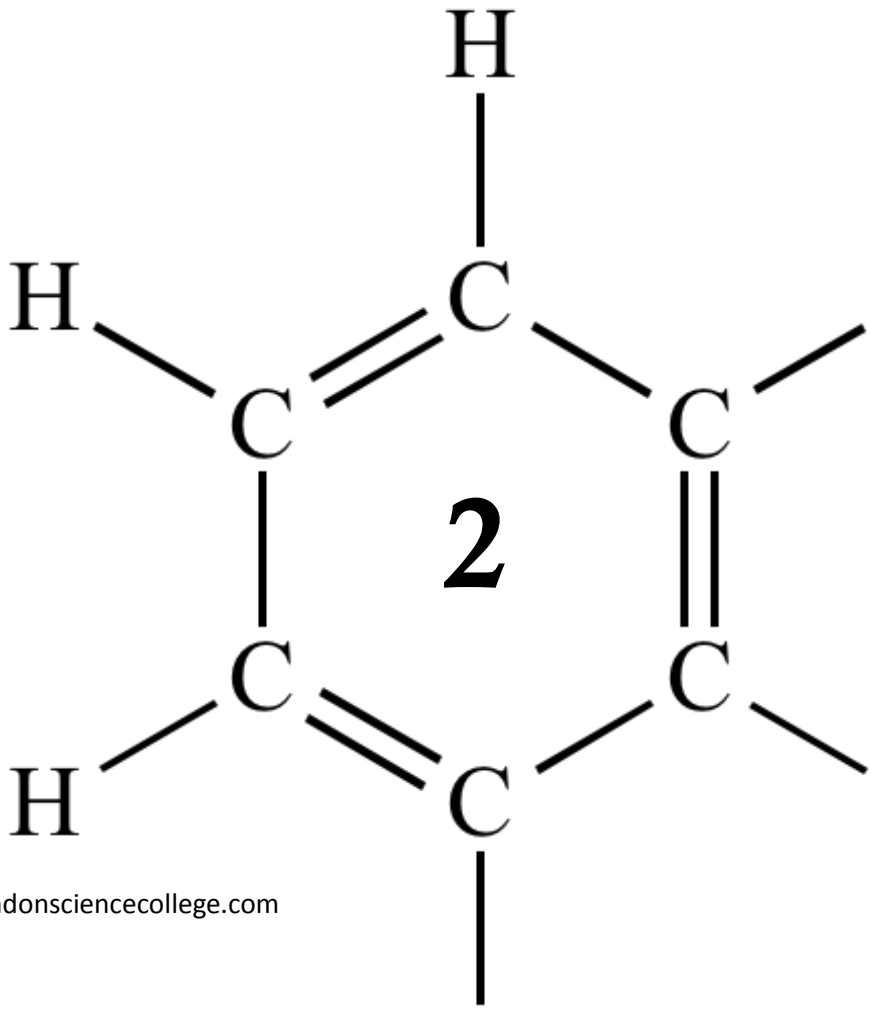
LONDON SCIENCE COLLEGE

AQA AS CHEMISTRY

ORGANIC ANAYLSIS



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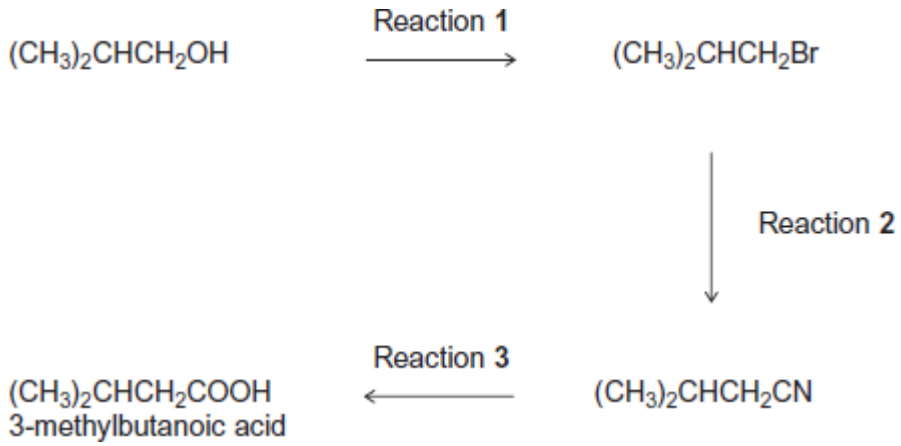
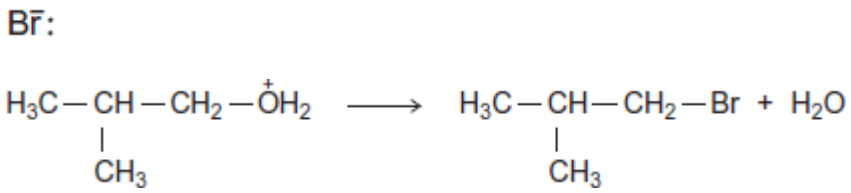
1 The carboxylic acid 3-methylbutanoic acid is used to make esters for perfumes.
The following scheme shows some of the reactions in the manufacture of this carboxylic acid.



(a) One of the steps in the mechanism for Reaction **1** involves the replacement of the functional group by bromine.

(i) Use your knowledge of organic reaction mechanisms to complete the mechanism for this step by drawing **two** curly arrows on the following equation.



(2)

(ii) Deduce the name of the mechanism in part (i).

Give the IUPAC name of $(CH_3)_2CHCH_2Br$

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(2)

(b) Reaction **3** is an acid-catalysed reaction in which water is used to break chemical bonds when the CN functional group is converted into the COOH functional group.
Infrared spectroscopy can be used to distinguish between the compounds in this reaction.

Deduce the name of the type of reaction that occurs in Reaction **3**.

Identify **one** bond in $(CH_3)_2CHCH_2CN$ and a **different** bond in $(CH_3)_2CHCH_2COOH$ that can be used with infrared spectroscopy to distinguish between each compound.
For each of these bonds, give the range of wavenumbers at which the bond absorbs.
Use **Table A** on the Data Sheet when answering this question.

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(3)

(c) When 3-methylbutanoic acid reacts with ethanol in the presence of an acid catalyst, an equilibrium is established. The organic product is a pleasant-smelling ester.

$$(CH_3)_2CHCH_2COOH + CH_3CH_2OH \rightleftharpoons \underset{\text{an ester}}{(CH_3)_2CHCH_2COOCH_2CH_3} + H_2O$$

The carboxylic acid is very expensive and ethanol is inexpensive. In the manufacture of this ester, the mole ratio of carboxylic acid to ethanol used is 1 to 10 rather than 1 to 1.

(i) Use Le Chatelier's principle to explain why a 1 to 10 mole ratio is used. In your explanation, you should **not** refer to cost.

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(Extra space) .....

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(3)

(ii) Explain how a catalyst increases the rate of a reaction.

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(Extra space) .....

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(2)

(Total 12 marks)

2 The following pairs of compounds can be distinguished by simple test-tube reactions.

For each pair, give a suitable reagent that could be added separately to each compound to distinguish between them.
Describe what you would observe in each case.

(a) AgBr(s) and AgI(s)

Reagent .....

Observation with AgBr(s).....

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Observation with AgI(s) .....

.....

(3)

(b) HCl(aq) and HNO_3(aq)

Reagent .....

Observation with HCl(aq) .....

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Observation with HNO_3(aq) .....

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(3)

(c) Cyclohexane and cyclohexene

Reagent .....

Observation with cyclohexane .....

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Observation with cyclohexene .....

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(3)

(d) Butanal and butanone

Reagent .....

Observation with butanal .....

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Observation with butanone .....

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(3)
(Total 12 marks)

3 Haloalkanes are used in the synthesis of other organic compounds.

(a) Hot concentrated ethanolic potassium hydroxide reacts with 2-bromo-3-methylbutane to form two alkenes that are structural isomers of each other. The major product is 2-methylbut-2-ene.

(i) Name and outline a mechanism for the conversion of 2-bromo-3-methylbutane into 2-methylbut-2-ene according to the equation.

$(CH_3)_2CHCHBrCH_3 + KOH \longrightarrow (CH_3)_2C{=}CHCH_3 + KBr + H_2O$

Name of mechanism .....

Mechanism

(4)

(ii) Draw the **displayed formula** for the other isomer that is formed.

(1)

(iii) State the type of structural isomerism shown by these two alkenes.

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(1)

(b) A small amount of another organic compound, **X**, can be detected in the reaction mixture formed when hot concentrated ethanolic potassium hydroxide reacts with 2-bromo-3-methylbutane.
Compound **X** has the molecular formula $C_5H_{12}O$ and is a secondary alcohol.

(i) Draw the **displayed formula** for **X**.

(1)

(ii) Suggest **one** change to the reaction conditions that would increase the yield of **X**.

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(1)

(iii) State the type of mechanism for the conversion of 2-bromo-3-methylbutane into **X**.

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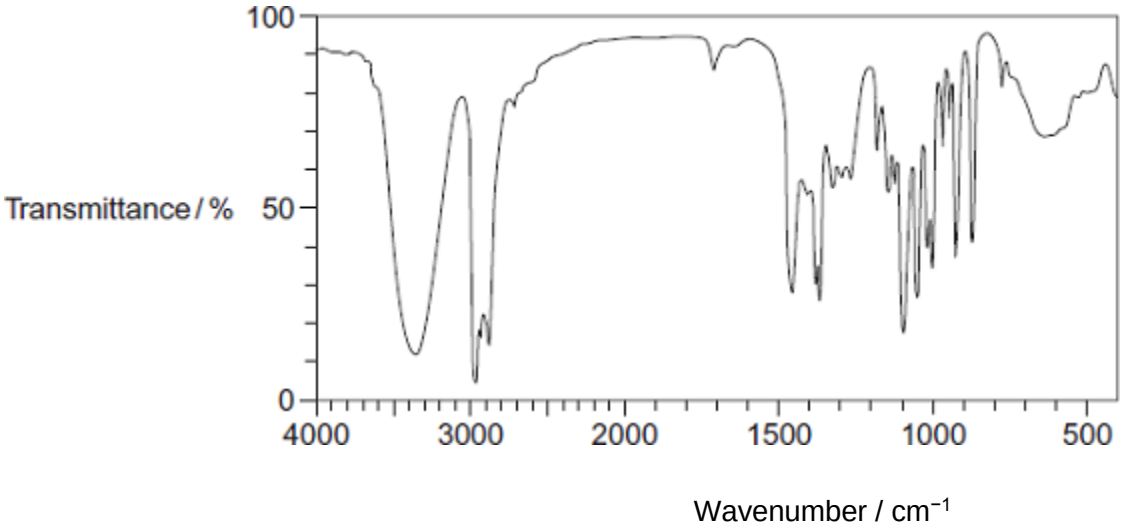
(1)

(iv) Identify **one** feature of this infrared spectrum of a pure sample of **X** that may be used to confirm that **X** is an alcohol.
You may find it helpful to refer to **Table 1** on the Data Sheet.



Feature .....

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(1)
(Total 10 marks)

4 Explain how infrared spectroscopy can be used to show that an aldehyde is definitely pentanal.

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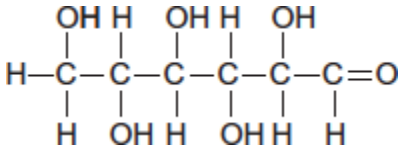
(Total 2 marks)

5 Glucose is an organic molecule. Glucose can exist in different forms in aqueous solution.

(a) In aqueous solution, some glucose molecules have the following structure.



(i) Deduce the empirical formula of glucose.

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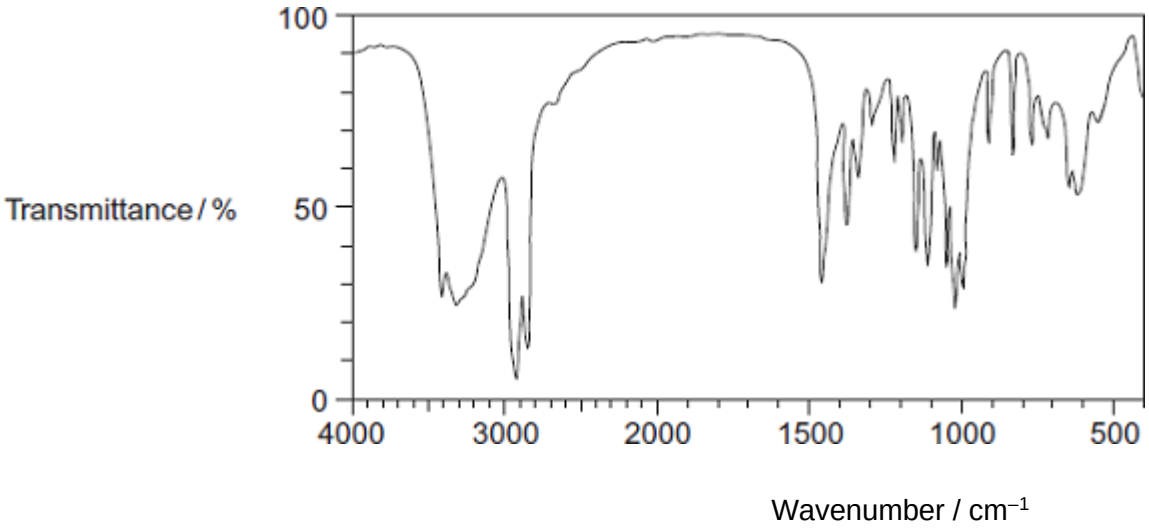
(1)

(ii) Consider the infrared spectrum of solid glucose.



State why it is possible to suggest that in the solid state very few molecules have the structure shown.
You may find it helpful to refer to **Table 1** on the Data Sheet.

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(1)

(b) In the absence of oxygen, an aqueous solution of glucose can be fermented to produce ethanol for use in alcoholic drinks.

Write an equation for this fermentation reaction.
Give **two** other essential conditions for the production of ethanol in this fermentation.

Equation

.....

Condition 1 .....

Condition 2 .....

(3)

(c) Any ethanol present in the breath of a drinker can be detected by using a breathalyser. The ethanol is converted into ethanoic acid. The breathalyser has negative and positive electrodes. A current is measured and displayed in terms of alcohol content.

The overall redox equation is as follows

$$CH_3CH_2OH(l) + O_2(g) \longrightarrow CH_3COOH(l) + H_2O(l)$$

(i) Draw the displayed formula for ethanoic acid.

(1)

(ii) Deduce a half-equation for the reduction of atmospheric oxygen to water in acidic solution at one electrode of the breathalyser.

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(1)

(iii) Deduce a half-equation for the oxidation of ethanol in water to ethanoic acid at the other electrode of the breathalyser.

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(1)

(iv) The earliest breathalysers used laboratory chemicals to oxidise the ethanol to ethanoic acid. Detection was by a colour change.

Identify a reagent or combination of reagents that you would use in the laboratory to oxidise ethanol to ethanoic acid.
State the colour **change** that you would expect to see.

Reagent or combination of reagents .....

Colour change .....

(2)

(d) The fermentation of glucose from crops is the main method for the production of ethanol. The product is called bioethanol. The European Union has declared that bioethanol is carbon-neutral.

(i) State the meaning of the term *carbon-neutral*.

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(Extra space) .....

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(1)

(ii) Other than carbon-neutrality, state the **main** advantage of the use of glucose from crops as the raw material for the production of ethanol.

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(1)

(iii) Give *one* disadvantage of the use of crops for the production of ethanol.

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(1)
(Total 13 marks)

6 The manufacture of food grade phosphoric acid for use in cola drinks begins with the production of pure white phosphorus from the mineral fluoroapatite, $Ca_5F(PO_4)_3$

(a) Complete the following equation for the manufacture of phosphorus.

$$....Ca_5F(PO_4)_3 + 9SiO_2 + ...C \longrightarrow 9CaSiO_3 + CaF_2 + ...CO + ...P$$

(1)

(b) As the phosphorus cools, it forms white phosphorus, P_4

Give the oxidation state of phosphorus in each of the following.

P_4 .....

H_3PO_4 .....

(2)

(c) Fertiliser grade phosphoric acid is manufactured from sulfuric acid and calcium phosphate. Use the following precise relative atomic mass data to show how mass spectrometry can be used to distinguish between pure sulfuric acid (H_2SO_4) and pure phosphoric acid (H_3PO_4) which both have M_r = 98 to two significant figures.

Atom	Precise relative atomic mass
^{1}H	1.00794
^{16}O	15.99491
^{31}P	30.97376
^{32}S	32.06550

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(1)

(d) Concentrated phosphoric acid is used as a catalyst in the hydration of propene to form the alcohol $CH_3CH(OH)CH_3$ as the main organic product.
The industrial name for this alcohol is isopropyl alcohol.

(i) State the meaning of the term *catalyst*.

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(Extra space) .....

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(1)

(ii) State the meaning of the term *hydration*.

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(Extra space) .....

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(1)

(iii) Write an equation for the hydration of propene to form isopropyl alcohol.
Give the IUPAC name for isopropyl alcohol.

Equation .....

IUPAC name .....

(2)
(Total 8 marks)

7 Chloromethanes, such as dichloromethane and trichloromethane, are produced in industry as they have many uses.
Trichloromethane has been used in the manufacture of the refrigerant chlorodifluoromethane.

(a) Chlorine can react with dichloromethane (CH_2Cl_2) to form trichloromethane ($CHCl_3$).

(i) Write an equation for each of the following steps in the mechanism for this reaction.

Initiation step

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First propagation step

.....

Second propagation step

.....

(3)

(ii) Give **one** essential condition for this reaction and name the type of mechanism.

Essential condition .....

Type of mechanism .....

(2)

(b) An organic product, **X**, with M_r = 154.0 is obtained when chlorine reacts with trichloromethane.

(i) Write an equation for the overall reaction of chlorine with trichloromethane to form **X**, by the same mechanism as that outlined in part (a)(i).

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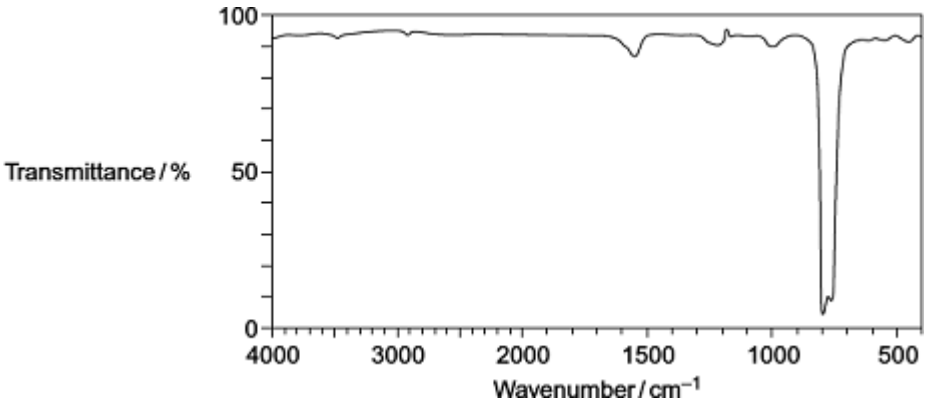
(1)

(ii) The following infrared spectrum was obtained for a sample of **X** produced in this reaction.



Use this infrared spectrum to explain why it is possible to deduce that this sample of **X** contains no trichloromethane.
You may find it helpful to refer to **Table 1** on the Data Sheet.

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(Extra space) .....

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(2)

(c) Explain, with the aid of equations and the intermediates that form in the ozone layer, why the European Union has banned the use of chlorodifluoromethane ($CHClF_2$) as a refrigerant.

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(Extra space) .....

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(4)

(d) The compound 2,3,3,3-tetrafluoropropene is the refrigerant used in all new car air conditioners.

(i) Draw the displayed formula for 2,3,3,3-tetrafluoropropene.

(1)

(ii) Give **one** reason why 2,3,3,3-tetrafluoropropene is a more **environmentally** acceptable refrigerant than chlorodifluoromethane.

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(1)

(Total 14 marks)

8 The reaction of butane-1,4-diol with butanedioic acid produces the polymer PBS used in biodegradable packaging and disposable cutlery.
Butanedioic acid is produced by two different processes.

Process 1

- Aqueous sodium hydroxide reacts with 1,4-dibromobutane to make butane-1,4-diol.
- Butane-1,4-diol is oxidised to butanedioic acid.

Process 2

- Glucose reacts with carbon dioxide in the presence of microorganisms to produce butanedioic acid directly.
- The carbon dioxide used in this process is obtained from a local factory that produces bioethanol.

(a) Deduce **one** safety reason and one environmental reason why **Process 2** is preferred to **Process 1**.

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(Extra space) .....

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(2)

(b) (i) Name and outline a mechanism for the following reaction that occurs in **Process 1**.

$$BrCH_2CH_2CH_2CH_2Br + NaOH \longrightarrow BrCH_2CH_2CH_2CH_2OH + NaBr$$

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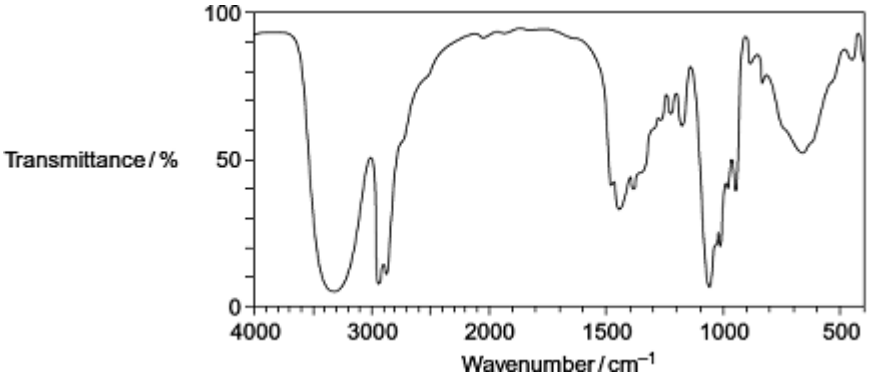
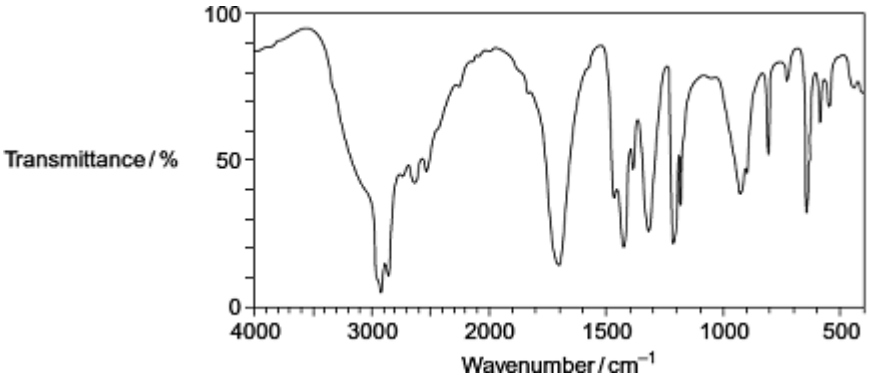
(3)

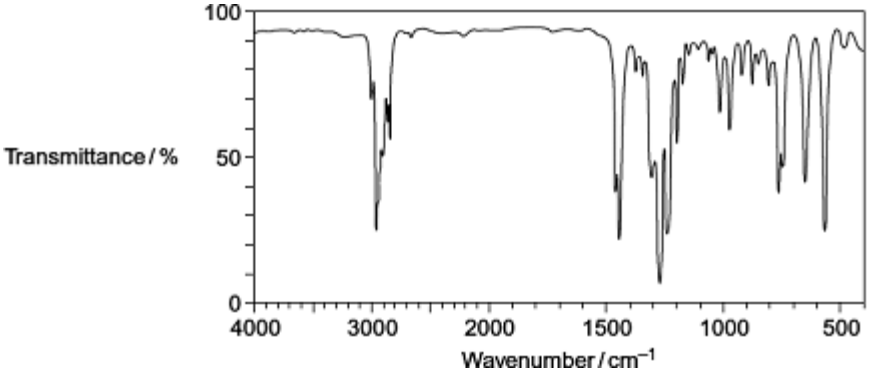
(ii) The infrared spectra shown are those of three compounds.

Compound **A** 1,4-dibromobutane
Compound **B** butane-1,4-diol
Compound **C** butanedioic acid

Identify the compound responsible for each spectrum by writing the correct letter, **A**, **B** or **C**, in the box next to each spectrum.
You may find it helpful to refer to **Table 1** on the Data Sheet.







(3)

(c) In the production of bioethanol, glucose ($C_6H_{12}O_6$) is converted into a dilute aqueous solution of ethanol and carbon dioxide.

Give the name of this process and state **three** essential conditions necessary to produce a good yield of ethanol.

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(4)

(d) State the class of alcohols to which the diol butane-1,4-diol belongs.

Identify a suitable reagent or combination of reagents for the conversion of butane-1,4-diol into butanedioic acid ($HOOCCH_2CH_2COOH$).

Write an equation for this oxidation reaction using [O] to represent the oxidising agent.

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(3)
(Total 15 marks)

9 The table shows the structures and names of three compounds with M_r = 72.0

Compound	Formula	Name
1	$CH_3CH_2CH_2CHO$	butanal
2	$CH_3CH_2CH_2CH_2CH_3$	pentane
3	$CH_3CH_2COCH_3$	butanone

(a) Explain why M_r values, measured to five decimal places, cannot distinguish between compounds **1** and **3** but can distinguish between compounds **1** and **2**.

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(2)

(b) A simple chemical test, using either Fehling's solution or Tollens' reagent, can be used to distinguish between compound **1** and compound **3**.
Choose one of these two reagents and state what you would observe with each of compound **1** and compound **3**.

Chosen reagent .....

Observation with compound **1**.....

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Observation with compound **3**.....

.....

(2)
(Total 4 marks)