CHAPTER 6: REDOX TITRATIONS WITH SODIUM THIOSULPHATE.

Most of the thiosulphate titrations involve use of standard iodine solution or iodine liberated from a given chemical reaction. The titration is thus called iodimetry or iodometry.

Theory of reaction between Iodine solution and Sodium thiosulphate

Iodine is an oxidizing agent while the thiosulphate is a reducing agent. The thiosulphate is oxidized to tetrathionate ions as in equation below.

$$2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2e^- \quad \text{..... Equation. (i)}$$

Iodine on the other hand is reduced to Iodine ions as in equation below.

$$I_2(aq) + 2e^- \rightarrow 2I^-(aq) \quad \text{..... Equation (ii)}$$

Adding equation (i) and (ii), the overall equation obtained is

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

(a) IODIMETRIC TITRATIONS:

These involve ***direct*** use an excess of standard solution of iodine in volumetric analysis. The iodine solution acts as an oxidizing agent in iodimetry.

Question.

(a) Give two advantages of using iodine as a primary standard in volumetric analysis.

Iodine is obtained in a high state of purity. ✔

Iodine can be accurately used in making standard solutions. ✔

(b) Explain why iodine is not a good primary standard?

Iodine is highly volatile ✔ *and this varies its concentration on standing,* ✔ *hence not recommended for a primary standard.*

Iodine has poor solubility in water. ✔

Question.

Iodine is dissolved in potassium iodide solution rather than water during iodimetry. Explain.

Iodine has a low water solubility ✔ *but dissolves in moderately concentrated*

potassium iodide solution due to the formation of a soluble triiodide ion complex, $I_3^-(aq)$ ✔

Equation; $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$ ✔

Equilibrium attained between iodine and triiodide ions ensures that even when iodine molecules are removed from the solution by a reaction, the triiodide ion readily dissociate in solution ✔ *and liberating more iodine molecules,* ✔ *so the dissolved iodine behaves as if they are all free iodine. An explanation of Le Chatelier's principle.*

NOTE:

1. Iodine is standardized by titration with standard sodium thiosulphate solution.
2. The thiosulphate is not a primary standard and is standardized by potassium permanganate solution or potassium iodate or potassium dichromate.
3. Hydrochloric acid and nitric acid are not used to standardize sodium thiosulphate.
4. Acidified potassium dichromate is commonly associated with thiosulphate titrations.

Question.

Explain why,

(a) Sodium thiosulphate-5-water is not a good primary standard. ***(3marks)***

Sodium thiosulphate-5-water contains water of crystallization✔ *making its exact concentration difficult to determine.* ✔ *This is because the composition depends on humidity and temperature, that is to say, loses water of crystallization at high temperatures*✔ *and absorbs water at high humidity*✔ *. Consequently affecting it absolute relative molecular mass*✔ *and hence varying its concentration.* ✔

(b) Titrations involving sodium thiosulphate should not be carried out in acid conditions.

(3½marks)

In acidic medium, hydrogen ions in solution easily react with the thiosulphate ions✔ *depositing yellow precipitate of elemental sulphur,* ✔ *with bubbles of sulphur dioxide gas and formation of water*✔*; depleting thiosulphate ions from solution*✔*.*

Equations; $S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$ ✔ = 1½marks

(c) Sodium bicarbonate is added to analyte solution during iodimetry of sulphite ions with standard thiosulphate solution.
(7½marks)

During iodimetry; sulphite ions are oxidised sulphite ions with formation of hydrogen ions in solution resulting to an acid medium. ✔

Equation, $SO_3^{2-}(aq) + H_2O(l) + I_2(aq) \longrightarrow SO_4^{2-}(aq) + 2I^-(aq) + 2H^+(aq)$. ✔=1½marks

Sodium bicarbonate added to quickly react with the hydrogen ions forming bubbles of a colourless gas and water✔.

Equation;

$HCO_3^-(aq) + H^+(aq) \longrightarrow CO_2(g) + H_2O(l)$. ✔ = 1marks

This protects the thiosulphate ions from reacting with the hydrogen ions to deposit a yellow solid of sulphur, sulphur dioxide and water✔*, hence keeping them available to react with the excess iodine in solution.* ✔

Equation(s).

$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$ ✔ = 1½marks

$2S_2O_3^{2-}{}_{(aq)} + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$ ✔ = 1½marks

(d) Sodium thiosulphate solution becomes cloudy with formation of a yellow precipitate on standing in air. ***(4marks)***

When left exposed to air, sodium thiosulphate solution readily absorbs carbon dioxide from air this forming weak carbonic acid. ✔ *Carbonic acid formed, ionizes in producing hydrogen ions that decompose the thiosulphate ions to deposit elemental sulphur, sulphur dioxide and water*✔ *which initially appears as a cloudy solution*✔ *but later settles as a yellow solid*✔.

$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$ ✔

Sodium thiosulphate solution absorbs atmospheric oxygen from air; ✔ *hence easily oxidized to sulphate.* ✔

Atmospheric sulphur requiring bacteria may attack sodium thiosulphate solution causing decomposition. ✔

(b) IODOMETRIC TITRATIONS:

These involve titration of standard solution of thiosulphate ions with iodine liberated from an iodo-compound in given chemical reaction. ***(Iodo-compounds; containing***

excess iodide ions for example, potassium iodide solution is usually used).

- **Liberation of iodine in iodometry.**

A known amount of suitable oxidizing agent in acid medium, reacted with excess potassium solution. The iodide ions are reducing agents and they are therefore, oxidised to form aqueous iodine (oxidant) which can then be titrated with a standard solution of the thiosulphate ions from the burette.

- ***Common reactions that liberate aqueous iodine include;***

(i) $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \longrightarrow \mathbf{3I_2}(aq) + 3H_2O(l)$

(ii) $ClO_3^-(aq) + 6I^-(aq) + 6H^+(aq) \longrightarrow \mathbf{3I_2}(aq) + Cl^-(aq) + 3H_2O(l)$

(iii) $OCl^-(aq) + 2I^-(aq) + 2H^+(aq) \longrightarrow \mathbf{I_2}(aq) + Cl^-(aq) + 2H_2O(l)$

(iv) $2MnO_4^-(aq) + 10I^-(aq) + 16H^+(aq) \longrightarrow \mathbf{3I_2}(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$

(v) $Cr_2O_7^{2-}(aq) + 6I^-(aq) + 14H^+(aq) \longrightarrow \mathbf{3I_2}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

(vi) $H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \longrightarrow \mathbf{I_2}(aq) + 2H_2O(l)$

(vii) $2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow \mathbf{I_2}(aq) + Cu_2I_2(s)$

(viii) $Cl_2(aq) + 2I^-(aq) \longrightarrow \mathbf{I_2}(aq) + 2Cl^-(aq)$

Detection of end point

The end point of all titrations involving thiosulphate ions and iodine is detected by the use of ***starch solution as indicator***.

Starch solution is added towards the end point and in the presence of free iodine. It produces a deep blue solution. This blue colour is discharged as soon sufficient sodium thiosulphate is added giving a colourless solution which serves as the end point.

General procedure

Sodium thiosulphate solution in the burette is run into iodine solution in the conical flask until the brown colour of solution turns pale yellow. At this point, about $3cm^3$ of starch is added producing a blue coloured solution. Then the thiosulphate solution is then added drop by drop until the blue solution just turns colourless at end point.

Question.

1. *Why is starch indicator added close to the end point rather than at the beginning*

of the experiment?

Adding starch close to the end point gives a sharp endpoint detection, while avoiding the formation of excess starch iodine complex which would difficult to decompose

2. *Why should the starch solution used in iodometry be freshly prepared?*

Starch solution deteriorates quickly on standing.

SAMPLE P525/1&2 CALCULATION QUESTIONS ON IODOMETRY

1. $10.0cm^3$ of a sample of commercial bleach containing chlorine was diluted to $250cm^3$ with water. $25.0cm^3$ of this solution was transferred into a clean conical flask and potassium iodide solution was added to liberate iodine. The iodine mixture required $23.2cm^3$ of a 0.1M sodium thiosulphate solution for complete neutralization. Calculate the molar concentration of chlorine in the commercial bleach.(UNEB 2015 P2 No.5). ***(3marks)***

Solution.

Moles of sodium thiosulphate

$1000cm^3$ of solution contain 0.1moles of sodium thiosulphate.

$23.5cm^3$ of solution contain $\frac{0.1x23.2}{1000}$ ✓ *= 0.00232molesof sodium thiosulphate.* ✓

Moles of liberated iodine.

From equation, $2S_2O_3^{2-}{}_{(aq)} + I_{2\,(aq)} \longrightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-{}_{(aq)}$

2moles of sodium thiosulphate reacted with 1mole of liberated iodine

0.00232moles of sodium thiosulphate reacted with $\frac{0.00232x1}{2}$ ✓*= 0.00116moles of iodine.* ✓

Moles of chlorine in the bleach.

From equation, $Cl_2\,(aq) + 2I^-\,(aq) \longrightarrow I_2\,(aq) + 2Cl^-\,(aq)$

Or; $OCl^-\,(aq) + Cl^-\,(aq) + 2H^+\,(aq) + 2I^-\,(aq) \longrightarrow I_2\,(aq) + 2Cl^-\,(aq) + H_2O\,(l)$

1mole of iodine was liberated by 1mole of chlorine in commercial bleach

0.00116molles of iodine were therefore liberated by 0.00116moles of chlorine in bleach. ✔

Molar concentration of chlorine in the commercial bleach.

25.0cm^3 of solution contain 0.00116moles of chlorine.

1000cm^3 of solution contains $\frac{0.00116 \times 1000}{25.0}$ ✔*= 0.0454M Cl_2* ✔

TRIAL P525/1&2 QUESTIONS ON IODOMETRY

Answer in your revision book for submission.

2. 2.835g of iodine and 6g of potassium iodide are dissolved in distilled water and made up to 250cm^3. A 25.0cm^3 portion titrated against sodium thiosulphate solution required 17.5cm^3 of the solution. Calculate the concentration of the thiosulphate solution.
3. 1.015g of potassium iodate(V) are dissolved and made up to 250cm^3. To a 25.0cm^3 portion are added an excess of potassium iodide and dilute sulphuric acid. The solution is titrated with a solution of sodium thiosulphate, starch solution is being added near the end point. 29.8cm^3 of thiosulphate were required. Calculate the concentration of the thiosulphate solution.
4. A standard solution is made by dissolving 1.015g of potassium dichromate(VI) and making up to 250cm^3. A 25.0cm^3 portion is added to excess potassium iodide and dilute sulphuric acid, and the iodine liberated is titrated with sodium thiosulphate solution. 19.2cm^3 of this solution are needed. Find the concentration of the thiosulphate solution.
5. A domestic bleach in solution is diluted by pipetting 10.0cm^3 and making this volume up to 250cm^3. A 25cm^3 portion of the solution is added to an excess of potassium iodide and ethanoic acid and titrated against sodium thiosulphate solution of concentration 0.1moldm^{-3}, using starch indicator. The volume required is 21.3cm^3. Calculate the percentage of available chlorine in the bleach.

P525/3 QUESTIONS ON IODOMETRY

EXPERIMENT 15: **UNEB 2018**

You are provided with the following;

FA1 which is approximately 0.1M sodium thiosulphate solution.

FA2 which is a solution containing 2.5gdm-3 of potassium iodate.

Solid Y, which is a salt containing dichromate ions.

1M sulphuric acid solution.

5% potassium iodide solution.

Starch solution.

You are required to standardize FA1 and use it to determine the percentage by mass of Y.

In acid solution, iodate and dichromate ions (VI) ions react with potassium iodide to liberate iodine according to the following equations.

$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \longrightarrow \mathbf{3I_2}(aq) + 3H_2O(l)$

$Cr_2O_7^{2-}(aq) + 6I^-(aq) + 14H^+(aq) \longrightarrow \mathbf{3I_2}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

The liberated iodine in both cases reacts with thiosulphate ions according to the equation.

$2S_2O_3^{2-}{}_{(aq)} + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

PART 1

PROCEDURE:

(a) Pipette 25.0 (or 20.0) cm of FA2 into a clean conical flask and add an equal volume of 0.1M sulphuric acid using a measuring cylinder, followed by 10cm3 of 5% potassium iodide solution.

(b) Titrate the iodine liberated FA1, using starch indicator.

(c) Repeat the titration until you obtain consistent results.

(d) Record your results in the Table I below.

Results

Volume of pipette used.....cm^3 ***(½marks)***

Table I

BURETTE READINGS	**I**	**II**	**II**
Final burette reading (cm^3)			
Initial burette reading (cm^3)			

Volume of FA_1 used (cm^3)			

(4½marks)

Titre values used to calculate average volume of **FA_1** used are; ***(½marks)***

..... and ..... cm^3

Therefore average volume of **FA_1** used= ..... cm^3. ***(2½marks)***

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(a) Calculate the number of moles of iodine liberated by **FA_2.** ***(2½ marks)***

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(b) Determine the concentration of **FA_1** in $moldm^{-3}$ ***(2marks)***

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PART 2

PROCEDURE:

(a) Weigh accurately about 1.2g of Y. dissolve it in minimum amount of distilled water and transfer the solution into 250cm3 volumetric flask. Make the solution up to the mark with distilled water and label it FA3.

(b) Pipette 25.0 (or 20.0) cm3 of FA3 into a clean conical flask and add an equal volume of 1M sulphuric acid using a measuring cylinder, followed by 10cm3 of 5% potassium iodide solution. Titrate the iodine liberated with FA1 using starch indicator.

(c) Repeat the titration until you obtain consistent results.

(d) Record your results in the Table II below.

Results

Mass of weighing bottle + **Y** = ... g ***(½marks)***

Mass of empty weighing bottle = ... g ***(½marks)***

Mass of **Y** used = ... g ***(½marks)***

Volume of pipette used ..... cm^3 ***(½marks)***

Table II

BURETTE READINGS	**I**	**II**	**II**
Final burette reading (cm^3)			
Initial burette reading (cm^3)			
Volume of FA_1 used (cm^3)			

(4½marks)

Titre values used to calculate average volume of **FA_1** used are; ***(½marks)***

..... and ..... cm^3

Therefore average volume of **FA_1** used= ..... cm^3. ***(2½marks)***

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(a) Calculate the number of moles iodine liberated by **FA_3.** ***(2marks)***

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(b) Determine the :

(i) Concentration of **FA_3** in $moldm^{-3}$. ***(2½marks)***

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(ii) Mass of chromium in Y and hence its percentage. (Cr = 52). ***(3½marks)***

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EXPERIMENT 16: **(ENTEBBE MOCK 2019)**

You are provided with the following:

FA1; which is approximately 0.1 M sodium thiosulphate solution

FA2; which is a solution prepared by dissolving 1.0 g of potassium iodate(V) in 250 cm^3 of distilled water

Liquid **X**, which is a commercial bleaching agent containing sodium hypochlorite (sodium chlorate(I))

You are required to standardize FA1 and use it to determine the percentage of chlorine in the commercial bleaching agent.

Theory

In acid medium, iodate(V) ions react with iodide ions according to the following equation:

IO_3^- *(aq)* + $6H^+$ *(aq)* + 5 I^- *(aq)* ⟶ 3 I_2 *(aq)* + $3H_2O$ *(l)*

In acid medium, hypochlorite ions react to produce chlorine which displaces iodine according to the following equations:

OCl^- (aq) + 2 H^+ (aq) + 2 Cl^- (aq) ⟶ Cl_2 (aq) + H_2O (l)

Cl_2 (aq) + 2 I^-(aq) ⟶ I_2 (aq) + 2 Cl^-(aq)

The liberated iodine reacts with thiosulphate ions according to the fooling equation:

$2S_2O_3^{2-}$ (aq) + I_2 (aq) ⟶ $S_4O_6^{2-}$ (aq) + $2I^-$ (aq)

Procedure A

(a) Pipette 10.0 cm^3 of ***FA2*** into a conical flask and add an equal volume of 1.0 M sulphuric acid using a measuring cylinder followed by 10.0 cm^3 of 0.5 M potassium iodide solution. Titrate the liberated iodine with ***FA1*** from the burette until the mixture is pale yellow. Add 2 cm^3 of starch indicator and continue the titration until end point. Repeat the titration until you obtain consistent results.

Record your observations in Table I below.

Results

Volume of pipette used..... cm^3 ***(½marks)***

Table I

BURETTE READINGS	**I**	**II**	**II**
Final burette reading (cm^3)			
Initial burette reading (cm^3)			
Volume of FA_1 used (cm^3)			

(4½marks)

Titre values used to calculate average volume of **FA_1** used are; ***(½marks)***

..... and ..... cm^3

Therefore average volume of **FA_1** used=..... cm^3. ***(2½marks)***

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Questions:

(a) Calculate the concentration of ***FA1*** in $moldm^{-3}$. ***(6marks)***

Procedure B

(a) Transfer 30.0 cm^3 of liquid **X** into 250 cm^3 volumetric flask. Add distilled water up to the mark. Label the solution ***FA3***.

Pipette 10.0 cm^3 of ***FA3*** into a conical flask and add an equal volume of 1.0 M sulphuric acid using a measuring cylinder followed by 10 cm^3 of 0.5 M potassium iodide solution. Titrate the liberated iodine with ***FA1*** from the burette until the mixture is pale yellow. Add starch indicator and continue the titration until the end

point. Repeat the titration to obtain consistent results.

Record your results in table II below.

Results

Volume of pipette used ..... cm^3 ***(½marks)***

Table I

BURETTE READINGS	**I**	**II**	**II**
Final burette reading (cm^3)			
Initial burette reading (cm^3)			
Volume of FA_1 used (cm^3)			

(4½marks)

Titre values used to calculate average volume of **FA_1** used are; ***(½marks)***

..... and ..... cm^3

Therefore average volume of **FA_1** used= ..... cm^3. ***(2½marks)***

Questions:

(a) Calculate the number of moles of

(i) Sodium thiosulphate in ***FA1*** that reacted. ***(1½ marks)***

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(ii) Iodine liberated by 10.0 cm^3 of ***FA3***. ***(1½ marks)***

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(iii) Aqueous chlorine in 30 cm^3 of ***X***. ***(2½ marks)***

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(b) Determine the

(i) mass of chlorine in 30 cm^3 of ***X.*** *(Cl = 35.5)* ***(02 marks)***

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(ii) Percentage by mass of chlorine in ***X.*** ***(01 mark)***

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EXPERIMENT 17: **(ASSHU-RWENZORI MOCK 2017)**

You are provided with the following

FA_1 which is approximately 0.1M sodium thiosulphate solution.

FA_2 which is a solution containing 3.5g per litre of potassium iodate.

Solid **U** which is a hydrated copper (II) salt.

10% potassium iodine solution 1M hydrochloric acid.

You are required to determine;

(a) the concentration of thiosulphate on FA_1

(b) the percentage of copper in R.

Theory

In acidic solution potassium iodide, react with iodate ions according to the equation.

$IO^-_{3(aq)} + 6H^+_{(aq)} + 5I^-_{(aq)} \rightarrow 3I_{2(aq)} + 3H_2O_{(l)}$

Also copper (II) ions react with potassium iodide to form copper (I) iodide according to the following equation.

$2CU^{2+}_{(aq)} + 4I^-_{(aq)} \rightarrow Cu_2I_{2(s)} + I_{2(aq)}$

The iodine liberated on both reactions can be titrated with the thiosulphate according to the equation.

$2S_2O^{2-}_{3(aq)} + I_{2(aq)} \rightarrow S_4O^{2-}_{6(aq)} + 2I^-_{(aq)}$

PROCEDURE (A)

Pipette 25cm^3 or 20cm^3 of **FA_2** into a conical flash add an equal volume of 1.0M hydrochloric acid followed by about 10cm^3 of 10% aqueous potassium iodide. Titrate the mixture with **FA_1** until the solution in the flask turns pale yellow. Add 3 – 4 drops of starch indicator and continue the titration until the blue colour of the starch turns colourless. Repeat the titration to obtain consistent results. Record your results in table **1** below.

Results

Volume of pipette used ..... cm^3 ***(½marks)***

Table I

BURETTE READINGS	**I**	**II**	**II**
Final burette reading (cm^3)			
Initial burette reading (cm^3)			
Volume of FA_1 used (cm^3)			

(4½marks)

Titre values used to calculate average volume of **FA_1** used are; ***(½marks)***

..... and ..... cm^3

Therefore average volume of **FA_1** used= ..... cm^3. ***(2½marks)***

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Calculate;

(i) the number of moles of iodate ions in FA_2. ***(03 marks)***

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(ii) the molarity of the thiosulphate ions in FA_1. ***(03 marks)***

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PROCEDURE (B)

Weigh accurately about 6.0g of **U** and transfer it to a 250cm^3 volumetric flash and add about 100cm3 of distilled water to dissolve, followed by sodium carbonate solution until there is a slight precipitate formed. Add dilute ethanoic acid drop wise until the precipitate dissolves and then make up the solution to the mass until distilled water, label the solutions **FA_3**.

Pipette 25.0 (or 20.0) cm^3 of **FA_3**into a conical flash, and add 10cm^3 of the potassium iodide solution and titrate the mixture with **FA_1** until the solution is pale yellow. Add starch indicator and continue the titrations until the blue colour of iodine turns colourless.

Repeat the titration to obtain consistent results. Record your results on table **2**

Results

Mass of weighing bottle + **U** = ……g ***(½marks)***

Mass of empty weighing bottle = ……g ***(½marks)***

Mass of **U** used = ……g ***(½marks)***

Volume of pipette used……cm^3 ***(½marks)***

Table II

BURETTE READINGS	**I**	**II**	**II**
Final burette reading (cm^3)			
Initial burette reading (cm^3)			
Volume of FA_1 used (cm^3)			

(4½marks)

Titre values used to calculate average volume of **FA_1** used are; ***(½marks)***

..... and ..... cm^3

Therefore average volume of **FA_1** used= ..... cm^3. ***(2½marks)***

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Calculate;

(i) The number of moles of copper (II) ions in 250cm^3 of **FA_3.** ***(3½marks)***

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(ii) The concentration of copper (II) ions in **FA_3** in mol/litre. ***(02marks)***

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(iii) the percentage of copper in **U** (Cu = 64) ***(2½marks)***

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