NATIONAL JUNIOR COLLEGE
SH 2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9729/02

Paper 2 Structured Questions

Tues 21 Aug 2018
2 hours

Candidates answer **all** questions on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid/tape.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

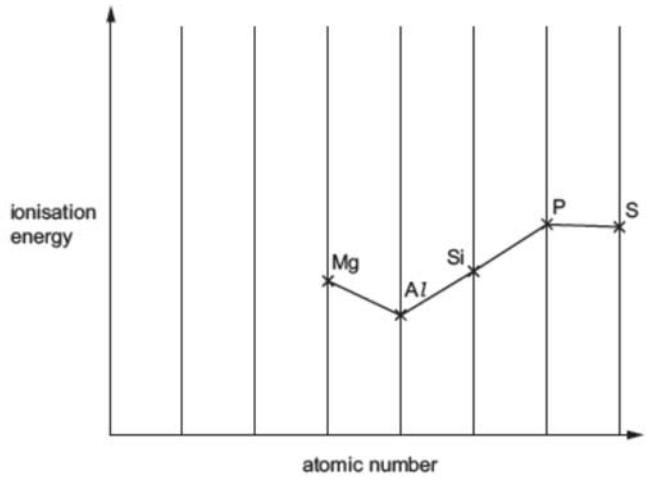
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use			
1	/8		
2	/14		
3	/13		
4	/11		
5	/14		
6	/15		
Penalty units			
Penalty sf			
Paper 2	/75		

Answer <u>ALL</u> questions on the space provided.
This paper consists of **18** printed pages.

1 The properties of elements and their compounds show similarities, differences and trends depending on the positions of the elements.

(a) The elements in the third period, and their compounds, show trends in their physical and chemical properties.
A sketch graph of the first ionisation energies of five successive elements in the third period is shown.



(i) Sketch on the graph, the position of the ionisation energy of the two elements that come before Mg in this sequence.

[1]

(ii) Explain, with reference to electronic arrangements, the decreases in first ionisation energy between Mg and A*l* and between P and S.

Mg and A*l*: .....

.....

.....

P and S: .....

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.....

[2]

(b) The chlorides of the elements in the third period behave in different ways when added to water, depending on their structure and bonding.
L is a chloride of an element in Period 3. A students investigated **L** and the results are as given below.

- **L** is a white crystalline solid with a melting point of 987 K.
- **L** dissolves in water to form a weakly acidic solution.
- Addition of NaOH(aq) to an aqueous solution of **L** produces a white precipitate, **M** .

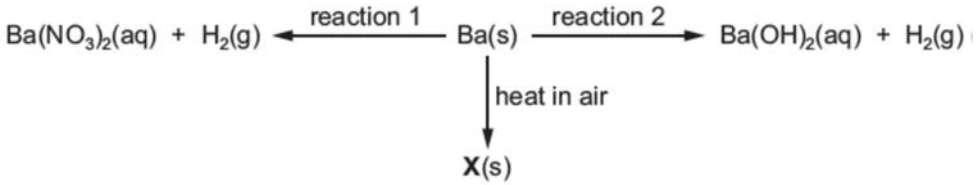
(i) Identify **L** and **M.**

L: ……. M: ……..
[1]

(ii) Write an equation to illustrate the formation of the weakly acidic solution.

…… [1]

(c) Some reactions based on the Group 2 metal barium, Ba, are shown below.



(i) State the reagent needed for each of reactions 1 and 2.

Reaction 1 **……...**

Reaction 2 **……...**
[2]

(ii) Write an equation for the formation of **X**.

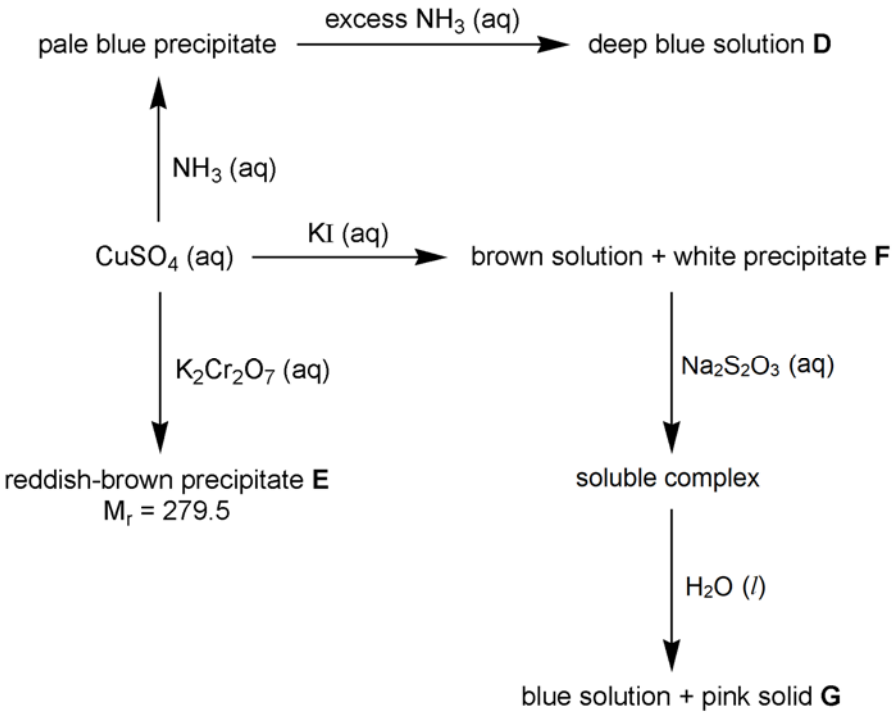
……

[1]

[Total: 8]

2 The use of *Data Booklet* is relevant to this question.

(a) Copper(II) sulfate, an inorganic compound that has wide uses in organic syntheses and in engraving of zinc plates for intaglio printmaking, can undergo a series of reactions as shown below.



(i) Identify **D**, **E**, **F** and **G**.

D: …… **E**: ……

F: …… **G**: ……

[4]

(ii) With the aid of relevant equations, account for the formation of the deep blue solution **D** from the pale blue precipitate.

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[2]

(b) **(i)** By quoting relevant data, account for the trend in the thermal stabilities from HC*l* to HI.

……

……

……

[2]

(ii) Identify a transition metal cation that can be used to differentiate the oxidising abilities of Br_2 and I_2. Explain your answer with appropriate workings.

[3]

(iii) Suggest a series of steps to verify the presence of chloride and iodide ions in a mixture, given the following reagents:

- Aqueous silver nitrate
- Aqueous ammonia
- Aqueous nitric acid
- Filter paper
- Filter funnel

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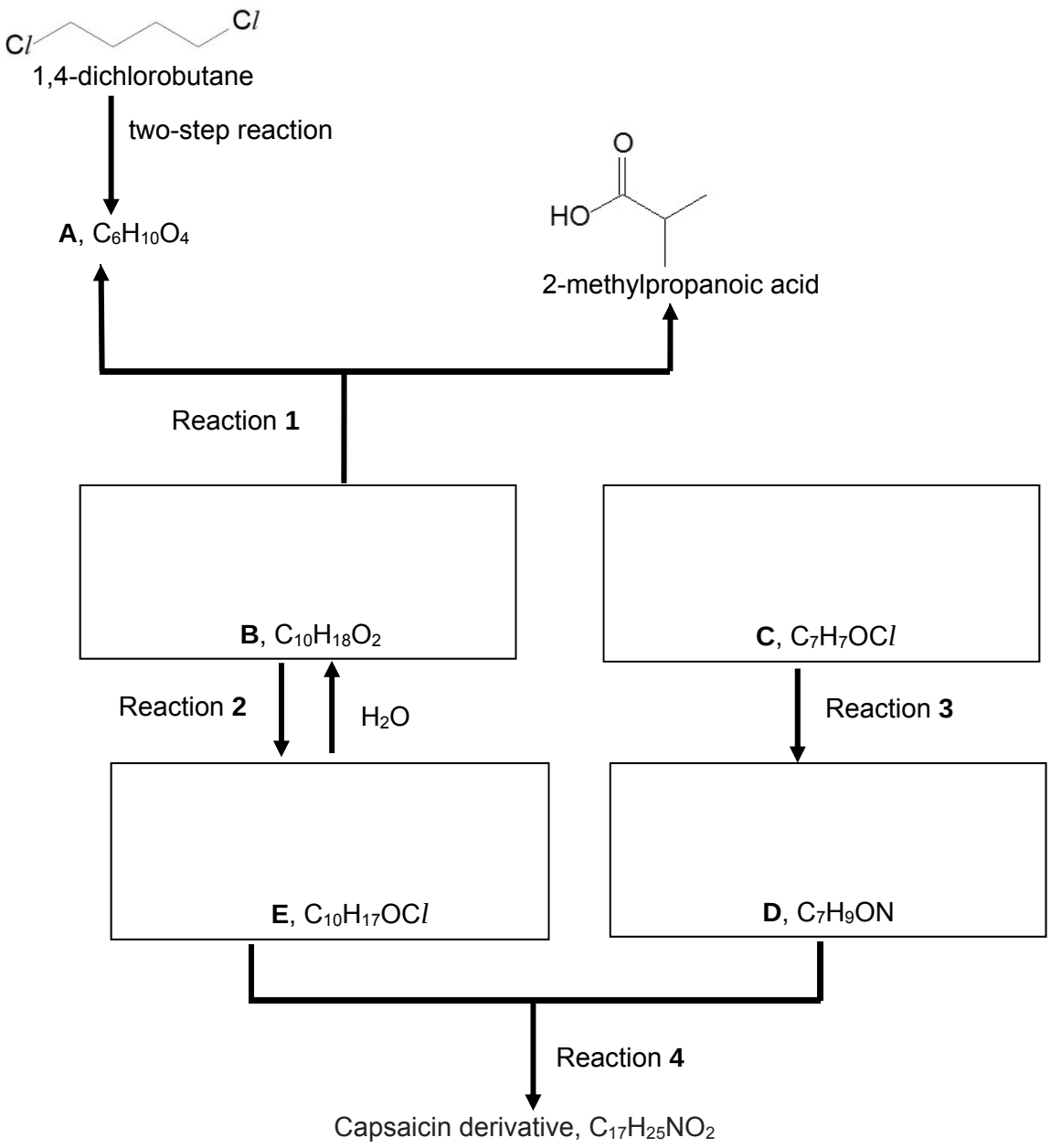
[3]

[Total: 14]

3 Capsaicin is an active component of chili peppers. The reaction scheme involving the formation of a derivative of Capsaicin, $C_{17}H_{25}NO_2$, is shown below.



Compounds **A** to **D** react with sodium metal.
Compounds **A** and **B** react with aqueous sodium carbonate.
Compound **C**, Compound **D** and the capsaicin derivative reacts with aqueous sodium hydroxide but does not react with aqueous sodium carbonate.
Compounds **B** and **E** also react with cold acidified $KMnO_4$.

(a) Name the functional group common to compounds **A** and **B**.

.....

[1]

(b) Compound **A** can be synthesised from 1,4-dichlorobutane in two steps.
Suggest reagents and conditions for the synthesis, and the intermediate product for the reaction.

Step 1: **……**

Step 2: **……**

Intermediate product:

[3]

(c) There are two functional groups in compound **B**. Suggest the identity of the functional group in **B** that reacts with cold acidified $KMnO_4$.

Functional group that reacts with cold acidified $KMnO_4$: **……**

[1]

(d) Hence, draw the structure of compound **B** in the box on pg 6 and state the reagents and conditions for reaction **1**.

Reagents and conditions for reaction **1**: **……**

[2]

(e) Compound **C** reacts with hot ethanolic silver nitrate to produce a white ppt.
Draw the structure of Compounds **C** and **D** in the box on pg 6.
Name the type of reaction for reaction **3**.

Type of reaction for reaction **3**: **……**

[3]

(f) Compound **E** readily hydrolyses in water to produce Compound **B**.

Draw the structure of compound **E** in the box on pg 6, and hence state the reagents and conditions for reaction **2**.

Reagents and conditions for reaction **2**: **……**
[2]

(g) Compounds **D** and **E** react to produce the Capsaicin derivative.

Draw the structure of the Capsaicin derivative.

[1]

[Total: 13]

4 On 11 May 2018, Mount Merapi on Central Java, Indonesia erupted, causing the local airport to be closed. The eruption was reported to be caused by accumulation of volcanic gases. The volcanic ash and gases spewed can be dangerous to planes passing through the plume. The most abundant volcanic gas is harmless water vapour. However, significant amounts of carbon dioxide, sulfur dioxide, hydrogen sulfide and hydrogen halides are also emitted.

When carbon dioxide is emitted from volcanoes, it typically becomes diluted to low concentrations very quickly and is not life threatening. However, cold carbon dioxide gas can flow into low-lying areas where it can reach much higher concentrations. Breathing air with more than 3% CO_2 can quickly lead to headaches, dizziness, increased heart rate and difficulty breathing. At about 15%, unconsciousness and death can result quickly.

Table 1.1: Volcanic gas composition in area **A**

Gas	Volume Percentage
Water vapour, H_2O	87.1
Carbon dioxide, CO_2	Rapidly increasing
Sulfur dioxide, SO_2	0.5
Hydrogen, H_2	0.7
Carbon monoxide, CO	0.01
Hydrogen sulfide, H_2S	0.23
Hydrochloric acid, HCl	2.89
Hydrofluoric acid, HF	2.55

Composition of the volcanic gases are typically expressed in terms of volume percentage, which can be calculated as follows

$$volume\ percentage = \frac{volume\ of\ gas}{Total\ volume}$$

However, percentages are only additive for ideal gases.

(a) (i) State **two** assumptions of the kinetic theory of gases.

……

……

……

[2]

(ii) Under what conditions of temperature and pressure would you expect the behaviour of carbon dioxide to be most like that of an ideal gas?

……

[1]

(iii) Suggest a reason why at low temperature, carbon dioxide would sink rapidly and accumulate to high concentrations.

……

……

……
[2]

(iv) People living in area A were evacuated as the level of carbon dioxide and temperature of surroundings were increasing rapidly.
Given that 0.30 mg of CO_2 was present in 10 cm^3 of gas mixture at 43^oC and 11.2 kPa, determine the volume percentage of carbon dioxide present.

Hence comment on the possible danger if people remained in the area.

Volume percentage of carbon dioxide = ……

……

……
[3]

(b) Hydrogen sulfide can react with methane in the following equation.

$$CH_4(g) + 2\ H_2S(g) \rightleftharpoons CS_2(g) + H_2(g)$$

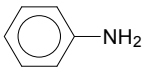
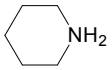
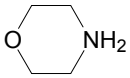
1 mol of CH_4, 2 mol of H_2S, 1 mol of CS_2 and 1 mol of H_2 was allowed to reach equilibrium at a constant temperature and pressure of 960^{o}C and 2 atm.

Given that partial pressure of CS_2 was found to be 0.5 atm at equilibrium, determine the value of K_p, giving its units.

[3]

[Total: 11]

5 **(a)** The following table contains the pK_b values of different nitrogen organic compounds.

Compound	pK_b
$(CH_3)_3CNH_2$ 2-amino-2-methylpropane	3.19
 phenylamine	9.38
 piperidine	2.88
 morpholine	5.17
N_2H_4 hydrazine	5.17, 11.05

(i) Suggest a reason why pK_b of morpholine is higher than piperidine.

Morpholine has an electronegative O that exert ***electron withdrawing effect***, it reduces the availability of lone pair on N to accept H^+, therefore Morpholine is a weaker base hence a higher pK_b value.

Examiners Comments:
Most students are able to identify that O is electronegative and hence able to exert electron withdrawing effect. There are a handful who thought that the lone pair will delocalise into O. This is impossible as the 2 atoms are not adjacent to each other and no orbital overlap exists.

(ii) Suggest a reason why pK_b of phenylamine is so much higher than 2-amino-2-methylpropane.

Lone pair on N of phenylamine is delocalised into the benzene ring, making lone pair much less available to receive H^+ than lone pair of N in $(CH_3)_3CNH_2$, phenylamine is a weaker base hence a higher pKb value than $(CH_3)_3CNH_2$.

Examiners Comments:
Most students are able to recognise that the lone pair on N can delocalise into the ring and hence a reduction in availability of lone pair for donation to a proton. Do use the correct key word "delocalisation" as some students will use terms like "dissociate" or "diffuse" into the ring which is not very accurate.

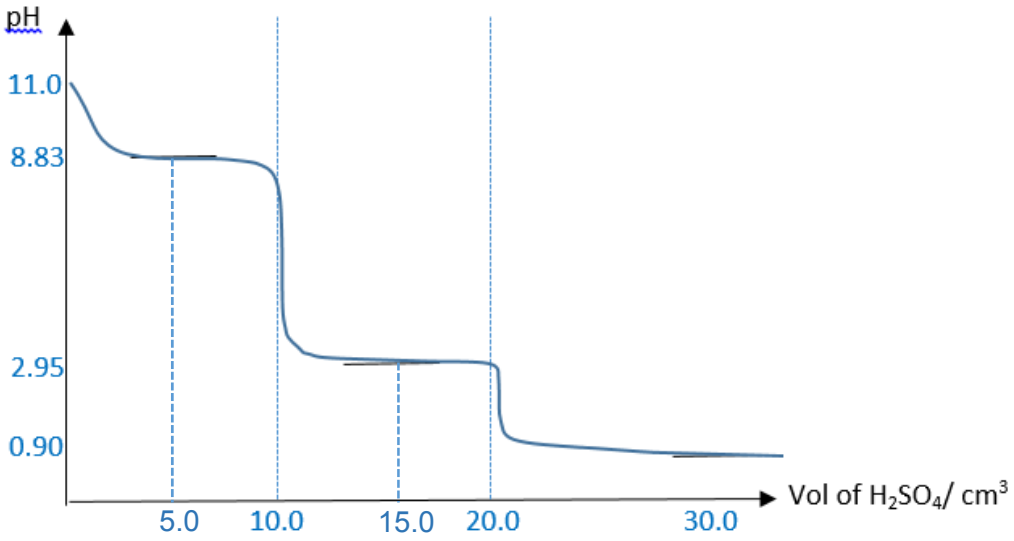
[2]

(b) 10.0 cm^3 of an aqueous mixture containing 0.5 mol dm^{-3} of hydrazine was placed in a conical flask and the initial pH was found to be 11.0.

Sketch the pH–volume graph on the axis provided when 10.0 cm^3 of the aqueous mixture was titrated with 0.25 mol dm^{-3} dilute sulfuric acid until a total volume of 30.0 cm^3 of dilute sulfuric acid was added.

Your sketch should include the following points

- Initial pH of hydrazine
- pH of the reaction mixture when 30.0 cm^3 of H_2SO_4 is added.
- Maximum buffer points (if any)



Initial pH = 11.0 given in question

volume of H_2SO_4 required for the 1st equiv point = 10.0 cm^3
total vol of H_2SO_4 required for 2nd equiv point = 20.0 cm^3

Max buffer points occur at 5 and 15 cm^3.
pOH = pK_b at max buffer pts
pH = 14- pOH
pH are 14 – 5.17 = 8.83 and 14 – 11.05 = 2.95 respectively.

Final pH
Amt of unreacted H^+ = (2 x 10/1000 x 0.25) = 0.005 mol (since H_2SO_4 is diprotic)
$[H^+]$ = 0.005 x 1000/ 40 = 0.125 $moldm^{-3}$
pH = 0.90

Examiners Comments:
Students did badly for this question.
Most students did not manage to recognise two equivalence point (represented by 2 steep slope).
To identify how many equivalence point(s) there is, students need to **focus on the analyte**. If the analyte is (1) weak **and** (2) multi-protic, then it will have multiple equivalence points.

Most students also could not calculate the volume of H_2SO_4 used correctly. To do so, since both acid and base are diprotic,

$N_2H_4 + H_2A \rightarrow N_2H_6^{2+} + A^{2-}$
Mol ratio is 1:1

Hence **total volume** of acid required is 20 cm^3

[3]

(c) Student **M** suggested a 2–step process as shown, to synthesise 2-amino-2-methylpropane from a suitable alkane.

C_4H_{10} (**A**) $\xrightarrow{\text{step 1}}$ C_4H_9Cl (**B**) $\xrightarrow{\text{step 2}}$ $C_4H_{11}N$

(i) Identify the structures of compounds **A** and **B**, and suggest reagents and conditions for each of the two steps.

$(CH_3)_3CH$ Structure of **A**	$(CH_3)_3CCl$ Structure of **B**

Step 1: limited Cl_2, UV. light

Step 2: excess NH_3 in ethanol, heat in sealed tube

[4]

(ii) Outline the mechanism for step 1.

			[3]

(iii) A student **N** suggested an alternative synthetic route for the synthesis of 2-amino-2-methylpropane, using an alkene as a starting material.

Explain why this synthetic route will give a higher yield as compared to the suggested route in **c(ii).**

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[2]

[Total: 14]

6 1–chloro–1–phenylethane undergoes hydrolysis with hydroxide ions to produce 1–phenylethanol, as shown in the equation below.

$$\underset{\text{1-chloro-1-phenylethane}}{C_6H_5CHClCH_3} + OH^- \rightarrow \underset{\text{1-phenylethanol}}{C_6H_5CH(OH)CH_3} + Cl^-$$

(a) The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in the solution at a given time after the reaction has been quenched.

(i) Suggest a suitable quenching agent that can be used to stop the reaction effectively.

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[1]

(ii) Using your answer in **(i)**, describe a suitable method for determining the order of reaction with respect to OH^-, given the following.

- Solution **A**, 1.0 mol dm^{-3} 1-chloro-1-phenylethane
- Solution **B**, 0.10 mol dm^{-3} sodium hydroxide
- 0.10 mol dm^{-3} hydrochloric acid
- Quenching agent [as suggested in **(i)**]
- Stopwatch
- Standard laboratory equipment

Specific details of volumes and time is not required.

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[3]

(b) The rate of this reaction was measured using different initial concentrations of the two reagents and the results are shown below.

Experiment	$[C_6H_5CHClCH_3]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Relative rate
1	0.05	0.10	1.0
2	0.10	0.20	2.0
3	0.15	0.10	3.0

(i) Deduce the order of reaction with respect to each of the reagents. Explain your reasoning.

Order with respect to $C_6H_5CHClCH_3$ = ……

Order with respect to OH^- = ……

[2]

(ii) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

rate = …… mol dm^{-3} s^{-1}

units of *k* = …… .

[2]

(c) **(i)** By making use of your answer in **(b)(i)**, describe the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions.
In your answer, you should show relevant charges, lone pairs, dipoles and show movement of electrons by curly arrow.

[3]

(ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane. Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers.
Explain your answer.

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[2]

(iii) 1-chloro-2-ethyl benzene, $C_6H_4ClCH_2CH_3$, is an isomer of 1-chloro-1-phenylethane, $C_6H_5CHClCH_3$. The ease of hydrolysis for each of the 2 compounds is different. Explain why.

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[2]

[Total: 15]