washing the rubber (the ammonia and phosphates used will cause eutrophication)
- toxic hydrogen sulfide may be breathed in by workers
- harmful acids may get into the soil and water or affect workers handling the sheets of rubber
- wood smoke produces particulates which are harmful to health and can cause cancer
- collection and transport of rubber from lots of small areas requires lorries and therefore further pollution from dust / combustion of diesel fuel.

Self-assessment questions

- 1 a Raise 2 (for two gas jars) to the power of the number of molecules (4):
 $2^4 = 2 \times 2 \times 2 \times 2 = 16$
- b As there are 16 ways, the probability of any one of these arrangements is 1 in 16.
- c i spontaneous (because there are more ways of spreading out the sugar molecules when they dissolve)
- ii spontaneous (because there are more ways of spreading out the ammonia molecules when they mix with the air molecules)
- iii not spontaneous (because ice forms at 0 °C and the energy transferred from the surroundings at 10 °C gives the molecules enough energy to move semi-independently of each other and so there are a greater number of ways of arranging the energy in the liquid than in the solid)
- iv spontaneous (because there is enough energy given to the molecules at 20 °C for some of them to escape, thus allowing more spreading out of molecules in the vapour than in the liquid)
- v not spontaneous (because the strength of the bonding between water molecules alone is greater than the strength between water and oil molecules; so the oil molecules cannot mix and spread between the water molecules)
- vi not spontaneous (because the temperature is not high enough to break bonds in the limestone (calcium carbonate); the ions in the calcium carbonate remain ordered)

2 a Bromine is a liquid, so its molecules are able to rotate / slide over each other so there is more disorder (higher entropy) than in iodine, which is a solid, in which the molecules cannot move.

b Both are gases but methane, CH_4 , is a more complex molecule with two different types of atom. Complex molecules tend to have greater entropy values than simpler molecules.

c Mercury is a liquid, so its atoms are able to rotate / slide over each other so there is more disorder (higher entropy) than in sodium, which is a solid, in which the atoms cannot move.

d Although SO_3 has only one oxygen atom more than SO_2 , which makes SO_3 a slightly more complex molecule, SO_2 has a much greater entropy because it is a gas, whereas SO_3 is a liquid. The particles in gases move freely from place to place and so there is more disorder are many more ways of spreading out the energy than in liquids whose particles can only rotate / slide over each other and vibrate.

3 a The entropy of the reactants is greater. Two gases (high entropy and two molecules) are being converted to a solid (low entropy and one molecule).

b Difficult to decide. The product SO_2 is a gas, which is likely to have a higher entropy than oxygen because it is a more complex molecule. However, there are two molecules on the left and only one on the right. The entropy of the solid sulfur, however, is low.

(The entropies in $\text{J K}^{-1} \text{mol}^{-1}$:

$$S^\ominus[\text{S(s)}] = 31.8$$

$$S^\ominus[\text{O}_2(\text{g})] = 205$$

$$S^\ominus[\text{SO}_2(\text{g})] = 248.1$$

show that the sum of the entropies of the reactants and the entropy of the product are similar.)

c The entropy of the reactants is greater. One of the reactants, carbon dioxide, is a gas, so has a very high entropy. This outweighs the entropies of the products which are both solids. Solids have low entropies.

d The entropy of the reactants is greater. One of the reactants, chlorine, is a gas, so has a very high entropy. This outweighs the entropies of the single product which is a solid. Solids have low entropies.

e The entropy of the products is greater. Two gases are produced (2 moles of gases) both of which have high entropy. The reactants have only one gas (1 mole of gas). The entropies of the solids are much smaller than those of the gases and so can be ignored.

f Difficult to decide. There are equal numbers of moles of gases on each side of the equation. We would have to know the individual values of the entropies of each molecule.

g The entropy of the products is greater. Reactants: potassium has low entropy because it is a solid; water has medium entropy because it is a liquid.

Products: aqueous potassium hydroxide has medium entropy (not only is it a liquid, but potassium ions and hydroxide ions are spread out randomly in the solution); hydrogen has high entropy because it is a gas. If we assume that water and aqueous potassium hydroxide have similar entropies, the production of hydrogen gas causes the entropy of the products to be greater.

h The entropy of the products is greater because carbon dioxide is a gas and therefore has more disorder than either magnesium carbonate or the magnesium oxide.

$$\begin{aligned} \Delta S_{\text{system}}^\ominus &= \sum S_{\text{products}}^\ominus - \sum S_{\text{reactants}}^\ominus \\ &= 2 \times S^\ominus[\text{H}_2\text{O(l)}] + S^\ominus[\text{O}_2(\text{g})] - 2 \times S^\ominus[\text{H}_2\text{O}_2(\text{l})] \end{aligned}$$

$$= (2 \times 69.90) + 205.0 - 2 \times 109.6$$

$$= 344.8 - 219.2$$

$$\Delta S_{\text{system}}^\ominus = +125.6 \text{ J K}^{-1} \text{mol}^{-1}$$

$$\begin{aligned} \Delta S_{\text{system}}^\ominus &= \sum S_{\text{products}}^\ominus - \sum S_{\text{reactants}}^\ominus \\ &= S^\ominus[\text{N}_2\text{O(g)}] + 2 \times S^\ominus[\text{H}_2\text{O(g)}] - S^\ominus[\text{NH}_4\text{NO}_3(\text{s})] \\ &= 219.7 + 2 \times 109.6 - 151.1 \end{aligned}$$

$$= 438.9 - 151.1$$

$$\Delta S_{\text{system}}^{\ominus} = +287.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \text{c } \Delta S_{\text{system}}^{\ominus} &= \sum S_{\text{products}}^{\ominus} - \sum S_{\text{reactants}}^{\ominus} \\ &= 2 \times S^{\ominus}[\text{MgO(s)}] - \{2 \times S^{\ominus}[\text{Mg(s)}] + S^{\ominus}[\text{O}_2(\text{g})]\} \end{aligned}$$

$$= 2 \times 26.90 - \{(2 \times 32.70) + 205.0\}$$

$$= 53.8 - 270.4$$

$$\Delta S_{\text{system}}^{\ominus} = -216.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \text{d } \Delta S_{\text{system}}^{\ominus} &= \sum S_{\text{products}}^{\ominus} - \sum S_{\text{reactants}}^{\ominus} \\ &= 2 \times S^{\ominus}[\text{NaCl(s)}] - \{2 \times S^{\ominus}[\text{Na(s)}] + S^{\ominus}[\text{Cl}_2(\text{g})]\} \end{aligned}$$

$$= 2 \times 72.10 - \{(2 \times 51.20) + 165.0\}$$

$$= 144.2 - 267.4$$

$$\Delta S_{\text{system}}^{\ominus} = -123.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \text{e } \Delta S_{\text{system}}^{\ominus} &= \sum S_{\text{products}}^{\ominus} - \sum S_{\text{reactants}}^{\ominus} \\ &= 3 \times S^{\ominus}[\text{MgO(s)}] + 2 \times S^{\ominus}[\text{Fe(s)}] \\ &\quad - \{3 \times S^{\ominus}[\text{Mg(s)}] + S^{\ominus}[\text{Fe}_2\text{O}_3(\text{s})]\} \end{aligned}$$

$$= (3 \times 26.90) + (2 \times 27.30) - \{(3 \times 32.70) + 87.40\}$$

$$= 135.3 - 185.5$$

$$\Delta S_{\text{system}}^{\ominus} = -50.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{5 a } \text{enthalpy change} = -393.5 \times 1000$$

$$= -393\,500 \text{ J mol}^{-1}$$

$$\text{temperature in K} = 0 + 273 \text{ K} = 273 \text{ K}$$

$$\begin{aligned} \Delta S_{\text{surroundings}}^{\ominus} &= \frac{\Delta H_{\text{reaction}}^{\ominus}}{T} \\ &= \frac{-(-393\,500)}{273} \end{aligned}$$

$$= +1441 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{b } \text{enthalpy change} = +307.9 \times 1000$$

$$= +307\,900 \text{ J mol}^{-1}$$

$$\text{temperature in K} = 330 + 273 = 603 \text{ K}$$

$$\begin{aligned} \Delta S_{\text{surroundings}}^{\ominus} &= \frac{\Delta H_{\text{reaction}}^{\ominus}}{T} \\ &= \frac{-(-307\,900)}{603} \end{aligned}$$

$$= +510.62 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{c } \text{enthalpy change} = -271.1 \times 1000$$

$$= -271\,100 \text{ J mol}^{-1}$$

$$\text{temperature in K} = 298 \text{ K}$$

$$\begin{aligned} \Delta S_{\text{surroundings}}^{\ominus} &= \frac{\Delta H_{\text{reaction}}^{\ominus}}{T} \\ &= \frac{-(-271\,100)}{298} \end{aligned}$$

$$= +909.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{d } \text{enthalpy change} = +34.30 \times 1000$$

$$= +34\,300 \text{ J mol}^{-1}$$

$$\text{temperature in K} = -3 + 273 \text{ K} = 270 \text{ K}$$

$$\begin{aligned} \Delta S_{\text{surroundings}}^{\ominus} &= \frac{\Delta H_{\text{reaction}}^{\ominus}}{T} \\ &= \frac{-(+34\,300)}{270} \end{aligned}$$

$$= -127.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \text{6 a } \Delta S_{\text{system}}^{\ominus} &= \sum S_{\text{products}}^{\ominus} - \sum S_{\text{reactants}}^{\ominus} \\ &= S^{\ominus}[\text{H}_2\text{S(g)}] - \{S^{\ominus}[\text{S(s)}] + S^{\ominus}[\text{H}_2(\text{g})]\} \\ &= 205.7 - \{31.80 + 130.6\} \end{aligned}$$

$$= 205.7 - 162.4$$

$$\Delta S_{\text{system}}^{\ominus} = +43.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \Delta S_{\text{surroundings}}^{\ominus} &= \frac{\Delta H_{\text{reaction}}^{\ominus}}{T} \\ &= \frac{-(-20.6 \times 1000)}{298} \\ &= +69.1 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S_{\text{total}}^{\ominus} &= S_{\text{system}}^{\ominus} + S_{\text{surroundings}}^{\ominus} \\ &= +43.3 + (+69.1) \end{aligned}$$

$$\Delta S_{\text{total}}^{\ominus} = +112 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \text{b } \Delta S_{\text{system}}^{\ominus} &= S_{\text{products}}^{\ominus} - S_{\text{reactants}}^{\ominus} \\ &= S^{\ominus}[\text{C}_2\text{N}_2(\text{g})] - \{2 \times S^{\ominus}[\text{C(s)}] + S^{\ominus}[\text{N}_2(\text{g})]\} \end{aligned}$$

$$= 242.1 - \{2 \times 5.700 + 191.6\}$$

$$= 242.1 - 203.0$$

$$\Delta S_{\text{system}}^{\ominus} = +39.10 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \Delta S_{\text{surroundings}}^{\ominus} &= \frac{\Delta H_{\text{reaction}}^{\ominus}}{T} \\ &= \frac{-(+307.9 \times 1000)}{298} \\ &= -1033 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S_{\text{total}}^{\ominus} &= S_{\text{system}}^{\ominus} + S_{\text{surroundings}}^{\ominus} \\ &= +39.10 - 1033 \end{aligned}$$

$$\Delta S_{\text{total}}^{\ominus} = -994 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \text{c } \Delta S_{\text{system}}^{\ominus} &= S_{\text{products}}^{\ominus} - S_{\text{reactants}}^{\ominus} \\ &= S^{\ominus}[\text{P}_4\text{O}_{10}(\text{s})] - \{4 \times S^{\ominus}[\text{P(s)}] + 5 \times S^{\ominus}[\text{O}_2(\text{g})]\} \end{aligned}$$

$$= 228.9 - \{4 \times 41.10 + 5 \times 205.0\}$$

$$= 228.9 - 1189.4$$

$$\Delta S_{\text{system}}^{\ominus} = -960.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{surroundings}}^{\ominus} = \frac{\Delta H_{\text{reaction}}^{\ominus}}{T}$$

$$= \frac{-(-2984 \times 1000)}{298}$$

$$= +10\,013 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

$$= -960.5 + 10\,013$$

$$\Delta S_{\text{total}}^{\ominus} = 9053 \text{ J K}^{-1} \text{ mol}^{-1}$$

d $\Delta S_{\text{system}}^{\ominus} = \sum S_{\text{products}}^{\ominus} - \sum S_{\text{reactants}}^{\ominus}$

$$= 3 \times S^{\ominus}[\text{CO}_2(\text{g})] + 4 \times S^{\ominus}[\text{H}_2\text{O}(\text{l})] - \{S^{\ominus}[\text{C}_3\text{H}_8(\text{g})] + 5 \times S^{\ominus}[\text{O}_2(\text{g})]\}$$

$$= (3 \times 213.6) + (4 \times 69.90) - \{269.9 + 5 \times 205.0\}$$

$$= 920.4 - 1294.9$$

$$\Delta S_{\text{system}}^{\ominus} = -374.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{surroundings}}^{\ominus} = \frac{\Delta H_{\text{reaction}}^{\ominus}}{T}$$

$$= \frac{-(-2219.2 \times 1000)}{298}$$

$$= +7447 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

$$= -374.5 + 7446.9$$

$$\Delta S_{\text{total}}^{\ominus} = +7072 \text{ J K}^{-1} \text{ mol}^{-1}$$

- 7 a** $\Delta S_{\text{surroundings}}^{\ominus}$ is calculated from $-\Delta H_{\text{reaction}}^{\ominus} / T$. So, as the temperature, T , increases, the value of $\Delta S_{\text{surroundings}}^{\ominus}$ gets less negative if the value of $\Delta H_{\text{reaction}}^{\ominus}$ is positive. The enthalpy change of the surroundings may then be sufficiently low so that $\Delta S_{\text{system}}^{\ominus} + \Delta S_{\text{surroundings}}^{\ominus}$ is a positive entropy change.

- b i** a system in which there is exchange of energy with the surroundings but no loss or gain of matter to or from the surroundings
- ii** The volume of gas is decreased, so the carbon dioxide molecules are closer together. The closer the molecules, the lower the degree of randomness or disorder and the lower the entropy. So the position of equilibrium shifts towards the left, where there are fewer gas molecules. The calcium carbonate and calcium oxide play little part because their entropy is very low.

- iii** zero; this is because at equilibrium $S_{\text{total}}^{\ominus} (\text{forward reaction}) = S_{\text{total}}^{\ominus} (\text{backward reaction})$

- 8 a** Step 1: convert the value of $\Delta H_{\text{r}}^{\ominus}$ to J mol^{-1} $-184.6 \times 1000 = -184\,600 \text{ J mol}^{-1}$

Step 2: calculate $\Delta S_{\text{system}}^{\ominus}$

$$\Delta S_{\text{system}}^{\ominus} = \sum S_{\text{products}}^{\ominus} - \sum S_{\text{reactants}}^{\ominus}$$

$$= 2 \times S^{\ominus}[\text{HCl}(\text{g})] - (S^{\ominus}[\text{H}_2(\text{g})] + S^{\ominus}[\text{Cl}_2(\text{g})])$$

$$= 2 \times 186.8 - (130.6 + 165.0)$$

$$= 373.6 - 295.6$$

$$\Delta S_{\text{system}}^{\ominus} = +78.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

Step 3: calculate ΔG^{\ominus}

$$\Delta G^{\ominus} = \Delta H_{\text{reaction}}^{\ominus} - T\Delta S_{\text{system}}^{\ominus}$$

$$= -184\,600 - (298 \times +78.0)$$

$$\Delta G^{\ominus} = -207\,844 \text{ J mol}^{-1}$$

$$= -208 \text{ kJ mol}^{-1} \text{ (to 3 significant figures)}$$

As the value of ΔG^{\ominus} is negative, the reaction is spontaneous at 298 K.

- b** Step 1: convert the value of $\Delta H_{\text{r}}^{\ominus}$ to J mol^{-1} $-890.3 \times 1000 = -890\,300 \text{ J mol}^{-1}$

Step 2: calculate $\Delta S_{\text{system}}^{\ominus}$

$$\Delta S_{\text{system}}^{\ominus} = S_{\text{products}}^{\ominus} - S_{\text{reactants}}^{\ominus}$$

$$= S^{\ominus}[\text{CO}_2(\text{g})] + 2 \times S^{\ominus}[\text{H}_2\text{O}(\text{l})] - S^{\ominus}[\text{CH}_4(\text{g})] + 2 \times S^{\ominus}[\text{O}_2(\text{g})]$$

$$= 213.6 + (2 \times 69.9) - (186.2) - (2 \times 205.0)$$

$$= 353.4 - 596.2$$

$$\Delta S_{\text{system}}^{\ominus} = -242.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

Step 3: calculate ΔG^{\ominus}

$$\Delta G^{\ominus} = \Delta H_{\text{reaction}}^{\ominus} - T\Delta S_{\text{system}}^{\ominus}$$

$$= -890\,300 - (298 \times -242.8)$$

$$\Delta G^{\ominus} = -817\,946 \text{ J mol}^{-1}$$

$$= -818 \text{ kJ mol}^{-1} \text{ (to 3 significant figures)}$$

As the value of ΔG^{\ominus} is negative, the reaction is spontaneous at 298 K.

- c** Step 1: convert the value of $\Delta H_{\text{r}}^{\ominus}$ to J mol^{-1}

$$-510.9 \times 1000 = -510\,900 \text{ J mol}^{-1}$$

Step 2: calculate $\Delta S_{\text{system}}^{\ominus}$

$$\Delta S_{\text{system}}^{\ominus} = \sum S_{\text{products}}^{\ominus} - \sum S_{\text{reactants}}^{\ominus}$$

$$= S^{\ominus}[\text{Na}_2\text{O}_2(\text{s})] - \{(2 \times S^{\ominus}[\text{Na}(\text{s})] + S^{\ominus}[\text{O}_2(\text{g})])\}$$

$$= 95.0 - (2 \times 51.2) + 205.00$$

$$= 95.0 - 307.4$$

$$\Delta S_{\text{system}}^{\ominus} = -212.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

Step 3: calculate ΔG^{\ominus}

$$\begin{aligned}\Delta G^{\ominus} &= \Delta H_{\text{reaction}}^{\ominus} - T\Delta S_{\text{system}}^{\ominus} \\ &= -510\,900 - (298 \times -212.4)\end{aligned}$$

$$\Delta G^{\ominus} = -447\,604.8 \text{ J mol}^{-1}$$

$$= -448 \text{ kJ mol}^{-1} \text{ (to 3 significant figures)}$$

As the value of ΔG^{\ominus} is negative, the reaction is spontaneous at 298 K.

- d** Step 1: convert the value of ΔH_r^{\ominus} to J mol^{-1}

$$-641.3 \times 1000 = -641\,300 \text{ J mol}^{-1}$$

Step 2: calculate $\Delta S_{\text{system}}^{\ominus}$

$$\Delta S_{\text{system}}^{\ominus} = S_{\text{products}}^{\ominus} - S_{\text{reactants}}^{\ominus}$$

$$= S^{\ominus}[\text{MgCl}_2(\text{s})] - (S^{\ominus}[\text{Mg}(\text{s})] + S^{\ominus}[\text{Cl}_2(\text{g})])$$

$$= 89.6 - (37.2 + 165.0)$$

$$\Delta S_{\text{system}}^{\ominus} = -108.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

Step 3: calculate ΔG^{\ominus}

$$\begin{aligned}\Delta G^{\ominus} &= \Delta H_{\text{reaction}}^{\ominus} - T\Delta S_{\text{system}}^{\ominus} \\ &= -641\,300 - (298 \times -108.1)\end{aligned}$$

$$\Delta G^{\ominus} = -609\,086.2 \text{ J mol}^{-1}$$

$$= -609 \text{ kJ mol}^{-1} \text{ (to 3 significant figures)}$$

As the value of ΔG^{\ominus} is negative, the reaction is spontaneous at 298 K.

- e** Step 1: convert the value of ΔH_r^{\ominus} to J mol^{-1}

$$+167.5 \times 1000 = +167\,500 \text{ J mol}^{-1}$$

Step 2: calculate $\Delta S_{\text{system}}^{\ominus}$

$$\Delta S_{\text{system}}^{\ominus} = \sum S_{\text{products}}^{\ominus} - \sum S_{\text{reactants}}^{\ominus}$$

$$= S^{\ominus}[\text{Ag}_2\text{O}(\text{s})] + S^{\ominus}[\text{CO}_2(\text{g})] - S^{\ominus}[\text{Ag}_2\text{CO}_3(\text{g})]$$

$$= 121.3 + 213.6 - 167.4$$

$$\Delta S_{\text{system}}^{\ominus} = +167.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

Step 3: calculate ΔG^{\ominus}

$$\begin{aligned}\Delta G^{\ominus} &= \Delta H_{\text{reaction}}^{\ominus} - T\Delta S_{\text{system}}^{\ominus} \\ &= +167\,500 - (298 \times +167.5)\end{aligned}$$

$$\Delta G^{\ominus} = -33\,165 \text{ J mol}^{-1}$$

$$= 33.2 \text{ kJ mol}^{-1} \text{ (to 3 significant figures)}$$

As the value of ΔG^{\ominus} is positive, the reaction is not spontaneous at 298 K.

- 9** B ($-39.4 \text{ kJ mol}^{-1}$)

10 a $\Delta G_{\text{reaction}}^{\ominus} = \Delta G_{\text{products}}^{\ominus} - \Delta G_{\text{reactants}}^{\ominus}$

$$\begin{aligned}\Delta G_{\text{reaction}}^{\ominus} &= 2 \times \Delta G_f^{\ominus} [\text{H}_2\text{O}(\text{l})] + \Delta G_f^{\ominus} [\text{O}_2(\text{g})] - 2 \times \Delta G_f^{\ominus} [\text{H}_2\text{O}_2(\text{l})] \\ &= 2 \times (-273.2) + 0 - 2 \times (-120.4) \\ &= -546.4 - (-240.8)\end{aligned}$$

$$\Delta G_{\text{reaction}}^{\ominus} = -305.6 \text{ kJ mol}^{-1}$$

The value of $\Delta G_{\text{reaction}}^{\ominus}$ is negative. So under standard conditions, hydrogen peroxide should spontaneously decompose to water and oxygen.

b $\Delta G_{\text{reaction}}^{\ominus} = \Delta G_{\text{products}}^{\ominus} - \Delta G_{\text{reactants}}^{\ominus}$

$$\begin{aligned}\Delta G_{\text{reaction}}^{\ominus} &= \Delta G_f^{\ominus} [\text{N}_2\text{O}(\text{g})] + 2 \times \Delta G_f^{\ominus} [\text{H}_2\text{O}(\text{g})] - \Delta G_f^{\ominus} [\text{NH}_4\text{NO}_3(\text{s})] \\ &= (+104.2) + 2 \times (-228.6) - (-184.0)\end{aligned}$$

$$\Delta G_{\text{reaction}}^{\ominus} = -169.0 \text{ kJ mol}^{-1}$$

The value of $\Delta G_{\text{reaction}}^{\ominus}$ is negative. So under standard conditions, ammonium nitrate will spontaneously decompose to $\text{N}_2\text{O}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$.

c $\Delta G_{\text{reaction}}^{\ominus} = \Delta G_{\text{products}}^{\ominus} - \Delta G_{\text{reactants}}^{\ominus}$

$$\begin{aligned}\Delta G_{\text{reaction}}^{\ominus} &= 2 \times \Delta G_f^{\ominus} [\text{MgO}(\text{s})] - \{2 \times \Delta G_f^{\ominus} [\text{Mg}(\text{s})] + \Delta G_f^{\ominus} [\text{O}_2(\text{g})]\} \\ &= 2 \times (-569.4) - (0 + 0)\end{aligned}$$

$$\Delta G_{\text{reaction}}^{\ominus} = -1138.8 \text{ kJ mol}^{-1}$$

The value of $\Delta G_{\text{reaction}}^{\ominus}$ is negative. So under standard conditions, magnesium will spontaneously react with oxygen.

11 a $E_{\text{cell}}^{\ominus} = -0.13 + (+0.14) = +0.01 \text{ V}$

$$\text{electrons transferred} = 2$$

substitute the values into the expression $\Delta G^{\ominus} = -nFE_{\text{cell}}^{\ominus}$.

$$\begin{aligned}\Delta G^{\ominus} &= -2 \times 96\,500 \times (+0.01) \\ &= -1.93 \text{ kJ mol}^{-1}\end{aligned}$$

The value of ΔG^{\ominus} is very small and negative and $E_{\text{cell}}^{\ominus}$ is very small and positive, so both reactants and products are present and the products predominate. So K_c is just above 1

b $E_{\text{cell}}^{\ominus} = +0.77 + (-0.8) = -0.03 \text{ V}$
 electrons transferred = 1
 substitute the values into the
 expression $\Delta G^{\ominus} = -nFE_{\text{cell}}^{\ominus}$.
 $\Delta G^{\ominus} = -1 \times 96\,500 \times (-0.03)$
 $= +2.9 \text{ kJ mol}^{-1}$

The value of ΔG^{\ominus} is very small
 and positive and $E_{\text{cell}}^{\ominus}$ is very small
 and negative, so both reactants and
 products are present and the reactants
 predominate. So K_c is below 1 e.g. 0.01

c $E_{\text{cell}}^{\ominus} = -1.66 + (+2.33) = +0.67 \text{ V}$
 electrons transferred = 3
 substitute the values into the
 expression $\Delta G^{\ominus} = -nFE_{\text{cell}}^{\ominus}$.
 $\Delta G^{\ominus} = -3 \times 96\,500 \times (+0.67)$
 $= -194 \text{ kJ mol}^{-1}$

The value of ΔG^{\ominus} is large and
 negative and $E_{\text{cell}}^{\ominus}$ is large and positive,
 so the reaction goes more or less to
 completion. So K_c has a high value.

Exam-style questions

1 a i Graphite is softer than diamond. [1]

Graphite has weak forces between
 the layers but diamond has only
 strong (covalent) bonding / greater
 rigidity in bonding in diamond
 than graphite. [1]

ii $\Delta S_{\text{system}}^{\ominus} = \sum S_{\text{products}}^{\ominus} - \sum S_{\text{reactants}}^{\ominus}$
 $= 2.40 - 5.70 = -3.30 \text{ J K}^{-1} \text{ mol}^{-1}$ [1]

iii The entropy change is negative. [1]

b entropy of product greater (no marks
 alone but maximum 1 mark for
 question if not present) Graphite has
 very low entropy because it is a solid
 with only one type of atom and oxygen
 has high entropy because it is a gas. [1]

Carbon dioxide has high entropy
 because it is a gas and higher than
 oxygen as it is a more complex molecule /
 has three atoms rather than two. [1]

[Total: 6]

2 a $\Delta S_{\text{system}}^{\ominus} = \sum S_{\text{products}}^{\ominus} - \sum S_{\text{reactants}}^{\ominus}$
 $= 2 \times S^{\ominus} [\text{CO}_2(\text{g})] + 3 \times S^{\ominus} [\text{H}_2\text{O}(\text{l})]$
 $- \{S^{\ominus} [\text{C}_2\text{H}_5\text{OH}(\text{l})] + 3 \times S^{\ominus} [\text{O}_2(\text{g})]\}$

$$= (2 \times 213.6) + (3 \times 69.90) - \{160.7 + (3 \times 205.0)\}$$

$$= 636.9 - 775.7$$

$$\Delta S_{\text{system}}^{\ominus} = -138.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{surroundings}}^{\ominus} = \frac{-\Delta H_{\text{reaction}}^{\ominus}}{T}$$

$$= \frac{-(-1367 \times 1000)}{298}$$

$$= +4587.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

$$= -138.8 + 4587.2$$

$$\Delta S_{\text{total}}^{\ominus} = +4448 \text{ J K}^{-1} \text{ mol}^{-1}$$

Correct multiplication of data and use
 of $\Delta S_{\text{system}}^{\ominus} = \sum S_{\text{products}}^{\ominus} - \sum S_{\text{reactants}}^{\ominus}$
 i.e. $2 \times 213.6 + 3 \times 69.90 -$

$$\{160.7 + 3 \times 205.0\} \quad [1]$$

Correct answer for $S_{\text{system}}^{\ominus} =$
 $-138.8 \text{ J K}^{-1} \text{ mol}^{-1} / 139 \text{ (J K}^{-1} \text{ mol}^{-1})$ [1]

Correct application of relationship for
 $\Delta S_{\text{surroundings}}^{\ominus}$ ($\times 1000$, division by 298
 and $-$ sign in relationship) [1]

$$\Delta S_{\text{surroundings}}^{\ominus} = +4587.2 \text{ (J K}^{-1} \text{ mol}^{-1}) \quad [1]$$

Correct use of $\Delta S_{\text{total}}^{\ominus} = S_{\text{system}}^{\ominus}$
 $+ \Delta S_{\text{surroundings}}^{\ominus} / +4448 \text{ (J K}^{-1} \text{ mol}^{-1})$ [1]

Correct units for entropy, $\text{J K}^{-1} \text{ mol}^{-1}$,
 anywhere in question. [1]

b $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}$
 $-174.9 \quad 2(-394.4) + 3(-237.2)$ [1]

use of $\sum G_{\text{products}}^{\ominus} - \sum G_{\text{reactants}}^{\ominus}$
 $-1500.4 - (-174.9)$ [1]

$$= -1325.5 \text{ kJ mole}^{-1} \quad [1]$$

c Use of $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ [1]
 $-1325.5 \times 1000 = \Delta H^{\ominus} - 298 \times$
 $(-138.3) \text{ (in joules)} \quad [1]$

$$\Delta H^{\ominus} = -1325500 + 41213.4 =$$

$$-1284286.6 \text{ J mol}^{-1} / -1284.3 \text{ kJ mol}^{-1} \quad [1]$$

[Total: 12]

3 a Molecules in ice do not move from
 place to place / only vibrate. So
 entropy is low. [1]

Molecules in water can rotate / slide
 over each other. So entropy is higher. [1]

b When water is being heated the
 molecules are moving faster and more
 randomly. [1]

Entropy increases due to more ways of spreading the energy. [1]

When water boils the entropy increases by a larger amount [1]

because the molecules in gas have more random movement than in liquid / more ways of spreading the energy in gas compared with a liquid. [1]

c Water is hydrogen bonded [1]

which gives it some structure so that entropy is lower. [1]

Bromine only has temporary dipole-induced dipole forces between molecules [1]

so movement of the molecules is more free so entropy is higher. [1]

d When 2 g potassium chloride added it dissolves and the ions spread out randomly in the water / move freely compared with the ionic lattice where they cannot move. [1]

There are more ways of arranging the particles of K^+ , Cl^- and water so the entropy increases. [1]

Adding more potassium chloride increases the number of particles of K^+ and Cl^- dissolved so there are more ways of arranging the ions and so the entropy increases. [1]

The percentage increase in entropy is smaller because there are already ions present. This reduces the number of arrangements available to the ions compared with when dissolved in water alone. [1]

[Total: 14]

4 a $\Delta H_f^\ominus [BaCO_3(s)] + \Delta H_{reaction}^\ominus = \Delta H_f^\ominus [BaO(s)] + \Delta H_f^\ominus [CO_2(s)]$
 $-1216.0 + \Delta H_{reaction}^\ominus = -553.5 + -393.5$

$$\Delta H_{reaction}^\ominus = +269.0 \text{ kJ mol}^{-1}$$

Correct application of Hess cycle. [1]

$$\Delta H_{reaction}^\ominus = +269 \text{ kJ mol}^{-1} \quad [1]$$

b $\Delta S_{system}^\ominus = S_{products}^\ominus - S_{reactants}^\ominus$
 $= S^\ominus [BaO(s)] + S^\ominus [CO_2(g)] - S^\ominus [BaCO_3(s)]$
 $= 70.40 + 213.6 - 112.1$
 $= 284.0 - 112.1$

$$\Delta S_{system}^\ominus = +171.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{surroundings}^\ominus$$

$$= \frac{-\Delta H_{reaction}^\ominus}{T}$$

$$= \frac{-(+269 \times 1000)}{298}$$

$$= -902.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{total}^\ominus = \Delta S_{system}^\ominus + \Delta S_{surroundings}^\ominus$$

$$= 71.9 + (-902.7)$$

$$\Delta S_{total}^\ominus = -730.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

Correct answer for

$$\Delta S_{system}^\ominus = +171.9 \text{ (J K}^{-1} \text{ mol}^{-1}) \quad [1]$$

Correct application of relationship for

$\Delta S_{surroundings}^\ominus$ ($\times 1000$, division by 298 and $-$ sign in relationship) [1]

$$\Delta S_{surroundings}^\ominus = (-902.7) \text{ (J K}^{-1} \text{ mol}^{-1}) \quad [1]$$

Correct use of $\Delta S_{total}^\ominus = -730.8$ (J K⁻¹ mol⁻¹) [1]

Correct units for entropy, J K⁻¹ mol⁻¹ [1]

c use of $\Sigma G_{products}^\ominus - \Sigma G_{reactants}^\ominus$
 $(-525.1 + (-394.4)) - (-1137.60)$ [1]
 $= +218.1 \text{ kJ mole}^{-1}$ [1]

d Reaction is not feasible at 298 K because the value of ΔG^\ominus is large and positive [1]

e $\Delta S_{total}^\ominus = \Delta S_{system}^\ominus + \Delta S_{surroundings}^\ominus$
 $0 = 171.9 + \Delta S_{surroundings}^\ominus$

So $\Delta S_{surroundings}^\ominus$ must be $-171.9 \text{ J K}^{-1} \text{ mol}^{-1}$

By substitution:

$$\Delta S_{surroundings}^\ominus = \frac{-\Delta H^\ominus}{T}$$

$$= \frac{-(+269 \times 1000)}{T}$$

$$= -171.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

So $-171.9 \times T = -269000$ and $T = 1565 \text{ K}$

For $\Delta S_{surroundings}^\ominus = -171.9 \text{ J K}^{-1} \text{ mol}^{-1}$

if ΔS_{total}^\ominus is zero [1]

Correct application of relationship

for $\Delta S_{surroundings}^\ominus$ ($\times 1000$, division by 298 and $-$ sign in relationship and value = $-171.9 \text{ (J K}^{-1} \text{ mol}^{-1})$) [1]

$$T = 1565 \text{ (K)} / 1292 \text{ (}^\circ\text{C)} \quad [1]$$

Correct unit of temperature, i.e. K (allow $^\circ\text{C}$ if answer 1292) [1]

[Total: 14]

5 a i Entropy of NaCl is low because it is ordered / ions only vibrate. [1]

Entropy of water is medium / higher than for NaCl because it is less ordered (or has degree of disorder). [1]

Dissolved ions have more disorder so greater entropy because free to move. [1]

Entropy of water decreases because of the hydration layer around the ions. (Allow: entropy of water doesn't change much.) [1]

So entropy increases (dependent on suitable arguments indicating entropy of solution greater than entropy of NaCl and water). [1]

[If entropy decreases given as an answer, max. 3 marks for question.]

ii Entropy of H₂O(g) is high because the particles are disordered. [1]

Entropy of H₂O(l) is medium / lower because the particles are less ordered than in H₂O(g). [1]

So entropy decreases (dependent on suitable arguments indicating entropy of vapour greater than entropy of liquid). [1]

[If entropy increases given as an answer, max. 1 mark for question.]

b i Entropy increases from CH₄ to C₄H₁₀ and then decreases to C₃H₁₂. [1]
CH₄ to C₄H₁₀ are in the same state but there are more atoms / more electrons / more complex molecules as the series is ascended. [1]

C₃H₁₂ is a liquid, so the entropy is relatively lower (compared with gaseous molecules of similar size); [1]
less randomness / disorder in liquid than in gas. [1]

ii Allow values between 280 and 310 J K⁻¹ mol⁻¹ (actual value 295.9). [1]

[Total: 13]

6 a i The free energy change when 1 mole of a compound [1]
is formed from its elements under standard conditions. [1]

ii 2C(graphite) + 3H₂(g) → C₂H₆(g)

(allow 2C(s))

correct reactants and product [1]

correct state symbols [1]

b i $\Delta G^{\ominus} = \Delta H_{\text{reaction}}^{\ominus} - T\Delta S_{\text{system}}^{\ominus}$ [1]

ii ΔG^{\ominus} is negative. [1]

$\Delta H_{\text{reaction}}^{\ominus}$ needs to be taken into account. [1]

If value of $\Delta H_{\text{reaction}}^{\ominus}$ is negative enough, its value will overcome the positive value of the $-T\Delta S_{\text{system}}^{\ominus}$ term / overcome the large negative value of $\Delta S_{\text{system}}^{\ominus}$. [1]

c $\Delta G_{\text{reaction}}^{\ominus} = \Delta G_{\text{products}}^{\ominus} - \Delta G_{\text{reactants}}^{\ominus}$ [1]
(or correct use of relationship)

$$= 2 \times \Delta G^{\ominus} [\text{CO}_2(\text{g})] + 3 \times \Delta G^{\ominus} [\text{H}_2\text{O}(\text{l})] - \{ \Delta G^{\ominus} [\text{C}_2\text{H}_6(\text{g})] + 3 \frac{1}{2} \times \Delta G^{\ominus} [\text{O}_2(\text{g})] \}$$

$$= 2 \times (-394.4) + 3 \times (-237.2) - (-32.9 + 0)$$

$$= -1500.4 + 32.9$$

Correct use of mole ratios, i.e. $\times 2$ for carbon dioxide, etc. [1]

$$\Delta G_{\text{reaction}}^{\ominus} = -1467.5 \text{ kJ} \quad [1]$$

[Total: 11]

7 a $\Delta S_{\text{system}}^{\ominus} = \sum S_{\text{products}}^{\ominus} - \sum S_{\text{reactants}}^{\ominus}$ [1]
(or correct use of relationship)

$$= S^{\ominus} [\text{CaO}(\text{s})] + S^{\ominus} [\text{CO}_2(\text{g})] - S^{\ominus} [\text{CaCO}_3(\text{s})]$$

$$= 39.7 + 213.6 - 92.9$$

$$\Delta S_{\text{system}}^{\ominus} = +160.4 \text{ J K}^{-1} \text{ mol}^{-1} \quad [1]$$

b $\Delta H_{\text{reaction}}^{\ominus} = \Delta H_{\text{f}}^{\ominus} [\text{products}] - \Delta H_{\text{f}}^{\ominus} [\text{reactants}]$ (or correct use of relationship or enthalpy cycle) [1]

$$= \Delta H_{\text{f}}^{\ominus} [\text{CaO}(\text{s})] + \Delta H_{\text{f}}^{\ominus} [\text{CO}_2(\text{g})] - \Delta H_{\text{f}}^{\ominus} [\text{CaCO}_3(\text{s})]$$

$$= -631.5 + (-393.5) - (-1206.9)$$

$$\Delta H_{\text{reaction}}^{\ominus} = +181.9 \text{ kJ mol}^{-1} \quad [1]$$

c Use of $\Delta G^{\ominus} = \Delta H_{\text{reaction}}^{\ominus} - T\Delta S_{\text{system}}^{\ominus}$ [1]

Multiplication of $\Delta H_{\text{reaction}}^{\ominus}$ by 1000 [1]

Correct substitution of values from parts **a** and **b** [1]

$$\text{e.g. } \Delta G^{\ominus} = \Delta H_{\text{reaction}}^{\ominus} + T\Delta S_{\text{system}}^{\ominus}$$

$$= (181\,900 - (298 \times 160.4))$$

$\Delta G^\ominus = +134\,100 \text{ (J mol}^{-1}\text{) or } +134 \text{ (kJ mol}^{-1}\text{) (to 3 significant figures)}$ [1]

Correct units in answer or other relevant part of question. [1]

- d** As the value of ΔG^\ominus is positive, the reaction is not spontaneous at 298 K. [1]

$\Delta S^\ominus_{\text{system}}$ alone is not a good guide to whether a reaction is spontaneous or not. [1]

Because the surroundings are not taken into account / only of ΔG^\ominus takes account of the surroundings as well as the system. [1]

[Total: 12]

- 8 a** $\Delta S^\ominus_{\text{system}} = \sum S^\ominus_{\text{products}} - \sum S^\ominus_{\text{reactants}}$
(or correct use of relationship) [1]

$$= 2 \times S^\ominus [\text{H}_2\text{O(l)}] - (2 \times S^\ominus [\text{H}_2\text{(g)}]) + (S^\ominus [\text{O}_2\text{(g)}])$$

$$= 2 \times 69.9 - [(2 \times 130.6) + 205.0]$$

$$= 139.8 - 466.2$$

Correct use of mole ratios, i.e. $\times 2$ for water and hydrogen [1]

$$\Delta S^\ominus_{\text{system}} = -326.4 \text{ J K}^{-1} \text{ mol}^{-1}$$
 [1]

- b** Use of $\Delta G^\ominus = \Delta H^\ominus_{\text{reaction}} - T\Delta S^\ominus_{\text{system}}$ [1]

Multiplication of $\Delta H^\ominus_{\text{reaction}}$ by 1000 [1]

Correct substitution of values from part **a** [1]

$$\text{e.g. } \Delta G^\ominus = \Delta H^\ominus_{\text{reaction}} + T\Delta S^\ominus_{\text{system}}$$

$$= -561\,600 + (298 \times -326.4)$$

$$\Delta G^\ominus = -474\,000 \text{ (J) or } -474 \text{ (kJ)}$$

(to 3 significant figures) [1]

Correct units in answer or other relevant part of question. [1]

[Allow: kJ mol^{-1} or J mol^{-1} if referring to oxygen in equation.]

- c** As the value of ΔG^\ominus is negative, the reaction is spontaneous at 298 K. [1]

- d** Half the value for the answer to part **b**, i.e. -237 kJ mol^{-1} [1]

Because in the equation there are 2 moles of water / free energy change of formation refers to 1 mole of substance formed. [1]

[Total: 11]

- 9 a i** $+0.75 \text{ V}$ [1]

- ii** The sign of E^\ominus_{cell} is fairly large and positive [1]

- b i** use of $\Delta G^\ominus = -nFE^\ominus_{\text{cell}}$ [1]

$$-2 \times 96\,500 \times -0.94$$
 [1]

$$+181\,420 \text{ J mol}^{-1} / +181.4 \text{ kJ mol}^{-1}$$
 [1]

- ii** The value of ΔG^\ominus is large and positive so the reaction is not feasible. [1]

The position of equilibrium will be well over to the left / the reaction is not likely to happen, so the value of K_c will be very low e.g. 10^{-5} . [1]

- c i** use of $\sum G^\ominus_{\text{products}} - \sum G^\ominus_{\text{reactants}}$
(-77.6) - ($+65.5$) [1]

$$= -143.1 \text{ kJ mole}^{-1}$$
 [1]

- ii** use of $\Delta G^\ominus = -nFE^\ominus_{\text{cell}}$
 $E^\ominus_{\text{cell}} = -\frac{\Delta G^\ominus}{nF}$ [1]

$$= -\frac{(-143.1 \times 1000)}{2 \times 96\,500}$$
 [1]

$$= 0.74 \text{ V}$$
 [1]

[Total: 12]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 24

Science in context

An internet search engine will produce results that learners can use to explain how *cis*-platin interacts with DNA when treating cancerous tumours. Working together with a biology student could be beneficial when discussing the effect of *cis*-platin on DNA. Here is the basic mechanism:

- The *cis*-platin can be taken by patients in solution and can pass through cell membranes and into the nucleus of the cell. One of the chloride ion ligands is first replaced by a water molecule, forming the complex $[\text{PtCl}(\text{H}_2\text{O})(\text{NH}_3)_2]^+$.
- On contact with a DNA molecule, the water ligand is itself replaced by a guanine base as one of its nitrogen atoms forms a dative bond with the platinum ion.
- Then the remaining chloride ion is ideally positioned to interact with another adjacent guanine base. The chloride ion is replaced and the new platinum complex has formed a bridge in a DNA strand.
- This 'bridging' can also take place to a lesser extent between the two strands in DNA, as well as with the base adenine.

Discuss the use of drugs that can have harmful side-effects in small groups so that learners get the chance to voice their opinions. Ask each group to write four bullet points to summarise their discussion. Pin the summaries up to share with the whole class.

Self-assessment questions

- Ti $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
 - Cr $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
 - Co $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
 - Fe^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^0$
 - Ni^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^0$
 - Cu^+ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^0$
 - For scandium the only observed oxidation state is +3, so the electronic configuration of Sc^{3+} is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0$. This ion has no d electrons, so does not satisfy the definition of a transition element. The only ion of zinc is Zn^{2+} , with the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^0$. This ion has a completely filled, not a partially filled, d subshell – so zinc is not a transition element.
 - The +7 oxidation state involves all of the 3d and 4s electrons in manganese.
 - Oxidation state of vanadium in **a** = $(\text{VO}_2^+) = +5$; **b** $(\text{VO}^{2+}) = +4$;
c $(\text{V}^{3+}) = +3$; **d** $(\text{V}^{2+}) = +2$.
 - +4 as this involves all the 4d and 5s electrons, leaving the noble gas electronic configuration of krypton.
 - ZrO_2
- $$\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$$

$$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$$
 - $$6\text{Fe}^{2+}(\text{aq}) \rightarrow 6\text{Fe}^{3+}(\text{aq}) + 6\text{e}^-$$

$$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$$

$$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{Fe}^{2+}(\text{aq}) + 14\text{H}^+(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}(\text{l})$$
 - $$E^\ominus = +1.33 \text{ V} + (-0.77 \text{ V}) = +0.56 \text{ V}$$

The positive value indicates that the reaction as written is feasible and its relatively large value suggests that the reaction is likely to occur (although values of E^\ominus tell us nothing about the rate of a reaction).
 - 6

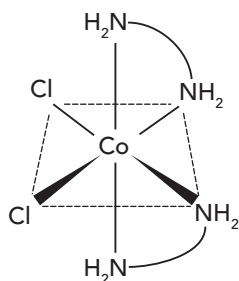
- e i $0.0153 \times 0.001 = 0.000\ 015\ 3\ \text{mol}$
 ii $0.000\ 015\ 3 \times 6 = 0.000\ 091\ 8\ \text{mol}$
 iii $\frac{0.000\ 091\ 8}{0.025} = 0.003\ 67\ \text{mol dm}^{-3}$

- 3 a i +3
 ii +2
 iii +3
 iv +3
 v +2

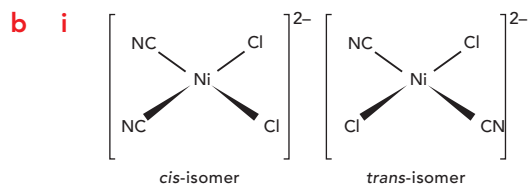


c ethanedioate ion (ox) and ethane-1,2-diamine (en)

- 4 a i 6
 ii

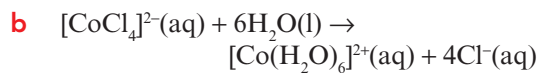


- iii They are mirror images, which are not superimposable.



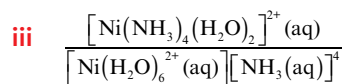
- ii Non-polar, as the charge is distributed perfectly symmetrically around the central nickel (with both cyanide ligands diagonally opposite each other in the square planar structure, and similarly with the two chloride ions).

- 5 a +2

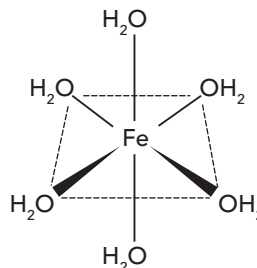


- c A

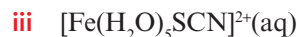
- 6 a i $\frac{[\text{PtCl}_2(\text{NH}_3)_2(\text{aq})][\text{Cl}^{-}(\text{aq})]^2}{[\text{PtCl}_4]^{2-}(\text{aq})[\text{NH}_3(\text{aq})]^2}$
 ii $\frac{[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^{+}(\text{aq})}{[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})[\text{Cl}^{-}(\text{aq})]^2}$



- b i $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$:



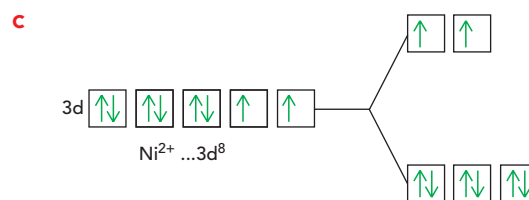
- ii SCN^{-} has a higher value of K_{stab} than H_2O . So the position of equilibrium is shifted to the right.



- iv Yes; a colour change is likely / possible. F^{-} has a higher value of K_{stab} than SCN^{-} . So F^{-} substitutes for SCN^{-} (and for water) because the position of equilibrium is shifted to the right.

- 7 a orbitals at the same energy level

- b The ligands in a complex cause the d orbitals to split, forming two sets of non-degenerate orbitals. The difference in the energy (ΔE) between the non-degenerate d orbitals corresponds to the energy of part of the visible spectrum of light. So when light travels through a solution or a solid containing the complex, an electron from one of the three lower non-degenerate orbitals absorbs that amount of energy (ΔE) and jumps into one of the two higher non-degenerate orbitals. This leaves the transmitted light coloured.



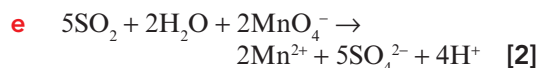
- d** Sc^{3+} ions have electronic configuration $[\text{Ar}]3d^04s^0$. If d-orbital splitting were to occur in a complex ion containing Sc^{3+} , there would be no electrons in the three 3d orbitals of lower energy, so visible light would not be absorbed in promoting an electron from a lower energy 3d orbital to a higher energy 3d orbital.
- e** Zn^{2+} ions have electronic configuration $[\text{Ar}]3d^{10}4s^0$. If d-orbital splitting were to occur in a complex ion containing Zn^{2+} , each of the 3d orbitals would contain two electrons, and would therefore be fully occupied. Visible light could not be absorbed in promoting an electron from a lower energy 3d orbital to a higher energy 3d orbital.

Exam-style questions

- 1 a** an element forming one or more compounds that contain an ion which has a partly filled 3d subshell [1]
- b** a molecule or ion capable of bonding to a positive ion by donating a lone-pair of electrons and forming a co-ordinate bond [1]
- c** a positive ion [1]
joined to one or more ligands [1]
[Total: 4]
- 2 a** $[\text{Ar}] 3d^6 4s^2$ or $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ [1]
- b** $[\text{Ar}] 3d^7$ or $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^0$ [1]
- c** $[\text{Ar}] 3d^1$ or $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^0$ [1]
[Total: 3]
- 3 a** e.g. FeCl_3 [1]
oxidation state +3 [1]
e.g. FeCl_2 [1]
oxidation state +2 [1]
- b** d orbitals split / form two sets of non-degenerate orbitals; [1]
an electron from one of the lower orbitals absorbs energy from visible light; [1]
and is promoted to one of the higher orbitals. [1]
[Total: 7]
- 4 a** $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$ [1]
pale blue precipitate [1]
- b** $\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4(\text{s}) + 4\text{NH}_3(\text{aq}) \rightarrow \text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{OH}^-(\text{aq})$ [1]
the precipitate dissolves [1]
giving a deep blue solution [1]
[Total: 5]
- 5 a** The electrode potential for the $\text{Cl}_2 / \text{Cl}^-$ redox system is more negative than the one for $\text{MnO}_4^- / \text{Mn}^{2+}$; [1]
this means that
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$ can gain electrons, proceeding to the right, and the reaction $\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$ can proceed to the left, forming Cl_2 . Chlorine is toxic, and this also gives an inaccurate titration result as the MnO_4^- reacts with the Cl^- as well as the Fe^{2+} . [1]
The electrode potential for the $\text{SO}_4^{2-} / \text{SO}_2$ redox system is more negative than the one for $\text{MnO}_4^- / \text{Mn}^{2+}$; [1]
this means that the reaction
 $\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{SO}_2 + 2\text{H}_2\text{O}$ can proceed to the left but not to the right and the acid is unchanged. [1]
- b** M_r of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 55.8 + 32.1 + 64.0 + 126.0 = 277.9$ [1]
amount (in mol) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
 $= \frac{5.56}{277.9} = 0.0200 \text{ mol}$ [1]
 $[\text{FeSO}_4] = \frac{0.02}{0.250} = 0.0800 \text{ mol dm}^{-3}$ [1]
- c i** $5\text{Fe}^{2+} + 8\text{H}^+ + \text{MnO}_4^- \rightarrow 5\text{Fe}^{3+} + 4\text{H}_2\text{O} + \text{Mn}^{2+}$ [2]
[1 mark for formulae; 1 mark for balancing]
- ii** when a permanent pink colour is obtained [1]
- d** amount in mol of Fe^{2+} (FeSO_4) in $25 \text{ cm}^3 = V \times C = 0.025 \times 0.0800 = 0.00200 \text{ mol}$
amount in mol of $\text{MnO}_4^- = \frac{1}{5} \times \text{amount in mol of Fe}^{2+}$
 $= 4.00 \times 10^{-4} \text{ mol}$ [1]

$$[\text{MnO}_4^-] = \frac{n}{V(\text{in dm}^3)}$$

$$= \frac{4.00 \times 10^{-4}}{0.0212} = 0.0189 \text{ mol dm}^{-3} \quad [1]$$



[1 mark for formulae; 1 mark for balancing]

amount in mol of $\text{MnO}_4^- = 0.0189 \times 0.025 = 4.73 \times 10^{-4} \text{ mol}$ [1]

amount in mol of SO_2

$$= \frac{5}{2} \times 4.73 \times 10^{-4} \text{ mol} = 1.18 \times 10^{-3} \text{ mol} \quad [1]$$

volume of SO_2 at r.t.p.

$$= 1.18 \times 10^{-3} \times 24 \text{ dm}^3 = 0.0283 \text{ dm}^3 \quad [1]$$

[Total: 17]

To make question 5e easier to answer, break it up:

1 How many moles of MnO_4^- are we given?

2 How many moles of SO_2 will this react with? (the reaction equation is needed here)

3 What is the volume of this number of moles of SO_2 ?

6 a i 4Cl^- (aq) in gap on left [1]

$6\text{H}_2\text{O}$ (l) in gap on right [1]

ii Yellow-green colour turns to light blue; [1]

excess water shifts position of equilibrium to the left; [1]

some of the Cl^- in the complex replaced by water molecules. [1]

iii One or more Cl^- replaced by ammonia [1]

because ammonia has greater value of K_{stab} (than Cl^-). [1]

b i bidentate ligands [1]

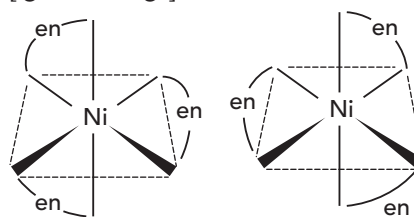
Ligands have two N lone pairs per ligand molecule available for complex formation. [1]

ii diaminoethane because it has a higher value of K_{stab} [1]

iii correct drawing of one isomer; [1]

correct drawing of mirror image; [1]

[ignore charge]



recognition of a single ligand attached to two points in the structure in either of the isomers; [1]

octahedral structure in either of the isomers [1]

[Total: 14]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 25

Science in context

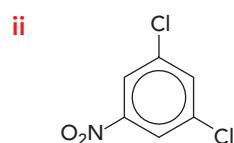
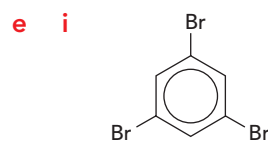
Most learners will be familiar with the work of Dmitri Mendeleev in developing the periodic table of elements, with its groups of similar elements, and his conviction of its veracity when changing the order of elements that did not align correctly when ordered by atomic weights – plus his leaving of gaps in his order for as yet undiscovered elements. Research will reveal his famous dream of playing the card game Patience that he claimed inspired his discovery.

The learners can then speculate on how our brains work, having come across two cases where chemists solved problems after dreaming. For example, both scientists were thinking deeply about how to solve a particular problem before they slept. It could be suggested that despite a person sleeping, the brain continues to mull over possible solutions to a problem. Some learners might even have experienced such a situation themselves, e.g. with a tricky homework problem that they could not complete but suddenly know how to work it out when they woke up the next morning. Then a selection of pairs can feedback a report of their theory to the whole class.

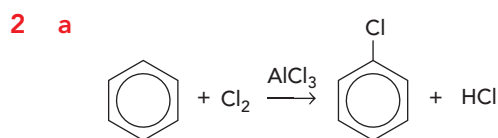
Self-assessment questions

- 1 a 6
- b p (or 2p) orbitals
- c electrons that are free to move around the molecule in the π bonding system above and below the plane of the carbon atoms in the benzene ring
- d In benzene the six electrons in the π bonding system are no longer associated with any particular carbon atoms in the molecule, whereas in hex-3-ene the two electrons in the π bond in the centre of the molecule are only

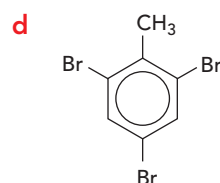
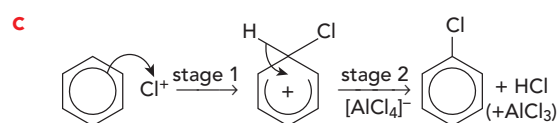
found above or below the central two carbon atoms.



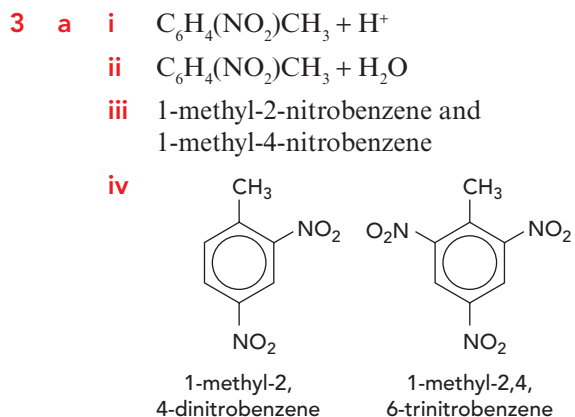
- f i 2-methylphenol
ii 1-bromo-2,3-dichlorobenzene



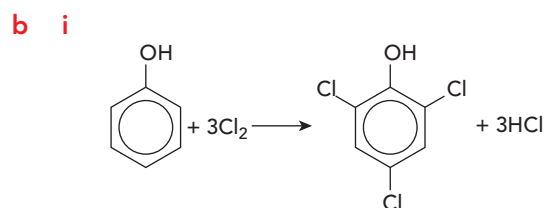
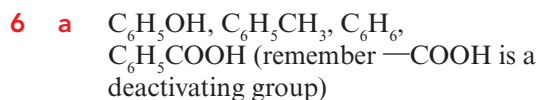
b electrophilic substitution



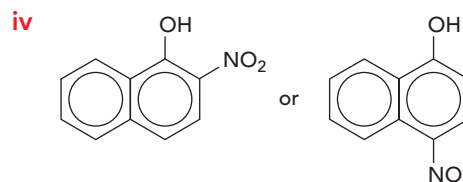
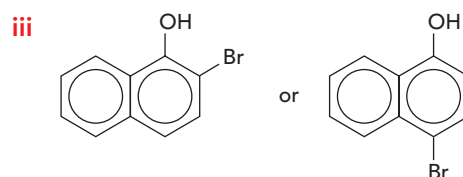
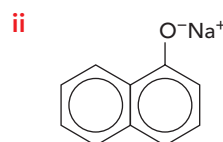
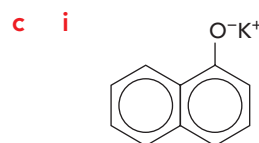
- e The hydrogen atoms in the $-\text{CH}_3$ side-chain would be all or partially replaced by Br atoms.
f free-radical substitution



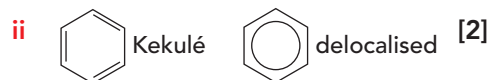
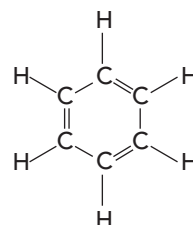
- b i sulfur atom
 ii $\text{C}_6\text{H}_6 + \text{SO}_3 \rightarrow \text{C}_6\text{H}_5\text{SO}_3\text{H}$
- 4 a i $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3 + \text{HCl}$
 ii $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{HCl}$
 b i propylbenzene
 ii (aryl) ketone
 c With hexylbenzene, the hexyl side chain would be oxidised to form an aryl carboxylic acid (and the purple potassium manganate(VII) solution would be decolourised), whereas no reaction would occur with hexane.
- d i Heat / hydrogen / nickel or platinum catalyst
 ii A
- 5 a HCl , CH_3COOH , $\text{C}_6\text{H}_5\text{OH}$, H_2O , $\text{C}_3\text{H}_7\text{OH}$
 b Methanol is less acidic than phenol because methanol has an electron-donating methyl group attached to the oxygen atom in the methoxide ion that is formed on dissociation. This has the effect of concentrating more negative charge on this oxygen atom, which more readily accepts an H^+ ion, re-forming undissociated methanol. On the other hand, the phenoxide ion, $\text{C}_6\text{H}_5\text{O}^-$ (aq), has its negative charge spread over the whole ion as the benzene ring draws in electrons from the oxygen atom, reducing the attraction of this ion for H^+ ions.
 c i Phenylamine, sodium nitrate(III) / sodium nitrite and dilute hydrochloric acid (water)
 ii ice / below 10°C



- ii A catalyst of AlCl_3 would be needed.



Exam-style questions



[Total: 5]



b iron(III) bromide / iron / aluminium bromide [1]

c steamy fumes; [1]

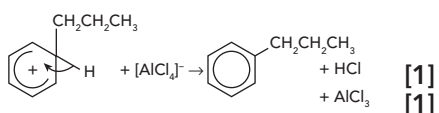
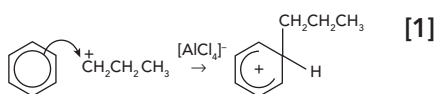
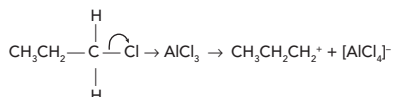
bromine decolourised [1]

d i AlCl_3 [1]

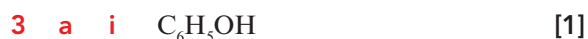
ii Cl^+ [1]

iii propylbenzene [1]

iv [1]

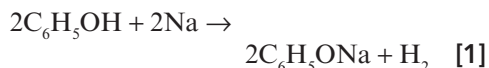


[Total: 11]

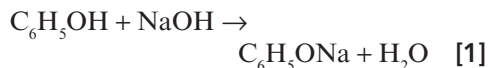


ii $\text{C}_6\text{H}_5\text{OH}$ [1]

b gas evolved / effervescence / fizzing [1]



c acid-base / neutralisation [1]

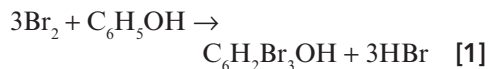


d sodium phenoxide [1]

e 2,4,6-tribromophenol; [1]

bromine water decolourised; [1]

white precipitate; [1]



Benzene reacts with liquid bromine but not with bromine water; [1]

benzene monosubstitutes while phenol trisubstitutes; [1]

benzene needs catalyst. [1]

f The benzene ring in phenol is activated [1]

by the electron-donating —OH group; [1]

the lone-pair electrons on the oxygen of the —OH group [1]

can overlap with the π electron system on the ring. [1]

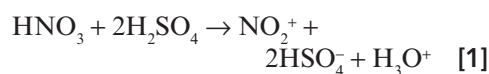
[Total: 18]

4 a electrophilic [1]

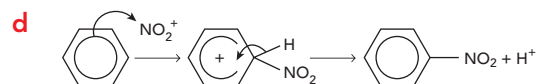
substitution [1]

b concentrated nitric acid; [1]

concentrated sulfuric acid; [1]



c = between 25 °C and 60 °C [1]



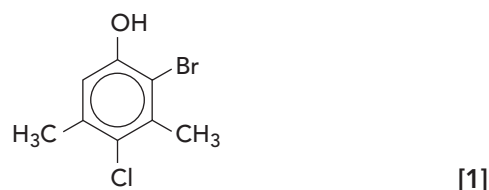
curly arrow starts at the delocalised π electrons and finishes on the nitrogen atom in NO_2^+ ; [1]

intermediate with part circle inside hexagon and positive charge in middle; [1]

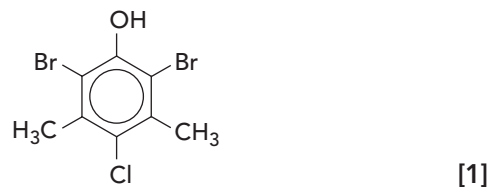
loss of H^+ with curly arrow from C—H bond back to ring [1]

e i $\text{C}_8\text{H}_9\text{OCl}$ [1]

ii either the mono-substituted (monobromo-) compound



or the di-substituted (dibromo-) compound



[Total: 12]

- 5 a** A diagram showing planar molecule, p orbitals and overlap earns a maximum of 2 marks. [2]
- For overlap of the p orbitals forming π bonds; [1]
- electrons delocalised; [1]
- C—C bonds all the same length. [1]
- b** Cyclohexene has a double bond; [1]
- benzene's π electrons [1]
- are delocalised. [1]
- And either:*
- The bromine molecule is not polarised enough for reaction [1]
- and needs a catalyst to polarise it. [1]
- Or:*
- The double bond in the cyclohexene has sufficient electron density [1]
- to polarise the bromine molecule and cause reaction. [1]
- [Total: 10]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 26

Science in context

This can be a whole-class discussion after going through the passage on *trans*-fatty acids, using it to remind learners of the structure of alkenes and carboxylic acids, as well as *cis/trans* isomerism.

Give the learners 5–10 minutes to discuss the three questions then ask for answers to the problems set. The answers should include the raising of the melting points of plant oils to make spreadable margarine; the furring of arteries as a result of a higher than normal proportion of low-density lipoproteins (bad cholesterol) compared with high-density lipoproteins (good cholesterol), leading to high blood pressure, strokes and heart attacks; choose a diet that does not contain a high proportion of processed *trans*-fatty acids.

Self-assessment questions

- 1 a $\text{CH}_3\text{CCl}_2\text{COOH}$, $\text{CH}_3\text{CHClCOOH}$, $\text{CH}_3\text{CH}_2\text{COOH}$
- b The electron-withdrawing carbonyl group in the ethanoic acid molecule weakens the O—H bond in the —COOH group, making it more likely for an ethanoic acid molecule to lose an H^+ ion than it is for an ethanol molecule. Secondly, delocalisation of electrons around the —COO[−] group stabilises the ethanoate ion. This is not possible in the ethoxide anion formed when ethanol loses an H^+ ion.
- c Methanoic acid would be the stronger acid, as ethanoic acid has an electron-donating methyl group next to the —COOH group, which does not aid the breaking of the O—H bond. Also, once the ethanoate anion is formed the methyl group tends to increase the concentration of the negative charge on the —COO[−] end of the ion, making it more attractive to H^+ ions than a

methanoate anion. Therefore ethanoic acid molecules are more likely to exist in the undissociated form, whereas methanoic acid molecules are less likely to exist in the undissociated form.

- 2 a because the methanoic acid formed would be oxidised to carbon dioxide (and water)
 - b $(\text{COOH})_2 \rightarrow 2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$
 $(\text{COOH})_2 + [\text{O}] \rightarrow 2\text{CO}_2 + \text{H}_2\text{O}$
 - c i to speed up the reaction because the redox reaction is initially slow before the Mn^{2+} ions form and act as a catalyst
 - ii 25 cm^3 of $0.0500 \text{ mol dm}^{-3}$ ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4$, contains $\frac{(0.0500 \times 25)}{1000} = 0.00125$ moles
- 2 moles of KMnO_4 will react with 5 moles of $\text{H}_2\text{C}_2\text{O}_4$ so 0.00125 moles of $\text{H}_2\text{C}_2\text{O}_4$ will react with $\frac{2}{5} \times 0.00125$ moles of KMnO_4
- Therefore there are $\frac{2}{5} \times 0.00125$ moles of KMnO_4 in 8.65 cm^3 of its solution so the number of moles of KMnO_4 in 1000 cm^3 (i.e. its concentration) is:
- $$\left(\frac{2}{5} \times 0.00125\right) \times \frac{1000}{8.65} \text{ moles dm}^{-3}$$
- making the concentration of KMnO_4 solution $0.0578 \text{ mol dm}^{-3}$ (to 3 significant figures)
- 3 a $\text{CH}_3\text{CH}_2\text{COOH} + \text{SOCl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{COCl} + \text{SO}_2 + \text{HCl}$
 - b $3\text{HCOOH} + \text{PCl}_3 \rightarrow 3\text{HCOCl} + \text{H}_3\text{PO}_3$
(heat is required for this reaction to occur)
 - c $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COCl} + \text{POCl}_3 + \text{HCl}$

4 a The carbonyl carbon in an acyl chloride carries a greater partial positive charge than the carbon atom bonded to the oxygen atom in an alcohol. This is because it has two strongly electronegative atoms (oxygen and chlorine) attached to the carbonyl carbon, compared with just the oxygen atom in an alcohol.

b propanoic acid and hydrogen chloride

c i $\text{CH}_3\text{CH}_2\text{COCl}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$, $\text{C}_6\text{H}_5\text{Cl}$

ii The hydrolysis of $\text{CH}_3\text{CH}_2\text{COCl}$ is far more vigorous than the hydrolysis of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$. The hydrolysis of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ needs a strong alkali and heating under reflux to bring about a reaction. The nucleophile is the negatively charged hydroxide ion, OH^- , as opposed to the neutral water molecule, which is sufficient to hydrolyse $\text{CH}_3\text{CH}_2\text{COCl}$ quickly at room temperature. That is because the carbon bonded to the chlorine atom in a $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ molecule is not as electron deficient as the carbon atom in $\text{CH}_3\text{CH}_2\text{COCl}$. In $\text{CH}_3\text{CH}_2\text{COCl}$ the carbon bonded to a chlorine atom is also attached to an oxygen atom. It has two strongly electronegative atoms pulling electrons away from it. Therefore the attack by the nucleophile is much more rapid. On the other hand, $\text{C}_6\text{H}_5\text{Cl}$, an aryl chloride, will not undergo hydrolysis. The p orbitals from the Cl atom overlap with the delocalised π electrons in the benzene ring. This causes the C—Cl bond to have some double bond character, making it stronger and more resistant to hydrolysis.

iii steamy white fumes (of HCl)

5 a i ethanoyl chloride and ethanol

ii butanoyl chloride and methanol

iii benzoyl chloride and phenol

b $\text{CH}_3\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_3 + \text{HCl}$

Exam-style questions

1 a i ethanol; [1]

ethanoic acid; [1]

a few drops of concentrated sulfuric acid as catalyst [1]

ii $\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$ [1]

b i phenol; [1]

benzoyl chloride; [1]

warm reaction mixture [1]

ii $\text{C}_6\text{H}_5\text{OH} + \text{C}_6\text{H}_5\text{COCl} \rightarrow \text{C}_6\text{H}_5\text{COOC}_6\text{H}_5 + \text{HCl}$ [1]

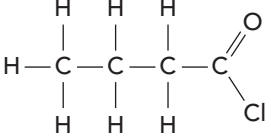
iii steamy white fumes (of hydrogen chloride) given off [1]

c The reactions with acyl chlorides happen more quickly than the reactions with carboxylic acids. [1]

The acyl chloride reactions also go to completion and do not form an equilibrium mixture like the reactions with carboxylic acids do. [1]

[Total: 11]

2 a



[1]

b i phosphorus(V) chloride, PCl_5 / phosphorus(III) chloride, PCl_3 / sulfur dichloride oxide, SOCl_2 [2]

ii $\text{C}_4\text{H}_9\text{COOH} + \text{PCl}_5 \rightarrow \text{C}_4\text{H}_9\text{COCl} + \text{POCl}_3 + \text{HCl}$

or

$3\text{C}_4\text{H}_9\text{COOH} + \text{PCl}_3 \xrightarrow{\text{heat}} 3\text{C}_4\text{H}_9\text{COCl} + \text{H}_3\text{PO}_3$

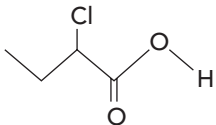
or

$\text{C}_4\text{H}_9\text{COOH} + \text{SOCl}_2 \rightarrow \text{C}_4\text{H}_9\text{COCl} + \text{SO}_2 + \text{HCl}$ [1]

iii Chlorine atom withdraws electrons from the —COOH group [1]

weakening the O—H bond so it is easier for 2-chlorobutanoic acid to lose an H^+ ion. [1]

iv



[1]

v 2,2-dichlorobutanoic acid /
2,3-dichlorobutanoic acid [1]

vi The hydrolysis of butanoyl
chloride is more vigorous than
the hydrolysis of 1-chlorobutane,
which is more reactive than that
of chlorobenzene. [1]

This difference between butanoyl
chloride and 1-chlorobutane is
due to the carbon bonded to
the chlorine atom in butanoyl
chloride being more strongly δ^+
than in 1-chlorobutane. [1]

This is because in butanoyl
chloride the carbon bonded to
the chlorine atom is also bonded
to an oxygen atom. So the
carbonyl carbon has two highly
electronegative atoms pulling
electrons away from it. Therefore,
the attack by the nucleophile,
 H_2O , is much more rapid. [1]

Chlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$,
will not undergo hydrolysis
(unless subjected to very harsh
conditions). The carbon atom
bonded directly to the chlorine
atom is part of the delocalised
bonding around the benzene ring. [1]

(A lone pair of electrons from the
Cl atom tends to overlap with the
electrons in the benzene ring). This
causes the C—Cl bond be stronger
and more difficult to break, so
hydrolysis is very difficult. [1]

[Total: 13]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 27

Science in context

After reading the Science in Context passage about William Perkin, ask learners to work in small groups to carry out the three tasks. Discussion of the role of serendipity in scientific discovery should bring out the chance element but also the astute responses of the pioneering scientists who then recognise the potential importance of their stroke of luck.

Research on the internet should reveal some cases of serendipitous discoveries in chemistry. For example, saccharin used as an artificial sweetener discovered by Constantine Fahlberg (there is a link with William Perkin here as both were experimenting with coal tar when their discoveries were made); Teflon discovered by Roy Plunkett; Super Glue discovered by Harry Coover; Vaseline discovered by Robert Chesebrough. Ask each group to give one of their examples, and a brief explanation of what happened in that particular discovery, rotating around the class until there are no new suggestions.

The structure that all the dyes have in common is the $-N=N-$ group. This is called an 'azo' group; hence the name 'azo dyes'.

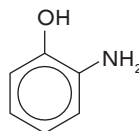
Self-assessment questions

- 1 a i pentylamine
 ii dipropylamine
 iii ethylammonium chloride
- b Diethylamine is a stronger base than ethylamine because it has two ethyl groups each releasing electrons to its N atom, making the lone pair more readily available to bond with an H^+ ion than it is in ethylamine, which only has one electron-donating ethyl group.
- 2 a i The vapour of butanenitrile and hydrogen gas are passed over

a nickel catalyst; alternatively sodium and ethanol are used to reduce the butanenitrile.

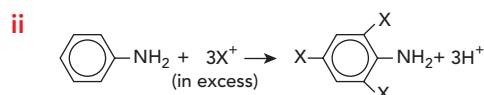
- ii 1-bromopropane
 iii nitriles and amides (nitro-alkanes also acceptable)

- b i 2-aminophenol, $C_6H_4(OH)NH_2$



- ii reduction

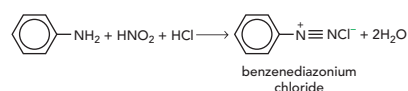
- 3 a i Phenylamine, because of the greater electron density around the benzene ring, because the lone pair of the nitrogen atom is delocalised into the π bonding electron system.



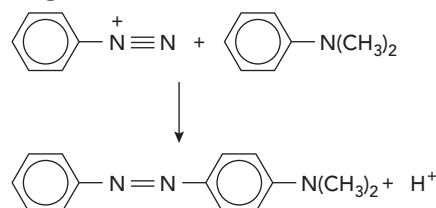
- b i The benzenediazonium ion will decompose, giving off nitrogen gas, above $10^\circ C$. The nitrous acid used as a reactant also decomposes above $10^\circ C$.

- ii $NaNO_2 + HCl \rightarrow HNO_2 + NaCl$

- iii Step 1



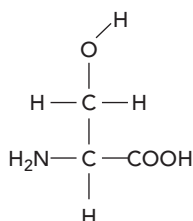
Step 2



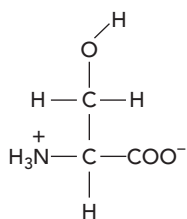
4 a i A

- ii They have relatively high melting points for organic compounds of their molecular mass because of the strong electrostatic forces of attraction between the oppositely charged parts of the zwitterions formed.

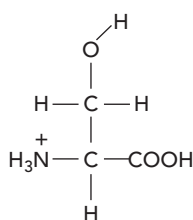
b i



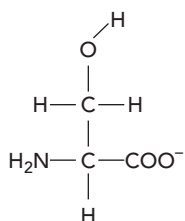
ii



iii

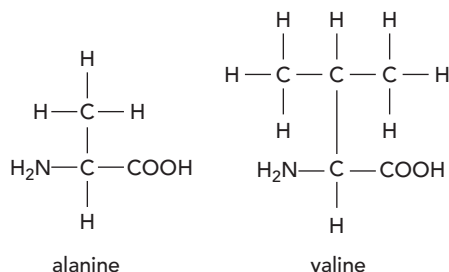


iv

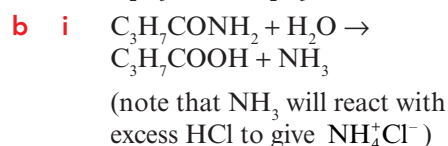
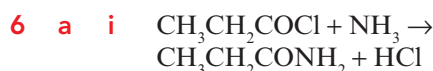
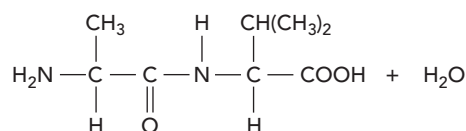
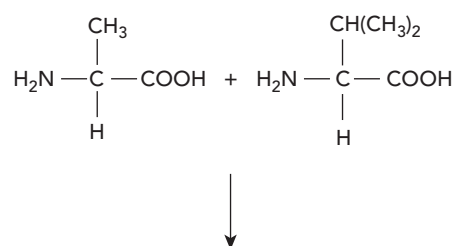


- v The isoelectric point of serine is the pH value at which there is no overall charge on an aqueous solution of serine.

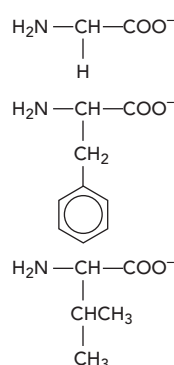
5 a



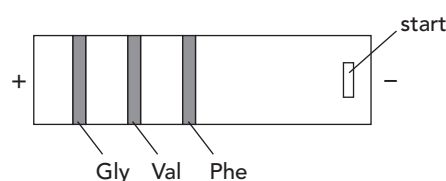
b



7 a



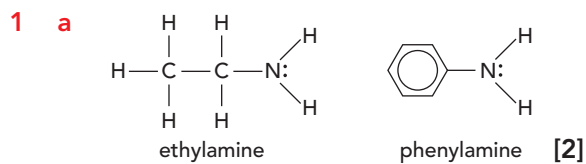
b i



- ii The molecules are separated according to size, with the smallest (glycine) moving furthest, and the largest (phenylalanine) moving the shortest distance. Each of the ions will have a -1 charge at pH 10, so the size of the ions is the only factor involved in their separation.

c The amino acid would remain in position / not move.

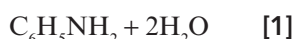
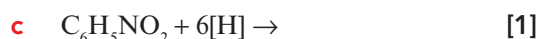
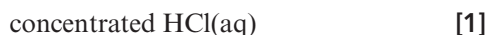
Exam-style questions



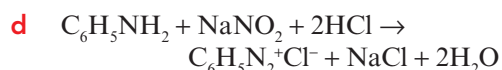
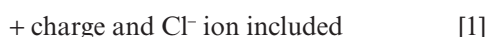
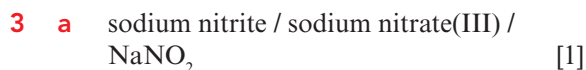
[1 mark for each structure]



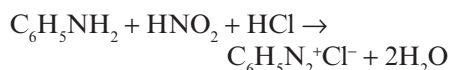
[Total: 5]



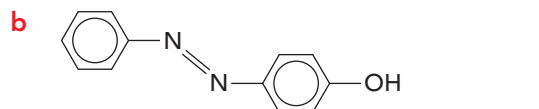
[Total: 5]



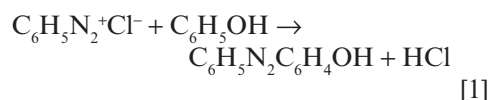
or



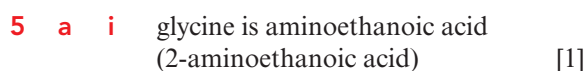
[Total: 8]



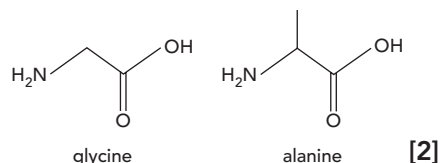
or



[Total: 6]

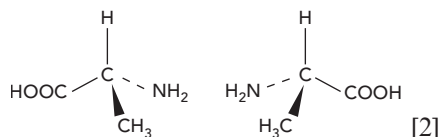


ii

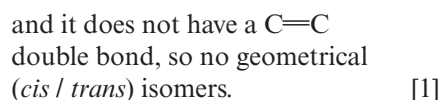
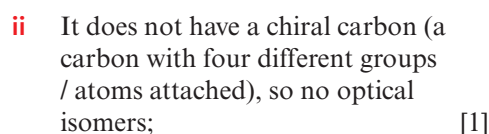


[1 mark for each structure]

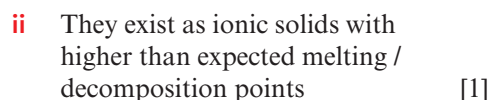
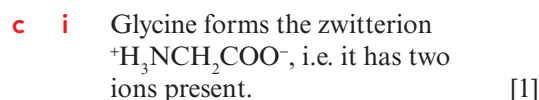
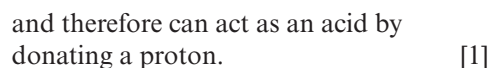
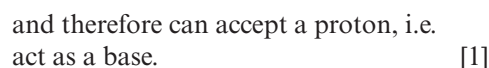
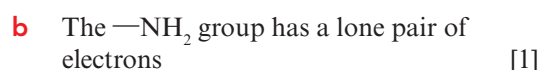
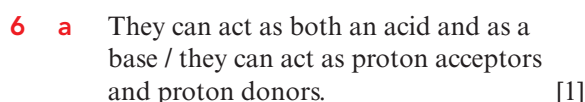
b i



[1 mark for each structure]



[Total: 8]



because of the electrostatic attraction between oppositely charged ions on neighbouring zwitterions.

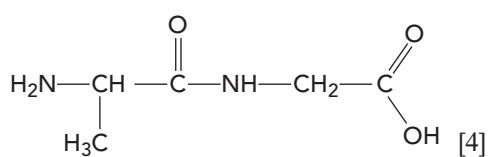
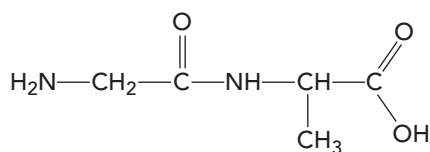
[1]

They are soluble in water

[1]

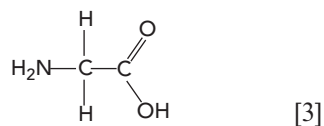
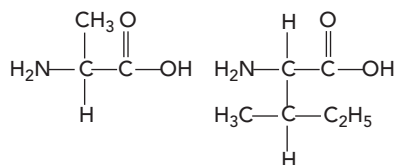
because of the interactions between the charged groups and polar water molecules.

[1]

d

[2 marks for each structure]

[Total: 14]

7 a i

[3]

[1 mark for each structure]

ii the second one in the diagram above

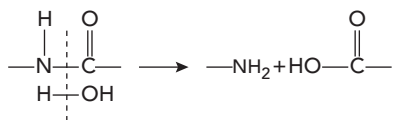
[1]

b i —CO—NH— / amide / peptide bond / link

[1]

ii Hydrolysis means splitting of a bond / breaking down a compound using water.

[1]



[2]

[1 mark for showing which bond breaks, 1 mark for products]

iii electrophoresis

[1]

iv It works because ions move at different rates towards the oppositely charged electrode

[1]

depending on the size / mass of ions

[1]

and charge on the ions;

[1]

larger ions will move more slowly;

[1]

more highly charged ions will move more quickly.

[1]

[Total: 14]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

Coursebook answers

Chapter 28

Science in context

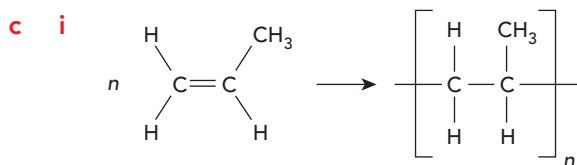
The points put forward by each pair or group of learners should be:

- delocalisation of alternate double bonds in the π bonding running down the length of the polymer chain
- a sketch that shows the long carbon backbone of the polymer linked by single (sigma bonds) and two long, continuous orbitals above and below the carbon chain (pi bonds)
- any sensible suggestion for applications, e.g. in circuits used in aircraft manufacture, portable electrical appliances.

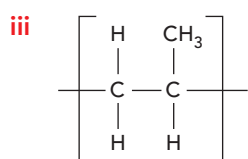
Ask different pairs to give their suggestion to one of the bulleted tasks for the whole class to discuss.

Self-assessment questions

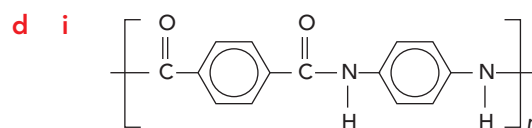
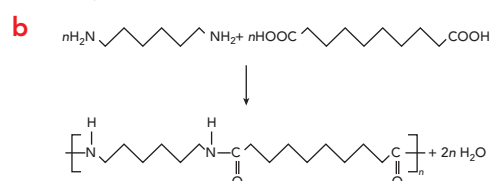
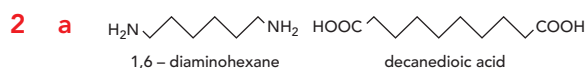
- 1 a addition polymers from **ii** and **iii**;
condensation polymers from **i**, **iv** and **v**
- b Addition polymers have monomers that are alkenes; condensation polymers have monomers that are not alkenes but that have two functional groups per molecule. **i** and **iv** both have an —NH_2 group and a —COOH group. **v** has an —OH group and a —COOH group.



ii addition polymerisation

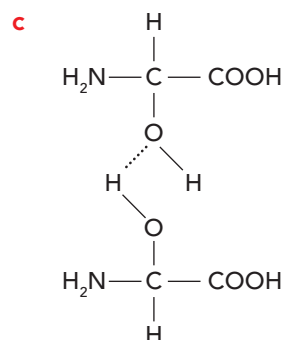


d Condensation polymerisation



ii The highly regular structure enables a network of extensive hydrogen bonding between the polymer chains (at the amide links) to be established so it is very difficult to separate the polymer chains.

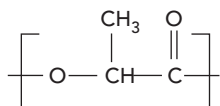
- 3 a amine / amino group, —NH_2 , and carboxylic acid, —COOH
- b Any amino acid that has a hydrocarbon side-chain, e.g. alanine, valine, leucine, isoleucine, phenylalanine. Glycine, the simplest amino acid, also has a non-polar side-chain.



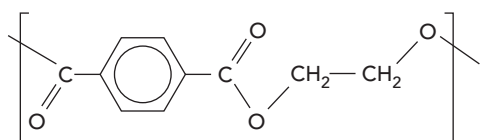
d A

- e An amino acid when it is part of a peptide chain. 'Residue' means what is left after something has been removed. In this case it is water that has been removed by the condensation of the amino acids.

4 a



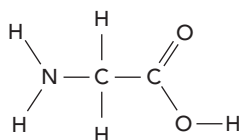
b



5 a

condensation polymerisation

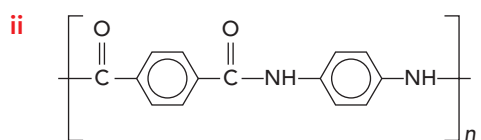
b



Exam-style questions

- 1 a polymer formed when many monomers combine, with the simultaneous elimination of many small molecules (e.g. water) [2]

- b i small molecule that combines with other monomer molecules to form a polymer [1]



correct chain structure [1]

correct brackets [1]

- iii polyamide [1]

- c extensive / very many hydrogen bonds [1]
between the $>\text{C}=\text{O}$ and $-\text{NH}$ groups [1]
on neighbouring / linear polymer chains [1]

[Total: 9]

- 2 a a diol; [1]

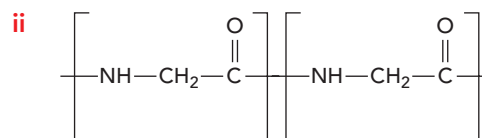
a dicarboxylic acid [1]

- b correct repeat unit [1]

with ester linkage [1]

[Total: 4]

- 3 a i 2-aminoethanoic acid / aminoethanoic acid [1]



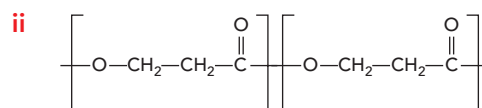
correct chain structure [1]

brackets round repeat unit [1]

- iii amide / peptide [1]

- iv hydrogen bonding [1]

- b i $\text{HOCH}_2\text{CH}_2\text{COOH}$ [1]



correct chain structure [1]

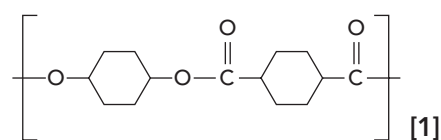
brackets round repeat unit [1]

- iii ester [1]

- iv dipole-dipole [1]

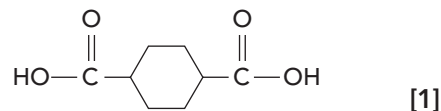
[Total: 10]

4 a i



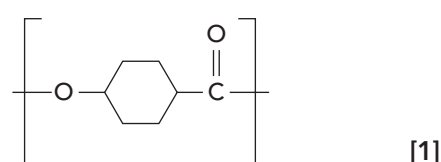
[1]

- ii $\text{HO}-\text{C}_6\text{H}_{10}-\text{OH}$ [1]



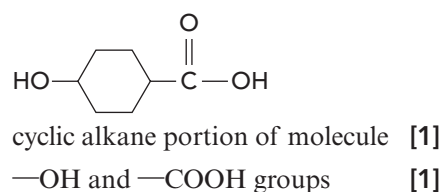
[1]

b i



[1]

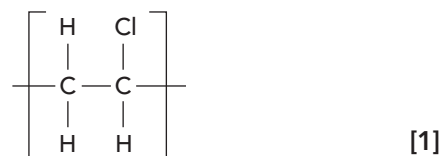
ii



cyclic alkane portion of molecule [1]

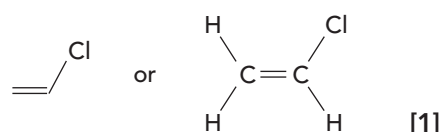
 $-\text{OH}$ and $-\text{COOH}$ groups [1]

c i

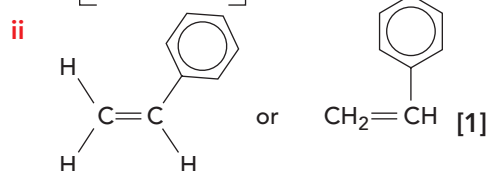
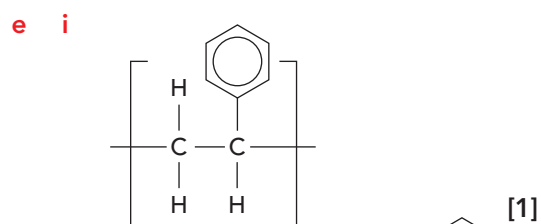
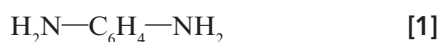
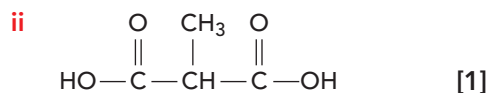
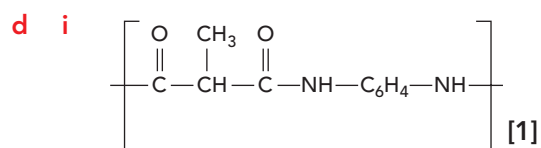


[1]

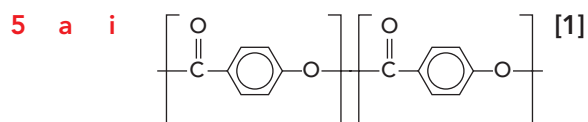
ii



[1]

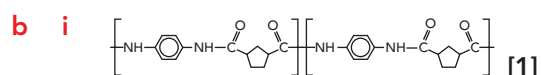


[Total: 13]



ii ester link [1]

iii dipole-dipole attraction [1]



ii amide link [1]

iii hydrogen bonding [1]

[Total: 6]

6 a A substance is biodegradable if it is broken down in the environment; [1]

by living organisms / microorganisms. [1]

b Biodegradable polymers will not persist in the environment; [1]

less litter; [1]

no problems with disposal, e.g. burning / landfill. [1]

c Disposable packaging; [1]

it is biodegradable so does not take up space in landfill sites. [1]

Medical sutures and bandages; [1]

the product of biodegradation is natural / non-toxic. [1]

[Total: 9]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 29

Science in context

Ask learners to work in small groups to discuss the development of new medicinal drugs. Points covered should be the importance of computers in analysing data to discover the structure of pathogens, as well as their role in the modelling of potential drugs to fit into, bond with and deactivate the active site on the pathogen.

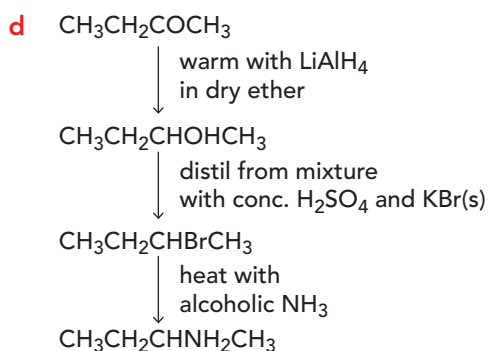
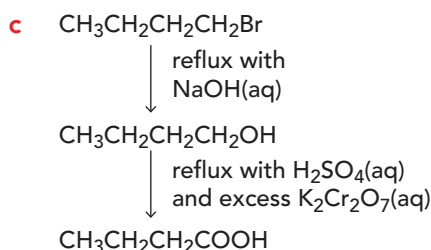
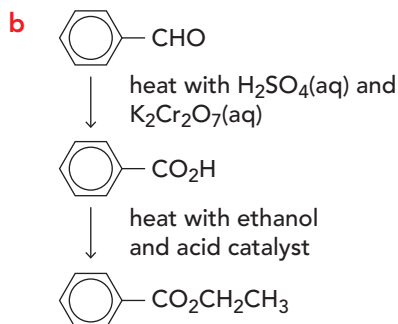
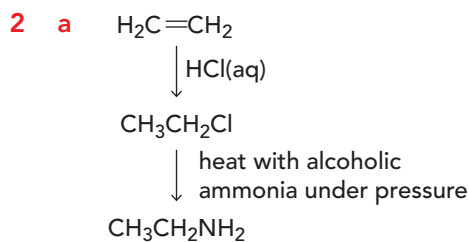
Discuss the ‘trial and error’ methods used and compare them with modern modelling techniques in a whole class plenary. Scientists can design specifically shaped molecules that can block active sites on enzymes and molecules and so interfere with the reproduction of a virus within its host cell. However, even with modern technology and our ability to determine the genetic code of a pathogen, the search for an effective anti-viral drug or for a vaccine to combat a new virus is both time-consuming, often involving large teams of scientists and extensive tests to ensure patient safety, and is inevitably a very costly process.

Note that the Science in Context passage in Chapter 30 covers the founder of the ribbon diagrams shown in Figure 29.2.

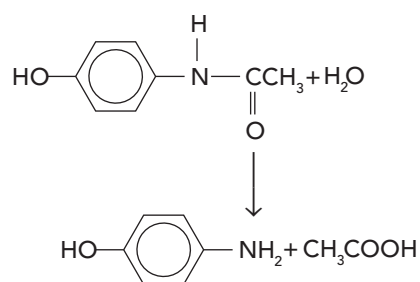
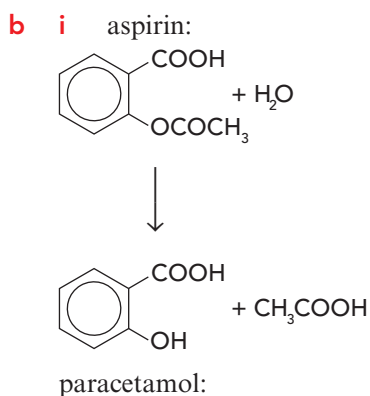
Self-assessment questions

- 1 a i less dosage required; reduces risk of side effects as the unwanted enantiomer might present a health hazard
- ii reduces the chances of litigation against the drug company as a result of side effects caused by the unwanted enantiomer; possibly cheaper as don't waste the unwanted enantiomer

- b points to include:
- racemic mixture produced in traditional synthetic routes
 - this results in the need to separate the mixture of enantiomers
 - this can use large volumes of organic solvents, which have to be disposed of, along with the unwanted enantiomer
 - the process will also use more chemicals, which require natural resources
 - enzymes are stereospecific
 - whole organisms can be used (without having to isolate enzymes)
 - fewer steps in process, resulting in more efficiency
- c Thalidomide was prescribed to pregnant women as a sedative during the early 1960s. It was for a time the preferred sedative during pregnancy as the alternatives, such as valium, were addictive. Unfortunately, one of the two optical isomers of thalidomide proved to have disastrous side effects, causing babies to be born with congenital deformities (teratogenicity). Not surprisingly, thalidomide was quickly withdrawn from use and law-suits were filed against the manufacturers to compensate those affected and to help finance their care. If the optical isomer that had therapeutic effects, without side effects, had been purified and given as a medicine, this still wouldn't have solved the problem. The ‘good’ optical isomer is converted into the ‘bad’ optical isomer in the body, with the same outcome.



- 3 a i** carboxylic acid and ester
ii hydroxy / alcohol / phenol and amide



ii hydrolysis

c A = sodium propanoate; B = propanoic acid; C = propanoyl chloride; D = propanamide

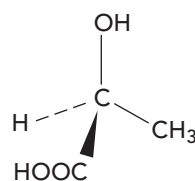
d i Stage 1: add conc. nitric acid and conc. sulfuric acid to make nitrobenzene
 Stage 2: add tin / conc. hydrochloric acid to reduce nitrobenzene to phenylamine
 Step 3: add sodium nitrate(III) and hydrochloric acid, followed by sodium hydroxide solution, at a temperature between 0°C and 5°C to phenylamine

ii add phenol in aqueous sodium hydroxide

iii D

Exam-style questions

- 1 a i** 2-hydroxypropanoic acid [1]
ii [1]



Question 1 part **a ii** asks you to draw the other optical isomer of lactic acid. To help yourself to get it right, redraw the isomer of lactic acid shown here on the left-hand side of a sheet of paper, then put a vertical mirror line down the centre of the paper. Now draw the other isomer. Start with a C in the middle and a vertical bond to an OH – this doesn't change. Then draw in the other three groups. In the first isomer they were (left to right)

—CH₃, —COOH, —H. In the second isomer they will be —H, —COOH, —CH₃. The forward / backwards direction of their bonds doesn't change. The —H is going backwards, the —COOH is coming forwards, the —CH₃ is neither backwards nor forwards.

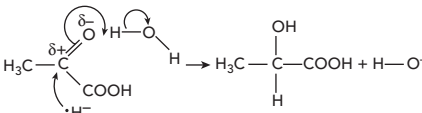
- iii It has a chiral carbon atom / four different groups bonded to same carbon atom. [1]

- b i acidified potassium dichromate; [1]
heat / distil [1]

- ii $\text{CH}_3\text{CH}(\text{OH})\text{COOH} + [\text{O}] \rightarrow \text{CH}_3\text{COCOOH} + \text{H}_2\text{O}$ [2]
[1 mark for reactants, 1 mark for products]

- c i sodium tetrahydridoborate(III) / borohydride / NaBH₄; [1]
warm [1]

- ii $\text{CH}_3\text{COCOOH} + 2[\text{H}] \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{COOH}$ [2]
[1 mark for reactants, 1 mark for products]

- d i  [1]

- for dipoles [1]
for curly arrow from lone-pair electrons on hydride [1]
for curly arrow from C=O to between O and H atoms [1]
for curly arrow from H—O bond onto oxygen [1]
for products [1]

- ii Question 1 part d i asks you for a mechanism you probably haven't studied. Think logically and use what you know from other topics and from the question:
The reaction involves addition of 2H to a ketone – the mechanism will be nucleophilic addition.
The question says that the first step involves nucleophilic attack on the carbon of the ketone group by an H[−] ion.

The question says that there is water present.

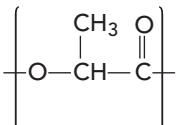
CH₃COCOOH is planar around the carbonyl carbon and there is attack from hydride above and below plane of molecule; [1]

this gives equal amounts of the two optical isomers of CH₃CH(OH)COOH. [1]

These cancel each other out, so there is no rotation of plane-polarised light. [1]

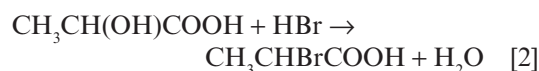
- e i Each molecule of lactic acid contains an alcohol / —OH group and a carboxylic acid / —COOH group, [1]
which react with each other / form an ester link between the monomers. [1]

- ii condensation polymerisation [1]

- iii  [1]

[Total: 23]

- 2 Step 1, preparation of 2-bromopropanoic acid:

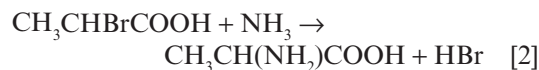


[1 mark for reactants, 1 mark for products]

reagents used are:

- concentrated sulfuric acid [1]
and sodium (or potassium) bromide [1]

Step 2, preparation of 2-aminopropanoic acid:



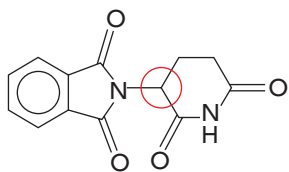
[1 mark for reactants, 1 mark for products]

reagents and conditions are:

- in ethanol (as solvent); [1]
heat [1]
in sealed tube (or under pressure) [1]

[Total: 9]

3 a [1]



b amine (allow amino); [1]

ketone [1]

c reduction; [1]

add an aqueous solution of NaBH_4 or LiAlH_4 in dry ether [1]

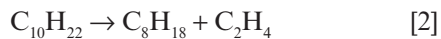
d Each enantiomer differs in its 'pharmaceutical activity' / one enantiomer might be effective but the other could induce serious side effects; [1]

minimises the risk of side effects / reduces the patient's dosage / the pure enantiomer is more potent / has better therapeutic activity [1]

cuts costs of production as less drug is needed / protects companies from possible legal action (litigation) for damages by patients who suffer bad side effects. [1]

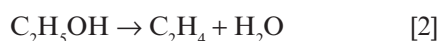
[Total: 8]

4 a i octane (C_8H_{18}) [1]



ii cracking [1]

b i ethanol [1]



ii elimination / dehydration [1]

[Total: 8]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter 30

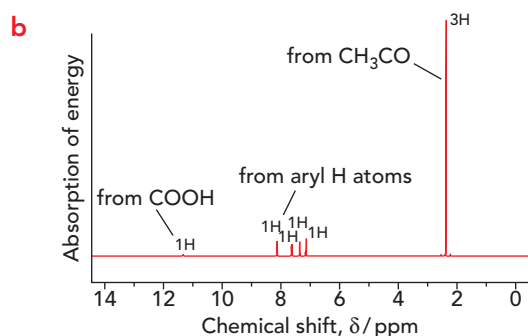
Science in context

Try to organise groups so that each group contains a biology student when discussing proteins in the first task. The simplification offered by ribbon diagrams is useful when looking at the active sites in protein molecules. Learners can link back to Chapter 29, where molecular modelling is considered.

Before starting the second task, the group should decide on how they will present their findings to the rest of the class. Members of the group can then research different aspects of the life and work of Jane Richardson. For example, one can cover her early life, another her life after joining Duke University, and a third could look at her contributions to the advancement of science.

Self-assessment questions

- 1 a C
b 0.53
- 2 a adsorption
b Hexane would rise furthest on the alumina as it has a greater affinity for non-polar methylbenzene than for the polar alumina stationary phase. Polar propanone has the greater affinity for the polar alumina than hexane does and is less soluble in methylbenzene so does not move as far as hexane over the alumina in a given time.
- 3 a i Retention time is measured as the time it takes for a substance to travel through the stationary phase and be detected.
ii The areas under the peaks give the relative proportions of each component of the mixture.
b the height of the peaks
- 4 a Its formula is $\text{Si}(\text{CH}_3)_4$ so all its H atoms are equivalent (i.e. they are all in the same molecular environment) so it only gives one, sharp absorption. It is also inert (it does not react with samples being tested), volatile (easily removed from the sample after NMR analysis) and mixes well with most organic compounds.
b i CCl_4
ii It has no hydrogen atoms so it won't produce a peak in the NMR spectrum.
iii Deuterium nuclei do not absorb radio waves in the range we use for NMR so there will be no peaks to interfere with the sample's NMR spectrum.
- 5 a two peaks, with areas in the ratio 1 : 3
b single peak (as all the H atoms are equivalent)
c two peaks, with areas in the ratio 2 : 3
d four peaks, with areas in the ratio 1 : 2 : 2 : 3
e three peaks, with areas in the ratio 1 : 1 : 6
f single peak (as all the H atoms are equivalent)
- 6 a Paracetamol: there are two peaks from single protons with relatively high chemical shifts, corresponding to the —OH and —NH protons in paracetamol (whereas you would expect aspirin to have one peak between 11 and 12 ppm at the high end of the spectrum from its —COOH proton).



- 7 a** The single —OH peak would disappear from the NMR spectrum.
- b** Two peaks (from the —OH and —NH protons) would disappear from the NMR spectrum of paracetamol but only one peak would disappear from aspirin's spectrum (from the —COOH peak).
- 8 a i** The carbon atom in the benzene ring that is bonded to the ethyl group as this is the closest to, and therefore most affected by, the ethyl side-chain.
- ii** Three lines, as there are three equivalent carbon atoms (two at the 2 and 6 positions in the benzene ring, two at the 3 and 5 positions, and one at the 4 position), each affected to a slightly different extent by the presence of the ethyl side-chain (off the carbon atom in the 1 position).
- b** a single peak (as all six carbon atoms are equivalent), at chemical shift between 110 and 160 ppm
- c i** three peaks; one for the carbon atom in the —CH₃ group, one for the —CH₂ group, and one for the —CH₂OH group
- ii** two peaks; one for the equivalent carbon atoms in the two —CH₃ groups, and one for the central carbon atom bonded to the —OH group, i.e. >CHOH

Exam-style questions

The 'Analytical techniques' section involves less knowledge to recall than other chapters, but it does contain ideas and skills that you must learn how to apply. Practise these questions, and the self-assessment questions in the text, until you are confident in applying ideas and skills. Questions 2, 3, 4 and 5 are good examples of this.

- 1 a** A = recorder response [1]
 B = time of injection [1]
 C = retention time [1]
- b** total area $\left(\frac{1}{2} \times 2 \times 50\right)$ [1]
 $+ \left(\frac{1}{2} \times 1 \times 80\right)$ [1]
 $+ \left(\frac{1}{2} \times 2 \times 60\right)$ [1]
 = 150 [1]
- percentage of pentan-1-ol = $\frac{50}{150} \times 100\%$ [1]
 = 33.3 % [1]
- c** The stationary phase is non-polar; [1]
 the less polar compounds are adsorbed more strongly on the column and have longer retention times; [1]
 octane has more electrons than pentane so stronger van der Waals' forces between octane and column. [1]
- d i** The order would be reversed / changed (and overall retention times would increase). [1]
- ii** The pentan-1-ol is the most polar molecule [1]
 and would be retained the longest. [1]
- e** Can quickly provide an accurate measure of the quantity of any anabolic steroid present; [1]
 the amounts present are small and gas-liquid chromatography is very sensitive. [1]
- f** The compounds can be identified immediately by their fragmentation patterns; [1]
 compare results to database or there is no need for running standards in order to identify the unknowns. [1]

- g** They are large compounds with large relative molecular masses; [1]
they have high boiling points and therefore are not volatile enough for separation using this method. [1]

[Total: 21]

2 a

Element	carbon	hydrogen	oxygen
Percentage	62.1	10.3	27.6
Mass in 100 g	62.1 g	10.3 g	27.6 g
Number of moles	$\frac{62.1}{12.0} = 5.18$	$\frac{10.3}{1.0} = 10.3$	$\frac{27.6}{16.0} = 1.73$
Relative number of atoms	$\frac{5.18}{1.73} = 3$	$\frac{10.3}{1.73} = 6$	$\frac{1.73}{1.73} = 1$

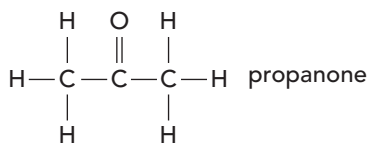
[1]

empirical formula = C_3H_6O [1]

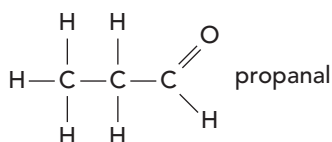
- b** molecular mass is 58 [1]

empirical formula mass = molecular mass, therefore the molecular formula = C_3H_6O [1]

- c i** [1]



[1]



- ii** it is propanal [1]

- iii** There are three peaks present in the ^1H NMR spectrum; [1]

propanone has only one type of proton [1]
and therefore it would have only one peak. [1]

- d** This is the peak for the $-\text{CH}_3$ protons; [1]
it is split into a triplet because of the two chemically different (non-equivalent) protons on the adjacent carbon (by applying the $n + 1$ rule in which $n = 2$). [1]

- e i** three lines as there are three non-equivalent carbon atoms in propanal [1]

the methyl carbon ($-\text{CH}_3$), the central carbon atom ($-\text{CH}_2-$ and the carbonyl carbon ($>\text{C}=\text{O}$) [1]

- ii** two lines as there are two non-equivalent carbon atoms in propanone [1]

the two (equivalent) methyl carbons ($-\text{CH}_3$), and the central carbon atom / carbonyl carbon ($-\text{C}=\text{O}$) [1]

[Total: 16]

3 a

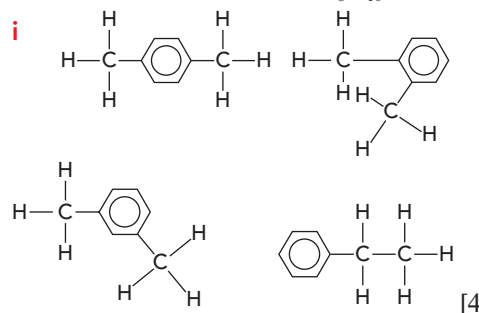
Element	carbon	hydrogen
Percentage	90.6	9.4
Mass in 100 g	90.6 g	9.4 g
Number of moles in 100 g	$\frac{90.6}{12.0} = 7.55$	$\frac{9.4}{1.0} = 9.4$
Relative number of atoms	$\frac{7.55}{7.55} = 1$	$\frac{9.4}{7.55} = 1.25$
Whole numbers	4	5

[1]

empirical formula = C_4H_5 [1]

- b** The m/e value for the penultimate peak on the mass spectrum = 106; [1]

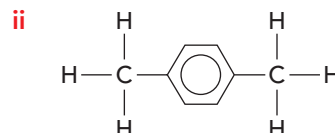
this is twice the empirical formula mass, so the molecular formula is C_8H_{10} . [1]

c i

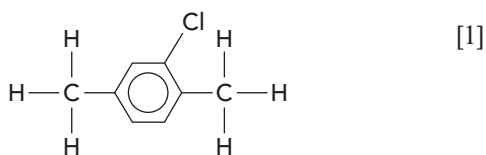
[4]

[1 mark for each structure]

- ii** [1]



This is because when chlorinated by electrophilic aromatic substitution it forms only the following compound:



The other possible isomers form several different compounds. [1]

The ^1H NMR spectrum shows two peaks as C has only two different types of proton; [1]

the other possible isomers have larger numbers of different types of proton. [1]

- d** The peak at $\delta = 7$ ppm [1]
 is the peak from the benzene ring protons; [1]
 the peak at $\delta = 2.3$ ppm [1]
 corresponds to the $-\text{CH}_3$ protons. [1]

[Total: 17]

4 a

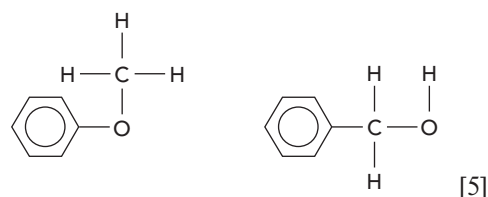
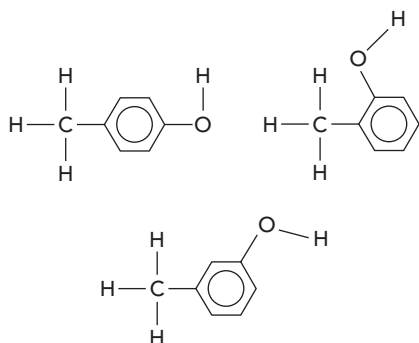
Element	carbon	hydrogen	oxygen
Percentage	77.8	7.41	14.8
Mass in 100 g	77.8 g	7.41 g	14.8 g
Number of moles in 100 g	$\frac{77.8}{12.0} = 6.48$	$\frac{7.41}{1.0} = 7.41$	$\frac{14.8}{16.0} = 0.925$
Relative number of atoms	$\frac{6.48}{0.925} = 7$	$\frac{7.41}{0.925} = 8$	$\frac{0.925}{0.925} = 1$

[1]

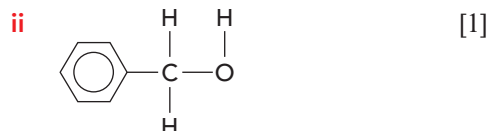
empirical formula = $\text{C}_7\text{H}_8\text{O}$ [1]

- b** The m/e value for the molecular-ion peak is 108; [1]
 this corresponds to the mass of the empirical formula,
 so molecular formula = empirical formula = $\text{C}_7\text{H}_8\text{O}$. [1]

c i



[1 mark for each structure]



- iii** The relative area of the peak at $\delta = 7.3$ ppm is 5, so there are five protons on the benzene ring; therefore D cannot be a disubstituted compound. [1]

The other mono-substituted compound has only two types of proton [1]

but the ^1H NMR spectrum of D has three peaks, corresponding to the three different types of proton in D. [1]

- d** There are three peaks because of the three chemically different types of proton in D: [1]
 the peak for five protons at $\delta = 7.3$ ppm is caused by the five benzene protons; [1]

[Total: 15]

5 a

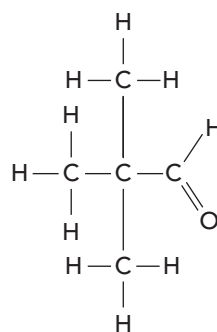
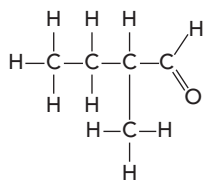
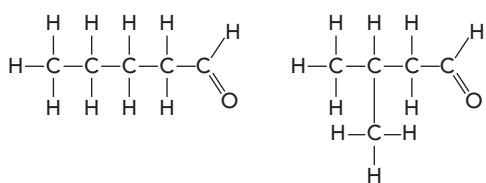
Element	carbon	hydrogen	oxygen
Percentage	69.8	11.6	18.6
Mass in 100 g	69.8 g	11.6 g	18.6 g
Number of moles in 100 g	$\frac{69.8}{12.0} = 5.82$	$\frac{11.6}{1.0} = 11.6$	$\frac{18.6}{16.0} = 1.16$
Relative number of atoms	$\frac{5.82}{1.16} = 5$	$\frac{11.6}{1.16} = 10$	$\frac{1.16}{1.16} = 1$

[1]

empirical formula = $\text{C}_5\text{H}_{10}\text{O}$ [1]

- b** The m/e value for the molecular-ion peak is 86 so its relative molecular mass is 86; [1]
 this is the same as the empirical formula mass, so the molecular formula is also $\text{C}_5\text{H}_{10}\text{O}$. [1]

c

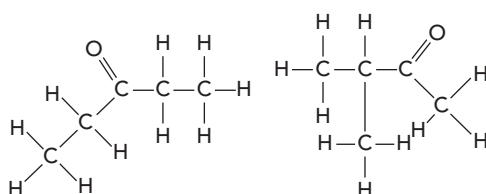
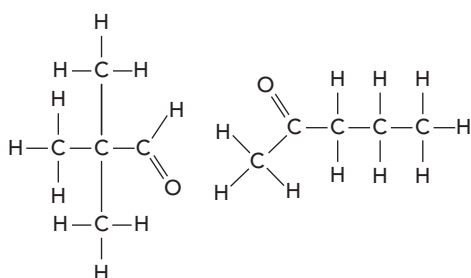


[1]

There is no splitting of the peaks because there are no adjacent carbons with chemically different protons on them.

[1]

[Total: 18]



[7]

[1 mark for each structure]

d

It must have a carbonyl group, because of the positive result with 2,4-DNPH.

[1]

It is an aldehyde, because of the positive result from the silver mirror test.

[1]

On the NMR spectrum there is an absorption at $\delta = 9.5$ ppm, characteristic of the aldehyde —CHO proton.

[1]

e

On the ^1H NMR spectrum there is an absorption at $\delta = 9.5$ ppm, characteristic of the aldehyde —CHO proton;

[1]

it has only two distinct peaks and therefore only two types of proton;

[1]

therefore E must be

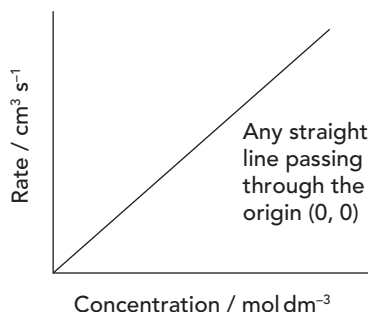
Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

> Coursebook answers

Chapter P1

Self-assessment questions

- 1
 - a temperature
 - b volume of gas given off in 30s
 - c concentration of the acid and surface area / mass of magnesium
 - d 10–50 °C (or alternatively the difference of 40 °C)
 - e 10 °C
 - f bar chart
- 2
 - a 12.65 cm³
 - b a suspension
 - c The solutions are both transparent but the sulfuric acid is colourless, whereas the copper(II) sulfate solution is pale blue.
 - d calcium carbonate
 - e
 - i thermometer or temperature sensor
 - ii gas syringe or measuring cylinder / burette full of water inverted in a trough of water
- 3
 - a –1600 J (the answer is a negative number, as the reaction is exothermic)
 - b The answer is given to 2 significant figures as the temperature is given to 2 significant figures, which is the least accurate data.
- 4
 - a Divide 20 cm³ by the time taken (in seconds) to collect that volume of gas.
 - b
 - i



- ii Choose two points on the line at least half as far apart as its total length. Then construct a right-angled triangle and calculate the change in rate divided by the change in concentration (change in y divided by change in x).
 - iii The rate would be halved.
- c As the concentration is doubled, the number of reactant particles is doubled in a given volume of solution. Therefore there will be twice as many collisions with energy greater than the activation energy in a given time and the rate of reaction will double.

Exam-style questions

- 1
 - a
 - i type of metal carbonate [1]
 - ii time (for limewater to turn cloudy) [1]
 - iii mass of carbonate [1]
 - b
 - i to improve accuracy by reducing effect of random errors / improve the reliability of data [1]

Metal carbonate	Time for limewater to turn milky / s			
	1st test	2nd test	3rd test	Mean

- [1] for main headings in table
 [1] for unit of time
 [1] for showing repeat tests and mean [3]
- c i** plus or minus 0.05 (allow 0.1) cm³ [1]
 percentage error is $(0.05/10) \times 100\% = 5\%$ (allow 10%) [1]
- ii** The time it takes for the limewater to turn cloudy [1]
 as stopping the timer at exactly the same point by eye in each test is very difficult to judge accurately / due to human error making accurate judgement of cloudiness [1]
- d** bar chart [1]
- [Total: 12]
- 2 a** heading 1/time (1/t)/s⁻¹ [1]
 values to enter 0.0033, 0.0050, 0.011, 0.017, 0.023, 0.027, 0.036 [2]
 [1 mark for values; 1 mark for 2 significant figures]
- b** volumetric / graduated / 25 cm³ pipette [1]
- c** Although the stopwatch can give more precise measurements, in this investigation the human error involved in reacting to the change in colour will mean that accuracy to one-hundredth of a second is not achievable. [2]
- d** $\frac{(40 \times 0.1)}{1000}$ [1]
 = 0.004 moles [1]
- e** The thiosulfate reacts with the iodine as it is formed until the thiosulfate is all used up. [1]
 Then the iodine, which continues to be formed, turns the starch blue/black [1]
 indicating that the reaction has reached the same point in each test (as the number of moles of thiosulfate is constant in each test). [1]
- [Total: 11]
- 3 a** magnesium ion / Mg²⁺ [1]
- b** Add an equal volume of dilute sodium hydroxide solution, followed an excess of sodium hydroxide [1]
 A white precipitate forms which remains insoluble in the excess sodium hydroxide [1]
- c** magnesium nitrate / Mg(NO₃)₂ [1]
- [Total: 4]

Exam-style questions and sample answers have been written by the authors. In examinations, the way marks are awarded may be different.

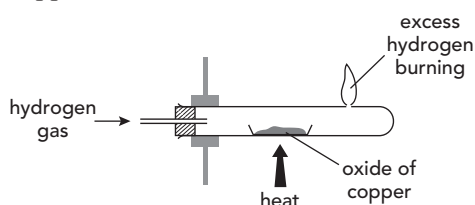
> Coursebook answers

Chapter P2

Self-assessment questions

- 1 a copper and water / steam

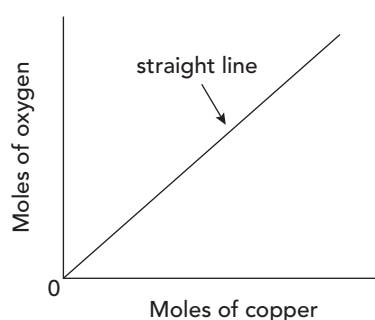
b



- c mass of (tube and) porcelain boat;
mass of (tube) boat and oxide of copper before heating;
mass of (tube) boat and its contents left after heating

- d i subtract the mass of (tube and) porcelain boat from the mass of (tube) boat and its contents left after heating
ii subtract the mass of (tube) boat and its contents left after heating from the mass of (tube) boat and oxide of copper before heating

e



- 2 a 0.44 %

b $\text{mol of Cu} = \frac{13.24}{63.5} = 0.209$

$\text{mol of O} = \frac{3.26}{16.0} = 0.204$

ratio of Cu:O = 1 : 1

formula = CuO

- c i anomalous result
ii omit / ignore this result or get that group to repeat their experiment
iii not all the copper oxide was reduced

Exam-style questions

- 1 a i The rate of diffusion will decrease as the M_r of the drug increases; [1]
any sensible explanation, e.g. because heavier molecules must move more slowly than lighter particles as their kinetic energy is the same at any given temperature. [1]
ii Rate of diffusion (units of distance/time, e.g. mm per hour) up y-axis and Relative molecular mass M_r (no units – allow g mol^{-1}) along x-axis; [1]
any negative line on graph (curve or straight line). [1]
b i relative molecular mass / M_r [1]
ii rate of diffusion (or time to travel a certain distance) [1]
c Use same concentration / moles per unit volume [1]
and same volume added to Petri dish. [1]
Measure calculated mass of dye powder on electric balance (measuring to 2 decimal places) and make up to required concentration in a volumetric flask. [1]
Keep all Petri dishes at the same temperature. [1]
Measure the distance the dye has penetrated the gelatin disc at regular time intervals. [1]

Have replicate plates running at same time or repeat experiments. [1]

- d** Wear protective gloves and eye protection when weighing dyes, and making and transferring solutions. [1]

Carry out experiment with all dishes in a fume cupboard. [1]

- e** A suitable table drawn, showing dyes and their relative molecular masses, time, distance; [1]

repeats/replication and rate of diffusion; [1]

e.g.

Dye	Relative molecular mass (or molecular mass in g mol^{-1})	Time / min or h	Distance dye travels / mm or cm				Rate of diffusion / mm or cm per min or h
			Test 1	Test 2	Test 3	Mean	
A	486						
B	534						
C	686						
D	792						
E	886						

[Total: 16]