Name:		Class:	

ST ANDREW'S JUNIOR COLLEGE

JC 2 Preliminary Exam

Chemistry **9647/02**

Higher 2 **31 August 2016**

Paper 2 **2 hours**

Candidates answer in the spaces provided on the question paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use:

Question	Marks
1	
2	
3	
4	
5	
6	
7	
Total (72 marks)	

This document consists of **27** printed pages including this page.

[Turn Over

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1 A student found a bottle of solid benzoic acid in the school laboratory. She was tasked to determine the standard enthalpy change of neutralisation of benzoic acid. The standard enthalpy change of neutralisation is when one mole of water is formed between an acid and a base.

$$H^+ (aq) + OH^- (aq) \rightarrow H_2O (l)$$

You may assume you are provided with the following:

- **FA 1**, aqueous sodium hydroxide, NaOH
- Solid benzoic acid
- Polystyrene (styrofoam) cups
- Apparatus normally found in a school laboratory

Before carrying out the experiment, an aqueous solution of 2.00 mol dm^{-3} benzoic acid (**FA 2**) is first prepared. Subsequently, in separate experiments, different volumes of **FA 2** and **FA 1** are mixed while keeping the total volume of the reaction mixture constant. In each experiment, the temperature rise, ΔT, is to be determined. A graph of ΔT against volume of **FA 1** used is then plotted.

Data from the graph can then be used to determine:

- the ΔT_{max},
- the concentration of **FA 1**,
- the enthalpy change of neutralisation between **FA 1** and **FA 2**.

It is given that 4.18 J is required to raise the temperature of 1 cm^3 of any solution by 1 ^oC.

(a) Write an equation to represent the standard enthalpy change of neutralisation between sodium hydroxide and benzoic acid.

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[1]

1 (b) (i) Write a detailed plan to prepare 2.00 mol dm^{-3} solution of **FA 2**.

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[3]

(ii) It is predicted that the maximum temperature change for the neutralisation would occur when the volume of **FA 1** mixed is between 25 cm^3 and 30 cm^3. The total volume of any mixture should be kept constant at 50 cm^3.

Write a detailed plan on how you could determine the temperature changes for the series of reactions between **FA 1** and **FA 2**.
Your plan should include details of:

- all essential experimental details,
- appropriate volumes of solutions to be used,
- a tabulation of the experimental data to be collected (including volumes used),
- how these measurements can be used to obtain the temperature change, ΔT.

1 (b) (ii)

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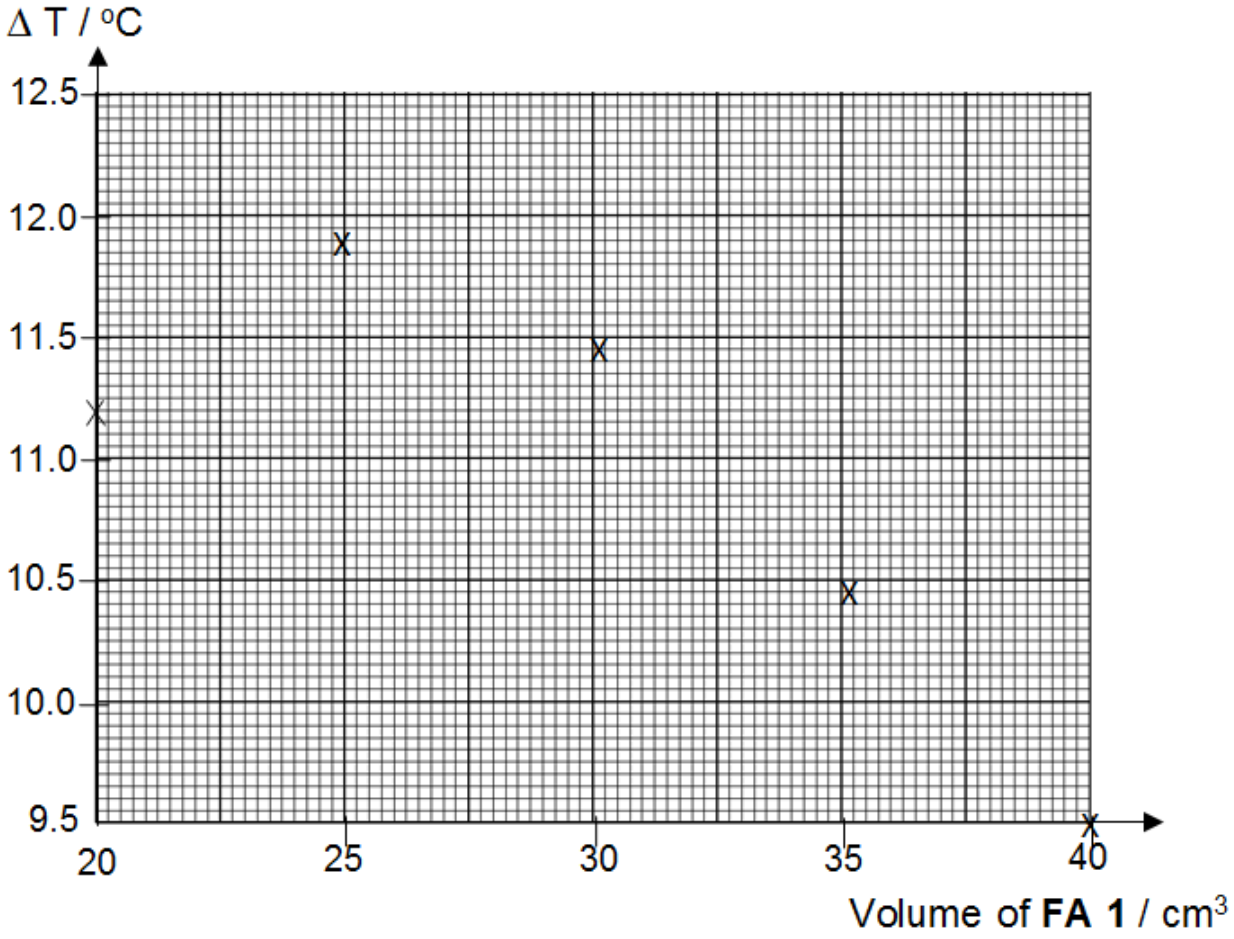
[5]

[Turn Over

1 (b) (iii) The following plots were plotted on a grid after another similar experiment was conducted. Draw suitable graphs through the plotted points.

[1]



1 (c) By using the graph in **(b)(iii)**, calculate

- the concentration of **FA 1**, given that the total volume of the mixture is 50 cm^3.
- the enthalpy change of neutralisation for the reaction between **FA 1** and **FA 2**.

[2]

[Total: 12]

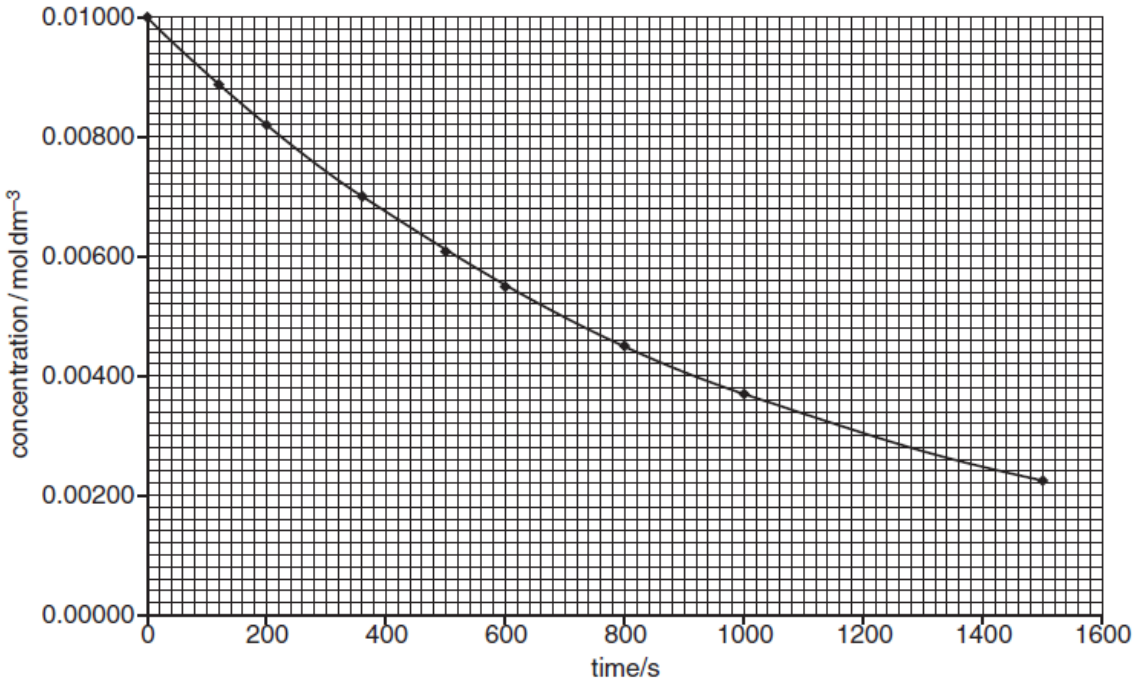
2 **(a)** Chromium carbonyl, also known as chromium hexacarbonyl, is a chemical compound with the formula $Cr(CO)_6$. $Cr(CO)_6$ is zerocovalent, meaning that Cr has an oxidation state of 0. Draw the structure of the complex and state the shape and bond angle around the Cr atom in the complex.

[2]

(b) Chromium hexacarbonyl undergoes the following ligand replacement reaction.

$$Cr(CO)_6 + PR_3 \longrightarrow Cr(CO)_5PR_3 + CO$$

Two separate experiments were carried out to study the rate of this reaction.
In the first experiment, the ligand PR_3 was in a large excess and $[Cr(CO)_6]$ was measured against time. The results are shown on the graph below.



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2 **(b)** In the second experiment, $Cr(CO)_6$ was in a large excess, and $[PR_3]$ was measured against time. The following results were obtained.

time / s	$[PR_3]$ / mol dm^{-3}
0	0.0100
120	0.0076
200	0.0060
360	0.0028

(i) On the graph, plot the data given in the table.

[1]

(ii) Use the graphs to determine the order of reaction with respect to $Cr(CO)_6$ and PR_3. In each case explain how you arrived at your answer.

$Cr(CO)_6$

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PR_3

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[2]

(iii) Write the rate equation for the reaction, and calculate a value for the rate constant, stating the units of the rate constant.

[3]

2 (b) (iv) Two possible mechanisms for this reaction are given below. State the mechanism which is consistent with the rate equation you have written in **(b)(iii)** and explain your answer.

Mechanism A $Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ slow
$Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5PR_3$ fast

Mechanism B $Cr(CO)_6 + PR_3 \rightarrow [OC\text{- - -}Cr(CO)_4\text{- - -}PR_3] \rightarrow Cr(CO)_5PR_3 + CO$
(transition state)

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[2]

[Total: 10]

3 This question refers to compounds of calcium and barium.

(a) Oil paints contain traces of red Ca^{2+} and green Ba^{2+} ions which give them their characteristic red and green colours respectively. Oil painting is typically done on canvas. During the manufacturing process of canvas, hydrogen orthoperiodate ions, HIO_6^{4-}, is left on the canvas.

Orthoperiodate salts are formed when orthoperiodate ions, IO_6^{5-}, reacts with the Ca^{2+} and Ba^{2+} ions in the paint, causing the decolourisation of the red and green colour of the paint. The equations below show the formation of IO_6^{5-} and its salts.

$$HIO_6^{4-}(aq) \rightleftharpoons H^+(aq) + IO_6^{5-}(aq) \qquad K_a = 4.04 \times 10^{-6} \text{ mol dm}^{-3}$$

$$5\,M^{2+}(aq) + 2\,IO_6^{5-}(aq) \rightarrow M_5(IO_6)_2(s) \qquad \text{where } M^{2+} \text{ is } Ca^{2+} \text{ or } Ba^{2+}$$

Relevant K_{sp} values are given in the table below :

Salt	K_{sp}
$Ca_5(IO_6)_2$	4.0×10^{-9}
$Ba_5(IO_6)_2$	1.6×10^{-15}

The painting was stored in a display cabinet at a low pH environment. Over the weekend, the electrical supply of the display cabinet was disrupted which resulted in an increase of the environment's pH. It was found that the green portions of the painting were decolourised due to the formation of solid barium orthoperiodate, $Ba_5(IO_6)_2$.

3 (a) Explain qualitatively why the green coloured areas of the painting were decolourised but not the red coloured areas when the pH increased.

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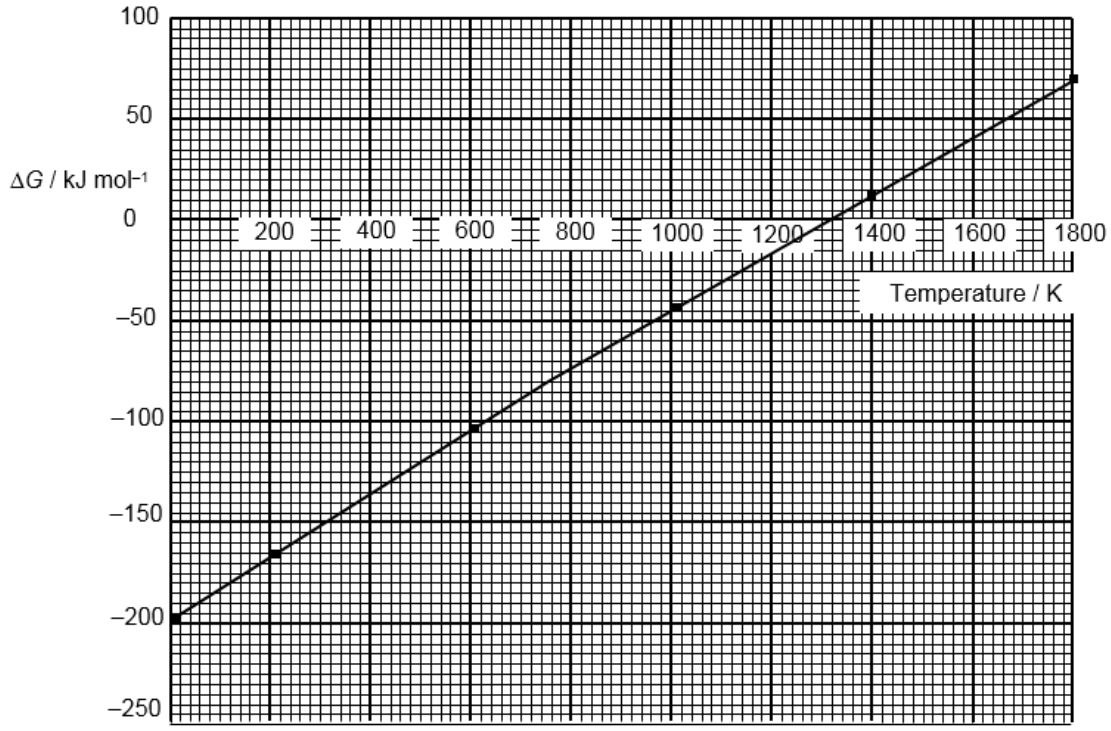
[3]

3 (b) ΔG, ΔH and ΔS are related by the following equation.

$$\Delta G = \Delta H - T\Delta S$$

The Ellingham diagram below shows how ΔG changes between 0 K and 1800 K for the following reaction.

$$CaO\ (s) + H_2O\ (l) \rightarrow Ca(OH)_2\ (s)$$



For the range of temperatures in the graph above, it can be assumed that the enthalpy change and the entropy change of the reaction remain approximately constant.

(i) Predict the sign of ΔS for the reaction, showing your reasoning.

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[2]

[Turn Over

3 (b) (ii) Using the graph, calculate ΔS.

[1]

(iii) Using the graph, determine ΔH.

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[1]

(iv) Determine the temperature above which the reaction become non-spontaneous.

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[1]

[Total: 8]

4 The table below gives data about some physical properties of the elements calcium, copper and chromium.

Physical Property	**Calcium**	**Copper**	**Chromium**
Relative atomic mass	40.1	63.5	52.0
Atomic radius / nm	0.197	0.128	0.117
Density / g cm^{-3}	1.54	8.92	7.20
First ionisation energy / kJ mol^{-1}	590	745	653

(a) **(i)** Explain why the first ionisation energy of copper and chromium are both higher than that of calcium.

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[2]

(ii) Use relative data from the table to explain qualitatively why the densities of copper and chromium are significantly greater than that of calcium.

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[1]

[Turn Over

4 (b) Chromium (III) nitrate is more acidic than chromium (II) nitrate. Explain with the aid of a relevant equation.

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[2]

(c) When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with gold and chromium impurities. It contained no other metal. In order to purify it, the alloy was made the anode of an electrolytic cell, with a pure copper cathode and aqueous copper (II) sulfate as the electrolyte.

Explain, with reference to E^{θ} values, what happens to the gold and chromium impurities during this purification process. The electrode reaction for the standard Au^{3+}/Au half cell is $Au^{3+}(aq) + 3e \rightleftharpoons Au(s)$ $\quad E^{\theta} = +1.50\ V$

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[3]

4 (d) A current of 1.8 A was passed through the cell described in **(c)** for 17 minutes, and the electrodes removed, washed, dried and weighed. It was found that some mass was lost from the anode.

After filtering it off and drying it, the deposit below the anode weighed 0.085 g. On adding an excess of hydroxide ions to the electrolyte, a grey-green precipitate was formed. Its mass was 0.304 g. (You may assume that negligible amount of copper ions remained in the electrolyte.)

(i) Calculate the expected increase in mass of the cathode.

[2]

(ii) Identify the grey-green precipitate.

grey-green precipitate: ……

[1]

(iii) It was found that the mass of copper removed from the alloy was 0.466 g. Calculate the masses of gold and chromium removed from the alloy. Hence calculate the total mass lost by the anode.

[3]

[Total: 14]

5 **(a)** A student conducted an experiment to identify the trend in thermal stability of hydrogen halides. The reaction occurred according to the following equation:

$$2HX(g) \rightleftharpoons H_2(g) + X_2(g)$$

The approximate K_c values for the above equilibrium at 500°C is shown in the table below.

Temperature /°C	K_c		
	HC*l*	**HBr**	**HI**
500	10^{-13}	10^{-9}	10^{-5}

(i) Using the Data Booklet, explain the trend in thermal stability of hydrogen halides down the group.

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[2]

(ii) Hence, deduce if the trend in **(a)(i)** agrees with the K_c data given above.

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[1]

5 (b) A student conducted another experiment to distinguish between samples of sodium chloride and phosphorus pentachloride. It was found that red onion water can be used as an indicator. The table below shows the colour of the indicator at various pH.

pH	Colour
Less than 7	Red
7	Violet

(i) To each unknown sample of chlorides, he added a few drops of red onion water. He recorded the colour of the indicator. Predict the identities of the chlorides.

Colour of red onion water	Identity of chloride
Red	
Violet	

[1]

(ii) With the aid of an equation, describe the action of water on phosphorus pentachloride.

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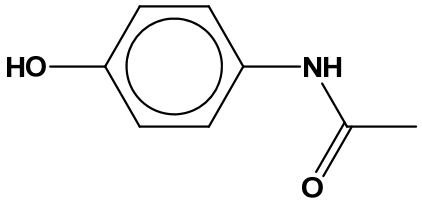
[2]

[Total: 6]

6 Paracetamol is an effective analgesic discovered by Joseph von Mering in 1893. Its structure is as shown.



(a) Explain why all the carbon-carbon bonds in benzene are of the same length.

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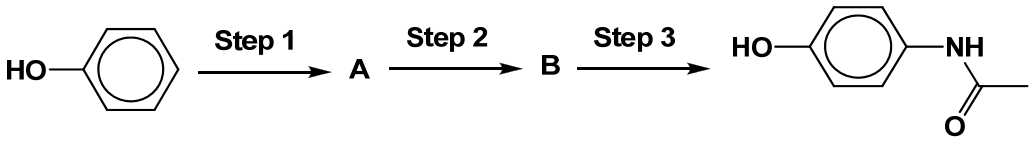
[1]

(b) **(i)** Paracetamol may be synthesised from phenol as shown.



State the reagents and conditions for steps **1** to **3**. Draw the structure of the intermediate product **B**.

Reagents and conditions:

Step **1**:

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Step **2**:

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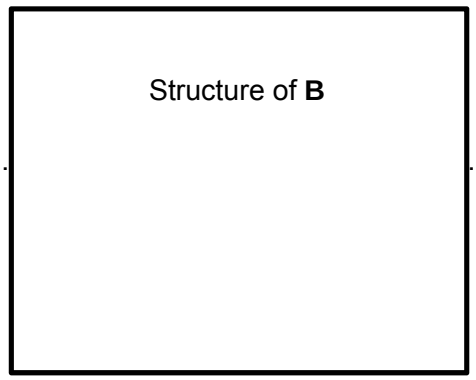
Step **3**:



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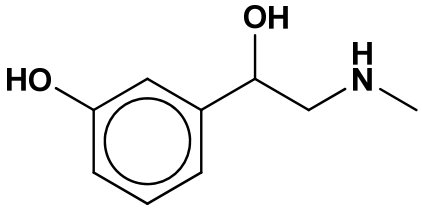
[4]

6 (b) (ii) Based on **Step 3** of the given reaction scheme, draw the structure of a possible side-product.

[1]

(iii) Phenylephrine is a decongestant which may be taken with paracetamol when a person is suffering from cold. The structure of phenylephrine is as shown.



State and explain how the basicity of phenylephrine might compare with that of paracetamol.

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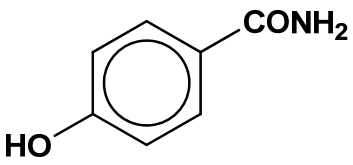
[2]

6 (b) (iv) Suggest a simple chemical test to distinguish between paracetamol and compound **A**.



Compound A

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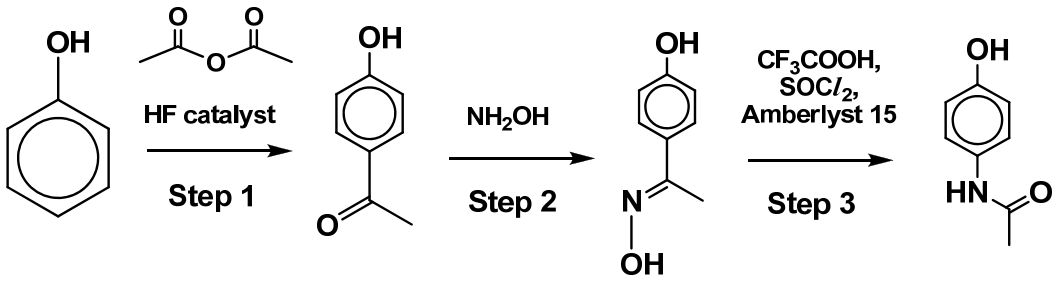
[2]

6 (c) (i) Hoechst and Celanese discovered a simpler synthetic route for paracetamol as shown.



State the types of reaction for steps **1** and **2**.

Step **1**:

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Step **2**:

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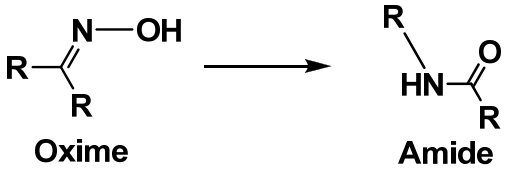
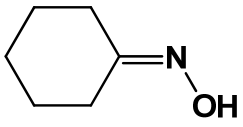
[2]

(ii) Step **3** is known as the Beckmann arrangement, where an oxime is converted into an amide.



Draw the structure of the product formed when 

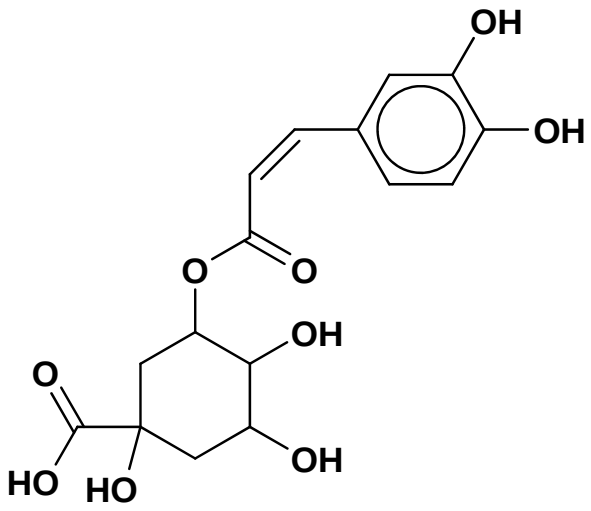
undergoes the Beckmann arrangement.

[1]

[Turn Over

[Total: 13]

7 Coffee beans contain chlorogenic acid, which is an antioxidant and an important biosynthetic intermediate. The structure of chlorogenic acid is as shown.



(a) State the number of moles of hot NaOH (aq) that will react with 1 mole of chlorogenic acid.

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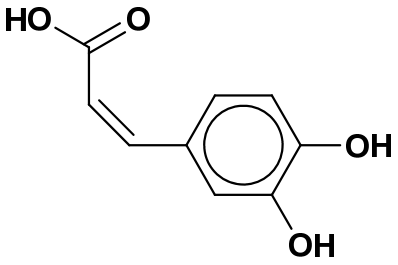
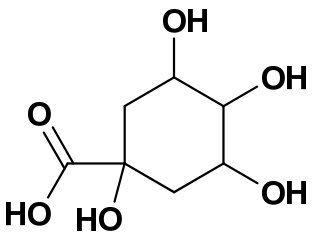
[1]

7 (b) On heating with dilute acid, chlorogenic acid produces two compounds, **X** and **Y**.

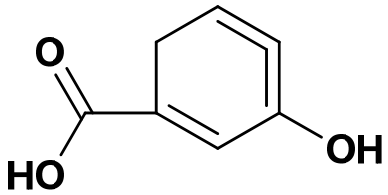


Compound **X**



Compound **Y**

When compound **Y** reacts with hot excess concentrated sulfuric acid, a product with a molecular formula of $C_7H_6O_3$ is formed. A student claims that the product formed has the following structural formula but the teacher disagrees.



Draw the correct structure of the product and explain what is wrong with the student's answer.

Structure of product

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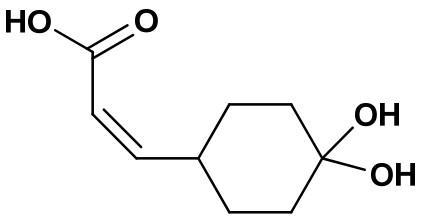
[2]

7 (c)



Compound **Z**

(i) Compound **Z** reacts with Br_2 (l) at room temperature and in the dark. Describe the mechanism showing curly arrows, charges, dipoles and any relevant lone pairs.

[3]

7 (c) (ii) The product of **(c)(i)** exists as a mixture of 4 stereoisomers. State the type of isomerism exhibited by the product and draw all the stereoisomers.

…...……

[3]

[Total: 9]

End of Paper