EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2019
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME							
CIVICS GROUP	1	8	–			INDEX NUMBER	

CHEMISTRY

9729/04

Paper 4 Practical

03 September 2019

2 hours 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidental Instructions

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on the work you hand in.
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 19 and 20.

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.

Shift
Laboratory

For Examiner's Use	
1	/ 18
2	/ 4
3	/ 19
4	/ 14
Total	/ 55

This document consists of **18** printed pages.

Answer **all** the questions in the spaces provided.

For Examiner's Use

1 Determination of the percentage by mass of water of crystallisation in $CuSO_4 \cdot nH_2O$

Copper forms compounds containing Cu^{2+} or Cu^{+} ions. Those compounds containing Cu^{2+} ions tend to be relatively stable.

The addition of an excess of potassium iodide, KI, to a solution of Cu^{2+} ions produces iodine, I_2, and a stable precipitate of CuI. To determine the concentration of Cu^{2+} via iodometric titration, it is necessary that all the Cu^{2+} ions are reduced to Cu^{+} ions. A brown suspension will be produced, which is an off-white precipitate of CuI in a yellow-brown solution of I_2.

equation 1 $\quad 2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$

I_2 has a relatively low solubility in water. However, the presence of an excess of I^{-} ions in the reaction mixture allows the soluble tri-iodide ion, I_3^{-}, to form as shown by equation 2. This ensures that the I_2 formed as shown in equation 1 is fully dissolved.

equation 2 $\quad I_2 + I^{-} \rightarrow I_3^{-}$

The I_3^{-} ions formed may be titrated against a standard solution of $Na_2S_2O_3$ as shown in equation 3.

equation 3 $\quad I_3^{-} + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 3I^{-}$

The solution should be titrated immediately after addition of KI because the I_2 may be adsorbed onto the CuI precipitate, rendering the end-point less sharp.

FA 1 is solid hydrated copper(II) sulfate, $CuSO_4 \cdot nH_2O$, where *n* is an integer.

You are also provided with

FA 2, 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$,
FA 3, 1.00 mol dm^{-3} potassium iodide, KI,
10% potassium thiocyanate, KSCN,
1% starch solution.

The presence of thiocyanate ion, SCN^{-}, in the titration mixture near to the end-point will affect the accuracy of the results. The procedure described is designed to improve on the accuracy.

In this experiment, you will determine the percentage by mass of water of crystallisation in $CuSO_4 \cdot nH_2O$. You will titrate a solution of **FA 1** against **FA 2**.

For Examiner's Use

(a) Preparing a solution of FA 1

1. Weigh accurately about 5.00 g of **FA 1** in a pre-weighed weighing bottle.

2. Transfer the solid into a 250 cm^3 beaker and reweigh the weighing bottle. Dissolve this solid in about 70 cm^3 of deionised water.

3. Transfer the solution to the graduated flask, labelled **FA 1 solution**. Rinse the beaker with deionised water several times, adding each rinsing to the graduated flask.

4. Make up the solution to 250 cm^3 with deionised water and mix thoroughly. This solution will be used in both **Question 1(b)** and **2(a)**.

Results

Mass of weighing bottle and **FA 1** / g	9.599
Mass of empty weighing bottle / g	4.596
Mass of emptied weighing bottle / g	4.599
Mass of **FA 1** used / g	5.000

Comments:
- This part was well done in general. This part was well done in general.
- A number omitted to include the mass of empty weighing bottle, as required by the question. Many also did not differentiate between the 'empty' and 'emptied' bottle in their table. It should be noted that there should not be two same headers within a table.
- A small number of students incorrectly referenced mass as "weight".

(b) Titration of solution of FA 1 against FA 2

(i) 1. Fill the burette with **FA 2**.

2. Use a pipette to transfer 25.0 cm^3 of **FA 1** solution into a 250 cm^3 conical flask.

3. Use a measuring cylinder to add about 15 cm^3 of **FA 3** into this flask.

4. Run **FA 2** from the burette into this flask. Near the end-point, when the brown solution becomes pale, add about 1 cm^3 of 1% starch solution.

5. Continue adding **FA 2** until the blue-black colour **just** disappears. Add 10 cm^3 of 10% KSCN solution using a measuring cylinder.

6. Continue adding **FA 2** slowly. The end-point is reached when the **solution** first becomes colourless. The white precipitate remains.

7. Record your titration results in the space provided on page **4**. Make certain that your recorded results show the precision of your working.

8. Swirl the reaction mixture and filter the mixture. Wash the residue twice with deionised water. Keep the residue for use in **2(a)**. The residue is **FA 4**.

For Examiner's Use

While you are waiting for the mixture to filter, continue with step 9.

9. Repeat points **1** to **7** as necessary until consistent results are obtained.

Titration results

Titration number	1	2
Final burette reading / cm^3	20.00	40.00
Initial burette reading / cm^3	0.00	20.00
Volume of **FA 2** solution used / cm^3	20.00	20.00
	✓	✓

- Table with correct headings (*'burette' must be stated)* and units.
- All burette readings recorded to the nearest 0.05 cm^3
- Titres for end-point must be within 0.10 cm^3

[5]

Comments:
- This part was well done in general.
- Common errors included using 'burette volumes' instead of burette readings, making reference to **FA 1** instead of **FA 2**, and recording volume as 'amount'.
- The accuracy of the titration was poor, with majority of the volumes obtained being significantly higher than the expected volume.

(ii) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

$$\text{volume of FA 2 used} = \frac{20.00 + 20.00}{2}$$
$$= 20.00 \text{ cm}^3$$

volume of **FA 2** = ...**20.00 cm^3**..... [1]

Comments:
- This part was well done in general. A small number of students incorrectly rounded their values off to 3 sf, although it was left as 2 dp in their final answer. It should be noted that the average volume calculated should follow the precision of the burette readings, i.e. to 2 dp, without rounding it to 3 significant figures.

(c) (i) Calculate the amount of iodine, I_2, liberated from 25.0 cm^3 of **FA 1** solution.

$$n_{S_2O_3^{2-}} \text{ used} = \frac{20.00}{1000} \times 0.100 = 2.00 \times 10^{-3} \text{ mol}$$

$$n_{I_2} = n_{I_3^-} = \frac{1}{2} n_{S_2O_3^{2-}} = \frac{1}{2} \times 2.00 \times 10^{-3} \text{ mol}$$
$$= 1.00 \times 10^{-3} \text{ mol}$$

amount of I_2 liberated from 25.0 cm^3 of **FA 1** solution = ...**1.00×10^{-3} mol**..... [1]

For Examiner's Use

(ii) Hence, calculate the amount of copper(II), Cu^{2+}, in 25.0 cm^3 of **FA 1** solution.

$$n_{Cu^{2+}} = 2n_{I_2} = 2 \times 1.00 \times 10^{-3} \text{ mol}$$
$$= 2.00 \times 10^{-3} \text{ mol}$$

amount of Cu^{2+}, in 25.0 cm^3 of **FA 1** solution = **2.00×10^{-3} mol** [1]

(iii) Determine the amount of $CuSO_4 \cdot nH_2O$ in 250 cm^3 of **FA 1** solution.

$$n_{CuSO_4 \cdot nH_2O} \text{ in 250 cm}^3 \text{ of FA 1 solution} = \frac{250}{25} \times 2.00 \times 10^{-3}$$
$$= 2.00 \times 10^{-2} \text{ mol}$$

amount of $CuSO_4 \cdot nH_2O$ in **FA 1** solution = **2.00×10^{-2} mol** [1]

Comments:
- Part **(c)** was well done in general. Common mistakes included using the wrong stoichiometric ratio for calculation in **(c)(i)** and **(c)(ii)**.

(iv) Use your answer to **1(c)(iii)** to calculate the M_r of $CuSO_4 \cdot nH_2O$, and hence the value of n.
[A_r: H, 1.0; O, 16.0; S, 32.1; Cu, 63.5]

$$M_r\left(CuSO_4 \cdot nH_2O\right) = \frac{5.000}{2.00 \times 10^{-2}}$$
$$= 250$$
$$n = \frac{250 - \left(63.5 + 32.1 + 16.0 \times 4\right)}{\left(1.0 \times 2 + 16.0\right)}$$
$$= 5.022$$
$$\approx 5$$

M_r of $CuSO_4 \cdot nH_2O$ = **250**

value of n = **5**

Comments:
- This part was well done in general.
- A small number of students incorrectly used 5 g as the mass of solid in their calculations instead of using the mass of **FA 1** that was transferred into the beaker for preparation of standard solution. Some incorrectly used the mass of **FA 1** weighed, rather than the mass of **FA 1** used when the two values were different.
- A few students did not follow the question and reversed the order by first determining the value of n, before using it to calculate the M_r of $CuSO_4 \cdot nH_2O$.

Hence, determine the percentage by mass of water of crystallisation in $CuSO_4 \cdot nH_2O$.
Show your working.

$$\text{percentage by mass of water of crystallisation} = \frac{5.022 \times (1.0 \times 2 + 16.0)}{250}$$
$$= 36.2\% \ (3 \text{ s.f.})$$

percentage by mass of water of crystallisation = **36.2%** [3]

Comments:
- This part was well done in general.

(d) Starch forms a dark blue-black complex with the tri-iodide ion, I_3^-. The starch indicator is not added at the beginning of the titration as the resulting complex at high I_3^- concentration is relatively stable, dissociating only slowly.

Predict and explain the effect of adding the starch indicator at the start of the titration on the M_r of $CuSO_4 \cdot nH_2O$ determined in **1(c)(iv)**.

Due to the slow release of I_3^- from the starch-I_3^- complex, the **end-point would have exceeded the equivalence point as the titration reaction is slower**, leading to a **larger titre volume**.

This would lead to a **larger amount of $CuSO_4 \cdot nH_2O$**, hence the M_r of $CuSO_4 \cdot nH_2O$ determined in **1(c)(iv)** would have been **smaller than the actual value**. [2]

Comments:
- This part poorly done for the explanation for the titre value being larger than expected.
- Otherwise, most students can conclude the effect of titre value on the M_r of $CuSO_4 \cdot nH_2O$.
- Minority of students mis-read this question.

For Examiner's Use

(e) (i) The solution should be titrated immediately after addition of KI because I_2 may be adsorbed onto the CuI precipitate, rendering the end-point less sharp. Explain how I_2 is adsorbed onto the CuI precipitate.

Similar to the formation of I_3^-, the **I^-** ion in CuI can **donate a lone pair of electrons to I_2 to form a dative bond with the I_2** molecule, leading to the adsorption of I_2 on the surface of the solid CuI. [1]

Comments:
- This part was poorly in general.
- Many students wrongly thought that dative bond had occur between Cu^{2+} and I_2. Or that the I_2 forms intermolecular id-id with CuI.

(ii) Hence, explain the effect **1(e)(i)** has on the amount of $CuSO_4 \cdot nH_2O$ determined in **1(c)(iii)**.

Due to adsorption of I_2 onto the CuI precipitate, the **titre reading will be lower** than expected since there will be **less I_2 to react**. Hence amount of $CuSO_4 \cdot nH_2O$ determined in **(c)(iii)** would be **smaller than the actual value**. [1]

Comments:
- This part was well done in general.
- Minority of students mis-read this question answered only about the amount of Cu^{2+} or M_r of $CuSO_4 \cdot nH_2O$

(iii) In step 5 of **1(b)(i)**, a colour change was observed when 10% KSCN solution was added to the mixture in the conical flask.

Suggest how the addition of KSCN to the mixture helps to improve the accuracy of titration.

SCN^- **displaces the adsorbed I_2 or I_3^- from the CuI**, allowing essentially **all** the I_2/I_3^- produced to react in the titration.

..... [1]

Comments:
- This part was poorly done in general.
- Many students simply state that addition of SCN^- made the colour change more obvious.
- Some students wrongly thought that K^+ will react with CuI.
- Some students were confused between Cu^+ and Cu^{2+}.

For Examiner's Use

(iv) Similar to the starch indicator, the 10% KSCN solution must not be added too early in the titration, although for a different reason from that given in **1(d)**.

The thiocyanate is also said to be a psuedohalide as it behaves chemically similar to a halide ion, also existing as thiocyanogen, $(SCN)_2$, which is similar to the parent halogen.

Suggest a reason why the KSCN solution should not be added at the start of the titration and the effect this has on the amount of $CuSO_4 \cdot nH_2O$ determined in **1(c)(iii)**.

The I_2 first produced could **oxidise SCN^- to $(SCN)_2$**, itself reduced back to I^-.

This will lead to **lower titre reading** and hence a **smaller amount** of

$CuSO_4 \cdot nH_2O$ in **(c)(iii)** than expected.

..... [1]

Comments:

- This part was poorly done in general.
- Many students wrongly thought that $(SCN)_2$ as added instead of SCN^-, hence wrongly concluded the reaction occur with I^-.
- Many students also wrongly thought that SCN^- with react with $S_2O_3^{2-}$ or Cu^{2+}.

[Total: 18]

For Examiner's Use

2 Investigation of inorganic reactions

Note: You should complete **Question 1(b)(i)** before starting **Question 2**.

A reaction in which one species is both reduced and oxidised is known as a disproportionation reaction.

In aqueous solution, $Cu^+(aq)$ ions are unstable as they spontaneously undergo a disproportionation reaction. However, stable Cu^+ compounds may be prepared by precipitation or by forming complex ions. Examples of precipitates are copper(I) iodide, CuI, and copper(I) thiocyanate, CuSCN. Examples of stable complex ions are $[CuCl_2]^-$ and $[Cu(NH_3)_2]^+$, both of which form colourless aqueous solutions.

FA 1 solution is the solution of $CuSO_4 \cdot nH_2O$ prepared in **1(a)**.
FA 2 is 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
FA 4 is the residue from **1(b)(i)**. This solid is copper(I) iodide, CuI.

Carry out the following tests. Carefully record your observations in Table 2.1.

If there is no observable change, write **no observable change**.

Table 2.1

	test	observations
(a)	Add 10 drops of **FA 1** solution to a test-tube. Add 10 drops of 10% KSCN solution dropwise, with shaking. Add **FA 2** slowly, with shaking, until no further change is seen.	Blue solution turns **green** initially. When more KSCN is added a **dark green/brown/black ppt** is formed. The dark green/brown/black ppt turns **white** upon addition of **FA 2**. White ppt **dissolves in excess** **FA 2** to give a **clear colourless solution**. [2]
(b)	Transfer 1 small spatula of **FA 4** into a clean test-tube, using the small plastic spatula. Add **FA 2** slowly, with shaking, until no further change is seen.	White **FA 4** **dissolves in excess** **FA 2** to give a **clear colourless solution**. [1]

Comments:
- In general, this part was poorly done. Many students did not state the initial change and only the final change.
- Most students did not dissolve the ppt in excess reagent properly, leading to erroneous results.
- Most did not state that when the ppt dissolved, it will give a clear colourless solution.

For Examiner's Use

(c) Suggest an explanation for your observations in **2(a)** and **2(b)** when **FA 2** is added in excess to the mixture.

Cu^+ forms a **stable water-soluble complex** with $S_2O_3^{2-}$:

$$Cu^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons \left[Cu(S_2O_3)_2\right]^{3-}(aq)$$

This causes $[Cu^+(aq)]$ to decrease, resulting in the **dissolution of the white CuSCN** formed in **2(a)** and the CuI in **2(b)** when the **I.P. falls below the respective K_{sp}**. [1]

Comments:
- This part was poorly done as many students were unable to obtain the correct observations for **2(a)** and **2(b)**.
- Those who did, explained incorrectly that complex formed using $I^-/Cu^{2+}/Cu$.

[Total: 4]

For Examiner's Use

3 Evaluate of the reliability of a gravimetric method in determining the percentage by mass of water of crystallisation in $CuSO_4 \cdot nH_2O$

FA 1 is solid hydrated copper(II) sulfate, $CuSO_4 \cdot nH_2O$. You are required to determine the percentage of water of crystallisation and the value of *n* in the salt.

When $CuSO_4 \cdot nH_2O$ is heated, the change in percentage weight loss with temperature is as shown in Fig 3.1.

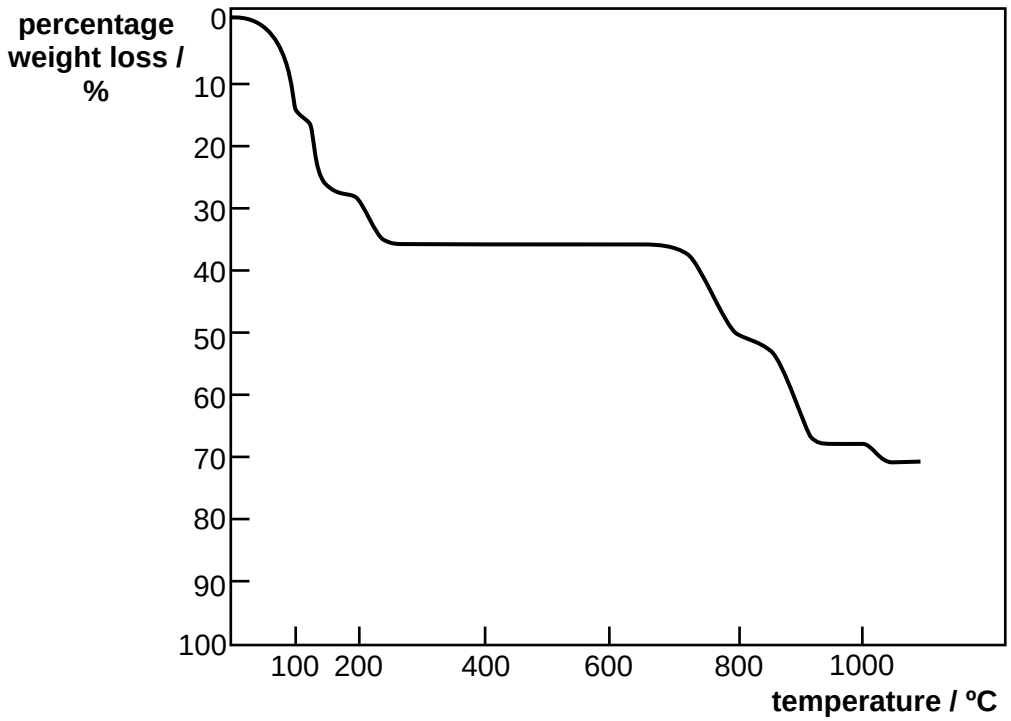

Fig. 3.1

There are four distinct regions of decomposition, listed below along with the approximate temperature range:

$$CuSO_4 \cdot nH_2O(s) \longrightarrow CuSO_4 \cdot H_2O(s) + (n-1)H_2O(g) \qquad 90–150\ ºC$$

$$CuSO_4 \cdot H_2O(s) \longrightarrow CuSO_4(s) + H_2O(g) \qquad 200–275\ ºC$$

$$CuSO_4(s) \longrightarrow CuO(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \qquad 700–900\ ºC$$

$$CuO(s) \longrightarrow Cu_2O(s) + \tfrac{1}{2}O_2(g) \qquad 1000–1100\ ºC$$

In this question, you will heat to dehydrate the $CuSO_4 \cdot nH_2O$ in **FA 1** and determine the mass of water lost. The data will be used to determine

- the percentage by mass of water of crystallisation in $CuSO_4 \cdot nH_2O$,
- the value of *n* in $CuSO_4 \cdot nH_2O$.

For Examiner's Use

(a) Thermal dehydration of $CuSO_4 \cdot nH_2O$

In this experiment, solid **FA 1** is heated gently in a boiling tube, over a luminous Bunsen flame, until **all** water has been driven off.

1. Weigh accurately between 2.00 g and 2.50 g of **FA 1** in the boiling tube provided. Record your weighings in the space provided below.

2. Heat the tube and content **gently** for 10 minutes.

Use a **luminous** Bunsen flame with the air-hole **closed** for this purpose. Ensure even heating of the sample and boiling tube.

3. Place the boiling tube into a **dry** 250 cm^3 beaker to cool.

You may wish to proceed with other experiments while waiting for the boiling tube to cool.

4. Weigh and record the mass of the cooled boiling tube containing the residue.

5. Repeat points 2 (heat gently for 2 minutes subsequently) to 4 as necessary until a constant mass is obtained.

6. **Turn off the Bunsen burner**.

(i) In an appropriate format in the space below, record all weighings.

Mass of empty boiling tube / g	30.883
Mass of boiling tube and **FA 1** / g	32.894
Mass of **FA 1** used / g	2.011
Mass of boiling tube and residue after first heating / g	32.174
Mass of boiling tube and residue after second heating / g	32.171

[4]

Comments:
- This part was surprisingly poorly attempted. Candidates are advised to familiarise themselves with the recording of experimental data in a single table.
- Many candidates did not record the mass of the empty boiling tube.
- Some candidates did not follow the instructions in Step 5. Some other candidates mistook the instruction and repeated steps 1 to 4 instead.

For Examiner's Use

(ii) Using your results, calculate the mass of water vapour evolved.

$$\text{mass of water vapour evolved} = 32.894 - 32.171$$
$$= 0.723 \text{ g } \textbf{[1]}$$

mass of H_2O evolved = **0.723 g** ..... [1]

Comments:
- This part was well done in general.

(iii) Using your answer to **3(a)(ii)**, calculate the percentage by mass of water of crystallisation in $CuSO_4 \cdot nH_2O$.

$$\text{mass of } \textbf{FA 1} \text{ used} = 32.894 - 30.883$$
$$= 2.011 \text{ g}$$

$$\text{percentage by mass of water of crystallisation} = \frac{0.723}{2.011}$$
$$= 36.0\% \text{ (3 s.f.) } \textbf{[1]}$$

percentage by mass of water of crystallisation = **36.0%** ..... [2]

Comments:
- This part was well done in general.

(iv) Determine the value of n in $CuSO_4 \cdot nH_2O$.

$$n_{H_2O} = \frac{0.723}{1.0 \times 2 + 16.0} = 0.04017 \text{ mol}$$

$$n_{CuSO_4} = \frac{2.011 - 0.723}{63.5 + 32.1 + 16.0 \times 4} = 8.070 \times 10^{-3} \text{ mol}$$

$$n = \frac{n_{H_2O}}{n_{CuSO_4}} = \frac{0.04017 \text{ mol}}{8.070 \times 10^{-3} \text{ mol}}$$
$$= 4.98$$
$$\simeq 5 \textbf{ [1]}$$

value of n = **5** ..... [2]

Comments:
- This part was not well attempted. Candidates should note that
- n is an integer (as stated in the question paper), and
- they should only use measurements and calculations from the same experiment (instead of using values from Q1).

(b) (i) Solid **FA 1** is a blue crystalline solid. Describe the appearance of the residue after heating.

White / Off-white / Greyish powder ..... [1]

Comments:
- This part is poorly attempted. Majority of the candidates only noted the white colour of the residue, but failed to note the **powder appearance** of the residue.
- Those who did not ensure heating **until water has been driven off** obtained pale blue or greenish blue residue which is not accepted.

(ii) Explain the difference in colour between solid **FA 1** and the residue.

Despite both containing Cu^{2+} with a **partially filled d subshell**, **water molecules** in **FA 1** **serve as ligands** to bind to Cu^{2+} causing the **d orbitals** to **split into two sets of different energies**, while in residue, **d orbital splitting does not occur** as there are no ligands and the d orbitals in Cu^{2+} are degenerate. **Visible light of a certain wavelength is absorbed by the former** hence appearing the complementary colour, while **visible light is not absorbed by the latter** and the reside **appears white**. ..... [3]

Comments:
- The explanations given lack accuracy and terminologies were not put together correctly.
- The common errors were as follows.
  - Many failed to identify the water in **FA 1** act as ligands and the act of heating drives off the water ligands. Hence the residue is anhydrous $CuSO_4$, **not Cu_2O or Cu_2I**. The Cu ion in **both** **FA 1** and residue contain partially filled d subshell.
  - Many were casual in the use of the phrase *"d orbital splitting"*. The d subshell or d orbitals split **into two sets of different energies** due to the water ligands in **FA 1**.
  - Some serious misuse of phrasings seen. For instance, "promotion of d orbitals from lower energy to higher energy?! **It is the d electron that get promoted** from the low energy d orbitals to the high energy d orbitals, not the orbitals.
- Many also did not realise that **having no d-d transition did not mean no energy is absorbed**. d-s transition can still take place in the residue where **energy can still be absorbed, but not in the visible light range**. Hence the all the wavelengths in visible light is transmitted and residue is white.

For Examiner's Use

(c) The intermediate monohydrate, $CuSO_4 \cdot H_2O$, formed during the dehydration is a white crystalline solid. Using your answer to **3(a)(iv)**, suggest and explain the likely identity of the copper(II)-containing complex ion present in solid **FA 1**.

This suggests that **one of the water molecule** (the last molecule) **is not bound to the Cu^{2+} as ligand**. Hence, the complex is **$[Cu(H_2O)_{n-1}]^{2+}$**. [1]

Comments:
- This part was poorly done. Majority of the candidates did not read the question carefully, suggesting only identity of the complex ion without any explanation at all. Hence those who have deduced correctly, but without explanation could not be award the one mark.
- Many could not did not see that if one of the water molecules is left in the intermediate, then the other (n – 1) water molecules will act as ligands and copper containing complex ion present in **FA 1** is **$[Cu(H_2O)_{n-1}]^{2+}$**.

(d) One potential source of error in this experiment is further decomposition of the anhydrous $CuSO_4$ residue when temperature goes above 700 ºC as seen in Fig. 3.1.

(i) How would this error affect the calculated results in **3(a)(iii)**?

There would be a **larger lost in mass** than expected, which is ascribed to the water of crystallisation, leading to a **larger percentage by mass** of water of crystallisation calculated in **3(a)(iii)**. [1]

Comments:
- This part was well done in general.
- Majority of students were able to relate to the larger mass loss to the SO_2/O_2 gases evolved or the lower/smaller mass of the residue formed.
- Some students say that the "% mass of water of crystallisation will be inaccurate". The effect was not clear and thus penalised.

For Examiner's Use

(ii) Describe two observations that would seen if further decomposition had occurred.

Black solid / residue copper(II) oxide will be seen **OR Brick-red solid / residue** copper(I) oxide will be seen;
Colourless, neutral gas which **rekindles/relights a glowing splint (O_2)** evolved;
Colourless, acidic gas which **turns aqueous acidified potassium manganate(VII) from purple to colourless** evolved (**SO_2**). .....[2]

Comments:
- This part was well-done.
- Majority of students gave the 2 latter gases and the observations from the test of those 2 gases. Some students thought that SO_2 gas was brown in colour.
- Students who gave black solid/residue but identify it to be Cu_2O were penalised.
- Some students did not indicate clearly the colour change for $KMnO_4$ e.g. "decolourise $KMnO_4$".

(e) (i) Comparing the titrimetric method in **1(b)** and the gravimetric method in **3(a)**, which of these two methods is less reliable? Explain your answer.

Gravimetric method; This is because the **temperature** of dehydration **cannot be controlled** using a Bunsen burner, hence it will be **difficult to prevent decomposition** of the anhydrous $CuSO_4$ first formed. ***or*** .....
The anhydrous $CuSO_4$ may **absorb moisture from the air during cooling**.
..... [1]

Comments:
- This part proved challenging to most students.
- Those who identified gravimetric method correctly often attributed it to uneven heating or not all H_2O could be evaporated when pg 12 of qns paper step 2 has asked them to ensure this. Many who identified gravimetric method thought they were decomposing the compound in this experiment saying "incomplete decomposition took place.". All these answers were not given credit.
- Out of the 2 explanations above, the 1st one on preventing further decomposition was more commonly given by students. There were few students, which gave the explanation regarding the ability of the anhydrous residue to absorb moisture from the air.

For Examiner's Use

(ii) Suggest one way in which the reliability of the method identified in **3(e)(i)** can be improved.

Carry out the dehydration of $CuSO_4 \cdot nH_2O$ in a vacuum oven under controlled temperature of 400 ºC (< 700 ºC) ***or***

Cool the anhydrous $CuSO_4$ in a **desiccator** [1]

Comments:

- This part was also challenging to majority of the students.
- The answer given in this part should align to method or explanation given in **(e)(i)** for credit to be given i.e. they should be discussing on the gravimetric method.
- Students who propose idea of temperature controlled environment OR oil/sand bath were given credit. Water bath was rejected since it will no longer exist when at a temperature of 200 ºC or higher. Those who mention this but mention "to ensure complete decomposition" were penalised since we are dehydrating and not decomposing it.
- Students who mention "cool residue in a dry (or not humid) environment" or to "stopper the residue during cooling to avoid absorbing moisture in the air" were also given credit.

[Total : 19]

For Examiner's Use

4 Planning

Besides the titrimetric method in **1(b)**, the amount of Cu^{2+} in a sample can be determined by gravimetric method involving precipitation of copper(I) thiocyanate, CuSCN.

The essential experimental conditions are:

1. *slight acidity* of the solution with respect to hydrochloric acid, since the solubility of the precipitate increases appreciably with decreasing pH;
2. *boiling* with ammonium hydrogensulfite, NH_4HSO_3, a *reducing agent*, to first reduce copper(II) to copper(I);

$$2Cu^{2+}(aq) + HSO_3^-(aq) + H_2O(l) \longrightarrow 2Cu^+(aq) + HSO_4^-(aq) + 2H^+(aq)$$

3. precipitation using a *slight excess of ammonium thiocyanate*, NH_4SCN, since a large excess increases the solubility of the copper(I) thiocyanate due to the formation of a thiocyanate complex.

$$Cu^+(aq) + SCN^-(aq) \longrightarrow CuSCN(s)$$

Isolation of the precipitate is achieved by filtering through a sintered-glass crucible shown in Fig. 4.1, which does not require the use of filter paper. At the same time, the crucible serves as a *container* to hold the precipitate during weighing and drying.

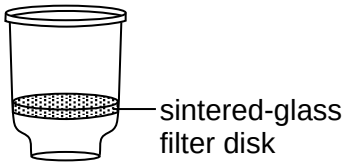

Fig. 4.1

The precipitate is washed with dilute NH_4SCN solution, containing a little NH_4HSO_3 to prevent any oxidation of the copper(I) salt. This is followed by washing with ethanol.

The precipitate (in the crucible) is dried by heating in a hot air oven at 110–120 ºC.

In the question, you are to plan a procedure that would allow you to determine the percentage purity of a sample of $Cu(NO_3)_2{\cdot}3H_2O$.

You can assume that you are provided with:

- 3.00 g of solid copper(II) nitrate trihydrate, $Cu(NO_3)_2{\cdot}3H_2O$ (solubility : 267 g / 100 cm^3 of water),
- 10 cm^3 of 1.00 mol dm^{-3} hydrochloric acid, HC*l*,
- 150 cm^3 of 0.10 mol dm^{-3} ammonium hydrogensulfite, NH_4HSO_3,
- 150 cm^3 of 0.25 mol dm^{-3} ammonium thiocyanate, NH_4SCN,
- 50 cm^3 of ethanol,
- sintered-glass crucible,
- the equipment normally found in a school or college laboratory.

For Examiner's Use

(a) Assuming that 2.50 g of $Cu(NO_3)_2{\cdot}3H_2O$ is used. Determine the minimum volume of 0.10 mol dm^{-3} ammonium hydrogensulfite, NH_4HSO_3, that is needed to convert all the $Cu^{2+}(aq)$ into $Cu^{+}(aq)$.

[A_r: Cu, 63.5; O, 16.0; N, 14.0; H, 1.0]

$$n_{Cu(NO_3)_2\cdot 3H_2O} = \frac{2.50}{63.5 + 2(14.0 + 16.0\times 3) + 3(1.0\times 2 + 16.0)} = \frac{2.50}{241.5} = 0.010352 \text{ mol}$$

$$\text{mininium } n_{HSO_3^-} \text{ required} = \frac{1}{2}\times n_{Cu^{2+}} = \frac{1}{2}\times 0.010352 = 0.005176 \text{ mol}$$

$$\text{mininium } V_{NH_4HSO_3} \text{ required} = \frac{0.005176}{0.10} = 0.05176 \text{ dm}^3 \approx 51.80 \text{ cm}^3$$

minimum volume of 0.10 mol dm^{-3} NH_4HSO_3 needed = **51.80 cm^3** ..... [1]

Comments:
- This part was well done in general.
- Despite the equation and hence 2:1 mole ratio of Cu^{2+}:HSO_3^- being given, a handful of students still use a wrong 1:1 stoichiometry in the calculation.
- A number of students also evaluated the numerical answer for $n(Cu(NO_3)_2{\cdot}3H_2O)$ wrongly despite writing down the correct string of A_r corresponding to the formula.

(b) Determine the minimum volume of 0.25 mol dm^{-3} ammonium thiocyanate, NH_4SCN, needed to precipitate all the $Cu^{+}(aq)$ produced in **4(a)**.

$$n_{Cu^+} = n_{Cu^{2+}} = 0.010352 \text{ mol}$$

$$\text{minimium } n_{SCN^-} = n_{Cu^+} = 0.010352 \text{ mol}$$

$$\text{mininium } V_{NH_4SCN} \text{ required} = \frac{0.01035}{0.25} = 0.04141 \text{ dm}^3 = 41.50 \text{ cm}^3$$

minimum volume of 0.25 mol dm^{-3} NH_4SCN needed = **41.50 cm^3** ..... [1]

Comments:
- This part was generally badly attempted as most students round *down* the volume of NH_4SCN needed instead of rounding *up* as question ask for the minimum volume.
- Accepted 41.60 cm^3 if student uses $n(Cu^+)$ = 0.0104 mol and 41.40 cm^3 if student uses $n(Cu^+)$ = 0.01035 mol. Otherwise, students are expected to round up to 41.50 cm^3 if they use $n(Cu^+)$ with 5 or higher significant figures.
- Again, despite the 1:1 stoichiometry for the precipitation reaction being given, a handful of students used a 2:1 molar ratio of Cu^+ : SCN^- instead.

For Examiner's Use

(c) Plan an investigation to determine the percentage purity of a 2.50 g sample of $Cu(NO_3)_2 \cdot 3H_2O$ based on the gravimetric method described above.

In your plan, you should include brief details of:

- the apparatus you would use,
- the quantities you would use,
- the procedure you would follow,

Procedure:

1. Weigh out **accurately about 2.50 g** of $Cu(NO_3)_2 \cdot 3H_2O$ into a clean and dry **weighing bottle** using an **analytical balance**.
2. Dissolve the solid in **50 cm^3 of deionised water** in a **250 cm^3 beaker**.
3. Add **1 cm^3 of 1.00 mol dm^{-3} HCl** by means of a **10 cm^3 measuring cylinder**.
4. Add in **70 cm^3 of 0.10 mol dm^{-3} NH_4HSO_3** by means of a **100 cm^3 measuring cylinder**.
5. Bring the solution to **boil over a Bunsen flame** for 5 minutes.
6. Turn off the Bunsen burner.
7. Add in **42 cm^3 of 0.25 mol dm^{-3} NH_4SCN slowly** to the mixture using a **50 cm^3 measuring cylinder, stirring with a glass rod**.
8. Allow the mixture to stand for 30 minutes at room temperature.
9. **Weigh** and **record** the **mass** of a **clean and dry sintered-glass crucible** using an **analytical balance**.
10. Filter the mixture through the sintered-glass funnel, and **wash the precipitate 3 times** with a mixture consisting of **10 cm^3** of **0.25 mol dm^{-3} NH_4SCN** and **1 cm^3** of **0.10 mol dm^{-3} NH_4HSO_3**.
11. **Wash** the precipitate **3 times with 10 cm^3 portions of** cold **ethanol**.
12. **Heat** the crucible and precipitate in a **hot air oven** at **110–120 °C** for **1 hour**.

For Examiner's Use

13. **Cool** the crucible in a dessicator. **Weigh and record** the **mass of the cooled crucible with the precipitate** using an **analytical balance**.

14. Repeat step 12 and 13 until **constant mass** of the crucible with precipitate is obtained within ±0.01g. [10]

Comments:

- This first part up till the precipitation of CuSCN was fairly well attempted.
- The latter part pertaining to isolation of the precipitate and obtaining the mass of the dry precipitate was generally poorly attempted.

Precipitation

- Despite given 3.00 g of solid $Cu(NO_3)_2 \cdot 3H_2O$ in the list and asked to determine the percentage purity of a 2.50 g sample, with the calculations in **4(a)** and **4(b)** dealing with 2.50 g of $Cu(NO_3)_2 \cdot 3H_2O$, a sizable number of students did not weigh out the desired mass of $Cu(NO_3)_2 \cdot 3H_2O$ as the first step (mark ref 44). Very commonly, the use of a weighing balance was not mentioned.
- Some students erroneously weighed the $Cu(NO_3)_2 \cdot 3H_2O$ into the crucible, possibly mis-reading the information "At the same time, the crucible serves as a *container* to hold the precipitate during weighing and drying".
- Quite a significant number of students prepared 250 cm^3 of a standard solution from the 2.50 g of $Cu(NO_3)_2 \cdot 3H_2O$ and pipetted out (or in the worst case, using a measuring cylinder to measure out) 10/25/50 cm^3 of the solution for subsequent reaction. They should use all the 2.50 g of $Cu(NO_3)_2 \cdot 3H_2O$.
- Among the students who prepared a standard solution, the better ones scaled the volume of NH_4HSO_3 (mark ref 46) and NH_4SCN calculated in **4(a)** and **4(b)** accordingly, which is still acceptable. Many failed to realise that they need to scale the two volumes and ended up using far excess of the two reagents. They did not realise that excess NH_4SCN will actually cause the ppt to dissolve due to formation of a complex. Students were not penalised though (mark ref 48).
- A number of students forgot to add HC*l* to acidify the solution, or more commonly, added too much HC*l* (maximum accepted is 5 cm^3; but adjusted if students add in water to dilute the solution) despite being told "slight acidity", or a few used the wrong acid (mark ref 45).
- A large number of students did not mention boiling and just describe heating the solution (mark ref 47). The heat source was also often not mentioned. Thermostatically controlled water bath is not accepted as water bath is not used to boil aqueous solution. A very small number used reflux, which is not needed for aqueous/non-organic system.
- A number of students also did not heat the solution at all and proceeded with addition of NH_4SCN. Although technically the Cu^{2+} would not have converted to Cu^{+} fully, students were not penalised for the subsequent parts.
- Many students added the NH_4SCN in far larger excess, without realising that the precipitate is actually soluble in excess of the reagent. However, they were not penalised giving benefit of doubt (mark ref 48).
- Some students did not use the values obtained in **4(a)** and **4(b)** in their plan at all.

For Examiner's Use

Isolation of Precipitate

- Most students did not understand that the sintered glass crucible is used to hold the ppt despite being told "At the same time, the crucible serves as a *container* to hold the precipitate during weighing and drying". Hence, most students did not pre-weigh the sintered glass crucible prior to filtration (mark ref 49).
- The idea that washing needs to be carried out with small volumes of the solution at least 2 times is also missing in almost all the students' scripts. However, this was only penalised once for either the NH_4HSO_3+NH_4SCN mixture (mark ref 50) or ethanol (mark ref 51). The absence of specific volume of the solutions used in washing was also not penalised.
- Most students understand the need to dry the precipitate in the oven, although a few heated the precipitate in a Bunsen flame.
- Most students did not mention the need to allow the heated crucible and ppt to cool before weighing (mark ref 52). Benefit of doubts were given should the student not mention the crucible but just made reference to heating the ppt.
- Only very few students appreciated the need to heat till constant mass (mark ref 53). Even then, those who realised the need, did not state the level of precision for constant mass in general, although they were not penalised.
- Many students thought of repeating the whole precipitation and isolation of precipitate, especially those who prepared a standard solution and took out aliquots for the precipitation, which is not the case for gravimetric determination.

Overall

- Very commonly, students did not give details on the volume of solution and choice of apparatus for the difference steps. One mark overall is deducted in these cases.

(d) Assuming that *m* g of CuSCN is obtained from 2.50 g of $Cu(NO_3)_2{\cdot}3H_2O$ sample in **3(c)**. Express the percentage purity of the sample in terms of *m*.

For Examiner's Use

[A_r: Cu, 63.5; S, 32.1; O, 16.0; N, 14.0; C, 12.0; H, 1.0]

$$n_{CuSCN} = \frac{m}{63.5 + 32.1 + 12.0 + 14.0} = \frac{m}{121.6} \text{ mol}$$

$$n_{Cu(NO_3)_2\cdot 3H_2O} = n_{CuSCN} = \frac{m}{121.6} \text{ mol [1]}$$

$$m_{Cu(NO_3)_2\cdot 3H_2O} = n_{Cu(NO_3)_2\cdot 3H_2O} \times \left[63.5 + 2\left(14.0 + 16.0 \times 3\right) + 3\left(1.0 \times 2 + 16.0\right)\right]$$
$$= \frac{m}{121.6} \times 241.5 \text{ g}$$

$$\text{percentage purity} = \frac{\frac{m}{121.6} \times 241.5}{2.50} \times 100\% = \underline{\mathbf{79.4}\boldsymbol{m}\%} \text{ [1]}$$

[2]

Comments:

- This part was fairly well attempted in general. Other methods of obtaining the % purity were accepted as well.
- Quite a handful of students thought erroneously that $n(Cu^{2+}) = 2n(Cu^{+})$.
- One common mistake is to determine the mass of Cu in the precipitate (instead of the mass of $Cu(NO_3)_2{\cdot}3H_2O$) and divide by 2.50 g (the mass of $Cu(NO_3)_2{\cdot}3H_2O$ used) to find the % purity.
- Another commonly observed mistake is to give 100*m*/2.50% as the % purity without realising that the *m* g refers to CuSCN and 2.50 g refers to $Cu(NO_3)_2{\cdot}3H_2O$ (despite being given in the question), which are different compounds altogether.

[Total : 14]