JURONG JUNIOR COLLEGE
2013 JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
CLASS		EXAM INDEX NUMBER	

CHEMISTRY

9647/02

Paper 2 Structured Questions

30 August 2013
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
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.

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	
2	
3	
4	
5	
6	
7	
Total	

This document consists of **18** printed pages and **2** blank pages.

For Examiner's Use

1 Planning (P)

Solubility of a substance is the ***maximum mass*** of the substance dissolved in a ***given volume*** of a particular solvent to give a ***saturated*** solution at a specified temperature.

The units of solubility is grams per hundred grams of water (*i.e.* g /100 g water).

When solid potassium nitrate is dissolved in water, the temperature of solution decreases.

$$KNO_3(s) = K^+(aq) + NO_3^-(aq)$$

To investigate how the solubility of potassium nitrate varies with temperature, a student demonstrated the experiment, at 30 °C, as follows.

The solid was added into 50 cm^3 of water in a small beaker until a saturated solution at 30 °C is obtained. The mixture was filtered and the filtrate was collected in a crucible.

The filtrate in the crucible was heated to evaporate off the water and the mass of potassium nitrate dissolved in 50 cm^3 of water was determined.

(a) Predict, in the form of a sketch graph, how the solubility of potassium nitrate changes if the solution temperature is increased. Explain your answer.

Explanation:

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…… [2]

(b) State and explain one limitation for heating the solid to dryness.

……

…… [1]

For Examiner's Use

1 (c) Consider the brief description of the experiment given on **Page 2**.

The prediction in **(a)** can be determined by performing a number of experiments.

Write a plan for such a series of experiments. In your plan, you should use the same volume of water to dissolve the solid as described on **Page 2**.

Your plan should also ensure that the temperature of each solution is between 30 °C and 70 °C.

You may assume that you are provided with the following:

- a bottle of pure anhydrous solid potassium nitrate,
- thermometer covering the temperature range of 0 °C to 100 °C,
- thermostat to maintain the temperature of water–bath,
- crucible,
- deionised water and
- apparatus normally found in a school or college laboratory.

Your plan should include the following:

- the choice of number of experiments to conduct to ensure a wide range of results suitable for analysis;
- the choice of temperature for each experiment;
- all essential experimental details including the apparatus used and measurements recorded.

Experimental procedure:

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For Examiner's Use

1 (c) ....

[7]

For Examiner's Use

1 (d) The following data was collected for the experiment conducted at 30 °C.

mass of crucible /g	***x***
mass of crucible with solid residue /g	***y***

Outline how you would calculate the solubility of potassium nitrate, at 30 °C, given that the density of water is 1 g cm^{-3}.

[1]

(e) State one safety precaution which must be taken in this experiment.

……..……

……..…… [1]

[Total: 12]

For Examiner's Use

2 The equation for the reaction of iodine with propanone in the presence of H^+ is shown below.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + HI$$

The following experiment is carried out as part of an investigation into the mechanism of the iodination of propanone which is catalysed by H^+.

Experimental procedure:

1. 50 cm^3 of iodine solution was added to 25 cm^3 of sulfuric acid in a conical flask.
2. 25 cm^3 of propanone solution was added to the mixture and a timer started.
3. A 10 cm^3 of sample was drawn out from the conical flask after one minute and added immediately to 20 cm^3 of sodium hydrogen carbonate solution in a conical flask.
4. The resulting mixture from step 3 was then titrated with a standard solution of sodium thiosulfate, $Na_2S_2O_3$.
5. Steps 3 to 4 were repeated for subsequent 10 cm^3 samples withdrawn at three minute intervals.

(a) **(i)** Explain why each sample was added to sodium hydrogen carbonate solution in step 3.

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(ii) Write an ionic equation for the reaction occurring in step 4 of the experimental procedure.

……

(iii) To determine the order of reaction with respect to iodine, propanone is used in large excess. Explain why it is not necessary to use sulfuric acid in large excess.

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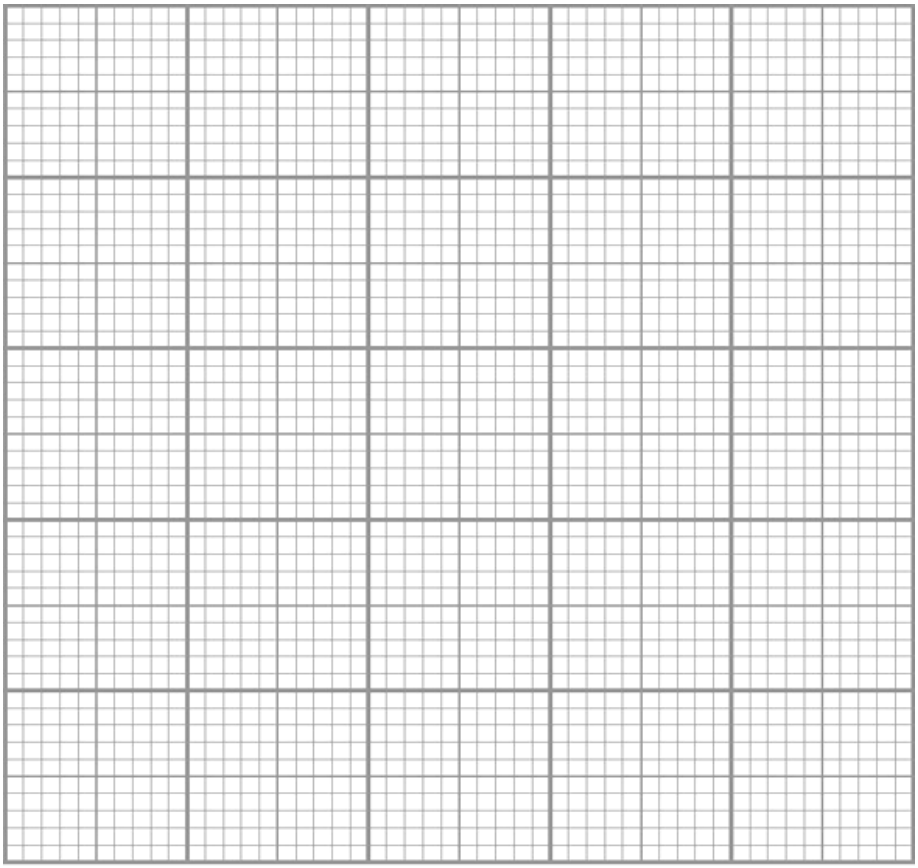
…… [3]

For Examiner's Use

2 (b) The following results were obtained in the experiment.

Time/ min	Volume of sodium thiosulfate solution used / cm^3
1	19.0
4	16.0
7	13.0
10	10.0
13	7.0
16	4.0
19	1.0

(i) Plot a graph of the volume of sodium thiosulfate solution used against time.



(ii) Use your graph to deduce the order of reaction with respect to [iodine].

Order with respect to [iodine] = ……..

(iii) In another experiment, when the concentration of propanone was doubled, the gradient of the graph also doubled. Deduce the order with respect to [propanone] in the rate equation.

Order with respect to [propanone] = ……..

(iv) Given that the overall order of reaction between iodine and propanone is two, deduce the rate equation for this reaction.

……..... [4]

For Examiner's Use

2 (c) $CH_3COCH_3 + I_2 \longrightarrow CH_3COCH_2I + HI$

The reaction between iodine and propanone has the following mechanism and energy profile diagram.

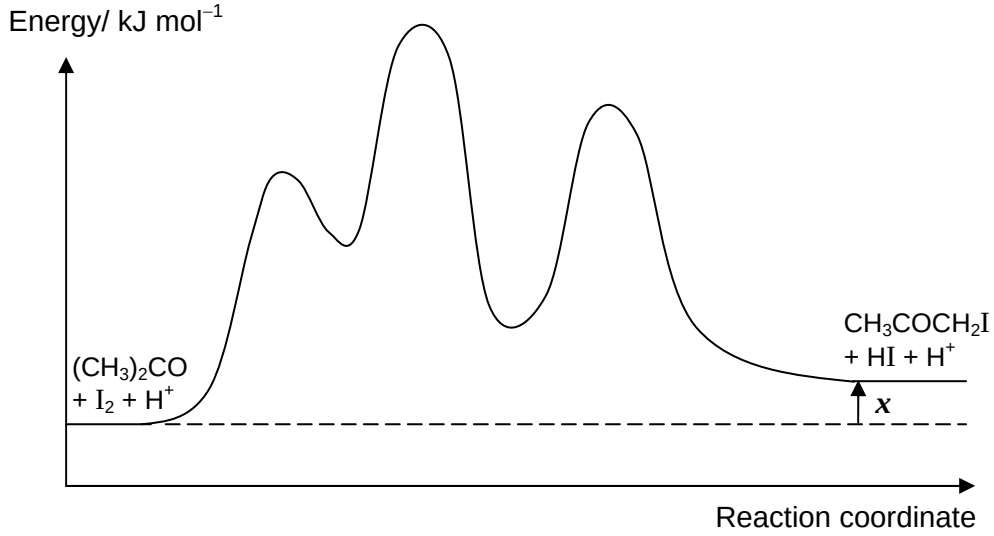
Mechanism:

Step 1: $H_3C-\overset{\overset{O}{\|}}{C}-CH_3 + H^+ \longrightarrow H_3C-\overset{\overset{+O-H}{\|}}{C}-CH_3$

Step 2: $H_3C-\overset{\overset{+O-H}{\|}}{C}-CH_3 \longrightarrow H_3C-\overset{\overset{OH}{|}}{C}=CH_2 + H^+$

Step 3: $H_3C-\overset{\overset{OH}{|}}{C}=CH_2 + I_2 \longrightarrow H_3C-\overset{\overset{O}{\|}}{C}-CH_2I + HI$

Energy profile diagram:



(i) Using appropriate data from the *Data Booklet*, calculate a value for ***x*** in the energy profile diagram.

(ii) The value of ***x*** calculated in **(c)(i)** shows a deviation from its theoretical value. Suggest a reason for the discrepancy between these two values.

……

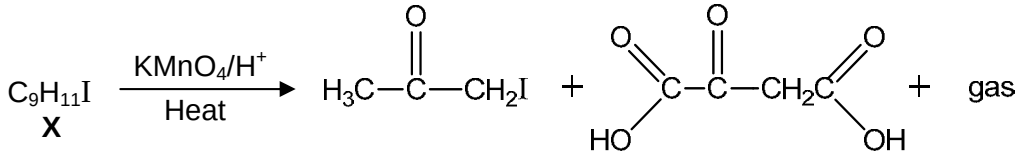
……

(iii) Using your answer in **(b)(iv)** and the proposed mechanism in **(c)**, label the activation energy clearly on the energy profile diagram above. [4]

For Examiner's Use

2 (d) Iodopropanone, CH_3COCH_2I, can also be produced from a 6-membered cyclic compound **X** with the molecular formula $C_9H_{11}I$.

When compound **X** is heated with acidified potassium manganate(VII), iodopropanone, oxaloacetic acid and a gas which forms white precipitate in limewater is produced.



iodopropanone oxaloacetic acid

(i) In the above reaction, 1 mole of compound **X** produces 50 dm^3 of gas at 27 °C and 1 atm. Calculate the number of moles of gas produced.
Give your answer to the **nearest whole number**. [1 atm = 101 kPa]

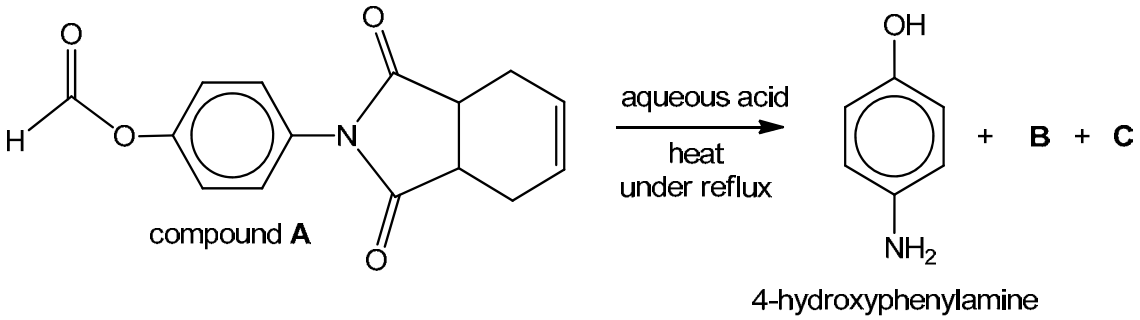
(ii) Deduce the structural formula of compound **X**.

[3]

[Total: 14]

For Examiner's Use

3 When compound **A** is heated under reflux with aqueous acid, 4-hydroxyphenylamine together with cyclic compound **B** and non-cyclic compound **C** are formed.



(a) Draw the structural formulae of compounds **B** and **C** in the boxes provided below. [2]

Cyclic compound **B**	Non-cyclic compound **C**

(b) When cyclic compound **B** is heated with hydrogen and nickel, compound **D** is formed. Suggest the structural formula of compound **D**.

Structural formula of **D**:

[1]

(c) When non-cyclic compound **C** reacts with $LiAlH_4$ in dry ether, compound **E** is formed. Suggest the structural formula of compound **E**.

Structural formula of **E**:

[1]

For Examiner's Use

3 (d) When 1:2 ratio of compound **D** and **E** are heated with a trace amount of concentrated sulfuric acid, compound **F** is formed.

Draw the displayed formula of compound **F**.

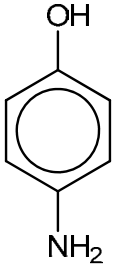
[1]

(e) 4-hydroxyphenylamine can react with ethanoic acid at room temperature to produce compound **G** ($C_8H_{11}O_3N$). Suggest a structure for compound **G**, and state the type of reaction undergone.

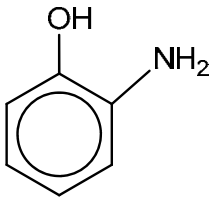
Structure of **G**:

Type of reaction: …… [2]

(f) 4-hydroxyphenylamine and 2-hydroxyphenylamine have the same molecular formula but different melting points.



4-hydroxyphenylamine
(melting point = 190°C)



2-hydroxyphenylamine
(melting point = 174°C)

Explain the difference in melting points between these two compounds.

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…… [2]

[Total: 9]

For Examiner's Use

4 **(a)** An alkene **K**, C_6H_{12}, exhibits geometric isomerism. **K** is reacted with chlorine in the presence of ultraviolet light to form only three structural isomers of $C_6H_{11}Cl$ in the ratio 1 : 2 : 3.

(i) Give the structural formula of **K**.

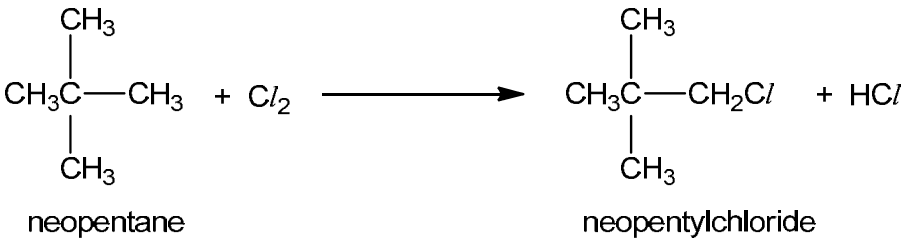
(ii) Give the structures of the three monochlorinated alkenes isomers that are formed in this reaction.

Isomers

[3]

(b) Alkanes can react with chlorine under suitable condition to form different monochlorinated products. The equations below show the reaction of pentane and neopentane with chlorine under such condition.

$$\underset{\text{pentane}}{CH_3(CH_2)_3CH_3} + Cl_2 \longrightarrow \underset{\text{1-chloropentane}}{CH_3(CH_2)_3CH_2Cl} + HCl$$



neopentane neopentylchloride

Explain why neopentane will give a better yield of monochlorinated product as compared to pentane.

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…… [1]

[Total: 4]

For Examiner's Use

5 Elements **X**, **Y** and **Z** are three elements found in the range of proton numbers from 9 to 17. Information of these three elements and their compounds is given below.

(a) Elements **X** and **Y** exist as diatomic molecules which form silver-containing compounds with the formula Ag**X** and Ag**Y**.

X reacts with **Y** to form $\mathbf{XY_3}$. Draw the shape of $\mathbf{XY_3}$ using **X** and **Y** to represent the two elements in your diagram.

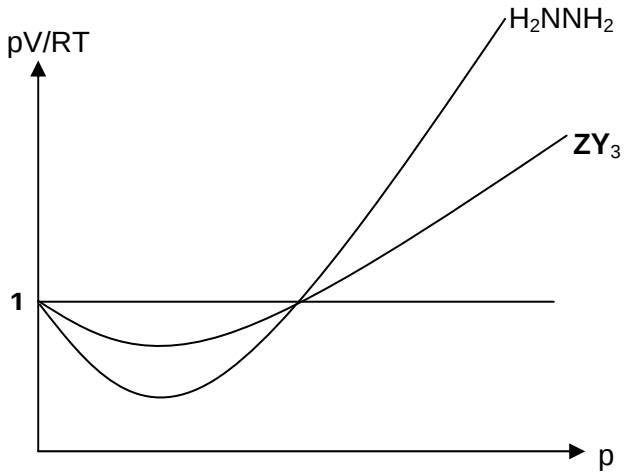
[1]

(b) $\mathbf{ZY_3}$ is a molecule with a trigonal pyramidal shape.

Identify elements **X**, **Y** and **Z**.

Element **X**: ……. Element **Y**: ……. Element **Z**: ……. [3]

(c) **(i)** The plots of pV/RT against pressure, p, for $\mathbf{ZY_3}$ and H_2NNH_2 at 500 K are shown below.



Explain the difference in the two graphs based on the kinetic theory of gases.

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(ii) Sketch on the same axes in **(c)(i)**, a graph that represents H_2NNH_2 at 800 K. [3]

[Total: 7]

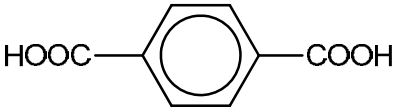
For Examiner's Use

6 Diacids can ionise successively in water according to the following equations.

$$HOOC{-}R{-}COOH \rightleftharpoons HOOC{-}R{-}COO^- + H^+ \qquad pK_{a1}$$

$$HOOC{-}R{-}COO^- \rightleftharpoons {}^-OOC{-}R{-}COO^- + H^+ \qquad pK_{a2}$$

The pK_a values of suberic acid and terephthalic acid are shown in the table below.

Compound	pK_{a1}	pK_{a2}
$HOOC{-}(CH_2)_6{-}COOH$ **suberic acid**	4.5	5.5
 **terephthalic acid**	3.5	4.8

(a) (i) Explain why the pK_{a2} value for both acids are higher than their pK_{a1} value.

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(ii) Suggest why the pK_{a1} value of terephthalic acid is lower than the pK_{a1} value of suberic acid.

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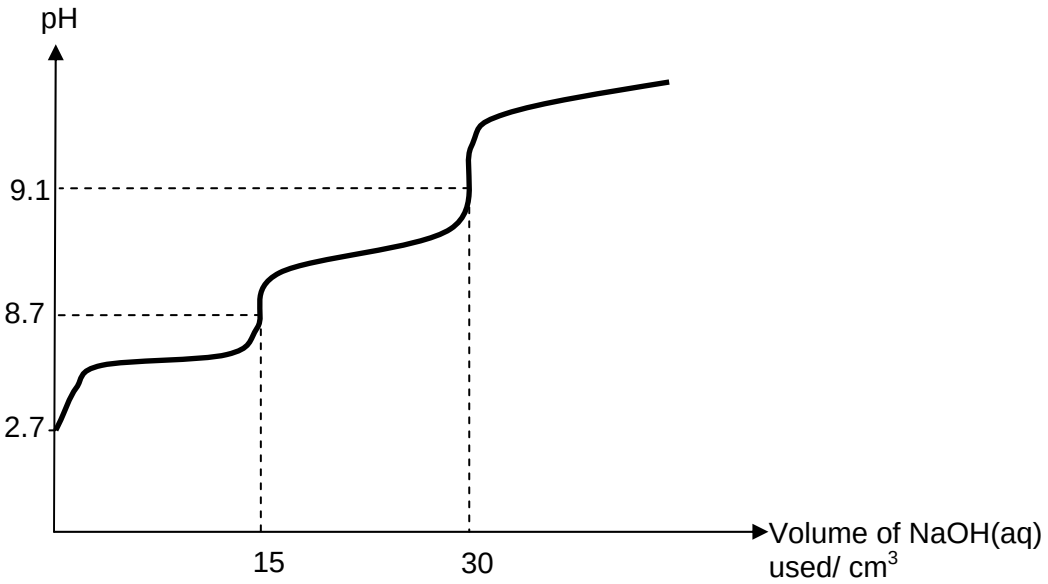
..... [2]

For Examiner's Use

6 (b) A bottle of acid, containing **either** terephthalic acid or suberic acid, has its label torn off. A student titrated 25 cm^3 of the acid with 0.200 mol dm^{-3} of NaOH(aq) and the following titration curve was observed.



(i) State the volume of NaOH(aq) required to form a $HOOC–R–COO^-$/ $^-OOC–R–COO^-$ buffer with maximum buffering capacity.

Volume of NaOH(aq) = ……. cm^3

(ii) Using the graph above, calculate the concentration of the acid in the bottle.

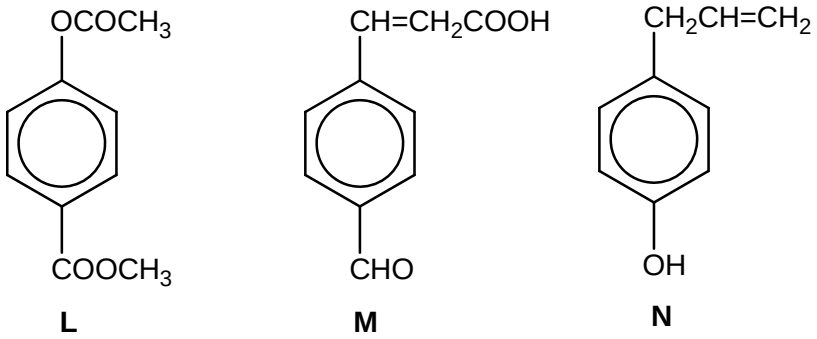
(iii) Using information from the graph and your answer in **(b)(ii)**, calculate the K_{a1} value of the unknown acid.

(iv) Hence, identify the unknown acid.

Identity of unknown acid = …… [5]

For Examiner's Use

6 (c) Terephthalic acid, HOOC–C$_6$H$_4$–COOH, can be formed in a one step reaction from one of the following compounds.



L **M** **N**

(i) State which of the compounds **L**, **M** or **N** can be used to synthesise terephthalic acid. Suggest the reagent and conditions required in this one step reaction.

Compound: ……

Reagent and conditions: ……

(ii) Answer this part of the question by using only the letters **L**, **M** or **N**. In each case, state which compounds will give the result described. You may use the letters more than once.

(A) Which compounds do not react with 2,4-dinitrophenylhydrazine?

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(B) Which compounds do not react with Fehling's solution?

……

(C) Which compounds react with cold aqueous potassium hydroxide?

……

(iii) Compound **N** can undergo an addition reaction with HBr. Describe the mechanism of the reaction between compound **N** and HBr to form the major product.

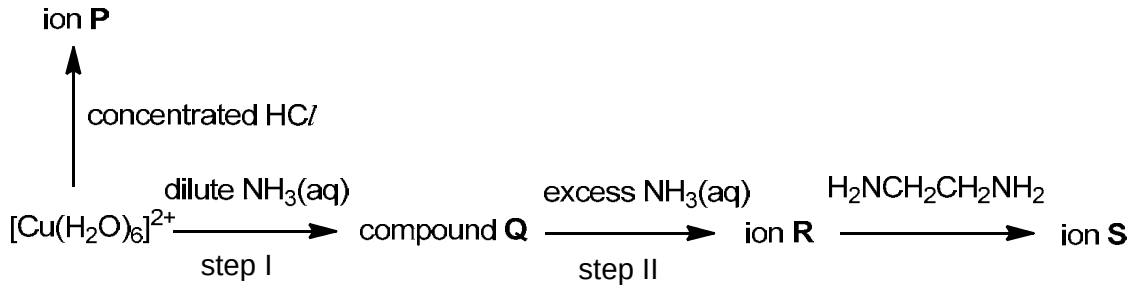
(You may use R to represent HO–C$_6$H$_4$–.)

[7]

[Total: 14]

For Examiner's Use

7 This question is about some reactions of copper compounds



(a) Complete the electronic configuration in s, p, d, f notation for Cu atom, where [Ar]: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Cu: [Ar] …… [1]

(b) **(i)** Identify ion **P**.

Ion **P**: ……

(ii) Copper forms an octahedral complex with fluorine with the formula CuF_6^{4-}. Suggest why ion **P** is formed instead of $CuCl_6^{4-}$.

Explanation:

……

……

…… [2]

(c) Describe the observations in step I and II and write balanced equations for the two reactions.

Observations in step I: ……

Equation: ……

Observations in step II: ……

Equation: …… [3]

For Examiner's Use

7 (d) Ethylenediamine, $H_2NCH_2CH_2NH_2$, (abbreviated as **en**) is a bidentate ligand. When a dilute aqueous solution containing ethylenediamine is added to ion **R**, a purple solution of ion **S** is formed. The following shows the stability constant, K_{stab}, for the formation of three possible copper complexes with the **en** ligand from $[Cu(H_2O)_6]^{2+}$.

$$[Cu(H_2O)_6]^{2+} + \mathbf{en} = [Cu(H_2O)_4(\mathbf{en})]^{2+} + 2H_2O \quad K_{stab1} = 3.55 \times 10^{10}$$

$$[Cu(H_2O)_6]^{2+} + 2\mathbf{en} = [Cu(H_2O)_2(\mathbf{en})_2]^{2+} + 4H_2O \quad K_{stab2} = 3.98 \times 10^{19}$$

$$[Cu(H_2O)_6]^{2+} + 3\mathbf{en} = [Cu(\mathbf{en})_3]^{2+} + 6H_2O \quad K_{stab3} = 3.98 \times 10^{18}$$

(i) From the K_{stab} values shown above, what is the likely formula of ion **S**?

Ion **S**: ……

(ii) Draw a diagram to illustrate the structure of ion **S**.

You should show the following clearly in your diagram.

- how the ligands are bonded to the copper ion.
- the shape around copper in the ion.

(iii) Explain why H_2NNH_2 cannot act as a bidentate ligand.

……

…… [4]

(e) Water, ammonia and ethylenediamine are common ligands used in transition metal chemistry. From the reactions given in the scheme on **Page 18**, arrange these three ligands in order of increasing ligand strength. Explain your answer.

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…… [2]

[Total: 12]