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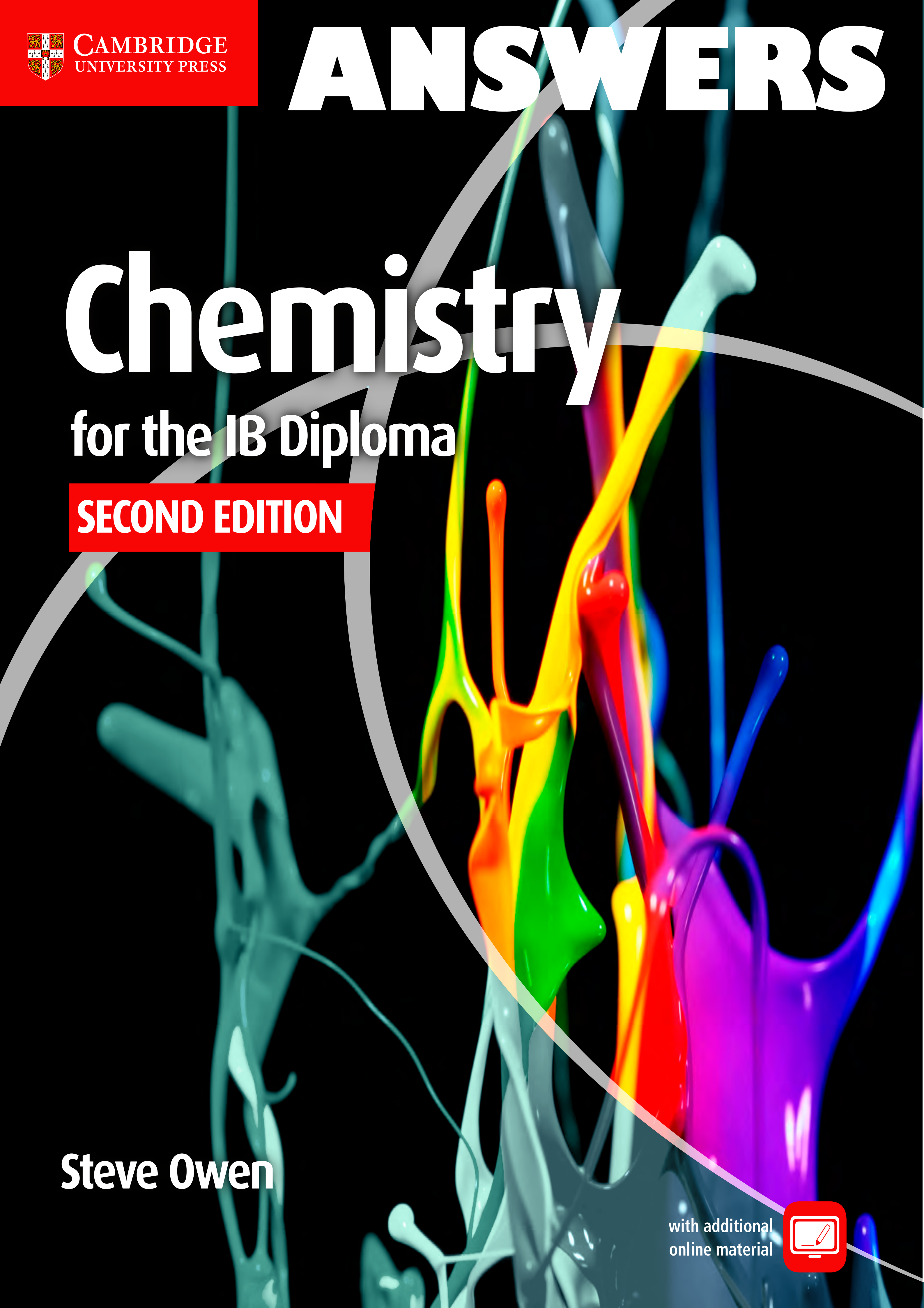
ANSWERS

Chemistry

for the IB Diploma

SECOND EDITION



Steve Owen

with additional
online material

Answers to exam-style questions

Topic 1

1 C

2 B

3 D

4 A

5 B

6 B

7 C

8 A

9 B

10 D

11 volume of ammonia in $dm^3 = \frac{227}{1000} = 0.227\,dm^3$

no. moles of ammonia $= \frac{\text{volume}}{\text{molar volume}} = \frac{0.227}{22.7}$

$= 0.0100\,mol$

From the equation, two moles of NH_3 produce one mole of N_2.

$0.0100\,mol\ NH_3 \rightarrow 0.00500\,mol\ N_2$

$0.00500\,mol$ of N_2 has a volume of 0.00500×22.7, i.e. $0.1135\,dm^3$. This is $0.1135 \times 1000 = 113.5\,cm^3$, which is the theoretical yield of N_2.

percentage yield $= \frac{85}{113.5} \times 100 = 75\%$

Alternative method: NH_3 and N_2 are both gases and so we do not have to convert to moles. From the equation, two moles of NH_3 react to give one mole of N_2. Therefore two volumes of NH_3 react to give one volume of N_2, so 227 cm^3 of NH_3 react to give $\frac{227}{2}$, i.e. $113.5\,cm^3$ of N_2. This is the theoretical yield of N_2.

The rest of the method is the same as above. **[3]**

12 a Because the masses of the two substances are given, we must check to see if one of the substances is limiting.

molar mass of $Mn_3O_4 = 228.82\,g\,mol^{-1}$

no. moles of $Mn_3O_4 = \frac{100\,000}{228.82} = 437.0\,mol$

molar mass of $Al = 26.98\,g\,mol^{-1}$

no. moles of $Al = \frac{100\,000}{26.98} = 3706\,mol$

$437.0\,mol$ of Mn_3O_4 will react with $437.0 \times 8/3$, i.e. 1165 mol. The number of moles of Al is greater than this, so Al is present in excess and Mn_3O_4 is the limiting reactant. So Mn_3O_4 must be used in all calculations.

3 mol Mn_3O_4 produces 9 mol Mn. Therefore 437.0 mol of Mn_3O_4 will produce 437.0×3, i.e. 1311, mol of Mn.

molar mass of $Mn = 54.94\,g\,mol^{-1}$

mass of of $Mn = 1311 \times 54.94$, i.e. 72 030 g, i.e. 72.03 kg. **[4]**

b $3Mn_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Mn$

200.0 kg of Mn is $\frac{200\,000}{54.94}$, i.e. 3640 mol.

This number of moles is produced from $\frac{3640}{3}$, i.e. 1213 mol Mn_3O_4. The mass of 1213 mol Mn_3O_4 is $1213 \times 228.82 = 277\,661\,g$, i.e. 277.7 kg. To convert to tonnes, we divide by 1000 to get 0.2777 tonnes.

Therefore, the percentage Mn_3O_4 in the ore $= \frac{0.2777}{1.23} \times 100$, i.e 22.6%. **[3]**

13 a A hydrocarbon contains carbon and hydrogen only. The percentage hydrogen in the hydrocarbon is $100 - 88.8$, i.e. 11.2%.

	C	**H**
	88.8	11.2
divide by A_r	$\frac{88.8}{12.01}$	$\frac{11.2}{1.01}$
moles	7.39	11.09
divide by smallest	$\frac{7.39}{7.39}$	$\frac{11.09}{7.39}$
ratio	1	1.5

Multiplying by 2 to get whole numbers, we get C_2H_3, which is the empirical formula. **[3]**

b To do this, we have to work out the relative molecular mass of the hydrocarbon.

Use $PV = nRT$ to calculate the number of moles.

Convert volume in cm^3 to volume in m^3:

$\frac{98.9}{(1 \times 10^6)} = 9.89 \times 10^{-5}\,m^3$

$P = 1.00 \times 10^5\,Pa$ $\quad V = 9.89 \times 10^{-5}\,m^3$ $\quad n = ?$

$R = 8.31\,J\,K^{-1}\,mol^{-1}$ $\quad T = 320\,K$

$n = \frac{PV}{RT}$

$n = \frac{1.00 \times 10^5 \times 9.89 \times 10^{-5}}{8.31 \times 320}$

$n = 3.72 \times 10^{-3}\,mol$

relative molecular mass $= \frac{\text{mass}}{\text{no. moles}} = \frac{0.201}{3.72 \times 10^{-3}}$

$= 54.0$

The empirical formula mass

$= (2 \times 12.01) + (3 \times 1.01) = 27.05$ and

$\frac{54.0}{27.05} = 2$

Therefore the molecular formula is $(C_2H_3)_2$, i.e. C_4H_6. **[3]**

14 a volume of CO_2 in $m^3 = \frac{258}{1\,000\,000}$

$= 2.58 \times 10^{-4}\,m^3$

$P = 1.10 \times 10^5\,Pa \quad V = 2.58 \times 10^{-4}\,m^3 \quad n = ?$

$R = 8.31\,J\,K^{-1}\,mol^{-1} \quad T = 300\,K$

$n = \frac{PV}{RT}$

$n = \frac{1.10 \times 10^5 \times 2.58 \times 10^{-4}}{8.31 \times 300}$

$= 0.0114\,mol$ **[3]**

b The number of moles of $CaCO_3$ that must react to produce this number of moles of CO_2 is worked out from the chemical equation:

no. moles of $CaCO_3 = 0.0114\,mol$

molar mass of $CaCO_3 = 100.09\,g\,mol^{-1}$

mass of $CaCO_3 = 0.0114 \times 100.09 = 1.14\,g$

percentage $CaCO_3$ in the limestone $= \frac{1.14}{1.20} \times 100$

$= 95.0\%$ **[3]**

15 a In this question the number of moles of copper(II) nitrate is equivalent to the number of moles of Cu^{2+} and the number of moles of potassium iodide is equivalent to the number of moles of I^-.

no. moles of copper(II) nitrate $= \frac{25.0}{1000} \times 0.100$

$= 2.50 \times 10^{-3}\,mol$

no. moles of potassium iodide $= \frac{15.0}{1000} \times 0.500$

$= 7.50 \times 10^{-3}\,mol$

From the ionic equation we can deduce that two moles of $Cu(NO_3)_2$ will react with four moles of KI. Therefore $2.50 \times 10^{-3}\,mol$ of $Cu(NO_3)_2$ will react with $2 \times 2.50 \times 10^{-3}$, i.e. $5.00 \times 10^{-3}\,mol$ of KI. The number of moles of potassium iodide present is greater than this, so the KI is present in excess. **[3]**

b We must use the number of moles of the limiting reactant ($Cu(NO_3)_2$) for subsequent calculations. From the chemical equation, 2 mol Cu^{2+} react to form 1 mol I_2. Therefore $2.50 \times 10^{-3}\,mol$ of $Cu(NO_3)_2$ will react to form $\frac{2.50 \times 10^{-3}}{2}$, i.e. $1.25 \times 10^{-3}\,mol$ I_2.

molar mass of $I_2 = 253.80\,g\,mol^{-1}$

mass of $I_2 = 1.25 \times 10^{-3} \times 253.80$, i.e. $0.317\,g$ **[3]**

16 a molar mass of $PbI_2 = 461.0\,g\,mol^{-1}$

moles of $PbI_2 = \frac{0.1270}{461.0} = 2.755 \times 10^{-4}\,mol$ **[2]**

b $Pb(NO_3)_2(aq) + MI_2(aq) \rightarrow PbI_2(s) + M(NO_3)_2(aq)$ **[1]**

c From the chemical equation, we can deduce that the number of moles of MI_2 is the same as the number of moles of PbI_2. Therefore the number of moles of MI_2 is $2.755 \times 10^{-4}\,mol$. **[1]**

d We know the mass of $2.755 \times 10^{-4}\,mol$ of MI_2 is $0.0810\,g$. The molar mass of MI_2 is $\frac{0.0810}{2.755 \times 10^{-4}}$, i.e. $294.0\,g\,mol^{-1}$. Some of this mass is due to the two I^- ions in the formula – these contribute 2×126.90 to the mass, i.e. 253.8. The relative atomic mass of M is $294.0 - 253.8 = 40.20$. We know that this is a group 2 element, so from the periodic table we can see that it must be calcium. **[3]**

17 a molar mass of $BaSO_4 = 233.40\,g\,mol^{-1}$

no. moles of $BaSO_4$ formed $= \frac{3.739 \times 10^{-2}}{233.40}$

$= 1.602 \times 10^{-4}\,mol$ **[2]**

b $CuSO_4(aq) + BaCl_2(aq) \rightarrow BaSO_4(s) + CuCl_2(aq)$ **[1]**

c From the chemical equation we can deduce that the number of moles of $CuSO_4$ is the same as the number of moles of $BaSO_4$. Therefore the number of moles of $CuSO_4$ is $1.602 \times 10^{-4}\,mol$. **[1]**

d Only $10.00\,cm^3$ of the original solution ($100.0\,cm^3$) was used in the reaction, so the number of moles of $CuSO_4$ that were dissolved in water was $10.00 \times 1.602 \times 10^{-4}\,mol$, i.e. $1.602 \times 10^{-3}\,mol$. **[1]**

e $0.4000\,g$ of hydrated copper sulfate ($CuSO_4{\cdot}xH_2O$) contains $1.602 \times 10^{-3}\,mol$ of $CuSO_4$. The molar mass of $CuSO_4$ is $159.62\,g\,mol^{-1}$. The mass of $CuSO_4$ present in the sample is $1.602 \times 10^{-3} \times 159.62$, i.e. $0.2557\,g$ of $CuSO_4$. The rest of the hydrated copper sulfate is water. Therefore the mass of water present in the sample is $0.4000 - 0.2557$, i.e. $0.1443\,g$.

no. moles of water $= \frac{0.1443}{18.02} = 8.008 \times 10^{-3}\,mol$

ratio of no. moles of water to no. moles of $CuSO_4$

$= \frac{8.008 \times 10^{-3}}{1.602 \times 10^{-3}} = 4.999$

This will be a whole number in the formula. Therefore the value of x is 5, and the formula is $CuSO_4{\cdot}5H_2O$. **[3]**

Answers to exam-style questions

Topic 2

1 B

2 B

3 A

4 B

5 C

6 B

7 C

8 C

9 C

10 A

11 **a** *Atomic number:* the number of protons in the nucleus of an atom; *isotopes:* different atoms of the same element with different mass numbers, i.e. different numbers of neutrons in the nucleus. **[3]**

b The number of protons is given by the atomic number, 26. The number of neutrons is the mass number − the atomic number, i.e. $57 - 26 = 31$. This is an atom, so the number of electrons equals the number of protons: 26. **[2]**

c **i** Mass spectrometer **[1]**

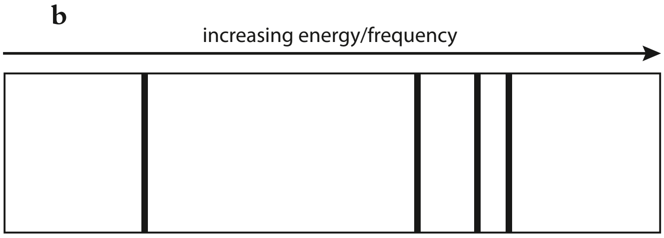
ii relative molecular mass =

$$\frac{(5.80 \times 54) + (91.16 \times 56) + (3.04 \times 57)}{100} = 55.91$$

[2]

12 **a** *Continuous spectrum:* all frequencies/wavelengths of light present; *line spectrum:* only certain frequencies/wavelengths of light present. **[2]**

b



[2]

c An electron is promoted to a higher energy level; the electron is unstable at this higher level and falls to a lower energy level; as it falls from a higher energy level to a lower one, the energy difference is given out in the form of a photon of light. This gives a line in the spectrum. **[3]**

d $E = h\nu$

Energy of photon emitted when electron falls from level 5 to level 3 is $6.63 \times 10^{-34} \times 2.34 \times 10^{14}$

i.e. 1.55×10^{-19} J

Energy of photon emitted when electron falls from level 6 to level 3 is $6.63 \times 10^{-34} \times 2.74 \times 10^{14}$

i.e. 1.82×10^{-19} J

In both cases the electron falls to the same lower level, so the difference in energy between these is the energy difference between level 6 and level 5. Therefore the energy difference between these levels is $1.82 \times 10^{-19} - 1.55 \times 10^{-19}$ i.e. 2.70×10^{-20} J (if more significant figures are carried through or the energy is calculated by subtracting the frequencies from each other the answer 2.65×10^{-20} J is obtained). **[2]**

13 **a** $1s^22s^22p^63s^23p^64s^1$ **[1]**

b $K^+(g) \rightarrow K^{2+}(g) + e^-$ (gaseous symbols are essential) **[2]**

c There are various contributing factors here. The most important one is that when the first electron is removed, it is removed from the fourth shell (main energy level), but the second electron is removed from the third shell; an electron in the third shell is closer to the nucleus and therefore more strongly held.

Other factors may also be mentioned: the first electron is removed from a neutral atom, but the second is removed from a positive ion − it is more difficult to remove a negatively charged electron from a positive ion than from a neutral atom; once the first electron has been removed, there is less electron–electron repulsion − all electrons are pulled in more closely and the ion is smaller so all electrons are held more tightly. **[3]**

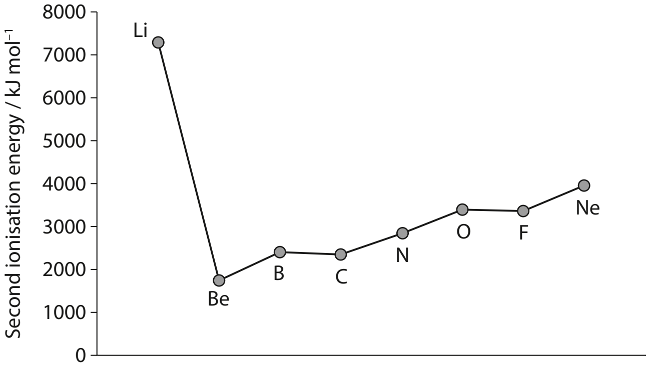
d The first ionisation of Ca is higher; in both cases the electron is removed from the same shell (main energy level) and subshell (4s), so the amount of shielding is approximately the same; Ca has a higher nuclear charge than K, so the outer electron is attracted more strongly to the nucleus. A calcium atom is also smaller than a potassium atom and so the outer electron is held closer to the nucleus and therefore more strongly attracted. **[3]**

14 **a** $1s^22s^22p^6$ **[1]**

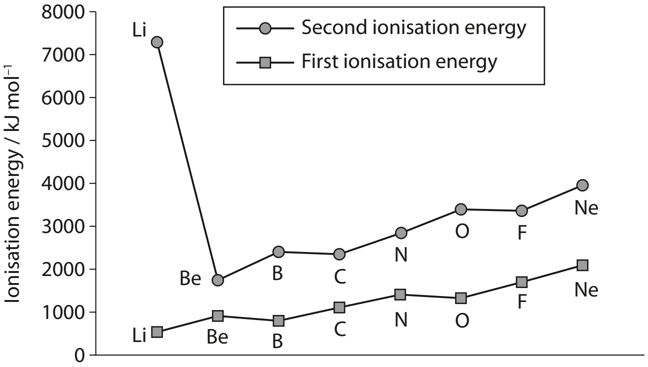
b The atom is Ne; there are various ions: N^{3-}, F^-, Na^+, Mg^{2+}, Al^{3+}. (C^{4-} and Si^{4+} do not form under normal conditions.) **[2]**

c The electron configuration of O is $1s^22s^22p^4$; the electron configuration of N is $1s^22s^22p^3$; O has two electrons paired up in the same p orbital, whereas nitrogen has only one electron in each p orbital; there is greater repulsion between two electrons in the same p orbital, so one of the electrons is easier to remove. **[2]**

d



Lithium has a very high value, as the second electron is removed from the first shell (main energy level). The rest of the graph is like that of the first ionisation energy graph except it is shifted one position to the right (see below), as all the ions have one fewer electron than the parent atom. There is a dip between the first ionisation energies of Be ($1s^22s^2$) and B ($1s^22s^22p^1$) because the electron is being removed from the 2p subshell for B but from the 2s subshell for Be. Once the 1+ ions are formed, the dip occurs between B^+ ($1s^22s^2$) and C^+ ($1s^22s^22p^1$). **[3]**



Answers to exam-style questions

Topic 3

1 B

2 A

3 C

4 B

5 B

6 C

7 B

8 C

9 B

10 C

11 **a** **i** Aluminium and sodium are in the same period in the periodic table, and therefore have the same number of shells of electrons. The shielding from inner shells of electrons is approximately the same in both, but aluminium has a higher nuclear charge (more protons) than sodium, and therefore the outer electrons are attracted more strongly. **[2]**

ii An Al atom forms a 3+ ion by losing its three outer shell electrons. If the Al atom and the Al^{3+} ion are compared, they both have the same number of protons in the nucleus, but the Al^{3+} ion has one fewer shell of electrons. The Al^{3+} ion is therefore smaller than the Al atom. A Cl atom forms a 1− ion by gaining one electron. If the Cl atom and the Cl^- ion are compared, they have the same number of protons in the nucleus, but Cl^- has one extra electron, so there is greater electron–electron repulsion for the same nuclear charge pulling in the electrons. The electron cloud expands and the ion is larger than the atom. **[4]**

iii K forms the K^+ ion, but Cl forms the Cl^- ion. These have the same number of electrons, but K^+ has a higher nuclear charge (19+) than Cl^- (17+), so the electrons are pulled in more strongly and the K^+ ion is smaller. **[2]**

b **i** First electron affinity: $Cl(g) + e^- \rightarrow Cl^-(g)$
First ionisation energy: $Mg(g) \rightarrow Mg^+(g) + e^-$ **[2]**

ii A chlorine atom is smaller than a bromine atom; so when an electron is accepted into the outer shell of Cl it is closer to the nucleus – and so more strongly attracted to it. **[2]**

iii A chlorine atom is smaller and has a higher nuclear charge than a magnesium atom. However, Cl and Mg have the same number of electron shells, and so approximately the same amount of shielding from inner shells. So, the outer electron is held more tightly in Cl and is more difficult to remove. **[2]**

12 **a** **i** $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

ii $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ **[2]**

b Ligands are negative ions or neutral molecules that possess at least one lone pair of electrons; a lone pair is used to form a coordinate (dative) covalent bond between the ligand and the transition metal ion to form a complex ion. **[2]**

c Cl^- is a negatively charged ligand and four Cl^- ions have a total charge of 4−; the overall charge on the complex ion is 2−; therefore the oxidation number of Cu must be +2. **[1]**

d CuBr contains the Cu^+ ion, which has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$; it has no unpaired electrons and will therefore be diamagnetic. Br^- also has no unpaired electrons. **[2]**

e **i** The $[Cu(H_2O)_6]^{2+}$ complex ion contains the Cu^{2+} ion, which has a partially filled 3d subshell. The d orbitals are split into two groups in the complex ion. Energy in the form of a certain frequency of visible light is absorbed to promote an electron from the lower set of d orbitals to the upper set. The light transmitted has the complementary colour to the light absorbed. **[3]**

ii $[Cu(NH_3)_2]^+$ contains the Cu^+ ion, which has a full 3d subshell. There is no space available in the upper set of d orbitals to promote an electron to, so light in the visible region of the spectrum cannot be absorbed. **[2]**

iii According to the spectrochemical series, Br^- is a weaker field ligand than H_2O and therefore causes less splitting of the 3d orbitals. The wavelength of light absorbed by $[Cu(H_2O)_5Br]^+$ will therefore be longer than that absorbed by $[Cu(H_2O)_6]^{2+}$; longer wavelength corresponds to lower energy. **[2]**

Answers to exam-style questions

Topic 4

1 C

2 B

3 A

4 D

5 A

6 C

7 A

8 B

9 D

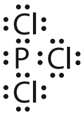
10 B

11 B

12 D

13 **a** Pairs of electrons in the outer shell of the central atom repel each other; they take up positions in space to be as far away from each other as possible in order to minimise this repulsion. Pairs of electrons may be bonding pairs and lone pairs; lone pairs cause greater repulsion than bonding pairs of electrons. **[4]**

b **i** The Lewis structure for PCl_3 is:

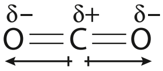


There are four pairs of electrons around the central atom. The basic shape (distribution of electron pairs) is tetrahedral; because one of the pairs of electrons is a lone pair, the actual shape of the molecule is trigonal pyramidal. The bond angle will be slightly less than that in a tetrahedron (109.5°), so predictions in the range 100–108° will generally be accepted.

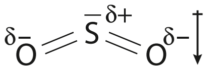
ii The Lewis structure for CO_2 is:

The four electrons in each double bond are constrained to be in the same region of space, so there are two electron domains around the C. The shape is linear and the bond angle is 180°. **[4]**

c CO_2 is a linear molecule and so, although each individual C=O bond is polar, the dipoles cancel out.



Because there is a lone pair of electrons on the S in SO_2, the molecule is bent and the dipoles do not cancel out – one end of the molecule is δ+ and the other is δ−. **[3]**



d $|C\equiv O|$

CO has a triple bond between the C and the O, whereas CO_2 has double bonds between the C and O atoms; the C–O bond in CO is shorter than that in CO_2; there are six electrons between the atoms in a triple bond but only four electrons between the atoms in a double bond; with more electrons between the atoms, there is greater attraction between the nuclei and the bonding electrons. **[3]**

14 **a** Sodium oxide has a giant ionic structure in which the ions are held in a lattice structure by strong electrostatic forces of attraction between positive ions and negative ions. Because the electrostatic attractions between the oppositely charged ions are strong, a lot of energy is required to overcome them, and the melting point is high. Na_2O does not conduct electricity when solid, because the ions are held tightly in the lattice structure. When molten, the Na^+ and O^{2-} ions are free to move, and so the liquid conducts electricity. **[4]**

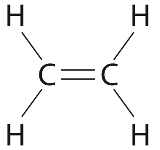
b Sodium and magnesium have metallic bonding, which is the electrostatic attraction between positively charged ions and delocalised electrons. Mg^{2+} has a higher positive charge than Na^+, so there is a stronger attraction for the delocalised electrons. Mg^{2+} is smaller than Na^+, so the nucleus of the ion is closer to the delocalised electrons and the attraction is stronger. In Mg there are more delocalised electrons per atom, and therefore more attractions holding the lattice together. **[3]**

c These are all covalent molecular substances. The strength of London forces increases with relative molecular mass. AsH_3 has a higher relative molecular mass than PH_3, so the London forces are stronger between AsH_3 molecules, and the boiling point is higher. Although NH_3 has the lowest relative molecular mass, it has an H atom joined directly to an N atom, and therefore there will be hydrogen bonding between the molecules. Hydrogen bonding is a stronger intermolecular force than London forces, and therefore the intermolecular forces between NH_3 molecules are stronger than those between PH_3 molecules. **[3]**

d Silicon dioxide has a giant covalent structure, but carbon dioxide is covalent molecular. When silicon dioxide is melted, strong covalent bonds between the atoms must be broken. This requires a lot of energy, so SiO_2 has a high melting point. When carbon dioxide is melted, only the weak London forces between molecules must be overcome. This requires relatively little energy, and CO_2 has a lower melting point. **[3]**

15 a Hybridisation is the mixing of atomic orbitals to form a new set of orbitals that are better arranged in space for bonding. The number of hybrid orbitals formed is the same as the initial number of atomic orbitals. **[2]**

b There are three electron domains around each C in C_2H_4:



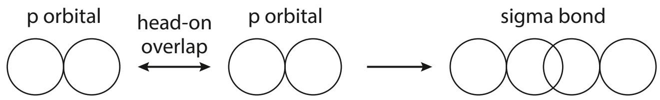
The electron domains are arranged in a trigonal planar array around each C. The type of hybridisation that gives a trigonal planar array of orbitals is sp^2. Therefore the C atoms in C_2H_4 are sp^2 hybridised.

There are two electron domains around each C in C_2H_2:

$$H-C\equiv C-H$$

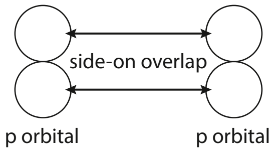
The electron domains are arranged in a linear array around each C. The type of hybridisation that gives a linear arrangement of orbitals is sp. Therefore, the C atoms in C_2H_2 are sp hybridised. **[2]**

c A sigma bond is a head-on overlap of atomic orbitals that results in the electron density lying along the internuclear axis:



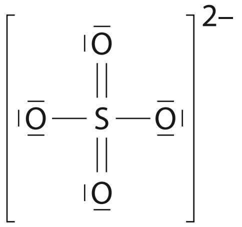
There is one sigma bond between the two C atoms in ethene and ethyne, and there are sigma bonds between the C and H atoms in ethene and ethyne.

A pi bond is a side-on overlap between two p orbitals. This results in the electron density in the pi bond lying above and below the internuclear axis:



The double bond in ethene is made up of a sigma bond and a pi bond. The triple bond in ethyne is made up of one sigma bond and two pi bonds. **[4]**

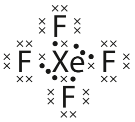
16 a i The Lewis structure of the SO_4^{2-} ion is:



The concept of formal charge could be used to decide between alternative Lewis structures – that with all single bonds has higher formal charges, therefore the structure shown is preferred.

There are four electron domains around the S, and therefore the shape is tetrahedral. The bond angle is 109.5°, although two of the bonds in the Lewis structure are shown as double bonds and may be expected to repel single bonds more strongly, the structure is delocalised and all bonds are equivalent.

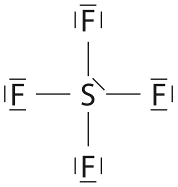
ii The Lewis structure of XeF_4 is:



There are six electron domains around the Xe, and therefore the distribution of these electron pairs is octahedral. The two lone pairs go opposite each other, and the shape of the molecule is square planar.

The bond angles are the same as in an octahedron: i.e. 90°.

iii The Lewis structure for SF_4 is:

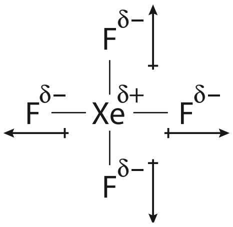


There are five electron domains around the S atom. The basic shape (arrangement of electron pairs) is trigonal bipyramidal. The lone pair in a trigonal bipyramid always goes around the middle, so the actual shape is 'see-saw' shaped:

The bond angles in a trigonal bipyramid are 90° and 120°. The lone pair causes these bond angles to close up slightly, and so we can predict bond angles of about 88° and 118°.

[6]

b XeF_4 is non-polar because, although each individual bond is polar, the square planar shape means that the dipoles cancel:



[2]

c SO_2 has two double bonds between the S and the O atoms, but SO_4^{2-} has a delocalised structure in which the π components of the double bonds are shared equally between all four sulfur–oxygen bonds. The bond order in SO_2 is 2, but that in SO_4^{2-} is 1.5. The sulfur–oxygen bond length in SO_2 would be expected to be shorter than that in SO_4^{2-}. **[2]**

Answers to exam-style questions

Topic 5

1 B

2 C

3 B

4 D

5 C

6 B

7 D

8 D

9 B

10 A

11 **a** The average amount of energy required to break one mole of covalent bonds in a gaseous molecule under standard conditions. 'Average' refers to the fact that the bond enthalpy is different in different molecules and therefore the value quoted is the average amount of energy to break a particular bond in a range of molecules. **[2]**

b

Bond broken	**Bond energy / kJ mol^{-1}**	**No. bonds**	**Total energy / kJ mol^{-1}**
C–H	412	5	2060
C–C	348	1	348
C–O	360	1	360
O–H	463	1	463
O=O	496	3	1488
Total energy to break all bonds			4719

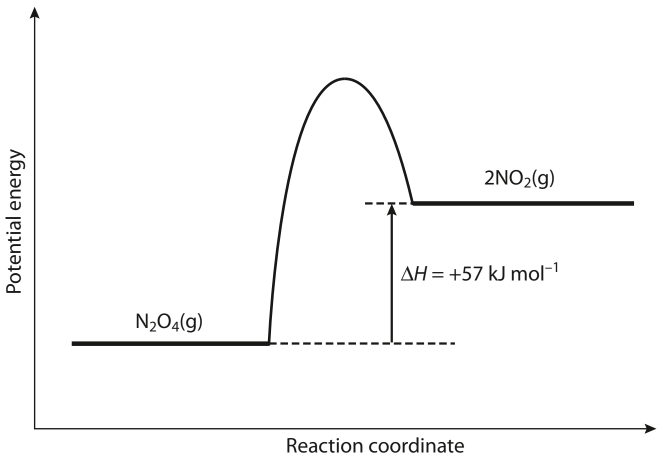
Bond made	**Bond energy / kJ mol^{-1}**	**No. bonds**	**Total energy / kJ mol^{-1}**
C=O	743	4	2972
O–H	463	6	2778
Total energy released when bonds made			5750

$\Delta H_r = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$

$\Delta H_r = 4719 - 5750 = -1031\,\text{kJ mol}^{-1}$ **[3]**

c Two of the substances involved are in the liquid state, but bond enthalpies can be used only when all substances are in the gaseous state. When substances are not in the liquid state, energy must also be supplied to overcome intermolecular forces, or energy is released when intermolecular forces are formed. **[2]**

d



N_2O_4 is more stable because it is at a lower energy level. **[3]**

12 **a** The enthalpy change when one mole of a substance is formed from its elements in their standard states under standard conditions (100 kPa pressure). **[2]**

b $4H_2(g) + 3C(s) + \frac{1}{2}O_2(g) \rightarrow C_3H_7OH(l)$ **[2]**

c $\Delta H = \Sigma\Delta H_f\,(\text{products}) - \Sigma\Delta H_f\,(\text{reactants})$

$= [(3 \times -394) + (4 \times -286)] - [-316]$

$= (-1182 + -1144) + 316$

$= -2010\,\text{kJ mol}^{-1}$ **[3]**

d The equation for the complete combustion of propan-1-ol is:

$C_3H_7OH(l) + 4\frac{1}{2}O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

To calculate the entropy change we use:

$\Delta S = \Sigma S(\text{products}) - \Sigma S(\text{reactants})$

$\Delta S^{\ominus} = [(3 \times 214) + (4 \times 69.9)] - [(1 \times 196.6) + (4.5 \times 205)]$

$\Delta S^{\ominus} = -197.5\,\text{J K}^{-1}\,\text{mol}^{-1}$

The sign of ΔS is negative because the reaction involves a decrease in the number of moles of gas (4.5 on the left-hand side but only 3 on the right-hand side) and therefore the energy is less spread out in the products. **[3]**

e For the complete combustion of propan-1-ol:

$\Delta H^{\ominus} = -2010\,\text{kJ mol}^{-1}$

$\Delta S^{\ominus} = -197.5\,\text{J K}^{-1}\,\text{mol}^{-1}$

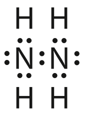
At 298 K:

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$$\Delta G^{\ominus} = -2010 - 298 \times \left(\frac{-197.5}{1000}\right)$$

Therefore, $\Delta G^{\ominus} = -1951\,\text{kJ mol}^{-1}$. $\Delta G^{\ominus}$ is negative, so the reaction is spontaneous at 25 °C. **[3]**

13 a [1]



b $N_2(g) + 2H_2(g) \rightarrow N_2H_4(g)$ [2]

c

Bond broken	**Bond energy / kJ mol^{-1}**	**No. bonds**	**Total energy / kJ mol^{-1}**
N≡N	944	1	944
H–H	436	2	872
Total energy to break all bonds			1816

Bond made	**Bond energy / kJ mol^{-1}**	**No. bonds**	**Total energy / kJ mol^{-1}**
N–N	163	1	163
N–H	388	4	1552
Total energy released when bonds made			1715

$\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$

$\Delta H = 1816 - 1715 = 101\,\text{kJ mol}^{-1}$ [3]

d We have been given enthalpy change of formation data, so we can use the equation:

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

The enthalpy change of formation of elements in their standard states is zero. Substituting known values we get:

$-622 = (2 \times -286) - \Delta H_f(N_2H_4(l))$

Rearranging this we get:

$\Delta H_f(N_2H_4(l)) = 50\,\text{kJ mol}^{-1}$ [3]

e We have calculated ΔH_f values in parts **c** and **d** and can use these in the equation:

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

$\Delta H = 101 - 50 = 51\,\text{kJ mol}^{-1}$ [2]

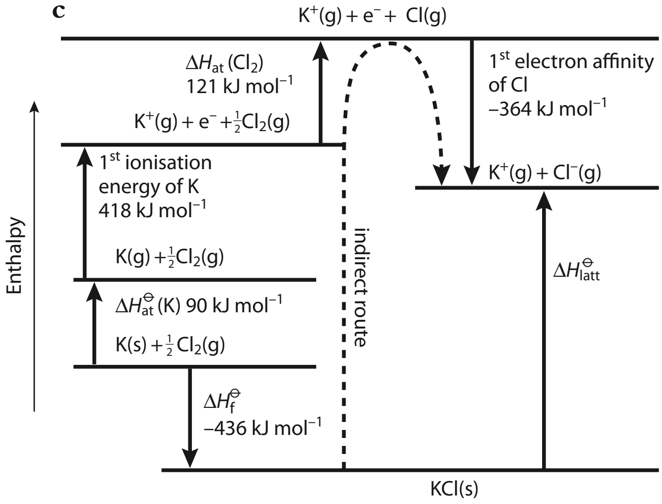
14 a Lattice enthalpy is the enthalpy change when one mole of an ionic compound is broken apart into its constituent gaseous ions under standard conditions. [2]

b **i** $KCl(s) \rightarrow K^+(g) + Cl^-(g)$

ii $Cl(g) + e^- \rightarrow Cl^-(g)$

iii $K(g) \rightarrow K^+(g) + e^-$ [3]

c



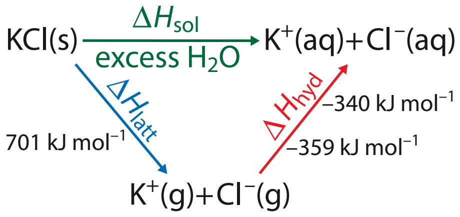
The enthalpy change for the indirect route is the same as that for the direct route:

$\Delta H_{\text{latt}} = -(-436) + 90 + 418 + 121 - 364$

$= 701\,\text{kJ mol}^{-1}$ [5]

d Calcium chloride contains 2+ and 1− ions, whereas potassium chloride contains 1+ and 1− ions. The electrostatic attraction between more highly charged ions is greater, so there are stronger electrostatic attractions in the calcium chloride lattice and more energy is required to break the lattice apart. The Ca^{2+} ion is also smaller than the K^+ ion, and this will also lead to the electrostatic attraction between the Ca^{2+} ion and the Cl^- ion being greater. [2]

e Using the lattice enthalpy from part **c**, a cycle can be constructed:



$\Delta H_{\text{sol}} = 701 - 340 - 359 = 2\,\text{kJ mol}^{-1}$ [2]

Answers to exam-style questions

Topic 6

1 C

2 A

3 B

4 C

5 C

6 C

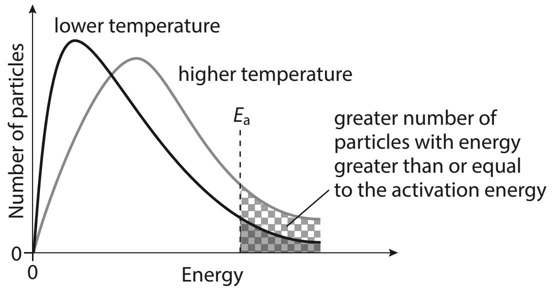
7 A

8 C

9 D

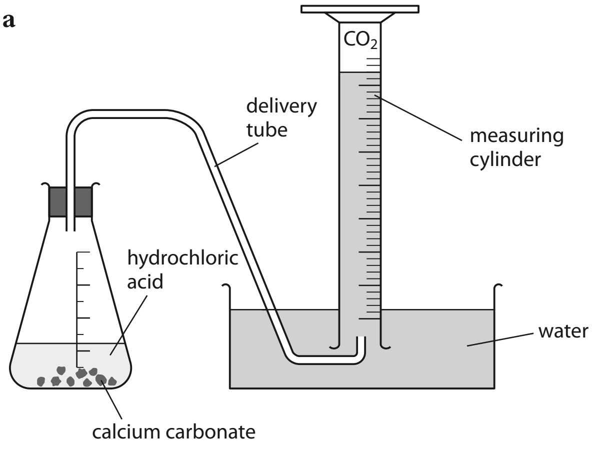
10 B

11 There are two factors that contribute to the increase in rate of reaction with increase in temperature. The first is that as the temperature increases the particles have more kinetic energy and so are moving faster; the particles collide more often. This is only, however, a small effect. The second factor is that at the higher temperature there are more particles with energy greater than the activation energy; therefore there is a greater chance that a collision will result in reaction and there will be more successful collisions per unit time. This is the more important factor in explaining why the rate of reaction increases with temperature. This can be shown on the Maxwell–Boltzman distribution – the checked area represents the number of particles with energy greater than the activation energy at the higher temperature.



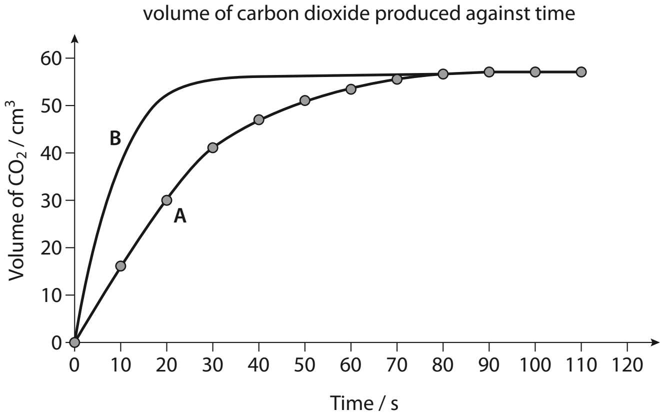
[4]

12 **a**



The volume of carbon dioxide produced is measured every 10 s. **[3]**

b and **d** **b[2] d[2]**



c The rate is fastest at the beginning, because the graph has its maximum gradient (slope) there. The concentration of HCl is highest at the beginning, so there are the most collisions per unit time. **[2]**

e i No. moles of $CaCO_3 = \frac{1.00}{100.09} = 9.99 \times 10^{-3}$ mol

No. moles of HCl $= \frac{20.0}{1000} \times 0.300$

$= 6.00 \times 10^{-3}$ mol

From the chemical equation: 6.00×10^{-3} mol HCl react with 3.00×10^{-3} mol $CaCO_3$. Therefore $CaCO_3$ is in excess. The number of moles of CO_2 formed is obtained by using the number of moles of the limiting reactant (HCl): 6.00×10^{-3} mol HCl produces 3.00×10^{-3} mol CO_2.

volume of $CO_2 = 3.00 \times 10^{-3} \times 24.0$

$= 0.0720\ dm^3$

There are 1000 cm^3 in 1 dm^3, so the volume in cm^3 is 72.0 cm^3. **[3]**

ii The most likely reason is that some gas will escape before the bung is put in the flask. **[1]**

13 a The power of a reactant's concentration in the experimentally determined rate equation. The overall order of reaction is the sum of the powers of the concentration terms in the experimentally determined rate equation. **[2]**

b From experiment 2 to 1, when the concentration of X is doubled, the rate of reaction also doubles, so the order of reaction with respect to X is 1.
From experiment 3 to 2, when the concentration of Y is doubled, the rate of reaction also doubles, so the order of reaction with respect to Y is 1.
The rate expression is rate $= k[\mathrm{X}][\mathrm{Y}]$ **[4]**

c From experiment 1, $[\mathrm{X}] = 0.500\,\mathrm{mol\,dm^{-3}}$ and $[\mathrm{Y}] = 0.500\,\mathrm{mol\,dm^{-3}}$. Substituting these values and the value of the rate into the rate expression we get:

$3.20 \times 10^{-3} = k \times 0.500 \times 0.500$

Rearranging this we get $k = 0.0128$.

The units of k are obtained by substituting units into the rate expression:

$\cancel{\mathrm{mol\,dm^{-3}}}\,\mathrm{s^{-1}} = k \times \mathrm{mol\,dm^{-3}} \times \cancel{\mathrm{mol\,dm^{-3}}}$

$\mathrm{s^{-1}} = k \times \mathrm{mol\,dm^{-3}}$

Rearranging this we get:

$\dfrac{\mathrm{s^{-1}}}{\mathrm{mol\,dm^{-3}}} = k$

$k = \mathrm{mol^{-1}\,dm^{3}\,s^{-1}}$

Therefore, $k = 0.0128\,\mathrm{mol^{-1}\,dm^{3}\,s^{-1}}$. **[2]**

d This can be worked out in two ways. In the first, the values can be substituted into the rate expression:

rate $= k[\mathrm{X}][\mathrm{Y}]$

rate $= 0.0128 \times 0.100 \times 0.100$

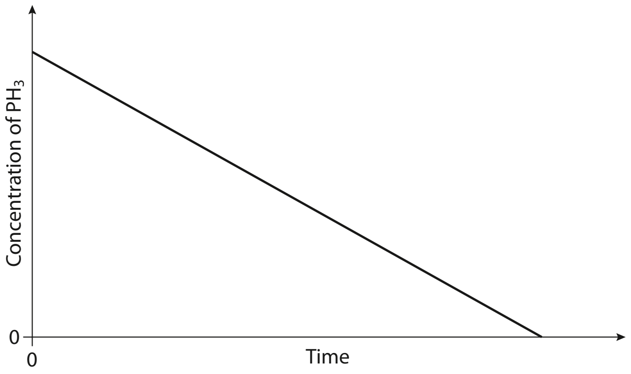
$= 1.28 \times 10^{-4}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$

In the second method, the concentration of X is $\frac{1}{5}$ its value in experiment 1 and the reaction is first order with respect to X, so dividing the concentration of X by 5 will reduce the rate by a factor of 5; the concentration of Y is $\frac{1}{5}$ its value in experiment 1 and the reaction is first order with respect to Y, so dividing the concentration of Y by 5 will reduce the rate by a factor of 5. If we take these two factors together, the rate in the new experiment will be $\frac{1}{25}$ times the rate in experiment 1. **[2]**

rate $= 3.20 \times 10^{-3} \times \frac{1}{25} = 1.28 \times 10^{-4}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$

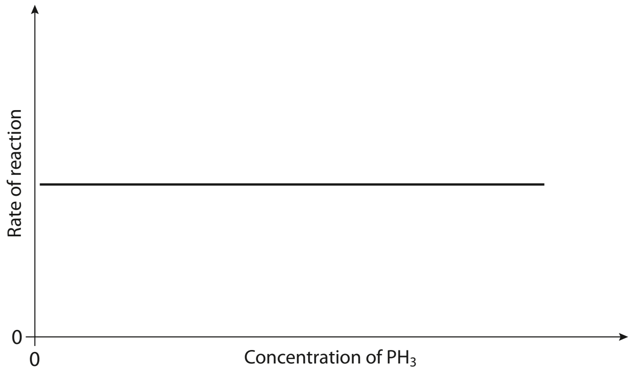
e The rate constant increases as the temperature increases. This is because more particles have energy greater than or equal to the activation energy at a higher temperature. **[2]**

14 a



[2]

b



[2]

15 a The rate equation cannot be derived directly from the stoichiometric equation because the reaction could occur in more than one step. This reaction is unlikely to occur in one step, because that would involve three molecules all colliding at the same time, which is statistically extremely unlikely. **[2]**

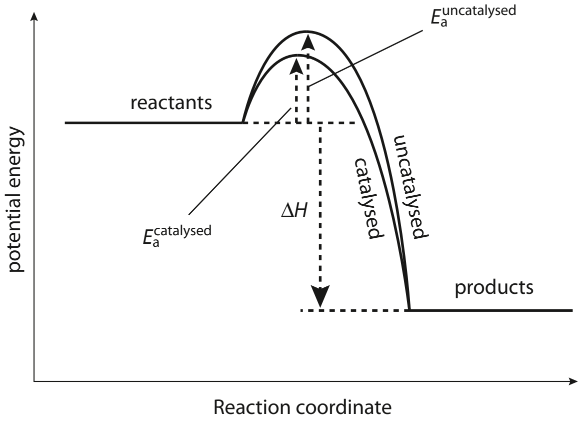
b The rate-determining step is the slowest step in a reaction mechanism: that is, the step with highest activation energy. **[1]**

c $\mathrm{NO + NO \rightarrow N_2O_2}$ **rate-determining step**
$\mathrm{N_2O_2 + O_2 \rightarrow 2NO_2}$ **fast**

The rate expression contains $[\mathrm{NO}]^2$, which indicates that two molecules of NO are involved up to and including the rate-determining step – molecularity of the rate-determining step is 2 because there are two reactant molecules involved. There is no O_2 in the rate equations, which indicates that O_2 can be involved in the mechanism only in a fast step after the rate-determining step. **[4]**

d All the concentrations will be decreased by a factor of 2. The rate of the reaction depends on the concentration of NO squared, so if the concentration is halved the rate will decrease by a factor of 2^2. So the rate will be decreased by a factor of 4. **[2]**

e


$E_a^{\text{uncatalysed}}$
reactants
uncatalysed
catalysed
ΔH
$E_a^{\text{catalysed}}$
products
potential energy
Reaction coordinate

[4]

Answers to exam-style questions

Topic 7

1 C

2 B

3 A

4 A

5 C

6 A

7 D

8 B

9 C

10 D

11 **a** In dynamic equilibrium, macroscopic properties are constant/the concentrations of all reactants and products remain constant. The rate of the forward reaction is equal to the rate of the reverse reaction. [2]

b **i** The position of equilibrium shifts to the right because the forward reaction is endothermic. As the temperature is increased, the position of equilibrium shifts in the direction that minimises the effect of the change – to the right (endothermic direction) – to take in heat. The value of the equilibrium constant increases because more H_2O and CO are present at equilibrium. The expression for the equilibrium constant is:

$$K_c = \frac{[H_2O][CO]}{[H_2][CO_2]}$$

The concentrations of H_2O and CO are on the top of this expression. **[3]**

ii The position of equilibrium does not change; there is the same number of moles of gas on both sides of the equation. The value of the equilibrium constant does not change; only a change in temperature affects the value of the equilibrium constant. **[2]**

iii The position of equilibrium and the value of the equilibrium constant do not change; a catalyst speeds up the forward and reverse reactions equally. **[2]**

12 **a** $K_c = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]}$ **[1]**

b As the temperature increases, the value of the equilibrium constant increases. This means that the position of equilibrium has shifted to the right (more NO present at equilibrium). The forward reaction is therefore endothermic; when the temperature increases the position of equilibrium shifts in the endothermic direction to take in heat and minimise the effect of the change. **[3]**

13 **a** $K_c = \frac{[NO_2(g)]^2}{[N_2O_4(g)]}$ **[1]**

b The mixture will become browner. The forward reaction is endothermic, and as the temperature is increased, the position of equilibrium shifts in the endothermic direction (to the right) to take in heat and minimise the effect of the change, so there will be more NO_2 (brown) in the equilibrium mixture. **[3]**

c The equilibrium mixture will be less brown/more colourless at higher pressure. There are fewer moles of gas on the left-hand side and as the pressure is increased, the position of equilibrium will shift to the left to minimise the effect of the change. More N_2O_4 (colourless) will be present at equilibrium. The value of the equilibrium constant will not change. Only a change in temperature affects the value of the equilibrium constant. **[4]**

d

	$N_2O_4(g) \rightleftharpoons$	$2NO_2(g)$
initial no. moles/mol	0.200	0.00
equilibrium no. moles/mol	0.140	

The number of moles of N_2O_4 that has reacted is $0.200 - 0.140 = 0.060$ mol. From the chemical equation we can see that 1 mol N_2O_4 reacts to form 2 mol NO_2. Therefore 0.060 mol N_2O_4 react to form $2 \times 0.060 = 0.120$ mol NO_2, so 0.120 mol NO_2 are present at equilibrium.

The volume of the container is $4.00\,dm^3$.

Equilibrium concentrations are worked out using:

concentration = no. moles/volume

Therefore the equilibrium concentrations are:

$$[N_2O_4] = \frac{0.140}{4.00} = 0.0350\,mol\,dm^{-3}$$

$$[NO_2] = \frac{0.120}{4.00} = 0.0300\,mol\,dm^{-3}$$

The expression for K_c is:

$$K_c = \frac{[NO_2(g)]^2}{[N_2O_4(g)]}$$

The values can be put into this expression:

$$K_c = \frac{0.0300^2}{0.0350} = 0.0257$$ **[4]**

14 a i $K_c = \dfrac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]}$ **[1]**

ii

	$2SO_2(g) +$	$O_2(g) \rightleftharpoons$	$2SO_3(g)$
initial no. moles/mol	0.120	0.120	0.00
equilibrium no. moles/mol			0.060

From the chemical equation we can work out that 0.030 mol O_2 must have reacted to produce 0.060 mol SO_3 (the mole ratio is 1 : 2 in the equation). Therefore the number of moles of O_2 left at equilibrium is $0.120 - 0.030 = 0.090$ mol.

The volume of the reaction vessel is 2.00 dm^3.

$$\text{concentration} = \frac{\text{no. moles}}{\text{volume}}$$

Therefore:

$$\text{concentration of } O_2 \text{ at equilibrium} = \frac{0.090}{2.00}$$

$= 0.045\ mol\,dm^{-3}$ **[2]**

iii To work out the equilibrium constant, we need the equilibrium concentrations of all species.

	$2SO_2(g) +$	$O_2(g) \rightleftharpoons$	$2SO_3(g)$
initial no. moles/mol	0.120	0.120	0.00
equilibrium no. moles/mol		0.090	0.060

From the chemical equation we can work out that 0.060 mol SO_2 must have reacted to produce 0.060 mol SO_3 (the mole ratio is 2 : 2 in the equation). Therefore the number of moles of SO_2 left at equilibrium is $0.120 - 0.060 = 0.060$ mol.

The volume of the reaction vessel is 2.00 dm^3.

$$\text{concentration} = \frac{\text{no. moles}}{\text{volume}}$$

Therefore:

$$\text{concentration of } SO_2 \text{ at equilibrium} = \frac{0.060}{2.00}$$

$= 0.030\ mol\,dm^{-3}$

	$2SO_2(g) +$	$O_2(g) \rightleftharpoons$	$2SO_3(g)$
initial no. moles/mol	0.120	0.120	0.00
equilibrium no. moles/mol	0.060	0.090	0.060
equilibrium concentration/ mol dm^{-3}	0.030	0.045	0.030

$$K_c = \frac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]}$$

Substituting in the equilibrium concentrations we get:

$$K_c = \frac{0.030^2}{0.030^2 \times 0.045} = 22$$ **[3]**

b i $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

We have been given enthalpy change of formation values and can therefore use the equation:

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

To calculate the enthalpy change for the reaction.

$\Sigma\Delta H_f(\text{products}) = 2 \times -395 = -790\ kJ\,mol^{-1}$

$\Sigma\Delta H_f(\text{reactants}) = 2 \times -297 = -594\ kJ\,mol^{-1}$

The enthalpy change of formation of $O_2(g)$ is zero, as it is an element in its standard state.

$\Delta H_r = -790 - (-594) = -196\ kJ\,mol^{-1}$ **[2]**

ii The reaction is exothermic in the forward direction; so as the temperature is increased from 1100 K to 1500 K the position of equilibrium shifts in the endothermic direction, i.e. to the left. There will be less SO_3 present at equilibrium and because SO_3 appears on the top of the K_c expression, the value of K_c will be lower at 1500 K. **[2]**

15 a $K_c = \dfrac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$ **[1]**

b The expression for the equilibrium constant for this reaction would be:

$$K_c = \frac{[H_2(g)][I_2(g)]}{[HI(g)]^2}$$

This is the inverse of the equilibrium constant expression in **a** so the value of the equilibrium constant is $\dfrac{1}{54.0}$, i.e. 0.0185. **[1]**

c

	$H_2(g) +$	$I_2(g) \rightleftharpoons$	$2HI(g)$
initial no. moles/mol	0.00	0.00	2.00
equilibrium no. moles/mol	x	x	$2 - 2x$
equilibrium concentration/mol dm^{-3}	$\dfrac{x}{4.00}$	$\dfrac{x}{4.00}$	$\dfrac{(2-2x)}{4.00}$

We will assume that when the HI comes to equilibrium $2x$ moles react. From the chemical equation we can see that $2x$ moles of HI will form x moles of H_2 and x moles of I_2.

$$K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

Substituting the equilibrium concentrations we get:

$$K_c = \frac{\left[\frac{(2-2x)}{4.00}\right]^2}{\left(\frac{x}{4.00}\right)\left(\frac{x}{4.00}\right)}$$

Because the number of moles is the same on both sides of the chemical equation (two moles of HI and a total of two moles of H_2 and I_2), the volumes cancel out:

$$K_c = \frac{(2-2x)^2}{(x)(x)}$$

We are given that $K_c = 54.0$, so we can write:

$$54.0 = \frac{(2-2x)^2}{x^2}$$

The right-hand side is a perfect square, and taking the square root of both sides we get:

$$\sqrt{54.0} = \frac{2-2x}{x}$$

$$7.39 = \frac{2-2x}{x}$$

Rearranging this we get:

$$7.39x = 2-2x$$

$$9.39x = 2$$

$$x = \frac{2}{9.39} = 0.214\,\text{mol}$$

This is the equilibrium number of moles of H_2, and to determine the equilibrium concentration we must divide by the volume:

$$\text{equilibrium concentration of } H_2 = \frac{0.214}{4.00}$$

$= 0.0535\,\text{mol}\,\text{dm}^{-3}$ **[3]**

Answers to exam-style questions

Topic 8

1 C

2 A

3 B

4 C

5 B

6 B

7 B

8 A

9 B

10 D

11 **a** $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

or

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

The conjugate base is formed when ethanoic acid acts as an acid and loses a proton (H^+). The conjugate base is therefore CH_3COO^- **[2]**

b A strong acid dissociates completely in solution; a weak acid dissociates only partially. **[2]**

c **i** HCl is a strong acid so dissociates completely:

$[H^+(aq)] = 1.00 \times 10^{-3}\,mol\,dm^{-3}$

$pH = -\log_{10}[H^+(aq)] = \log_{10} 1.00 \times 10^{-3} = 3.00$

ii Ethanoic acid is a weak acid and will be less dissociated than the same concentration of hydrochloric acid. The pH will thus be greater than 3, e.g. 4. (Values in the range 3.5–6 should be accepted.) **[3]**

d **i** $Mg + 2CH_3COOH \rightarrow (CH_3COO)_2Mg + H_2$

magnesium ethanoate and hydrogen gas **[2]**

ii Equal concentrations of the two acids must be reacted with magnesium; the strong acid will react more vigorously with magnesium because the strong acid has a higher concentration of H^+ ions. **[2]**

12 **a** $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ **[1]**

b $K_w = [H^+(aq)][OH^-(aq)]$ **[1]**

c NaOH is a strong base; so ionises fully

$[OH^-(aq)] = 0.10\,mol\,dm^{-3}$

$[H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}$

$[H^+(aq)] = 1.0 \times 10^{-13}\,mol\,dm^{-3}$

$pH = -\log[H^+(aq)] = -\log 1.0 \times 10^{-13} = 13$ **[3]**

d Barium hydroxide will have a higher pH; barium hydroxide has the formula $Ba(OH)_2$ and is a strong base; a $0.10\,mol\,dm^{-3}$ solution will ionise to produce $[OH^-(aq)] = 0.20\,mol\,dm^{-3}$; a higher concentration of $OH^-(aq)$; so a higher pH. **[2]**

13 **a** $pH = -\log_{10}[H^+(aq)]$ **[1]**

b $K_a = 10^{-pK_a}$

$K_a = 10^{-4.82} = 1.51 \times 10^{-5}$

The equation for the dissociation of butanoic acid is:

$CH_3CH_2CH_2COOH(aq) \rightleftharpoons CH_3CH_2CH_2COO^-(aq) + H^+(aq)$

The expression for K_a is:

$$K_a = \frac{[CH_3CH_2CH_2COO^-(aq)][H^+(aq)]}{[CH_3CH_2CH_2COOH(aq)]}$$

Because one molecule of $CH_3CH_2CH_2COOH$ dissociates to form one $CH_3CH_2CH_2COO^-$ ion and one H^+ ion, the concentrations of $CH_3CH_2CH_2COO^-$ and H^+ ions in the solution will be equal:

$[CH_3CH_2CH_2COO^-(aq)] = [H^+(aq)]$

We will make the assumption that the dissociation of the acid is negligible compared with the concentration of the acid; that is, we will assume that the concentration of the acid at equilibrium is the same as the initial concentration, $0.150\,mol\,dm^{-3}$ in this case. These terms are substituted into the K_a expression:

$$1.51 \times 10^{-5} = \frac{[H^+(aq)]^2}{0.150}$$

$[H^+(aq)]^2 = 1.51 \times 10^{-5} \times 0.150 = 2.27 \times 10^{-6}$

$[H^+(aq)] = \sqrt{(2.27 \times 10^{-6})}$

$= 1.51 \times 10^{-3}\,mol\,dm^{-3}$

$pH = -\log_{10}[H^+(aq)]$

$pH = -\log_{10}(1.51 \times 10^{-3}) = 2.82$ **[4]**

c It will be higher than 7, because sodium butanoate is the salt of a strong base (NaOH) and a weak acid (butanoic acid). When sodium butanoate dissolves in water, the two ions separate from each other; the solution contains $CH_3CH_2CH_2COO^-(aq)$ and $Na^+(aq)$ ions. The $CH_3CH_2CH_2COO^-$ ion is the conjugate base of the weak acid butanoic acid and so, acting as a base, will react with water molecules to accept a proton according to the equilibrium:

$CH_3CH_2CH_2COO^-(aq) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2COOH(aq) + OH^-(aq)$

The concentration of OH^- ions in the solution has been increased and the solution is alkaline. **[3]**

d **i** The equation for the reaction is:

$$CH_3CH_2CH_2COOH(aq) + NaOH(aq) \rightarrow CH_3CH_2CH_2COONa(aq) + H_2O(l)$$

$$\text{no. moles of butanoic acid} = \frac{25.00}{1000} \times 0.150$$

$= 3.75 \times 10^{-3}$ mol

From the chemical equation: one mole of butanoic acid react with one mole of sodium hydroxide. Therefore 3.75×10^{-3} mol butanoic acid reacts with 3.75×10^{-3} mol sodium hydroxide. So there are 3.75×10^{-3} mol present in 27.60 cm^3 of sodium hydroxide.

The concentration of sodium hydroxide is:

$$\frac{3.75 \times 10^{-3}}{(27.60/1000)} = 0.136\,mol\,dm^{-3}$$ **[3]**

ii NaOH is a strong base and therefore completely ionises in solution:

$[OH^-(aq)] = 0.136\,mol\,dm^{-3}$

$pOH = -\log_{10}[OH^-(aq)]$

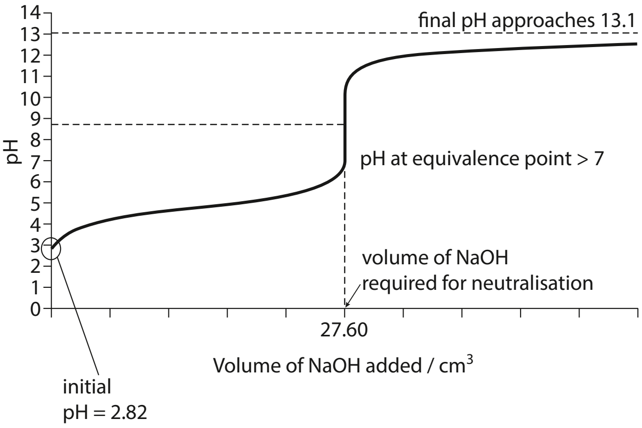
$pOH = -\log_{10} 0.136 = 0.866$

Assuming that the temperature is 25 °C:

$14 = pH + pOH$

$pH = 14 - 0.866 = 13.1$ **[3]**

iii



The values quoted are from the previous parts of the question. The pH at the equivalence point is higher than 7 because sodium butanoate is formed in the titration. The final pH will approach the pH of the sodium hydroxide solution used. **[3]**

iv The most suitable indicator for a strong base–weak acid titration is phenolphthalein. The range of the indicator (8.3–10.0) comes entirely within the very steep part of the titration curve. **[2]**

14 **a** $CH_3CH_2COOH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COO^-(aq) + H_3O^+(aq)$

or

$CH_3CH_2COOH(aq) \rightleftharpoons CH_3CH_2COO^-(aq) + H^+(aq)$ **[2]**

b $K_a = 10^{-pK_a}$

For ethanoic acid, $K_a = 10^{-4.76}$

$= 1.74 \times 10^{-5}$

For propanoic acid, $K_a = 10^{-4.87}$

$= 1.35 \times 10^{-5}$

Ethanoic acid is the stronger acid, because it has a higher K_a value. A higher K_a indicates that a greater proportion of the acid molecules have dissociated. **[4]**

c The equation for the dissociation of propanoic acid is:

$CH_3CH_2COOH(aq) \rightleftharpoons CH_3CH_2COO^-(aq) + H^+(aq)$

The expression for K_a is:

$$K_a = \frac{[CH_3CH_2COO^-(aq)][H^+(aq)]}{[CH_3CH_2COOH(aq)]}$$

Because one molecule of CH_3CH_2COOH dissociates to form one $CH_3CH_2COO^-$ ion and one H^+ ion, the concentration of $CH_3CH_2COO^-$ and H^+ ions in the solution will be equal:

$[CH_3CH_2COO^-(aq)] = [H^+(aq)]$

We will make the assumption that the dissociation of the acid is negligible compared with the concentration of the acid; so the concentration of the acid at equilibrium is the same as the initial concentration, 0.250 $mol\,dm^{-3}$ in this case.

These terms and the K_a value are substituted into the K_a expression:

$$1.35 \times 10^{-5} = \frac{[H^+(aq)]^2}{0.250}$$

$[H^+(aq)]^2 = 1.35 \times 10^{-5} \times 0.250 = 3.37 \times 10^{-6}$

$[H^+(aq)] = \sqrt{(3.37 \times 10^{-6})} = 1.84 \times 10^{-3}\,mol\,dm^{-3}$

$pH = -\log_{10}[H^+(aq)]$

$pH = -\log_{10}(1.84 \times 10^{-3}) = 2.74$ **[4]**

d $CH_3CH_2COO^-(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COOH(aq) + OH^-(aq)$ **[1]**

e $K_a \times K_b = K_w$ for a conjugate acid–base pair. Assuming that the temperature is 25 °C and therefore that $K_w = 1.00 \times 10^{-14}$.

K_a for propanoic acid is 1.35×10^{-5}, so

$1.35 \times 10^{-5} \times K_b = 1.00 \times 10^{-14}$

$K_b = 7.41 \times 10^{-10}$ **[2]**

f We can write an expression for K_b for $CH_3CH_2COO^-$

$$K_b = \frac{[CH_3CH_2COOH(aq)][OH^-(aq)]}{[CH_3CH_2COO^-(aq)]}$$

One $CH_3CH_2COO^-$ ion reacts with one H_2O molecule to form one CH_3CH_2COOH molecule and one OH^- ion; therefore:

$[CH_3CH_2COOH(aq)] = [OH^-(aq)]$

We will use the approximation that the amount of $CH_3CH_2COO^-$ that reacts with water is negligible compared with its concentration and take $[CH_3CH_2COO^-(aq)]$ to be $0.200\,mol\,dm^{-3}$.

Substituting known values into the K_b expression:

$$7.41 \times 10^{-10} = \frac{[OH^-(aq)]^2}{0.200}$$

$[OH^-] = 1.22 \times 10^{-5}\,mol\,dm^{-3}$

$pOH = -\log_{10}[OH^-(aq)]$

$pOH = -\log_{10} 1.22 \times 10^{-5} = 4.91$

$pOH + pH = pK_w$

At 25 °C, $pOH + pH = 14$; therefore:

$pH = 14 - 4.91 = 9.09$ **[4]**

15 a $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ **[1]**

b $K_w = [H^+(aq)][OH^-(aq)]$

Because one H_2O molecule dissociates to form one H^+ ion and one OH^- ion, in pure water the concentration of H^+ ions is equal to the concentration of OH^- ions. We can therefore write $K_w = [H^+(aq)]^2$ for pure water. So, at 40 °C:

$5.48 \times 10^{-14} = [H^+(aq)]^2$

$[H^+(aq)] = \sqrt{(5.48 \times 10^{-14})}$

$[H^+(aq)] = 2.34 \times 10^{-7}\,mol\,dm^{-3}$

$pH = -\log_{10}[H^+(aq)]$

$pH = -\log_{10}(2.34 \times 10^{-7}) = 6.63$ **[3]**

c pOH for a neutral solution at 323 K will be the same as the pH, i.e. 6.63. This solution has a pOH of 7.0. A higher pOH indicates a lower concentration of OH^- ions than in a neutral solution; therefore the solution is acidic.

or

K_w is 5.48×10^{-14} at 323 K. Therefore

$pK_w = 13.26$.

$pK_w = pH + pOH$

If $pOH = 7.0$, the pH of this solution is $13.26 - 7.0 = 6.26$.

This solution has a lower pH than the neutral pH at this temperature and is, therefore, acidic. **[3]**

d K_w for water at 288 K is $10^{-14.34}$, i.e. 4.57×10^{-15}.

K_w is 5.48×10^{-14} at 323 K.

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

As the temperature increases, the value of K_w increases and therefore more water dissociates. The position of equilibrium shifts to the right as the temperature increases, so the reaction to the right must be endothermic. When the temperature increases, the position of equilibrium shifts in the endothermic direction to take in heat and minimise the effect of the change. **[3]**

16 a A buffer solution is one that resists changes in pH when small amounts of acid or base are added. **[2]**

b If some hydrochloric acid is added to this solution, the extra H^+ added reacts with the NH_3 in the solution:

$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$

If some sodium hydroxide is added to the solution, the extra OH^- added reacts with the NH_4^+ in the solution:

$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$ **[2]**

c $K_b = 10^{-pK_b}$ $K_b = 10^{-4.75}$

Therefore, $K_b = 1.78 \times 10^{-5}$.

The ionisation of ammonia is shown by the equation:

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

The expression for K_b is:

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

One NH_3 molecule ionises to produce one NH_4^+ and one OH^- ion. This means that the concentration of NH_4^+ is equal to the OH^- concentration and we can write:

$$K_b = \frac{[OH^-(aq)]^2}{[NH_3(aq)]}$$

We will make the approximation that the concentration of NH_3 at equilibrium is equal to the initial concentration, i.e. that the ionisation of the base is negligible compared with its concentration. Therefore we take $[NH_3(aq)]$ to be $0.125\,mol\,dm^{-3}$. If we substitute this value and the value for K_b into the expression for K_b we get:

$$1.78 \times 10^{-5} = \frac{[OH^-(aq)]^2}{0.125}$$

$[OH^-(aq)]^2 = 1.78 \times 10^{-5} \times 0.125 = 2.22 \times 10^{-6}$

$[OH^-(aq)] = 1.49 \times 10^{-3}\,mol\,dm^{-3}$

$pOH = -\log_{10}[OH^-(aq)]$

$pOH = -\log_{10}(1.49 \times 10^{-3}) = 2.83$ **[3]**

d The amount of HCl that has been added is half the amount required for neutralisation; at the half-neutralisation point, $pOH = pK_b$ because $[NH_3(aq)] = [NH_4^+(aq)]$; therefore $pOH = 4.75$.

So $pH = 14 - 4.75 = 9.25$ **[3]**

Answers to exam-style questions

Topic 9

1 A

2 C

3 C

4 C

5 C

6 C

7 C

8 B

9 C

10 D

11 a Oxidation is the loss of electrons. **[1]**

b i +7; O is the more electronegative element and has an oxidation number of -2; $4 \times -2 = -8$, so the oxidation number of Mn must be +7 in order to cancel out all but one of the negative charges and leave an overall charge of -1. **[1]**

ii Fe^{2+}, because it has been oxidised. **[1]**

iii Separate into its two half-equations:

$MnO_4^-(aq) + H^+(aq) \rightarrow Mn^{2+}(aq) + H_2O(l)$

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$

Each is balanced separately by following the procedure given on page **376** or they can be looked up in the IB Chemistry data booklet:

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

The number of electrons is balanced by multiplying the bottom equation by 5 and then the equations can be recombined:

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$ **[2]**

c i Number of moles of $KMnO_4$ = $(21.50/1000) \times 5.00 \times 10^{-3} = 1.08 \times 10^{-4}$ mol **[1]**

ii Number of moles of Fe^{2+} is five times the number of moles of MnO_4^- from the balanced equation for the reaction, so no. of moles of $Fe^{2+} = 5 \times 1.08 \times 10^{-4} = 5.38 \times 10^{-4}$ mol **[1]**

iii Number of moles of Fe^{2+} in 250.0 cm^3 solution $= 10 \times 5.38 \times 10^{-4} = 5.38 \times 10^{-3}$ mol

This is the number of moles of iron in five iron tablets.

The mass of iron in 5 iron tablets is:

$5.38 \times 10^{-3} \times 55.85 = 3.00 \times 10^{-1}$ g

So the mass of iron in one iron tablet is:

$3.00 \times 10^{-1}/5 = 6.00 \times 10^{-2}$ g **[3]**

iv 6.00×10^{-2} g is 60.0 mg of iron per tablet; the manufacturer's claim seems to be wrong. However, some solution would be lost in the filtering process and there could have been other systematic errors in the experiment. **[2]**

12 a A species that donates electrons (to another substance) and is itself oxidised. **[1]**

b i $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ **[2]**

ii Copper is less reactive than lead; it is unable to displace lead ions from solution. **[1]**

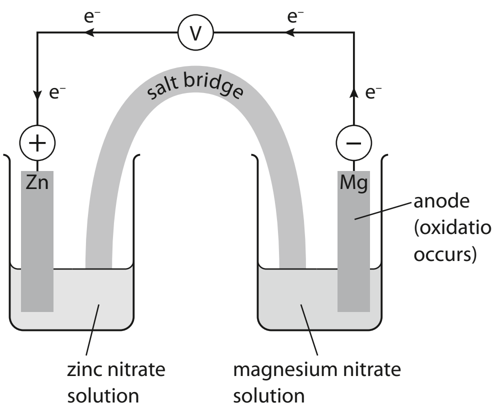
iii magnesium (most reactive) > zinc > lead > copper (least reactive)

Zinc can displace copper and lead from solution but cannot displace magnesium, so zinc must be more reactive than lead and copper but less reactive than magnesium. Copper cannot displace lead, therefore must be less reactive than lead. **[1]**

iv Magnesium is the strongest reducing agent; it will displace the other metals from solution. This means that magnesium will reduce Zn^{2+} to Zn, Pb^{2+} to Pb and Cu^{2+} to Cu. Zinc is able to reduce only lead and copper ions, lead can reduce only copper ions and copper cannot reduce the ions of any of these metals. **[3]**

v $Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s)$ **[2]**

c i



[3]

ii $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

The zinc ion gains electrons; this is reduction. **[2]**

13 a In solid sodium chloride, the ions are fixed in position in the lattice structure (they can only vibrate); when the sodium chloride is melted the ions are free to move around. **[2]**

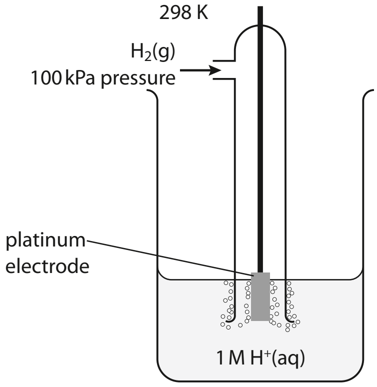
b At the anode, the product is chlorine:

$2Cl^- \rightarrow Cl_2 + 2e^-$

At the cathode, the product is sodium:

$Na^+ + e^- \rightarrow Na$ **[3]**

14 a



[5]

b i $Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$ −1.18 V

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ +0.77 V

The more negative electrode potential is reversed: $1.18 + 0.77 = +1.95\,V$.

The standard cell potential is +1.95 V. **[1]**

ii $2Fe^{3+}(aq) + Mn(s) \rightarrow 2Fe^{2+}(aq) + Mn^{2+}(aq)$ **[2]**

iii The anode is the electrode at which oxidation occurs; Mn is oxidised, so this is the anode. **[2]**

iv From the Mn electrode to the platinum electrode (Fe^{2+}/Fe^{3+} half-cell). **[1]**

v The salt bridge completes the circuit; allows ions to flow into/out of the half-cells and prevents a build-up of charge. **[2]**

vi $\Delta G^\ominus = -nFE^\ominus = -2 \times 96\,500 \times 1.95$

$= -376\,000\,J\,mol^{-1}$

$= -376\,kJ\,mol^{-1}$

$\Delta G^\ominus$ is negative; the reaction is spontaneous. **[3]**

15 a MnO_4^- is the strongest oxidising agent. It has the most positive electrode potential and therefore the strongest tendency to gain electrons/be reduced. **[2]**

b From the standard electrode potentials it can be seen that $Cr_2O_7^{2-}$ will oxidise Br^- ions but not Cl^- ions. $Cr_2O_7^{2-}$ has a more positive standard electrode potential than Br_2 and a less positive electrode potential than Cl_2. It is thus a stronger oxidising agent than Br_2 but weaker than Cl_2. This could also be explained by working out the cell potentials. The cell potential for the reaction with Br^- ions is positive (+0.24 V), but the cell potential for the reaction with Cl^-, is negative (-0.03 V). A positive cell potential indicates a spontaneous reaction.

To work out the overall equation for the reaction between $Cr_2O_7^{2-}$ and Br^- the half-equation for Br_2/Br^- must be reversed because the bromide ions are oxidised:

$2Br^-(aq) \rightarrow Br_2(l) + 2e^-$

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

The top equation must be multiplied by 3 so that the electrons balance:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Br^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3Br_2(l)$ **[3]**

c $2Cl^-(aq) + Br_2(l) \rightarrow Cl_2(g) + 2Br^-(aq)$

Using the standard electrode potentials we can work out that the cell potential for this reaction is: $-1.36 + 1.09 = -0.27\,V$.

The cell potential is negative, so the reaction will not be spontaneous and the sign of $\Delta G^\ominus$ will be positive. **[2]**

d i HCOOH: +2 HCHO: 0

The oxidation number of C decreases, so HCOOH is reduced. **[3]**

ii There is the same number of C atoms on both sides. The H atoms must then be balanced by adding another H^+ to the left hand side so that there are 2 H^+ on that side. The O atoms are balanced. The total charge on the left hand side is now 1+ but there is no charge on the right hand side, therefore an extra electron must be added to the left hand side.

$HCOOH(aq) + 2H^+(aq) + 2e^- \rightarrow HCHO(aq) + H_2O(l)$ **[1]**

iii MnO_4^- will oxidise methanal to methanoic acid (MnO_4^- has a more positive electrode potential).

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$HCHO(aq) + H_2O(l) \rightarrow HCOOH(aq) + 2H^+(aq) + 2e^-$

To balance the number of electrons, the top equation must be multiplied by 2 and the bottom equation by 5:

$$2MnO_4^-(aq) + 16H^+(aq) + 5HCHO(aq) + 5H_2O(l) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5HCOOH(aq) + 10H^+(aq)$$

H^+ ions and H_2O molecules can then be cancelled from each side:

$2MnO_4^-(aq) + 6H^+(aq) + 5HCHO(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5HCOOH(aq)$ **[2]**

iv The reaction mixture may need to be heated as the reaction may have a high activation energy. **[1]**

16 a Because the solution is concentrated, chlorine will be formed at the anode, rather than oxygen.
At the anode the product is chlorine gas:
$2Cl^- \rightarrow Cl_2 + 2e^-$
At the cathode the product is hydrogen gas:
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
Hydrogen is produced at the cathode rather than sodium because sodium is a reactive metal and so it is more difficult to reduce sodium ions to sodium than it is to reduce water to hydrogen. **[4]**

b i Oxygen gas is formed at the anode:
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ **[2]**

ii The electrolyte will become less blue as the copper ions, which are responsible for the blue colour, are removed at the cathode.
The electrolyte will become more acidic as H^+ ions are produced at the anode. The electrolyte will become sulfuric acid because copper ions are removed from the solution and replaced by H^+ ions. **[2]**

c i Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ **[2]**

ii The colour of the electrolyte will not change – it will remain the same shade of blue – as the concentration of copper ions in the solution will remain constant. Copper ions are produced at the anode at the same rate as they are used up at the cathode. **[2]**

Answers to exam-style questions

Topic 10

1 A

2 C

3 B

4 C

5 C

6 D

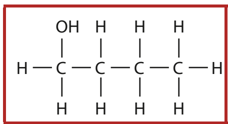
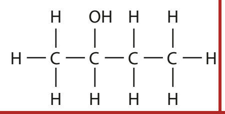
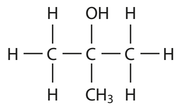
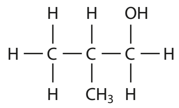
7 C

8 A

9 C

10 B

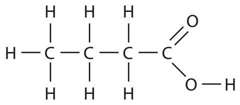
11 **a** Alcohols contain the –OH functional group.

	butan-1-ol
	butan-2-ol
	2-methylpropan-2-ol
	2-methylpropan-1-ol

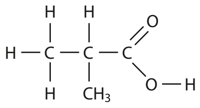
[4]

b Only primary alcohols can be oxidised to a carboxylic acid. Primary alcohols have only one C attached to the carbon with the OH group on it. Butan-1-ol and 2-methylpropan-1-ol are primary alcohols. The only change that occurs is that the $-CH_2OH$ group of the primary alcohol becomes a –COOH group in the carboxylic acid – the rest of the carbon skeleton remains unchanged.

butan-1-ol becomes:



2-methylpropan-1-ol becomes:

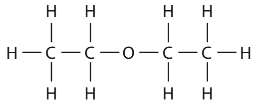


Suitable oxidising agents are: acidified potassium dichromate(VI), $K_2Cr_2O_7/H^+$ or just $Cr_2O_7^{2-}/H^+$ colour change: orange to green

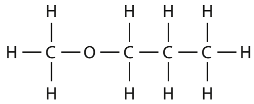
or

acidified potassium manganate(VII), $KMnO_4/H^+$ or MnO_4^-/H^+ colour change: purple to colourless **[6]**

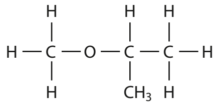
c The isomer must have the same molecular formula but no –OH group. Possible isomers are:



ethoxyethane



1-methoxypropane



2-methoxypropane

[2]

12 **a** $C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$ **[1]**

b **i** free radical substitution **[1]**

ii *Homolytic fission* occurs in the initiation step. In the presence of ultraviolet light the Cl–Cl bond breaks so that one electron goes to each Cl atom:

$Cl_2 \xrightarrow{UV} 2Cl\bullet$

A *free radical* is an atom/group of atoms with an unpaired electron. In this case, $Cl\bullet$ is a free radical. A $CH_3CH_2\bullet$ free radical is also formed in this reaction.

A *termination step* occurs when two free radicals react together – this ends a chain reaction. There are three possible termination steps in this mechanism:

$Cl\bullet + Cl\bullet \rightarrow Cl_2$ Termination

$Cl\bullet + \bullet CH_2CH_3 \rightarrow CH_3CH_2Cl$ Termination

$\bullet CH_2CH_3 + \bullet CH_2CH_3 \rightarrow C_4H_{10}$ Termination

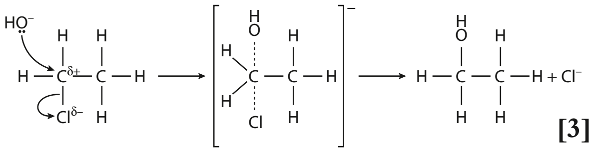
[4]

c **i** $CH_3CH_2Cl + NaOH \rightarrow CH_3CH_2OH + NaCl$

or, as an ionic equation:

$CH_3CH_2Cl + OH^- \rightarrow CH_3CH_2OH + Cl^-$ **[1]**

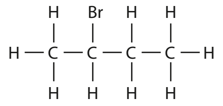
ii Chloroethane is a primary halogenoalkane and therefore reacts by an S_N2 mechanism:



[3]

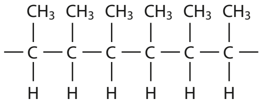
13 a Both compounds must be shaken with bromine water. But-2-ene decolorises the bromine water (orange to colourless), but there is no change with butane. **[3]**

b



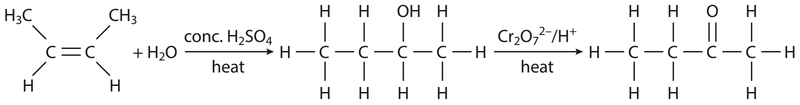
[1]

c Only the C=C part of the molecule reacts – all other groups remain unchanged:



[2]

d Butanone can be obtained by oxidation of a secondary alcohol, butan-2-ol.
To convert but-2-ene to an alcohol we must add water across the double bond:



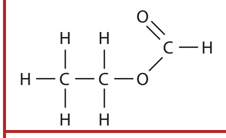
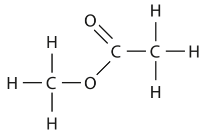
[5]

14 a

	C	**H**	**O**
Percentage	48.6	8.2	43.2
Divide by A_r	48.6 / 12.01	8.2 / 1.01	43.2 / 16.00
Moles	4.05	8.12	2.7
Divide by smallest	4.05 / 2.7	8.12 / 2.7	2.7 / 2.7
Ratio	1.5	3.01	1

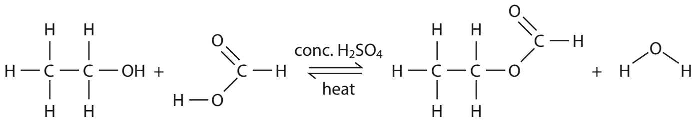
Multiplying by 2 to get whole numbers we get $C_3H_6O_2$, which is the empirical formula. The empirical formula mass is $(3 \times 12.01 + 6 \times 1.01 + 2 \times 16) = 74.09$. The empirical formula mass is the same as the relative molecular mass, so the molecular formula is the same as the empirical formula. The molecular formula is $C_3H_6O_2$. **[3]**

b i Esters contain the COOC functional group:

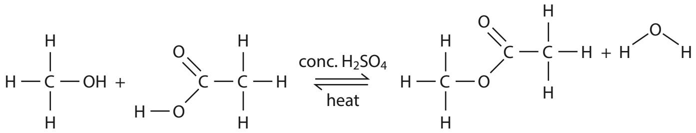
	ethyl methanoate
	methyl ethanoate

[4]

ii

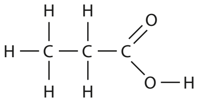


or



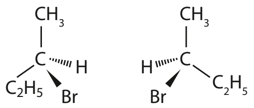
[2]

c Acids react with magnesium to form hydrogen, so this isomer must be a carboxylic acid:



$$2CH_3CH_2COOH + Mg \rightarrow (CH_3CH_2COO)_2Mg + H_2$$ **[3]**

15 a 2-bromobutane has a chiral centre, i.e. a C atom with four different groups attached.



[3]

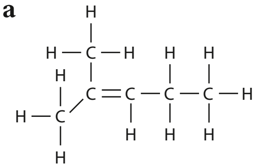
b i 'N' stands for 'nucleophilic'. A nucleophile is a molecule/negatively charged ion, possessing a lone pair of electrons, which is attracted to a more positively charged region in a molecule (region with lower electron density) and donates a lone pair of electrons to form a covalent bond. **[1]**

ii The S_N2 mechanism occurs with inversion of configuration at the carbon attached to the halogen. Which enantiomer of the product is formed can be predicted from knowing the configuration of the enantiomer you started with. **[2]**

iii 1-bromobutane will react more quickly than 2-bromobutane via an S_N2 mechanism. There is less steric hindrance around the C with the Br in 1-bromobutane, because there is only one alkyl group attached to this C. It is therefore easier for the nucleophile to get in to attack the C in 1-bromobutane.
An alternative explanation is in terms of the transition state. The transition state will be more crowded in 2-bromobutane, because there are two alkyl groups around the five

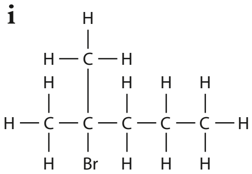
co-ordinate C. This makes the transition state less stable for 2-bromobutane, and so the activation energy is higher. This means that this reaction will occur more slowly. **[2]**

16 a



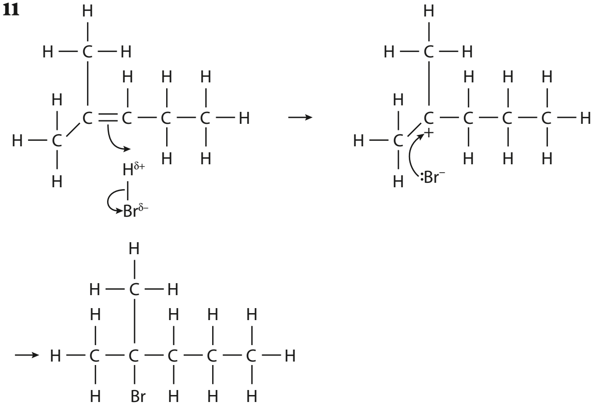
[1]

b i



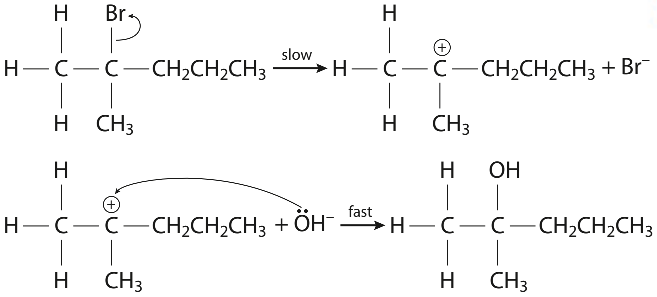
This is an addition reaction and H–Br will add across the C=C. The alkene is unsymmetrical so we can use Markovnikov's rule to predict the major product. The H of the H–Br will become attached to the C which has more Hs already attached; that is, carbon 3. **[2]**

ii



The major product is formed because when the H joins to the C atom with more H atoms attached a tertiary carbocation is formed. This is more stable than the secondary carbocation that would be formed if the bond broke the other way. The tertiary carbocation is more stable because there are more electron-releasing alkyl groups attached to the C with the positive charge. **[5]**

c



[3]

d X cannot be oxidised because it is a tertiary alcohol. **[1]**

Answers to exam-style questions

Topic 11

1 B

2 A

3 A

4 C

5 C

6 B

7 C

8 D

9 A

10 B

11 a Experiment B has produced the more precise values because there is a smaller spread of values. The range of values in experiment A is $53.2 - 49.2 = 4$. The range of values in experiment B is $51.2 - 50.6 = 0.6$. The smaller range in experiment B indicates more precise data. **[2]**

b The mean value in experiment A is 51.2. The mean value in experiment B is 50.9. The mean value in experiment B is closer to the literature value and therefore this is the more accurate experiment. **[3]**

12 a percentage error =

$$\frac{|\text{experimental value} - \text{accepted value}|}{|\text{accepted value}|} \times 100$$

$$\text{percentage error} = \frac{|56.1 - 55.2|}{55.2} \times 100 = 1.6\%$$

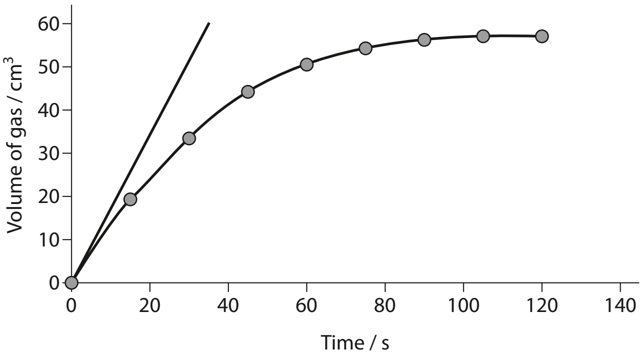
[1]

b percentage uncertainty due to random

$$\text{uncertainties} = \frac{0.5}{56.1} \times 100 = 0.9\%$$

The percentage error (1.6%) is larger than that due to random uncertainties (0.9%) and therefore the student is not correct. This experiment contains systematic errors. **[2]**

13 a



[3]

b A tangent is drawn at the initial point of the graph as shown.

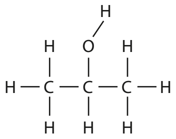
The gradient of this tangent is $\frac{56}{32} = 1.8\,\text{cm}^3\,\text{s}^{-1}$.

The initial rate of reaction is therefore $1.8\,\text{cm}^3\,\text{s}^{-1}$. This value is given to two significant figures, because the original data were given to two significant figures. The units are obtained by dividing the units on the *y*-axis by those on the *x*-axis. **[3]**

14 a There is an absorption band in the range 1700–1750 cm^{-1}, which suggests the presence of a C=O group; so molecule **I** can be eliminated (also no O–H absorption in the spectrum). There is no very broad band absorption in the range 2400–3400 cm^{-1}, which is characteristic of carboxylic acids, so molecule **III** can be eliminated. There is no absorption band in the range 1000–1300 cm^{-1}, indicating that no C–O bond is present, so molecule **IV** (and **III** and **I**) can be eliminated. So this must be the spectrum of molecule **II**. **[4]**

b Both propanal and propanone contain the same bonds and will have very similar absorption bands in the region around 1500 cm^{-1}. However, propanal has three peaks in its NMR spectrum (three different chemical environments for H) while propanone has only one, so they can be distinguished easily using NMR. Propanone has only one peak in the NMR spectrum because it is symmetrical and all the H atoms are chemically equivalent. **[4]**

15 **a**

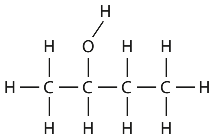


Note that the full structural formula must show the O–H bond. **[1]**

b The three peaks arise because there are three different chemical environments for the protons (hydrogen atoms) in propan-2-ol. **[2]**

c The integration trace gives the relative numbers of protons (hydrogen atoms) in each environment. This is obtained by finding the ratio of the heights of the vertical steps in the trace. **[2]**

d **i**



[1]

ii The molecule is non-symmetrical and so there are five peaks in its NMR spectrum. The ratio of the areas under the peaks is the same as the ratio of the numbers of hydrogen atoms in each environment – 3 : 1 : 1 : 2 : 3. **[2]**

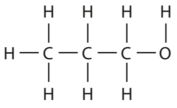
16 **a** The relative molecular mass is obtained from the highest-mass peak in the mass spectrum – 60 in this case. **[1]**

b Z contains C, H and O and the only two possible combinations of these that add up to a relative molecular mass of 60 are C_3H_8O and $C_2H_4O_2$. **[2]**

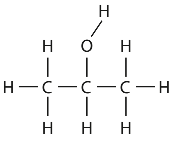
c m/z 31 could be due to CH_3O^+ or CH_2OH^+; m/z 29 could be due to $C_2H_5^+$ or CHO^+ **[2]**

d The absorption band at about 3350 cm^{-1} suggests the presence of an O–H bond. No absorptions in the range 1600–1800 cm^{-1} suggests that there is no C=C or C=O present. **[2]**

e Z cannot have the formula $C_2H_4O_2$ because this requires the presence of a double bond. Therefore Z has the molecular formula C_3H_8O and possible structural formulas that contain an O–H group are:



propan-1-ol



propan-2-ol

[2]

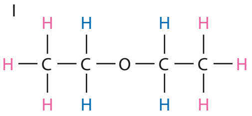
f There are four different chemical environments for hydrogen atoms in propan-1-ol but only three in propan-2-ol because it is symmetrical. There are four peaks in the NMR spectrum, indicating four different chemical environments for hydrogen atoms – so **Z** must be propan-1-ol.

We could also measure the vertical heights of the steps in the integration trace – this works out to be 1 : 2 : 2 : 3, which corresponds with the numbers of hydrogen atoms in each environment in propan-1-ol. **[4]**

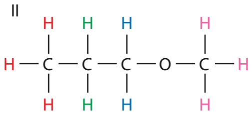
17 **a** The signal caused by the proton (hydrogen atom) in bold type is not split by the protons on the same carbon atom because they are chemically equivalent. There is one hydrogen atom on the adjacent carbon atom, so the signal due to the bold proton is split into a 1 : 1 doublet (if we add 1 to the number of hydrogens on the adjacent carbon atom we get 2 – i.e. a doublet). **[2]**

b This can be approached in two ways. The first is to draw the isomers of $C_4H_{10}O$:

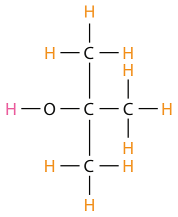
I



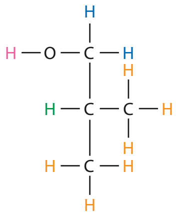
II



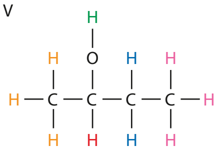
III



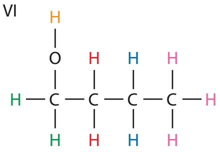
IV



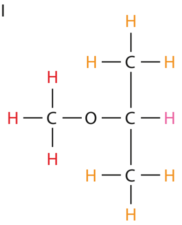
V



VI



VII

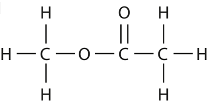


There are two sets of peaks in the NMR spectrum and only two of these isomers (**I** and **III**) have two different chemical environments for hydrogen. These can be distinguished by using the integration trace. The ratio of the heights of the steps is 1 : 1.5, or 2 : 3, so the compound must be isomer **I**. This has hydrogen atoms (protons) in two different chemical environments and the numbers of protons in each are in the ratio 4 : 6, or 2 : 3.

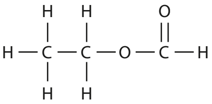
The second way is to consider the splitting pattern and the integration trace. The ratio of the heights of the steps is 1 : 1.5, or 2 : 3. There are 10 protons (hydrogen atoms) in this molecule and if they are divided in the ratio 2:3 there are 4 protons in one chemical environment and 6 in the other. The splitting pattern is a quartet and a triplet – the quartet indicates three hydrogen atoms on the adjacent carbon atom, and the triplet indicates two hydrogen atoms on the other adjacent carbon atom. These two peaks together are characteristic of an ethyl group, CH_3CH_2. So with ten protons there must be two ethyl groups, and the compound is isomer **I**. **[4]**

c The isomers are:

I



II

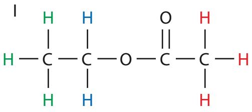


Isomer **I** has two different chemical environments for hydrogen atoms, so there will be two sets of peaks in its NMR spectrum. The ratio of the areas under these peaks will be 1:1. There are no hydrogen atoms on adjacent carbon atoms, so the spectrum will consist of two singlets.

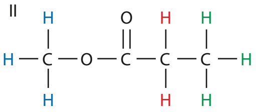
Isomer **II** has three different chemical environments for hydrogen atoms, so there will be three sets of peaks in its NMR spectrum. The ratio of the areas under these peaks will be 3:2:1. There are three hydrogen atoms on one carbon atom and two on the adjacent carbon atom, so the peak with area 3 will be a triplet and the peak with area 2 will be a quartet – the third peak will be a singlet. The quartet will have a chemical shift similar to that of three of the protons in isomer I because the protons (hydrogen atoms) are in the same type of environment but all other chemical shifts will occur in different ranges. **[5]**

d The isomers are:

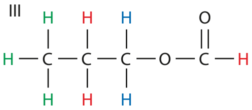
I



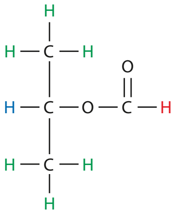
II



III



IV

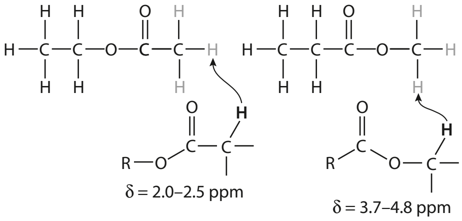


The NMR spectrum shows three sets of peaks and so there are three different chemical environments for hydrogen atoms (protons). This means that isomer **III** can be eliminated because it has four different environments.

The ratio of the heights of the vertical steps in the integration trace is 3:2:3. There is a total of 8 hydrogen atoms in one molecule so this ratio indicates the numbers in each environment. This means isomer **IV** can be eliminated because its ratio of hydrogen atoms in different environments is 6:1:1.

The splitting pattern is singlet, quartet, triplet. Putting this together with the information from the integration trace we can say the following about atom arrangements – there are three Hs with no Hs on an adjacent carbon atom; two Hs with three Hs on an adjacent carbon atom; and three Hs with two Hs on an adjacent carbon atom. The latter two signals indicate the presence of an ethyl group. Both isomers **I** and **II** have the splitting pattern shown in the spectrum and so they have to be distinguished using chemical shifts.

If we consider the singlet in the spectra of isomers **I** and **II**, we can predict the following chemical shifts using Table **11.14**:



The singlet in the spectrum occurs at δ 3.7 ppm, so we can conclude that the compound responsible for the spectrum is isomer **II** – methyl propanoate. **[6]**