NAME _____ CLASS **22S**

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2023

CHEMISTRY **9729/03**

Higher 2 **13 September 2023**

Paper 3 Free Response **2 hour**

Candidates answer on the Question paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces at the top of this page.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.
Write the Question number of the Question you have attempted, in the box provided below.

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

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

For Examiner's Use	
1	**20**
2	**22**
3	**18**
4 or 5	**20**
Penalty (delete accordingly)	
Lack **3sf** in final answer	**–1 / NA**
Missing/wrong **units** in final ans	**–1 / NA**
Bond linkages	**–1 / NA**
Total	**80**

This document consists of **32** printed pages.

[Turn Over

Section A

Answer **all** the questions in this section.

For Examiner's Use

1 Carbon monoxide, CO, occurs in the exhaust gases of internal combustion engines. Other gases in the exhaust gases include oxides of nitrogen, NO_x.

(a) CO and NO can be removed from the exhaust gases by a catalytic converter to form CO_2 and N_2. Construct a balanced equation for this reaction. [1]

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(b) Explain why N_2 gas behaves more like an ideal gas than CO gas at 20.0 °C and 101 kPa. [2]

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(c) A mixture of carbon monoxide and hydrogen is known as *synthesis gas*. *Synthesis gas* is used as a feedstock for the manufacture of methanol.

$$CO(g) + 2H_2(g) \ll CH_3OH(g) \qquad \Delta H = -91.0 \text{ kJ mol}^{-1}$$

A temperature of 550 K and pressure of 60 atm are used in this reaction with a catalyst. When the reaction reached equilibrium, a mixture of gases was extracted. It contained 364 g of carbon monoxide, 5 g of hydrogen, and 171 g of methanol.

(i) Calculate the value of K_p for this reaction at 550 K. [3]

(ii) Explain the effect of increasing temperature on the equilibrium yield of methanol. [1]

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For Examiner's Use

For Examiner's Use

(d) Liquid methanol could be used instead of petrol in a conventional internal combustion engine.

(i) Some enthalpy changes are given in Table 1.1.

Table 1.1

	ΔH /kJ mol^{-1}
standard enthalpy change of formation of $CO_2(g)$	−394
standard enthalpy change of formation of $H_2O(l)$	−286
standard enthalpy change of formation of CO(g)	−111
standard enthalpy change of $CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$	−129

Use the enthalpy changes provided in Table 1.1 to construct a fully labelled energy cycle to find the standard enthalpy change of combustion of liquid methanol, ΔH_c ($CH_3OH(l)$). [3]

(ii) Both methanol and *synthesis gas* can be used as fuels.

Suggest one advantage in converting *synthesis gas* to methanol. [1]

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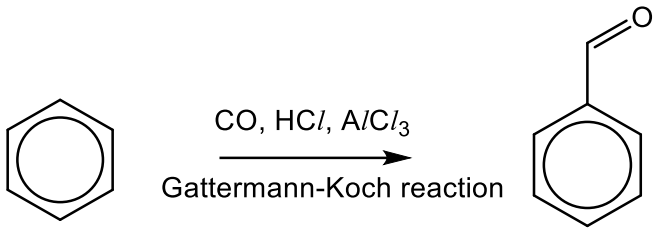
(e) Carbon monoxide reacts with benzene in the presence of hydrogen chloride and aluminium chloride in the Gattermann-Koch reaction to give benzaldehyde.

For Examiner's Use



In this reaction, CO and HC*l* react to form methanoyl chloride, HCOC*l.*

Similar to how A*l*C*l*$_3$ generates the electrophile in the halogenation of benzene, A*l*C*l*$_3$ reacts with HCOC*l*, producing a carbocation that can then attack a benzene ring.

(i) Suggest an equation for the formation of the carbocation that functions as an electrophile for the Gattermann-Koch reaction. [1]

(ii) Suggest the mechanism for the Gattermann-Koch reaction to form benzaldehyde from benzene.

In your answer, include the movement of electron pairs using curly arrows. [2]

(iii) The Gattermann-Koch reaction is a substitution reaction. Explain why benzene undergoes substitution more readily than addition reaction. [1]

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For Examiner's Use

(f) Carbon monoxide and methanol are used in an industrial process to form methyl methacrylate. An alternative route to obtain methyl methacrylate from propanone is proposed in Fig. 1.1.

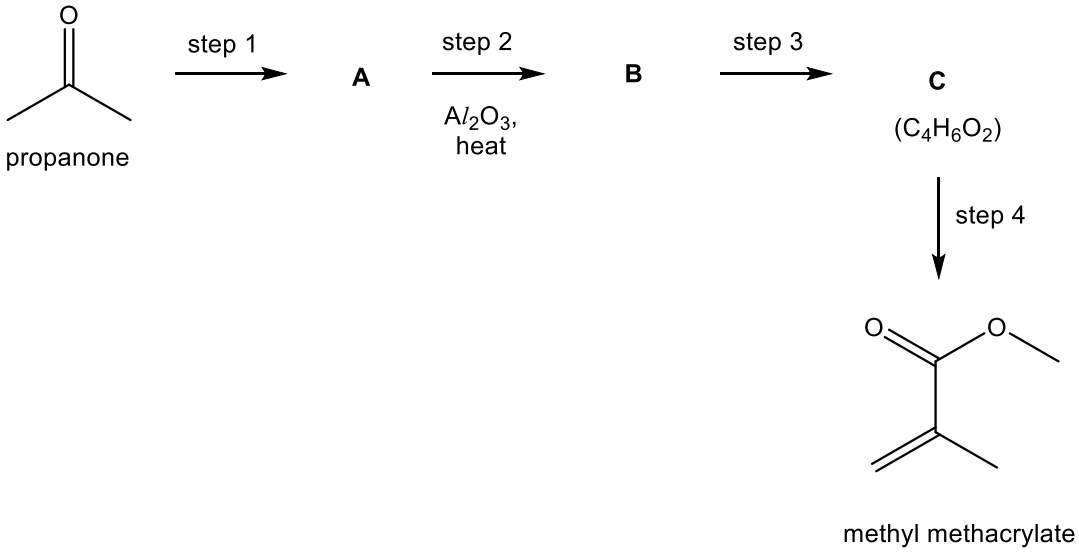

Fig. 1.1

(i) Suggest the structures of compounds **A**, **B** and **C**. [3]

(ii) Suggest reagents and conditions for step 1 and for step 3. [2]

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[Total: 20]

For Examiner's Use

2 This question is about some Group 14 elements and their compounds.

(a) Carbon, silicon and germanium are the first three elements of Group 14. They have the same type of structure. The melting points of these three elements are given below.

element	melting point / K
C	>3823
Si	1683
Ge	1210

In terms of structure and bonding, explain why the melting points of these elements decrease from carbon to germanium. [2]

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(b) Describe how the reactions of the chlorides of silicon and aluminium with water differ. Include the approximate pH value of any resulting solutions and write equations where appropriate. [3]

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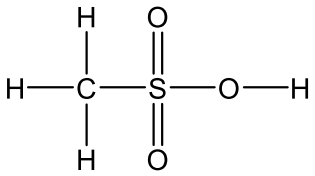
(c) The numerical values of K_a for three acids are given in Table 2.1.

For Examiner's Use

Table 2.1

name of acid	formula of acid	K_a
methanoic acid	HCO_2H	1.78×10^{-4}
ethanoic acid	CH_3CO_2H	1.74×10^{-5}
methanesulfonic acid	CH_3SO_2OH	1.26×10^{-2}

The structure of methanesulfonic acid is given below.



Suggest an explanation for the differences in K_a values of the three acids. [2]

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(d) **(i)** Carboxylic acids form esters which can be hydrolysed by aqueous alkali. The overall equation representing the alkaline hydrolysis of an ester is given below.

$$RCO_2R' + OH^- \rightarrow RCOO^- + R'OH$$

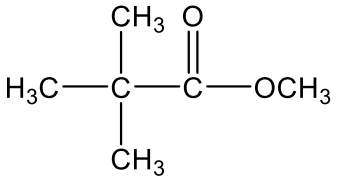
The mechanism of the alkaline hydrolysis of esters takes place in three steps. The first two steps are described below.

- The first step involves the reaction of OH^- with the C=O group of the ester.
- In the second step, RCOOH and $R'O^-$ are formed.

Use the information provided to draw out the mechanism for the first two steps of the alkaline hydrolysis of methyl ethanoate, $CH_3CO_2CH_3$. Show all relevant charges, dipoles, lone pairs and curly arrows. [3]

For Examiner's Use

(ii) Suggest why the rate of alkaline hydrolysis is slower when methyl ethanoate is replaced with the following ester.



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(e) Ester **D** has the molecular formula, $C_8H_{14}O_4$. When **D** is hydrolysed with aqueous alkali, followed by acidification, compounds **E** and **F** are produced.

For Examiner's Use

- **F** gives effervescence when Na_2CO_3(aq) is added but **E** does not.
- **F** gives an orange precipitate with 2,4-dinitrophenyhydrazine but **E** does not.
- **F** does not react with Fehling's solution.
- Prolonged heating of **E** under reflux with acidified $K_2Cr_2O_7$(aq) gives **F**.
- Compounds **D**, **E** and **F** give a yellow precipitate when warmed with alkaline I_2(aq).

Suggest the structures of **D**, **E** and **F** and explain the reactions described. [7]

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For Examiner's Use

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For Examiner's Use

(f) Tin forms an oxide, **G**, which contains Sn^{2+} and Sn^{4+}. A sample of **G** was dissolved in aqueous acid to form solution **H**. Solution **H** was divided into two portions.

- A 25.0 cm^3 sample of one portion of solution **H** was titrated with 0.0200 mol dm^{-3} $KMnO_4$ solution. 18.50 cm^3 of the $KMnO_4$ solution was required for complete reaction.
- Hydrogen gas was bubbled through the other portion of **H** for some time. 25.0 cm^3 sample of the resulting solution was titrated with 0.0200 mol dm^{-3} $KMnO_4$ solution as before and required 27.70 cm^3 of the $KMnO_4$ solution for complete reaction.

The equation for the reaction of Sn^{2+} and MnO_4^- is shown.

$$2MnO_4^- + 16H^+ + 5Sn^{2+} \rightarrow 2Mn^{2+} + 8H_2O + 5Sn^{4+}$$

(i) Use the results of the two titrations to calculate

- the amount of Sn^{2+} in 25.0 cm^3 of solution **H**.
- the amount of Sn^{2+} in 25.0 cm^3 of the solution that was treated with H_2 gas. [2]

(ii) Hence, deduce the ratio of Sn^{4+}: Sn^{2+} in the oxide and suggest the formula of oxide **G**. [2]

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[Total: 22]

For Examiner's Use

3 This question is about some compounds of nitrogen.

(a) Airbags in cars help to protect the driver and passengers during a collision.

A version of airbag contains a mixture of sodium azide, NaN_3, potassium nitrate, KNO_3, and silicon dioxide, SiO_2.

A heavy collision completes an electrical circuit which ignites a pellet of sodium azide. The sodium azide decomposes to sodium metal and nitrogen gas as shown in reaction 1.

Reaction 1 $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$

The sodium metal produced is removed by reaction 2.

Reaction 2 $2KNO_3(s) + 10Na(s) \rightarrow 5Na_2O(s) + K_2O(s) + N_2(g)$

(i) In an ignition, a sample of sodium azide in the airbag described above decomposes, inflating an airbag to a volume of 75 dm^3 at a pressure of 1.50×10^5 Pa and temperature of 35.0 °C.

By considering reactions 1 and 2, calculate the mass of sodium azide in this airbag. [3]

(ii) SiO_2 is added in the airbag to react away K_2O and Na_2O. Using either K_2O or Na_2O, write an equation for the reaction of SiO_2 with your chosen Group 1 oxide. [1]

(iii) Given that the azide ion, N_3^-, contains two double bonds, draw a 'dot-and-cross' diagram to show the bonding in an azide ion. [1]

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For Examiner's Use

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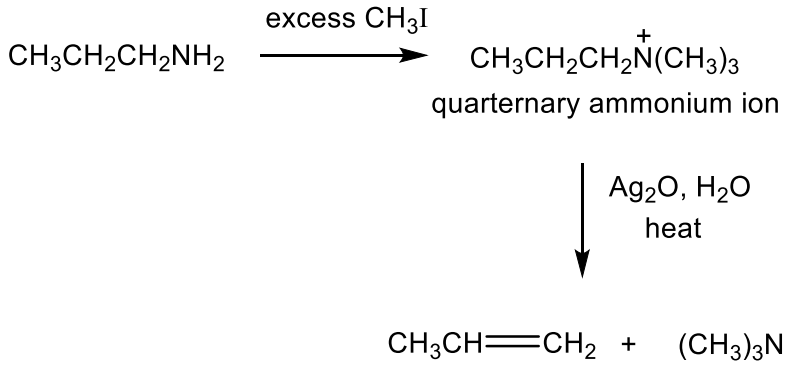
(b) Sodium azide can be used to form organic azides which are useful reagents in the synthesis of amines.

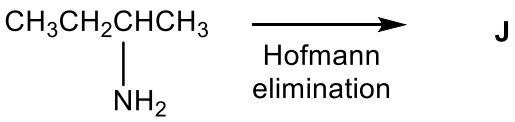
Amines can undergo elimination reaction to give alkenes through the Hofmann elimination. The reaction goes through a quaternary ammonium ion, which on heating with moist Ag_2O, produces the alkene and a tertiary amine.

In Hofmann elimination, the less substituted alkene is formed as the major product over the more substituted alkene.

An example of the two-stage process of the Hofmann elimination is given below.



(i) Using the above information, suggest the structure of compound **J**.



[1]

(ii) Compound **N** can be synthesised in 3 steps as shown in Fig. 3.1. Step 2 involves the Hofmann elimination.

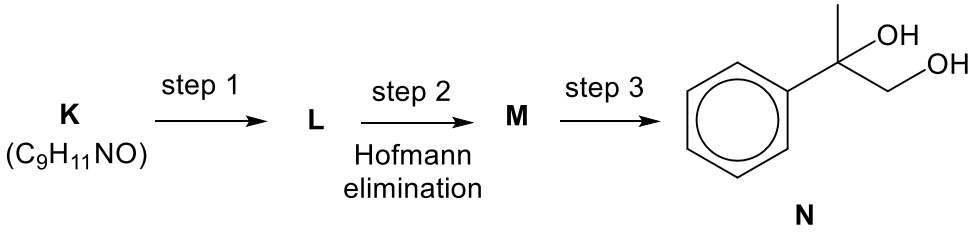


Fig. 3.1

Suggest the reagents and conditions required for steps 1 and 3 and suggest the structures of organic compounds **K**, **L** and **M**. [5]

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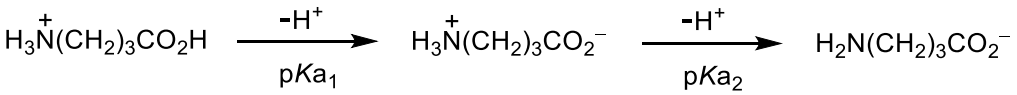
(c) 4-aminobutanoic acid is a neurotransmitter. The fully protonated 4-aminobutanoic acid, $^{+}NH_3(CH_2)_3CO_2H$, has two pK_a values.

For Examiner's Use



pK_{a1}	pK_{a2}
4.8	10.7

(i) Calculate the pH of a 0.10 mol dm^{-3} solution of $^{+}NH_3(CH_2)_3CO_2H$ (ignore the effect of the second dissociation on the pH). [1]

(ii) Sketch a labelled pH-volume added curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} of $^{+}NH_3(CH_2)_3CO_2H$.

In your curve, indicate clearly

- the volume of NaOH(aq) at the equivalence points and
- the pH and volume of NaOH(aq) at the points of maximum buffering capacity. [3]

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For Examiner's Use

(d) Barium amide, $Ba(NH_2)_2$, decomposes when heated to form barium nitride, Ba_3N_2, and ammonia as the only products.

(i) Write an equation for this reaction. [1]

(ii) Given that the variation in the thermal stability of Group 2 amides is similar to that of Group 2 carbonates, suggest whether calcium amide, $Ca(NH_2)_2$, will decompose more or less readily than $Ba(NH_2)_2$. Explain your answer. [2]

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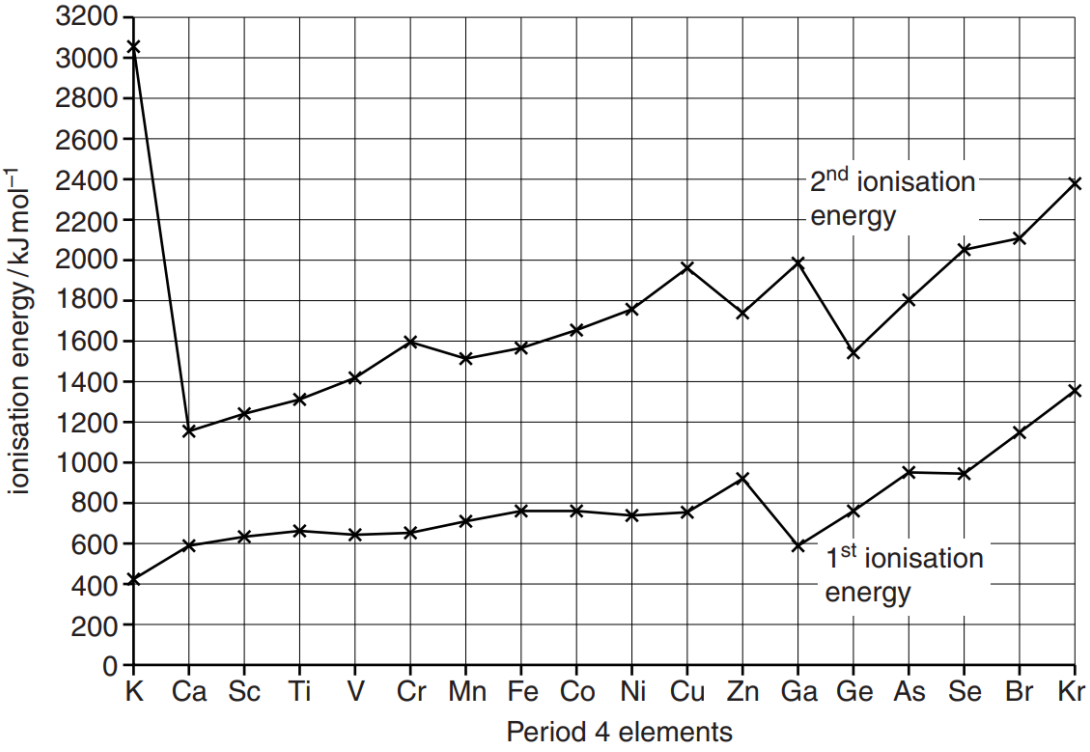
[Total: 18]

Section B

Answer **one** question from this section.

For Examiner's Use

4 **(a)** The patterns of the first and second ionisation energies across Period 4 are shown.



(i) Explain what is meant by the term *first ionisation energy*. [1]

(ii) Explain why the first ionisation energies of the elements Sc to Cu are relatively invariant. [1]

(iii) Explain why the increase between the first and second ionisation energies for both Cr and Cu is bigger than that for the rest of the transition elements shown. [2]

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For Examiner's Use

(b) When air is bubbled through an aqueous solution containing $CoCl_2$, NH_4Cl and NH_3, and the resulting solution evaporated, crystals of a salt **X** can be isolated. **X**, which contains an octahedral ion, has the following composition by mass:

Co, 25.2 %; N, 24.1 %; H, 5.1 %; C*l*, 45.6 %.

On adding an excess of $AgNO_3$(aq) to an aqueous solution containing 0.01 mol of **X**, 0.01 mol of AgC*l*(s) is precipitated.

(i) Calculate the empirical formula of **X**.

Identify the complex cation of **X** and suggest the oxidation number of the cobalt atom in **X**. [3]

(ii) The complex cation of **X** exists in two stereoisomeric forms. One has an overall dipole moment while the other does not.

Suggest the type of isomerism that is possible in the complex cation of **X**.

Draw relevant diagrams to illustrate the isomerism. [2]

For Examiner's Use

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(c) Chloroquine is a common drug administered to patients suffering from malaria. A proposed synthesis route for chloroquine is shown in Fig. 4.1 below.

For Examiner's Use

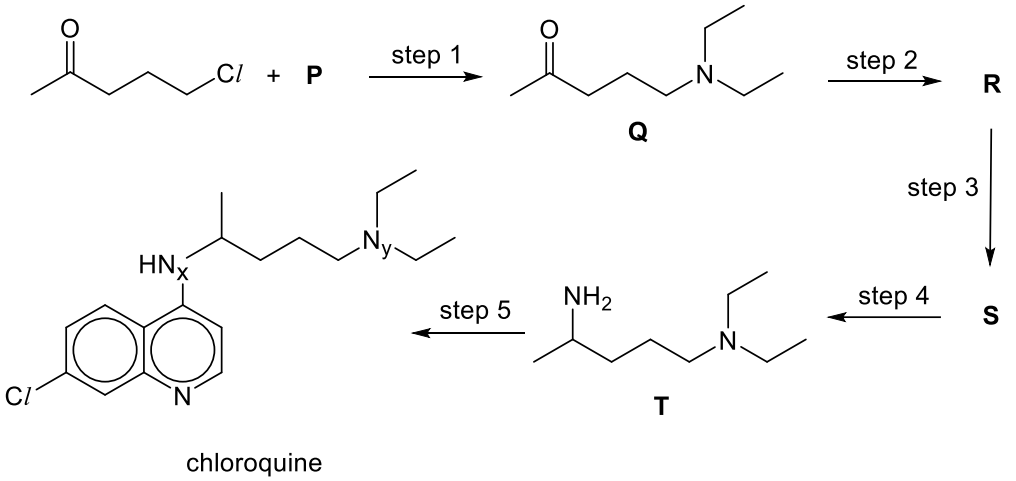

Fig. 4.1

(i) Draw the structure of **P**. [1]

(ii) Name the type of reaction for step 1. [1]

(iii) Suggest reagents and conditions for steps 2, 3 and 4, and draw the structures of compounds **R** and **S**. [5]

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For Examiner's Use

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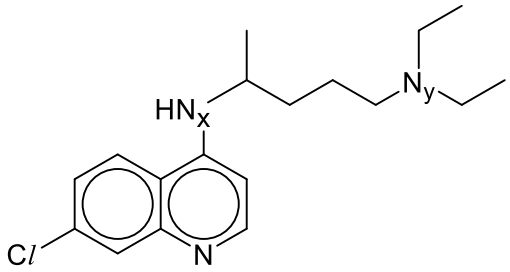
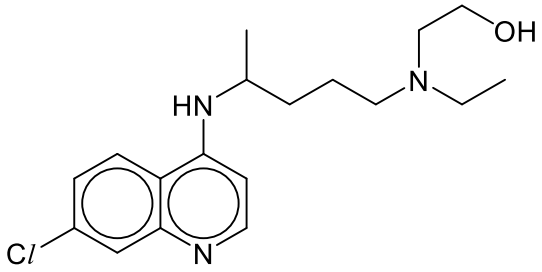
(d) **(i)** Suggest reasons to explain how the basicity of the nitrogen functional group labelled N_x would compare to that labelled N_y in chloroquine.

For Examiner's Use



chloroquine [2]

(ii) Describe a simple chemical test to distinguish between chloroquine and hydroxychloroquine, giving observations for each compound.



hydroxychloroquine [2]

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For Examiner's Use

5 Copper and iron are versatile transition metals that form a wide array of complexes due to their ability to exhibit multiple oxidation states. These complexes showcase diverse chemical and biological roles, ranging from catalysis to electron transfer processes.

(a) **(i)** Write the electronic configuration of Cu atom. [1]

(ii) Explain why the radius of Cu^{+} ion is larger than Cu^{2+}. [1]

(iii) Explain why complexes of Cu(II) are coloured, whereas complexes of Cu(I) are colourless. [3]

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For Examiner's Use

(b) Cu(I) is stable in insoluble salts and in some complexes.

The addition of KI(aq) to $CuSO_4$(aq) produces a white precipitate of CuI and a brown solution of iodine.

The solution turns colourless and the white precipitate dissolves when excess aqueous sodium thiosulfate is added.

(i) Using relevant *E* values from the *Data Booklet*, explain the observations when KI(aq) is added to $CuSO_4$(aq). [2]

(ii) Suggest why the white precipitate dissolves when excess aqueous sodium thiosulfate is added. [1]

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(c) The stability constant, K_{stab}, of a complex is the equilibrium constant for the formation of the complex ion in a solvent.

For Examiner's Use

Copper forms complex ions in aqueous solution, such as $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and $[Cu(en)(H_2O)_4]^{2+}$, where en is the bidentate ligand, ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$.

$[Cu(H_2O)_6]^{2+} + 4NH_3 \ll [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$ equilibrium 1

$[Cu(H_2O)_6]^{2+} + en \ll [Cu(en)(H_2O)_4]^{2+} + 2H_2O$ equilibrium 2

Table 5.1 lists the values of stability constants for these two complexes.

Table 5.1

	colour	stability constant, K_{stab}
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	dark blue	1.74×10^2
$[Cu(en)(H_2O)_4]^{2+}$	purple	3.98×10^{10}

(i) With reference to the value of K_{stab} in equilibrium 1 and the difference in ligand strength, explain why $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is formed when excess $NH_3(aq)$ is added to $Cu^{2+}(aq)$. [2]

(ii) Using the information in Table 5.1, predict and explain what will be observed when en is added to a solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$. [2]

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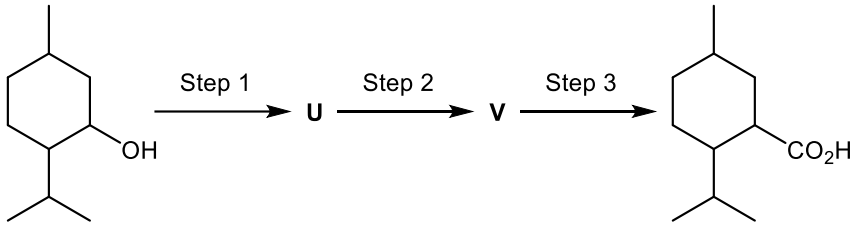
For Examiner's Use

(d) Menthol is one of the constituents of peppermint oil. It can undergo a series of reactions to form compound **W**.



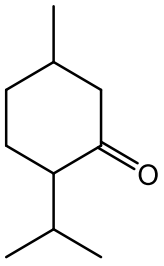
menthol **W**

(i) Suggest reagents and conditions for steps 1 and 2, and draw the structures of compounds **U** and **V**. [4]

(ii) Menthone is another constituent of peppermint oil.

Describe a simple chemical test that would give an observable change for menthone but not for menthol.

State clearly all the observations you would expect to see.



menthone [2]

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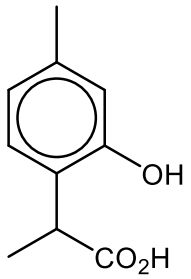
For Examiner's Use

(e) When compound **Y** is reacted with an excess of $NaHCO_3$(aq), compound **Z** is formed which has the molecular formula $NaC_{10}H_{11}O_3$.



Compound **Y**

(i) Suggest the structure of compound **Z**. [1]

(ii) Explain why compound **Z** contains only 1 Na atom/ion although $NaHCO_3$ is in excess. [1]

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Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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