

X813/77/02

Chemistry Section 1 — Questions

FRIDAY, 12 MAY 9:00 AM – 12:00 NOON

Instructions for the completion of Section 1 are given on *page 02* of your question and answer booklet X813/77/01.

Record your answers on the answer grid on page 03 of your question and answer booklet.

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

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

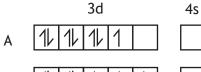


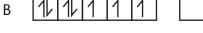


SECTION 1 — 25 marks

Attempt ALL questions

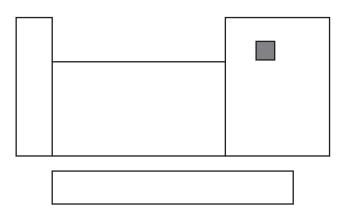
1. Which of the following electronic configurations shows the ground state arrangement of electrons in the 3d and 4s subshells of an atom?





- D 111111 1
- 2. Which of the following shapes can only be formed by compounds that contain non-bonding electron pairs?
 - A Linear
 - B Tetrahedral
 - C Trigonal pyramidal
 - D Trigonal bipyramidal

3.



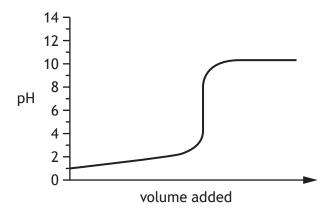
In which block of the periodic table is the shaded element?

- A s
- Вр
- C d
- D f

4. Which line in the table is correct for transition metal catalysts?

	Heterogenous catalyst	Homogeneous catalyst
Α	adsorption onto active sites	same state as reactants
В	full d subshell	different state to reactants
С	same state as reactants	can change oxidation state
D	different state to reactants	adsorption onto active sites

5.



The titration curve above shows how the pH changes when a

- A weak acid is added to a strong alkali
- B strong alkali is added to a weak acid
- C strong acid is added to a weak alkali
- D weak alkali is added to a strong acid.

6. Which line in the table is correct for an acidic buffer?

	Species absorbing excess H ₃ O ⁺ ions	Species providing H ₃ O ⁺ ions
Α	weak base	conjugate acid
В	conjugate base	conjugate acid
С	weak base	weak acid
D	conjugate base	weak acid

- 7. Which of the following statements is correct for a feasible reaction under standard conditions?
 - Α The standard free energy change is negative and the equilibrium favours products.
 - В The standard free energy change is negative and the equilibrium favours reactants.
 - C The standard free energy change is positive and the equilibrium favours products.
 - D The standard free energy change is positive and the equilibrium favours reactants.
- 8. At 298 K,

$$\frac{1}{2}$$
N₂(g) + O₂(g) \rightarrow NO₂(g) $\Delta G^{\circ} = +51.8 \text{ kJ mol}^{-1}$

$$\Delta G^{\circ} = +51.8 \text{ kJ mol}^{-1}$$

$$N_2(g) + 2O_2(g) \rightarrow N_2O_4(g)$$
 $\Delta G^{\circ} = +97.7 \text{ kJ mol}^{-1}$

$$\Delta G^{\circ} = +97.7 \text{ kJ mol}^{-1}$$

What is the free energy change ΔG° , in kJ mol⁻¹, for the conversion of nitrogen dioxide to one mole of dinitrogen tetroxide?

- Α -45.9
- В -5.9
- С +5.9
- D +45.9
- **9.** Which of the following processes is endothermic and has a positive ΔS value?
 - Α Carbon burning
 - В Snowflakes forming
 - C Ethoxyethane evaporating
 - Ammonia gas and hydrogen chloride gas forming solid ammonium chloride
- **10.** The reaction $X + 2Y \rightarrow Z$ has the rate equation shown below.

$$rate = k[X][Y]$$

Which of the following could represent the rate determining step?

- A $X + Y \rightarrow intermediate$
- B $Y + Y \rightarrow intermediate$
- $C X + Y \rightarrow Z$
- $D XY + Y \rightarrow Z$

11. Which line in the table is correct for a carbon-carbon single bond in an alkane?

	Overlap of atomic orbitals	Symmetry of molecular orbital
Α	end-on	symmetrical
В	end-on	asymmetrical
С	side-on	symmetrical
D	side-on	asymmetrical

12. Which line in the table is correct for a chromophore that absorbs blue-green light?

	Movement of electrons	Colour observed
Α	HOMO to LUMO	blue-green
В	LUMO to HOMO	blue-green
С	HOMO to LUMO	red
D	LUMO to HOMO	red

- **13.** Which of the following compounds does **not** exhibit hydrogen bonding between its molecules?
 - A Ethanol
 - B Ethylamine
 - C Ethanoic acid
 - D Ethoxyethane
- 14. A haloalkane can be converted into a ketone by reaction with
 - A aqueous sodium hydroxide followed by oxidation
 - B ethanolic potassium cyanide followed by hydrolysis
 - C ethanolic sodium hydroxide followed by addition
 - D potassium in ethanol followed by substitution.

The organic product X is

- A 2-methylbutanal
- B 2-methylbut-1-ene
- C 2-methylbutan-1-ol
- D 2-methylbutanoic acid.

16.
$$CH_3CH_2COOH \xrightarrow{NH_3} X \xrightarrow{heat} Y + H_2O$$

The formula for Y will be

- A CH₃CH₂CH₂CN
- B CH₃CH₂CH₂CONH₂
- C CH₃CH₂CH₂CH₂NH₂
- D CH₃CH₂CH₂COONH₄
- 17. Which of the following compounds is **not** an isomer of methoxypropane?
 - A CH₃CH₂COCH₃
 - B CH₃CH₂OCH₂CH₃
 - C CH₃CH(OH)CH₂CH₃
 - D CH₃CH(CH₃)CH₂OH
- **18.** Which of the following compounds can exhibit geometric isomerism?
 - A CH₂CHBr
 - B CHClCHCH₃
 - C CH₃CH₂CHCCl₂
 - D CH₃C(CH₃)CHCH₃
- 19. In which of the following techniques will the test compound always be destroyed?
 - A Mass spectrometry
 - B Infrared spectroscopy
 - C Melting point analysis
 - D Proton NMR spectroscopy

20. Which line in the table correctly describes the action of a drug?

	Type of drug	Binding site	Response
A	antagonist	receptor binding site	produces a response similar to the body's natural response
В	antagonist	enzyme active site	blocks the body's natural response
С	enzyme inhibitor	receptor binding site	produces a response similar to the natural action of the enzyme
D	enzyme inhibitor	enzyme active site	blocks the action of the enzyme

21. The structural formulae of three antihistamine drugs are shown.

Which of the following is the largest structural fragment that is common to all three molecules?

A	
В	
С	CI
D	N N

22. A compound was found to have the percentage composition by mass as shown below.

oxygen 38.6%

This compound has the formula

- A VO
- B VO_2
- $C V_2O$
- D V_2O_3
- 23. Which of the following compounds could be used as a primary standard?
 - A Calcium carbonate
 - B Hydrochloric acid
 - C Sodium carbonate
 - D Sodium hydroxide
- 24. The total mass of the Earth's atmosphere has been determined to be 5.1×10^{18} kg. What mass, in kg, of carbon dioxide is in the Earth's atmosphere if the concentration of

What mass, in kg, of carbon dioxide is in the Earth's atmosphere if the concentration of carbon dioxide is 420 ppm?

- A 1.2×10^{13}
- B 2.1×10^{15}
- C 1.2×10^{16}
- D 2.1×10^{18}
- **25.** The concentration of Pb^{2+} ions in a solution can be determined using the following sequence of reactions:

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$$

$$PbCrO_4(s) + 2Cl^-(aq) \rightarrow PbCl_2(s) + CrO_4^{2-}(aq)$$

$$2CrO_4^{2-}(aq) + 6l^{-}(aq) + 16H^{+}(aq) \rightarrow 2Cr^{3+}(aq) + 3l_2(aq) + 8H_2O(\ell)$$

How many moles of iodine are formed from one mole of Pb2+ ions in the solution?

- A 0.75
- B 1.5
- C 3.0
- D 6.0

[END OF SECTION 1. NOW ATTEMPT THE QUESTIONS IN SECTION 2 OF YOUR QUESTION AND ANSWER BOOKLET.]

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Mark

X813/77/01

Chemistry
Section 1 — Answer grid
and Section 2

FRIDAY, 12 MAY 9:00 AM – 12:00 NOON



Full name of centre			Town	
Forename(s)		Surr	name	Number of seat
	th			
Date of bir	CII			

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.





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	$+\frac{1}{2}$



page 05

- (a) (continued)
 - (iii) Distress flares also contain oxidising agents.
 - (A) Potassium perchlorate, KClO₄, can be used as the oxidising agent. Determine the oxidation state of chlorine in the perchlorate ion, ClO_4^- .

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

$$\begin{array}{c|c} H & & H \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$$

5-aminotetrazole

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

(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.

$$4Fe(s) + 3O2(g) \rightarrow 2Fe2O3(s)$$

Substance	$\Delta H_{ m f}^{ m o}$ (kJ mol $^{-1}$)	<i>S</i> ° (J K ^{−1} mol ^{−1})
Fe(s)	_	27.3
O ₂ (g)	_	205
Fe ₂ O ₃ (s)	-824	87.4

Using information from the table, calculate

(A)
$$\Delta H^{\circ}$$
, in kJ mol⁻¹

1

(B)
$$\Delta S^{\circ}$$
, in J K⁻¹ mol⁻¹

1

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

2

MARKS DO NOT WRITE IN THIS MARGIN

1. (b) (continued)

(ii) Some oxygen candles contain sodium chlorate, NaClO₃, which decomposes at high temperatures to produce oxygen.

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

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



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

$$2 \text{HgCl}_2(\text{aq}) \; + \; \text{C}_2 \text{O}_4^{\; 2-}(\text{aq}) \; \rightarrow \; 2 \text{Cl}^-(\text{aq}) \; + \; 2 \text{CO}_2(\text{g}) \; + \; \text{Hg}_2 \text{Cl}_2(\text{s})$$

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

Experiment	[HgCl ₂] (mol l ⁻¹)	[C ₂ O 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

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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

1

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.

(ii) The isolated precipitate was washed.

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

(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.

MARKS DO NOT WRITE IN THIS MARGIN

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.



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.

2+ NH_2

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

1

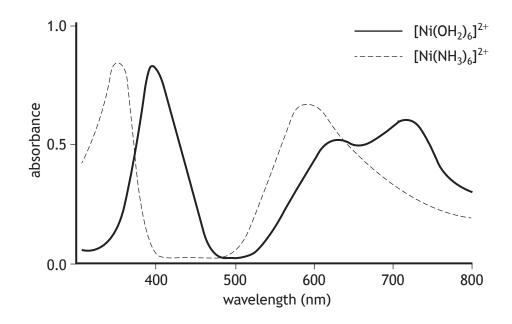
(ii) State the coordination number of nickel in this complex.

(continued) 5.

- (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



page 15

- 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.



(continued)

(b) Hydroiodic acid, HI(aq), was prepared from iodine, I₂(aq), and hydrogen sulfide, H₂S(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



6. (continued)

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

$$R^{1} - C - C - R^{3} \qquad \qquad R^{1} - C \qquad R^{2} \qquad \qquad R^{3} \qquad \qquad R^{4}$$

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

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, H₂CO₃(aq).

$$H_2O(\ell) + CO_2(g) \rightleftharpoons H_2CO_3(aq)$$
 $\Delta H - ve$

Explain the effect rising seawater temperatures will have on the concentration of ${\rm CO_2}$ dissolved in the oceans.

(b) Carbonic acid, H₂CO₃(aq), dissociates as shown.

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

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

(ii) State the role of H₂O in the above equilibrium.



7. (continued)

- (c) The average pH of pre-industrial ocean surface water is recorded to be 8.2. The increased CO₂ 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.

(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.

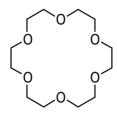
(ii) Name a suitable control substance that could be used to validate this procedure.

1

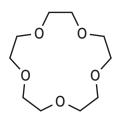


- Crown ethers are a group of cyclic organic compounds.
 - (a) Crown ethers act as ligands and form complexes with alkali metal ions according to their size. They have names indicating the total number of atoms in the ring and the number of oxygen atoms.

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



1

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

(c) Potassium permanganate is insoluble in non-polar solvents. 18-crown-6 can be used to help dissolve potassium permanganate, KMnO₄, 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 cm³ of solution.

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.

$$C_6H_{12}O$$
 H
 $CH(OH)CH_3$
 $C=C$
 H_5C_2
 H

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



1

- Cyclohexene is a cycloalkene. 10.
 - (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.

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

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



Draw a structural formula for the product of this reaction.

(continued) 10.

- (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 Cl₂ molecules become polarised.

1

(ii) Draw a structural formula for the intermediate formed when cyclohexene reacts with Cl₂.

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



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.

$$\mu = Qr$$

and

 $Q = partial charge \times e$

where: $\boldsymbol{\mu}$ 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.

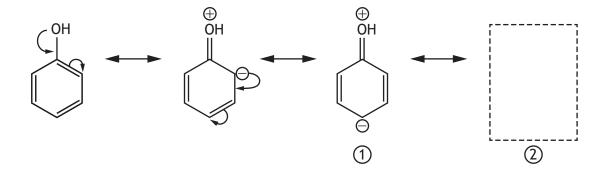
11. Paracetamol can be synthesised in several reaction steps.

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

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

(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

11. (continued)

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

$$HO \longrightarrow NO_2 \longrightarrow HO \longrightarrow NH_2$$

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.

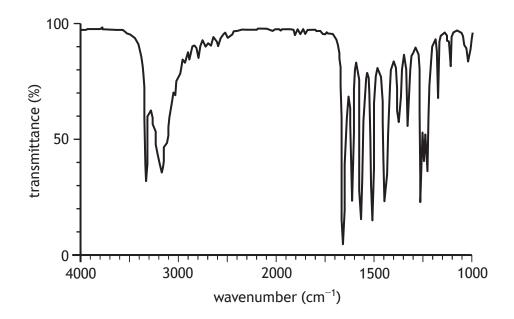
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(d) Outline the steps that should be carried out to purify paracetamol by recrystallising from distilled water.

1

11. (continued)

- (e) Infrared spectroscopy and ¹H 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.

(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.



11. (e) (continued)

(ii) Analysis of a high resolution ¹H 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.

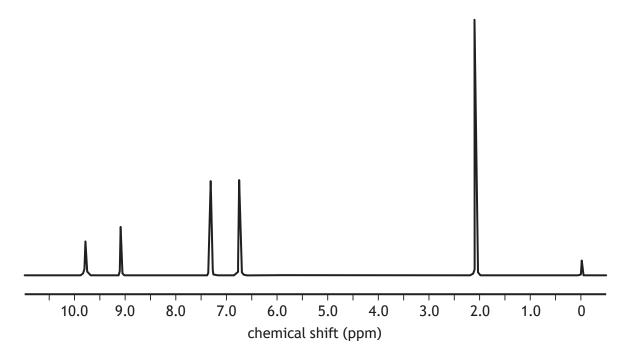
(An additional diagram, if required, can be found on page 34.)

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

1

(e) (continued) 11.

> (iii) The low resolution ¹H 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 ¹H NMR spectrum.

1

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

2

[END OF QUESTION PAPER]

