

Teacher Guide

George Facer

Edexcel

AS Chemistry

2nd Edition

philip allan
UPDATES



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2nd Edition

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Introduction

This Teacher Guide accompanies the *Edexcel AS Chemistry* textbook (2nd edition), by George Facer, published by Philip Allan Updates.

The answers to the end-of-chapter questions are not model answers. They are designed to help the student understand the answer. The examiner notes after the answer, indicated by the icon , are additional points to help the student:

- understand what is required
- avoid some common errors

Answers to the chapter summary worksheets (see the textbook CD-ROM) are given at the end of each chapter of this Teacher Guide.

The answers to the practice unit tests are model answers that include all that examiners look for when awarding marks, together with some extra explanation. Each marking point is indicated by a .

Relative atomic mass values are not given in the questions, because the student is expected to use the periodic table. All Edexcel's theory exam papers have a periodic table printed on the back page. The textbook has an identical version inside the back cover.

This guide includes a CD-ROM, designed so that answers to individual questions and the explanatory comments can be cut and pasted and then issued to students after they have done their homework.

A-level examiners are instructed not to be too literal in following the mark scheme. The important point is that what has been written is correct and answers the question. There are several occasions in this Guide when different wording is used from that in the textbook, but either is equally acceptable. An example of this is:

- textbook — the bombarding electrons in a mass spectrometer have a high kinetic energy
- answer — the electrons are fast moving

Some answers are expanded to show the logic of the calculation. For instance, the conversion of 23.7 cm³ of solution to dm³ in the answer to Question 9 of the first chapter is set out as

$$23.7 \text{ cm}^3 \times \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} = 0.0237 \text{ dm}^3$$

Specific terms used in exam questions

State

This means that no explanation is required and so none should be given. However, in this Guide an explanation is often given in order to help the student understand why the answer is correct.

Name

If the name of a substance is asked for, examiners will accept either the name or the formula, but if both are given, both must be correct. The command word 'identify' is often used. The answer here can be a name or a formula. If the formula is required, only the formula and not the name will score the mark.

Molecular formula

The added up formula, such as $C_2H_4Cl_2$, is what is required. This is normally the answer to questions involving percentage composition of compounds.

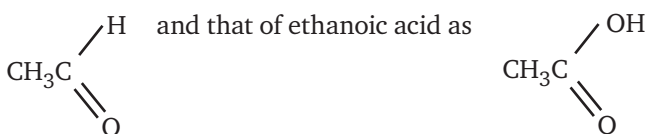
Give the formula (of an organic substance)

An unambiguous formula must be given. Butanoic acid is $CH_3CH_2CH_2COOH$ or $C_2H_5CH_2COOH$, not C_3H_7COOH , which could also be methylpropanoic acid.

Ethanal is CH_3CHO , not CH_3COH ; ethyl ethanoate is $CH_3COOC_2H_5$ or $CH_3CO_2C_2H_5$, not $CH_3OCOC_2H_5$ (ethyl ethanoate or methyl propanoate).

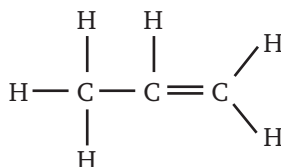
Give the structural formula

The bonding in the functional group containing a π -bond must be clearly shown. For example, the structural formula of ethene should be written as $H_2C=CH_2$, that of ethanal as



Give the full structural formula (displayed formula)

All the atoms and the bonds between them should be shown. For example, propene is:



Observations

The colour before as well as after the test must be given in the answer. For example, bromine water changes from brown to colourless, not 'is decolorised', and acidified potassium dichromate(vi) goes from orange to green, not 'goes green'.

Gas evolved is not an observation (it is a deduction). Bubbles of gas or effervescence are observations.

Hydrogen chloride is observed as misty fumes, not as a white smoke.

Preferred colours

Flame tests

Cation	Preferred colour	Acceptable colours
Lithium	Red	Carmine, deep red, magenta or crimson
Sodium	Yellow (not orange)	—
Potassium	Lilac	Mauve or purple
Calcium	Red or brick red	Orange-red
Strontium	Crimson	Red
Barium	Pale green	Apple green or yellowy-green



Indicators (alkali in the burette, acid in the conical flask)

Indicator	Starting colour	End-point colour	Not
Methyl orange	Red	Orange or peach	Yellow or pink
Phenolphthalein	Colourless	Pink	Red or purple

Indicators (acid in the burette, alkali in the conical flask)

Indicator	Starting colour	End-point colour	Not
Methyl orange	Yellow	Orange or peach	Red or pink
Phenolphthalein	Red or purple	Colourless	Clear

Significant figures

If a question asks for appropriate or a specific number of significant figures, the answer must be given to the correct number of significant figures.

Never round up to one figure, even if the answer is 5.0. The exception to this is when calculating the number of atoms or the number of molecules of water of crystallisation in a formula.

In calculations from titration data, always give the answer to three or more significant figures.

Do not round up to less than three significant figures in intermediate steps in a calculation.

Signs

Always give a + or a – sign in your answers to ΔH questions and to those on oxidation numbers.

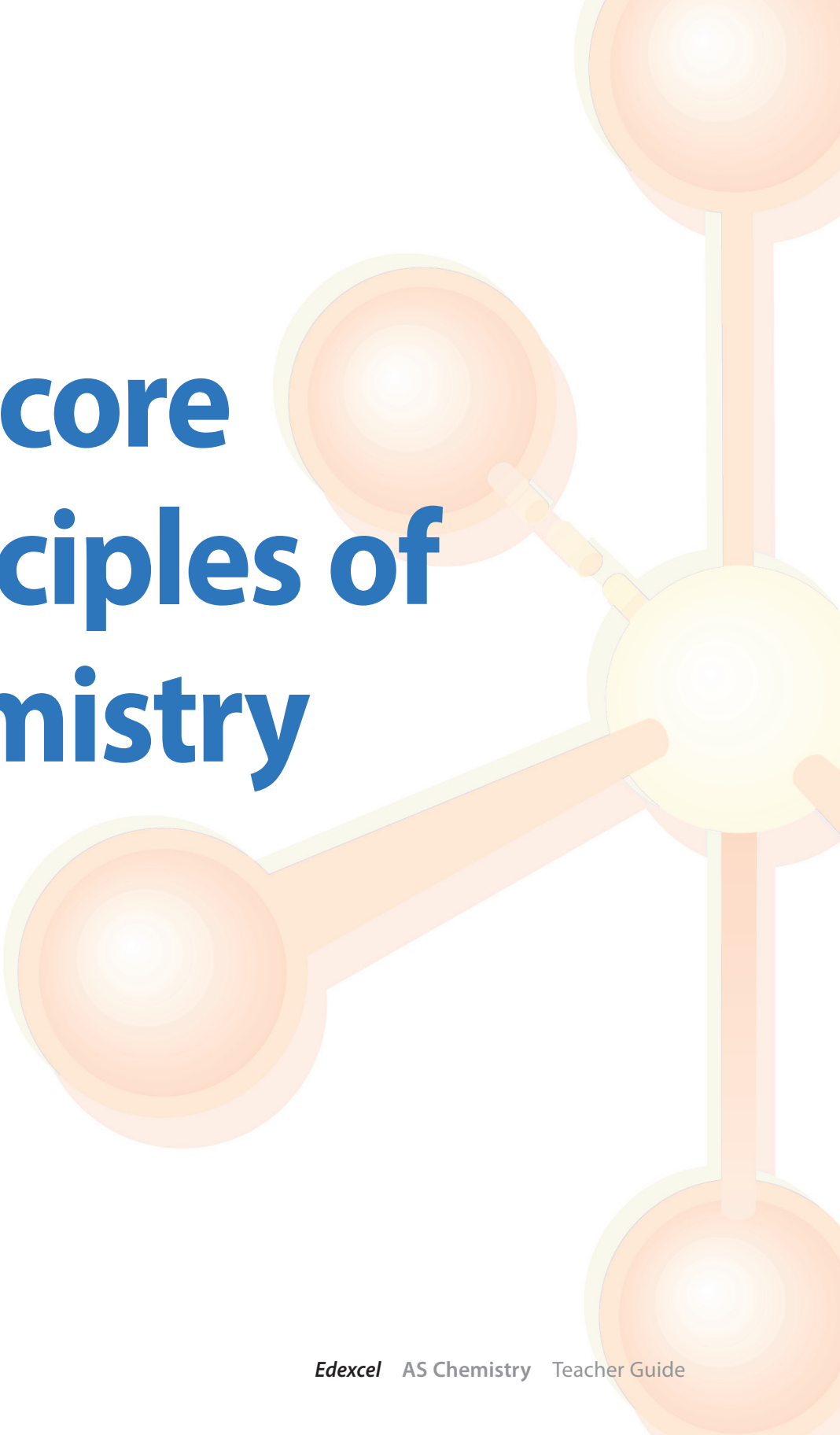
Conditions

You must state:

- the temperature range necessary or whether the substance has to be heated under reflux
- the name of the solvent
- the name of any catalyst required

Unit 1

The core principles of chemistry



1 Fundamental concepts

1 The element in group 5 and period 3 is phosphorus, P.

- e Look at the periodic table printed on the last page of an exam paper or at the back of the textbook. The group number is written at the top of the group and the period number on the left-hand side.

2 The most reactive element in group 2 is radium, Ra.

- e Metals become more reactive down a group. The metal at the bottom of group 2 is radium.

3 The only two elements that are liquids are bromine and mercury.

- e Some people think that francium is a liquid at room temperature. However, only a few francium atoms have ever been made and those underwent rapid radioactive decay, so no-one has seen enough of the element to be sure of its physical state.

4 The ion is $3+$, i.e. X^{3+} .

- e Electrons are negatively charged, so loss of electrons results in a positively charged ion. A neutral atom has the same number of positively charged protons as negatively charged electrons. When electrons are lost, there are more protons than electrons, resulting in a positively charged ion.

5 $12 \text{ kg} = 12\,000 \text{ g}$

- e There are 1000 g in 1 kg. Remember that the number of grams is always bigger than the number of kilograms.

6 $1.2 \times 10^6 \text{ g} = 1.2 \text{ tonnes}$

- e 1 tonne contains 1000 kg, and each kg weighs 1000 g, so there are 10^6 (a million) grams in 1 tonne.

7 $0.0234 \text{ g} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 23.4 \text{ mg}$

- e There are 1000 mg in 1 g, so what you have to do in this calculation is to multiply the mass in grams by the ratio 1000 mg/1 g. Note how the unit g cancels, leaving mg as the final unit.

8 $22.4 \text{ dm}^3 \times \frac{1000 \text{ cm}^3}{1 \text{ dm}^3} = 22\,400 \text{ cm}^3$

- e $1 \text{ dm}^3 = 1000 \text{ cm}^3$, so the volume in dm^3 has to be multiplied by the ratio $1000 \text{ cm}^3/1 \text{ dm}^3$.

9 $\text{volume in dm}^3 = \frac{\text{volume in cm}^3}{1000}$

so $23.7 \text{ cm}^3 = 0.0237 \text{ dm}^3$

This is the same as $23.7 \text{ cm}^3 \times \frac{1 \text{ dm}^3}{1000 \text{ cm}^3}$

- e $1000 \text{ cm}^3 = 1 \text{ dm}^3$, so the volume in cm^3 has to be divided by 1000.
The volume in dm^3 is always less than the volume in cm^3 . This type of conversion is often required in titration calculations.

10 a 1 mol of CO_2 contains 6.02×10^{23} carbon dioxide molecules. Each molecule contains three atoms, so there are $3 \times 6.02 \times 10^{23} = 1.81 \times 10^{24}$ atoms.

b 1 mol of CaCl_2 contains 1 mol of Ca^{2+} ions and 2 mol of Cl^- ions. Therefore, there are $2 \times 6.02 \times 10^{23} = 1.20 \times 10^{24}$ Cl^- ions in 1 mol of CaCl_2 .

- e The Avogadro constant, N_A ($6.02 \times 10^{23} \text{ mol}^{-1}$), is the number of molecules or groups of ions in 1 mol of the substance.



- 11 a** The ratio of N_2 to H_2 in the equation is 1:3. Therefore, 0.246 mol of H_2 react with $\frac{1}{3} \times 0.246 = 0.0820$ mol of N_2 .
- e** As with the unit conversion questions, what you are really doing is multiplying by a ratio, this time of moles. Thus to convert mol of H_2 to mol of N_2 , you multiply by the ratio 1 mol N_2 /3 mol H_2 (obtained from the equation). The unit 'mol H_2 ' cancels, leaving 'mol N_2 ' as the unit of the answer.
- $$0.246 \text{ mol H}_2 \times \frac{1 \text{ mol N}_2}{3 \text{ mol H}_2} = 0.0820 \text{ mol N}_2$$
- The data were given to three significant figures, so you should give your answer to three significant figures.
- b** The ratio of ammonia, NH_3 , to H_2 is 2:3. Therefore, 0.246 mol of H_2 produces $\frac{2}{3} \times 0.246 = 0.164$ mol of ammonia.
- e** As before, the 0.246 mol H_2 is multiplied by a ratio, this time by $\frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2}$.
- 12** The ratio of calcium hydroxide to nitric acid in the equation is 1:2. Therefore, 0.0642 mol of nitric acid react with
- $$0.0642 \text{ mol HNO}_3 \times \frac{1 \text{ mol Ca(OH)}_2}{2 \text{ mol HNO}_3} = 0.0321 \text{ mol Ca(OH)}_2$$
- 13 a** 1.202 is written to four significant figures.
- e** The zero in the middle of a number is always counted as a significant figure.
- b** 3.30 is written to three significant figures.
- e** The zero at the end of a number in decimals is always counted as a significant figure.
- c** 0.002220 is written to four significant figures.
- e** For numbers less than 1, do not count the zero before the decimal point or any that follow immediately after the decimal point.
- d** 2.34×10^{-3} is written to three significant figures.
- e** The power of 10 in scientific notation is not counted as a significant figure.
- 14 a** 2.3447 expressed to three significant figures is 2.34.
- e** Do not round from five significant figures to four and then to three significant figures. The fourth figure is a 4, which is less than 5, so the preceding digit is not altered.
- b** 0.04375 expressed to three significant figures is 0.0438.
- e** When the final digit is 5, round the preceding digit up.
- c** 4.872499 expressed to three significant figures is 4.87.
- d** 1.524×10^{-5} expressed to three significant figures is 1.52×10^{-5} .
- e** Ignore the 10^{-5} when rounding, but don't forget to put it into the answer.

2 Atomic structure and the periodic table



- 1 Relative isotopic mass refers to the relative mass of one atom of an isotope of an element. It is *not* an average. The relative atomic mass refers to the natural mixture of all the isotopes of that element, and so is a weighted average. Thus, the relative isotopic mass of chlorine-35 is the mass of one chlorine-35 atom relative to one-twelfth of the mass of a carbon-12 atom. The relative atomic mass of chlorine is the average mass of an atom of chlorine (taking into account the relative abundance of the two isotopes of chlorine) relative to one-twelfth of the mass of a carbon-12 atom.
- 2 a Isotopes have the same number of protons but a different number of neutrons. Therefore, B and D are isotopes of element number 17 (chlorine). B is a ^{35}Cl atom and D is a $^{37}\text{Cl}^+$ ion. Isotopes can be neutral (atoms) or charged (ions).
- b Atoms are neutral if the number of electrons is the same as the number of protons. Thus B and F are neutral atoms.
- e B is a ^{35}Cl atom and F is an ^{40}Ar atom.
- c Cations are positively charged ions because they have more protons than electrons. A, C and D are cations.
- e A is K^+ , C is Mg^{2+} and D is Cl^+ .
- d Anions are negatively charged ions because they have more electrons than protons. Element E (Br^-) is the only anion.
- e For atoms and ions to have the same electronic configuration, they must have the same number of electrons. Element A (K^+) and F (Ar) both have 18 electrons, arranged 2,8,8.
- 3 There are two reasons. The more important is that most elements consist of a mixture of isotopes (tin has ten naturally occurring isotopes) and so the average mass is not a whole number. The second reason is that the relative mass of an isotope is not quite a whole number. For example, the relative mass of sodium (which has only one isotope, ^{23}Na) is 22.9898. This is because protons and neutrons do not have a mass of exactly one and when they join to form a nucleus, some of their mass is changed into energy.
- 4 Let the % of ^{65}Cu be x . This means that the % of ^{63}Cu is $(100 - x)$.

$$\text{relative atomic mass} = \frac{65x + 63(100 - x)}{100} = 63.5$$

$$65x + 63(100 - x) = 6350$$

$$65x - 63x = 6350 - 6300 = 50$$

$$2x = 50$$

$$x = 25$$

The abundances of the two isotopes are $^{65}\text{Cu} = 25.0\%$ and $^{63}\text{Cu} = 75.0\%$.

- e Note that the answer is given to three significant figures, because the data in the question were given to three significant figures.

- 5 The relative atomic mass is the sum of the % of each isotope multiplied by its mass, all divided by 100.

$$\text{relative atomic mass of silicon} = \frac{(28 \times 92.2) + (29 \times 4.7) + (30 \times 3.1)}{100} = 28.1$$

- e Note that the value given on your calculator is 28.109. However, this must be changed to the one decimal place required by the question.

Always check that your answer agrees with the value given in the periodic table at the back of the exam paper, but remember that most values in the table have been rounded up to one decimal place.

- 6 Look in the periodic table for element number 13. This is aluminium. Aluminium has 13 protons and 14 neutrons and therefore has a relative mass of 27 (13 + 14). The particle in the question has three electrons fewer than the number of protons, so it has a charge of 3+. The particle is:



- 7 a The peaks in a mass spectrum are caused by positive ions. Bromine exists as Br_2 molecules and there are two isotopes of bromine, of relative masses 79 and 81. The peak at m/e 158 is caused by the $({}^{79}\text{Br}-{}^{79}\text{Br})^+$ ion, the one at 160 by the $({}^{79}\text{Br}-{}^{81}\text{Br})^+$ ion and the one at 162 by the $({}^{81}\text{Br}-{}^{81}\text{Br})^+$ ion.

- b The peaks at 158 (due to the ion containing the Br-79 isotope only) and at 162 (due to the ion containing the Br-81 isotope only) are the same height, so the relative abundance of the two isotopes must be the same.

- e Students studying statistics will know that in a 50:50 mixture of the two isotopes, the chance of a ${}^{79}\text{Br}-{}^{79}\text{Br}$ molecule is

$$\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$$

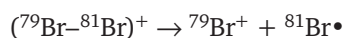
It is the same for ${}^{81}\text{Br}-{}^{81}\text{Br}$. However, the chance of a ${}^{79}\text{Br}-{}^{81}\text{Br}$ molecule is

$$2 \times \frac{1}{2} \times \frac{1}{2}$$

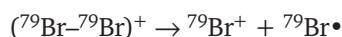
as there are two ways (head-tail and tail-head) of obtaining this species. Thus, the peak heights are

$$\frac{1}{4} : \frac{1}{2} : \frac{1}{4} \text{ or } 1:2:1$$

- c The energy of the bombardment in the mass spectrometer may cause the molecular ion to dissociate into an atom and a monatomic ion. The equation for the formation of the peak at 79 is either:



or



- e Note that the singly charged molecular ion only forms one positive ion. The other particle is a neutral free radical.

- 8 Positive ions are formed when the vaporised atom or molecule is bombarded with fast-moving electrons. The kinetic energy of these electrons is great enough to cause the removal of an electron from the outermost orbital of the atom or of one of the bonding electrons in the molecule.

- e They can also be formed by rapid laser-induced evaporation of a solution of protonated large molecules, such as pharmaceuticals.

- 9 The third shell has three types of orbitals, *s*, *p* and *d*. There are one *s*-orbital, three *p*-orbitals and five *d*-orbitals, making a total of nine orbitals.

- e Each orbital can hold two electrons, which is why the third shell can hold 18 electrons.

10 The lowest energy level is the 4s-orbital, followed in increasing order by the 4p-, 5s-, 4d-, 5p-, 6s- and 5d-orbitals.

e Remember that the d-orbitals fill 'late', after the next s-orbital has been filled.

11 Phosphorus: [Ne] 3s² 3p³

Cobalt: [Ar] 4s² 3d⁷

The answer [Ar] 3d⁷ 4s² is equally acceptable.

12 Sodium in its ground state is 1s² 2s² 2p⁶ 3s¹. In an excited state, the 3s-electron is promoted to a higher level such as the 3p level, so one answer is 1s² 2s² 2p⁶ 3p¹. Another correct answer is 1s² 2s² 2p⁶ 4s¹.

13 The boxes must show electrons with their spins ↑ or ↓.

The answer is: 3s

3p



14 Periodicity is the term used to describe a regular pattern of physical or chemical properties. An example is that the first ionisation energies reach a maximum value at regular intervals (at each noble gas).

15 Boron has a nuclear charge of +5 and the electronic configuration 2,3. Thus, it has two inner shielding electrons. Its effective nuclear charge is approximately +3 (+5 – 2). Magnesium has 12 protons in its nucleus and the electronic configuration 2,8,2. Therefore, there are ten inner shielding electrons, giving it an approximate nuclear charge of +2 (+12 – 10). Bromine has 35 protons and the electronic configuration 2,8,18,7. The nucleus is shielded by 28 inner electrons, so the approximate effective nuclear charge is +7 (+35 – 28).

Bromine has the largest effective nuclear charge and magnesium the smallest.

e Remember that the effective nuclear charge is approximately equal to the nuclear charge (number of protons) minus the number of inner (shielding) electrons.

The argument used in this answer ignores the repulsion between electrons in the outer orbit, which reduces the effective nuclear charge from that calculated.

16 Negative ions are bigger than their parent neutral atoms; positive ions are smaller. Thus the order of increasing radius is K⁺ < Cl < Cl⁻.

17 a K(g) → K⁺(g) + e⁻

b Ar(g) → Ar⁺(g) + e⁻

c Br(g) → Br⁺(g) + e⁻

e Note that all the species on the left are gaseous atoms that *lose* one electron.

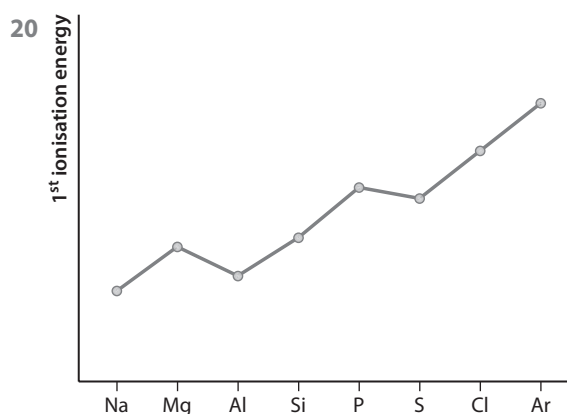
18 F⁴⁺(g) → F⁵⁺(g) + e⁻

e The fifth ionisation energy is the energy for the removal of the fifth electron, and *not* for the removal of five electrons.

19 a Mg(g) + e⁻ → Mg⁻(g)

b N(g) + e⁻ → N⁻(g)

e Note that all the species on the left are gaseous atoms that *gain* one electron.



The general trend in the first ionisation energy is upwards as the effective nuclear charge increases. Moving from sodium to argon, the nuclear charge steadily increases. However, the number of shielding electrons remains the same because these elements all have ten inner electrons.

There is a slight decrease at aluminium because the outer electron is in the $3p$ -orbital and is, therefore, at a higher energy level than the $3s$ -electrons in magnesium. Thus less energy is required to remove it.

There is another dip at sulfur. This is because the electronic configuration of sulfur is $[\text{Ne}] 3s^2 3p_x^2 3p_y^1 3p_z^1$. The two electrons in the $3p_x$ -orbital repel each other, making it slightly easier to remove one of them.

21 Helium has two electrons that are totally unshielded and so are extremely difficult to remove. Neon has ten protons in the nucleus and the $2p$ -electrons are shielded by two inner ($1s$) electrons; argon has 18 protons and the $3p$ -electrons are shielded by ten inner electrons; and lastly krypton has 36 protons with the $4p$ -electrons shielded by 28 electrons. So although the nuclear charge increases, so does the number of shielding electrons. These two effects cancel each other out.

The ionisation energy decreases from neon to krypton because the radii of the outer electron shells increase, which results in the electrons being held less firmly and, therefore, being easier to remove.

22 There is a big jump in ionisation energy between the sixth and the seventh values. The seventh electron is therefore being removed from an inner shell. Therefore, element X has six outer electrons and is in group 6 of the periodic table.



Chapter Summary Worksheet (textbook CD-ROM)

- 1 (i) The answer is C. In a group 4 element, the successive ionisation energies steadily rise from first to fourth. There is a big jump as an electron is removed from an inner shell/orbit.
- (ii) The answer is A. The general trend in a period is an increase, with slight dips at the third and sixth elements in periods 2 and 3. Answer A fits this pattern.
- (iii) The answer is D. There is always a steady decrease in first ionisation energy as a group is descended.
- 2 The answer is C. The lowest frequency means the smallest energy difference. Energy levels become closer together as the orbit number increases. Therefore, $3 \rightarrow 2$ is of lower energy than $2 \rightarrow 1$.
- 3 The answer is C. The third orbit has three types of orbital, *s*, *p* and *d*. There is just one $3s$ -orbital, but three $3p$ - and five $3d$ -orbitals, making a total of nine different orbitals in the third orbit.
- e Remember that each orbital can hold two electrons, so the third orbit can hold $2 \times 9 = 18$ electrons.
- 4 The answer is B. All four ions have the electron configuration of neon. Positive ions are smaller than isoelectronic negative ions and highly charged positive ions are smaller than cations with lower charge. (The opposite is true for negative ions.) Thus Al^{3+} is smaller than Na^+ , which is smaller than F^- ; O^{2-} is the largest of the four ions.
- 5 The answer is B. Electron affinity is the energy change for the addition of an electron to each of one mole of gaseous atoms or ions. The first electron affinity is the energy change per mole for adding one electron to a gaseous atom, here $\text{Cl}(\text{g})$, to form a gaseous ion with a single negative charge.
- 6 The answer is D. Bromine is Br_2 . There are no lines at 159 and 161, so there cannot be a ^{80}Br isotope because this would give an ion of mass 159 ($79 + 80$) and one of mass 161 ($80 + 81$). The lines in a mass spectrum are caused by positive ions, so the answer must be $(^{79}\text{Br}-^{81}\text{Br})^+$ because $79 + 81 = 160$.

3 Formulae, equations and moles

e Remember:

- Put words into your calculation so that both you and the examiner can follow the calculation through. Not only will this help you, it will enable the examiner to award 'consequential' marks, should you make an error early in the calculation.
- Check the number of significant figures for each answer. The data are almost always given to three significant figures, so the answers should also be given to three significant figures.
- Do not confuse decimal places with significant figures. For example, 0.012 is a number to three decimal places, but to two significant figures. When counting significant figures in numbers less than 1, do not count the zeros before or immediately after the decimal point.
- Putting units into the calculation acts as a check to see if you have used the correct 'formula'. For instance, if you thought that moles = mass \times molar mass, the units of amount of substance (moles) would come out as $\text{g} \times \text{g mol}^{-1}$ or $\text{g}^2 \text{mol}^{-1}$, which is absurd.
- Always think about the magnitude of your answer and see if it is reasonable. If not, check your working. When you have finished, redo the calculation on your calculator to check that you have not made a calculator error.
- If the volume of 1 mol of gas is given in dm^3 , convert gas volumes from cm^3 to dm^3 . Do this by dividing the volume in cm^3 by 1000. The dm^3 volume is smaller than the cm^3 volume.

1 The compound contains 72.6% rubidium, so oxygen makes up 27.4%.

Element	Divide by r.a.m.	Divide by smallest
Rubidium	$72.6/85.5 = 0.849$	$0.849/0.849 = 1$
Oxygen	$27.4/16.0 = 1.71$	$1.71/0.849 = 2.01 \approx 2$

The empirical formula of the compound is RbO_2 .

- e This might seem unlikely, but rubidium, like potassium, forms a superoxide of formula RbO_2 , which contains the O_2^- ion.

Make sure that you show all the steps clearly. Marks are awarded for dividing by the relative atomic mass and then by the smallest number. A common error is to divide by the atomic number instead of the atomic mass.

2

Element	Divide by r.a.m.	Divide by smallest
Carbon	$17.8/12.0 = 1.48$	$1.48/0.991 = 1.5$
Hydrogen	$3.0/1.0 = 3.0$	$3.0/0.991 = 3.0$
Bromine	$79.2/79.9 = 0.991$	$0.991/0.991 = 1.0$

The simplest whole number ratio of 1.5:3:1 is obtained by multiplying them all by 2, i.e. 3:6:2. The empirical formula is $\text{C}_3\text{H}_6\text{Br}_2$.

- e After division by the smallest number, you should round the values to 1 decimal place. If the ratio is not a whole number ratio, try to obtain integers by multiplying all the numbers by 2. If that fails, multiply by 3.

3 a

Element	Divide by r.a.m.	Divide by smallest
Carbon	$36.4/12.0 = 3.03$	$3.03/3.03 = 1$
Hydrogen	$6.1/1.0 = 6.1$	$6.1/3.03 = 2$
Fluorine	$57.5/19.0 = 3.03$	$3.03/3.03 = 1$

The empirical formula is CH_2F .

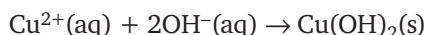
- b The mass of the empirical formula is $(12.0 + 2.0 + 19.0) = 33.0$. This is half the molar mass, so the molecular formula is $\text{C}_2\text{H}_4\text{F}_2$.



- e** To find the molecular formula, multiply the empirical formula by the ratio of molar mass divided by empirical mass. In this example it is $66.0/33.0$, which equals 2.
- 4 a** Calcium ions are $2+$ and chloride ions are $1-$, so the formula is CaCl_2 .
- b** Silver ions are $1+$ and nitrate ions are $1-$, so the formula is AgNO_3 .
- c** Copper(II) is Cu^{2+} and phosphate is PO_4^{3-} . For a neutral compound you need three copper ions and two phosphate ions, making charges of $+6$ and -6 . Therefore, the formula is $\text{Cu}_3(\text{PO}_4)_2$.
- d** Aluminium is $3+$ and oxide is $2-$, so aluminium oxide is Al_2O_3 .
- e** There are two ways of working out formulae of ionic compounds. One way is to make sure that the total positive charge equals the total negative charge (see part c). The other way, if the charges are not the same, is to swap them round. Copper is $2+$ and phosphate $3-$, so there are three copper ions and two phosphate ions in the formula.
- 5 a** As there is one manganese ion to each carbonate ion, the charges have the same numerical value. Carbonate ions are $2-$, so the manganese ions in this compound must be $2+$.
- b** The charge on two vanadium ions must equal the charge on three sulfate ions. Each sulfate is -2 , so three sulfate ions have a total charge of -6 . This means that two vanadium ions have a total charge of $+6$, so each has a charge of $+3$.
- 6 a** molar mass of $\text{Ca}(\text{OH})_2 = 40.1 + 2 \times (16.0 + 1.0) = 74.1 \text{ g mol}^{-1}$
- b** molar mass of $\text{Al}_2(\text{SO}_4)_3 = (2 \times 27.0) + 3 \times [32.1 + (4 \times 16.0)] = 342.3 \text{ g mol}^{-1}$
- c** molar mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 55.8 + 32.1 + (4 \times 16.0) + 7 \times (2.0 + 16.0) = 277.9 \text{ g mol}^{-1}$
- e** In calculating molar mass, make sure that you use the relative atomic masses (the larger numbers), not the atomic numbers, from the periodic table. Molar mass has the units of g mol^{-1} . Relative molecular mass has no units. The numbers are the same.
- 7** The balanced equations are:
- a** $\text{P}_4 + 5\text{O}_2 \rightarrow \text{P}_4\text{O}_{10}$ or $2\text{P}_2\text{O}_5$
- e** Phosphorus(V) oxide exists as the dimer P_4O_{10} , but $2\text{P}_2\text{O}_5$ on the right of the equation would be acceptable.
- b** $4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$
- c** $2\text{Mg}(\text{NO}_3)_2 \rightarrow 2\text{MgO} + 4\text{NO}_2 + \text{O}_2$
- e** In part c, balance the oxygen atoms last. Remember that the number of oxygen atoms on the right-hand side of the equation must be an even number, because $\text{Mg}(\text{NO}_3)_2$ contains an even number of oxygen atoms.
- d** $2\text{LiOH} + \text{H}_2\text{SO}_4 \rightarrow \text{Li}_2\text{SO}_4 + 2\text{H}_2\text{O}$
- e** $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$
- e** Make sure that this equation balances for charge. Having one Fe^{3+} ion on the left-hand side and one Fe^{2+} on the right-hand side balances the number of Fe ions, but the charge on the left would not equal the charge on the right.
- f** $2\text{C}_8\text{H}_{18} + 25\text{O}_2 \rightarrow 16\text{CO}_2 + 18\text{H}_2\text{O}$ or $\text{C}_8\text{H}_{18} + 12\frac{1}{2}\text{O}_2 \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O}$
- e** The only source of oxygen on the left-hand side of the equation is O_2 , so the number of oxygen atoms on the right-hand side must be an even number. Therefore, there must be an even number of H_2O molecules on the right. This requires two C_8H_{18} molecules on the left.
- 8** For equations a–c, the simplest way is to realise that the component ions of the compound combine to give the precipitate. All other ions are spectators.

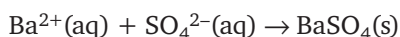


- a The precipitate is $\text{Cu}(\text{OH})_2$, so the ionic equation is:

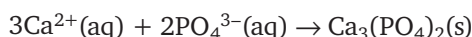


- e Do not forget state symbols in all ionic equations.

- b The precipitate is BaSO_4 , so the ionic equation is:

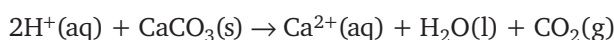


- c The precipitate is $\text{Ca}_3(\text{PO}_4)_2$, so the ionic equation is:

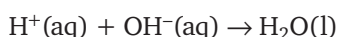


- d Aqueous solutions of strong acids are totally ionised, so when they react as acids, the ionic equation contains $\text{H}^+(\text{aq})$. Solids, even if ionic, must be written in full.

The ionic equation is:



- e Aqueous alkalis are fully ionised, so in neutralisation reactions $\text{OH}^{-}(\text{aq})$ ions are in the equation. The reaction is between H^+ and OH^{-} ions and the ionic equation is:



- 9 For solids:

$$\text{moles} = \frac{\text{mass}}{\text{molar mass}}$$

a amount of $\text{CaCO}_3 = \frac{1.11 \text{ g}}{[40.1 + 12.0 + (3 \times 16.0)] \text{ g mol}^{-1}} = 0.0111 \text{ mol}$

b amount of $\text{Ba}(\text{OH})_2 = \frac{2.22 \text{ g}}{[137.3 + 2 \times (16.0 + 1.0)] \text{ g mol}^{-1}} = 0.130 \text{ mol}$

- e Make sure that you give your answer to the correct number of significant figures. Here, the data in the question are given to three significant figures, so the answer is also given to three significant figures.

- 10 mass = moles \times molar mass

a mass of 0.0100 mol $\text{H}_2\text{SO}_4 = 0.0100 \text{ mol} \times [2.0 + 32.1 + (4 \times 16.0)] \text{ g mol}^{-1} = 0.981 \text{ g}$

b mass of 100 mol Na = $100 \text{ mol} \times 23.0 \text{ g mol}^{-1} = 2300 \text{ g}$

11 molar mass of the hydrated salt = $\frac{\text{mass}}{\text{moles}} = \frac{4.56 \text{ g}}{0.0185 \text{ mol}} = 246 \text{ g mol}^{-1}$

MgSO_4 contributes $[24.3 + 32.1 + (4 \times 16.0)] = 120.4 \text{ g mol}^{-1}$;
therefore, $246 - 120.4 = 125.6 \text{ g mol}^{-1}$ is due to x moles of water:

$$x(2.0 + 16.0) = 125.6$$

$$x = \frac{125.6}{18.0} = 6.98$$

The number of molecules of water of crystallisation must be a whole number, so hydrated magnesium sulfate contains seven molecules of water of crystallisation.

12 a moles of water = $\frac{\text{mass}}{\text{molar mass}} = \frac{1.2 \text{ g}}{18.0 \text{ g mol}^{-1}} = 0.0667 \text{ mol}$

$$\text{number of molecules} = 0.0667 \text{ mol} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 4.0 \times 10^{22}$$

- e Note that the mass data were given to two significant figures.



b molecules of water in 1.2 mol = $1.2 \text{ mol} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 7.2 \times 10^{23}$

e The number of molecules is the number of moles multiplied by Avogadro's constant, which is $6.02 \times 10^{23} \text{ mol}^{-1}$. Therefore, to calculate the number of molecules, masses have first to be converted into moles.

13 number of molecules in 0.0100 mol $\text{CO}_2 = 0.0100 \times 6.02 \times 10^{23} = 6.02 \times 10^{21}$

There are two oxygen atoms in each molecule of CO_2 , so:

number of oxygen atoms in 0.0100 mol $\text{CO}_2 = 2 \times 6.02 \times 10^{21} = 1.20 \times 10^{22}$

14 moles of $\text{Ba}(\text{OH})_2 = \frac{\text{mass}}{\text{molar mass}} = \frac{10.0 \text{ g}}{(137.3 + 34.0) \text{ g mol}^{-1}} = 0.05838 \text{ mol}$

There are two OH^- ions per formula unit of $\text{Ba}(\text{OH})_2$, so:

number of hydroxide ions = $2 \times 0.05838 \times 6.02 \times 10^{23} = 7.03 \times 10^{22}$

e Remember that the number of atoms, molecules or ions is always a huge number, usually around 10^{23} . The number of moles is usually less than 1.



Chapter Summary Worksheet (textbook CD-ROM)

1 The answer is B. Aluminium has a valency of three (Al^{3+}) and chlorine has a valency of 1 (Cl^-). Swapping the valencies gives the formula AlCl_3 .

2 The answer is D. $M_r = (1 \times \text{Ca}) + (2 \times \text{O}) + (2 \times \text{H}) = 40.1 + 32.0 + 2.0 = 74.1 \approx 74 \text{ g mol}^{-1}$.

e You must not use atomic numbers ($\text{Ca} = 20$, $\text{O} = 8$ and $\text{H} = 1$).

3 The answer is D.

$$M_r = (2 \times \text{Na}) + (1 \times \text{C}) + (3 \times \text{O}) + (10 \times \text{H}_2\text{O}) = 46.0 + 12.0 + 48.0 + (10 \times 18.0) = 286.0 \text{ g mol}^{-1}$$

4 The answer is B. Phosphorus(v) has a valency of 5 and oxygen a valency of 2. Swapping over the valencies gives the formula P_2O_5 .

e Phosphorus pentachloride exists as the dimer P_4O_{10} but the formula P_2O_5 is also acceptable.

5 The answer is C. Equation A balances for atoms (three calcium atoms and two phosphate groups on each side). It also balances for charge: left-hand side has $6+$ and $6-$ charges, which is neutral, as is the right-hand side.

Equation B has two lead, four nitrogen and twelve oxygen atoms on each side, so it balances.

Equation C balances for atoms, but not for charge. The charges on the left-hand side are $3+$ and $2+ = 5+$. On the right-hand side they are $2+$ and $4+ = 6+$.

e Beware. This is an example of a negative question — 'does *not* balance'. The answer that is chemically *wrong* is, therefore, the correct response. You will find several questions of this type in your A-level exams.

6 The answer is A.

$$\text{moles} = \text{concentration} \times \text{volume in dm}^3 = 0.10 \text{ mol dm}^{-3} \times 25/1000 \text{ dm}^3 = 0.0025 \text{ mol}$$

e Remember that you have to divide by 1000 to convert a volume in cm^3 to one in dm^3 . The fact that there are 2NaOH in the equation is irrelevant.

4 Calculations from chemical equations

e Remember:

- Put words into your calculation so that both you and the examiner can follow the calculation through. Not only will this help you, it will enable the examiner to award 'consequential' marks, should you make an error early in the calculation.
- Check the number of significant figures for each answer. The data are almost always given to three significant figures, so the answers should also be given to three significant figures.
- Do not confuse decimal places with significant figures. For example, 0.012 is a number to three decimal places, but to two significant figures. When counting significant figures in numbers less than 1, do not count the zeros before or immediately after the decimal point.
- Putting units into the calculation acts as a check to see if you have used the correct 'formula'. For instance, if you thought that moles = mass \times molar mass, the units of amount of substance (moles) would come out as $\text{g} \times \text{g mol}^{-1}$ or $\text{g}^2 \text{mol}^{-1}$, which is absurd.
- Always think about the magnitude of your answer and see if it is reasonable. If not, check your working. When you have finished, redo the calculation on your calculator to check that you have not made a calculator error.
- If the volume of 1 mol of gas is given in dm^3 , convert gas volumes from cm^3 to dm^3 . Do this by dividing the volume in cm^3 by 1000. The dm^3 volume is smaller than the cm^3 volume.
- Convert solution volumes in cm^3 to volumes in dm^3 before multiplying by the concentration. The volume in dm^3 equals the volume in cm^3 divided by 1000.

$$1 \text{ molar mass of Fe}_2(\text{SO}_4)_3 = (2 \times 55.8) + 3 \times [32.1 + (4 \times 16.0)] = 399.9 \text{ g mol}^{-1}$$

$$\text{molar mass of Fe(OH)}_3 = 55.8 + (3 \times 17.0) = 106.8 \text{ g mol}^{-1}$$

$$\text{amount of Fe}_2(\text{SO}_4)_3 \text{ (in moles)} = \frac{\text{mass}}{\text{molar mass}} = \frac{12.7 \text{ g}}{399.9 \text{ g mol}^{-1}} = 0.03176 \text{ mol}$$

$$\begin{aligned} \text{moles Fe(OH)}_3 &= \text{moles Fe}_2(\text{SO}_4)_3 \times \frac{\text{number of Fe(OH)}_3 \text{ in equation}}{\text{number of Fe}_2(\text{SO}_4)_3 \text{ in equation}} \\ &= 0.03176 \text{ mol} \times 2 = 0.06352 \text{ mol} \end{aligned}$$

$$\text{mass of Fe(OH)}_3 = \text{moles} \times \text{molar mass} = 0.06352 \text{ mol} \times 106.8 \text{ g mol}^{-1} = 6.78 \text{ g}$$

- e** It is a good idea to work out the molar masses of the two substances involved before starting the rest of the calculation.

$$2 \text{ molar mass of AgNO}_3 = 107.9 + 14.0 + (3 \times 16.0) = 169.9 \text{ g mol}^{-1}$$

$$\text{amount (in moles) of AgNO}_3 = \frac{\text{mass}}{\text{molar mass}} = \frac{12.6 \text{ g}}{169.9 \text{ g mol}^{-1}} = 0.07416 \text{ mol}$$

$$\text{ratio of Cu:AgNO}_3 = 1:2$$

$$\text{so, amount of copper} = \frac{1}{2} \times 0.07416 = 0.03708 \text{ mol}$$

$$\begin{aligned} \text{mass of copper needed} &= \text{moles} \times \text{molar mass} \\ &= 0.03708 \text{ mol} \times 63.5 \text{ g mol}^{-1} = 2.35 \text{ g} \end{aligned}$$

- e** The answer 2.35 g was obtained keeping all the numbers on the calculator during the calculation. If the rounded up value of 0.0371 mol is used, the answer 2.36 g is obtained. Either would score full marks.

A common error is to calculate the molar mass of AgNO_3 as $2 \times 170 \text{ g mol}^{-1}$ because there are 2 moles of it in the equation. This is wrong. The number of moles of a substance depends only on its mass and *not* on the reaction. The stoichiometry comes into play when moles of one substance are converted to moles of another substance. This type of calculation can be done either by mass ratio or by converting

to moles, then using the reaction stoichiometry and finally converting back to mass. The second method fits all types of calculation, so is the better one to use.

$$3 \text{ molar mass of NaNO}_3 = 23.0 + 14.0 + (3 \times 16.0) = 85.0 \text{ g mol}^{-1}$$

$$\text{amount of NaNO}_3 = \frac{\text{mass}}{\text{molar mass}} = \frac{33.3 \text{ g}}{85.0 \text{ g mol}^{-1}} = 0.392 \text{ mol}$$

$$\text{ratio of O}_2:\text{NaNO}_3 = 1:2$$

$$\text{so, amount of oxygen} = \frac{1}{2} \times 0.392 = 0.196 \text{ mol}$$

$$\begin{aligned} \text{volume of oxygen} &= \text{moles} \times \text{molar volume} \\ &= 0.196 \text{ mol} \times 25.0 \text{ dm}^3 \text{ mol}^{-1} \\ &= 4.90 \text{ dm}^3 \end{aligned}$$

$$4 \text{ amount (moles) of hydrogen, H}_2 = \frac{\text{mass}}{\text{molar mass}} = \frac{3000 \text{ g}}{2.0 \text{ g mol}^{-1}} = 1500 \text{ mol}$$

$$\text{ratio of NH}_3:\text{H}_2 = 2:3$$

$$\text{so, theoretical amount (moles) of ammonia produced} = \frac{2}{3} \times 1500 = 1000 \text{ mol}$$

$$\begin{aligned} \text{theoretical yield (mass) of NH}_3 &= \text{moles} \times \text{molar mass} \\ &= 1000 \text{ mol} \times 17 \text{ g mol}^{-1} \\ &= 17\,000 \text{ g} \end{aligned}$$

$$\text{percentage yield} = \frac{\text{actual yield of product} \times 100}{\text{theoretical yield of product}} = \frac{2550 \text{ g} \times 100}{17\,000 \text{ g}} = 15.0\%$$

- e When calculating the percentage yield, the yields can be expressed in moles or in mass units. Calculating both yields in moles gives:

$$\text{actual amount (moles) of NH}_3 = \frac{2550 \text{ g}}{17.0 \text{ g mol}^{-1}} = 150 \text{ mol}$$

$$\text{so, percentage yield} = \frac{150 \text{ mol} \times 100}{1000 \text{ mol}} = 15.0\%$$

$$\text{The percentage yield is not } \frac{\text{mass of product} \times 100}{\text{mass of reactant}}.$$

$$5 \text{ amount (in moles)} = \text{concentration} \times \text{volume}$$

$$= 0.0545 \text{ mol dm}^{-3} \times \frac{23.4}{1000} \text{ dm}^3 = 0.00128 \text{ mol}$$

- e Be careful about units. The concentration is in mol dm⁻³, but the volume is in cm³. The volume in cm³ must be divided by 1000 to convert it into a volume in dm³.

$$6 \text{ volume} = \frac{\text{moles}}{\text{concentration}} = \frac{0.00164 \text{ mol}}{0.106 \text{ mol dm}^{-3}} = 0.0155 \text{ dm}^3 = 15.5 \text{ cm}^3$$

- e Volumes of solutions less than 1 dm³ are usually expressed in cm³.

$$7 \text{ amount (moles) of H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \text{concentration} \times \text{volume}$$

$$= 0.0500 \text{ mol dm}^{-3} \times \frac{500}{1000} \text{ dm}^3 = 0.0250 \text{ mol}$$

$$\text{molar mass of H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = 2.0 + (2 \times 12.0) + (4 \times 16.0) + (2 \times 18.0) = 126.0 \text{ g mol}^{-1}$$

$$\begin{aligned} \text{mass of hydrated ethanedioic acid needed} &= \text{moles} \times \text{molar mass} \\ &= 0.0250 \text{ mol} \times 126.0 \text{ g mol}^{-1} = 3.15 \text{ g} \end{aligned}$$



$$8 \text{ a amount (moles) of Fe} = \frac{\text{mass}}{\text{molar mass}} = \frac{4.50 \text{ g}}{55.8 \text{ g mol}^{-1}} = 0.0806 \text{ mol}$$

$$\begin{aligned} \text{amount of copper(II) sulfate} &= \text{concentration} \times \text{volume in dm}^3 \\ &= 2.00 \text{ mol dm}^{-3} \times 0.0500 \text{ dm}^3 = 0.100 \text{ mol} \end{aligned}$$

As 0.100 is greater than 0.0806, iron is the limiting reagent.

e As the substances react in a 1:1 ratio, the one with fewer moles is the limiting reagent.

b ratio of Cu to Fe in the equation = 1:1

so, amount (moles) of copper = amount of iron = 0.0806 mol

$$\text{mass of copper} = \text{moles} \times \text{molar mass} = 0.0806 \text{ mol} \times 63.5 \text{ g mol}^{-1} = 5.12 \text{ g}$$

c Copper sulfate is in excess, so the solution will still be blue.

e If copper sulfate had been the limiting reagent, the solution would be colourless at the end of the reaction.



e The stoichiometric ratio is not 1:1, so the amount of sodium sulfate that would be produced from both sodium hydroxide and sulfuric acid reacting completely has to be calculated. The limiting reagent is the one that gives the smaller amount of product.

b molar mass of sodium hydroxide = 23.0 + 16.0 + 1.0 = 40.0 g mol⁻¹

$$\text{amount (moles) of NaOH} = \frac{\text{mass}}{\text{molar mass}} = \frac{21.5 \text{ g}}{40.0 \text{ g mol}^{-1}} = 0.5375 \text{ mol}$$

$$\begin{aligned} \text{amount (moles) of Na}_2\text{SO}_4 \text{ that would be produced if NaOH were the limiting reagent} \\ = \frac{1}{2} \times 0.5375 = 0.269 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{amount (moles) of H}_2\text{SO}_4 &= \text{concentration} \times \text{volume in dm}^3 \\ &= 1.00 \text{ mol dm}^{-3} \times 0.500 \text{ dm}^3 = 0.500 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{amount (moles) of Na}_2\text{SO}_4 \text{ that would be produced if H}_2\text{SO}_4 \text{ were the limiting reagent} \\ = 0.500 \text{ mol, which is more than 0.269 mol from NaOH} \end{aligned}$$

Therefore, sodium hydroxide is the limiting reagent.

c molar mass of Na₂SO₄ = (2 × 23.0) + 32.1 + (4 × 16.0) = 142.1 g mol⁻¹

$$\begin{aligned} \text{mass of sodium sulfate produced} &= \text{moles} \times \text{molar mass} \\ &= 0.269 \text{ mol} \times 142.1 \text{ g mol}^{-1} = 38.2 \text{ g} \end{aligned}$$

d Sodium hydroxide is the limiting reagent, so there will be an excess of sulfuric acid. Therefore, red litmus will stay red and blue litmus will turn red.

e Even though there are more moles of sodium hydroxide than sulfuric acid, the sodium hydroxide is the limiting reagent because 2 moles of it are needed for every mole of sulfuric acid.



Chapter Summary Worksheet (textbook CD-ROM)

1 The answer is D. There are two ways of calculating the answer:

$$\text{amount (moles) Mg} = \frac{6.075}{24.3} = 0.25 = \text{moles MgCl}_2$$

$$\text{mass of MgCl}_2 = 0.25 \text{ mol} \times \text{molar mass} = 0.25 \times 95.3 = 23.825 \text{ g}$$

or

$$24.3 \text{ g of Mg produces } 95.3 \text{ g of MgCl}_2$$

$$\text{so } 6.075 \text{ g produces } 95.3 \times \frac{6.075}{24.3} = 23.825 \text{ g of MgCl}_2$$

e Option A used some atomic numbers rather than atomic masses. The formula for magnesium chloride is MgCl_2 — option B used MgCl and C used Mg_2Cl .

2 The answer is D.

$$\text{amount (moles)} = \frac{\text{mass}}{\text{molar mass}} = 0.0250$$

there are 5 ions per formula, so there are $5 \times 0.025 = 0.125 \text{ mol}$ of ions

$$\text{number of ions} = 0.125 \times 6.02 \times 10^{23} = 7.53 \times 10^{22}$$

e Option A is the number of moles, B is the moles of ions and C is the number of 'molecules' or ion groups.

3 The answer is A.

$$\begin{aligned} \text{amount (moles) of rubidium} &= \frac{\text{mass}}{\text{atomic mass}} \\ &= \frac{8.55 \text{ g}}{85.5 \text{ g mol}^{-1}} = 0.100 \text{ mol} \end{aligned}$$

$$\text{mass of } 0.100 \text{ mol of RbO}_2 = 0.100 \text{ mol} \times 117.5 \text{ g mol}^{-1} = 11.75 \text{ g}$$

so A is the correct answer

4 The answer is B.

$$\begin{aligned} \text{amount (moles) of CuO} &= \frac{\text{mass}}{\text{molar mass}} \\ &= \frac{7.95 \text{ g}}{79.5 \text{ g mol}^{-1}} = 0.100 \text{ mol} \end{aligned}$$

theoretical yield = $0.100 \text{ mol} \times \text{molar mass of hydrated copper sulfate}$

$$= 0.1 \times 249.6 = 24.96 \text{ g}$$

$$\text{percentage yield} = \frac{\text{actual yield of product}}{\text{theoretical yield of product}} \times 100$$

$$= \frac{23.0 \times 100}{24.96} = 92.1 = 92\% \text{ to two significant figures}$$

so B is the correct answer.

5 The answer is B.

$$\begin{aligned} \text{amount (moles) of Al} &= \frac{\text{mass}}{\text{atomic mass}} \\ &= \frac{1.076 \text{ g}}{27.0 \text{ g mol}^{-1}} = 0.03985 \text{ mol} \end{aligned}$$

$$\text{amount (moles) of hydrogen} = \frac{3}{2} \times 0.03985 = 0.05978 \text{ mol}$$

$$\text{so volume} = 0.05978 \times 24.0 = 1.43 \text{ dm}^3$$

5 Energetics

1 heat change, $Q = \text{mass} \times \text{specific heat capacity} \times \text{change in temperature}$

$$Q = 50.0 \text{ g} \times 0.450 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1} \times (100 - 21.0)^\circ\text{C} = 1778 \text{ J} = 1.78 \text{ kJ}$$

- e The specific heat capacity is measured in joules, so the calculation gives a heat change in joules. It is usual to give the answer in kilojoules, so the value 1778 is divided by 1000. The data were given to three significant figures, so the answer should also be given to three significant figures.

2 heat change, $Q = \text{mass} \times \text{specific heat capacity} \times \text{change in temperature}$

$$Q = 9.45 \times 1000 \text{ J} = 100 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1} \times \Delta T$$

$$\Delta T = \frac{9450 \text{ J}}{100 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1}} = 22.6^\circ\text{C}$$

$$\text{final temperature} = 18.2^\circ\text{C} + 22.6^\circ\text{C} = 40.8^\circ\text{C}$$

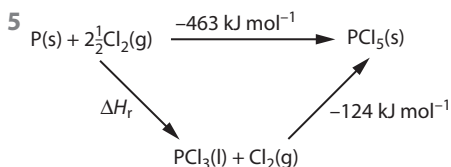
- e Don't forget to convert the heat energy in kilojoules into joules.



4 a $\text{C}_4\text{H}_{10}(\text{g}) + 6\frac{1}{2}\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l})$

- e The equation must only have 1 mol of butane, because enthalpies of combustion are defined per mole of substance burnt. It is a thermochemical equation, so state symbols must be included. Water is a liquid at 298 K and 1 atm pressure.

b $4\text{C}(\text{s}) + 5\text{H}_2(\text{g}) \rightarrow \text{C}_4\text{H}_{10}(\text{g})$



$$\Delta H_r + (-124) = -463$$

$$\Delta H_r = -463 + 124 = -339 \text{ kJ mol}^{-1}$$

- e Remember to label the cycle with ΔH values.

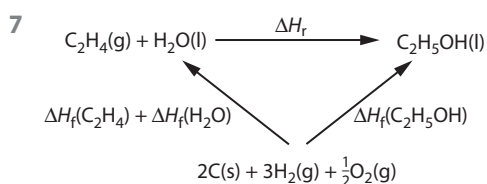
6 Enthalpy of **formation** data are given, so it is correct to use the expression:

$$\Delta H_r = \sum n\Delta H_f (\text{products}) - \sum n\Delta H_f (\text{reactants})$$

where n is the number of moles of each substance in the equation.

$$\Delta H_r = \{(2 \times -111) + (3 \times -286)\} - (-84.7) = -995 \text{ kJ mol}^{-1}$$

- e The enthalpy of formation of oxygen gas is zero.

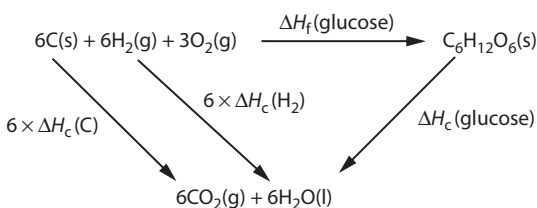
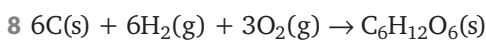


- e Always label a Hess's law diagram with either ΔH or the values of ΔH .

$$\begin{aligned}
 \Delta H_f(\text{C}_2\text{H}_4) + \Delta H_f(\text{H}_2\text{O}) + \Delta H_r &= \Delta H_f(\text{C}_2\text{H}_5\text{OH}) \\
 +52.3 + (-286) + \Delta H_r &= -278 \\
 \Delta H_r &= -278 - 52.3 + 286 \\
 &= -44.3 \text{ kJ mol}^{-1}
 \end{aligned}$$

- e You can check your answer by using $\Delta H_r = \sum n\Delta H_f(\text{products}) - \sum n\Delta H_f(\text{reactants})$:

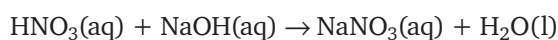
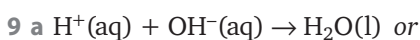
$$\Delta H_r = (-278) - (-286 + 52.3) = -44.3 \text{ kJ mol}^{-1}$$



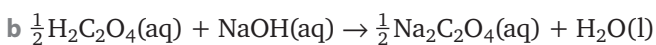
By Hess's law:

$$\begin{aligned}
 \Delta H_f(\text{glucose}) &= [6 \times \Delta H_c(\text{C})] + [6 \times \Delta H_c(\text{H}_2)] - \Delta H_c(\text{glucose}) \\
 \Delta H_f(\text{glucose}) &= [6 \times (-393.5)] + [6 \times (-285.8)] - (-2816) = -1260 \text{ kJ mol}^{-1}
 \end{aligned}$$

- e A Hess's law diagram has to be drawn because the calculation cannot be carried out using the formula, $\Delta H_r = \Delta H(\text{products}) - \Delta H(\text{reactants})$.

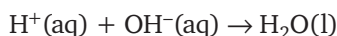


- e Nitric acid is a strong acid and is therefore totally ionised. This means that the ionic equation for neutralisation can be given as the answer.



- e Ethanedioic acid is a weak acid, so an ionic equation should not be written. The definition of enthalpy of neutralisation is per mole of water produced and not per mole of acid. Thus, $\frac{1}{2}\text{H}_2\text{C}_2\text{O}_4$ is used in the equation.

10 Strong acids are totally ionised in dilute solution, so whatever the acid, the reaction is always:



Thus the enthalpy of neutralisation always has approximately the same value.

- e In practice, enthalpies of neutralisation of strong acids are not *exactly* the same because of the different enthalpies of solution of the salts formed.

11 The C=C and the H-Br bonds are broken (endothermic) and new C-C, C-H and C-Br bonds are formed (exothermic).

Bonds broken/kJ mol ⁻¹		Bonds formed/kJ mol ⁻¹	
C=C	+612	C-C	-348
H-Br	+366	C-H	-413
		C-Br	-276
Total	+978		-1037

$$\Delta H_r = +978 - 1037 = -59 \text{ kJ mol}^{-1}$$

- e There is no need to break all the bonds in propene and then make them again. Think about which bonds break in the reaction and which are made. Bond breaking is always endothermic and bond making always exothermic.

12 The C=C and the Cl-Cl bonds are broken (endothermic) and C-C and two C-Cl bonds are made (exothermic).

Bonds broken/kJ mol ⁻¹		Bonds formed/kJ mol ⁻¹	
C=C	+612	C-C	-348
Cl-Cl	+242	2 × C-Cl	-ΔH _B × 2

$$\Delta H_r = -217.4 = +612 + 242 + (-348) + [2 \times (-\Delta H_B)]$$

$$2 \times \Delta H_B = +612 + 242 - 348 + 217.4 = +723.4 \text{ kJ}$$

$$\text{C-Cl bond enthalpy, } \Delta H_B = \frac{1}{2} \times (+723.4) = +362 \text{ kJ mol}^{-1}$$

- e The C-H bond enthalpy is given in the data in case you want to break all the bonds in the molecule and then remake all the bonds. In this way of calculating the answer, four C-H bonds would be broken and then remade.

13 Procedure:

- Weigh out 16 g (0.1 mol) of anhydrous copper sulfate.
 - Pour 100 cm³ of distilled water into an expanded polystyrene cup.
 - Place the cup firmly in an empty beaker and measure the temperature to 0.2°C every 30 seconds for 3 minutes.
 - On the fourth minute, add the copper sulfate and stir with a glass rod.
 - Measure the temperature every 30 seconds until the temperature stops rising and then for another 3 minutes.
- e A good way to write plans is to use bullet points. This stops the answer from becoming a rambling account from which important points might be omitted.

Calculation:

- Plot the points on a piece of graph paper with the temperature on the y-axis.
- Draw a smooth line using the readings for the first 3 minutes and another line for the last 3 minutes.
- Extrapolate these lines back to the 4-minute point.
- Measure the temperature difference between these two lines at the 4-minute point (the time when the copper sulfate was added). This is the corrected temperature change, ΔT.

$$\text{heat change, } Q = \text{mass of solution} \times \text{specific heat capacity of solution} \times \Delta T$$

- e This is often written as $mc\Delta T$.

$$\Delta H = \frac{-Q}{\text{moles of copper sulfate taken}}$$

ΔH is negative if the temperature rises (an exothermic reaction) or positive if the temperature falls (an endothermic reaction).



It is assumed that:

- no heat is lost to the surroundings
- the density of the solution is 1 g cm^{-3}
- the specific heat capacity of the solution is approximately the same as for water ($4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$)
- there would be no further heat change on diluting the solution

14 ΔH for this reaction cannot be measured directly because too much heat is required to decompose calcium carbonate. The clue is in the substances that the question allows you to use to plan an indirect route:

calcium carbonate + acid \rightarrow calcium chloride + water + carbon dioxide

calcium chloride + water \rightarrow calcium oxide + acid



On adding these two equations, the equation in the question is obtained:



$$\text{so } \Delta H = \Delta H_1 + \Delta H_2$$

ΔH_1 is the heat change for the reaction of calcium carbonate with hydrochloric acid; $-\Delta H_2$ is the heat change for the reaction of calcium oxide with hydrochloric acid. If ΔH_1 and ΔH_2 are found by experiment, ΔH for the reaction can be calculated.

To find ΔH_1 :

- Weigh out a known amount of calcium carbonate — for example, about 5 g.
- Place 100 cm^3 of 2.0 mol dm^{-3} hydrochloric acid (an excess) in a polystyrene cup supported in a beaker.
- Measure the temperature of the acid every 30 s for 3 minutes.
- At 3.5 minutes, add the calcium carbonate slowly, making sure that none fizzes over.
- When all the calcium carbonate has been added, measure the temperature every 30 s until the temperature stops rising and then for a further 3 minutes.
- Plot a graph of temperature against time. Draw straight lines through the points up to 3 minutes and another line for the last 3 minutes. Extrapolate these lines back to the 3.5-minute point and measure the difference in temperature of the two points at 3.5 minutes.

$$\Delta H_1 = \frac{-(100 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1} \times \Delta T)}{\text{moles of CaCO}_3}$$

- Repeat for the reaction between calcium oxide and hydrochloric acid.

$$-\Delta H_2 = \frac{-(100 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1} \times \Delta T)}{\text{moles of CaO}}$$

- $\Delta H_r = \Delta H_1 + \Delta H_2$
- ⓔ Beware of signs. Both reactions are exothermic, so their ΔH values are negative. To obtain ΔH_2 , the equation for the second reaction has to be reversed.

15 a heat change, $Q = \text{mass} \times \text{specific heat capacity} \times \text{change in temperature}$

$$Q = 80.0 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1} \times (24.9 - 18.5)^\circ\text{C} = 2140 \text{ J} = 2.14 \text{ kJ}$$

amount (moles) of ethanoic acid = concentration \times volume

$$= 1.00 \text{ mol dm}^{-3} \times 0.0400 \text{ dm}^3 = 0.0400 \text{ mol}$$

$$\Delta H_{\text{neut}} = \frac{-Q}{\text{moles}} = \frac{-2.14 \text{ kJ}}{0.0400 \text{ mol}} = -53.5 \text{ kJ mol}^{-1}$$

- ⓔ Do not forget to convert the volume of acid from cm^3 to dm^3 . The temperature rose, so the reaction is exothermic and ΔH is negative.

b There must be an excess of sodium hydroxide to ensure that all the acid reacts.

$$\begin{aligned} \text{16 amount (moles) of magnesium sulfate} &= \frac{\text{mass}}{\text{molar mass}} \\ &= \frac{6.0 \text{ g}}{120.4 \text{ g mol}^{-1}} = 0.0498 \text{ mol} \end{aligned}$$

$$\text{heat produced} = \text{moles} \times -\Delta H = 0.0498 \text{ mol} \times 91 \text{ kJ mol}^{-1} = 4.53 \text{ kJ} = 4530 \text{ J}$$

$$\text{heat} = \text{mass} \times \text{specific heat capacity} \times \Delta T$$

$$\begin{aligned} \text{so } \Delta T &= \frac{\text{heat}}{\text{mass} \times \text{specific heat capacity}} \\ &= \frac{4530 \text{ J}}{56 \text{ g} \times 4.08 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}} = 19.8^\circ\text{C} \end{aligned}$$

$$\text{17 a } \Delta T = 40.2 - 18.5 = 21.7^\circ\text{C}$$

$$\text{heat produced, } Q = mc\Delta T = 175 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1} \times 21.7^\circ\text{C} = 15870 \text{ J} = 15.87 \text{ kJ}$$

$$\begin{aligned} \text{amount (moles) methanol} &= \frac{\text{mass}}{\text{molar mass}} \\ &= \frac{0.85 \text{ g}}{32 \text{ g mol}^{-1}} = 0.02656 \text{ mol} \end{aligned}$$

$$\begin{aligned} \Delta H_c &= \frac{-Q}{\text{moles}} \\ &= \frac{-15.87 \text{ kJ}}{0.02656 \text{ mol}} = -598 \text{ kJ mol}^{-1} \end{aligned}$$

e Remember that the mass required is the mass of water heated, *not* the mass of methanol burnt. Also the reaction is exothermic (the temperature increased), so the sign of ΔH is negative. Getting these wrong are common errors.

b The two main reasons why the value is less exothermic than the data book value are that:

- not all the heat produced is absorbed by the water and some heats the air around the beaker and the beaker itself
- the reaction produces gaseous water and the data book value is for the production of liquid water. The change $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ is exothermic.

Other reasons are that combustion might not have been complete or some methanol might have evaporated between blowing out the flame and weighing the burner.

$$\begin{aligned} \text{18 amount (moles) of propane gas burnt} &= \frac{\text{volume}}{\text{molar volume}} \\ &= \frac{0.208 \text{ dm}^3}{24.0 \text{ dm}^3 \text{ mol}^{-1}} = 0.00867 \text{ mol} \end{aligned}$$

$$\text{heat change, } Q = \text{mass} \times \text{specific heat capacity} \times \text{change in temperature}$$

$$= 100 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1} \times (61.5 - 19.4)^\circ\text{C} = 17600 \text{ J} = 17.6 \text{ kJ}$$

$$\Delta H_c(\text{propane}) = \frac{-17.6 \text{ kJ}}{0.00867 \text{ mol}} = -2.03 \times 10^3 \text{ kJ mol}^{-1}$$

e Remember:

- to convert the volume of gas from cm^3 to dm^3
- the temperature rose, so the reaction is exothermic and ΔH is negative
- to give your answer to three significant figures because the data are expressed to three significant figures

The answer is lower than the book value because of considerable heat losses during the experiment.



Chapter Summary Worksheet (textbook CD-ROM)

1 The answer is A.

$$\Delta T = 52.4 - 18.3 = 34.1^{\circ}\text{C}$$

$$\text{heat produced, } Q = \text{mass} \times \text{specific heat capacity} \times \Delta T$$

$$= 25 \text{ g} \times 4.2 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1} \times 34.1^{\circ}\text{C} = 3581 \text{ J (to 4 s.f.)}$$

2 The answer is A.

$$\text{amount (moles) of copper sulfate} = \text{concentration} \times \text{volume in dm}^3$$

$$= 0.500 \text{ mol dm}^{-3} \times 0.0250 \text{ dm}^3 = 0.0125 \text{ mol}$$

3 The answer is B.

$$\Delta H = \frac{-Q}{\text{moles}}$$

$$= \frac{-2970}{0.104} = -286000 \text{ J mol}^{-1} = -286 \text{ kJ mol}^{-1}$$

- e There are two points that need careful consideration. First, the data are in joules (J) but the four choices are in kilojoules (kJ), so the number obtained has to be divided by 1000. The second point is that heat is produced, so the reaction is exothermic and ΔH is negative, so options A and C are wrong.

4 The answer is C. The data are about enthalpy of formation and reaction, so you can use the formula:

$$\Delta H_r = \Sigma n \Delta H_f(\text{products}) - \Sigma n \Delta H_f(\text{reactants})$$

$$= \Delta H_f(\text{CO}_2) + 2 \times \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{CH}_4)$$

This rearranges to:

$$\Delta H_f(\text{H}_2\text{O}) = \frac{1}{2} \{ \Delta H_r + \Delta H_f(\text{CH}_4) - \Delta H_f(\text{CO}_2) \} = \frac{1}{2} \{ -803 + (-75) - (-394) \} = -242 \text{ kJ mol}^{-1}$$

- e Do not forget that there are two water molecules in the equation, so you must have $2 \times \Delta H_f(\text{H}_2\text{O})$. (The n in the formula means that you have to use the stoichiometric numbers from the equation.)
- 5 The answer is A. When gaseous water turns to liquid water, heat is produced because the process is exothermic. Therefore, $\Delta H_f(\text{H}_2\text{O})(\text{l})$ is more exothermic than $\Delta H_f(\text{H}_2\text{O})(\text{g})$, so option A is correct.
- 6 The answer is B. The definition of any enthalpy of combustion is for 1 mol of the substance being burnt. Options A and C are incorrect because the equations have $2\text{C}_4\text{H}_{10}$ on the left. Option C is also wrong because combustion must be complete. Option D is incorrect because it is not combustion. Water is a liquid under standard conditions, so B is the correct answer.

6 Bonding

1 There are two reasons why magnesium has a higher melting temperature than sodium. First, each magnesium atom provides two electrons to the metallic bond whereas each sodium atom supplies one electron. Second, the Mg^{2+} ion formed is smaller than the Na^+ ion. These two factors result in the forces between the delocalised electrons and the positive ions being stronger in magnesium than in sodium. Therefore, more energy is required to break up the lattice in magnesium and melt the solid.

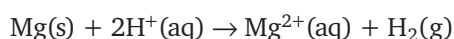
- e To obtain full marks you must state something about each substance — this is an important point that applies to all comparison questions.

Students often fail to make the final point linking the strength of the force to the energy required to separate the particles.

2 a $\text{Mg} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2$

- e State symbols should be included if the reaction produces a precipitate. Otherwise, unless they are specifically asked for, it is not necessary to include them.

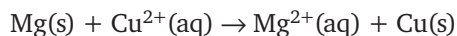
The ionic equation is:



- e An ionic equation should always include state symbols.

b $\text{Mg}(\text{s}) + \text{CuSO}_4(\text{aq}) \rightarrow \text{MgSO}_4(\text{aq}) + \text{Cu}(\text{s})$

The ionic equation is:



- e Magnesium is above both hydrogen and copper in the reactivity series so it is oxidised both by hydrogen ions and by copper ions.

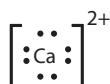
3 a An ionic bond is the electrostatic attraction between a positively charged ion (the cation) and a negatively charged ion (the anion).

- e An ionic bond is the attraction between ions, not the losing and gaining of electrons by the constituent atoms.

b Calcium has an electron configuration $[\text{Ar}] 4s^2$. Fluorine has the electron configuration $[\text{He}] 2s^2 2p^5$. Each calcium atom loses two electrons to form a Ca^{2+} ion that has the electron configuration of the noble gas argon. These two electrons are gained by two fluorine atoms and two F^- ions are formed, each with the electron configuration $[\text{He}] 2s^2 2p^6$, which is that of the noble gas neon. These ions attract each other, forming the bond.

- e You must give the electron configuration before and after the formation of the ions.

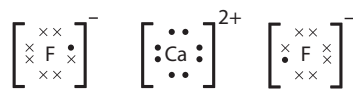
c The electron configuration diagram for a calcium ion is:



The electron configuration diagram of a fluoride ion is:



Note that in calcium fluoride, there are two fluoride ions for each calcium ion. Therefore, the dot-and-cross diagram for the compound calcium fluoride is:



- e The calcium ion has eight electrons in its outer orbit, which is the third shell. These must be shown in the dot-and-cross diagram.

4 In decreasing order of size of radius: $\text{Na} > \text{Cl}^{-} > \text{Mg} > \text{Cl} > \text{Na}^{+} > \text{Mg}^{2+}$

- e Atoms get bigger when they gain electrons and form negative ions. The species Cl^{-} , Cl , Na and Mg have electrons in three shells; the positive ions, Na^{+} and Mg^{2+} , have electrons in two shells. Therefore the positive ions are the smallest. Moving across the periodic table, neutral atoms become smaller, so a magnesium atom is smaller than a sodium atom and a chlorine atom is smaller than a magnesium atom. Cl^{-} is larger than Cl , and Na is larger than Cl . Na and Cl^{-} are similar in radius, but a sodium atom is slightly bigger than a chloride ion.

5 In decreasing order of polarising power: $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^{+} > \text{K}^{+}$

- e Polarising power depends on the charge on the ion and on its radius. Aluminium, magnesium and sodium are all in period 3. Of the three ions, aluminium has the highest charge and the smallest radius, so it is the most polarising. Potassium is in period 4, so it has the largest radius and, as it is only $1+$, its polarising power is the smallest.

6 A covalent bond and a dative covalent bond both consist of a pair of electrons shared by two atoms. In a covalent bond each atom donates one electron; in a dative covalent bond both electrons come from the same atom.

- e The bond is the attraction between the two atoms caused by the sharing of a pair of electrons.

7 The dot-and-cross diagram for carbon monoxide is: $\times \text{C} \times \times \text{O} \cdot$

- e The molecule has two covalent bonds, so two pairs (each consisting of a dot and a cross) are drawn between the two atoms. In addition, a lone pair of electrons from the oxygen atom forms a dative covalent bond to the carbon, so two more dots are drawn between the atoms to represent this bond. Do not forget to draw two additional dots on the oxygen and carbon atoms, which represent the lone pairs. Each covalent bond is represented by a single line between the atoms. A dative covalent bond is represented by an arrow from the atom supplying the two electrons to the atom that does not provide any electrons to the bond. In this example, the arrowhead would point towards the carbon atom:



It is usual to show the electrons from one atom as crosses and from the other atom as dots, but all electrons are the same and so could be shown as all crosses or all dots. Questions of this type normally ask for only the outer electrons to be drawn. However, if all electrons are required, you must draw the inner electrons as well.

8 The electron configuration of nitrogen is $[\text{He}] 2s^2 2p^3$ and of phosphorus is $[\text{Ne}] 3s^2 3p^3$. Both elements have five electrons in the valence shell. However, the maximum number of electrons in the second shell, which is the outer shell of nitrogen, is eight. This means that nitrogen can only form three covalent bonds. The three unpaired $2p$ -electrons and three electrons from the other atoms in the molecule are shared. This fills the $2p$ -orbital and the second shell. The valence electrons of phosphorus are in the third shell, which can hold up to 18 electrons. One of the $3s$ -electrons is promoted into an empty $3d$ -orbital and its five unpaired electrons are used to form five covalent bonds.

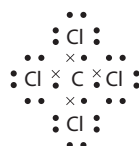
- e Do not say that nitrogen has *no* empty orbitals into which it can promote a $2s$ -electron. It does not have an empty orbital in the second shell. The empty orbitals in the third shell cannot be used in bonding because too much energy is required to promote a $2s$ -electron into a third-shell orbital. In addition to forming three covalent bonds, nitrogen can also provide two electrons to form a dative covalent bond, as in the NH_4^{+} ion.

9 A σ -bond is caused by the head-on overlap of two atomic orbitals. The shared electrons are on the line between the centres of the two atoms. A π -bond is the result of a sideways overlap of two p -orbitals (or a p - and a d -orbital), so that the shared electrons are above and below the line joining the centres of the two atoms.

- e A σ -bond can be caused by the overlap of:
- two s -orbitals, as in hydrogen
 - one s - and one p -orbital, as in HCl
 - two p -orbitals, as in Cl_2

A π -bond is always found together with a σ -bond, making a double bond.

10 a The dot-and-cross-diagram for carbon tetrachloride, CCl_4 , is:



- e Carbon tetrachloride has four σ -bonds.

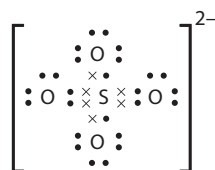
b The dot-and-cross-diagram for carbon dioxide, CO_2 , is:



- e Carbon dioxide has one σ - and one π -bond between each oxygen atom and the central carbon atom.

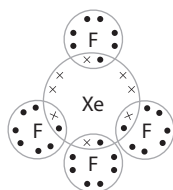
Apart from in carbon monoxide, carbon has four bonds in all of its compounds.

c The dot-and-cross-diagram for the sulfate ion, SO_4^{2-} , is:



- e The sulfur atom has the electron configuration $[\text{Ne}] 3s^2 3p^4$. It can form six covalent bonds because one $3s$ - and one $3p$ -electron are promoted into empty $3d$ -orbitals. Two of these bonds are π -bonds and four are σ -bonds.

d The dot-and-cross-diagram for xenon tetrafluoride, XeF_4 , is:



- e The heavier noble gases can form compounds. Xenon has the electron configuration $[\text{Kr}] 4d^{10} 5s^2 5p^6$. Electrons can be promoted from its $5p$ -orbitals into empty $5d$ -orbitals and bonds can then form. The energy requirement for this is quite high, so it is only energetically favourable if strong bonds, such as those with the small element fluorine, are formed.

11 The strongest of these three bonds is C–C; the weakest is C–Br.

- e A general rule is that small atoms form strong bonds. Carbon has a smaller atomic radius than chlorine, which, in turn, is smaller than bromine. Therefore, the carbon–carbon bond is the strongest of the three and carbon–bromine the weakest.



Chapter Summary Worksheet (textbook CD-ROM)

- 1 The answer is C. Metals conduct electricity by a flow of electrons that are delocalised. When molten or dissolved, ionic compounds conduct electricity by the movement of ions.
- 2 The answer is A. The strength of a metallic bond depends mainly on the ionic radius and charge. Solid aluminium has a lattice of Al^{3+} ions that are more highly charged and are smaller than Mg^{2+} , K^+ or Na^+ ions, and there are three more delocalised electrons per ion. These three factors all make the metallic bond in aluminium the strongest.
- 3 The answer is A. All metals form positive ions (cations).
 - a The first ionisation energies of metals are *less* than those of non-metals. Not all metals react with acids to give hydrogen (Cu, Ag, Pt do not). Oxides of metals are either basic (MgO) or amphoteric (Al_2O_3).
- 4 The answer is B. The sum of the ionic radii in sodium chloride is the radius of Na^+ plus the radius of Cl^- . A metallic radius is always slightly bigger than the corresponding ionic radius (the ions are not touching), so the answer is B not C. Option D is incorrect because, in the same period, $2+$ ions are smaller than $1+$ ions.
- 5 The answer is D. The magnitude of the lattice energy depends mostly on the charge of the ions and the sum of their radii. Ca^{2+} is more highly charged than Na^+ or K^+ . The O^{2-} ion is more charged than Cl^- and is smaller than Cl^- and S^{2-} . Therefore, CaO has the highest exothermic lattice energy.
- 6 The answer is A. Covalent character is caused by polarisation of the anion. The greater the degree of covalency, the greater is the difference between the Born–Haber and the theoretical lattice energies. Small, highly charged ions are the most polarising; large and highly charged anions are the easiest to polarise. Mg^{2+} is smaller than Ca^{2+} and the ion is more highly charged than Na^+ or K^+ . I^- is larger than Cl^- , so the I^- ion in MgI_2 is the most polarised. Therefore, magnesium iodide has the greatest covalent character.
- 7 The answer is B. It is impossible to have two σ -bonds between the same two atoms. The sideways overlap of two p -orbitals results in a π -bond that is part of a double bond, but not all of it.
- 8 The answer is C. The strength of a covalent bond depends mostly on the small size of the atoms. (There are exceptions to this. For example, the $\text{F}-\text{F}$ bond is weaker than the $\text{Cl}-\text{Cl}$ bond.) The second-period atoms, nitrogen and oxygen, are smaller than the third-period atoms, phosphorus and sulfur. The trend across a period is for the atoms to become *smaller*, so an oxygen atom has a smaller radius than a nitrogen atom. Therefore, the $\text{O}-\text{H}$ covalent bond is the strongest of the four.
- 9 The answer is C. The definition is for the formation of *one* mole of atoms from the element in its standard state. Bromine is a liquid at 1 atm pressure and 298 K, so the answer is C.
 - a Option A represents twice the enthalpy of atomisation.
- 10 The answer is D. Do not confuse ionisation energy (always loss of an electron) with electron affinity (always gain of an electron). The second ionisation energy is for the removal of an electron from each ion of a mole of gaseous $1+$ ions forming a mole of $2+$ ions.
 - a Option C is the sum of the first and second ionisation energies. Option B is the second electron affinity and A is the sum of the first and second electron affinities.

- 11 The answer is A. This is a difficult question, possibly best attempted by drawing out the structures of the species. PCl_4^+ comes from a PCl_5 molecule (which has five covalent σ -bonds) that loses a Cl^- ion. The other species all contain dative bonds. In NH_4^+ , there is a dative bond between the lone pair of electrons on the nitrogen of NH_3 and an H^+ . In PCl_6^- , it is between a Cl^- ion and a PCl_5 molecule. In Al_2Cl_6 there are two dative bonds, one to each aluminium atom in an AlCl_3 molecule from the other AlCl_3 molecule.

7 Introduction to organic chemistry

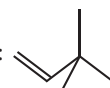
1 a $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{Br}$ is called 1-bromopropan-2-ol.

b $\text{CH}_2\text{ClCH}_2\text{COOH}$ is called 3-chloropropanoic acid.

e There are three carbon atoms in the chain, so the stem name is prop-.

c $\text{CH}_2=\text{CHC}(\text{CH}_3)_3$ is called 3,3-dimethylbut-1-ene.

e There are four carbon atoms in the chain, as can be seen from the skeletal formula:



2 a The formula of 1,2-dichloro-1,2-difluoroethene is $\text{F}(\text{Cl})\text{C}=\text{C}(\text{Cl})\text{F}$.

b The formula of 1-hydroxybutanone is $\text{CH}_3\text{CH}_2\text{COCH}_2\text{OH}$.

c The formula of 2-amino-3-chloropropanoic acid is $\text{CH}_2\text{ClCH}(\text{NH}_2)\text{COOH}$.

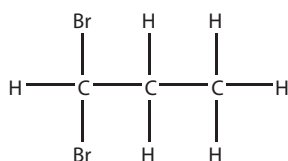
3 a The functional groups in $\text{CH}_2\text{OHCOCH}(\text{NH}_2)\text{COOH}$ are:

- $-\text{OH}$ (alcohol)
- $-\text{NH}_2$ (amino)
- $\text{C}=\text{O}$ (in a ketone)
- $-\text{COOH}$ (carboxylic acid)

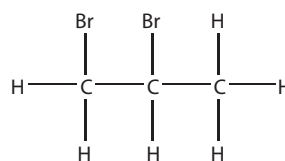
b The functional groups in $\text{CH}_2=\text{CHCH}(\text{OH})\text{CHO}$ are:

- $\text{C}=\text{C}$ (alkene)
- $\text{C}=\text{O}$ (in an aldehyde)
- $-\text{OH}$ (alcohol)

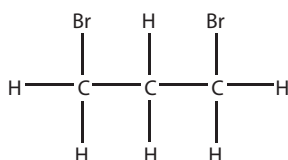
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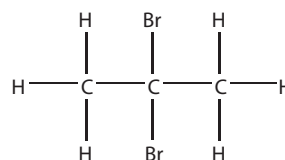
1,1-dibromopropane



1,2-dibromopropane



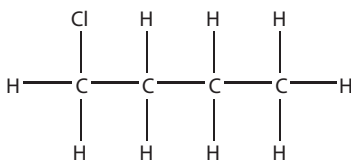
1,3-dibromopropane



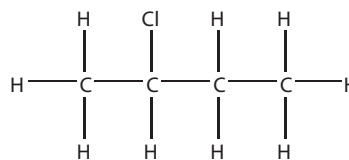
2,2-dibromopropane

e 2,3-dibromopropane is identical to 1,2-dibromopropane.

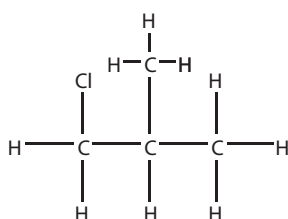
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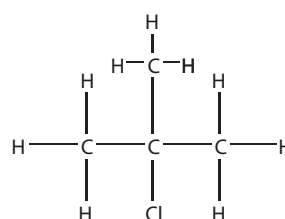
1-chlorobutane



2-chlorobutane



1-chloro-2-methylpropane



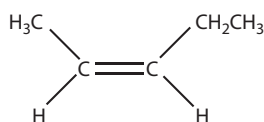
2-chloro-2-methylpropane

- e Start by drawing the longest chain — here it is four carbon atoms. Then, add chlorine to different positions on that chain. Next, branch the chain and see if chlorine could go in different positions. Putting the chlorine in the top CH₃ in place of a hydrogen ion is another way of writing 1-chloro-2-methylpropane (the molecule is bent through 90°).

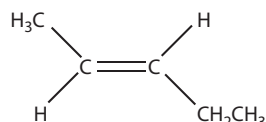
6 There are three pentene isomers:



Pent-1-ene

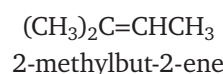
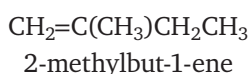
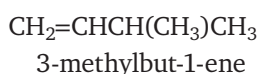


(Z)-pent-2-ene
cis-pent-2-ene



(E)-pent-2-ene
trans-pent-2-ene

and there are three butene isomers:

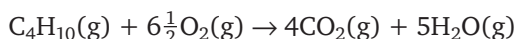


- e A chain of three is impossible, because to achieve this the central carbon atom would have to have five bonds (one double and three single).

7 The major organic product is hexachloroethane, CCl₃CCl₃.

8 $2\text{C}_4\text{H}_{10}(\text{g}) + 13\text{O}_2(\text{g}) \rightarrow 8\text{CO}_2(\text{g}) + 10\text{H}_2\text{O}(\text{g})$

or



- e Complete combustion of organic compounds produces carbon dioxide and water.

9 $(\text{CH}_3)_2\text{C}=\text{CHCH}_3 + \text{HI} \rightarrow (\text{CH}_3)_2\text{CICH}_2\text{CH}_3$

The gases are mixed at room temperature.

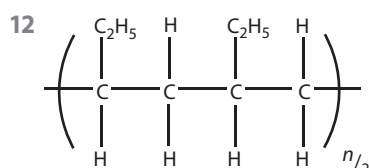
- e The major product is 2-iodo-2-methylbutane. Applying Markovnikoff's rule, hydrogen adds on to the carbon atom that has more hydrogen atoms already directly attached — in this case, one hydrogen atom rather than none.

10 The purple colour of the potassium manganate(VII) solution would be replaced by a brown precipitate. The organic product is butane-2,3-diol, CH₃CH(OH)CH(OH)CH₃.

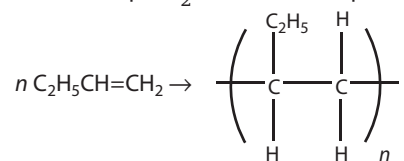
- e Do not forget to state the original colour as well as the final appearance. The brown precipitate is manganese(IV) oxide, MnO₂.

11 In the reaction between ethene and bromine, bromine attacks the electron-rich π-bond. In ethane, all the bonds are σ-bonds, so there is no centre of high-electron density. The propagation step of the photochemical substitution reaction with ethane involves the reaction of a bromine radical with an ethane molecule. This is a slow reaction. It is energetically unfavourable because of the relatively weak C–Br bond that is formed.

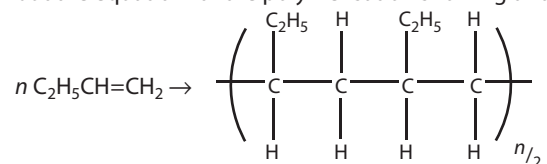
- e The mechanism of the reaction between ethene and bromine is electrophilic addition; between ethane and bromine it is free-radical substitution.



- e The subscript is $\frac{n}{2}$ because the equation for the polymerisation showing one repeat unit is:

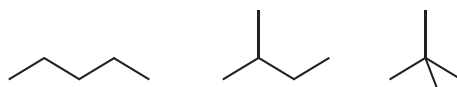


but the equation for the polymerisation showing two repeat units is:

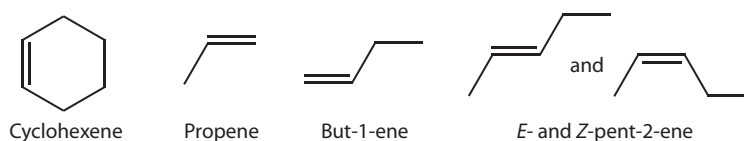


Chapter Summary Worksheet (textbook CD-ROM)

- 1 The answer is B. The compounds are all alkanes because they have the general formula C_nH_{2n+2} . One isomer has a carbon chain of five atoms; another has a chain of four with the fifth carbon atom on the second carbon in the chain. The third compound has a chain of three carbon atoms with two CH_3 groups on the middle carbon of the chain:

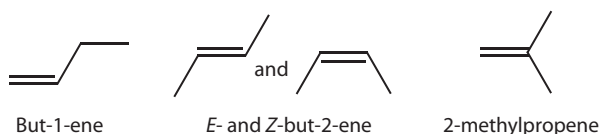


- 2 The answer is D. Geometric isomerism is only possible if there are two different atoms or groups on both the carbon atoms of the double bond. Pent-2-ene has a CH_3 group and a hydrogen atom on one carbon of the $C=C$ group and a C_2H_5 group and a hydrogen atom on the other, so it exists as two geometric isomers:



- e Cyclohexene has one hydrogen atom on each of the carbon atoms in the $C=C$ group. Propene and but-1-ene have two hydrogen atoms on one of the carbon atoms. Therefore, none can form geometric isomers.

- 3 The answer is C. The isomers are but-1-ene and the two geometric isomers of but-2-ene and 2-methylpropene:



- 4 The answer is B. Ethane and methylpropane are alkanes and have only σ -bonds. When ethene polymerises, the double bond breaks, so poly(ethene) does not contain any double bonds. Cyclohexene has a double bond, which consists of a σ -bond and a π -bond, so B is the correct response.

- 5 The answer is D. The general formula for the homologous series of alkanes is C_nH_{2n+2} .

- 6 The answer is B. The important step that determines the rate of reaction is that between the halogen radical and the alkane.

- e Option A is not correct because the reaction is between chlorine *radicals* and the alkane *not* chlorine molecules. Options C and D are incorrect — the $Cl-Cl$ bond is the stronger.

- 7 The answer is B. The initial attack is by a δ^+ Br atom. Therefore, all the possible products must contain bromine. This means that option B is false and is the correct answer to this negative question.

- e The intermediate carbocation, $CH_2BrCH_2^+$, can pick up a Br^- , H_2O (followed by loss of H^+) or a Cl^- , so all the other options are true.

- 8 The answer is A. When the double bond breaks, the two groups add on to the previously double-bonded carbon atoms. Therefore, option B is incorrect. Potassium ions do not replace H in OH groups, so options C and D are also incorrect.

- 9 The answer is C. First, the reaction of alkenes with hydrogen halides is an addition reaction. Second, the attack is by δ^+ hydrogen in HBr . The attacking reagent is an electrophile, so the reaction is electrophilic addition.

10 The answer is B. The simplest way of working this out is:

$$\frac{\text{volume of oxygen}}{\text{volume of octane}} = \frac{\text{moles of oxygen in equation}}{\text{moles of octane in equation}}$$
$$= \frac{25}{2} = \frac{12.5}{1}$$

$$\text{volume of oxygen} = 12.5 \times \text{volume of octane} = 12.5 \times 10 = 125 \text{ cm}^3$$

$$\text{volume of air needed} = 5 \times \text{volume of oxygen} = 5 \times 125 = 625 \text{ cm}^3$$

e You have to multiply the volume of oxygen by 5 because air is 20% (one-fifth) oxygen.

An alternative way of carrying out the calculation is to work out the moles of octane:

$$\text{amount (moles) of octane} = \frac{\text{volume}}{\text{molar volume}}$$
$$= \frac{10 \text{ cm}^3}{24000 \text{ cm}^3 \text{ mol}^{-1}} = 4.17 \times 10^{-4}$$

$$\text{amount (moles) of oxygen} = 4.17 \times 10^{-4} \times \frac{25}{2} = 0.00521$$

$$\text{volume of oxygen} = \text{moles} \times 24000 = 125 \text{ cm}^3$$

$$\text{volume of air} = 5 \times 125 = 625 \text{ cm}^3$$

Practice Unit Test 1

Section A

1 The answer is D. Average mass refers to the relative atomic mass only. The mass is quoted relative to $\frac{1}{12}$ the mass of a carbon atom.

2 The answer is A. 'Parts per million' is a measure by mass. 1 dm^3 of water weighs 1000 g. Here, this contains $5.4 \times 10^{-6} \times 1000 \text{ g}$ of Al^{3+} . So there are $5.4 \times 10^3 \text{ g} = 5.4 \text{ mg}$ of Al^{3+} ions in the solution.

3 The answer is A.

$$\begin{aligned} \text{amount (moles)} &= \frac{\text{mass}}{\text{molar mass}} \\ &= \frac{10 \text{ g}}{100 \text{ g mol}^{-1}} = 0.1 \text{ mol} \\ \text{concentration} &= \frac{\text{moles}}{\text{volume}} \\ &= \frac{0.1 \text{ mol}}{0.250 \text{ dm}^3} = 0.40 \text{ mol dm}^{-3} \end{aligned}$$

4 The answer is B.

$$1 \text{ dm}^3 \text{ of gas} = \frac{1}{24} = 0.0417 \text{ mol}$$

butane forms carbon dioxide in a 1:4 molar ratio

$$\text{so amount (moles) of carbon dioxide produced} = 4 \times 0.0417 = 0.167 \text{ mol}$$

$$\text{mass} = \text{moles} \times \text{molar mass} = 0.167 \text{ mol} \times 44.0 \text{ g mol}^{-1} = 7.3 \text{ g}$$

5 The answer is A. Atom economy is the number of atoms in the desired product compared with the number of atoms in the starting materials, expressed as a percentage. In this example it is:

$$8 \times \frac{100}{15} = 53.3\%$$

6 The answer is C.

molar mass of ethanol = 46.0 g mol^{-1} ; molar mass of ethanoic acid = 60.0 g mol^{-1}

$$\begin{aligned} \text{amount (moles) of ethanol} &= \frac{\text{mass}}{\text{molar mass}} \\ &= \frac{23 \text{ g}}{46.0 \text{ g mol}^{-1}} = 0.50 \text{ mol} \end{aligned}$$

maximum theoretical yield of ethanoic acid = 0.5 mol as the reaction has a 1:1 ratio

$$\begin{aligned} \text{maximum theoretical mass of ethanoic acid} &= \text{moles} \times \text{molar mass} \\ &= 0.5 \text{ mol} \times 60.0 \text{ g mol}^{-1} = 30.0 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{percentage yield} &= \frac{\text{actual yield}}{\text{maximum theoretical yield}} \times 100 \\ &= \frac{16 \text{ g}}{30.0 \text{ g}} \times 100 = 53.3\% \end{aligned}$$

- e The percentage yield is never equal to the actual mass of product $\times 100$ divided by the mass of reactant. In this instance, such a calculation would give the answer 69.6%, i.e. option D.

7 The answer is B.

$$\begin{aligned} \text{amount (moles) of calcium chloride} &= \frac{\text{mass}}{\text{molar mass}} \\ &= \frac{111.1 \text{ g}}{111.1 \text{ g mol}^{-1}} = 1.000 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{number of formula units} &= \text{moles} \times \text{Avogadro constant} \\ &= 1.000 \times 6.02 \times 10^{23} = 6.02 \times 10^{23} \end{aligned}$$

$$\text{number of ions} = 3 \times 6.02 \times 10^{23} = 1.81 \times 10^{24}$$

- e Do not forget that calcium chloride has three ions per formula, one Ca^{2+} and two Cl^- .

8 The answer is B.

$$20 \text{ nmol of steroid per dm}^3 = 2.0 \text{ nmol of steroid per } 100 \text{ cm}^3 = 2.0 \times 10^{-9} \text{ mol per } 100 \text{ cm}^3$$

(1 nmol = 10^{-9} mol)

$$\text{number of molecules} = \text{moles} \times \text{Avogadro constant} = 2.0 \times 10^{-9} \times 6.02 \times 10^{23} = 1.204 \times 10^{15}$$

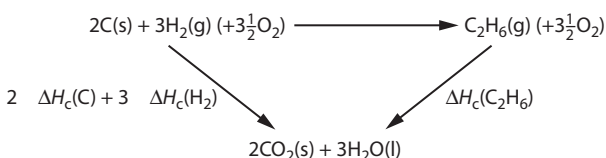
9 The answer is B.

$$\begin{aligned} \Delta H_r &= \Sigma \Delta H_f(\text{products}) - \Sigma \Delta H_f(\text{reactants}) \\ &= 2 \times -395 - (2 \times -297 + 0) = -196 \text{ kJ mol}^{-1} \end{aligned}$$

- 10 The answer is B. You cannot use 'products – reactants' here because you are not given enthalpy of formation data. The question has to be solved using a Hess's law cycle (direct ΔH = sum of indirect ΔH values).

The direct route is: elements \rightarrow ethane.

The indirect route is: elements (and oxygen) \rightarrow combustion products \rightarrow ethane (and oxygen):



The equation is:

$$\begin{aligned} 2\text{C(s)} + 3\text{H}_2\text{(g)} &\rightarrow \text{C}_2\text{H}_6\text{(g)} \\ \text{so, } \Delta H_f(\text{C}_2\text{H}_6) &= 2 \times \Delta H_c(\text{C}) + 3 \times \Delta H_c(\text{H}) - \Delta H_c(\text{C}_2\text{H}_6) \\ &= (2 \times -395) + (3 \times -286) - (-1560) = -88 \text{ kJ mol}^{-1} \end{aligned}$$

- 11 The answer is A. Beware! ΔH_f is for the formation of 1 mol. It is equal to one-half of ΔH_r because the equation has 2 moles of ammonia, NH_3 , on the right-hand side. ΔH_r is found from bond enthalpies. (Remember that bond breaking is endothermic and bond making is exothermic.)

$$\text{bonds broken} = 1 \times \text{N}\equiv\text{N} \text{ and } 3 \times \text{H-H} = +946 + (3 \times 436) = +2254 \text{ kJ}$$

$$\text{bonds made} = 6 \times \text{N-H} = 6 \times -391 = -2346 \text{ kJ}$$

$$\Delta H_r = +2254 + (-2346) = -92 \text{ kJ}$$

$$\text{so } \Delta H_f = 0.5 \times -92 = -46 \text{ kJ mol}^{-1}$$



12 The answer is D. The indirect route is:

$$2 \times \text{equation (i)} - \text{equation (ii)}$$

$$\text{so the enthalpy change} = 2 \times (-y) - (-z) = z - 2y$$

- e Since the equation relates to the decomposition of NaHCO_3 , the NaHCO_3 is on the left-hand side. Therefore, equation 1 must be in the direction given in the data. Na_2CO_3 is on the right-hand side, so you must reverse equation 2.

13 The answer is C.

$$\Delta T = 18.7 - 22.4 = -3.7^\circ\text{C}$$

$$\text{heat change, } Q = \text{mass} \times \text{specific heat capacity} \times \Delta T$$

$$= 100 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1} \times 3.7 = 1546.6 \text{ J} = 1550 \text{ J (3 s.f.)}$$

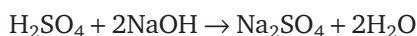
- e You must use the mass of the water being heated, *not* the mass of the solute. The latter gives option A as the answer.
- 14 The answer is A. A thermometer reading that is always 2° too high gives readings for both the starting and the final temperatures that are 2° too high. This has no effect on the value of ΔT , and so none on the accuracy of the experiment.
- e The reason that option D is incorrect is that it would result in not all the acid being neutralised, which would affect the value of ΔH .

15 The answer is D. The reaction is exothermic, so the value of ΔH is negative. Options A and C can, therefore, be ignored.

$$\text{amount (moles) of sulfuric acid} = \text{concentration} \times \text{volume in dm}^3$$

$$= 0.500 \text{ mol dm}^{-3} \times 0.025 \text{ dm}^3 = 0.0125 \text{ mol}$$

The data are for the equation:



$$\begin{aligned} \text{so } \Delta H \text{ per mole of } \text{H}_2\text{SO}_4 \text{ reacted} &= \frac{-\text{heat produced}}{\text{moles}} \\ &= \frac{-1.46 \text{ kJ}}{0.0125 \text{ mol}} = -116.8 \text{ kJ} \end{aligned}$$

The definition of enthalpy of neutralisation is per mole of water produced *not* per mole of sulfuric acid reacted, so:

$$\text{enthalpy of neutralisation} = \frac{1}{2} \times -116.8 = -58.4 \text{ kJ mol}^{-1}$$

- 16 The answer is C. When determining the significant figures for numbers less than 1, the zero in front of the decimal point and zeros immediately after the decimal point are not counted, whereas zeros at the end of the number are counted. Written in scientific notation, the number is 2.10×10^{-2} , which is clearly to three significant figures.
- 17 The answer is A. Ionisation energy relates to a gaseous atom losing an electron and becoming a positive ion.
- 18 The answer is A. Oxygen has the electronic configuration $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$. When an O^+ ion is formed the electron in the highest energy level is lost — one of the $2p_x$ electrons.
- 19 The answer is B. The chain is five carbon atoms long, so the stem name is pent-. The highest priority atoms attached to the $\text{C}=\text{C}$ group are the oxygen (atomic number 8) on the left-hand

carbon and the carbon (atomic number 6) on the right-hand carbon of the double bond. These are on opposite sides of the double bond and so the prefix *E* is given to the name.

- 20 The answer is B. A is wrong as there is always restricted rotation about a carbon dioxide bond. C and D are wrong as 2-methylbut-2-ene does not have geometric isomers.
- 21 The answer is C. The peak at 158 is caused by $(^{79}\text{X}-^{79}\text{X})^+$ and that at 162 by $(^{81}\text{X}-^{81}\text{X})^+$. Since there is no peak at 159, there cannot be an ^{80}X isotope ($^{79}\text{X}-^{80}\text{X}$ has a mass of 159). This cuts out options A, B and D. The double intensity of the peak at 160 is caused by the two ways of combining ^{79}X and ^{81}X — $(^{79}\text{X}-^{81}\text{X})^+$ and $(^{81}\text{X}-^{79}\text{X})^+$ (similar to the way that, when tossing two coins, the chances of the head–tail combination is twice as likely as either head–head or tail–tail).
- 22 The answer is B. The compound does not decolorise bromine water, so it cannot be an alkene. Therefore, option B is false and is the correct answer.
- 23 i The answer is B. There is a big jump after the third ionisation energy when an electron is removed from an inner shell.
- ii The answer is A. The ionisation energies decrease down a group as the atomic radius increases.
- iii The answer is C. In a period, there is a general upward trend with a slight dip between the second and third elements. This is because the electron is being removed from a higher-energy *p*-orbital, rather than from an *s*-orbital, as is the case for the second element.

Section B

- 24 a i Ionisation is achieved by the bombardment of the gaseous substance with a beam of high-energy (fast-moving) electrons ✓.
- ii The ions formed are then accelerated by an electrical potential ✓.
- iii They are then deflected by a magnetic field ✓. (Heavier ions are deflected less.)
- b relative atomic mass = $\frac{(53.94 \times 5.94) + (55.93 \times 91.78) + (56.94 \times 2.28)}{100}$ ✓ = 55.83 ✓
- c Rock dating ✓ — Use a mass spectrometer to measure the relative amounts of a radioactive isotope and its daughter isotope in the rock sample ✓. Assuming that there is no other source of the daughter element, the age of the rock can be calculated knowing the half-life of the radioactive isotope ✓.
- or
- Carbon-14 dating of organic materials ✓ — the relative amount of carbon-14 to carbon-12 is measured in a mass spectrometer ✓. If the approximate age is known, then the ratio of ^{14}C to ^{12}C when the organic material was grown can be estimated. Knowing the half-life ✓ of carbon-14, the age of the material can be calculated.
- or
- Catching drug cheats ✓ — a sample of the urine of an athlete is separated into component substances and placed in a mass spectrometer. The mass/charge ratio of the molecular ion ✓ is measured and compared with a data base ✓ of known performance-enhancing drugs.

- 25 a** The first ionisation energy of an element is the energy required to remove one electron ✓ from each of a mole ✓ of gaseous atoms ✓ of that element.
- b i** Sodium has a nuclear charge of +11 and the outer electron is shielded by ten inner electrons. The effective nuclear charge is therefore about +1. In magnesium, the nuclear charge of +12 is also shielded by ten inner electrons, so its effective nuclear charge is about +2 ✓. Also, the atomic radius of a magnesium atom is less than that of a sodium atom ✓. Together these factors result in it being harder to remove an electron from a magnesium atom than from a sodium atom ✓. Therefore, magnesium has a larger first ionisation energy.
- ii** Aluminium has the electronic configuration [Ne] 3s² 3p¹ and that of magnesium is [Ne] 3s² ✓. The 3p-electron is at a higher energy level than a 3s-electron and so is slightly easier to remove. In addition, the 3s-electrons partially shield the 3p-electron ✓.

Element	Divide by r.a.m. ✓	Divide by smallest
Sodium	36.5/23.0 = 1.59	1.59/0.79 = 2.0
Sulfur	25.4/32.1 = 0.79	0.79/0.79 = 1
Oxygen	38.1/16.0 = 2.38	2.38/0.79 = 3.0

The empirical formula is Na₂SO₃ ✓.

- e** Make sure that you show all your working. The working for the second step (dividing by the smallest) is often omitted by candidates.

26 a i Free-radical substitution ✓

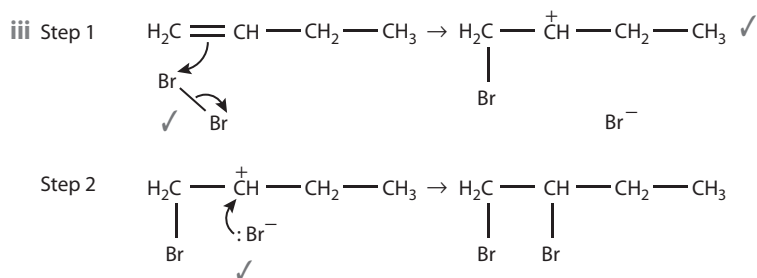
ii Electrophilic addition ✓

- e** The equations are CH₃CH₃ + Cl₂ → CH₃CH₂Cl + HCl (substitution) and CH₂=CH₂ + Cl₂ → CH₂ClCH₂Cl (addition).

- b i** A homologous series is a series of compounds that all have the same general formula ✓. Each one differs from the next by CH₂ ✓ and either they have similar chemical properties or they show a trend in physical properties ✓.

ii CH₂=CHCH₂CH₃ + Br₂ → CH₂BrCHBrCH₂CH₃ ✓

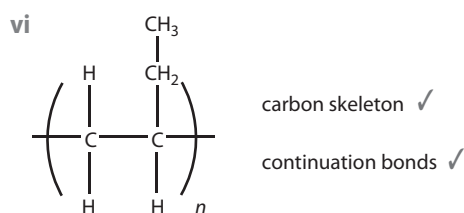
- e** Do not use the 'added-up' formulae C₄H₈ and C₄H₈Br₂ as they are not specific.



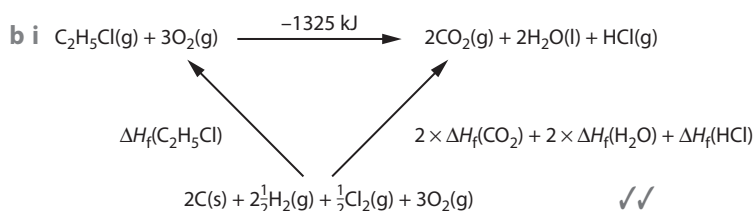
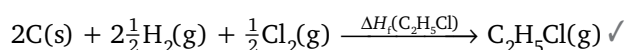
iv 1-bromobutan-2-ol/CH₃BrCH(OH)CH₂CH₃

- v** The purple ✓ potassium manganate(VII) solution turns to a brown precipitate ✓. The organic product is CH₂OHCH(OH)CH₂CH₃/butan-1,2-diol ✓.

- e** Don't give the name *and* the formula in case one is wrong. +1 and -1 score 0.



- 27 a The standard enthalpy of formation, ΔH_f^\ominus , is the enthalpy change when 1 mol ✓ of a substance is formed from its elements ✓ in their standard states under standard conditions of 1 atm pressure and a stated temperature (usually 298 K) ✓.



- e The formulae in the Hess's law cycle are awarded 1 mark. Labelling with arrows in the correct directions gains the second mark. Make sure that you label the Hess's law diagram either with symbols or ΔH values.

Note that when chloroalkanes burn, hydrogen chloride gas is one of the products.

- ii $\Delta H_f(\text{C}_2\text{H}_5\text{Cl}) + (-1325) = [2 \times \Delta H_f(\text{CO}_2)] + [2 \times \Delta H_f(\text{H}_2\text{O})] + \Delta H_f(\text{HCl}) \checkmark$

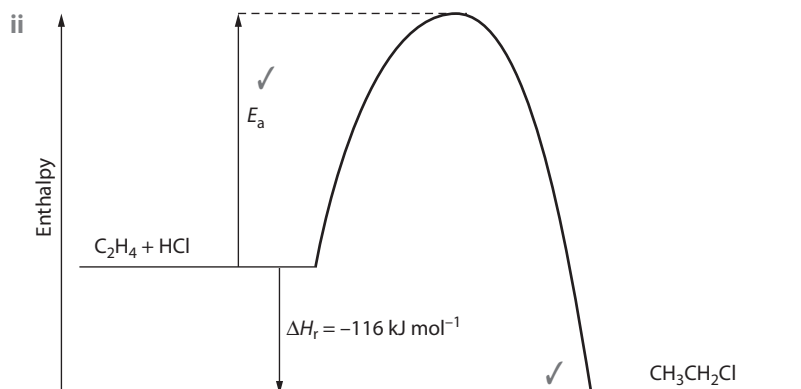
$$\Delta H_f(\text{C}_2\text{H}_5\text{Cl}) = [2 \times (-394)] + [2 \times (-286)] + (-92.3) + 1325 = -127.3 \text{ kJ mol}^{-1} \checkmark$$

c i

Bonds broken/kJ mol ⁻¹		Bonds made/kJ mol ⁻¹	
C=C	+612	C-C	-347
H-Cl	+432	C-H	-467
		C-Cl	-346
Total	+1044 ✓	Total	-1160 kJ ✓

$$\Delta H_r = +1044 - 1160 = -116 \text{ kJ mol}^{-1} \checkmark$$

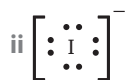
- e Remember that bond breaking is always endothermic (+) and bond making is always exothermic (-). Another way of doing this calculation is to break all the bonds in the reactants. Broken 4 × C-H, 1 × C=C and 1 × H-Cl; made 5 × C-H, 1 × C-C and 1 × C-Cl.



- e 1 mark is for showing the energy level of products as lower than the energy level of reactants and for labelling ΔH_r . The hump with activation energy shown gains a second mark.

iii The bond enthalpies used in the calculation are the average of the enthalpies of the bonds in a range of different compounds ✓.

e The C–Cl bond enthalpy in C_2H_5Cl is slightly different from the C–Cl bond enthalpy in CH_3Cl .



e For parts (i) and (ii), there is 1 mark for both electronic configurations being correct and 1 mark for both charges being correct.

b i The difference between the two values in magnesium iodide is 383 kJ. For magnesium fluoride, it is 44 kJ. The iodide ion has the same charge as the fluoride ion ($1-$) but it has a much bigger radius ✓. This means that the anion is much more polarised ✓ by the Mg^{2+} ion, so magnesium iodide has more covalent character ✓ than magnesium fluoride. This causes its lattice energy obtained from the Born–Haber cycle to have a higher value than the theoretical value calculated on the basis of the compound being wholly ionic.

e The marks are for:

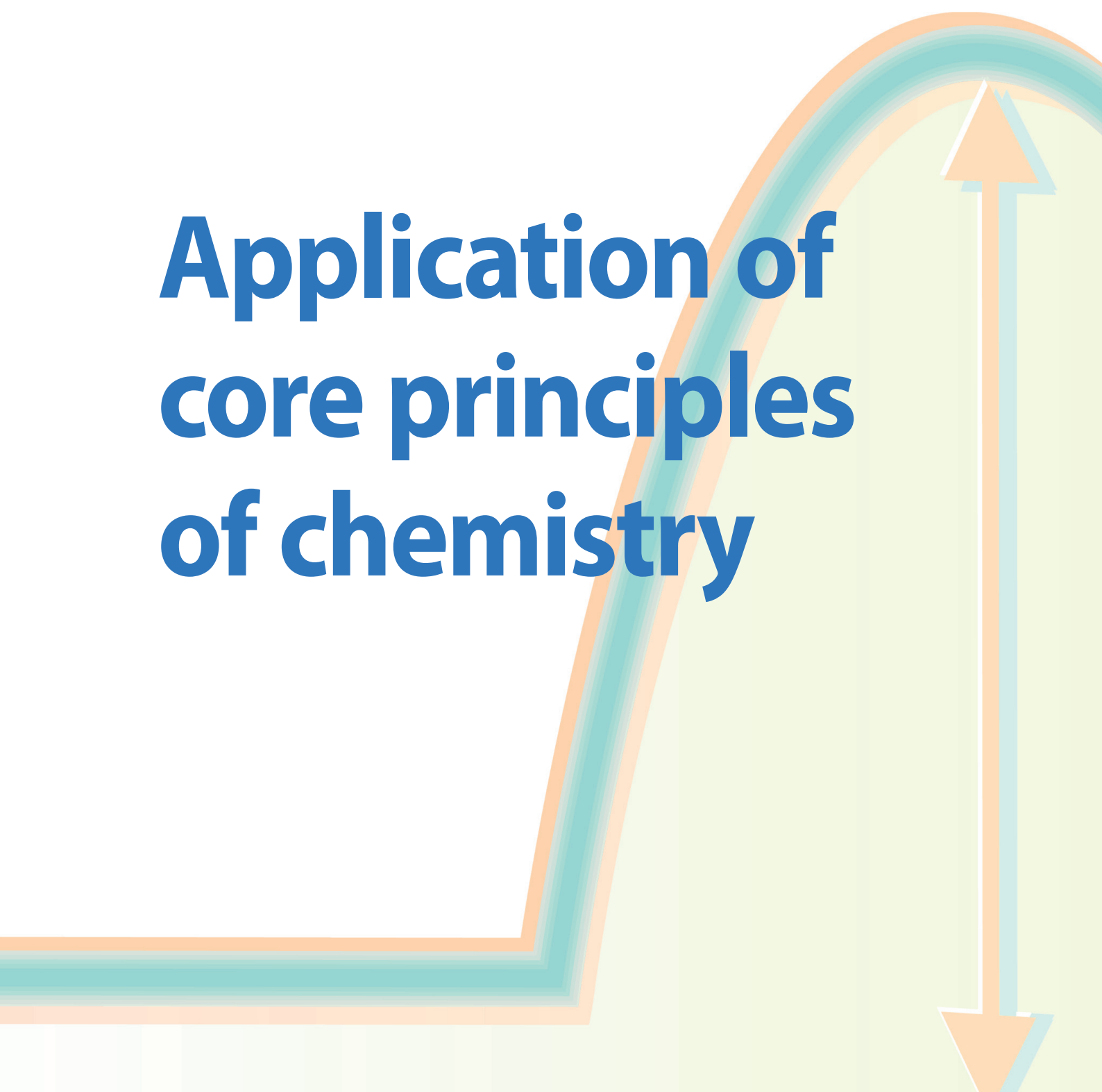
- size and charge of anions
- a comparison of polarisation of the anions
- comparison of covalent character

Do not confuse ions with atoms. This is a common error. To score the first mark, you must either state that the charges on the two anions are the same or give the charge. Do not say that magnesium iodide is covalent — say that it has 'some covalent character'.

ii The main factors that determine lattice energy are ionic radius and charge. Calcium and magnesium ions are both $2+$, but calcium ions have a smaller radius ✓ than magnesium ions and are, therefore, more strongly attracted ✓ to the fluoride ions. This means that the lattice energy of magnesium fluoride is more exothermic than that of calcium fluoride.

Unit 2

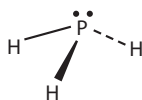
Application of core principles of chemistry

A decorative graphic on the right side of the page. It features a thick, multi-layered line that starts as a horizontal bar at the bottom left, then curves upwards and to the right, forming a rainbow-like arch. The colors of the arch transition from orange at the bottom to light blue at the top. From the peak of the arch, a vertical double-headed arrow extends both upwards and downwards. The arrow is also multi-layered, with orange and light blue colors.

8 Shapes of molecules and ions, bond polarity and intermolecular forces

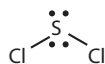
- 1 a Iodine is in group 7 and has the electron configuration $[\text{Kr}] 4d^{10} 5s^2 5p^5$, so there are seven electrons in its valence (outer) orbit. Three of these electrons are used to form bonds with the three chlorine atoms. Therefore, there are four unused electrons, i.e. two lone pairs.
- b Oxygen is in group 6 and has the electron configuration $[\text{He}] 2s^2 2p^4$. Two of the six valence (outer shell) electrons are used in bonding with the two fluorine atoms. Therefore, there are four unused electrons, i.e. two lone pairs.
- c Carbon is in group 4 and has the electron structure $[\text{He}] 2s^2 2p^2$. There are four valence electrons that are all used in bonding, since one σ - and one π -bond are formed with each of the two oxygen atoms. Therefore, there are no lone pairs.
- e To work out the number of lone pairs (essential when predicting the shape of a molecule), you must calculate the number of electrons in the outer orbit of the central atom. These are the valence electrons. Subtract the number of bonds from the number of valence electrons to find the number of unused electrons. The number of lone pairs is half the number of unused valence-shell electrons.

2 a



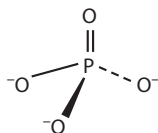
Phosphorus is in group 5 of the periodic table, so it has five valence electrons. It forms three covalent bonds in PH_3 , so it has one lone pair. The electron pairs are arranged tetrahedrally around the central atom because all four pairs repel each other to the position of maximum separation. The three hydrogen atoms take up a pyramidal arrangement around the phosphorus atom.

b



Sulfur is in group 6 of the periodic table, so it has six valence electrons. It forms two covalent (σ) bonds and so has four ($6 - 2$) unused electrons. Therefore, there are two bond pairs and two lone pairs around the sulfur atom. This means that a tetrahedral arrangement of electron pairs produces the least repulsion between the electron pairs. The two chlorine atoms are arranged in a bent (v-shaped, non-linear) shape around the sulfur atom.

c

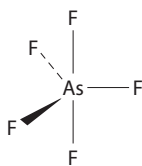


The phosphorus atom, $[\text{Ne}] 3s^2 3p^3$, is bonded to one oxygen atom by a double ($\sigma + \pi$) bond and to the other three oxygen atoms by single bonds. It forms five bonds, so there are no lone pairs.

There are four sets of electrons around the phosphorus atom. These repel each other to a position of maximum separation. Therefore, the ion has a tetrahedral shape.

- e When counting the number of electron pairs around the central atom, count a double ($\sigma + \pi$) bond as one set. Thus the number of σ -bonds and lone pairs determines the electron arrangement around the central atom. In this example there are four σ -bonds and no lone pairs, so the electron arrangement is tetrahedral.

d



Arsenic is in the same group of the periodic table as phosphorus. Therefore, it has five valence electrons. One 4s-electron is promoted into an empty 4d-orbital and all five electrons are used in bonding to the five fluorine atoms. Thus, there are no lone pairs. The five (bonding) pairs of electrons repel each other and the molecule has the shape of a trigonal bipyramid.

e Practise drawing this awkward shape.

e



Carbon is in group 4 of the periodic table and has four valence electrons. All these electrons are used in bonding (one σ -bond to the hydrogen atom and one σ - and two π -bonds to the nitrogen, making a total of four bonds). Therefore, there are no lone pairs on the carbon. The two sets of electrons repel each other and the molecule is linear.

e For all questions about shapes of molecules or ions you must first work out the number of valence (outer shell) electrons on the central atom, the number of bonds and hence the number of lone pairs. This gives you the arrangement of the electron pairs. The lone pairs are 'invisible' but repel the bond pairs and so affect the shape of the molecule or ion.

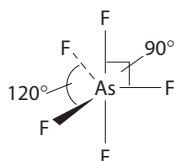
3 a The bond angle in the PH_3 trigonal pyramid is less than 109.5° (the tetrahedral angle). This is because of the greater repulsion between a lone pair and a bond pair than between two bond pairs.

e The bond angle might be expected to be the same as in ammonia (107°), but, for complex reasons, it is less than this.

b The bond angle in the non-linear SCl_2 molecule is considerably less than the tetrahedral angle. This is because of the strong lone pair–lone pair repulsion. The angle is similar to that in water, which is 104.5° .

c The bond angle in the tetrahedral PO_4^{3-} ion is 109.5° .

d



The bond angles in the trigonal bipyramidal AsF_5 molecule are 120° between the fluorine atoms and the arsenic atom in the triangular plane, and 90° between the top or bottom fluorine atom and those in the plane.

e The bond angle in the linear HCN molecule is 180° .

4 a The bond is polar, with the iodine atom being δ^+ and the chlorine atoms δ^- . This is because chlorine is more electronegative than iodine and draws the bonding electrons towards itself. Iodine has two lone pairs of electrons, so the molecule is not trigonal planar and, therefore, has a dipole moment.

- b** Fluorine is the most electronegative element and so is δ^- and the less electronegative oxygen is δ^+ .
- The shape of this molecule is bent because of the two lone pairs on the oxygen atom. Therefore, the molecule is polar.
- e** This is the only bond in which the oxygen atom is δ^+ and, therefore, oxygen has a positive oxidation number.
- c** Oxygen is more electronegative than carbon, so the C=O bonds are polar with the carbon atom δ^+ and the oxygen atoms δ^- . However, as the molecule is linear and so symmetrical, the polarities cancel out and the molecule is non-polar.
- d** Carbon and iodine both have electronegativities of 2.5, so the bond is non-polar. The C–H bond is polar as carbon is more electronegative than hydrogen, which becomes δ^+ . As the molecule is not symmetrical, it is polar.
- 5 a** The small radius and high electronegativity of the nitrogen atom result in the formation of hydrogen bonds between ammonia molecules. Instantaneous induced dipole forces (dispersion forces) are also present.
- b** Methane is non-polar, so the only intermolecular forces are dispersion forces.
- c** Oxygen fluoride is very polar, but does not contain hydrogen and so cannot form hydrogen bonds. Its intermolecular forces are permanent dipole–dipole forces and dispersion forces.
- e** All molecules have dispersion forces between them. Hydrogen bonds are a special type of permanent dipole–dipole forces.
- 6** Both hydrogen fluoride and hydrogen chloride are very polar molecules containing a δ^+ hydrogen atom and a δ^- halogen atom. However, a chlorine atom is too big to form a hydrogen bond with a δ^+ hydrogen in another molecule. Only very small atoms, such as fluorine, oxygen and nitrogen, can form hydrogen bonds with δ^+ hydrogen atoms.
- 7 a** Solid chlorine is a simple molecular substance.
- b** Vanadium is a metallic solid, with a delocalised cloud of electrons between vanadium ions.
- c** Lithium fluoride is ionic.
- d** Glucose is a hydrogen-bonded molecular solid. The δ^+ hydrogen atoms in the –OH groups form intermolecular hydrogen bonds with the δ^- oxygen atoms in other molecules.
- e** Silicon tetrachloride is a simple molecular substance.
- 8 a** In graphite, each carbon atom forms three σ -bonds with three other carbon atoms in the same plane. The fourth $2p$ -electron is in an orbital above and below the hexagonal plane of the carbon atoms. These p -orbitals overlap with their neighbours and the electrons become delocalised. These electrons are mobile and solid graphite conducts electricity by the movement of these electrons under an applied potential. In diamond, each carbon atom is covalently bonded to four others in a giant three-dimensional tetrahedral arrangement. All the electrons are fixed between the atoms and cannot move through the solid. Therefore, diamond does not conduct electricity.
- e** Remember that metals and graphite conduct electricity by a flow of electrons, whereas molten or dissolved ionic compounds conduct by a flow of ions.

- b** Although all the π -electrons in a fullerene molecule are delocalised, they are not connected to neighbouring fullerene molecules and so do not conduct electricity. However, C_{60} polymers do conduct. When C_{60} molecules react with potassium metal, the resulting compound conducts as a solid.
- 9** The fullerene C_{60} has the unusual optical property of being transparent to light of low-to-medium brightness and becoming opaque when the light is intense. It could be used as a coating for sensitive optical devices, allowing low-intensity light through but preventing intense light from damaging the optics of the device.
- or*
- Carbon nanotubes are much stronger than steel. Bundles of these nanotubes are light in weight and incredibly strong. They conduct electricity as efficiently as does copper. They could, therefore, be used in electrical apparatus that has to withstand high tensile forces.
- 10 a** Solid silicon forms a giant atomic lattice similar to diamond. To melt it, a huge amount of energy must be supplied to break the four covalent bonds to each atom. Therefore, the solid has a very high melting temperature (1410°C). Phosphorus is a simple molecular solid, consisting of an arrangement of P_4 molecules. The forces between these molecules are weak dispersion forces. Therefore, less energy, and hence a lower temperature, is needed to separate the P_4 molecules and melt the solid.
- e** When answering questions about melting solids, you should first state the type of solid and the forces that hold the particles together. Then, discuss the relative strength of these forces and relate them to the energy required to separate the particles and break up the solid (lattice) structure.
- b** In solid sodium, there is a cloud of delocalised electrons (a 'sea' of electrons) amongst a lattice of sodium ions. These electrons are not fixed in position and, therefore, are able to move under an applied electric potential. These mobile electrons are the reason why solid sodium conducts electricity. Solid sodium chloride consists of a lattice of alternate sodium and chloride ions, which are fixed in position. The ions cannot move when an electric potential is applied, so solid sodium chloride does not conduct electricity.
- e** In *molten* sodium chloride the ions are free to move and conduct electricity.
- 11** The general trend in boiling temperature from PH_3 to BiH_3 is upward. The intermolecular forces involved are permanent dipole–dipole forces and dispersion forces. As the polarity of the bonds decreases down the group, the permanent dipole–dipole forces decrease slightly. However, as the number of the electrons in the molecules increases from 18 in PH_3 to 86 in BiH_3 , the strength of the dispersion forces increases considerably. Therefore, an increasing amount of energy is required to separate the molecules and boil the substances. Ammonia, NH_3 , is an anomaly. The dispersion forces between ammonia molecules are much weaker than in the other group 5 hydrides. However, because the nitrogen atom is so small and considerably δ^- , it forms hydrogen bonds with the δ^+ hydrogen atoms in neighbouring molecules. These intermolecular hydrogen bonds are much stronger than the dispersion forces, which are the dominant forces in the other hydrides. Therefore, ammonia has an anomalistic high boiling temperature.
- e** When answering questions about boiling, you should first state the type of force between the particles in the substances. Discuss the relative strengths of these forces and relate them to the energy required to separate the molecules.
- 12** Propanone has 32 electrons per molecule and butane has 34. This means that the dispersion forces are almost identical. Propanone is very polar because of the large difference in electronegativity between carbon and oxygen, whereas butane is non-polar. Thus propanone has

significant permanent dipole–dipole intermolecular forces as well as dispersion forces, whereas butane only has dispersion forces. Therefore, more energy is required to separate propanone molecules than is required to separate butane molecules.

13 Hydrogen bromide is more polar than hydrogen iodide, so it has stronger permanent dipole–dipole intermolecular forces. However, the dispersion forces are stronger in hydrogen iodide because it has 54 electrons as opposed to 36 in hydrogen bromide. This increase in the strength of the dispersion forces more than compensates for the decrease in permanent dipole–dipole forces and, therefore, hydrogen iodide has a higher boiling temperature.

- Ⓔ Permanent dipole–dipole forces play little part in the value of the boiling temperature. It has been calculated that the contribution of this force in HCl is about 10% of that of the dispersion force. This is because the molecules are constantly moving around and rotating, so the δ^+ end of one molecule is rarely next to the δ^- end of another molecule. They only become important when comparing polar and non-polar molecules that have a similar number of electrons (see Question 12).

14 The solubility of a covalent molecular substance in water depends mostly on the strength of the hydrogen bonds that are formed with the water molecules. The nitrogen in ammonia, NH_3 , is δ^- and has a lone pair of electrons. Therefore, it forms a hydrogen bond with a δ^+ hydrogen atom in a water molecule. The δ^+ hydrogen atoms in an ammonia molecule form hydrogen bonds with δ^- oxygen atoms in water molecules. The energy released by the formation of these hydrogen bonds compensates for breaking the intermolecular hydrogen bonds between ammonia molecules and those between water molecules.

The δ^- chlorine atom in chloromethane is too large to form hydrogen bonds. The hydrogen atoms in chloromethane are not sufficiently δ^+ and are not bonded to an electronegative atom. Thus chloromethane cannot form hydrogen bonds with water molecules. Therefore, it is insoluble in water.

- Ⓔ It is a common misconception that polar solvents, such as water, dissolve polar solutes. The dipole–dipole forces are too weak to compensate for the disruption of the hydrogen bonding between water molecules.

15 The energy cycle for an ionic solid dissolving is:

- ionic solid \rightarrow separate gaseous ions (endothermic and equal to $-\text{lattice energy}$)
- gaseous ions bonding with water molecules \rightarrow solution (exothermic as with all bond formation)

If these factors balance, the ionic solid dissolves. Magnesium, Mg^{2+} , ions are small and highly charged, so they bond strongly with the δ^- oxygen atoms in water. The Cl^- ions bond to the δ^+ hydrogen atoms. Each magnesium ion is bonded to six water molecules. Enough energy is released in the formation of this hydrated ion, and the hydrated chloride ion, to compensate for the large lattice energy value.

16 Hydrogen bonding makes a substance water-soluble. Large residues, particularly of benzene rings, render a substance lipid-soluble.

A molecule of aspirin has one $-\text{COOH}$ group and a large residue. The $-\text{COOH}$ group forms hydrogen bonds with water molecules, making it water-soluble and insoluble in lipids. The benzene ring cannot form hydrogen bonds with water and the ester group does so only weakly, making it insoluble in water but lipid-soluble. The result of these opposing factors is that aspirin is slightly soluble in both water and lipids.

Ibuprofen has a $-\text{COOH}$ group and a long hydrocarbon tail. This makes it less water-soluble but significantly more lipid-soluble.

Chapter Summary Worksheet (textbook CD-ROM)

- 1 The answer is C. Sulfur is in group 6, so it has six valence electrons. Two are used in bonding (one to each hydrogen), so there are two lone pairs. Therefore, there are two bonding pairs and two lone pairs. These four electron pairs arrange themselves in a tetrahedron, which means that the bonding pairs are not linear and the molecule is V-shaped.

e Do not confuse the distribution of electrons — tetrahedral — with the shape of the molecule. It is the relative position of the *atoms* that determines the shape.
- 2 The answer is C. Sulfur forms three double bonds, one with each of the oxygen atoms. Therefore, all six valence electrons are used in bonding, so there are no lone pairs. The three pairs of σ -bonding electrons repel to a position of maximum separation, which is trigonal planar.
- 3 The answer is B. Xenon has eight electrons in its outer orbit. Four of these are used in bonding, one to each fluorine atom. Therefore, there are four electrons remaining, so there are two lone pairs.
- 4 The answer is A. All four compounds have polar bonds, but compounds B, C and D are symmetrical, so the dipoles cancel and the molecules are non-polar.
- 5 The answer is D. There are no intermolecular hydrogen bonds because the chlorine atom is too large to form them. Covalent bonds are strong, but do not occur *between* the molecules of hydrogen chloride. Although the H–Cl bond is polar, the permanent dipole–dipole forces are weaker than the induced (London or dispersion) forces.

e It is a common misconception that permanent dipole forces are stronger than induced (London) forces.
- 6 The answer is B. Fluorine in hydrogen fluoride, HF, is more δ^- than the oxygen in water and it also has a smaller radius. This means that a *single* hydrogen bond between the hydrogen atom in one hydrogen fluoride molecule and the fluorine atom in another is stronger than a *single* hydrogen bond between water molecules. However, there are twice as many intermolecular hydrogen bonds in water.

e Statement D is true but does not answer the question.
- 7 The answer is A. There are no lone pairs around the hydrogen, so the covalent bond pair and the hydrogen bond pair are at 180° to each other.

e The angle around the hydrogen-bonded hydrogen atom is always 180° , even in complex molecules such as DNA and proteins.
- 8 The answer is C. All the statements are true, but only option C explains why graphite is less dense than diamond.

e The packing within the plane in graphite is closer than that in diamond, but the layers in graphite are much further apart than are the bonded atoms in both forms of carbon.
- 9 The answer is A. Diamond is a giant atomic structure with strong covalent bonds between the atoms. Silicon carbide is similar in that each silicon atom is bonded to four carbon atoms and each carbon atom to four silicon atoms. To melt either structure, many strong covalent bonds have to be broken. This only happens at an extremely high temperature.

e Neither diamond nor silicon carbide forms molecules and neither is ionic, so options B, C and D are incorrect.

- 10 The answer is C. Statements A, B and C are all true. However, only the lower number of electrons results in weaker intermolecular forces, which is why C is the correct response.
- e Statement D is incorrect because hydrogen chloride is more polar than hydrogen iodide. This is because chlorine is more electronegative than iodine.
- 11 The answer is A. Butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, has fewer electrons and so has weaker induced forces. Pentane, dimethylpropane and methylbutane (options A, C and D respectively) are isomers and, therefore, have the same number of electrons. The straight-chain pentane has better packing and, hence, stronger intermolecular forces than its branched isomers.

9 Oxidation and reduction: redox

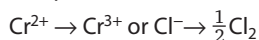
1 a Cr^{2+} to Cr^{3+} is oxidation because the Cr^{2+} ion loses an electron to become a Cr^{3+} ion.

b HI to I_2 is oxidation. The I^- ion in HI loses an electron to become an I atom, which then joins with another I atom to form an I_2 molecule.

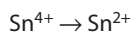
c Sn^{4+} to Sn^{2+} is reduction. The Sn^{4+} ion gains two electrons to become an Sn^{2+} ion.

d Cl^- to Cl_2 is oxidation because each Cl^- ion loses an electron.

e If a species loses an electron, it becomes more positive or less negative. For example:



If a species gains electrons, it becomes less positive. For example:



2 a $\text{Cr}^{2+}(\text{aq}) \rightarrow \text{Cr}^{3+}(\text{aq}) + \text{e}^-$

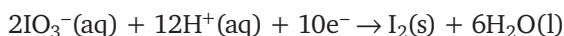
b $2\text{HI}(\text{aq}) \rightarrow \text{I}_2(\text{s}) + 2\text{H}^+(\text{aq}) + 2\text{e}^-$ or $\text{HI}(\text{aq}) \rightarrow \frac{1}{2}\text{I}_2(\text{s}) + \text{H}^+(\text{aq}) + \text{e}^-$

c $\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$

d $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$ or $\text{Cl}^-(\text{aq}) \rightarrow \frac{1}{2}\text{Cl}_2(\text{g}) + \text{e}^-$

e Note that all the equations balance for charge. This is why it helps to put the minus on the symbol for the electron.

3 a $\text{IO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \frac{1}{2}\text{I}_2(\text{s}) + 3\text{H}_2\text{O}(\text{l})$ or



The oxidation number of iodine changes from +5 to 0, so there must be five electrons for each IO_3^- ion. The change is reduction, so the electrons are on the left-hand side of the equation. Six hydrogen ions are needed to form three molecules of water with the three oxygen atoms from the IO_3^- ion. Note that the overall charge on each side of the equation is zero.

b $\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

The oxidation number of manganese changes by two from +4 to +2. Therefore, it is reduced. There must be two electrons on the left-hand side of the equation. Four hydrogen ions are needed to form two molecules of water with the two oxygen atoms from MnO_2 . Note that the overall charge on each side of the equation is +2.

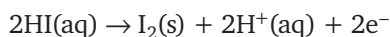
c $\text{VO}_2^+(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

The oxidation number of vanadium in VO_2^+ is +5; $(x + 2 \times (-2) = +1; x = +5)$.

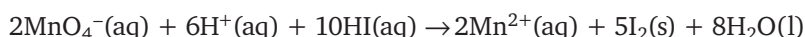
In VO^{2+} , it is +4; $(x + (-2) = +2; x = +4)$.

Therefore, vanadium is reduced. The change in oxidation number is -1, so one electron is needed on the left-hand side of the equation. Two hydrogen ions are required to form one molecule of water with the oxygen atom removed from the VO_2^+ ion.

4 a The two half-equations are:

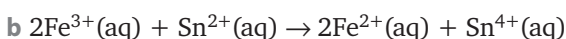
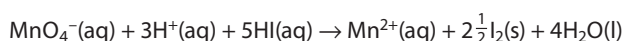


The overall equation is found by multiplying the first equation by 2 and the second equation by 5 and then adding them together:



Manganate(vii) ions are reduced to Mn^{2+} ions, which is a change in oxidation number of five per manganese. The oxidation number of each iodine atom changes by one, so 5HI are needed per MnO_4^- . Two MnO_4^- ions will produce $8\text{H}_2\text{O}$, so the equation needs six hydrogen ions to go with the ten hydrogen atoms from 10HI to form the eight molecules of water. Note that the overall charge on each side is +4.

- e The following equation is also acceptable:

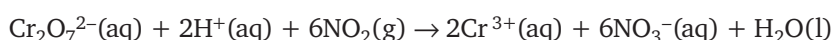


The oxidation number of tin changes by two going from +2 to +4. Therefore, two Fe^{3+} ions are needed to balance the change. Note that the equation balances for charge, both sides being +8.

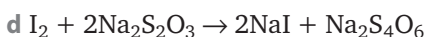
- c The two half-equations are:



The overall equation is found by multiplying the second equation by 6 and then adding it to the first equation:



The dichromate(vi) is in an acid solution to provide H^+ . Dichromate(vi) ions are reduced to Cr^{3+} ions, a change in oxidation number of three per chromium atom or six per $\text{Cr}_2\text{O}_7^{2-}$ ion. The oxidation number of nitrogen changes from +4 in NO_2 to +5 in NO_3^- , so there must be six NO_2 molecules in the equation to balance the change in oxidation numbers. There are 19 oxygen atoms on the left-hand side of the equation, so there must be one water molecule on the right-hand side and, hence, two hydrogen ions on the left. Note that the overall charge on each side is zero.



There are four sulfur atoms in $\text{Na}_2\text{S}_4\text{O}_6$, so $2\text{Na}_2\text{S}_2\text{O}_3$ are needed.

- e You are told the formulae of all the substances, so this is simply an exercise in balancing. You do not need to work out any oxidation numbers.

If you succeeded with these four examples, you are a real expert in redox equations. These examples are considerably harder than those you will meet in the AS exam.

- 5 a The oxidation number of iodine in I_2O_7 is +7.

Each oxygen is -2, so the seven oxygen atoms have a total of -14. Thus each of the two iodine atoms is +7.

- b The oxidation number of iodine in IO_3^- is +5.

The three oxygen atoms each have the oxidation number -2, giving a total of -6. The charge on the ion is -1, so:

$$\begin{aligned} x + 3(-2) &= -1 \\ x + (-6) &= -1 \\ x &= +6 - 1 = +5 \end{aligned}$$

- c** The oxidation number of iodine in KIO_4 is +7.

The oxidation number of potassium is +1; each oxygen is -2, so:

$$\begin{aligned} +1 + x + 4(-2) &= 0 \\ x &= +8 - 1 = +7 \end{aligned}$$

- d** The oxidation number of iodine in $\text{Ba}(\text{IO}_2)_2$ is +3.

The oxidation number of barium is +2, each oxygen is -2, so:

$$\begin{aligned} +2 + 2x + 4(-2) &= 0 \\ 2x &= +8 - 2 = +6 \\ x &= +3 \end{aligned}$$

- 6 a** The vanadium in V^{3+} is in the +3 oxidation state.

- b** The vanadium in VO_2^+ is in the +5 state (see the answer to Question 3c).

- c** The vanadium in VO^{2+} is in the +4 state (see the answer to Question 3c).

- 7 a** The oxidation number of nitrogen in NO_2 is +4.

The oxidation number of each oxygen atom is -2, so two oxygen atoms total -4.

The molecule is neutral, so the oxidation number of nitrogen is +4.

- b** The oxidation number of nitrogen in NO_2^- is +3.

The oxidation number of oxygen is -2, so two oxygen atoms total -4. The ion is -1, so:

$$\begin{aligned} x - 4 &= -1 \\ x &= +3 \end{aligned}$$

- c** The oxidation number of nitrogen in N_2O_5 is +5.

The oxidation number of each oxygen atom is -2, so five oxygen atoms total -10. The molecule is neutral, so:

$$\begin{aligned} 2x - 10 &= 0 \\ 2x &= +10 \\ x &= +5 \end{aligned}$$

- d** The oxidation number of nitrogen in N_2H_4 is -2.

The oxidation number of each hydrogen atom is +1, so four hydrogen atoms total +4. Therefore, the oxidation number of each nitrogen atom is -2.

- 8 a** The oxidation number of bromine in KBr is -1.

In KBrO_3 the oxidation number of bromine is +5.

$$\begin{aligned} +1 + x + 3(-2) &= 0 \\ x &= +6 - 1 = +5 \end{aligned}$$

In Br_2 the oxidation number of bromine is zero.

- b** An oxidising agent is reduced. The oxidation number of bromine changes from +5 in KBrO_3 to zero in Br_2 . The oxidation number has decreased, so the bromine in the KBrO_3 has been reduced. Therefore, KBrO_3 is the oxidising agent. It has oxidised the bromine in KBr from the -1 state to zero.

9 The oxidation number of the carbon atoms in the $\text{C}_2\text{O}_4^{2-}$ ion is +3:

$$2x + 4(-2) = -2$$

so,

$$2x = -2 + 8 = +6$$

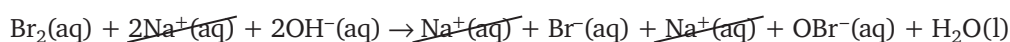
$$x = +3$$

The carbon atom in CO_2 is in the +4 state, so each carbon atom changes by +1. The total change in oxidation number per $\text{C}_2\text{O}_4^{2-}$ ion is +2.

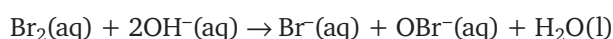
10 The molecular equation is:



Converting this to ions gives:



Cancelling the spectator ions gives the final ionic equation:

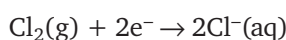


e Water and bromine are not ionic, and so must be written as molecules.

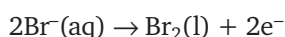
11 $2\text{Cu}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s})$

e There must be two Cu^+ ions on the left-hand side of the equation, so that one can be oxidised to Cu^{2+} and one reduced to Cu.

12 a Chlorine is reduced. The half-equation is:



The bromide ions in NaBr are oxidised. The half-equation is:

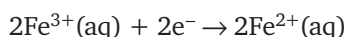


The chlorine gains these electrons, so it is the oxidising agent (becoming reduced to Cl^- ions).

The bromine has given electrons to the chlorine, so the bromide ions are the reducing agent (becoming oxidised to Br atoms, which form Br_2).

e Remember that, in a redox reaction, oxidising agents are reduced and reducing agents are oxidised.

b The iron(III) ions are reduced to iron(II) ions:



The hydrogensulfite(IV) ions, HSO_3^- , are oxidised to sulfate(VI) ions, SO_4^{2-} :



The Fe^{3+} ions have been reduced, so they are the oxidising agent.

The HSO_3^- ions have been oxidised, so they are the reducing agent.



Chapter Summary Worksheet (textbook CD-ROM)

- 1 The answer is C. The oxidation number of tin goes from +2 in SnCl_2 to +4 in SnCl_4 , so tin is oxidised. The oxidation number of iron goes from +3 in FeCl_3 to +2 in FeCl_2 , so iron is reduced. Oxidation plus reduction equals redox.
- e Option A is incorrect because the oxidation number of hydrogen stays at +1 and that of oxygen stays at -2, so there is no redox reaction. Option B is incorrect because the oxidation state of chromium is +6 in both CrO_4^{2-} and in $\text{C}_2\text{O}_7^{2-}$, so there is no redox reaction. Option D is incorrect because the oxidation state of copper is +2 in both CuO and CuSO_4 .
- 2 The answer is C. Note that this is a negative question — ‘is *not* disproportionation’. The copper is reduced from +2 to +1 and oxidised from 0 to +1, but there are two different copper species on the left-hand side of the equation and only one on the right, so it is not a disproportionation reaction. In A, the oxygen in H_2O_2 is in the -1 oxidation state and is simultaneously oxidised to zero in O_2 and reduced to -2 in H_2O . In B, the chlorine in Cl_2 is oxidised to OCl^- (zero \rightarrow +1) and reduced to Cl^- (zero \rightarrow -1). In D, the manganese in MnO_4^{2-} is in the +6 state. It is oxidised to MnO_4^- (+7) and simultaneously reduced to MnO_2 (+4).
- e The reverse reaction, $2\text{CuCl}_2^-(\text{aq}) \rightarrow \text{CuCl}_2(\text{aq}) + \text{Cu}(\text{s}) + 2\text{Cl}^-(\text{aq})$ is a disproportionation.
- 3 The answer is B. Sodium tetrathionate, $\text{Na}_2\text{S}_4\text{O}_6$, is neutral, so the oxidation numbers add up to zero. Each Na is +1, each oxygen is -2, totalling +2 -12 = -10. There are four sulfur atoms, so the oxidation number of each must equal 10 divided by 4, i.e. 2.5.
- 4 The answer is A. The oxidation numbers in potassium superoxide add up to zero and, as it is a superoxide, the oxidation number of oxygen is not -2. (It is also not -2 in peroxides.) The oxidation number of potassium is *always* +1, so the oxidation numbers of the two oxygen atoms must add up to -1. Therefore, the oxidation number of oxygen in potassium superoxide is $-\frac{1}{2}$.
- 5 The answer is A. The oxidation number of manganese changes from +7 to +2, which is a change of five. Therefore, there must be five electrons in the equation. An alternative way to work this out is that the half-equation must balance for charge. The charge on the right-hand side is +2, so that on the left-hand side must also be +2. This is achieved if there are five electrons:

$$1- + 5- + 8+ = 2+$$

10 The periodic table: group 2

1 The first ionisation energy of an element is the energy change when one electron is removed from each atom of a mole of gaseous atoms of that element to form one mole of gaseous singly charged positive ions. The equation for the first ionisation of calcium is:



e Since ionisation energies are always endothermic, the definition can be expressed in terms of the energy required to remove one electron.

2 The nuclear charge increases down the group, but the number of inner shielding electrons increases by the same amount. However, the atomic radius increases down the group. Thus, the outer electrons are further from the nucleus and so are held less firmly. This means that less energy is required to remove a 3s-electron from a magnesium atom than is required to remove a 2s-electron from a beryllium atom. Less still is needed to remove a 4s-electron from a calcium atom and so on.

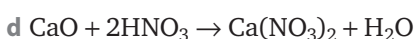
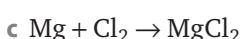
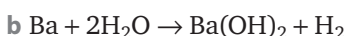
e Do not just say that shielding increases down the group — there is more to shield. The critical point is that the atomic radius increases. The further an electron is from the nucleus, the easier it is to remove.

3 Calcium has atomic number 20 and the electron configuration 2,8,8,2. Potassium has atomic number 19 and the electron configuration 2,8,8,1. In calcium, the nuclear charge of 20 is shielded by 18 inner electrons. In potassium, the nuclear charge of 19 is also shielded by 18 inner electrons. Thus the outer electrons in calcium are less well shielded and are harder to remove. In addition, a calcium atom has a smaller radius than a potassium atom making it even harder to remove one of its outer (4s) electrons.

e Remember that, across a period, the atomic radius *decreases* as the atomic number increases. This is because of the increasing pull of the nucleus on the shells of electrons.

4 The electron configuration of magnesium is $1s^2 2s^2 2p^6 3s^2$. The first ionisation energy is for the removal of one of the 3s-electrons and the second is for the removal of the other 3s-electron, but from a positive ion. This makes the second ionisation energy larger than the first. The 3s-electrons are shielded by the two electrons in the first shell and the eight electrons in the second shell. The third ionisation involves removing an electron from the 2p-subshell. This electron is only shielded by the inner two 1s-electrons. Therefore, it experiences a much stronger pull from the nucleus than the better shielded 3s-electrons. Thus there is a big jump between the second and third ionisation energies.

e A simpler answer, which would just score the marks, would be to state that the third electron comes from an inner shell and so is harder to remove. The explanation above shows *why* it is harder to remove.



e Remember that the valency of all the group 2 elements is 2, so the formula of a group 2 oxide is MO, of a hydroxide is $\text{M}(\text{OH})_2$, of a chloride is MCl_2 and of a nitrate is $\text{M}(\text{NO}_3)_2$, where M stands for a group 2 metal. The final equation is base + acid \rightarrow salt + water.



6 The thermal stability of group 1 nitrates increases down the group. This is because the polarising power of the cation decreases as the ionic radius increases. The lower the polarising power of the cation, the less the electron cloud of the anion is distorted. Thus it is harder to cause decomposition.

- e The ease of decomposition depends on the charge density of the cation. Charge density is loosely defined as the charge on the ion divided by its radius. In this example, all the group 1 cations have a charge of +1, but their radii increase down the group causing a decrease in charge density. In questions that ask for a comparison of the ease of decomposition of a group 1 nitrate with that of the nitrate of the group 2 element in the same period, two factors have to be compared. First, the group 2 cation is 2+ whereas the group 1 cation is 1+. Second, the ionic radius of the group 2 cation is smaller than that of the group 1 cation. These two factors result in the polarising power of the group 2 cation being greater than that of the group 1 cation and make the group 2 nitrate easier to decompose. A similar argument is used to compare the decomposition of carbonates.

$$\begin{aligned} 7 \text{ a amount (moles) of sulfuric acid} &= \text{concentration} \times \text{volume in dm}^3 \\ &= 0.0561 \text{ mol dm}^{-3} \times 0.0250 \text{ dm}^3 = 0.0014025 \text{ mol} \end{aligned}$$

$$\text{amount of sodium hydroxide in titre} = 2 \times 0.0014025 = 0.002805 \text{ mol}$$

$$\begin{aligned} \text{concentration of sodium hydroxide} &= \frac{\text{moles}}{\text{volume in dm}^3} \\ &= \frac{0.002805}{0.02345} = 0.1196 \text{ mol dm}^{-3} \\ &= 0.120 \text{ mol dm}^{-3} \end{aligned}$$

- e This calculation would probably be structured at AS. Remember to divide the volume in cm^3 by 1000 to convert it to a volume in dm^3 . Rounding to three significant figures at each stage gives the answer $0.119 \text{ mol dm}^{-3}$. This would score full marks, but do *not* round to two or one significant figure in a calculation.

$$\begin{aligned} \text{b concentration in g dm}^{-3} &= \text{concentration in mol dm}^{-3} \times \text{molar mass} \\ &= 0.1196 \text{ mol dm}^{-3} \times 40.0 \text{ g mol}^{-1} = 4.78 \text{ g dm}^{-3} \end{aligned}$$

- e Note that the units cancel to g dm^{-3} . If the concentration rounded to three significant figures had been used, the answer would be 4.80 g dm^{-3} .

8 molar mass of ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = 126.0 \text{ g mol}^{-1}$

$$\begin{aligned} \text{amount (moles) of the acid} &= \frac{\text{mass}}{\text{molar mass}} \\ &= \frac{3.05 \text{ g}}{126.0 \text{ g mol}^{-1}} = 0.02421 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{concentration} &= \frac{\text{moles}}{\text{volume in dm}^3} \\ &= \frac{0.02421 \text{ mol}}{0.250 \text{ dm}^3} = 0.0968 \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} 9 \text{ amount (moles) of sodium carbonate} &= \text{concentration} \times \text{volume in dm}^3 \\ &= 0.0525 \text{ mol dm}^{-3} \times 0.0250 \text{ dm}^3 = 0.0013125 \text{ mol} \end{aligned}$$

$$\text{amount (moles) of hydrochloric acid} = 2 \times 0.0013125 = 0.002625 \text{ mol}$$

$$\begin{aligned} \text{volume of acid} &= \frac{\text{moles}}{\text{concentration}} \\ &= \frac{0.002625 \text{ mol}}{0.100 \text{ mol dm}^{-3}} = 0.02625 \text{ dm}^3 = 26.25 \text{ cm}^3 \end{aligned}$$

- e Be careful with units. The volume comes out in dm^3 because the concentration is in mol dm^{-3} .

$$\begin{aligned}
 10 \text{ amount (moles) of hydrochloric acid} &= \text{concentration} \times \text{volume in dm}^3 \\
 &= 0.0050 \text{ mol dm}^{-3} \times 0.00755 \text{ dm}^3 = 3.775 \times 10^{-5} \text{ mol} \\
 &= \text{amount (moles) of potassium hydroxide}
 \end{aligned}$$

$$\begin{aligned}
 \text{mass of potassium hydroxide in } 100 \text{ cm}^3 \text{ of washings} &= \text{moles} \times \text{molar mass} \\
 &= 3.775 \times 10^{-5} \text{ mol} \times 56.1 \text{ g mol}^{-1} \\
 &= 0.002118 \text{ g}
 \end{aligned}$$

$$\text{concentration in ppm} = \frac{1000000 \times 0.002118}{100} = 21 \text{ ppm}$$

- e* In the final step, to obtain an answer in parts per million, the mass of potassium hydroxide must be multiplied by a million divided by the volume. The answer is rounded to two significant figures, because some data were given to two significant figures.

11 a

Element	Divide by r.a.m.	Divide by smallest
Barium	81.1/137.3 = 0.591	0.591/0.591 = 1
Oxygen	18.9/16.0 = 1.18	1.18/0.591 = 2

Therefore the empirical formula is BaO₂.

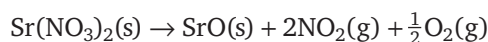
- b** The formula mass of BaO₂ is 169.3. This is the same as the molar mass, so the molecular formula is also BaO₂.

- 12 a When strontium nitrate is heated it first melts. On further heating a brown gas is seen bubbling off from the molten compound.

- e* Oxygen is produced but cannot be seen. Its presence can be detected by the relighting of a glowing splint. The brown gas is nitrogen dioxide.



or



- e* It is not essential to use state symbols because the question did not ask for them. However, they are useful as they identify the gases evolved. This is needed in part c.

- c** molar mass of strontium nitrate, Sr(NO₃)₂ = 211.6 g mol⁻¹

$$\begin{aligned}
 \text{amount (moles) of strontium nitrate} &= \frac{\text{mass}}{\text{molar mass}} \\
 &= \frac{2.12 \text{ g}}{211.6 \text{ g mol}^{-1}} = 0.01002 \text{ mol}
 \end{aligned}$$

there are 2.5 moles of gas per mole of strontium nitrate

$$\text{moles of gas} = 2.5 \times 0.01002 = 0.02504 \text{ mol}$$

volume = moles × molar volume

$$= 0.0250 \text{ mol} \times 24.0 \text{ dm}^3 \text{ mol}^{-1} = 0.601 \text{ dm}^3 = 601 \text{ cm}^3$$

- 13 Both magnesium and calcium ions are 2+. However, a magnesium ion has a smaller radius than a calcium ion. This means that a magnesium ion polarises a carbonate ion more than a calcium ion does. Therefore, magnesium carbonate is easier to decompose than calcium carbonate and does so at a lower temperature.

- e* It is important to write something about both the charges and radii of the two cations. Make sure that you do not use the word 'atom' when you mean 'ion'. This is a common error.



$$\begin{aligned}
 \text{14 amount (moles) of nitric acid, HNO}_3 &= \text{concentration} \times \text{volume} \\
 &= 0.100 \text{ mol dm}^{-3} \times 0.0176 \text{ dm}^3 \\
 &= 1.76 \times 10^{-3} \text{ mol}
 \end{aligned}$$

ratio of $\text{Ba(OH)}_2:\text{HNO}_3$ in the equation = 1:2

$$\text{so, amount of Ba(OH)}_2 = \frac{1}{2} \times 1.76 \times 10^{-3} \text{ mol} = 8.80 \times 10^{-4} \text{ mol}$$

$$\text{concentration of Ba(OH)}_2 = \frac{\text{moles}}{\text{volume}} = \frac{8.80 \times 10^{-4} \text{ mol}}{0.0250 \text{ dm}^3} = 0.0352 \text{ mol dm}^{-3}$$

- e Always start the calculation from the substance about which you have two pieces of data — in this case, the volume and concentration of the acid.

$$\begin{aligned}
 \text{15 amount (moles) of H}_3\text{PO}_4 &= \text{concentration} \times \text{volume} \\
 &= 0.100 \text{ mol dm}^{-3} \times 0.0250 \text{ dm}^3 = 0.00250 \text{ mol}
 \end{aligned}$$

ratio of $\text{NaOH}:\text{H}_3\text{PO}_4$ = 3:1

$$\text{so, amount of NaOH} = 3 \times 0.00250 \text{ mol} = 0.00750 \text{ mol}$$

$$\begin{aligned}
 \text{volume of NaOH solution} &= \frac{\text{moles}}{\text{concentration}} \\
 &= \frac{0.00750 \text{ mol}}{0.202 \text{ mol dm}^{-3}} = 0.0371 \text{ dm}^3 = 37.1 \text{ cm}^3
 \end{aligned}$$

$$\begin{aligned}
 \text{16 a amount (moles) of HCl in titration} &= \text{concentration} \times \text{volume} \\
 &= 0.110 \text{ mol dm}^{-3} \times 0.02335 \text{ dm}^3 \\
 &= 0.00257 \text{ mol}
 \end{aligned}$$

b ratio $\text{NaOH}:\text{HCl}$ = 1:1

$$\text{so, amount (moles) of NaOH in } 25.0 \text{ cm}^3 \text{ of diluted solution} = \text{amount (moles) HCl} = 0.00257 \text{ mol}$$

$$\text{c amount (moles) of NaOH in } 250 \text{ cm}^3 \text{ of diluted solution} = 10 \times 0.00257 \text{ mol} = 0.0257 \text{ mol} = \text{amount (moles) of NaOH in excess}$$

$$\begin{aligned}
 \text{d amount (moles) of NaOH originally taken} &= \text{concentration} \times \text{volume} \\
 &= 1.00 \text{ mol dm}^{-3} \times 0.0500 \text{ dm}^3 \\
 &= 0.0500 \text{ mol}
 \end{aligned}$$

$$\begin{aligned}
 \text{e amount (moles) of NaOH reacted with ibuprofen tablets} \\
 &= \text{amount taken} - \text{amount in excess} \\
 &= 0.0500 \text{ mol} - 0.0257 \text{ mol} = 0.0243 \text{ mol}
 \end{aligned}$$

f Ibuprofen and NaOH react in a 1:1 ratio. So, amount of ibuprofen in 25 tablets = amount of NaOH reacted = 0.0243 mol

$$\text{g amount (moles) of ibuprofen in 1 tablet} = \frac{0.0243}{25} \text{ mol} = 9.72 \times 10^{-4} \text{ mol}$$

$$\begin{aligned}
 \text{molar mass of ibuprofen, C}_{12}\text{H}_{17}\text{COOH} &= [(12 \times 12.0) + 17.0 + 12.0 + (2 \times 16.0) + 1.0] \\
 &= 206.0 \text{ g mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \text{mass of ibuprofen in 1 tablet} &= \text{moles} \times \text{molar mass} \\
 &= 9.72 \times 10^{-4} \text{ mol} \times 206.0 \text{ g mol}^{-1} \\
 &= 0.200 \text{ g} = 200 \text{ mg}
 \end{aligned}$$

- e This question is about a back titration. If such a question is asked at AS, it will be structured in a similar way to this one. However, you must have a clear idea of the different experimental stages:
- adding excess sodium hydroxide
 - after the reaction, making the solution up to 250 cm³
 - titrating portions of this diluted solution, containing excess sodium hydroxide, with standard acid



Chapter Summary Worksheet (textbook CD-ROM)

- 1 The answer is A. The most polarising cation is the one with the highest charge and the smallest radius. All these group 2 cations are 2+ and the ionic radius increases down the group. Therefore, Mg^{2+} is the most polarising.

e In questions about trends in a group, the answer will always be about the top or the bottom member — option A or D.
- 2 The answer is A. The more the anion is polarised, the greater is the covalent character of the compound. The Mg^{2+} ion is the most polarising, so MgCl_2 has the most covalent character.
- 3 The answer is D. All four metals have the same number of delocalised electrons, so the relative strengths of the metallic bonds depend mainly on the metallic radius. The metallic radius of magnesium is the smallest, so it has the strongest metallic bond. The metallic radius of barium is the largest, so it has the weakest metallic bond and, therefore, the lowest melting temperature.

e The type of packing also affects the melting temperature. However, this is less important than the charge and the metallic radius, and it is ignored at A-level.
- 4 The answer is A. Solubility is a balance between lattice energy and the sum of the hydration energies of the ions. Both the lattice energy and the hydration energy of the cations decrease down the group. However, because the hydroxide ion is of a similar size to the cations, the lattice energy decreases more and this causes the enthalpy of solution to be more exothermic (or less endothermic). Therefore, the hydroxides of the lower members of the group are more soluble.

e The lattice energy depends on the sum of the ionic radii. Therefore, it alters markedly when the cation and the anion are of similar size (e.g. with hydroxides). Thus solubility increases down the group. If the anion is much bigger than the cation (e.g. with sulfates), the decrease in the lattice energy is much less and solubility decreases down the group.
- 5 The answer is A. Only the nitrate of the most strongly polarising group 1 cation decomposes on heating to form the metal oxide, nitrogen dioxide and oxygen. Nitrates with less polarising cations decompose to the nitrite and oxygen. All the group 1 cations are 1+. Of these, lithium has the smallest ionic radius and so is the most strongly polarising. Therefore, on heating, lithium nitrate decomposes giving off brown fumes of nitrogen dioxide. When nitrates of the less polarising cations are heated, they do not produce brown fumes.

e The equations are:
$$2\text{LiNO}_3 \rightarrow \text{Li}_2\text{O} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 \quad \text{and} \quad \text{KNO}_3 \rightarrow \text{KNO}_2 + \frac{1}{2}\text{O}_2$$
- 6 The answer is D. The nitrate of the most polarising group 2 cation decomposes the most easily; that of the least polarising cation is the hardest to decompose and requires a higher temperature. Barium, Ba^{2+} , is the least polarising of the group 2 cations, so barium nitrate takes the longest time to produce brown fumes of nitrogen dioxide.

e Notice that the correct answers to these six multiple-choice questions about trends in a group are either the top element in the group or the bottom one — option A or D.
- 7 The answer is C. Methyl orange is yellow in alkaline solution, red in acid solution and a mixture of red and yellow — orange — when in neutral solution. In this example, the alkali is in the conical flask. Therefore, the colour at the start of the titration is yellow and becomes orange at the end point.

e If the indicator turns red, the end point has been overshoot, which is why option D is incorrect. If the alkali were in the burette and acid in the conical flask, the correct answer would be B.

8 The answer is B. The initial titre has an accuracy of $\pm 0.05 \text{ cm}^3$. The final reading is also accurate to $\pm 0.05 \text{ cm}^3$, making the total potential error $\pm 0.10 \text{ cm}^3$.

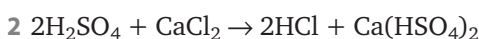
This makes the maximum percentage error $\frac{0.10 \times 100}{8.00} = 1.25\%$

11 The periodic table: group 7



b It is a disproportionation reaction. The chlorine, oxidation number zero, is oxidised to +1 in ClO^- and simultaneously reduced to -1 in Cl^- .

e This is a reaction that must be known. The reaction is with alkali, so the K^+ ions are spectator ions. Oxygen is more electronegative than chlorine, so the chlorine is in a positive oxidation state in the ClO^- ion.



e The equation forming the sulfate rather than the hydrogensulfate is also acceptable:
 $\text{H}_2\text{SO}_4 + \text{CaCl}_2 \rightarrow 2\text{HCl} + \text{CaSO}_4$

An observation is that steamy fumes are given off.

e Do not state as an observation that hydrogen chloride is given off — you can't tell by looking that the fumes are hydrogen chloride — or that the fumes are white. The latter indicates confusion with the result of adding ammonia to the steamy fumes. The reaction is similar to that of concentrated sulfuric acid with a group 1 chloride, such as sodium chloride.

3 Steamy fumes mixed with a brown gas would be seen. Three gases are produced:

- hydrogen bromide — the steamy fumes
- bromine — the brown gas
- sulfur dioxide — colourless, so is not observed

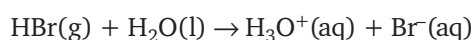
e This answer is the same as that for the reaction of concentrated sulfuric acid on sodium bromide.

4 Bromine is a brown gas or fuming brown liquid. It turns a solution of potassium iodide red-brown.

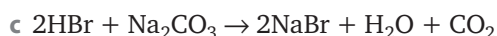
e Bromine also turns damp starch-iodide paper dark blue. Remember that the test paper must be *damp*. A mark is often lost because this is omitted.

5 a Gaseous hydrogen bromide is covalently bonded.

b Covalent hydrogen bromide reacts with water to produce ions:



These ions are hydrated and the energy released on hydration is greater than that required to break the H-Br covalent bond. Thus the reaction is energetically favourable and so hydrogen bromide dissolves in water. The solution is acidic because H_3O^+ ions are produced.



e Acids liberate carbon dioxide when added to carbonates.

6 a The oxidation number of iodine in KIO_3 is +5.

$$+1 + x + 3(-2) = 0$$

$$x = +6 - 1 = +5$$

The oxidation number of iodine in KI is -1.

$$+1 + x = 0$$

$$x = -1$$

The oxidation number of iodine in I_2 is zero.



b The iodide ions in KI are oxidised from -1 to zero. Therefore, potassium iodide is the reducing agent.

e Remember that in a redox reaction, a reducing agent becomes oxidised.

c Add a solution of starch, which will turn dark blue-black in the presence of iodine.

7 The first electron affinity requires an electron to be brought towards the positive nucleus of a neutral atom and into the outer orbit. This is an exothermic process. More energy is released the nearer an electron approaches the nucleus. Bromine has a smaller atomic radius than iodine, so the electron gets closer to the bromine nucleus than it does to the iodine nucleus. Therefore, more energy is released and the electron affinity is higher.

e The sign in thermochemistry gives the direction of the heat change. A more negative value means a bigger heat change.

8 One method is to dissolve the solid, add aqueous silver nitrate and observe the precipitate. Then add dilute ammonia. If the precipitate does not dissolve in dilute ammonia, concentrated ammonia is then added. Possible observations are:

- a white precipitate that is soluble in dilute ammonia. This indicates calcium chloride.
- a cream precipitate that does not dissolve in dilute ammonia but is soluble in concentrated ammonia. This indicates calcium bromide.
- a pale yellow precipitate that does not dissolve in either dilute or concentrated ammonia. This indicates calcium iodide.

A second method is to add concentrated sulfuric acid to the solid. Possible observations are:

- copious steamy fumes. This indicates calcium chloride.
 - steamy fumes mixed with a brown gas. This indicates calcium bromide.
 - clouds of violet vapour and a gas that smells of rotten eggs. A yellow deposit is left. This indicates calcium iodide.
- e** In each case, a hydrogen halide is first produced. Hydrogen chloride is such a weak reducing agent that it does not reduce the sulfuric acid. Hydrogen bromide is a stronger reducing agent and is partially oxidised to brown bromine vapour. Hydrogen iodide is a very strong reducing agent and is totally oxidised to iodine by the sulfuric acid, which is itself reduced to a mixture of yellow sulfur and hydrogen sulfide.

9 a $\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$

e As the iodine is reduced, the electrons are on the left-hand side of the equation. The oxidation number of each iodine atom is decreased by one. Therefore, two electrons are needed on the left-hand side of the equation.

b $\frac{1}{2}\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{ClO}^- + 2\text{H}^+ + \text{e}^-$

e As the chlorine is reduced, the electrons are on the right-hand side of the equation. The oxidation number of a chlorine atom is increased by one. Therefore, one electron is needed on the right-hand side of the equation.

c $\text{ClO}^- + 2\text{H}_2\text{O} \rightarrow \text{ClO}_3^- + 4\text{H}^+ + 4\text{e}^-$

e The oxidation number of chlorine changes from $+1$ to $+5$. Therefore, four electrons are needed on the right-hand side of the equation.

d $\text{ClO}^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O}$

e The oxidation number of chlorine changes from $+1$ to -1 . Therefore, two electrons are needed on the left-hand side of the equation.



Cancelling electrons, H⁺ and H₂O gives:



- e The equation was obtained by multiplying the answer to part d by two and then adding this equation to the answer to part c. In this way, the electrons cancel.

Remember that reduction half-equations always have electrons on the left-hand side; oxidation half-equations always have electrons on the right-hand side.

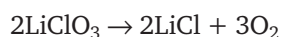
- 10 Chlorine is the stronger oxidising agent. It oxidises a solution of potassium bromide to bromine. The solution changes from colourless to brown. Iodine does not oxidise potassium bromide to bromine. Therefore, on mixing the two solutions, there is no colour change.

11 a

Element	Divide by r.a.m.	Divide by smallest
Lithium	7.75/6.9 = 1.12	1.12/1.11 = 1.0
Chlorine	39.25/35.5 = 1.11	1.11/1.11 = 1
Oxygen	53.0/16.0 = 3.31	3.31/1.11 = 3.0

The empirical formula is LiClO₃.

- b The molecular formula is also LiClO₃. The equation is:



$$\text{amount (moles) of oxygen} = \frac{\text{volume}}{\text{molar volume}} = \frac{1.77 \text{ dm}^3}{24 \text{ dm}^3} = 0.0738 \text{ mol}$$

$$\text{moles of LiClO}_3 = \text{moles of O}_2 \times \frac{\text{number of LiClO}_3 \text{ in equation}}{\text{number of O}_2 \text{ in equation}}$$

$$\text{so, amount (moles) of LiClO}_3 = 0.0738 \times \frac{2}{3} = 0.0492 \text{ mol}$$

$$\text{molar mass of LiClO}_3 = 6.9 + 35.5 + (3 \times 16.0) = 90.4 \text{ g mol}^{-1}$$

$$\text{mass of LiClO}_3 = \text{moles} \times \text{molar mass} = 0.0492 \text{ mol} \times 90.4 \text{ g mol}^{-1} = 4.45 \text{ g (or 4.44 g if the numbers were not rounded during any stage of the calculation)}$$

- e Remember that it is essential that the units of volume and molar volume are the same, i.e. *either* dm³ or cm³.

12 a amount (moles) of thiosulfate = concentration \times volume in dm³
 $= 0.133 \text{ mol dm}^{-3} \times 0.02645 \text{ dm}^3 = 0.003518 \text{ mol}$

b amount of iodine reacted with sodium thiosulfate = $\frac{1}{2} \times 0.003518 = 0.001759 \text{ mol}$

amount (moles) Fe³⁺ in 25 cm³ of solution = $2 \times 0.001759 = 0.003518 \text{ mol}$

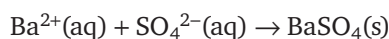
c amount (moles) Fe³⁺ in 250 cm³ of solution = $10 \times 0.003518 = 0.03518 \text{ mol}$

d mass of iron in sample = moles \times molar mass = $0.03518 \text{ mol} \times 55.8 \text{ g mol}^{-1} = 1.963 \text{ g}$

e percentage of iron in compound X = $\frac{1.963 \text{ g} \times 100}{16.95 \text{ g}} = 11.6\%$

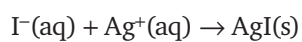
- e Always give intermediate answers to one more significant figure than the number of significant figures (usually three) justified in your answer.

- 13 The flame test shows that Z is a barium compound. This was confirmed by the formation of a white precipitate when dilute sulfuric acid was added:





The second test on the solution shows that Z contains iodide ions:



Silver iodide is a pale yellow solid that is insoluble in both dilute and concentrated ammonia.

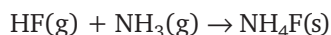
Therefore, the solid Z is barium iodide, BaI_2 .

- e In justifying your answer you must make sure that you use all the pieces of experimental evidence given in the question.



Chapter Summary Worksheet (textbook CD-ROM)

- 1 The answer is D. Hydrogen fluoride is a gas. It reacts with the base ammonia to form a smoke of solid ammonium fluoride in a similar way to the other hydrogen halides.



- e Hydrogen fluoride is a weaker acid than hydrogen chloride because the H–F bond is stronger than the H–Cl bond. It is the most difficult hydrogen halide to oxidise and does not react with concentrated sulfuric acid. None of the hydrogen halides disproportionates in water, although the elements chlorine and bromine do.

- 2 The answer is C. The chlorine in OCl^- is reduced from oxidation number +1 to zero and the chlorine in Cl^- oxidised from oxidation number –1 to zero. The chlorine on the left-hand side of this equation is in two different species, so the reaction cannot be disproportionation.

- e Option D is incorrect because the definition of synthesis is ‘making a compound from simpler species’. The term has been expanded to cover a series of reactions that make a desired product, for example in photosynthesis. Neither applies to the reaction in this question.

- 3 The answer is B. The oxidation numbers in a neutral compound add up to zero. The oxidation number of sodium is always +1 and that of oxygen is –2 (except in oxygen fluoride, peroxides and superoxides):

$$\text{so, } (2 \times +1) + (6 \times -2) = -10$$

The oxidation number of the four sulfur atoms must add up to +10, so the oxidation number of sulfur in $\text{Na}_2\text{S}_4\text{O}_6$ is $+\frac{10}{4} = +2.5$.

- 4 The answer is B. Beware — this is a negative question. Option B is false (and therefore the correct answer) because the electronegativities decrease down the group, so the electronegativity difference between the hydrogen and the halogen is less in HI than in HBr.

- e It is worth checking the other responses, unless you are totally sure that you have selected the correct answer. This is particularly important in negative questions such as this. Statement A is true because the oxidising power decreases from fluorine to astatine. Statement C is true because the reducing power of the anions increases down the group (as the oxidising power of the elements decreases). Statement D is also true — silver chloride is soluble in dilute ammonia, so it also dissolves in concentrated ammonia.

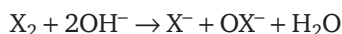
- 5 The answer is B. Iodine is present at the start and, when the colour has faded to pale straw, starch is added and an intense blue colour is produced. Sodium thiosulfate is then added dropwise until the blue colour disappears.

- e The starch must not be added too early otherwise a solid black complex is formed irreversibly with the iodine.

- 6 The answer is C. Do not confuse steamy fumes of the hydrogen halides (HF, HCl, HBr and HI) with the white smoke that is produced when a gaseous hydrogen halide is mixed with ammonia gas. Thus the answer is not option A. Concentrated sulfuric acid reacts with ionic bromides, such as silver bromide, to give steamy fumes of hydrogen bromide (together with some red–brown bromine gas and colourless sulfur dioxide).

- e The substances given in option B would produce bromine, which is a red–brown volatile liquid. Those in option D would react to form a colourless solution.

- 7 The answer is D. It is the halogens (apart from fluorine), *not* the hydrogen halides that react with alkali in disproportionation reactions:



Thus statement D is false and is the correct answer to this negative question.

④ Hydrogen bromide is oxidised by chlorine dissolved in water to give a brown solution of bromine. It reacts with silver ions to give a cream precipitate of silver bromide. Its intermolecular (dispersion/London/van der Waals) forces are stronger than those of hydrogen chloride, so it has a higher boiling point. Therefore, options A, B and C are all true statements.

8 The answer is A. It is essential that all the oxidising agent reacts, so excess potassium iodide is added to a measured volume of the solution of the oxidising agent. Option C is ambiguous. Which reaction?

12 Introduction to kinetics

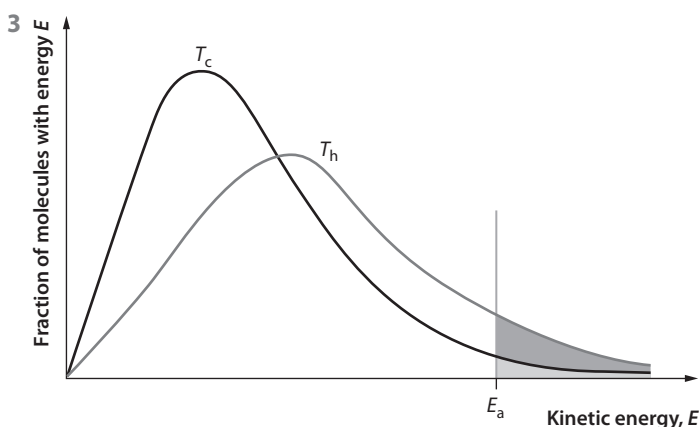
1 The main points of the collision theory are that:

- the molecules must collide
- ⓔ The rate depends on the frequency of collisions.
- for the collision to result in reaction, the energy of the colliding molecules must be equal to or greater than a specific value — the activation energy
- ⓔ Only a few collisions result in reaction. An increase in temperature causes an increase in this proportion. Reactions with high activation energy are slow at room temperature. They may even be too slow to be observed. The reactants are then said to be kinetically stable.
- the molecules must collide with the correct relative orientation

2 a The rate of an exothermic reaction is increased by an increase in temperature.

b The rate of an endothermic reaction is also increased by an increase in temperature.

- ⓔ Raising the temperature increases the rate of all reactions. For reversible reactions, the rate in the endothermic direction is increased more than the rate in the exothermic direction.



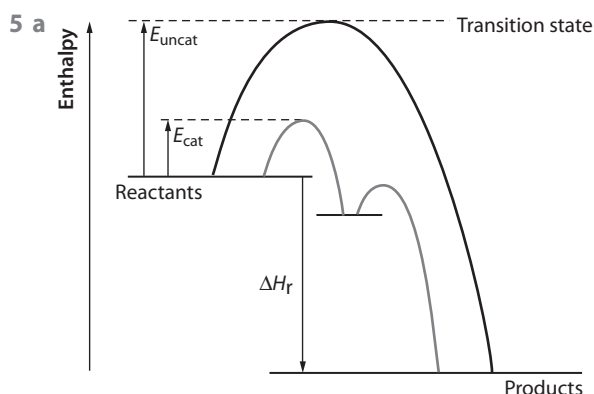
A decrease in temperature decreases the average kinetic energy of the molecules. Therefore, the area under the curve to the right of the activation energy is smaller for the T_c curve than for the T_h curve. This means that a smaller *proportion* of collisions have the necessary activation energy to result in reaction, so the reaction rate is slower. There is also a slight reduction in the frequency of collision, but this effect is swamped by the reduction in the proportion of successful collisions.

- ⓔ The crucial points are that:
 - the molecules have less energy
 - fewer colliding molecules have energy \geq activation energy (area under the curve to the right of the activation energy value)
 - a smaller *proportion* of the collisions result in reaction
 - the rate is slower

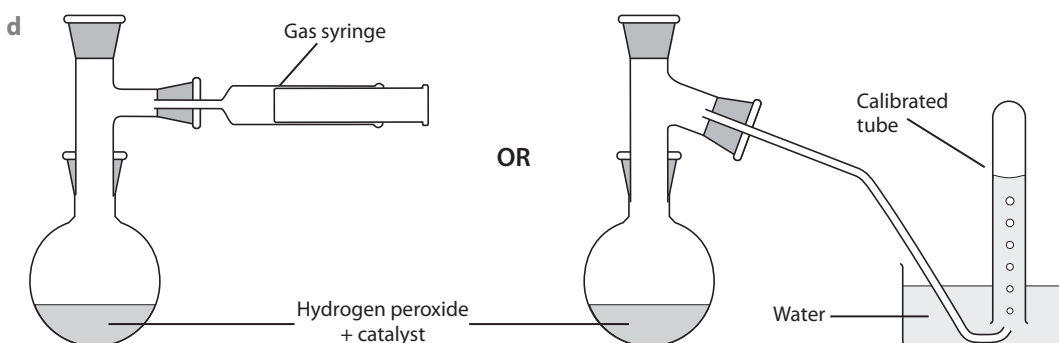
4 a Halving the volume results in the molecules being much closer together, so the frequency of collision increases. This results in a faster reaction, i.e. an increased reaction rate.

b The addition of more hydrogen increases the rate because the probability of a hydrogen molecule colliding with an iodine molecule is increased. It is the increase in the frequency of $\text{H}_2\text{-I}_2$ collisions that results in an increase in the rate.

- e Do not talk about *more* collisions, but about the increase in the *frequency* of collision or more collisions *per unit time*.



- b A heterogeneous catalyst is in a different phase from the reactants; a homogeneous catalyst is in the same phase as the reactants.
- c Platinum is a solid and hydrogen peroxide is in solution. They are in different phases, so platinum is a heterogeneous catalyst in this reaction.
- e Mixtures of solids can be in separate phases (e.g. salt and sand). Miscible liquids (ethanol and water) form a single phase; immiscible liquids (petrol and water) are in two phases. Gaseous mixtures are always in a single phase.



Measurements taken:

- mass of platinum and mass of an equal number of moles of manganese(IV) oxide
- in each case, time taken to produce a given volume of oxygen, e.g. 40 cm³

rate of reaction is proportional to $\frac{1}{\text{time}}$

$$\frac{\text{rate with platinum}}{\text{rate with manganese(IV) oxide}} = \frac{\text{time for manganese(IV) oxide}}{\text{time for platinum}}$$

6 a amount (moles) of magnesium = $\frac{\text{mass}}{\text{molar mass}}$

$$= \frac{0.06 \text{ g}}{24.3 \text{ g mol}^{-1}} = 0.0025 \text{ mol}$$

amount (moles) of acid = concentration \times volume in dm³

$$= 1.00 \text{ mol dm}^{-3} \times 0.025 \text{ dm}^3 = 0.025 \text{ mol}$$

b amount of acid reacted = 2 \times moles magnesium = 2 \times 0.0025 = 0.005 mol

$$\begin{aligned} \text{c percentage of acid reacted} &= \frac{\text{change} \times 100}{\text{original}} \\ &= \frac{0.005 \times 100}{0.025} = 20\% \end{aligned}$$

d i There is a large change in the amount of acid (and hence, because the volume remains constant, a large percentage change in concentration). This causes the rate to alter considerably during the time of the measurement, which means that in this instance the assumption that rate is proportional to $1/t$ is not very accurate.

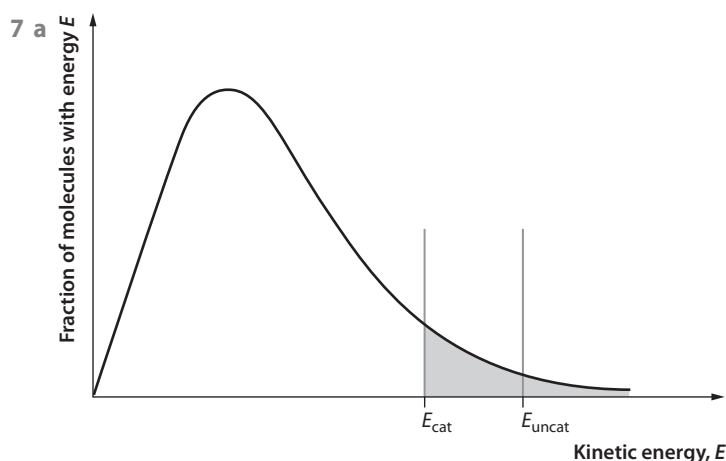
ii Take a larger volume of acid (50 cm^3 would mean a 10% change in concentration of the acid during the reaction).

or

Increase the initial concentration of the acid (a 2.0 mol dm^{-3} solution would mean a 10% change in concentration).

Either of these changes would make the assumption that rate is proportional to $1/t$ fair, because the rate would not change by more than 10% during the course of the experiment.

e The reaction is exothermic, so the temperature rises as the magnesium reacts. This alters the reaction rate. Increasing the volume of acid to 50 cm^3 would halve the temperature rise and so reduce the error caused by the exothermic nature of the reaction. Doubling the concentration would have no effect on the temperature rise.



The catalyst causes the reaction to go via a different route that has lower activation energy. The area under the curve to the right of E_{cat} is greater than that to the right of E_{uncat} . This means that a greater proportion of the colliding molecules have at least this smaller amount of energy. Therefore, more of the collisions result in reaction, so the rate increases.

e The Maxwell–Boltzmann distribution used to explain catalysis has one curve and two activation energies. To describe the effect of temperature, there are two curves and one activation energy.

b The platinum catalyst used in catalytic converters contains active sites where the catalysed reactions take place. The lead in this type of petrol would irreversibly bind to these sites, thus ‘poisoning’ the catalyst.

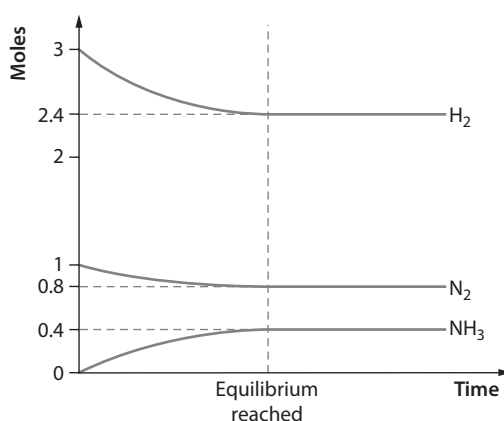


Chapter Summary Worksheet (textbook CD-ROM)

- 1 The answer is B. Remember that this is a negative question. A rise in temperature always increases the rate of reaction, so option A is a true statement and is not the correct answer. Neither reactant is a gas, so an alteration in pressure does not alter the rate. Therefore, statement B is false and is the correct answer. Addition of a catalyst and an increase in concentration both cause an increase in reaction rate, so statements C and D are also true and cannot, therefore, be correct answers in the context of this negative ('would *not* alter') question.
- 2 The answer is C. Pressure has no effect on the rate because the reactant calcium hydrogen-carbonate is in solution. This eliminates options A and B. Lowering the concentration and lowering the temperature both result in a decreased reaction rate, so C is the correct response.
- 3 The answer is B. A shorter time requires a faster rate. Smaller lumps of solid have a larger surface area resulting in an increase in rate. This highlights options B and C as potential answers. Option B is the correct response because the acid is more concentrated and the temperature higher than in option C. Each of these factors causes an increase in reaction rate and, hence, a shorter reaction time.
- 4 The answer is D. This is another negative question. Adding argon at constant volume will not alter the chances of a sulfur dioxide molecule colliding with an oxygen molecule and so will have no effect on the rate. Response D is false and so is the correct answer to this negative question.
 - e Decreasing the volume causes the frequency of collision to increase and increase the reaction rate. Option A is a true statement. Increasing the temperature results in more colliding molecules having energy $\geq E_a$. These molecules are more likely to react on collision, thus increasing the rate. A catalyst provides an alternative path with a lower activation energy. This results in more successful collisions, thus increasing the rate.
- 5 The answer is B. The faster the reaction, the lower is the activation energy.
 - e Statement C is not true. Many exothermic reactions (e.g. that between hydrogen and oxygen) are so slow that they do not occur at room temperature — the reactants are kinetically stable. Statement D is not true. A catalyst lowers the activation energy by providing an alternative route. It has no effect on the kinetic energy of the molecules. Only an increase in temperature causes an increase in kinetic energy.

13 Introduction to chemical equilibrium

- 1 a When the system has reached dynamic equilibrium, the rate of the forward reaction producing sulfur trioxide is exactly the same as the rate of the back reaction of sulfur trioxide decomposing into sulfur dioxide and oxygen. The term 'equilibrium' means that there is no change in the concentrations of any of the three substances over time. The term 'dynamic' means that both the forward and the back reactions are taking place at the same rate.
- b The state of dynamic equilibrium is reached when the rate of dissolving solid sodium chloride is equal to the rate at which sodium and chloride ions join to form solid sodium chloride. Once equilibrium has been established, the concentration of dissolved salt does not change.
- e The dynamic nature of this process is why the many tiny crystals gradually turn into a smaller number of slightly larger crystals on standing. Heating speeds up the process. Some precipitates consist of such tiny crystals that they pass through a filter paper. They can be filtered effectively if the suspension is allowed to stand or is heated.
- 2 At the start there is no ammonia. The amount of the ammonia rises as the amounts of hydrogen and nitrogen fall. When the system reaches equilibrium, there is no further change in the amounts of any of the substances.



- e The amounts of hydrogen and nitrogen decrease by 20%. Therefore, at equilibrium there will be 0.8 mol of N₂ and 2.4 mol of H₂ (0.8 × 3). 2 mol of NH₃ are formed from 1 mol of N₂, so 0.4 mol (2 × 0.2) of ammonia will be present at equilibrium.
- 3 To produce nickel metal from the complex, the position of the equilibrium has to be driven to the left. The reaction as written is exothermic, so the reverse (right-to-left) direction is endothermic. In order to drive the equilibrium in the endothermic direction, the temperature must be increased.
- e Remember that an increase in temperature drives a reversible reaction in the endothermic direction, and a decrease in temperature drives it in the exothermic direction. You should make it very clear in your answer that the reverse direction is endothermic. Avoid phrases such as 'an increase in temperature favours the endothermic direction'. An increase in temperature 'favours' (increases the rate of) both the forward and the reverse reaction. However, it increases the rate of the endothermic reaction more than that of the exothermic reaction, which is why the position shifts in the endothermic direction.
- 4 This esterification reaction is neither exothermic nor endothermic, so a change of temperature has no effect on the equilibrium position.
- e An increase in temperature speeds up the rate at which equilibrium is reached. This is why this reaction is always heated.



5 A decrease in temperature increases the solubility of the carbon dioxide. Therefore, lowering the temperature drives the position of equilibrium to the right. This is because the forward reaction is exothermic.

- e It may be easier to consider the effect of increasing temperature. This makes the carbon dioxide less soluble, so the position shifts to the left. The right-to-left direction is endothermic, so ΔH for the reaction as written is negative (exothermic).

6 Manufacturing processes require a high equilibrium yield that is obtained quickly at low cost.

The reaction is endothermic, so increasing the temperature would increase the yield. However, too high a temperature results in added expense because of heat loss and the corrosive effect of high-temperature steam. The extra cost of a temperature higher than 750°C would not be recovered by the slightly higher yield and faster rate. A catalyst is used so that equilibrium is reached rapidly at an economic temperature, i.e. the yield per hour of product is high enough to make the process economically viable.

- e In this example, rate and yield are both improved by an increase in temperature. No compromise temperature (rate versus yield) is needed.

7 This reaction is exothermic. However, it is very slow at ordinary temperatures. Increasing temperature would increase the reaction rate but reduce the yield at equilibrium. The compromise conditions are to use a catalyst, which makes the reaction fast enough at a moderate temperature (420°C) but does not reduce the yield too much. A lower temperature would result in the catalyst being ineffective because the rate would be too slow; a higher temperature would mean a faster rate, but a lower equilibrium yield. This would cause pollution problems with unreacted sulfur dioxide being released into the atmosphere, as well as being an uneconomic use of sulfur.

- e The Haber process and this reaction in the manufacture of sulfuric acid are both examples of the use of a compromise temperature. This is necessary because the processes are exothermic:
 - low temperature — good yield, poor rate
 - high temperature — good rate, low yield
 - compromise temperature — reasonable rate, reasonable yield

8 An increase in pressure drives the position of equilibrium to the side of the equation that has fewer gas molecules or moles.

a There are three gas molecules on the right and two on the left. An increase in pressure drives the equilibrium to the left.

b There are two gas molecules on the right and one on the left. An increase in pressure drives the position of equilibrium to the left, reducing the yield of hydrogen.

- e The C does not count as it is a solid and not a gas.

c There are nine gas molecules on the left and ten on the right. An increase in pressure drives the position of equilibrium to the left.

d There are one-and-a-half moles of gas on the left and one on the right. An increase in pressure drives the equilibrium to the right.

- e A good answer to this type of question will:
 - state the theory
 - count the moles or molecules of gas on each side (or state which is the endothermic direction for questions about an increase in temperature)
 - state the direction in which the position of equilibrium moves



- 9 a** On heating a mixture at equilibrium, the position of equilibrium shifts in the endothermic direction. In this example, the position shifts to the left. Therefore, the direction from right to left is endothermic and the reaction as written is exothermic. ΔH for the reaction of iodine monochloride with chlorine is negative.
- b** An increase in pressure drives the equilibrium to the side with fewer gas molecules. In this example, the left-hand side has one gas molecule and the right-hand side has none, so the position of equilibrium is driven to the right. This results in a higher percentage of iodine trichloride in the equilibrium mixture.
- e** Make sure that you answer the question. In this case it asks for the change in the equilibrium mixture *not* the change in the equilibrium position.
- c** The red-brown iodine monochloride would melt. The colour of the equilibrium mixture would become increasingly red-brown and less orange as the position of equilibrium shifts in the endothermic direction (to the left).
- 10** Adding concentrated hydrochloric acid greatly increases the concentration of chloride ions. Therefore, the position of equilibrium moves to the right, resulting in more lead chloride dissolving as it forms PbCl_4^{2-} ions.
- e** This is an example of the application of Le Chatelier's principle. As the concentration of one of the reactants is increased, the equilibrium shifts to remove the extra reactant added. Similarly, if one of the products of a reversible reaction is removed (e.g. by precipitation or neutralisation), the equilibrium shifts to the right to produce more product.



Chapter Summary Worksheet (textbook CD-ROM)

- 1 The answer is A. When an equilibrium mixture is heated, the position of equilibrium moves in the endothermic direction. In this example, this is from left to right. Therefore, the colour changes from pink (the hydrated ion) to blue (the chloro complex ion).
- 2 The answer is D. There are four gas molecules on each side of the equation, so a change in pressure has no effect on the equilibrium position. Therefore, options A and B are incorrect. The reaction is exothermic, so the temperature has to be lowered to drive the position of equilibrium in the endothermic direction. This means that option D is the correct answer.
- 3 The answer is A. The Pb^{2+} ions react with the CrO_4^- ions to form a precipitate of lead chromate(vi). The removal of the CrO_4^- ions causes the equilibrium position to shift to the right. This produces more CrO_4^- ions which react with more Pb^{2+} ions. This continues until all the Pb^{2+} ions are precipitated as yellow lead chromate(vi).
 - e D is wrong because there are enough CrO_4^{2-} ions in the equilibrium mixture to form a precipitate with lead ions. Lead chromate(vi), PbCrO_4 , is yellow not orange, so option B is incorrect.
- 4 The answer is C. An increase in temperature causes the equilibrium position to shift to the left (the endothermic direction). Therefore, less ammonia is present in the equilibrium mixture. However, equilibrium is reached faster, so less ammonia is made more quickly, i.e. option C.
 - e An increase in temperature increases the rate of both the exothermic and endothermic reactions, so option A is incorrect. Catalysts (apart from enzymes) work better at higher temperatures, so option B is also incorrect. Note that an increase in temperature increases the rate of the reaction in the endothermic direction more than it increases the rate in the exothermic direction. This is one explanation of why the equilibrium position shifts in the endothermic direction when the temperature is increased.

14 Further organic chemistry

1 a The electronegativity of carbon is 2.5. Chlorine is the most electronegative of the three halogens, with an electronegativity of 3.0. Therefore, the C–Cl bond is the most polar. All the molecules are asymmetrical, but as the C–Cl bond is the most polar, chloromethane is the most polar molecule.

e Electronegativity values would be given in an exam.

b Fluorine is the most electronegative element, so the C–F bond is more polar than the C–O bond or the O–H bond. Therefore, fluoromethane is more polar than methanol.

2 Solubility of an organic compound in water depends upon its ability to form hydrogen bonds with water molecules. Fluoromethane does not have any δ^+ hydrogen atoms, whereas the hydrogen of the –OH group in methanol is very δ^+ . Both molecules have small δ^- atoms, but the lack of δ^+ hydrogen in fluoromethane means that it is insoluble.

e An incorrect rule is that polar molecules dissolve in polar solvents such as water. The solute has to disrupt hydrogen bonds between water molecules, so equally strong (or stronger) solute–solvent interactions must be present. Thus, organic molecules that can hydrogen bond with water — rather than polar molecules such as CH_3F — will dissolve in water, as long as they do not have a long hydrophobic chain.

3 Ethanol and methanol form intermolecular hydrogen bonds of almost identical strength. In addition, both substances have instantaneous induced dipole–induced dipole (dispersion) forces between their molecules. These forces are stronger in ethanol than in methanol because ethanol has more electrons per molecule. The combined intermolecular forces are stronger in ethanol and so more energy is required to separate its molecules. Therefore, ethanol has a higher boiling temperature than methanol.

e Boiling simple covalent molecules is nothing to do with covalent bond strength because no covalent bonds are broken. All substances have dispersion forces between their molecules.

4 1-bromo-2-methylpropane, $\text{CH}_3\text{CH}(\text{CH}_3)_2\text{CH}_2\text{Br}$, forms:

a 2-methylpropan-1-ol, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$, with aqueous potassium hydroxide

b methylpropene, $(\text{CH}_3)_2\text{C}=\text{CH}_2$, with ethanolic alkali

c 1-amino-2-methylpropane, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$, with concentrated ammonia

5 The hydrolysis requires the carbon–halogen bond to be broken as the nucleophilic OH^- ion attacks the carbon atom. The carbon–iodine bond is weaker than the carbon–chlorine bond, so it breaks more easily. Therefore, hydrolysis of 2-iodopropane has a lower activation energy and so occurs at a faster rate.

e The C–I bond is weaker than C–Cl because the atomic radius of iodine is larger than that of chlorine. Remember: weak bond = small activation energy = fast rate.

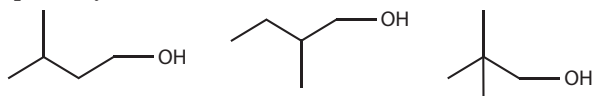
6 One common halogenated polymer is poly(chloroethene) or PVC. It has many uses, including window frames, drain pipes and guttering, and electrical insulation of wires. Like most man-made polymers it is non-biodegradable. Therefore, it can accumulate in landfill sites and, if discarded, can cause permanent litter.

Another example is PTFE, which is used as a coating on non-stick cooking utensils. It produces toxic fumes when disposed of by incineration.

- e Its stability to rainwater (even acid rain) and bacterial action are important properties of PVC. This is why, unlike wooden frames, UPVC window frames do not need the protection of regular painting.

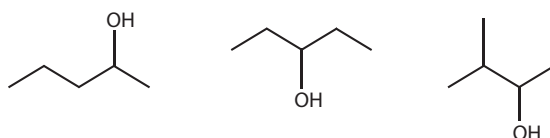
The lack of biodegradability is not caused by the strength of the bonds in the polymer. Natural polymers, such as proteins and carbohydrates, contain very strong bonds, but enzymes have evolved that catalyse their hydrolysis.

- 7 a $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ and $(\text{CH}_3)_3\text{CH}_2\text{OH}$ are examples of branched-chain primary alcohols. Their skeletal formulae are:



- b $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ is an example of an unbranched primary alcohol.

- c $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ and $(\text{CH}_3)_2\text{CHCH}(\text{OH})\text{CH}_3$ are examples of secondary alcohols. Their skeletal formulae are:



- d $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{CH}_3$ is an example of a tertiary alcohol.

- e Primary alcohols contain the CH_2OH group, secondary alcohols the $\text{CH}(\text{OH})$ group and tertiary alcohols have no hydrogen atoms on the carbon of the $\text{C}-\text{OH}$ group.

- 8 Shake a sample of each with bromine water. Hexene will decolorise it from brown to colourless, whereas hexanol and hexanoic acid will have no effect.

Add phosphorus pentachloride to samples of the remaining two liquids. Both will give steamy fumes. Next, add a solution of sodium hydrogencarbonate to samples of these two liquids. Only the hexanoic acid will give off bubbles of gas that turn limewater cloudy. Alternatively both liquids can be tested with damp blue litmus paper. Hexanol will have no effect but hexanoic acid will turn it red.

- e Remember that phosphorus pentachloride gives steamy fumes of hydrogen chloride with *any* compound containing an $-\text{OH}$ group — it is not specific to alcohols.

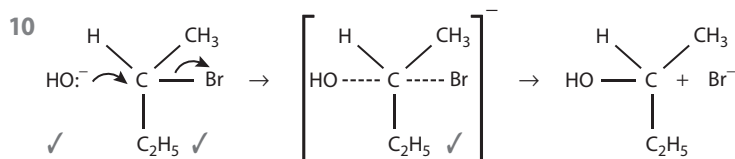
- 9 When heated under reflux with dilute sulfuric acid and potassium dichromate(vi), the organic substance remaining is:

- a the carboxylic acid $\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$ (from the primary alcohol)

- b the unchanged tertiary alcohol $\text{C}_2\text{H}_5\text{C}(\text{OH})(\text{CH}_3)_2$

- c the ketone $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$ (from the secondary alcohol)

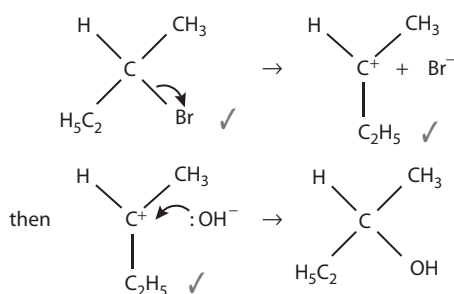
- e In reactions a and c, the solution changes from orange ($\text{Cr}_2\text{O}_7^{2-}$ ions) to green (Cr^{3+} ions). In b, it remains orange.



- e Marks for a mechanism such as this are for:

- a curly arrow from the oxygen of OH^- towards the carbon (on the opposite side to the bromine atom)
- a curly arrow from the $\sigma\text{-C}-\text{Br}$ bond to the bromine atom
- the negatively charged transition state showing partial bonds between the oxygen of the OH group and the carbon atom and between the carbon and bromine atoms

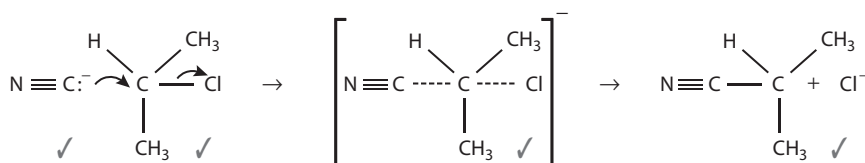
An alternative mechanism is:



- e The marks are for:
- a curly arrow from the σ -C-Br bond to the bromine atom
 - the intermediate carbocation
 - a curly arrow from the oxygen of the OH^- ion towards the positively charged carbon in the intermediate

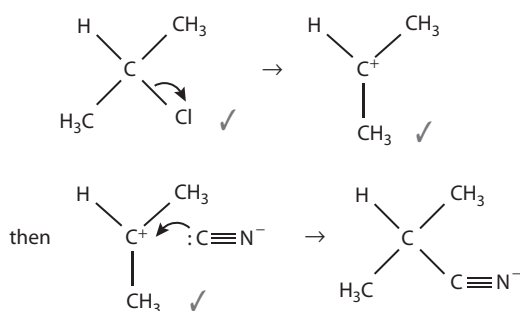
Either mechanism would score full marks.

11



- e Marks for a mechanism such as this are for:
- a curly arrow from the carbon atom of the CN^- ion towards the carbon (on the opposite side to the chlorine atom)
 - a curly arrow from the σ -C-Cl bond to the chlorine atom
 - the negatively charged transition state showing partial bonds between the carbon of the CN group and the central carbon atom and between the central carbon and chlorine atoms

An alternative mechanism is:



- e The marks are for:
- a curly arrow from the σ -C-Cl bond to the chlorine atom
 - the intermediate carbocation
 - a curly arrow from the carbon of the CN^- ion towards the positively charged carbon in the intermediate

You are not expected to know this mechanism, but you should be able to work it out from your knowledge of the mechanism of the reaction of a halogenoalkane with hydroxide ions. Either mechanism would score full marks.

- 12 2-iodopentane has a long hydrocarbon chain, which makes it almost insoluble in water. Therefore, there will be little contact between it and the OH^- ions from the aqueous sodium hydroxide. The organic substance is more soluble in aqueous ethanol and can, therefore, come into contact with the hydroxide ions.

13 The chloroalkane also contains hydrogen. The percentage of hydrogen is:

$$100 - (37.2 + 55.0) = 7.8\%$$

Element	Divide by r.a.m.	Divide by smallest
Carbon	$37.2/12.0 = 3.1$	$3.1/1.55 = 2.0$
Chlorine	$55.0/35.5 = 1.55$	$1.55/1.55 = 1.0$
Hydrogen	$7.8/1.0 = 7.8$	$7.8/1.55 = 5.0$

The empirical formula is C_2H_5Cl .

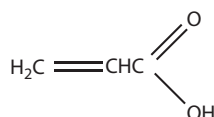
14 a

Element	Divide by r.a.m.	Divide by smallest
Carbon	$50/12.0 = 4.17$	$4.17/2.78 = 1.5$
Hydrogen	$5.6/1.0 = 5.6$	$5.6/2.78 = 2.0$
Oxygen	$44.4/16.0 = 2.78$	$2.78/2.78 = 1.0$

The empirical formula is $C_3H_4O_2$.

e The ratio calculated is 1.5:2:1, which is a whole number ratio of 3:4:2.

b The compound turns bromine water colourless, so it must contain a C=C bond. It is a carboxylic acid and, therefore, contains the $-COOH$ group. The simplest structural formula is:



Propenoic acid

15 a

Element	Divide by r.a.m.	Divide by smallest
Carbon	$53.3/12.0 = 4.44$	$4.44/2.23 = 1.99$
Hydrogen	$11.1/1.0 = 11.1$	$11.1/2.23 = 4.98$
Oxygen	$35.6/16.0 = 2.23$	$2.23/2.23 = 1$

The empirical formula of X is C_2H_5O .

e The error leading to 4.98 is caused by rounding up. The empirical formula $C_{199}H_{498}O_{100}$ is ridiculous.

b empirical mass = $(2 \times 12) + 5 + 16 = 45$

$$\frac{\text{molar mass}}{\text{empirical mass}} = \frac{90}{45} = 2$$

molecular formula mass = $2 \times$ empirical formula mass

molecular formula of X = $C_4H_{10}O_2$

c amount (moles) of X taken = $\frac{9.0 \text{ g}}{90 \text{ g mol}^{-1}} = 0.10 \text{ mol}$

$$\text{amount (moles) of HCl gas produced} = \frac{\text{volume}}{\text{molar volume}} = \frac{4.8 \text{ dm}^3}{24 \text{ dm}^3 \text{ mol}^{-1}} = 0.20 \text{ mol}$$

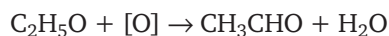
ratio of HCl:X = 2:1

Therefore, there are two $-OH$ groups per molecule of X. Thus, one structure for X is $CH_2OHCH_2CH_2CH_2OH$. Others are $CH_2OHCH(OH)CH_2CH_3$, $CH_2OHCH_2CH(OH)CH_3$, $(CH_3)_2C(OH)CH_2OH$ and $CH_2OHCH(CH_3)CH_2OH$.



e Substance X cannot be a carboxylic acid, as one $-COOH$ group would give rise to only 1 mole of HCl.

16 In the equation, there is a 1:1 ratio of ethanol to ethanal.



$$\text{amount (moles) of ethanol} = \frac{\text{mass}}{\text{molar mass}} = \frac{5.67 \text{ g}}{46 \text{ g mol}^{-1}} = 0.123 \text{ mol}$$

$$\text{theoretical yield of ethanal} = 0.123 \text{ mol} = 0.123 \text{ mol} \times 44 \text{ g mol}^{-1} = 5.41 \text{ g}$$

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 = \frac{4.88 \text{ g}}{5.41 \text{ g}} \times 100 = 90.2\%$$

- e The calculation can be done by mass ratios or by first calculating the moles of ethanol. The percentage yield of ethanal is given by:

$$100 \times \frac{\text{actual moles of ethanal}}{\text{theoretical moles of ethanal}}$$

The percentage yield is *not* $100 \times \frac{\text{mass of product}}{\text{mass of reactant}}$, which is a common error.

17 amount (moles) of 2-chloropropane = $\frac{\text{mass}}{\text{molar mass}} = \frac{78.5 \text{ g}}{78.5 \text{ g mol}^{-1}} = 1.00 \text{ mol}$

$$\text{amount of propene produced} = 30\% \text{ of } 1.00 \text{ mol} = 0.30 \text{ mol}$$

$$\text{amount of 2-iodopropane produced} = 90\% \text{ of } 0.30 \text{ mol} = 0.27 \text{ mol}$$

$$\text{mass of 2-iodopropane produced} = \text{mol} \times \text{molar mass}$$

$$= 0.27 \text{ mol} \times 170 \text{ g mol}^{-1} = 46 \text{ g}$$

18 molar mass of glyceryl tristearate = $(57 \times 12) + (110 \times 1) + (6 \times 16) = 890 \text{ g mol}^{-1}$

$$\text{amount (moles)} = \frac{100 \text{ g}}{890 \text{ g mol}^{-1}} = 0.112 \text{ mol}$$

$$\text{theoretical amount (moles) of sodium stearate (soap)} = 3 \times 0.112 \text{ mol} = 0.336 \text{ mol}$$

- e 1 mol of the fat produces 3 mol of soap.

$$\text{molar mass of sodium stearate} = (18 \times 12) + 35 + (2 \times 16) + 23 = 306 \text{ g mol}^{-1}$$

$$\text{theoretical mass of sodium stearate produced} = 0.336 \text{ mol} \times 306 \text{ g mol}^{-1} = 103 \text{ g}$$

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} = \frac{87.1 \text{ g}}{103 \text{ g}} \times 100 = 84.6\%$$

- e In an exam, you would be given the molar mass of glyceryl tristearate.

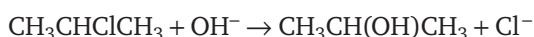


Chapter Summary Worksheet (textbook CD-ROM)

1 The answer is C. A nucleophile is either a negative ion or an atom in a molecule that has a lone pair of electrons that can be used to form a dative bond. H_3O^+ is a positive ion and is, therefore, an electrophile. So option C is false and is the correct answer to this negative question.

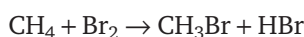
- e There is a lone pair of electrons on the nitrogen of the NH_2 group of CH_3NH_2 and on the oxygen of water. The iodide ion, I^- , is a negative ion with four lone pairs of electrons. These three substances are nucleophiles.

2 The answer is B. The reaction is:



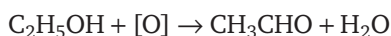
This is a substitution reaction. The attacking reagent is an OH^- ion. This is a nucleophile, so the reaction is nucleophilic substitution.

3 The answer is A. The overall reaction is:

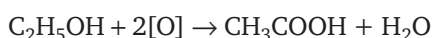


This is a substitution reaction. Ultraviolet light is needed to split bromine molecules into bromine radicals, so the mechanism is free radical.

4 The answer is D. The reaction is:



or if heated under reflux:



Both are oxidation reactions.

5 The answer is C. The reaction is:

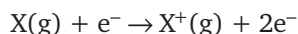


There is only one product, so this is an addition reaction. The propene is attacked by the δ^+ hydrogen in HBr. This accepts a pair of electrons from the π -bond in propene and is, therefore, an electrophile. The reaction is electrophilic addition.

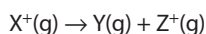
6 The answer is C. Acidified potassium dichromate is an oxidising agent and will oxidise primary and secondary alcohols (and aldehydes), but not tertiary alcohols (or ketones). Ethanol (option A) is a primary alcohol. Butan-2-ol (option B) and hexan-2-ol (option D) are secondary alcohols and so are oxidised. 2-methylpropan-2-ol, $\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)_2$, is a tertiary alcohol and so will not reduce dichromate(vi) ions to green Cr^{3+} ions.

15 Mass spectra, infrared spectra and the greenhouse effect

- 1 a** Positive ions are produced in a mass spectrometer by bombardment of gaseous atoms or molecules with fast-moving (high-energy) electrons:



- e** The positive ion often breaks into two fragments, one charged and one neutral:



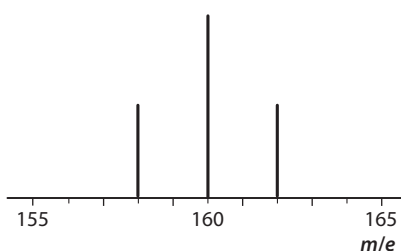
The X^+ ion is called the molecular ion. The m/e value of the Z^+ ion is less than that of the molecular ion by the mass of the neutral particle Y .

- b** The ions are accelerated towards the negative terminal of a cathode and pass through a hole in the cathode.
- c** The ions are deflected by a magnetic field perpendicular to the direction in which they are moving. Lighter ions are deflected more than heavier ions.

- 2** The peak at 74 is due to the molecular ion. The peak at 29 could be due to either $C_2H_5^+$ or CHO^+ . The $C_2H_5^+$ ion cannot be formed from either X or Y; CHO^+ could be formed from either. However, the peak at 31 is due to a CH_2OH^+ ion, which can only come from Y. Substance X would produce peaks at 15, due to CH_3^+ , and at 59, due to $CH(OH)CHO^+$. The absence of these two peaks confirms that the unknown substance is Y.

- e** You must answer the question fully by explaining all the peaks present and giving reasons why the other two peaks are absent.

- 3** The mass spectrum of molecular bromine is represented below:



There are two ways of obtaining a mass of 160: $^{79}\text{Br}-^{81}\text{Br}$ and $^{81}\text{Br}-^{79}\text{Br}$. Therefore, the peak at $m/e = 160$ is twice the height of that at 158, caused by $(^{79}\text{Br}-^{79}\text{Br})^+$, and that at 162, caused by $(^{81}\text{Br}-^{81}\text{Br})^+$.

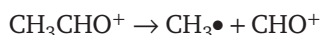
- e** The 1:2:1 ratio is similar to that obtained when tossing two coins at once. The chances of two heads, a head and a tail and two tails are in the ratio 1:2:1.

There are also two peaks at $m/e = 79$ and 81, caused by $^{79}\text{Br}^+$ and $^{81}\text{Br}^+$, formed from the decomposition of a molecular ion, but none at $m/e = 80$ as there is no ^{80}Br isotope.

- 4 a** The peak at $m/e = 29$ is due to the CHO^+ ion.

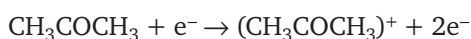
- e** It cannot be due to $C_2H_5^+$.

b The equation for the formation of this ion is:

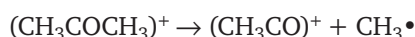


e Remember that the molecular ion decomposes into at least two fragments, one which is positively charged and one which is a neutral free radical.

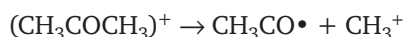
5 The molar mass of propanone, CH_3COCH_3 , is 58 g mol^{-1} . The peak at $m/e = 58$ is caused by the molecular ion $(\text{CH}_3\text{COCH}_3)^+$, which is formed by the process:



The peak at $m/e = 43$ is 15 units less than the molecular-ion peak. It is caused by the ion $(\text{CH}_3\text{CO})^+$ formed by the loss of CH_3 from the molecular ion:



The peak at $m/e = 15$ is due to a CH_3^+ ion, also formed by fragmentation of the molecular ion:



e A common error is to omit the positive charge on the ions whose m/e values are detected.

6 The energy of 1 photon is given by:

$$E = h\nu = 6.63 \times 10^{-34} \text{ Js} \times 5.7 \times 10^{14} \text{ s}^{-1} = 3.78 \times 10^{-19} \text{ J}$$

energy per mole of photons = Avogadro constant \times energy of 1 photon

$$= 6.02 \times 10^{23} \text{ mol}^{-1} \times 3.78 \times 10^{-19} \text{ J} = 228\,000 \text{ J mol}^{-1}$$

$$= 228 \text{ kJ mol}^{-1}$$

e The unit of frequency is Hz, which is measured by the number of peaks per second. Therefore, the unit is also s^{-1} .

$$\begin{aligned} \text{7 Energy needed to break one Cl-Cl bond} &= \frac{\text{bond energy in kJ mol}^{-1}}{\text{Avogadro constant}} \\ &= \frac{242 \text{ kJ mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 4.02 \times 10^{-22} \text{ kJ} = 4.02 \times 10^{-19} \text{ J} \\ &= \text{energy of 1 photon} = h\nu \end{aligned}$$

$$\begin{aligned} \text{frequency, } \nu &= \frac{\text{energy of 1 photon}}{\text{Planck's constant}} \\ &= \frac{4.02 \times 10^{-19} \text{ J}}{6.63 \times 10^{-34} \text{ Js}} = 6.06 \times 10^{14} \text{ s}^{-1} \end{aligned}$$

e The units of frequency are either s^{-1} or Hz, the values being the same in either unit. The answer to this question could be written as $6.06 \times 10^{14} \text{ Hz}$ or $6.06 \times 10^8 \text{ MHz}$

8 Polar molecules absorb energy in the infrared region of the electromagnetic spectrum. It is because oxygen is more electronegative than hydrogen and because the water molecule is not linear that a water molecule is polar. The light coming from the Sun contains higher frequencies than the infrared radiated by the Earth back towards space. The water vapour absorbs some of this infrared radiation, trapping energy in the atmosphere and so keeping the Earth warm.

e Polar water molecules also absorb in the microwave region, which is why aqueous liquids heat up in a microwave oven.

9 a Anthropogenic means caused directly or indirectly by mankind. Human beings have no input into a natural cause. A forest fire caused by lightning is a natural source of carbon dioxide; mining and burning coal is an anthropogenic cause of carbon dioxide.

- b** The two main anthropogenic sources of oxides of nitrogen are burning fuel at a high temperature in car and aeroplane engines and in the decay of nitrogen-containing chemical fertilisers — for example, ammonium nitrate. A natural source is the combination of nitrogen and oxygen in the air during a thunderstorm or bacterial decay of organic matter in the soil.
- 10** Spectrum A: the peak at wavenumber 1715 cm^{-1} is caused by a C=O bond and the peak at 1421 cm^{-1} by a C–C bond.
- Spectrum B: the peak at wavenumber 1716 cm^{-1} is caused by a C=O bond and the peak at 1416 cm^{-1} by a C–C bond, but the peak at 2986 cm^{-1} is caused by an O–H bond.
- Both propanal and propanoic acid have C=O and C–C bonds, but only propanoic acid has an O–H bond. Thus, spectrum B is that of propanoic acid and spectrum A that of propanal.
- e** The broadness of the peak around 3000 cm^{-1} is caused by the intermolecular hydrogen bonding of the –OH group on one molecule with the >C=O group on another.
- 11** The C–H bonds in the alkyl groups (–CH₃ and –CH₂–) give a peak at around 2900 cm^{-1} , the C=O bond in the ester gives a peak at around 1740 cm^{-1} and the C–C bond in the C₂H₅ group gives a peak at about 1430 cm^{-1} .

Chapter Summary Worksheet (textbook CD-ROM)

- 1 The answer is B. The fragment at $m/e = 29$ could be caused by either a CHO^+ ion or a C_2H_5^+ ion, so look for a molecule that does not have either of these groups.

 - e Note that all four molecules have the same molecular formula — they are isomers.
- 2 The answer is C. Look for a molecule that does not have any polar bonds. The Cl_2 molecule consists of two hydrogen atoms, which have the same electronegativity, so the bond is not polar.
- 3 The answer is B. The four molecules are isomers of molar mass 88.0 g mol^{-1} . Therefore, each has a molecular ion peak at $m/e = 88$. The peak at 45 is due to a COOH^+ ion, so the substance could be either B or C. The peak at 29 is due to a C_2H_5^+ ion, which shows that the compound must be option B. The infrared data are inconclusive. The peak at 3010 cm^{-1} could be due to a C–H bond in an alkene or to a hydrogen-bonded O–H in a carboxylic acid. The peak at 1715 cm^{-1} could be due to the C=O in a carboxylic acid, so it only rules out option A.

 - e If the peak at 3010 cm^{-1} were broad, it would be due to the O–H bond in a carboxylic acid and not to a C–H bond in an alkene.
- 4 The answer is D. This question is straightforward factual recall. As a rough guide, the more complex the molecule, the more ways it has of absorbing infrared radiation and so the higher is its global warming potential.
- 5 The answer is D. There is much more water vapour than there are other greenhouse gases in the air and in clouds. Water vapour is by far the greatest contributor to (natural) global warming.

 - e Anthropogenic carbon dioxide contributes less than 1% to the greenhouse effect.
- 6 The answer is B. Visible light is at a higher frequency and, therefore, a shorter wavelength than the infrared radiation emitted by the Earth.

 - e To be infrared active, a molecule must have at least one polar bond. If the dipoles cancel out, making the molecule non-polar, it would still be infrared active due to asymmetrical stretching. The symmetrical stretching in non-polar carbon dioxide is not infrared active because it does not result in a change in dipole moment. Ozone is not linear because the central oxygen atom has a lone pair of electrons.

16 Green chemistry

1 Advantages of hydrogen as a fuel for motor vehicles include:

- It does not cause pollution at the point of use when used to power a fuel cell. (If burnt in a traditional piston engine, nitrogen oxides are produced by the combination of the nitrogen and oxygen in air at the high temperature of the engine.)
- Its energy per gram is high. However, this is only an advantage if weight is crucial — for example, in a space rocket.

Disadvantages include:

- It cannot be stored as a liquid unless the temperature is kept below -240°C .
- Gaseous hydrogen must be stored in heavy high-pressure tanks.
- Refuelling with either cold liquid hydrogen or gaseous high-pressure hydrogen is dangerous.
- ⓐ Do not say that hydrogen fuel is carbon neutral. The hydrogen has to be manufactured. The two possibilities for manufacture are from methane and steam, which has a high carbon footprint, and by the electrolysis of water. The generation of electricity also has a high carbon footprint.

2 Bioethanol is made from sugar or grain. The processes of growing these crops and transporting them to factories are fuel intensive. Fermentation is exothermic, but the distillation required to obtain ethanol from the dilute solution uses a considerable amount of energy.

3 Transesterification is the conversion of one ester into another, by reacting it with either a carboxylic acid or an alcohol. An example is biodiesel, which is made by reacting vegetable oil (an ester of propane-1,2,3-triol and long-chain acids) with methanol in the presence of an alkaline catalyst. The products are the methyl esters of the acids and propane-1,2,3-triol.

4 The advantage of using algae as a source of biodiesel is that algae are potentially efficient in using the energy from sunlight to produce organic oils. It is also a useful way of utilising wastewater and does not need good agricultural land. The disadvantage is that the method has not yet been developed into a commercially viable process.

5 One reason why wind power is not carbon zero (carbon neutral) is that the manufacture and erection of the aero-generator — either on land farms and especially in offshore wind farms — release a great deal of carbon dioxide from the various processes involved. Another reason is that there must be back-up power stations burning fossil fuels for when the wind does not blow strongly enough to generate sufficient electricity.

6 Very much less electrical energy is used making aluminium from recycled cans than when manufacturing it from bauxite. Bauxite is a non-renewable resource, so recycling cans reduces the amount of the mineral that is used and preserves it for future generations.

7 The atom economy is the percentage of the atoms in the reactants that are converted into the desired product.

8 Plastics made from fossil fuels are not natural products, so enzymes have not evolved that can break them down. This means that they are not biodegradable. The energy from sunlight may cause the polymer to decompose, but this is a photochemical, rather than a biological, process.

9 Burning organic substances that contain chlorine can produce harmful products such as hydrogen chloride and chlorinated dioxins.

- 10 If something is biodegradable, it is broken down by bacteria into simpler molecules. A biodegradable plastic contains a filler such as starch. Enzymes break down this filler. The plastic becomes a powder, which occupies less space in a landfill site.
- 11 A free radical is a species, usually neutral, that has an unpaired electron. Examples are a chlorine atom, $\text{Cl}\cdot$, and a methyl radical, $\text{CH}_3\cdot$.
- 12 A (chemical) chain reaction is one in which a radical reacts with a molecule to produce a different radical and a product molecule. The new radical then takes part in a further reaction producing another radical and so on, until a chain-breaking process stops the reaction.
- ⓔ In nuclear physics a chain reaction is one in which a product of the first nuclear reaction causes a second nuclear reaction to take place. The fission of ^{235}U produces several neutrons, each of which is capable of causing further fission.
- 13 Under normal atmospheric conditions, the C–H bond in HCFCs is oxidised. Therefore, the chemical does not diffuse into the stratosphere where it would cause ozone depletion. CFCs do not contain any C–H bonds and are not oxidised easily. They diffuse into the stratosphere, where they are decomposed by ultraviolet radiation to produce chlorine radicals that initiate a chain reaction which removes ozone.



Chapter Summary Worksheet (textbook CD-ROM)

- 1 The answer is D. The only carbon footprint associated with hydroelectricity is that due to the construction of the dam and the generating plant, and the building of the power-transmission lines.
- e Biofuels require the use of traditional fuels by the farmer growing the crop and in the processing factories where the crop is turned into biofuel. Hydrogen is made either from methane (releasing carbon dioxide) or by the electrolysis of water (using fossil fuels to generate the electricity).
- 2 The answer is A. To be able to store enough hydrogen in the car it has to be either liquefied or compressed under extremely high pressure. It cannot be liquefied at temperatures above -240°C .
- e Being flammable is an essential property of a fuel. The energy density of hydrogen per kg is higher than that of other fuels.
- 3 The answer is A. For hydrocarbon fuels, the amount of carbon dioxide produced for a given amount of energy released decreases as the hydrogen-to-carbon ratio increases. The ratio for methane is 4:1, for butane is 2.5:1 (10:4) and for octane is 2.25:1 (9:4). Thus methane produces the least amount of carbon dioxide per kilojoule of energy released. Coal contains almost no hydrogen and so produces the most carbon dioxide per kJ.
- 4 The answer is C. Oils are esters and do not ferment to ethanol. Therefore, option C is false and is the correct answer to this negative question.
- e Bioethanol is made by converting carbohydrates such as starch or sugar into glucose, which is then fermented to ethanol and carbon dioxide. Therefore, options A, B and D are all true.
- 5 The answer is D. Algae can be used to make vegetable oils, not sugars. Hence, they are used in biodiesel production.
- e The final step in DMF production is the conversion of fructose to DMF. It is insoluble in water and has a high energy density, so statements A, B and C are all true.
- 6 The answer is A. There are 11 reactant atoms on the left-hand side of the equation and only 2 atoms of iron (the desired product) on the right.
- $$\text{atom economy} = \frac{2}{11} \times 100 = 18\%$$
- 7 The answer is D. Poly(propene) is a non-natural substance made from propene, which is derived from crude oil.
- e Silk and cellulose are natural polymers (silk is a polyamide and cellulose is a polysaccharide). Biopol is a polyester made from a natural organic chemical, so bacteria have evolved that break the polymer down.
- 8 The answer is A. Ultraviolet radiation splits oxygen molecules into oxygen radicals. When an oxygen radical reacts with another oxygen molecule, ozone is formed. The other chemicals in the list destroy ozone.

Practice Unit Test 2

Section A

- 1 The answer is A. Beryllium has only two valence electrons. These are used in bonding, so there are no lone pairs. The two bonding pairs repel to maximum separation — a linear arrangement.
- 2 The answer is C. Phosphorus has five valence electrons. Three of these are used in bonding, leaving one lone pair. The three bonding pairs and the one lone pair of electrons repel and the atoms take up a pyramidal position with the lone pair above the pyramid.
- e Boron has three valence electrons, so there are no lone pairs in BF_3 , which is therefore planar. Chlorine has seven valence electrons, so there are three bond and two lone pairs in ClF_3 and thus it is not pyramidal. All six valence electrons of sulfur are used in SO_3 , which is planar.
- 3 The answer is A. All four species contain polar bonds. Apart from HCN, they are symmetrical and their dipoles cancel. The hydrogen of HCN is δ^+ and the nitrogen is δ^- , so the molecule is polar (has a dipole moment).
- 4 The answer is D. The conditions for hydrogen bonding are a δ^+ hydrogen atom covalently bonded to a δ^- fluorine, oxygen or nitrogen atom. Only the amine, $\text{CH}_3\text{CH}_2\text{NH}_2$, fulfils these criteria.
- e Propanone and methoxymethane both have a δ^- oxygen atom but neither has a hydrogen atom joined to the oxygen. Fluoroethane has a very δ^- fluorine atom but, again, no hydrogen atom joined to it.
- 5 The answer is C. For molecules with a similar number of electrons, the intermolecular forces in decreasing strength are:
- hydrogen bonds > induced dipole > permanent dipole
- Hydrogen bonding (A) is impossible because there is neither a suitable δ^- atom nor a δ^+ hydrogen atom. Covalent bonds (D) are even stronger but are within the molecule (intramolecular) — they are not intermolecular forces. Permanent dipole forces (B) are usually weaker than induced dipole forces and in this example the bonds in $\text{C}_2\text{H}_5\text{I}$ are only very slightly polar.
- 6 The answer is B. Solubility of a molecular substance in water is determined mainly by the possibility of forming hydrogen bonds with the water. Of the four choices, only the two alcohols can do this. Methanol has a much shorter hydrophobic chain than pentanol and so is more soluble.
- 7 The answer is B. The oxidation number of chromium atoms in $\text{K}_2\text{Cr}_2\text{O}_7$ is +6 and in $\text{Cr}_2(\text{SO}_4)_3$ it is +3. Therefore, the oxidation number goes down by 3.
- 8 The answer is D. Equation A has two chlorine atoms on the right-hand side and only one on the left. Equation B does not balance for charge (left-hand side is +5; right-hand side is +6). Equation C has the electron on the wrong side (oxidation is loss of electrons, not gain).
- 9 The answer is B. The only group 1 nitrate that decomposes to produce nitrogen dioxide (brown fumes) is lithium nitrate. Group 2 nitrates decompose to give the metal oxide, oxygen and nitrogen dioxide. Sodium nitrate is the only one that does not give brown fumes of nitrogen dioxide, so is the correct response to this negative question.
- e Sodium nitrate decomposes into sodium nitrite, NaNO_2 , and oxygen.

10 The answer is C. Potassium produces a lilac flame.

11 The answer is B.

$$\begin{aligned}\text{amount (moles) of NaOH} &= \frac{\text{mass}}{\text{molar mass}} \\ &= \frac{1.2 \text{ g}}{40.0 \text{ g mol}^{-1}} = 0.030 \text{ mol} \\ \text{concentration} &= \frac{\text{moles}}{\text{volume in dm}^3} \\ &= \frac{0.030 \text{ mol}}{0.050 \text{ dm}^3} = 0.60 \text{ mol dm}^{-3}\end{aligned}$$

12 The answer is D. When calculating the mean, you must choose consistent titres. In this example, 26.65 cm³ and 26.45 cm³ are consistent and their mean is 26.55 cm³.

e 27.00 cm³ is different by more than 0.20 cm³ from the other titres, so it is not a consistent titre.

13 The answer is A.

$$\begin{aligned}\text{amount (moles) of hydrochloric acid} &= \text{concentration} \times \text{volume in dm}^3 \\ &= 0.0500 \text{ mol dm}^{-3} \times 0.02375 \text{ dm}^3 = 0.001188 \text{ mol}\end{aligned}$$

$$\text{ratio of Ba(OH)}_2\text{:HCl} = 1:2$$

$$\text{so moles of Ba(OH)}_2 = \frac{1}{2} \times 0.001188 = 5.94 \times 10^{-4} \text{ mol}$$

$$\begin{aligned}\text{concentration} &= \frac{\text{moles}}{\text{volume in dm}^3} \\ &= \frac{5.94 \times 10^{-4} \text{ mol}}{0.02500 \text{ dm}^3} = 0.02375 \text{ mol dm}^{-3}\end{aligned}$$

e The answer 0.02375 is obtained by no rounding up intermediate values during the calculation. This is the correct procedure. Rounding gives 0.02376.

14 The answer is C. Iron(III) ions oxidise iodide ions to iodine.

e Although equation A balances, chlorine is such a powerful oxidising agent that it oxidises iron to iron(III) chloride, FeCl₃. The reaction in choice B works the other way round because chlorine is a better oxidising agent than bromine. Option D is wrong for a number of reasons, including that, in this incorrect equation, chlorine is reducing the Fe³⁺ ions.

15 The answer is D. The strength of the hydrogen–halogen bond is the critical factor. The larger the halogen atom, the weaker the bond and the stronger is the acid. Hydrogen iodide, which has the weakest bond, is the strongest acid.

e In questions about trends in a group of the periodic table, the answer is always the element at either the top or the bottom of the group. If you do not know the answer, choose either the top or the bottom option — you have a 50% chance of getting it right.

16 The answer is A. Statement A is false. Hydrogen chloride and gaseous ammonia react to form a white smoke, not steamy fumes. Gaseous hydrogen chloride itself appears as steamy fumes.

e The other three statements are all true. Chlorine disproportionates with hot aqueous NaOH to form NaCl (–1 oxidation state) and NaClO₃ (+5 oxidation state).



Silver chloride is decomposed by light to metallic silver and chlorine. The blue complex with starch is used as the indicator in iodine titrations.

- 17 i The answer is B. An increase in pressure and an increase in temperature would both increase the rate.
- ii The answer is A. An increase in pressure drives the equilibrium to the right (the side with fewer gas molecules). A decrease in temperature drives the equilibrium to the right because the reaction left to right is exothermic.
- 18 The answer is C. Compound X has no effect on acidified potassium dichromate(vi), so it cannot be a primary or secondary alcohol. This rules out options B and D. It does not decolorise bromine water so it does not contain a C=C group, which also eliminates compound B. All four compounds react with sodium. It does not fizz with sodium hydrogencarbonate, so it is not an acid and is, therefore, not option A. It must be the tertiary alcohol in option C.
- 19 The answer is A. The only difference between these molecules is the halogen. Fluorine is the most electronegative so is more δ^- than the other halogens in these compounds. This makes the C-F bond, and hence the molecule, more polar.
- e Note the comment after Question 15 about periodic table trends.
- 20 The answer is D. The critical point is not the polarity of the carbon-halogen bond but its strength. Iodine has the largest radius of the four halogens, so it has the weakest carbon-halogen bond. Therefore, the hydrolysis of $\text{CH}_3\text{CH}_2\text{I}$ is the easiest and fastest.
- e Note the comment after Question 15 about periodic table trends.
- 21 The answer is D. Sulfuric acid is reduced by iodide, which is the strongest reducing agent of the four options. The iodide ions are oxidised to iodine, so there would be no hydrogen iodide to react with the alcohol.
- e Note the comment after Question 15 about periodic table trends.
- 22 The answer is B. A nucleophile contains a lone pair of electrons that are used to form a covalent bond. Nucleophiles are negative ions, or molecules that contain a covalently bonded oxygen or nitrogen atom. Radicals are not nucleophiles, so option B is the correct answer to this negative question.
- 23 The answer is C. The CN^- ion is a nucleophile and is substituted for the chlorine in the molecule. Reaction A is free-radical substitution. Reaction B is electrophilic addition and D is oxidation.
- 24 The answer is D. This type of arrow (full-headed) represents the movement of a pair of electrons. In this mechanism, the pair of electrons goes towards an atom (e.g. carbon) forming a new covalent bond, not an ionic bond.
- 25 The answer is B.

$$\begin{aligned} \text{amount (moles) of 2-chlorobutane} &= \frac{\text{mass}}{\text{molar mass}} \\ &= \frac{12.3 \text{ g}}{92.5 \text{ g mol}^{-1}} = 0.133 \text{ mol} \end{aligned}$$

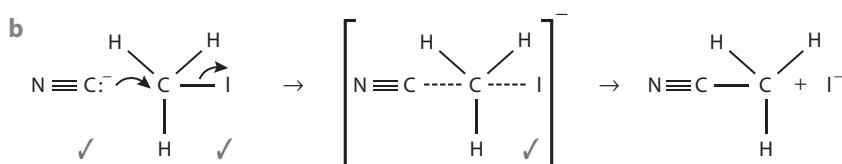
$$\begin{aligned} \text{theoretical yield of butan-2-ol} &= 0.133 \text{ mol} \\ &= 0.133 \text{ mol} \times 74.0 \text{ g mol}^{-1} = 9.84 \text{ g} \end{aligned}$$

$$\text{percentage yield} = \frac{7.54 \text{ g} \times 100}{9.84 \text{ g}} = 76.6\%$$

- e The percentage yield is never 'mass of product \times 100/mass of reactant'. You have to work out the theoretical yield and then calculate the actual yield as a percentage of the theoretical yield.
- 26 The answer is A. The i.r. peak at 1720 cm^{-1} indicates a C=O group (option A or B). Alcohols (and acids) react with sodium, so it cannot be option C or D. It has a peak in its mass spectrum at $m/e = 29$, which means that it has either a CHO or a C_2H_5 group (options A or C). The only molecule that fits all the data is the one in A.
- 27 The answer is A. Biodiesel is often mixed with petrodiesel, but does not have to be. McDonald's uses pure biodiesel made from its own old frying oil to power its lorries. Statements B, C and D are true. Algae can produce oils that can be converted to biodiesel using methanol in a transesterification reaction.
- 28 The answer is D. Ultraviolet light causes ozone to decompose into O_2 and an oxygen radical. Nitric oxides and CFCs are destroyers of ozone. HCFCs, however, are oxidised in the lower atmosphere and do not reach the stratosphere. Therefore, they do not destroy the ozone layer.

Section B

- 29 a Although the nuclear charge increases, the number of shielding electrons increases by the same amount ✓. The atomic radii increase down the group, making it easier to remove an outer electron ✓.
- e Do not give 'the amount of shielding increases' as the only reason — the amount to shield (the nuclear charge) also increases.
- b i $\text{Ca} + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{H}_2$ ✓
- ii $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$ ✓
- iii $2\text{Ca(NO}_3)_2 \rightarrow 2\text{CaO} + 4\text{NO}_2 + \text{O}_2$ ✓
- or
- $\text{Ca(NO}_3)_2 \rightarrow \text{CaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ ✓
- 30 a A nucleophile is a species with a lone pair of electrons that it uses to form a covalent bond ✓. It is usually a negative ion or a molecule with a covalently bonded oxygen or nitrogen atom.

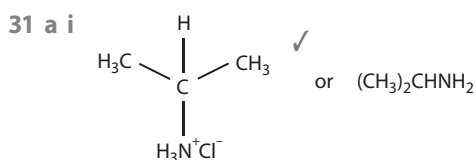


(An $\text{S}_{\text{N}}1$ mechanism would be accepted)

- e The marks are for:
- a curly arrow starting from the carbon of the CN^- ion and going towards the carbon in CH_3I
 - a curly arrow from the C-I σ -bond to the iodine atom of CH_3I
 - the transition state, which must be negatively charged and have partial bonds between the carbon of CN and the carbon of CH_3I and between the carbon of CH_3I and iodine
- c The C-I bond in 2-iodopropane is weaker than the C-Br bond in 2-bromopropane ✓, so the activation energy is lower ✓ and the reaction is faster.
- d An increase in temperature cause the molecules to have greater kinetic energy and, hence, to move faster. This results in an increase in the frequency ✓ of collisions and also means that more molecules have energy greater than or equal to the activation energy, E_{a} ✓. The

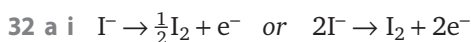
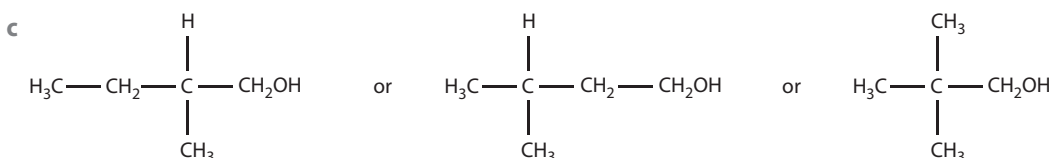
effect of this is to increase the *proportion* of molecules that react on collision ✓ and, therefore, to increase the rate. The energy factor has a much greater effect than the increase in the frequency of collision ✓.

- e Do not say that:
- there are more collisions — it is their frequency (number per second) that alters
 - there will be more successful collisions — ‘more of the collisions are successful’ or ‘a greater proportion of the collisions are successful’ will score the mark

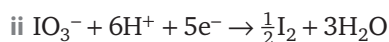


b The reagents are (red) phosphorus and iodine ✓.

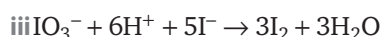
The condition is that the reagents must be damp ✓.



e This is an oxidation (OIL) reaction, so the electron in this half-equation is on the right-hand side and the reactant, iodide ion, is on the left.

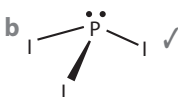


e This is a reduction (RIG) reaction, so the electron in this half-equation is on the left-hand side, as is the iodate(v) ion.



e ‘In acid solution’ means that there have to be hydrogen ions on the left-hand side of the equation.

This final equation is obtained by multiplying the equation in (i) by 5 and adding the result to the equation in (ii). The number of electrons on each side is then the same and, therefore, they cancel.



Phosphorus is in group 5 and has five valence electrons. Three of these are used in bonding with the iodine atoms, so there is one lone pair ✓. The three bond pairs and the lone pair repel each other to a position of maximum separation ✓, which is a pyramidal arrangement of atoms.

c The P–I bonds are polar, with the phosphorus atom δ^+ and the more electronegative iodine atoms δ^- ✓. The dipoles of the three bonds do not cancel ✓, so the molecule is polar.

e In this instance the dipoles do not cancel. However, if the dipoles do cancel, you must be careful to always use the word ‘dipole’ — *never* say ‘the charges cancel’.

If you did not realise that the phosphorus atom in PI_3 has a lone pair of electrons and, hence, state (wrongly) that the molecule is planar, you could score the marks in part (c) by saying that the dipoles cancel and that the planar molecule is not polar. This is an example of consequential marking.

- d** A molecule of phosphorus triiodide, PI_3 , contains 174 electrons (the sum of the atomic numbers of one atom of phosphorus and three atoms of iodine); a molecule of phosphorus trichloride, PCl_3 , contains 66 electrons ✓. This means that the induced dipole (London/dispersion/van der Waals) forces between phosphorus trichloride molecules are weaker ✓ than those between phosphorus triiodide molecules, so less energy is required to separate them. Therefore, phosphorus trichloride has the lower melting temperature.
- e** The first mark could be obtained by saying that phosphorus triiodide has more electrons than phosphorus trichloride (or that phosphorus trichloride has fewer electrons than phosphorus triiodide). Do *not* say that the strength of the intermolecular forces is connected with either the size of the molecules, the mass of the molecules, or the strength of the permanent dipole forces. Any comparison of covalent bond strength will fail to score because covalent bonds are not broken on melting.

Section C



- e** State symbols are not required as they were neither asked for nor is it a thermochemical question.

ii molar mass of butan-2-ol = 74.0 g mol^{-1} ✓

$$\begin{aligned} \text{volume of 1 mol} &= \frac{\text{mass}}{\text{density}} \\ &= \frac{74.0 \text{ g}}{0.80 \text{ g cm}^{-3}} = 92.5 \text{ cm}^3 \end{aligned}$$

1 mol releases 2650 kJ of heat energy

$$\text{so, energy density} = \frac{2650 \text{ kJ}}{92.5 \text{ cm}^3} = 28.6 \text{ kJ cm}^{-3} \text{ ✓}$$

iii 1 mol of 2-butanol produces $4 \times 44.0 = 176.0 \text{ g}$ of carbon dioxide and 2650 kJ of energy

$$\text{carbon footprint per 1000 kJ} = \frac{176.0 \text{ g} \times 1000 \text{ kJ}}{2650 \text{ kJ}} = 66.4 \text{ g} \text{ ✓ of carbon dioxide}$$

This is almost the same as the carbon footprint of petrol.

iv The peak at $m/e = 59$ is 15 less than the value for the molecular ion peak and is caused by the loss of CH_3 . The peak is due to either the $^+\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ ion or the $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})^+$ ion ✓.

The peak at $m/e = 45$ is 29 less than the value of the molecular ion peak and is caused by the loss of C_2H_5 . This peak is due to the $^+\text{CH}(\text{OH})\text{CH}_3$ ion ✓.

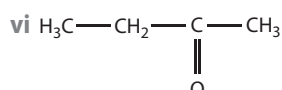
Peak A is at about 3350 cm^{-1} and is due to the hydrogen-bonded O–H bond stretch ✓.

Peak B is at about 2900 cm^{-1} and is due to the alkane C–H bond stretch ✓.

- e** When identifying peaks in mass spectra remember to include the charge. When identifying peaks in infrared spectra remember to include the wavenumber.

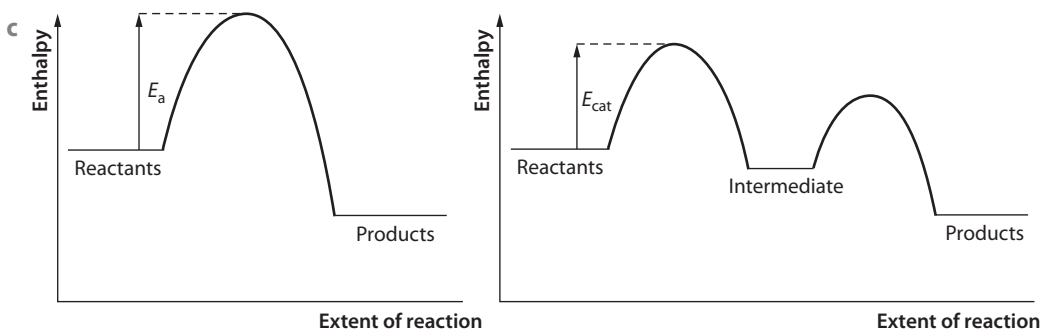
v Butan-2-ol is a secondary alcohol whereas 2-methylpropan-2-ol is a tertiary alcohol. Butan-2-ol will reduce acidified potassium dichromate solution from orange to green ✓, whereas 2-methylpropan-2-ol will not and the solution will stay orange ✓.

- e** Remember to state the observations with *both* organic substances.



- e The formula $\text{CH}_3\text{CH}_2\text{COCH}_3$ does not show the double bond in the $\text{C}=\text{O}$ group and so would not score the mark.
- b i Hydrogen will evaporate and an explosive mixture of hydrogen and air ✓ will build up in the enclosed space of the garage.
- ii The hydrogen has to be manufactured ✓.
This can be achieved by reacting methane with steam:

$$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$$
This produces carbon dioxide ✓ and requires the combustion of more methane to provide the heat energy for this endothermic reaction.
or
It can be manufactured by the electrolysis of water. Until most electricity is made from nuclear power or renewable resources, the generation of electricity involves burning fossil fuels and, therefore, produces carbon dioxide ✓.
- iii A homogeneous catalyst is in the same phase as the reactants (all in the gas phase or all dissolved in the same solvent). A heterogeneous catalyst is in a different phase from the reactants ✓.



- e The marks are for:
- labelled axes with levels marked reactants and products ✓ (the energy level of the products must be below that of the reactants) at the same energy level in both diagrams ✓
 - activation energies labelled, with E_a greater than E_{cat} ✓
 - in the catalyst diagram, an intermediate drawn and labelled ✓
- Note that it is acceptable for the two profiles to be drawn on the same set of axes.