FOR OFFICIAL USE

National Qualifications 2023

Mark

X813/77/01

Chemistry
Section 1 — Answer grid and Section 2

FRIDAY, 12 MAY

9:00 AM – 12:00 NOON

X8137701

Fill in these boxes and read what is printed below.

Full name of centre

Town

Forename(s)

Surname

Number of seat

Date of birth

Day Month Year

Scottish candidate number

You may refer to the Chemistry Data Booklet for Higher and Advanced Higher.

Total marks — 110

SECTION 1 — 25 marks

Attempt ALL questions.

Instructions for the completion of Section 1 are given on *page 02*.

SECTION 2 — 85 marks

Attempt ALL questions.

Write your answers clearly in the spaces provided in this booklet. Additional space for answers and rough work is provided at the end of this booklet. If you use this space you must clearly identify the question number you are attempting. Any rough work must be written in this booklet. You should score through your rough work when you have written your final copy.

Use **blue** or **black** ink.

Before leaving the examination room you must give this booklet to the Invigilator; if you do not, you may lose all the marks for this paper.

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X8137701

SECTION 1 — 25 marks

The questions for Section 1 are contained in the question paper X813/77/02.

Read these and record your answers on the answer grid on *page 03* opposite.

Use **blue** or **black** ink. Do NOT use gel pens or pencil.

1. The answer to each question is **either** A, B, C or D. Decide what your answer is, then fill in the appropriate bubble (see sample question below).

2. There is **only one correct** answer to each question.

3. Any rough working should be done on the additional space for answers and rough work at the end of this booklet.

Sample question

To show that the ink in a ball-pen consists of a mixture of dyes, the method of separation would be

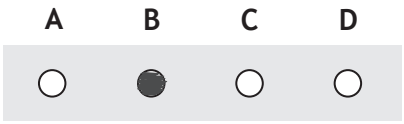
A fractional distillation

B chromatography

C fractional crystallisation

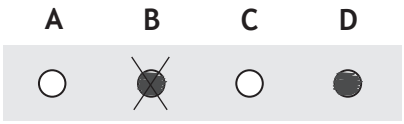
D filtration.

The correct answer is **B** — chromatography. The answer **B** bubble has been clearly filled in (see below).

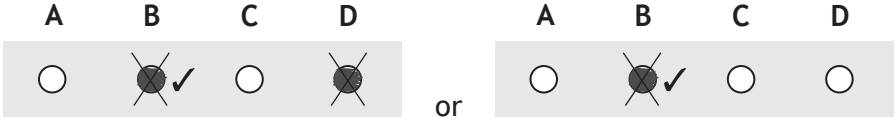


Changing an answer

If you decide to change your answer, cancel your first answer by putting a cross through it (see below) and fill in the answer you want. The answer below has been changed to **D**.



If you then decide to change back to an answer you have already scored out, put a tick (✓) to the **right** of the answer you want, as shown below:



SECTION 1 — Answer grid

0BJ25AD1

	A	B	C	D
1	○	○	○	○
2	○	○	○	○
3	○	○	○	○
4	○	○	○	○
5	○	○	○	○
6	○	○	○	○
7	○	○	○	○
8	○	○	○	○
9	○	○	○	○
10	○	○	○	○
11	○	○	○	○
12	○	○	○	○
13	○	○	○	○
14	○	○	○	○
15	○	○	○	○
16	○	○	○	○
17	○	○	○	○
18	○	○	○	○
19	○	○	○	○
20	○	○	○	○
21	○	○	○	○
22	○	○	○	○
23	○	○	○	○
24	○	○	○	○
25	○	○	○	○

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SECTION 2 — 85 marks

Attempt ALL questions

1. Distress flares and oxygen candles are used in emergency situations.

(a) Some distress flares contain lithium ions and burn with an intense red light.

(i) Explain, in terms of energy levels, why red light is emitted by lithium ions when distress flares are burned. **2**

(ii) Complete the table below showing the quantum numbers and values for an electron in a lithium ion, Li^+, in its ground state. **1**

Quantum number	n	l	m_l	
Value		0	0	$+\frac{1}{2}$

[Turn over

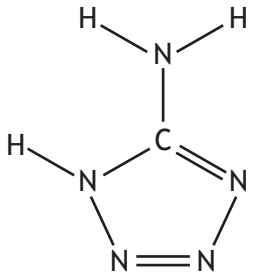
1. (a) (continued)

(iii) Distress flares also contain oxidising agents.

(A) Potassium perchlorate, $KClO_4$, can be used as the oxidising agent.

Determine the oxidation state of chlorine in the perchlorate ion, ClO_4^-. **1**

(B) In some distress flares, 5-aminotetrazole replaces perchlorate ions.



5-aminotetrazole

Determine the number of sigma bonds in a 5-aminotetrazole molecule. **1**

1. (continued)

(b) Oxygen candles can be used to supply oxygen in emergency situations.

(i) The initial energy required to start the oxygen candle can be provided by the combustion of iron.

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

Substance	ΔH_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
Fe(s)	–	27.3
$O_2(g)$	–	205
$Fe_2O_3(s)$	–824	87.4

Using information from the table, calculate

(A) ΔH°, in kJ mol^{-1} **1**

(B) ΔS°, in J K^{-1} mol^{-1} **1**

(C) the temperature, in K, below which the reaction is feasible. **2**

[Turn over

1. (b) (continued)

(ii) Some oxygen candles contain sodium chlorate, $NaClO_3$, which decomposes at high temperatures to produce oxygen.

1.00 mol $NaClO_3$ decomposes to produce 36.0 litres of O_2 and an average person consumes 0.380 litres of O_2 per minute.

Calculate the minimum mass of sodium chlorate required to supply oxygen to 5 people for 8 hours. **2**

[Turn over for next question

DO NOT WRITE ON THIS PAGE

2. The equation for the reaction between mercuric chloride and oxalate ions is shown.

$$2HgCl_2(aq) + C_2O_4^{2-}(aq) \rightarrow 2Cl^-(aq) + 2CO_2(g) + Hg_2Cl_2(s)$$

In an experiment to determine the kinetics for this reaction the following results were obtained.

Experiment	$[HgCl_2]$ (mol l^{-1})	$[C_2O_4^{2-}]$ (mol l^{-1})	Initial rate of reaction (mol l^{-1} s^{-1})
1	0.0840	0.200	0.860×10^{-6}
2	0.0840	0.400	3.44×10^{-6}
3	0.0420	0.400	1.72×10^{-6}
4	0.0320		2.11×10^{-6}

(a) Determine the order of the reaction with respect to

(i) $HgCl_2$ **1**

(ii) $C_2O_4^{2-}$ **1**

(b) Write the overall rate equation for the reaction. **1**

2. (continued)

(c) (i) Calculate a value for the rate constant, k, including the appropriate units. **2**

(ii) Calculate the initial oxalate concentration, in mol l^{-1}, for experiment 4. **1**

[Turn over

MARKS | DO NOT WRITE IN THIS MARGIN

3. Oxalic acid occurs naturally in spinach leaves. The percentage by mass of oxalic acid in spinach leaves was determined by soaking the leaves in water to dissolve the oxalic acid. The spinach leaves were removed from the mixture. Calcium chloride solution was then added to the oxalic acid solution to form a precipitate of calcium oxalate, as shown.

$$(COOH)_2(aq) + CaCl_2(aq) \rightarrow Ca(COO)_2(s) + 2HCl(aq)$$

(a) The calcium oxalate precipitate was isolated by filtration.

(i) Suggest what should be done to ensure the precipitation reaction has gone to completion. **1**

(ii) The isolated precipitate was washed.

State what else should be done to the precipitate before weighing to obtain an accurate mass. **1**

(b) 8.975 g of spinach leaves produced 0.075 g of precipitate.

Calculate the percentage by mass of oxalic acid in the spinach leaves. **2**

(c) A source of information gives the percentage by mass of oxalic acid in spinach leaves as 0.97%.

Suggest a reason for the difference between this quoted mass and your answer from part (b) above. **1**

4. Tap water naturally contains ions including Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Fe^{2+}, Mn^{2+}, Cu^{2+}, Cl^-, and SO_4^{2-}. Regular testing of tap water samples is carried out to ensure that the concentrations of ions are within recommended levels.

Using your knowledge of chemistry, describe how the concentrations of some of these ions in a tap water sample could be determined. **3**

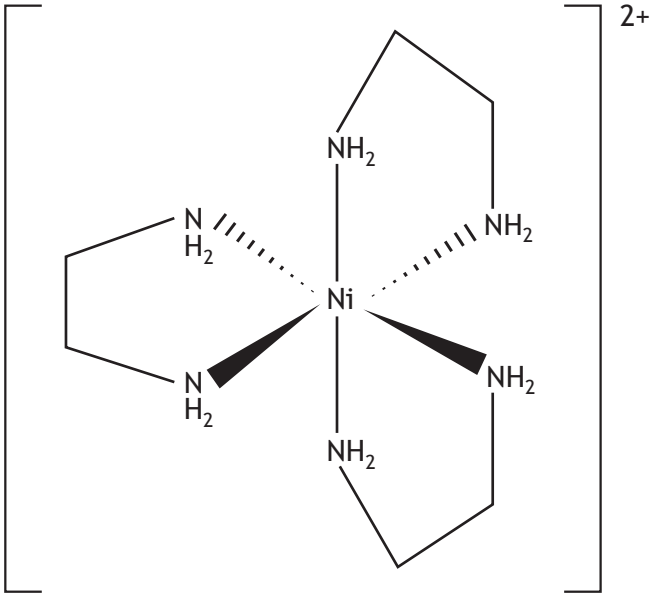
[Turn over

5. Nickel can form complex ions with different ligands.

(a) Write the electronic configuration, in terms of s, p and d orbitals, for the nickel ion in $[Ni(OH_2)_6]^{2+}$. **1**

(b) State the name of the complex ion $[Ni(NH_3)_6]^{2+}$. **1**

(c) The complex ion $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ has the structure shown.



(i) State the term used to classify the type of ligand in this complex. **1**

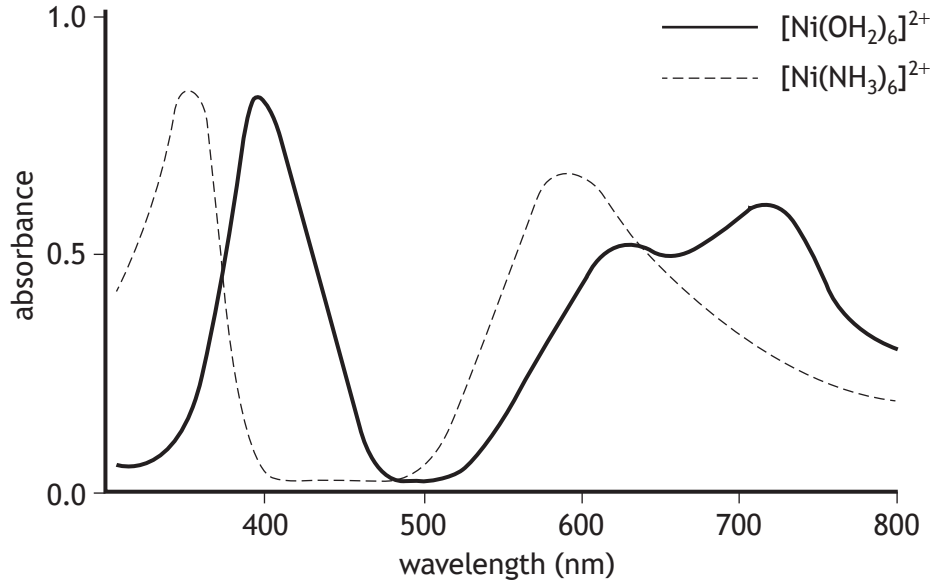
(ii) State the coordination number of nickel in this complex. **1**

5. (continued)

(d) Electron transitions involving the d subshell can give rise to colour in transition metal complexes.

(i) Explain fully why a solution of the complex ion $[Ni(OH_2)_6]^{2+}$ is green. **2**

(ii) The graph shows the absorption spectra for solutions of the complex ions $[Ni(OH_2)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$.



Using information from the graph, explain which ligand has the greater ability to split d orbitals. **1**

[Turn over

6. There are many different compounds containing hydrogen and iodine.

(a) Hydrogen gas and iodine gas combine directly to form hydrogen iodide, HI(g).

At constant temperature, an equilibrium is established.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(i) Write the expression for the equilibrium constant, *K*. **1**

(ii) 0.25 moles of $H_2(g)$ and 0.25 moles of $I_2(g)$ were mixed in a sealed 1.0 litre reaction vessel. At equilibrium, 0.015 moles of $I_2(g)$ were present.

Calculate the equilibrium constant, *K*, for this reaction. **2**

(iii) The rate of the reaction between $H_2(g)$ and $I_2(g)$ can be increased using light of wavelength 578 nm.

Calculate the energy, in kJ mol^{-1}, of light corresponding to this wavelength. **2**

6. (continued)

(b) Hydroiodic acid, HI(aq), was prepared from iodine, $I_2(aq)$, and hydrogen sulfide, $H_2S(g)$.

$$I_2(aq) + H_2S(g) \rightarrow 2HI(aq) + S(s)$$

Hydrogen sulfide gas was bubbled through 250 cm^3 of a solution containing 285 g of iodine. When the reaction was complete, the product mixture was separated by vacuum filtration and the filtrate was purified by distillation.

(i) Name the type of funnel that should be used to carry out vacuum filtration. **1**

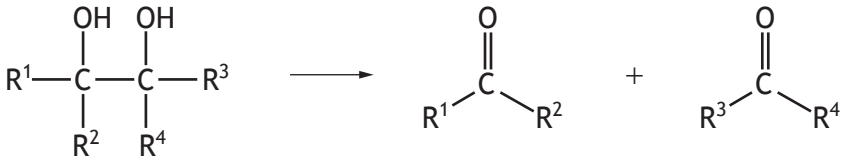
(ii) The distillate contained 251 g of HI.

Calculate the percentage yield for this reaction. **2**

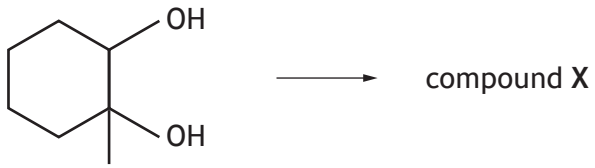
[Turn over

6. (continued)

(c) Periodic acid, H_5IO_6, can be used to oxidise diols with neighbouring hydroxyl groups into two aldehyde or ketone molecules.



The same oxidation reaction with 1-methylcyclohexane-1,2-diol and periodic acid gives only one product, compound **X**.



1-methylcyclohexane-1,2-diol

Draw a structural formula for compound **X**. **1**

7. Oceans are essential in reducing the concentration of carbon dioxide in the atmosphere. Around half of the carbon dioxide produced by burning fossil fuels dissolves in the surface water of oceans.

(a) Carbon dioxide dissolves in water to form carbonic acid, $H_2CO_3(aq)$.

$$H_2O(\ell) + CO_2(g) \rightleftharpoons H_2CO_3(aq) \qquad \Delta H \text{ –ve}$$

Explain the effect rising seawater temperatures will have on the concentration of CO_2 dissolved in the oceans. **1**

(b) Carbonic acid, $H_2CO_3(aq)$, dissociates as shown.

$$H_2CO_3(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \qquad pK_a = 6.35$$

(i) Explain how the strength of carbonic acid compares with that of ethanoic acid. **1**

(ii) State the role of H_2O in the above equilibrium. **1**

[Turn over

7. (continued)

(c) The average pH of pre-industrial ocean surface water is recorded to be 8.2. The increased CO_2 dissolved in the oceans has already reduced the pH of surface water and by the year 2100 the pH is predicted to be 7.9.

(i) Calculate the concentration, in mol l^{-1}, of hydronium ions, H_3O^+, in surface water with a pH of 8.2. **1**

(ii) Calculate the percentage increase in hydronium ion concentration between water with a pH of 8.2 and water with a pH of 7.9. **2**

(d) Acid in the ocean reacts with seashells containing calcium carbonate.

The percentage composition of calcium carbonate in seashells can be determined by carrying out a back titration using standard solutions of hydrochloric acid and sodium hydroxide.

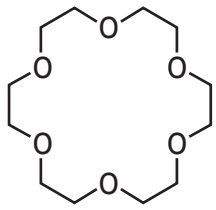
(i) Outline the steps that would be needed to carry out this back titration. **2**

(ii) Name a suitable control substance that could be used to validate this procedure. **1**

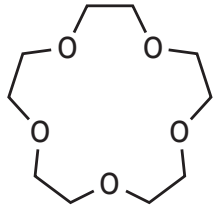
8. Crown ethers are a group of cyclic organic compounds.

(a) Crown ethers act as ligands and form complexes with alkali metal ions according to their size. They have names indicating the total number of atoms in the ring and the number of oxygen atoms.

One example of a crown ether is 18-crown-6, which is used to form complexes with K^+ ions.



(i) The crown ether shown below is used to form complexes with Na^+ ions.



Suggest a name for this crown ether. **1**

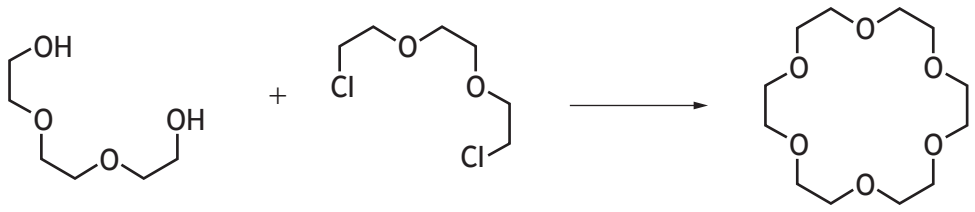
(ii) Draw a structure for a different crown ether that could be used to form a complex with Li^+ ions. **1**

(iii) State why crown ethers can act as ligands. **1**

[Turn over

8. (continued)

(b) 18-crown-6 can be prepared from triethylene glycol as shown.



triethylene glycol 18-crown-6

(i) Write the molecular formula for triethylene glycol. **1**

(ii) Suggest the type of chemical reaction taking place. **1**

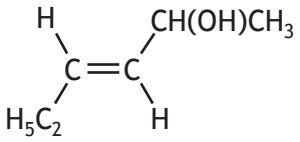
(c) Potassium permanganate is insoluble in non-polar solvents. 18-crown-6 can be used to help dissolve potassium permanganate, $KMnO_4$, in benzene by forming a complex with K^+ ions in a 1:1 ratio.

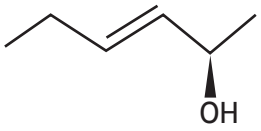
Calculate the maximum concentration of potassium permanganate solution, in mol l^{-1}, that can be obtained if excess potassium permanganate is added to benzene in the presence of 225 mg of 18-crown-6 (GFM 264 g) to make 350 cm^3 of solution. **2**

9. Molecules can be represented in different ways.

For example, some of the ways in which 3-hexen-2-ol can be represented are shown below.

$C_6H_{12}O$





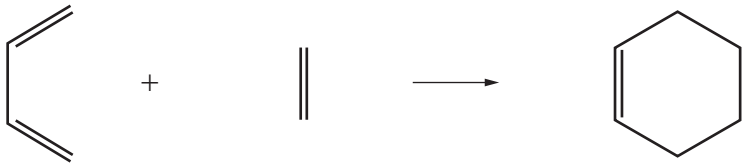
$CH_3CH_2CHCHCH(OH)CH_3$

Using your knowledge of chemistry, explain how the different information provided by these and other representations helps a chemist decide when to use particular representations. **3**

[Turn over

10. Cyclohexene is a cycloalkene.

(a) Cyclohexene can be synthesised by an addition reaction between buta-1,3-diene and ethene.

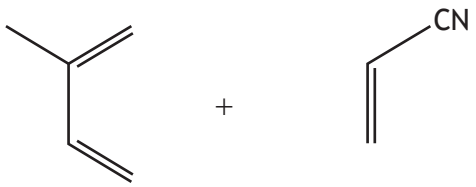


(i) Buta-1,3-diene has a conjugated system.

State what is meant by the term conjugated system. **1**

(ii) State the type of hybridisation that is adopted by the carbon atoms in buta-1,3-diene. **1**

(iii) A similar addition reaction can be used to make another cyclic compound.



Draw a structural formula for the product of this reaction. **1**

10. (continued)

(b) Cyclohexene reacts with Cl_2 to form 1,2-dichlorocyclohexane.

(i) In the first step of the reaction, Cl_2 molecules become polarised.

Explain why Cl_2 molecules become polarised. **1**

(ii) Draw a structural formula for the intermediate formed when cyclohexene reacts with Cl_2. **1**

(iii) 1,2-dichlorocyclohexane has geometric isomers and optical isomers.

(A) Explain why 1,2-dichlorocyclohexane has geometric isomers. **1**

(B) Draw a cyclic isomer of 1,2-dichlorocyclohexane that does not have an optical isomer. **1**

[Turn over

10. (continued)

(c) The reaction between cyclohexene and HCl produces chlorocyclohexane.

(i) Using structural formulae and curly arrow notation, outline the mechanism for this reaction. **2**

(ii) HCl has a permanent dipole. The size of a dipole is measured by its dipole moment and depends on the partial charge of the atoms and the bond length.

Dipole moment can be measured in units of Coulomb metres, Cm, or Debyes, D, and can be calculated using the following equations.

$$\mu = Qr \qquad \text{and} \qquad Q = \text{partial charge} \times e$$

where: μ is the dipole moment in Coulomb metres, Cm

Q is the charge in Coulombs, C

r is the bond length in metres, m

$e = 1.60 \times 10^{-19}$ C

$1\ D = 3.34 \times 10^{-30}$ Cm

Calculate the dipole moment, in D, of a hydrogen chloride bond, if the partial charge is 0.178 and the bond length is 0.127 nm. **2**

[Turn over for next question

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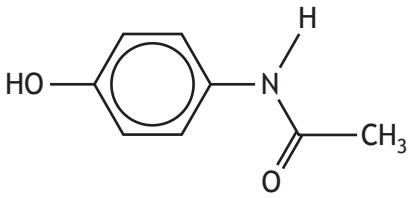
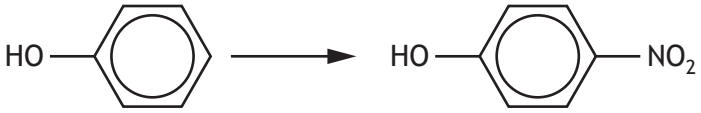
11. Paracetamol can be synthesised in several reaction steps.



paracetamol

(a) The first step is conversion of phenol into 4-nitrophenol as shown.

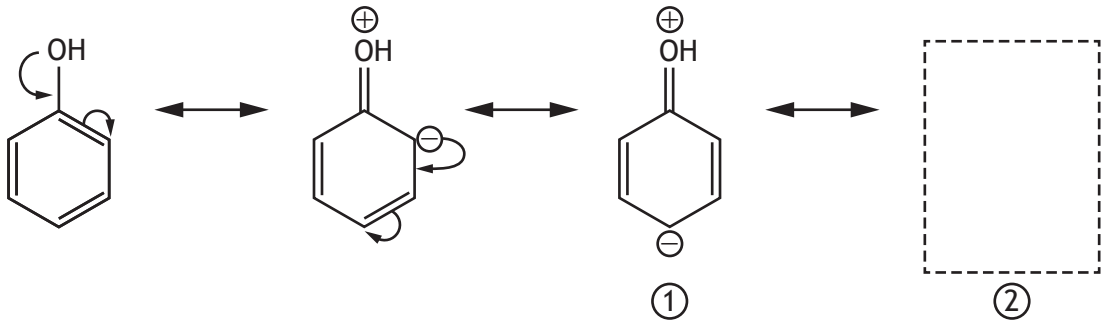


phenol 4-nitrophenol

(i) Write a formula for the electrophile in this reaction. **1**

11. (a) (continued)

(ii) 2-nitrophenol also forms in this reaction. This can be explained by considering the movement of delocalised electrons in phenol as shown.



(A) On structure (1), draw curly arrows to show how structure (2) forms. **1**
(An additional diagram, if required, can be found on *page 34*.)

(B) Draw a structural formula for structure (2). **1**

[Turn over

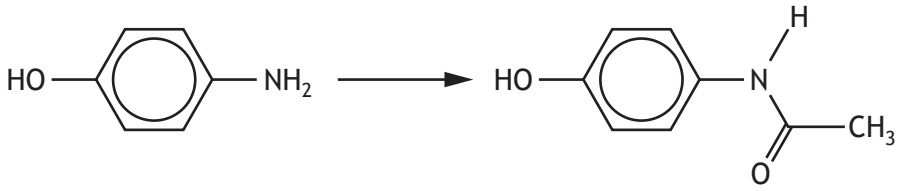
11. (continued)

(b) 4-nitrophenol is then reacted to make 4-aminophenol.

4-aminophenol

State the type of reaction taking place in this step. **1**

(c) 4-aminophenol is then converted into paracetamol.



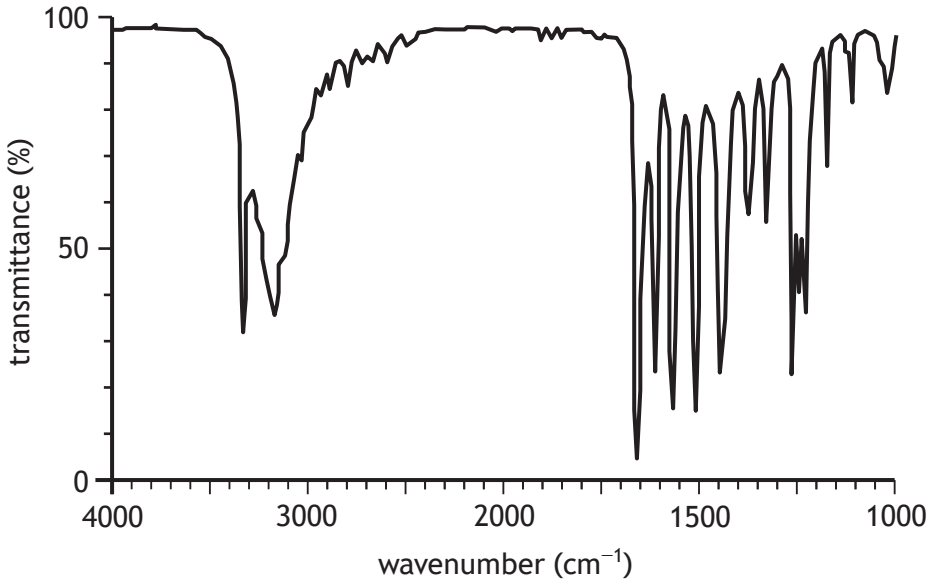
Suggest a reagent that could be used to carry out this reaction. **1**

(d) Outline the steps that should be carried out to purify paracetamol by recrystallising from distilled water. **2**

11. (continued)

(e) Infrared spectroscopy and ^{1}H NMR spectroscopy were used to confirm that paracetamol had been synthesised.

(i) The infrared spectrum of the recrystallised paracetamol is shown below.



(A) The peak at wavenumber 1660 cm^{-1} provides evidence that paracetamol has been synthesised.

Suggest the bond in paracetamol that gives rise to this peak. **1**

(B) By considering the functional groups present in paracetamol, suggest why the peaks that occur above 3000 cm^{-1} are difficult to assign to specific bonds. **1**

[Turn over

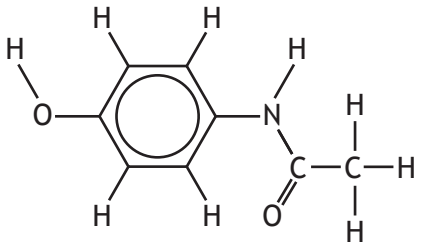
11. (e) (continued)

(ii) Analysis of a high resolution ^{1}H NMR spectrum of the recrystallised paracetamol gave the following information.

Chemical shift (ppm)	Height of integration curve (mm)	Type of multiplet
2.1	50	singlet
6.7	33	
7.3	33	
9.1	17	singlet
9.8	17	singlet

(A) Circle the proton environment on the structure below that is responsible for the peak at 2.1 ppm. **1**

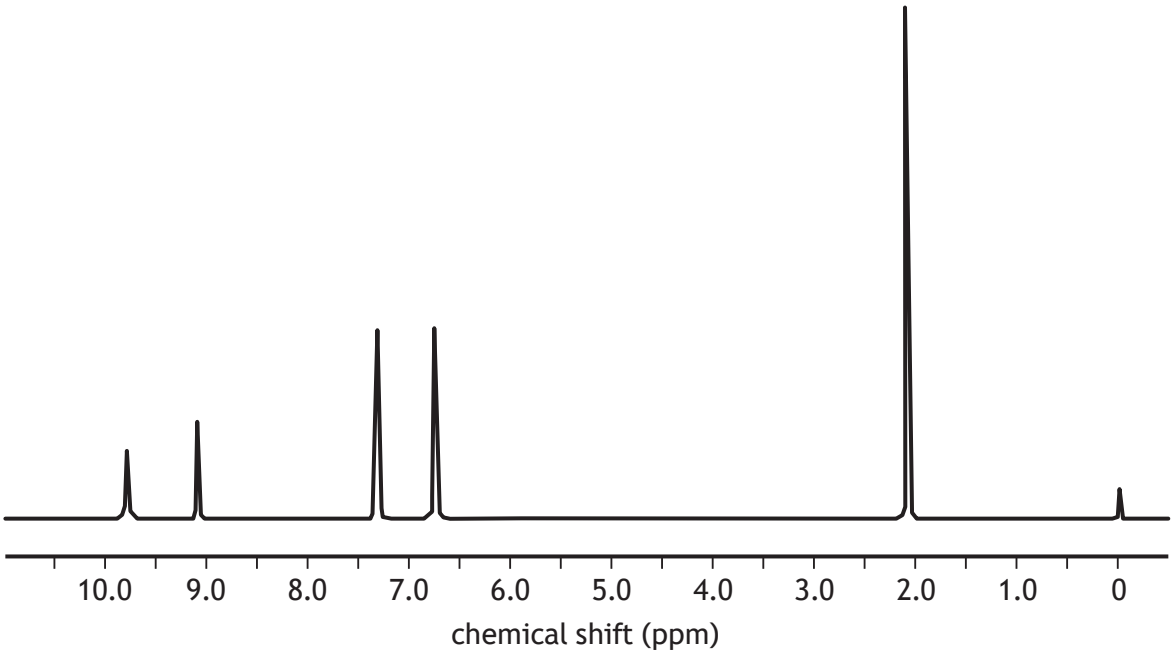
(An additional diagram, if required, can be found on *page 34*.)



(B) Complete the table by naming the multiplets that would be seen for the peaks at 6.7 and 7.3 ppm. **1**

11. (e) (continued)

(iii) The low resolution ^{1}H NMR spectrum of the recrystallised paracetamol is shown below.



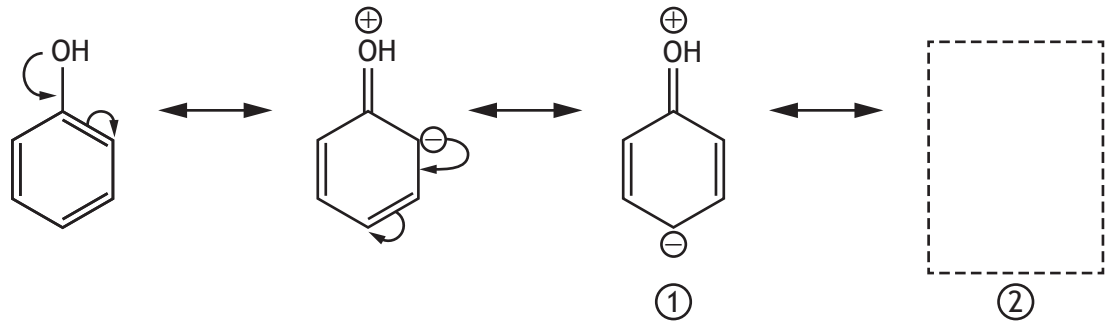
(A) Explain what conclusion can be made about the purity of the recrystallised paracetamol by considering this ^{1}H NMR spectrum. **1**

(B) Describe how the purity of the recrystallised paracetamol could be confirmed using a different technique. **2**

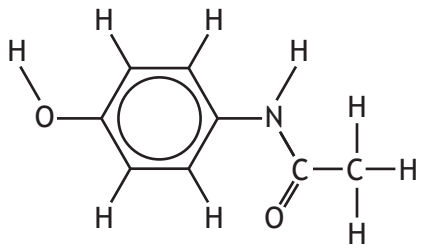
[END OF QUESTION PAPER]

ADDITIONAL SPACE FOR ANSWERS AND ROUGH WORK

Additional diagram for use with question 11 (a) (ii) (A)



Additional diagram for use with question 11 (e) (ii) (A)



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