I. PURPOSE OF THE EXPERIMENT
In this experiment (A) the mass of iodine (I₂) will be determined by direct titration method (Iodimetry). It was g / L of I₂.
(B) the mass of Copper (II) sulphate (CuSO₄) will be determined by indirect titration method (Iodometry). It was g / L of CuSO₄.

II. INTRODUCTION

Iodimetry
A reducing agent sodium thiosulphate (Na₂S₂O₆) was titrated directly with standard solution of iodine and I⁻ (iodide) is produced. Iodimetry is often used to determine the concentration of organic substances.

\[
\text{Iodine} \quad + \quad \text{Sodium thiosulphate} \quad \rightarrow \quad \text{Sodium iodide} \quad + \quad \text{Sodium persulphate}
\]

\[
\begin{align*}
\text{I}_2(\text{aq}) & \quad + \quad 2\text{Na}_2\text{S}_2\text{O}_3(\text{aq}) \quad \rightarrow \quad 2\text{NaI}(\text{aq}) \quad + \quad \text{Na}_2\text{S}_4\text{O}_6(\text{aq}) \\
1 \text{ mole} & \quad : \quad 2 \text{ mole} \quad \text{(Mole Ratio)}
\end{align*}
\]

Iodometry
Iodide (I⁻) is oxidized to iodine quantitatively and the liberated iodine is titrated with previously standardized sodium thiosulphate solution.
For example, when copper (II) sulphate solution is allowed to react with potassium iodide, iodine is liberated according to the chemical reaction as follows:

\[
\text{Copper (II) sulphate} + \text{Potassium iodide} \quad \rightarrow \quad \text{Copper (I) iodide} + \text{Potassium sulphate} + \text{Iodine}
\]

\[
\begin{align*}
(\text{i}) \quad 2\text{CuSO}_4(\text{aq}) & \quad + \quad 4\text{KI}(\text{aq}) \quad \rightarrow \quad 2\text{CuI}(\text{aq}) \quad + \quad \text{K}_2\text{SO}_4(\text{aq}) \quad + \quad \text{I}_2(\text{aq}) \\
2 \text{ mole} & \quad : \quad 1 \text{ mole}
\end{align*}
\]
The liberated iodine during the reaction is then titrated with standard sodium thiosulphate solution.

\[
\begin{align*}
\text{Iodine} \quad + \quad \text{Sodium thiosulphate} \quad \rightarrow \quad \text{Sodium iodide} \quad + \quad \text{Sodium persulphate}
\end{align*}
\]

\[
\begin{align*}
(\text{ii}) \quad \text{I}_2(\text{aq}) & \quad + \quad 2\text{Na}_2\text{S}_2\text{O}_3(\text{aq}) \quad \rightarrow \quad 2\text{NaI}(\text{aq}) \quad + \quad \text{Na}_2\text{S}_4\text{O}_6(\text{aq}) \\
1 \text{ mole} & \quad : \quad 2 \text{ mole} \quad \text{(Mole Ratio)}
\end{align*}
\]
Stoichiometrically, 2 moles of CuSO₄ will liberate 1 mole of I₂ from KI solution and 2 moles of Na₂S₂O₃ react with 1 mole of I₂.

Therefore ....2CuSO₄ = I₂ = 2Na₂S₂O₃

2 mole 1 mole
1 mole 2 mole

Indicator

In both cases starch is used as an indicator. Starch forms with I₃⁻ (tri-iodide ion) a dark blue complex, visible already with very tiny amounts of I₃⁻ present.

Notes:
1. Solid iodine is not very soluble in water. As a result, iodine solutions are usually prepared by dissolving the solid in the presence of potassium iodide. Iodine reacts with iodide to produce the tri-iodide ion:

   \[ I₂(aq) + I^-(aq) \rightarrow I₃^-(aq) \]

   Due to this reaction, solid iodine is soluble in solutions of iodide salts. However most of the dissolved iodine is actually present as tri-iodide, not as iodine. Thus, the reduction of iodine may be written as

   \[ I₃^-(aq) + 2e^- \rightarrow 3I^-(aq) \]

Iodine (or) tri-iodide ion is a much weaker oxidizing agent than potassium permanganate, potassium dichromate, and cerium (IV) sulphate. (Ref: standard reduction potential at 25°C)

In most direct titrations with iodine(iodimetry) a solution of iodine in potassium iodide is employed, and the reactive species is therefore the tri-iodide ion I₃⁻.

Strictly speaking, all equations involving reactions of iodine should be written with I₃⁻ rather than I₂.

   e.g.  \[ I₃^- (aq) + 2S_2O_3^{2-} (aq) \rightarrow 3I^- (aq) + S_4O_6^{2-} (aq) \]

   is more accurate than

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

2. Iodine / tri-iodide solutions are unstable for a variety of reasons.

   (a) aqueous iodine exerts a significant vapor pressure.

   (b) acid solutions of iodide is slowly air-oxidized to produce iodine.

   \[ 4I^- + O_2 + 4H^+ \rightarrow 2I_2 + 2H_2O \]

   (c) alkaline solutions of iodine will disproportionate to produce iodide and iodate, as follows:

   \[ 3I_2 + 6OH^- \rightarrow IO_3^- + 5I^- + 3H_2O \]

   Thus, iodine solutions are generally most stable at neutral pH values.
III. EXPERIMENTAL

3.1 Chemicals: (Iodimetry) I₂ solution, Standard Na₂S₂O₃ solution….M,
   Starch solution indicator
   (Iodometry) CuSO₄ solution, KI solution,
   Standard Na₂S₂O₃ solution……..M, Starch solution indicator.

3.2 Equipment: Titration set

3.3 Procedure I. (Iodimetry)
   Place the standard sodium thiosulphate solution in the buret. Transfer 10 mL of iodine solution in the 250mL Erlenmeyer flask (conical flask). Add 90 mL of distilled water into the iodine solution. Titrate the iodine solution with standard sodium thiosulphate till the solution turns pale yellow in colour. Then add 2 mL of starch indicator solution to get a blue colour. Continue the titration by addition of sodium thiosulphate solution till the blue colour disappears. This is the end point of the titration.

   Precautions (a) Keep the iodine solution (in the conical flask) covered. Remove cover only when adding standard sodium thiosulphate solution. (b) After each addition of titrant, swirl thoroughly.

Procedure II. (Iodometry)
   Place the standard sodium thiosulphate solution in the buret. Transfer 10 mL of CuSO₄ solution in the 125 mL Erlenmeyer flask (conical flask). Add 5 mL of 10% potassium iodide solution into a CuSO₄ solution. Titrate the liberated iodine with standard sodium thiosulphate solution until the brown colour of iodine fades, then add 2 mL of starch indicator solution to get the blue colour. Continue the titration till the blue colour turns into colourless (vita milk colour). This is the end point of the titration.
IV. RESULTS and DISCUSSION

(i) Molarity of I₂ solution………M
(ii) Mass content of “I₂ “ in 1 Liter of solution……g / L
(iii) Molarity of CuSO₄ solution……..M
(iv) Mass content of “CuSO₄” in 1 Liter of solution…….g / L

Discuss : Why iodine solution should be covered during titration process.

What are the sources of error in titrations involving iodine?

Why solutions containing iodide should be stored in amber glass bottles?

V. CONCLUSION

(Iodimetry) “I₂“ content in the given unknown iodine solution was determined.

(Iodometry) “CuSO₄” content in the given unknown CuSO₄ solution was determined.
1st Titration. (Iodimetry)

10 mL of Iodine solution $\equiv$ A mL of Standard Na$_2$S$_2$O$_3$ solution 0.1M

Indicator = starch solution

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<th>No.</th>
<th>Initial volume / mL</th>
<th>Final volume / mL</th>
<th>Difference / mL</th>
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Mean = A mL

**Calculation**

Iodine + Sodium Thiosulphate $\rightarrow$ Sodium Iodide + Sodium persulphate

I$_2$ (aq) + 2Na$_2$S$_2$O$_3$(aq) $\rightarrow$ 2NaI(aq) + Na$_2$S$_4$O$_6$(aq)

Mole Ratio of I$_2$ (aq) : Na$_2$S$_2$O$_3$(aq) = 1 : 2

\[
\frac{\text{moles of I}_2}{\text{moles of Na}_2\text{S}_2\text{O}_3} = \frac{1}{2} = \frac{M_{I_2} \cdot V_{I_2}}{M_{Na_2S_2O_3} \cdot V_{Na_2S_2O_3}}
\]

\[
\therefore 2M_{I_2} \cdot V_{I_2} = M_{Na_2S_2O_3} \cdot V_{Na_2S_2O_3}
\]

\[
M_{I_2} = \frac{M_{Na_2S_2O_3} \cdot x \cdot V_{Na_2S_2O_3}}{2V_{I_2}}
\]

(i) \[M_{I_2} = \frac{0.1M \cdot AmL}{2 \times 10 mL} = ^\prime ^\prime a''M\]

(ii) \[\frac{g}{L} \text{ of I}_2 = ^\prime ^\prime a''M \cdot x \cdot \text{molar mass of I}_2 \cdot (254 \cdot \frac{g}{mol}) = 254a\]
2\textsuperscript{nd} Titration. (Iodometry)

10 mL of CuSO\textsubscript{4} solution \(\equiv\) B mL of Standard Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solution 0.1M

Indicator = starch solution

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Mean = B mL

Calculation

Copper (II) sulphate + Potassium Iodide \(\rightarrow\) Copper(I)iodide + Potassium sulphate + Iodine

\[2\text{CuSO}_4\text{(aq)} + 4\text{KI (aq)} \rightarrow 2\text{CuI}_2\text{(aq)} + 2\text{K}_2\text{SO}_4\text{(aq)} + \text{I}_2\text{(aq)}\]

Iodine + Sodium Thiosulphate \(\rightarrow\) Sodium Iodide + Sodium persulphate

\[\text{I}_2\text{(aq)} + 2\text{Na}_2\text{S}_2\text{O}_3\text{(aq)} \rightarrow 2\text{NaI(aq)} + \text{Na}_2\text{S}_4\text{O}_6\text{(aq)}\]

Mole Ratio of

\[
\begin{align*}
\text{CuSO}_4\text{(aq)} : \text{I}_2\text{(aq)} : \text{Na}_2\text{S}_2\text{O}_3\text{(aq)} \\
2 & : 1 \\
1 & : 2
\end{align*}
\]

Mole Ratio of

\[
\begin{align*}
\text{CuSO}_4\text{(aq)} : \text{Na}_2\text{S}_2\text{O}_3\text{(aq)} \\
2 & : 2 \\
1 & : 1
\end{align*}
\]

\[
\frac{\text{moles of CuSO}_4}{\text{moles of Na}_2\text{S}_2\text{O}_3} = \frac{1}{1} = \frac{M_{\text{CuSO}_4} \cdot V_{\text{CuSO}_4}}{M_{\text{Na}_2\text{S}_2\text{O}_3} \cdot V_{\text{Na}_2\text{S}_2\text{O}_3}}
\]

\[\therefore M_{\text{CuSO}_4} \cdot V_{\text{CuSO}_4} = M_{\text{Na}_2\text{S}_2\text{O}_3} \cdot V_{\text{Na}_2\text{S}_2\text{O}_3}\]

\[M_{\text{CuSO}_4} = \frac{M_{\text{Na}_2\text{S}_2\text{O}_3} \cdot V_{\text{Na}_2\text{S}_2\text{O}_3}}{V_{\text{CuSO}_4}}\]

(i) \[M_{\text{CuSO}_4} = \frac{0.1M \times \text{BmL}}{10\text{mL}} = \text{"b" M}\]

(ii) \[\frac{\text{g CuSO}_4}{L} = \text{"b" M \times \text{molar mass of CuSO}_4(159.5 \frac{\text{g}}{\text{mol}})} = 159.5\text{b} \]