ERRATUM NOTICE

General Certificate of Education
January 2009
Advanced Level Examination

AQA

ASSESSMENT and
QUALIFICATIONS
ALLIANCE

CHEMISTRY   **CHM4**

Unit 4   Further Physical and Organic Chemistry

Tuesday 20 January 2009   9.00 am to 10.30 am

Instructions to Invigilators

Before the start of the examination please ask candidates to amend their question papers as follows.
(Please read out this message twice to ensure understanding.)

Turn to Page 12, Question 5(c) (ii)

Cross out the number '4' and insert the number '6' in its place.

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For this paper you must have
• a calculator.

Time allowed: 1 hour 30 minutes

Instructions
• Use black ink or black ball-point pen.
• Fill in the boxes at the top of this page.
• Answer **all** questions.
• Answer the questions in **Section A** and **Section B** in the spaces provided. Answers written in margins or blank pages will not be marked.
• Show all your working.
• Do all rough work in this book. Cross through any work you do not want to be marked.
• The Periodic Table/Data Sheet is provided on pages 3 and 4. Detach this perforated sheet at the start of the examination.
• **Section B** questions are provided on a perforated sheet. Detach this sheet at the start of the examination.

Information
• The maximum mark for this paper is 90.
• The marks for questions are shown in brackets.
• You are expected to use a calculator where appropriate.
• Write your answers to the questions in **Section B** in continuous prose, where appropriate. You will be assessed on your ability to use good English, to organise information clearly, and to use specialist vocabulary where appropriate.

Advice
• You are advised to spend about 1 hour on **Section A** and about 30 minutes on **Section B**.

*Areas outside
the box will
not be scanned
for marking*

SECTION A

Answer **all** questions in the spaces provided.

1   In this question, give all values of pH to 2 decimal places.

1   (a)   (i)   Write an expression for pH.

....

1   (a)   (ii)   Calculate the pH of a $0.150 \, mol \, dm^{-3}$ solution of hydrochloric acid.

....

....

(2 marks)

1   (b)   A $60.0 \, cm^3$ sample of $0.0850 \, mol \, dm^{-3}$ aqueous potassium hydroxide was partially
neutralised by the addition of $30.0 \, cm^3$ of $0.150 \, mol \, dm^{-3}$ hydrochloric acid.

1   (b)   (i)   Calculate the number of moles of potassium hydroxide used.

....

....

1   (b)   (ii)   Calculate the number of moles of hydrochloric acid added.

....

....

1   (b)   (iii)   Calculate the number of moles of potassium hydroxide remaining in excess in
the solution formed and hence calculate the pH at 298 K of this solution.

Moles of KOH ....

....

pH of solution formed ....

....

....

....

....

....

(7 marks)

9

The Periodic Table of the Elements

■ The atomic numbers and approximate relative atomic masses shown in the table are for use in the examination unless stated otherwise in an individual question.

Key

relative atomic mass —— 6.9 **Li** Lithium

atomic number —— 3

I	II			III	IV	V	VI	VII	0
1.0 **H** Hydrogen 1									4.0 **He** Helium 2
6.9 **Li** Lithium 3	9.0 **Be** Beryllium 4			10.8 **B** Boron 5	12.0 **C** Carbon 6	14.0 **N** Nitrogen 7	16.0 **O** Oxygen 8	19.0 **F** Fluorine 9	20.2 **Ne** Neon 10
23.0 **Na** Sodium 11	24.3 **Mg** Magnesium 12			27.0 **Al** Aluminium 13	28.1 **Si** Silicon 14	31.0 **P** Phosphorus 15	32.1 **S** Sulphur 16	35.5 **Cl** Chlorine 17	39.9 **Ar** Argon 18
39.1 **K** Potassium 19	40.1 **Ca** Calcium 20	45.0 **Sc** Scandium 21	...	69.7 **Ga** Gallium 31	72.6 **Ge** Germanium 32	74.9 **As** Arsenic 33	79.0 **Se** Selenium 34	79.9 **Br** Bromine 35	83.8 **Kr** Krypton 36
85.5 **Rb** Rubidium 37	87.6 **Sr** Strontium 38	88.9 **Y** Yttrium 39	...	114.8 **In** Indium 49	118.7 **Sn** Tin 50	121.8 **Sb** Antimony 51	127.6 **Te** Tellurium 52	126.9 **I** Iodine 53	131.3 **Xe** Xenon 54
132.9 **Cs** Caesium 55	137.3 **Ba** Barium 56	138.9 **La** Lanthanum 57 *	...	204.4 **Tl** Thallium 81	207.2 **Pb** Lead 82	209.0 **Bi** Bismuth 83	210.0 **Po** Polonium 84	210.0 **At** Astatine 85	222.0 **Rn** Radon 86
223.0 **Fr** Francium 87	226.0 **Ra** Radium 88	227 **Ac** Actinium 89 †							

Transition metals:

45.0 **Sc** Scandium 21, 47.9 **Ti** Titanium 22, 50.9 **V** Vanadium 23, 52.0 **Cr** Chromium 24, 54.9 **Mn** Manganese 25, 55.8 **Fe** Iron 26, 58.9 **Co** Cobalt 27, 58.7 **Ni** Nickel 28, 63.5 **Cu** Copper 29, 65.4 **Zn** Zinc 30

88.9 **Y** Yttrium 39, 91.2 **Zr** Zirconium 40, 92.9 **Nb** Niobium 41, 95.9 **Mo** Molybdenum 42, 98.9 **Tc** Technetium 43, 101.1 **Ru** Ruthenium 44, 102.9 **Rh** Rhodium 45, 106.4 **Pd** Palladium 46, 107.9 **Ag** Silver 47, 112.4 **Cd** Cadmium 48

138.9 **La** Lanthanum 57 *, 178.5 **Hf** Hafnium 72, 180.9 **Ta** Tantalum 73, 183.9 **W** Tungsten 74, 186.2 **Re** Rhenium 75, 190.2 **Os** Osmium 76, 192.2 **Ir** Iridium 77, 195.1 **Pt** Platinum 78, 197.0 **Au** Gold 79, 200.6 **Hg** Mercury 80

227 **Ac** Actinium 89 †

* 58 – 71 Lanthanides

| 140.1 **Ce** Cerium 58 | 140.9 **Pr** Praseodymium 59 | 144.2 **Nd** Neodymium 60 | 144.9 **Pm** Promethium 61 | 150.4 **Sm** Samarium 62 | 152.0 **Eu** Europium 63 | 157.3 **Gd** Gadolinium 64 | 158.9 **Tb** Terbium 65 | 162.5 **Dy** Dysprosium 66 | 164.9 **Ho** Holmium 67 | 167.3 **Er** Erbium 68 | 168.9 **Tm** Thulium 69 | 173.0 **Yb** Ytterbium 70 | 175.0 **Lu** Lutetium 71 |

† 90 – 103 Actinides

| 232.0 **Th** Thorium 90 | 231.0 **Pa** Protactinium 91 | 238.0 **U** Uranium 92 | 237.0 **Np** Neptunium 93 | 239.1 **Pu** Plutonium 94 | 243.1 **Am** Americium 95 | 247.1 **Cm** Curium 96 | 247.1 **Bk** Berkelium 97 | 252.1 **Cf** Californium 98 | 252.0 **Es** Einsteinium 99 | (257) **Fm** Fermium 100 | (258) **Md** Mendelevium 101 | (259) **No** Nobelium 102 | (260) **Lr** Lawrencium 103 |

Turn over ▶

Gas constant $R = 8.31$ J K^{-1} mol^{-1}

Table 1
Proton n.m.r. chemical shift data

Type of proton	δ/ppm
RCH$_3$	0.7–1.2
R$_2$CH$_2$	1.2–1.4
R$_3$CH	1.4–1.6
RCOCH$_3$	2.1–2.6
ROCH$_3$	3.1–3.9
RCOOCH$_3$	3.7–4.1
ROH	0.5–5.0

Table 2
Infra-red absorption data

Bond	Wavenumber/cm^{-1}
C—H	2850–3300
C—C	750–1100
C=C	1620–1680
C=O	1680–1750
C—O	1000–1300
O—H (alcohols)	3230–3550
O—H (acids)	2500–3000

2 In this question, give all values of pH to 2 decimal places.

2 (a) At 298 K, the pH of a $0.150 \, \text{mol dm}^{-3}$ solution of the weak acid HX is 3.48

2 (a) (i) Write an expression for the acid dissociation constant, K_a, for this acid.

....

....

2 (a) (ii) Calculate the value of K_a for this acid, HX, at 298 K.

....

....

....

....

(4 marks)

2 (b) The value of the acid dissociation constant, K_a, for a different weak acid HY is $2.65 \times 10^{-4} \, \text{mol dm}^{-3}$ at 298 K.

Calculate the pH of the buffer solution formed when a 0.0300 mol sample of the solid salt NaY is dissolved in $500 \, \text{cm}^3$ of a $0.250 \, \text{mol dm}^{-3}$ solution of the acid HY.

....

....

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....

....

(4 marks)

8

Turn over ▶

3 At a given temperature, in a closed container, a mixture of 0.360 mol of CO and 0.640 mol of H_2 was left to reach equilibrium according to the following equation.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H^{\ominus} = -90.0\,kJ\,mol^{-1}$$

At equilibrium, 0.120 mol of CH_3OH was present in the gaseous mixture.

3 **(a)** **(i)** Calculate the number of moles of CO and of H_2 in this equilibrium mixture.

Moles of CO ....

Moles of H_2 ....

3 **(a)** **(ii)** Calculate the mole fraction of CO in the equilibrium mixture.

....

....

....
(4 marks)

3 **(b)** **(i)** Write a general expression to show how the partial pressure of a gas is related to its mole fraction.

....

3 **(b)** **(ii)** The total pressure of the gases in the equilibrium mixture formed in part (a) was 268 kPa. Calculate the partial pressure of CO in this mixture.

....

....
(2 marks)

3 **(c)** A different equilibrium mixture of CO, H_2 and CH_3OH was prepared at a given temperature and a total pressure of 500 kPa. In this mixture, the partial pressure of CO was 75.0 kPa and the partial pressure of H_2 was 300 kPa.

3 **(c)** **(i)** Calculate the partial pressure of CH_3OH in this mixture.

....

....

3 **(c)** **(ii)** Write an expression for the equilibrium constant, K_p, for this reaction.

....

....

3 **(c)** **(iii)** Calculate a value for the equilibrium constant, K_p, at this temperature and give its units.

Calculation ....

....

....

Units ....

(5 marks)

3 **(d)** **(i)** State the effect, if any, at a constant temperature of an increase in total pressure on the mole fraction of CH_3OH and on the value of the equilibrium constant K_p.

Effect on mole fraction of CH₃OH ....

Effect on K_p ....

3 **(d)** **(ii)** State the effect, if any, at a constant pressure of an increase in temperature on the mole fraction of CH_3OH and on the value of the equilibrium constant K_p.
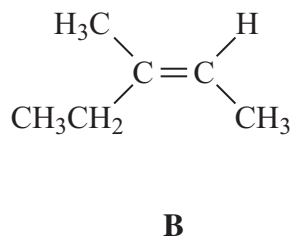
Effect on mole fraction of CH₃OH ....
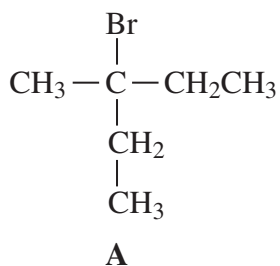
Effect on K_p ....

(4 marks)

15

Turn over for the next question

Turn over ▶

8

*Areas outside
the box will
not be scanned
for marking*

4 Compound **B** exists as a pair of stereoisomers which can be formed from compound **A**.

$$CH_3-\overset{\displaystyle Br}{\underset{\displaystyle \underset{\displaystyle CH_3}{CH_2}}{C}}-CH_2CH_3$$

$$\overset{\displaystyle H_3C}{\underset{\displaystyle CH_3CH_2}{}}C=C\overset{\displaystyle H}{\underset{\displaystyle CH_3}{}}$$

A   **B**

4 (a) Name compound **A**.

....

(1 mark)

4 (b) (i) Give the reagent and conditions used to convert **A** into **B** and name the type of reaction involved.

Reagent ....

Conditions ....

Type of reaction ....

4 (b) (ii) Draw the **structural** isomer of **B** which is also formed from **A** under the same conditions.

(4 marks)

4 (c) (i) Name the type of stereoisomerism shown by **B**.

....

4 (c) (ii) Explain why this type of stereoisomerism is possible in **B**.

....

....

....

(3 marks)

4 (d) (i) Suggest why the mass spectrum of **A** ($C_6H_{13}Br$) contains two molecular ion peaks of almost equal intensity at $m/z = 164$ and $m/z = 166$

....

....

....

4 (d) (ii) There is a major peak at $m/z = 85$ in the mass spectrum of **A**. Draw the structure of the species which gives rise to this peak. Give one reason why this peak is a major one.
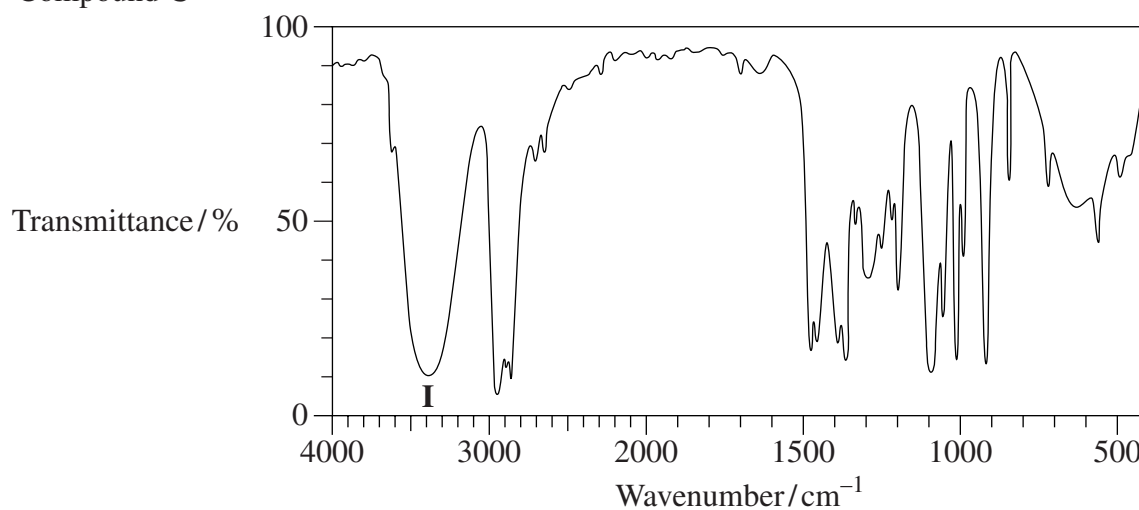
Structure

Reason ....

....

(4 marks)

12

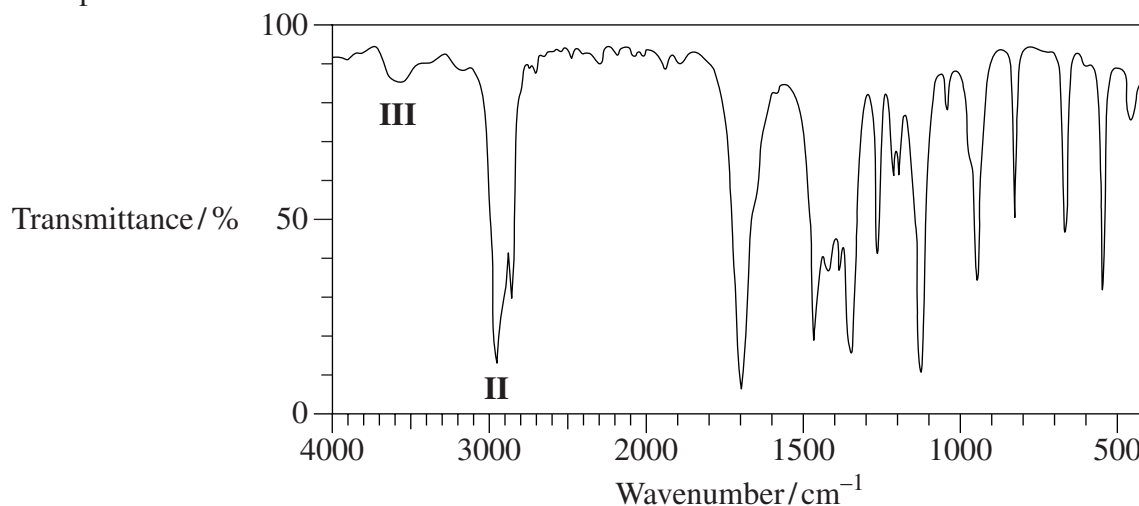**Turn over for the next question**

Turn over ▶

5 The infra-red spectra shown below are those of compound **C** and of compound **D**.

Compound **C**

Compound **D**

In the laboratory, a student converted **C** ($C_6H_{14}O$) into **D** ($C_6H_{12}O$) by heating **C** with acidified potassium dichromate(VI).

5 (a) (i) Identify the bonds responsible for the absorptions labelled **I** and **II** in the infra-red spectra above.

I ....

II ....

5 (a) (ii) The absorption labelled **III** is due to an impurity present in the sample of **D** made by the student. Suggest one possible impurity which would produce this absorption.

....

(3 marks)

5 (b) The proton n.m.r. spectrum of **C** ($C_6H_{14}O$) shows 4 peaks.

The table below gives the chemical shifts, δ values, for each of these peaks, together with their splitting patterns and integration values.

δ/ppm	3.47	1.63	1.12	0.89
Splitting pattern	quartet	singlet	doublet	singlet
Integration value	1	1	3	9

State what can be deduced about the structure of **C** from the presence of the following in its proton n.m.r. spectrum.

5 (b) (i) The singlet peak at $\delta = 0.89$

....

5 (b) (ii) The two peaks at $\delta = 3.47$ and $\delta = 1.12$

....

....

....

5 (b) (iii) Use the information in part (a) and part (b) to deduce the structure of **C**.

(4 marks)

Question 5 continues on the next page

Turn over ▶

5 (c) Draw the structures of the alcohols described below which are isomers of **C** ($C_6H_{14}O$):

5 (c) (i) a compound which is unaffected by acidified potassium dichromate(VI) and has 4 peaks in its proton n.m.r. spectrum,

5 (c) (ii) a compound which exists as optical isomers and has 4 peaks in its proton n.m.r. spectrum.

(2 marks)

5 (d) Draw the structure of an alcohol which is an isomer of **D** ($C_6H_{12}O$) but which has no absorption between 1620 and 1680 cm^{-1} in its infra-red spectrum.

(1 mark)

10

6 **(a)** **(i)** The rate equation for the reaction between compounds **E** and **F** at a given temperature is

$$rate = k[\mathbf{E}][\mathbf{F}]^2$$

The initial rate of reaction is $9.45 \times 10^{-4}\,mol\,dm^{-3}\,s^{-1}$ when the initial concentration of **E** is $0.76\,mol\,dm^{-3}$ and the initial concentration of **F** is $1.22\,mol\,dm^{-3}$. Calculate a value for the rate constant, *k*, at this temperature and state its units.

Value of k ....

....

....

Units of k ....

....

6 **(a)** **(ii)** Calculate the initial rate of reaction when the concentration of **E** is doubled and at the same time the concentration of **F** is halved but the temperature is not changed.

....

....

(4 marks)

6 **(b)** The following data were obtained by studying the reaction between compounds **G** and **H** at a constant temperature.

Experiment	Initial concentration of **G** / $mol\,dm^{-3}$	Initial concentration of **H** / $mol\,dm^{-3}$	Initial rate / $mol\,dm^{-3}\,s^{-1}$
1	0.20	0.25	6.80×10^{-3}
2	0.30	0.25	15.3×10^{-3}
3	0.60	0.50	61.2×10^{-3}

6 **(b)** **(i)** Deduce the order of reaction with respect to **G**.

....

....

6 **(b)** **(ii)** Deduce the order of reaction with respect to **H**.

....

....
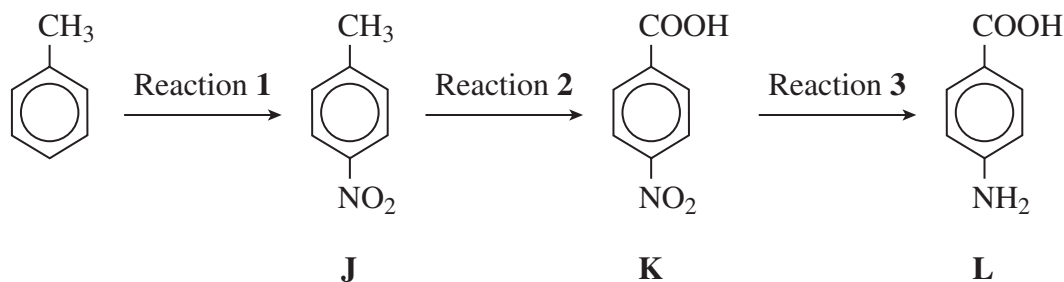
(2 marks)

6

Turn over ▶

SECTION B

Detach this perforated sheet.
Answer both questions **7** and **8** in the spaces provided on page 14 and pages 17–20.

7 Consider the reaction sequence shown below.

7 (a) Compound **J** is produced by the reaction of methylbenzene with the NO_2^+ ion. This ion is formed by the reaction of concentrated nitric acid with concentrated sulphuric acid.

State the role of concentrated nitric acid in its reaction with concentrated sulphuric acid.

Name and outline a mechanism for the reaction of methylbenzene with the NO_2^+ ion.
(5 marks)

7 (b) Name the type of reaction involved in the conversion of **J** into **K** (Reaction **2**).

Draw the structure of the compound formed when compound **K** reacts with methanol in the presence of a small amount of concentrated sulphuric acid.
(2 marks)

7 (c) Compound **L** is prepared by the reduction of **K** in Reaction **3**.

Give reagents and write an equation for Reaction **3**. Use [H] to represent the reducing agent.
(2 marks)

7 (d) In the presence of a catalyst, **L** can polymerise.

Name the type of polymerisation which occurs. Draw the repeating unit of the polymer and name the type of linkage involved.
(3 marks)

Turn over ▶

12

8 The intermediates, **X** and **Y**, shown below are formed by nucleophilic attack on two different compounds containing a carbonyl group.

$$CH_3CH_2 - \overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}} - CH_3 \qquad CH_3CH_2 - \overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\underset{\displaystyle H}{|}}{\overset{+}{N}} - H}{C}} - Cl$$

$$\qquad\qquad \textbf{X} \qquad\qquad\qquad\qquad \textbf{Y}$$
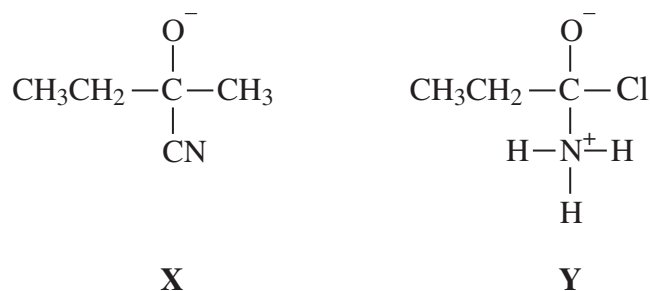
8 (a) Outline a mechanism for the complete reaction in which **X** is an intermediate.
Name the final product formed from **X**.

(5 marks)

8 (b) Outline a mechanism for the complete reaction in which **Y** is an intermediate.
Name this mechanism and name the final organic product formed from **Y**.

(6 marks)

8 (c) Species **Z** is shown below.

$$CH_3CH_2 - \overset{\overset{\displaystyle COO^-}{|}}{\underset{\underset{\underset{\displaystyle H}{|}}{\overset{+}{N}} - H}{C}} - H$$

$$\textbf{Z}$$
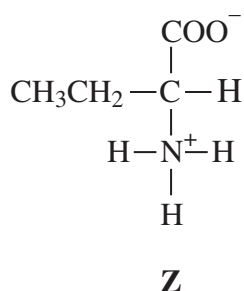
Name the type of species of which **Z** is an example and draw the product formed when **Z** reacts with an excess of aqueous sodium hydroxide.

(2 marks)

8 (d) Aspirin is an ester prepared industrially by the reaction of ethanoic anhydride with 2-hydroxybenzenecarboxylic acid shown below.

COOH
OH
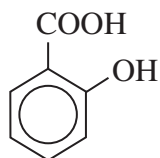
Write an equation for this reaction showing clearly the structure of aspirin.
Give **two** reasons why ethanoyl chloride is not used in this industrial preparation.

(5 marks)

END OF QUESTIONS

18

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