RAFFLES INSTITUTION
2016 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9647/02

Paper 2 Structured Questions **14 September 2016**
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces provided at the top of this page.
Write in dark blue or black pen in the spaces provided.
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.
A Data Booklet is provided. Do not write anything in it.
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	
1	/ **12**
2	/ **13**
3	/ **13**
4	/ **18**
5	/ **16**

Paper 1	Paper 2	Paper 3	Planning	Penalty	Total	Grade
/ 40	/ 60	/ 80	/ 12		/ 100	

This document consists of **24** printed pages.

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For examiner's use

1 Planning (P)

Copper plating is a method employed to coat an object's surface with a thin layer of copper. The object to be plated is lowered into an electrolyte containing Cu^{2+} ions, which are reduced on the surface of the object to form a thin layer of copper when an electric current is passed through the set-up.

This set-up can also be used to determine the Faraday constant (F), which is the charge carried by 1 mol of electrons, as described below.

A pre-weighed metal object and a pure copper rod are placed in a copper(II) sulfate solution, and then connected to an electrical source. After a sufficient duration, the mass of copper plated onto the metal object is determined by taking the difference between the object's mass before and after plating.

The mass of copper plated is dependent on the amount of electrical charge flowing through the circuit. The value of the Faraday constant may be determined graphically by repeating the experiment several times using different amounts of electrical charge, and plotting the collected data on a graph.

(a) The amount of electrical charge flowing through the circuit is dependent on time and electrical current.

Show that the relationship between the mass of copper plated onto the metal object and the time taken for the copper plating is given by:

$$m = \frac{63.5I}{2\mathrm{F}}t$$

where
m = mass of copper plated in grams (g),
I = current of circuit in amperes (A),
t = time in seconds (s)

[2]

(b) The value of the Faraday constant (F) is widely accepted by chemists to be 96500 C mol^{-1}.

Using this value and given an electrical power source that supplies a constant current of 0.500 A, calculate the **maximum time** (to the nearest second) for which copper plating can be carried out so that the mass of copper plated onto the metal object will not exceed 1.00 g.

maximum time = ……. [1]

For examiner's use

(c) By considering your answers to **(a)** and **(b)**, write a plan for determining the value of the Faraday constant in a laboratory.

You may assume that you are provided with:

- 0.0500 mol dm^{-3} copper(II) sulfate solution,
- 5 pieces of pure copper, each weighing **approximately** 1.5 g,
- 5 pieces of metal objects to be plated, each weighing exactly 2.00 g,
- an electrical power source that supplies a constant current of 0.500 A,
- distilled water,
- filter paper,
- the equipment and materials normally found in a school or college laboratory.

Your plan should include the following:

- a clearly labelled diagram of the set-up,
- details of how you would vary a variable of this experiment to collect 5 sets of data that will be used to calculate the Faraday constant,
- a sketch of the graph you would expect to obtain using the data collected and how the graph can be used to calculate the Faraday constant,
- the measures you would take to ensure the accuracy of the experiment.

Diagram for experimental set-up:

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For examiner's use

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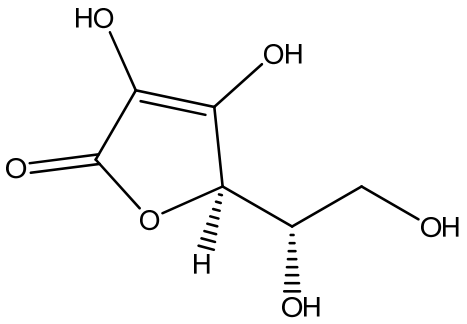
[9]

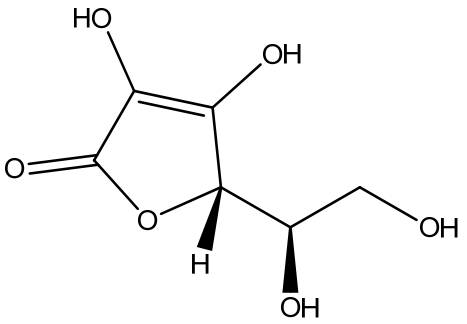
[Total: 12]

For examiner's use

2 **(a)** "Vitamin C" refers to a group of compounds which includes ascorbic acid and its salts.



ascorbic acid



compound **A**

Compound **A** is the mirror image of ascorbic acid.

(i) Besides compound **A**, ascorbic acid has two other stereoisomers. Draw the structures of these two isomers.

[2]

(ii) Pure ascorbic acid rotates plane-polarised light clockwise by 20° (or +20°).

Compound **A** was mixed with ascorbic acid, in an unknown proportion, in a beaker.

Plane-polarised light was shone through the beaker and it was found that the light had rotated 10° anti-clockwise (or −10°).

Calculate the percentage of ascorbic acid and compound **A** in the mixture.

% ascorbic acid = ……; % compound **A** = …… [2]

For examiner's use

(iii) Ascorbic acid is used as a food additive due to its solubility in water. Explain why ascorbic acid is soluble in water.

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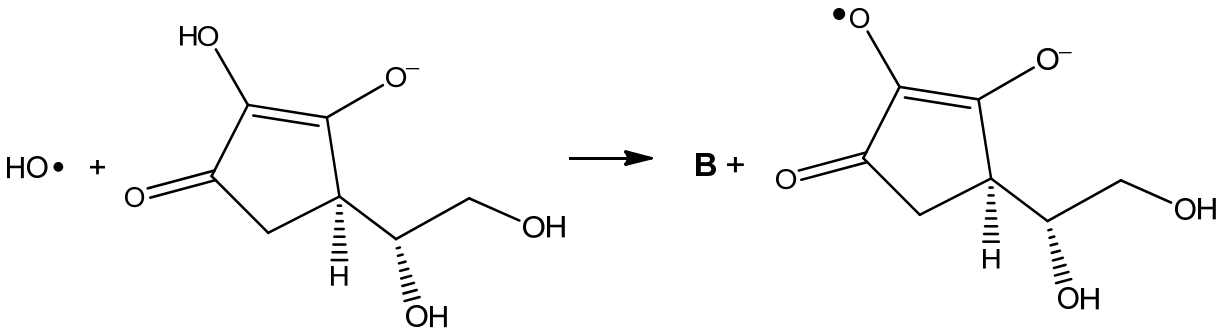
[1]

(b) Ascorbic acid has antioxidant properties and it exists mainly as the ascorbate ion at the physiological pH of 7.4.

An ascorbate ion reacts with a hydroxyl *free radical* in a 1:1 ratio to give product **B** and a radical anion **C** as shown below:



C

(i) Explain what is meant by a *free radical*.

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[1]

(ii) Suggest the identity of **B**.

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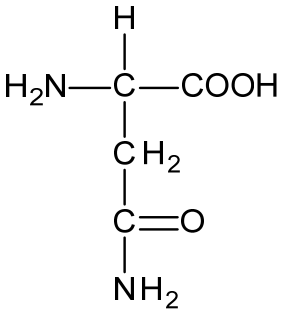
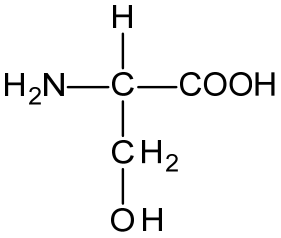
[1]

For examiner's use

(c) Asparagine and serine are important α-amino acids in the synthesis of proteins.



asparagine



serine

Suggest, with reagents and conditions, a simple chemical test to distinguish between the two α-amino acids.

Reagents and conditions:

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Observations:

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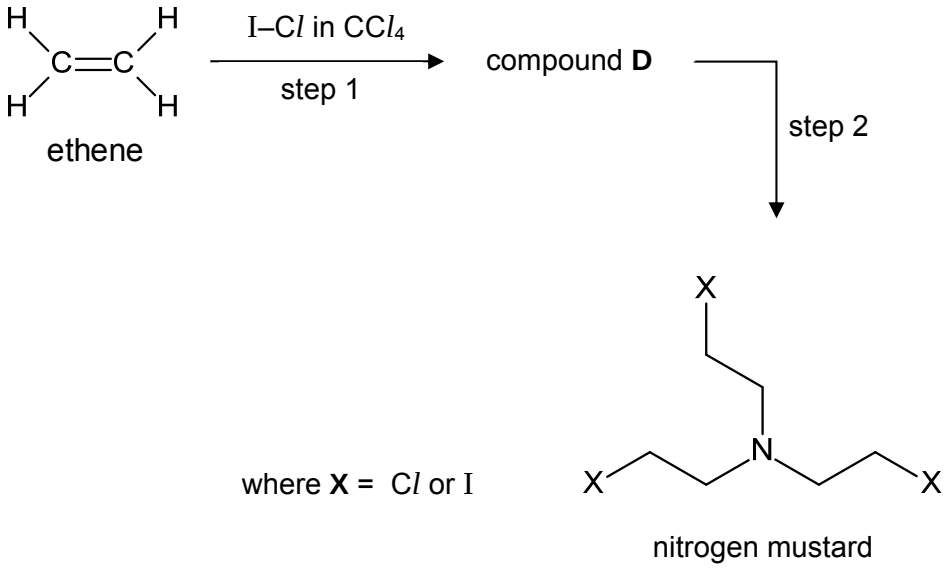
[2]

For examiner's use

(d) Nitrogen mustard gas is commonly used in chemotherapy for cancer.

It was suggested that the synthesis of nitrogen mustard can be carried out via the following pathway:



where **X** = C*l* or I

(i) Suggest the structure for compound **D**.

[1]

(ii) State and explain whether **X** (in nitrogen mustard) is more likely to be C*l* or I.

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[1]

(iii) Suggest the reagents and conditions for step 2.

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[2]

[Total: 13]

For examiner's use

3 *Use of the Data Booklet is relevant to this question.*

(a) Haemocyanin is the primary oxygen transport molecule found in the blood stream of lobsters.

Unlike haemoglobin which contains iron, haemocyanin contains copper that binds reversibly to oxygen molecules. Oxygenation of haemocyanin results in an oxidation reaction, and a colour change as shown below:

Cu(I)	⟶	Cu(II)
deoxygenated		oxygenated
colourless		blue

(i) Write the full electronic configuration of a Cu^{2+} ion.

……[1]

(ii) By considering your answer to **(a)(i)**, explain why oxygenated haemocyanin is coloured.

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[3]

(iii) Account for the absence of colour in deoxygenated haemocyanin.

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[1]

For examiner's use

(b) Bis(tartrate) complex of Cu^{2+}, which is present in Fehling's solution, is used to test for aldehydes.

(i) The reduction half-equation of bis(tartrate) complex of Cu^{2+} is given as:

$$2Cu^{2+}(complex) + 2OH^- + 2e^- \rightarrow Cu_2O + H_2O$$

Construct the half-equation for the oxidation of aldehyde (RCHO) under alkaline conditions, and hence, construct the overall equation.

Oxidation half-equation:

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Overall equation:

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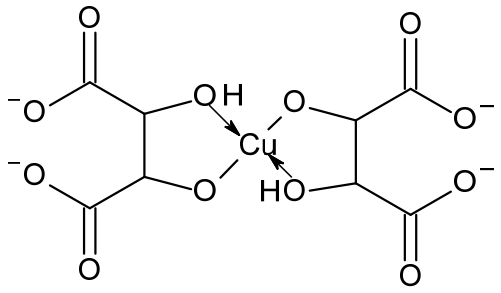
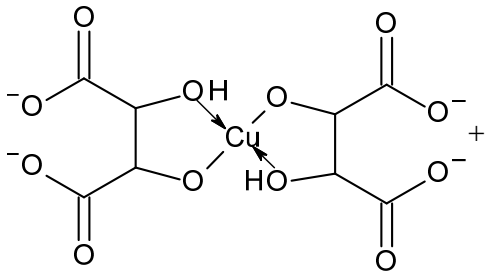
[2]

(ii) The bis(tartrate) complex of Cu^{2+} has the following structure:



It is synthesised by reacting aqueous Cu^{2+} ions with tartrate ions, $C_4H_4O_6^{2-}$, in an alkaline medium as shown below:

$2C_4H_4O_6^{2-} + Cu^{2+} + 2OH^- \rightarrow$  $+ 2H_2O$

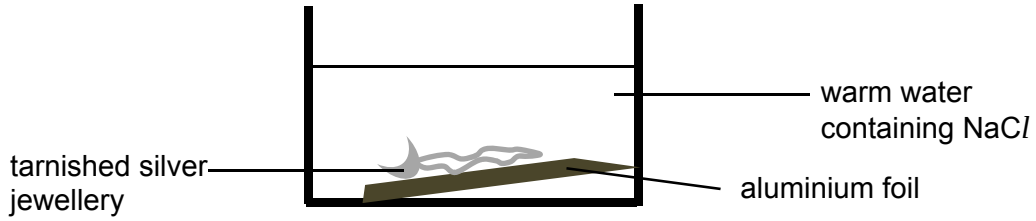
Draw the structure of the tartrate ion, $C_4H_4O_6^{2-}$.

[1]

For examiner's use

(c) Silver is a common metal used for jewellery. However, due to the increased amounts of hydrogen sulfide being released into the atmosphere by the combustion of fossil fuels, tarnishing of silver occurs relatively quickly, resulting in the formation of black silver sulfide.

Tarnished silver has a layer of silver sulfide, Ag_2S, on its surface. It may be restored easily by dipping it into warm water containing a piece of aluminium foil and a pinch of sodium chloride.



(i) The piece of aluminium acts as the anode which reduces the silver sulfide; itself being oxidised to aluminium sulfide. Write the balanced equation for this reaction.

……..…

[1]

(ii) A student calculated $E^{\ominus}_{cell}$ for this reaction using $E^{\ominus}(Ag^{+}/Ag)$ and $E^{\ominus}(Al^{3+}/Al)$.

However, the actual E_{cell} of this reaction is different from what he has calculated. Besides not being performed under standard conditions, suggest another reason to account for the difference.

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[1]

(iii) Suggest a purpose for the addition of sodium chloride in this reaction.

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[1]

For examiner's use

(iv) While carrying out this procedure, a faint aroma of rotten egg smell is given off. This is due to the further reaction of aluminium sulfide with water, producing aluminium hydroxide and hydrogen sulfide gas.

$$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2S$$

17.1 cm^3 of hydrogen sulfide gas was released at the end of the experiment, which was conducted at room temperature and pressure.

Using the information given and your answer to **(c)(i)**, calculate the percentage of silver that was tarnished if the original jewellery contained 2.00 g of pure silver.

[2]

[Total: 13]

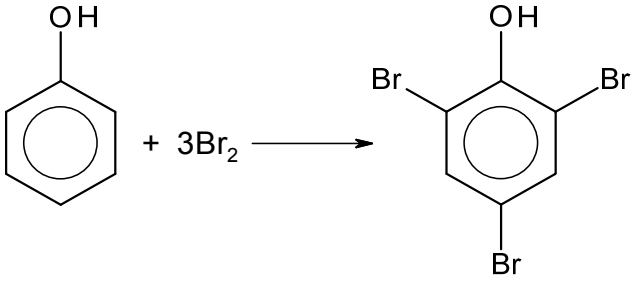
For examiner's use

4 Phenols and compounds containing the phenol functional group have many uses.

(a) One use of phenol is in studying the kinetics of the reaction between bromide and bromate(V) ions in acid solution.

The initial rate of this reaction can be studied by the "clock" method using phenol and methyl orange. The equations for the reactions are as follows:

$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$ reaction **I**



+ 3HBr reaction **II**

Br_2 + methyl orange (acid form) $\rightarrow$ bleached methyl orange + $2Br^-$ reaction **III**

pink colourless

Aqueous Br^- is added to acidified BrO_3^- solution containing a small and constant amount of phenol solution and methyl orange indicator. The Br_2 produced by reaction **I** will immediately react in reaction **II** until all the phenol has been used up. At that point, free Br_2 will be present in the solution and bleach the methyl orange reagent in reaction **III**. This causes the reaction mixture to turn from pink to colourless.

To study the kinetics of reaction **I**, KBr(aq), $KBrO_3$(aq) and H_2SO_4(aq), each with an initial concentration of 0.100 mol dm^{-3}, are reacted with 0.00010 mol dm^{-3} of phenol solution.

(i) Explain briefly why bromination of phenol occurs readily.

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[1]

(ii) It is noticed that the reaction mixture turns a little cloudy as the reaction progresses. Give a reason for the observation of cloudiness in the reaction mixture.

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[1]

For examiner's use

To find the order of reaction with respect to H^+, five experiments are conducted.

In all the experiments, 10 cm^3 of KBr(aq), 10 cm^3 of $KBrO_3$(aq), 5 cm^3 of phenol solution and 2 drops of methyl orange indicator are used, with water added to keep the total volume constant. The volume of H_2SO_4(aq) used and the time taken for the mixture to turn from pink to colourless for the 5 experiments are shown in the table below:

Experiment No.	Volume of H_2SO_4(aq), V / cm^3	V^2 / cm^6	Time taken for colour to change from pink to colourless, t / s	$\frac{1}{t}$ / s^{-1}
1	24.00	576	10.0	0.100
2	20.00	400	14.4	0.069
3	16.00	256	22.5	0.044
4	12.00	144	40.0	0.025
5	8.00	64	90.0	0.011

(iii) State the relationship between

- initial rate and t
- concentration of H^+ and V.

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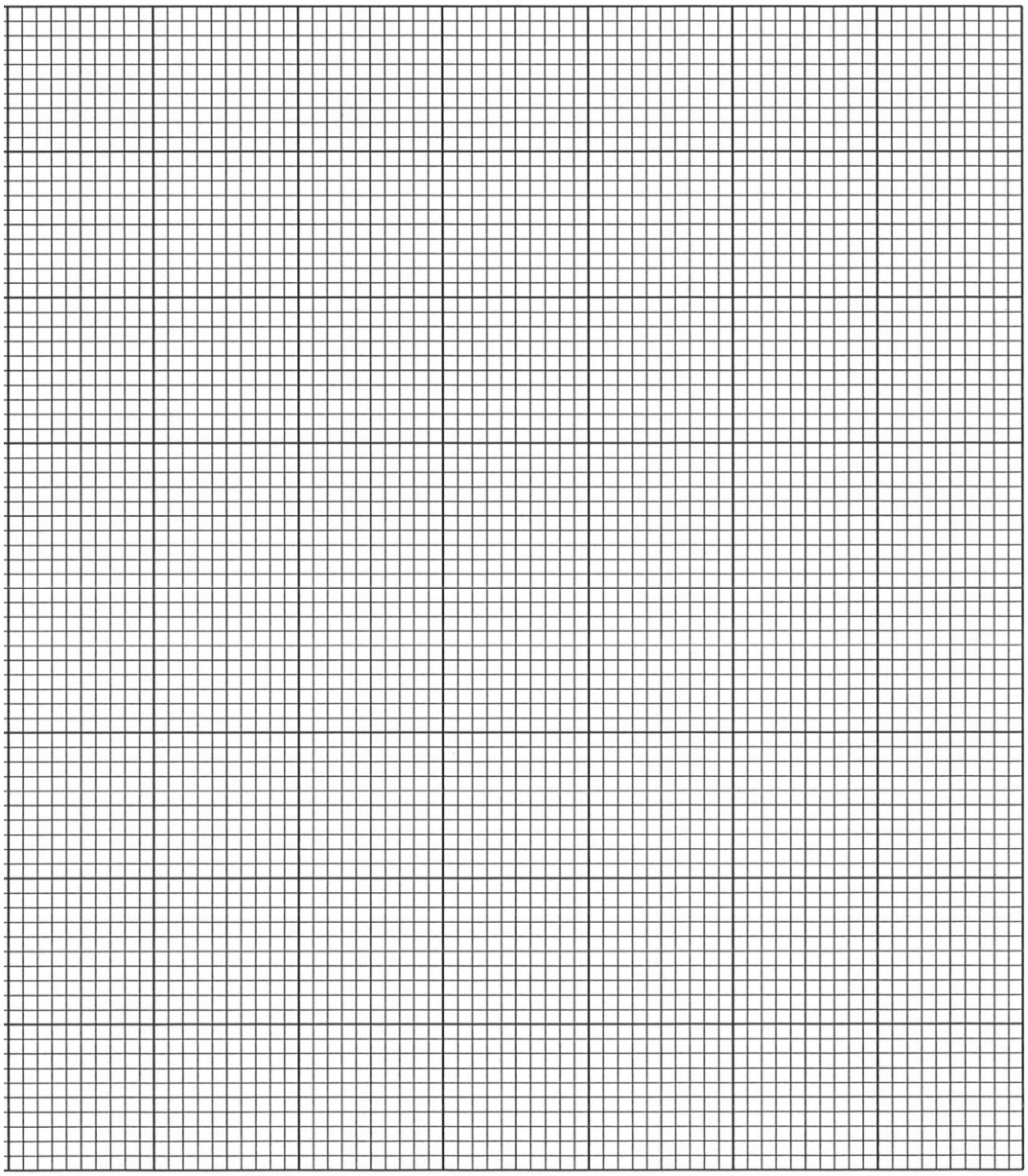
[1]

(iv) To determine the order of reaction with respect to H^+, use the data in the table above to plot a straight line graph on the grid provided on page 15. Label the axes clearly.

For examiner's use



[3]

(v) With reference to the graph, state the order of reaction with respect to H^+. Briefly explain your answer.

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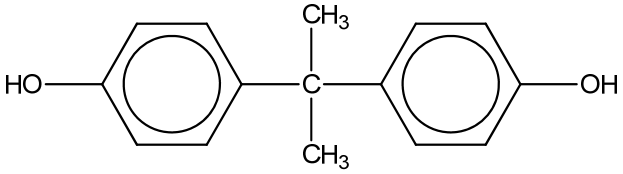
[2]

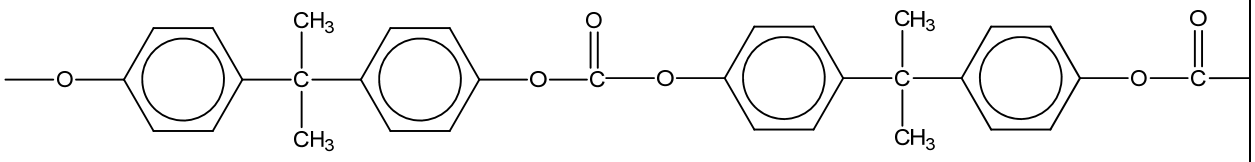
For examiner's use

(b) Bisphenol A, commonly known as BPA, has the structure shown below:



It is one of the two reactants used to make polycarbonate plastic which is a lightweight, high-performance polymer used in making containers, sports safety equipment and medical devices.

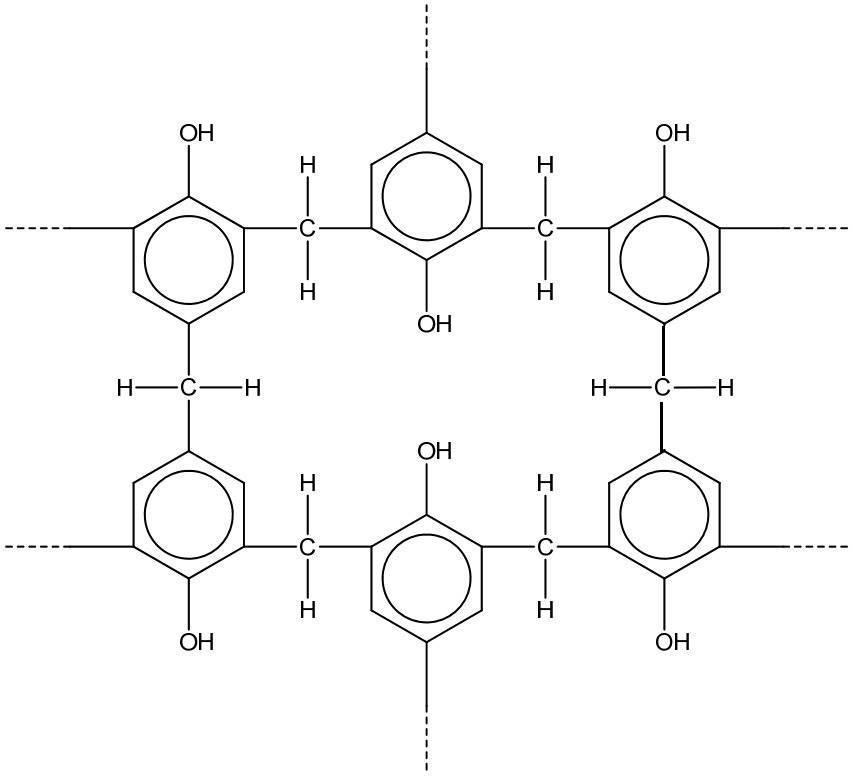
When reacted with compound **E**, BPA undergoes condensation to form polycarbonate plastic. The structure of the polycarbonate, showing two repeat units, is shown below:



(i) Compound **E** contains carbon, oxygen and halogen only. It reacts with aqueous silver nitrate to give a white precipitate. Draw the displayed formula of compound **E**.

[1]

Bakelite, a polymer made from the condensation reaction of phenol and methanal, has the structure shown below:



For examiner's use

(ii) With reference to their structures, explain why Bakelite is more rigid than polycarbonate plastic.

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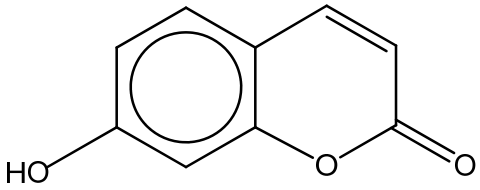
[1]

For examiner's use

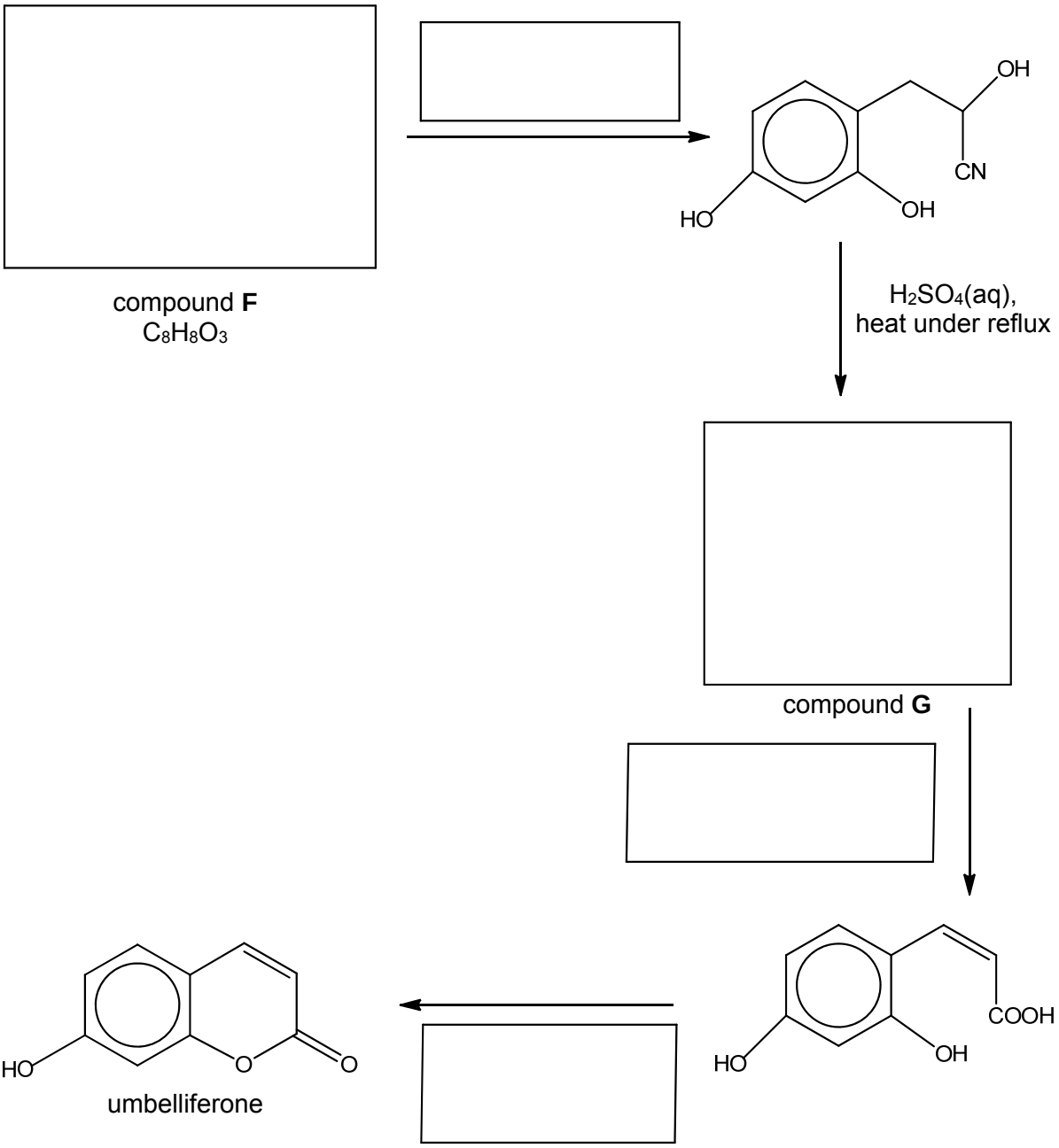
(c) Umbelliferone is a yellowish-white crystalline solid occurring naturally in carrots and is used as a sunscreen agent. It has the structure shown below:



The following reaction scheme shows how umbelliferone may be synthesised from compound **F**, which has a molecular formula of $C_8H_8O_3$.

In the boxes provided, fill in the missing

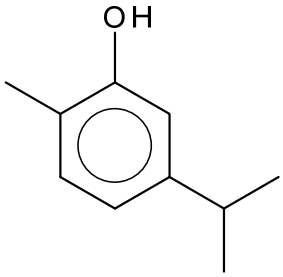
- reagents and conditions,
- structures of compounds **F** and **G**.



[5]

For examiner's use

(d) Thymol is a white crystalline solid with a pleasant odour and provides the distinctive strong flavour of the herb thyme. It has the structure shown below:



thymol

(i) Carvacrol is a *positional* isomer of thymol.

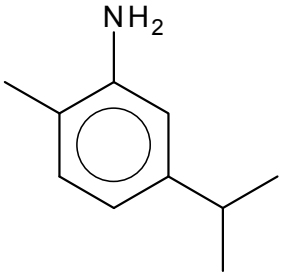
When warmed with acidified aqueous potassium manganate(VII), both thymol and carvacrol gave the same organic product.

Draw the structure of carvacrol.

[1]

For examiner's use

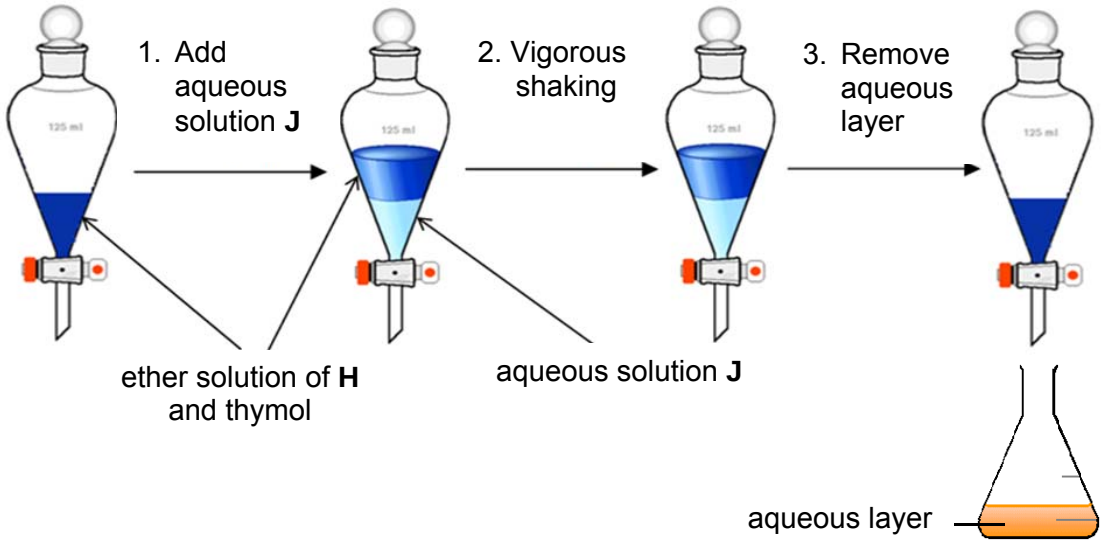
(ii) Compound **H** has the structure shown below:



compound **H**

To separate **H** from a mixture of **H** and thymol, the following method is used.

Using a separatory funnel, an ether solution of **H** and thymol is shaken with an aqueous solution **J**, and the aqueous layer is separated from the organic layer.



If the organic layer contains only compound **H** after separation, suggest a suitable reagent which can be used as aqueous solution **J**. Give a reason for your answer.

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[2]

[Total: 18]

For examiner's use

5 The table below gives data about some physical properties of some Group I and II elements.

property	potassium	calcium	strontium	barium	radium
relative atomic mass	39.1	40.1	87.6	137	–
atomic radius (metallic) / nm	0.227	0.197	0.215	0.217	0.220
ionic radius (2+) / nm	–	0.099	0.113	0.135	0.140
density / g cm^{-3}	0.890	1.55	2.60	3.50	5.50
1st ionisation energy / kJ mol^{-1}	418	590	548	502	509
2nd ionisation energy / kJ mol^{-1}	3070	1150	1060	966	979
solubility of sulfate in water (at 20 °C) / g per 100 cm^3	11.1	0.210	0.0130	0.000240	–

(a) Explain why the atomic radius of barium is larger than that of strontium.

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[2]

(b) Calcium and barium were separately added to cold water. Describe what you would observe and write equations for the reactions that occur.

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[3]

For examiner's use

(c) When added to water, potassium floats on the water surface. Explain whether calcium floats or sinks when it is first added to water.

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[1]

(d) Determination of the relative atomic mass of an element depends on information like the relative isotopic masses of the isotopes and the relative abundance of each of the isotopes. Suggest why no value is quoted for the relative atomic mass of radium in the table.

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[1]

(e) Write the expression for the solubility product, K_{sp}, of $SrSO_4$.

Using data given in the table on page 21, calculate the solubility product of $SrSO_4$ and state its units.

[3]

For examiner's use

(f) The ionic radius of the sulfate ion is much larger than the ionic radii of Group II metal ions. This results in the magnitude of the lattice energy of Group II sulfates to decrease only very slightly down the group.

(i) State and explain the trend of the enthalpy change of hydration of Group II sulfates down the group.

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[1]

(ii) The relationship between lattice energy, the enthalpy change of hydration and the enthalpy change of solution is given as follows:

$$\Delta H_{sol} = \Delta H_{hyd} - LE$$

Deduce the variation of the ΔH_{sol} of Group II sulfates down the group and hence explain the trend of the solubility of Group II sulfates shown in the table on page 21.

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[2]

For examiner's use

(g) Barium forms barium peroxide, BaO_2, on heating in oxygen.

The reaction involves the following energy change:

$O_2(g) + 2e^- \rightarrow O_2^{2-}(g)$ ΔH_1

By using the following data and those given in the table on page 21, construct a Born-Haber cycle for barium peroxide in the grid below and calculate ΔH_1.

enthalpy change of formation of barium peroxide	–630 kJ mol^{-1}
lattice energy of barium peroxide	–3443 kJ mol^{-1}
enthalpy change of atomisation of barium	+176 kJ mol^{-1}

[3]

[Total: 16]

– END OF PAPER –