FOR OFFICIAL USE

National Qualifications

Mark

X813/77/01

Chemistry
Section 1 — Answer grid and Section 2

Duration — 3 hours

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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SECTION 2 — 85 marks

Attempt ALL questions

1. Fireworks contain metal compounds and produce coloured light when ignited.

(a) Explain, in terms of electrons, how coloured light is produced when fireworks are ignited. **1**

(b) A firework produced coloured light with energy of 193 kJ mol^{-1}.

(i) Calculate the wavelength, in nm, of this coloured light. **2**

(ii) Identify the metal most likely to produce this coloured light. **1**

1. (continued)

(c) Fireworks also contain potassium nitrate, which decomposes when heated to produce oxygen.

$$2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g) \qquad \Delta H° = +250 \text{ kJ mol}^{-1}$$
$$\Delta S° = +509 \text{ J K}^{-1} \text{ mol}^{-1}$$

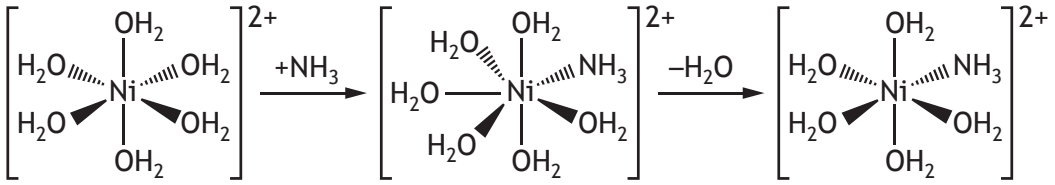
This reaction obeys the second law of thermodynamics.

(i) State the second law of thermodynamics. **1**

(ii) Calculate the temperature, in K, above which this reaction becomes feasible. **2**

2. Hexaaquanickel(II) can react with ammonia forming complex ion **X**.

A proposed mechanism for this reaction is shown.



hexaaquanickel(II) intermediate complex ion **X**

(a) State the shape of the hexaaquanickel(II) ion. **1**

(b) The intermediate has a pentagonal bipyramidal arrangement of bonds around the nickel.

State the co-ordination number of nickel in the intermediate. **1**

(c) Complex ion **X** is formed when a water molecule is removed from the intermediate.

(i) Name complex ion **X**. **1**

(ii) State why ammonia and water are classed as monodentate ligands. **1**

2. (continued)

(d) In an experiment to determine the rate equation for this reaction, some of the data obtained by a student is shown below.

$[[Ni(OH_2)_6]^{2+}]$ (mol l^{-1})	$[NH_3]$ (mol l^{-1})	*Initial rate* (mol l^{-1} s^{-1})
0·10	0·25	$1{\cdot}3 \times 10^2$

The student proposed the following rate equation.

$$rate = k\,[[Ni(OH_2)_6]^{2+}]\,[NH_3]$$

(i) Determine the overall order for this reaction. **1**

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

3. Benzene is a colourless, aromatic compound containing a conjugated system of pi (π) bonds.

benzene

(a) (i) State the type of hybridised orbitals found in benzene. **1**

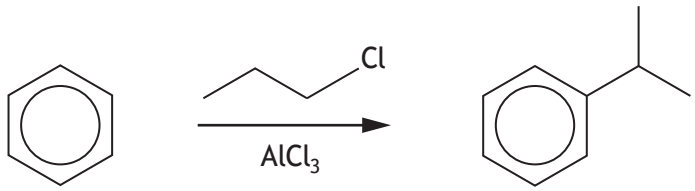
(ii) Explain how a pi bond is formed. **1**

(iii) Colour arises in some aromatic compounds due to absorption of visible light.

Explain why the conjugated system in benzene results in absorption of ultraviolet light and not visible light. **2**

3. (continued)

(b) Benzene can react with 1-chloropropane to form 2-phenylpropane.

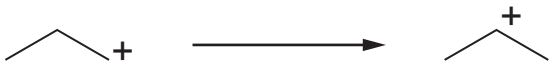


benzene 2-phenylpropane

(i) Name the type of chemical reaction taking place. **1**

(ii) Write the molecular formula for 2-phenylpropane. **1**

(iii) The reaction is thought to proceed via the carbocation rearrangement shown below.



Suggest why this rearrangement takes place. **1**

[Turn over

4. Limestone contains calcium carbonate and can be used to produce slaked lime, a component of cement.

The calcium carbonate content of limestone can be determined by volumetric analysis.

(a) State why a back titration is necessary for this volumetric analysis. **1**

(b) 1·30 g of limestone was reacted with 25·0 cm^3 of 1·50 mol l^{-1} hydrochloric acid. The resulting solution was transferred to a 100 cm^3 volumetric flask and made up to the mark with deionised water.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

25·0 cm^3 samples of this solution were then titrated against 0·300 mol l^{-1} sodium hydroxide.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

Titration	Titre volume (cm^3)
1	10·1
2	10·7
3	10·2

(i) Calculate the number of moles of hydrochloric acid that reacted with the calcium carbonate in the limestone. **2**

4. (b) (continued)

(ii) Only limestone with a calcium carbonate content greater than 95% can be used to produce slaked lime.

Determine whether this limestone sample could be used to produce slaked lime.

(Clearly show your working for the calculation.) **2**

[Turn over

4. (continued)

(c) **Using your knowledge of chemistry**, discuss possible sources of error in this volumetric analysis and how the accuracy of the final percentage could be checked. **3**

5. Cobalt chloride changes colour in the presence of water.

$$\underset{\text{blue}}{CoCl_2} + nH_2O \rightleftharpoons \underset{\text{pink}}{CoCl_2 \cdot nH_2O}$$

(a) (i) Write the electronic configuration, in terms of s, p and d orbitals, for the cobalt ion in blue $CoCl_2$. **1**

(ii) Determine the oxidation number for the cobalt ion in pink $CoCl_2 \cdot nH_2O$. **1**

(b) In a gravimetric analysis to determine the value of n, a weighed sample of $CoCl_2 \cdot nH_2O$ was converted into $CoCl_2$.

(i) Describe fully an experimental procedure that could be used to carry out this gravimetric analysis. **2**

5. (b) (continued)

(ii) In the gravimetric analysis, 0·372 g of $CoCl_2 \cdot nH_2O$ was converted into 0·204 g of $CoCl_2$.

Calculate the value of n.

(Clearly show your working for the calculation.) **2**

(c) The concentration of cobalt ions in a cobalt chloride solution can be determined by complexometric titration.

(i) Suggest a suitable complexometric reagent that could be used in this titration. **1**

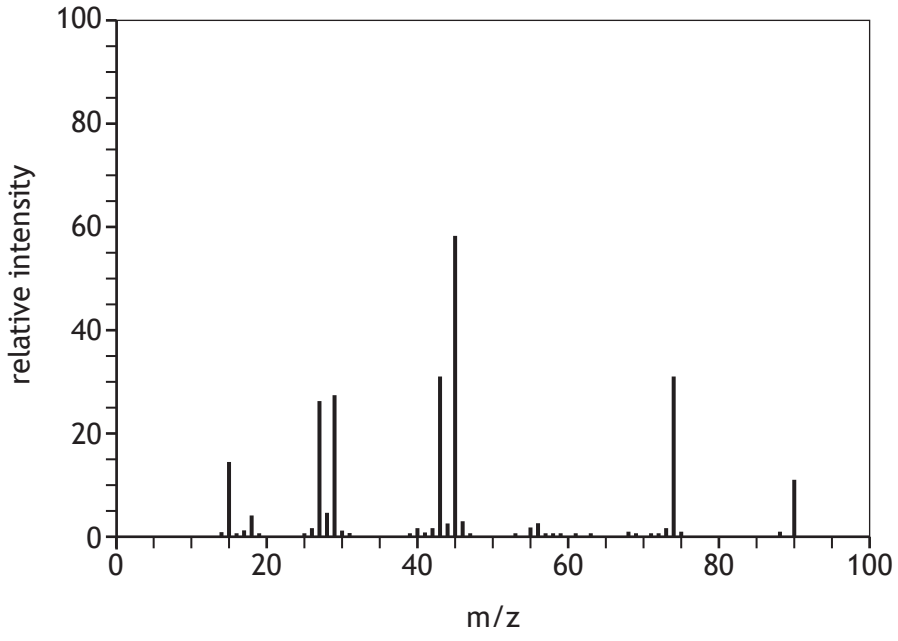
(ii) Suggest another analytical technique that could be used to determine the concentration of cobalt ions in a cobalt chloride solution. **1**

6. A sample of compound **X** was analysed to determine its structural formula. **MARKS** DO NOT WRITE IN THIS MARGIN

(a) Elemental microanalysis showed that compound **X** has a composition, by mass, of 40·0% carbon and 6·70% hydrogen.

Show, by calculation, that the empirical formula of **X** is CH_2O. **1**

(b) A simplified mass spectrum of compound **X** is shown below.



(i) Write the molecular formula of compound **X**. **1**

6. (b) (continued)

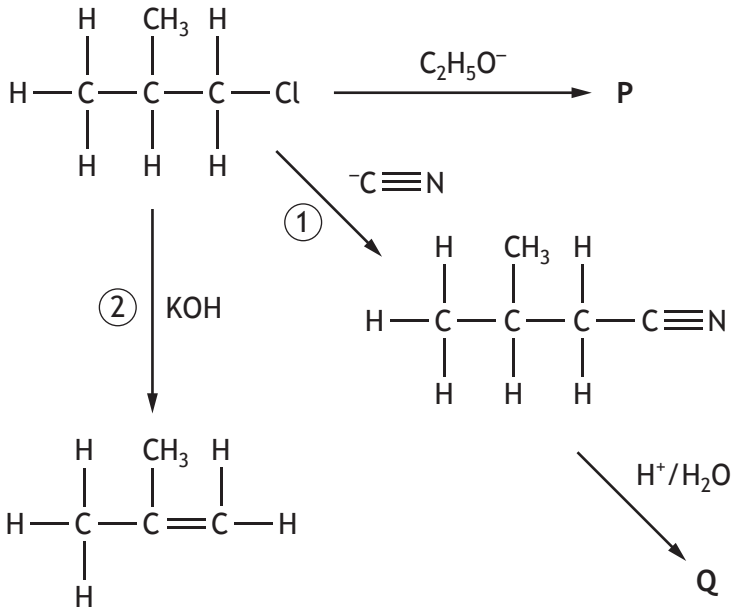
(ii) Suggest a possible ion fragment that may be responsible for the peak at m/z 45. **1**

(c) Compound **X** was found to rotate plane polarised light.

Considering all the evidence, draw a structural formula for compound **X**. **1**

[Turn over

7. Haloalkanes are useful starting materials in organic chemistry.



(a) Draw a structural formula for **P**. **1**

(b) State the class of compound to which **Q** belongs. **1**

7. (continued)

(c) Using structural formulae and curly arrow notation, outline the most likely mechanism for the formation of the nitrile in reaction (1). **2**

(d) (i) Suggest a solvent for use in reaction (2). **1**

(ii) Assuming the percentage yield for reaction (2) was 60·4%, calculate the volume of methylpropene produced from 1·85 g of 1-chloromethylpropane.

Take the molar volume of methylpropene to be 23·0 l mol^{-1}. **3**

8. A buffer solution was prepared by dissolving sodium ethanoate in dilute ethanoic acid.

(a) Write a formula for the conjugate base present in this buffer solution. **1**

(b) 250 cm^3 of buffer solution was prepared by dissolving 4·10 g of sodium ethanoate ($GFM = 82{\cdot}0$ g) in 0·500 mol l^{-1} ethanoic acid.

(i) Calculate the pH of this buffer solution. **3**

(ii) Explain why the pH of this buffer solution remains approximately constant when a small volume of water is added. **1**

8. (continued)

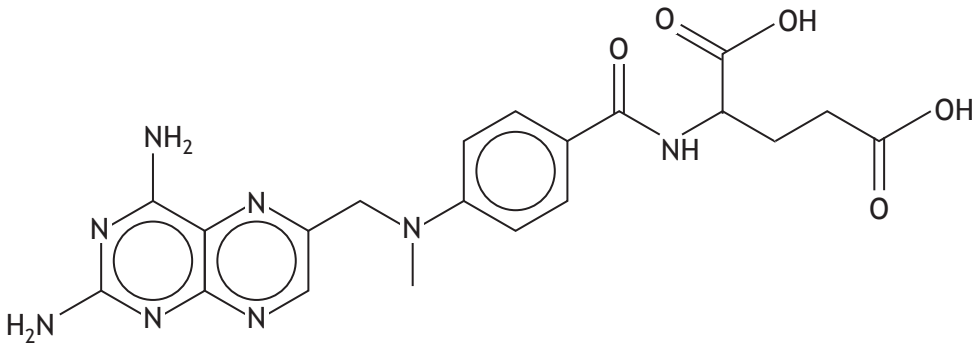
(c) Buffer capacity is a measure of how resistant a buffer solution is to pH changes. It can be defined as the number of moles of hydroxide ions required to raise the pH of a buffer solution by one pH unit.

A student prepared two different buffer solutions, both pH 5.

Describe an experimental procedure that could be carried out to determine which of the two solutions has the larger buffer capacity. **2**

[Turn over

9. Methotrexate is a drug commonly used to treat cancer in dogs. It binds to the active site of an enzyme, blocking the production of folic acid required for the synthesis of DNA.



methotrexate

(a) State what is meant by the term drug. **1**

(b) State the classification of drug used to describe methotrexate. **1**

(c) One treatment for dogs involves a dose of 0·68 mg per kg of bodyweight.

Calculate the concentration of methotrexate, in ppm, required to produce a 2·3 cm^3 dose to treat an 8·4 kg dog. **1**

9. (continued)

(d) Isomerism is an important concept in the research and development of the chemical synthesis of drug molecules.

Using your knowledge of chemistry, discuss isomerism and its role in chemical synthesis and drug action. **3**

[Turn over

10. The gram formula mass of some liquids can be determined using the following relationship.

$$PV = nRT$$

Where,

P is pressure in kilopascals, kPa

V is volume in litres, l

n is number of moles

R is 8·31 joules per kelvin per mole, $J\,K^{-1}\,mol^{-1}$

T is temperature in kelvin, K

In an experiment, 0·518 g of a liquid carbonyl compound was boiled producing 259 cm^3 of gas at a temperature of 353 K and a pressure of 101 kPa.

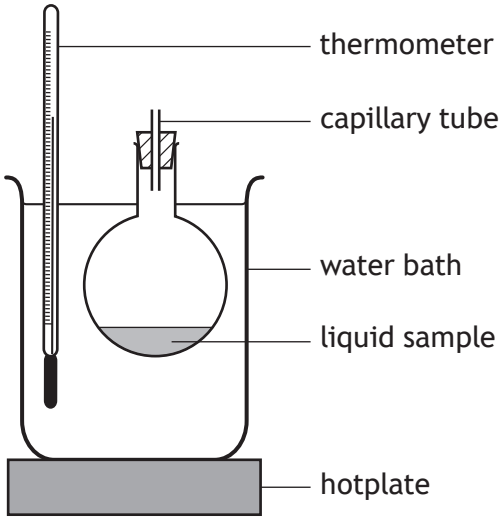
(a) (i) Use the data to calculate the gram formula mass of the liquid carbonyl compound. **2**

(Clearly show your working for the calculation.)

(ii) Using your answer to (a) (i), suggest a liquid carbonyl compound used in this experiment. **1**

10. (continued)

(b) The diagram shows the apparatus used in the experiment.



Suggest why this apparatus would not be suitable to determine the gram formula mass when the liquid sample is butanoic acid. **1**

[Turn over

11. Iodine solutions are prepared by dissolving iodine in aqueous potassium iodide. The following equilibrium is established.

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

(a) (i) Write an expression for the equilibrium constant, K, for this reaction. **1**

(ii) A solution of iodine was prepared by dissolving iodine in 0·239 mol l^{-1} aqueous potassium iodide.

The following data was obtained by analysing the equilibrium mixture.

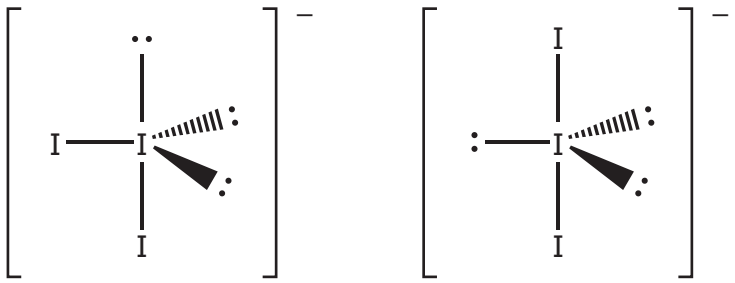
$$[I_2(aq)] = 1{\cdot}21 \times 10^{-3} \text{ mol } l^{-1}$$

$$[I_3^-(aq)] = 0{\cdot}116 \text{ mol } l^{-1}$$

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

11. (continued)

(b) Structures **A** and **B** show two possible arrangements of the electron pairs around the central iodine atom in a triiodide ion, I_3^-.



A **B**

•• denotes a non-bonding electron pair.

Explain fully why the electron pairs around the central iodine atom adopt structure **B** rather than structure **A**. **2**

[Turn over

12. The following reaction scheme starts with ethyl benzoate.

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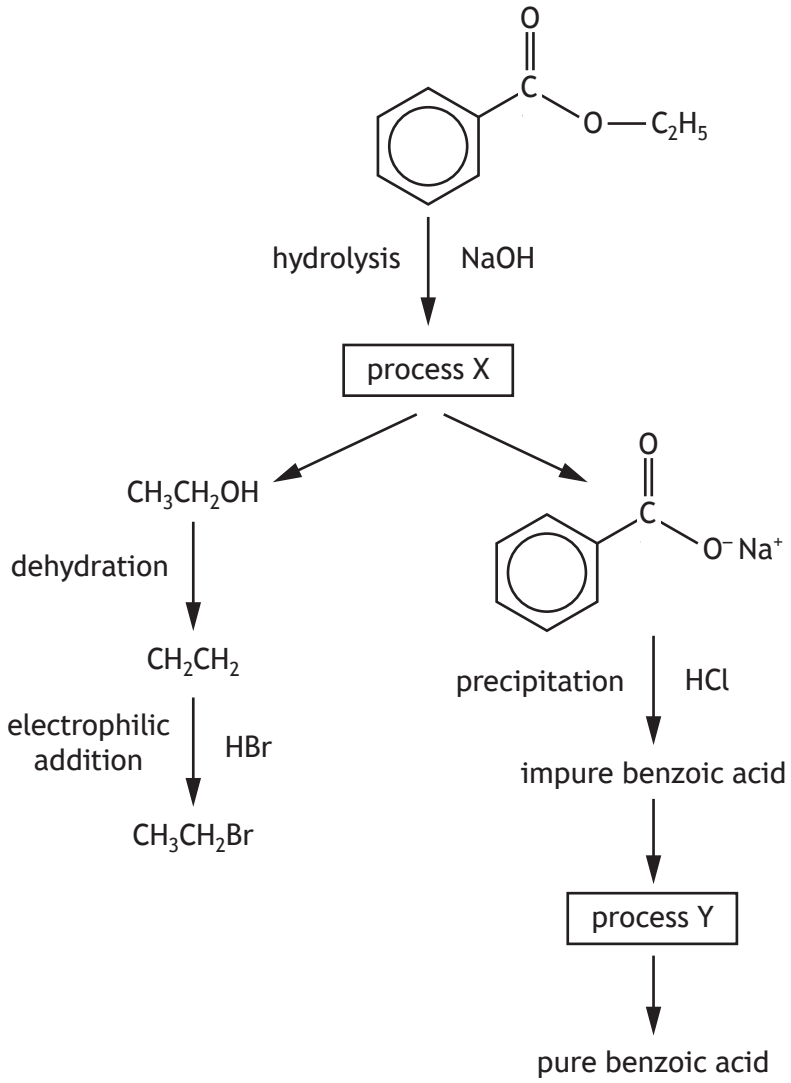


(a) Draw the skeletal formula for ethyl benzoate. **1**

(b) Suggest why the hydrolysis reaction mixture was heated under reflux. **1**

12. (continued)

(c) Name process **X**. **1**

(d) State another name for the dehydration reaction. **1**

(e) Identify the electrophile in the electrophilic addition reaction. **1**

(f) The impure precipitate of benzoic acid is produced by acidifying the alkaline sodium benzoate solution.

(i) Explain fully why an aqueous solution of sodium benzoate is alkaline. **2**

(ii) Name a technique that would be used to separate the impure precipitate from the reaction mixture. **1**

(g) Name process **Y**. **1**

12. (continued)

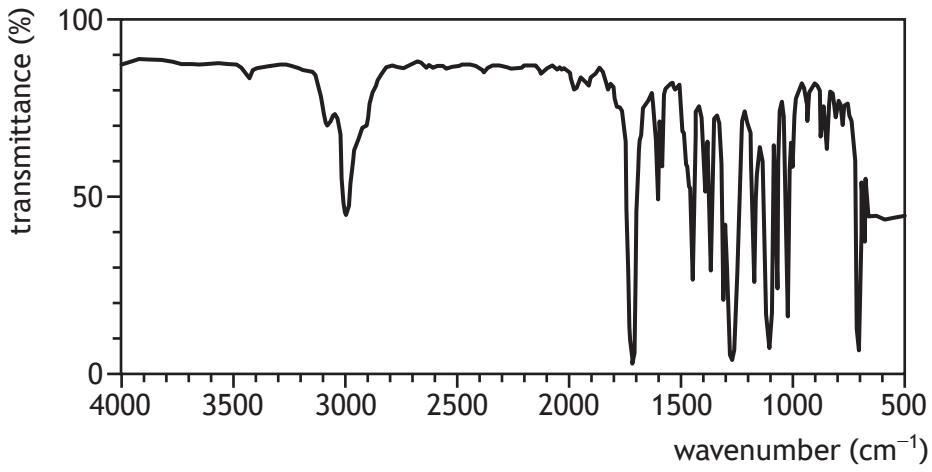
(h) The purity of the benzoic acid produced in process **Y** can be assessed using mixed melting point analysis.

(i) State what should be mixed with this sample of benzoic acid in a mixed melting point analysis. **1**

(ii) Explain how the results of a mixed melting point analysis would be used to assess the purity of this sample of benzoic acid. **2**

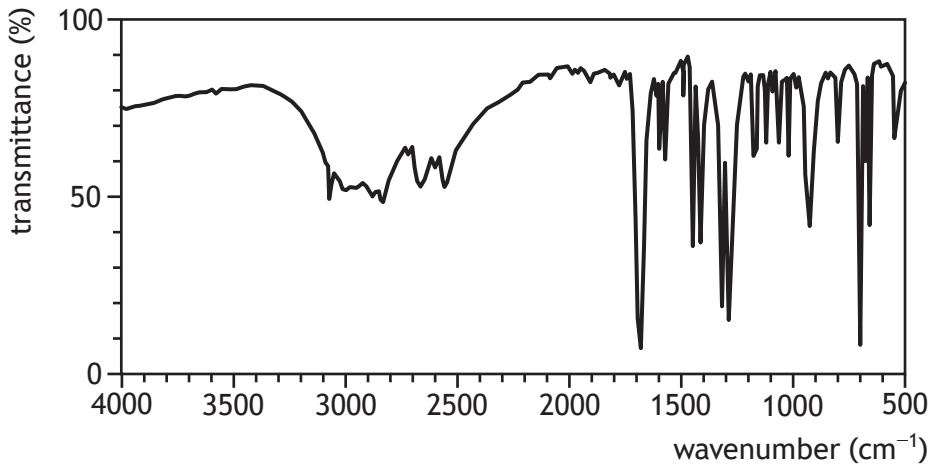
(i) Infrared spectra for three of the compounds in the reaction scheme are shown.

Spectrum A

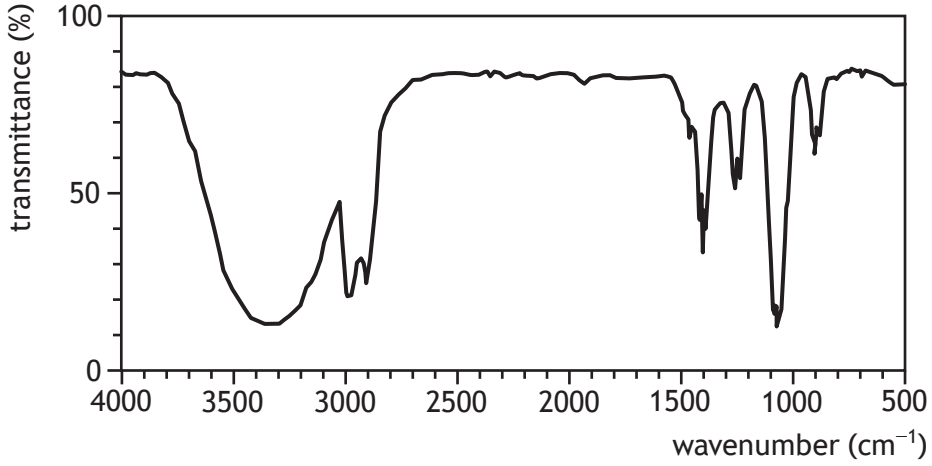


12. (i) (continued)

Spectrum B



Spectrum C



Identify the spectrum for ethanol and give a reason for your answer. **2**

[END OF QUESTION PAPER]