

Experiment no. 3:

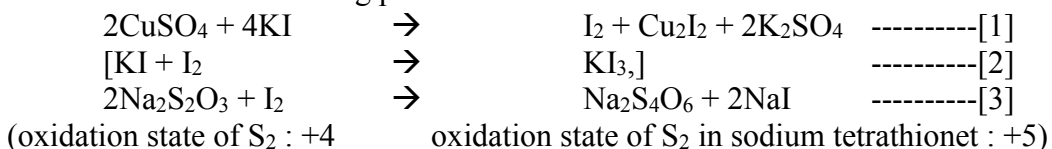
Objective: To determine the strength (in g/L) of the given unknown strength sodium thiosulphate (hypo) solution by a known strength (5.0000 g/L) standard copper sulphate solution.

Equivalent wt. of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$): 248.18

Equivalent wt. of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$): 249.68

Theory: The strength of sodium thiosulphate (hypo) solution is determined by iodometric method (**Note 1**). When KI is added to the solution of copper sulphate, an equivalent amount of I_2 is liberated along with the formation white precipitate (of cuprous iodide, Cu_2I_2). This *free* iodine (I_2), which remains in solution as $[\text{KI}_3]$ complex (**Note 2**) is then titrated with sodium thiosulphate solution using starch as indicator (**Note 3**). At the end point of the titration, the blue colour (due to formation of starch – iodine complex) of solution will disappear and a white precipitate of the Cu_2I_2 will remain in conical.

The reactions that are taking place are:



Procedure: Burette was rinsed and filled up to the zero mark with hypo solution. 10ml of supplied known strength copper sulphate solution was pipetted out in a clean conical flask. 5ml of 5% KI solution was added in that conical flask and mixed well (**Note 4**). The solution was kept for 1-2min. (**Note 5**). The solution became dark yellow due to the liberated I_2 which remains in the solution as KI_3 complex; stabilization of I_2 in water solution (eqn. 1). The liberated I_2 was titrated with hypo solution added from the burette. The dark yellow colour was faded slowly on addition of hypo solution. When the solution become light yellow (straw colour), 2-3 drops of freshly prepared starch solution (**Note 6**) was added as indicator (**Note 7**). The solution became deep blue in colour due to the formation of iodo-starch complex. Hypo solution was added further drop wise with constant stirring until the blue colour disappears (**Note 8**) and white precipitate of Cu_2I_2 remains. This was the end point of the titration. Burette reading was recorded. The titration was repeated until concordant readings were obtained.

Observation and Calculations:

Weight of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ salt dissolved in distilled water: 5.0000 g/L

Normality of the solution, $N_1 = 5.0000 / 249.68$

a) Titration of copper sulphate solution with unknown strength hypo solution:

Sl. No.	Vol. of copper sulphate solution taken (V_1)	Burette readings (ml)		Vol. of hypo soln. needed (ml)
		Initial	Final	
1.	10ml			
2.				
3.				
4.				

Concordant reading:ml (V_2)

Since, 1gram-equivalent wt. of copper sulphate \equiv 1gram-equivalent wt. of sodium thiosulphate

$$N_1 \times V_1 = N_2 \times V_2$$
$$N_2 = (5.0000 / 249.68 \times 10) / V_2 \quad (\text{where, } N_2 \text{ is the strength of hypo sol.})$$

Hence, strength of the unknown hypo solution = $N_2 \times \text{eq. wt. of sodium thiosulphate (g/L)}$

$$= [\{(5.0000 / 249.68) \times 10\} / V_2] \times 248.18 \text{ g/L}$$

Result: The strength of the supplied unknown strength hypo solution wasg/L

Note 1: In this redox titration, iodine was used indirectly as an oxidizing agent and is called iodometric titration. Oxidizing agent, CuSO_4 , liberates iodine from KI and that iodine was titrated with sodium thiosulphate solution (reducing agent). The amount of iodine liberated from iodide (i.e., KI) is equivalent to the quantity of the oxidizing agent (CuSO_4) present.

On the other hand, when the standard iodine solution is *directly* titrated by a reducing agent (such as sodium thiosulphate), then the titration is called as iodimetry titration.

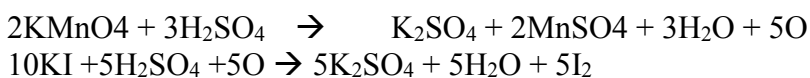
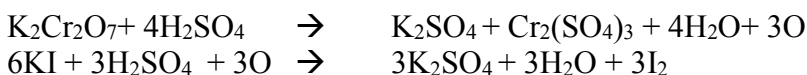
These two types of titration are also called iodine titration.

Examples of other oxidizing and reducing agents:

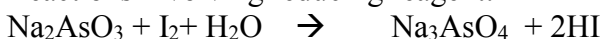
$\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 (oxidizing agents)

Arsenites, sulphites and stannous chloride (reducing agents)

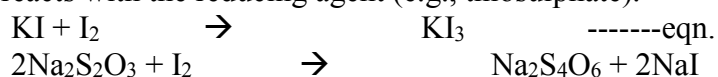
Reactions involving oxidizing reagents:



Reactions involving reducing reagent:



Note 2: I₂ (iodine) is volatile at room temperature and is not completely soluble in water. To keep the produced I₂ in solution, *excess* KI is added which makes [KI₃] complex (eqn.) and thus stabilizes in solution. This [KI₃] is a weak complex and readily liberate I₂ which reacts with the reducing agent (e.g., thiosulphate).



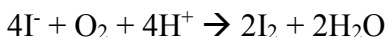
This amount of KI is more than the exact amount necessary to reduce Cu²⁺ (i.e., CuSO₄) to Cu¹⁺ (i.e., Cu₂I₂): 5% KI means 0.30N. 5ml 0.30N KI (eq. wt. 167) solution when added in 10ml 0.03N CuSO₄ (generally the strength of the supplied CuSO₄ solution), strength of KI solution becomes (5ml x 0.3N = 15ml x X) 0.1N. On the other hand, normality of 0.03N CuSO₄ in reaction mixture is 0.02N (10ml x 0.03N = 15ml x X). So the KI is added 5 times in excess.

Note 3: Starch solution (in water) is used as indicator. Starch can be divided into two types. The one with straight chain compound is called amylose (available from potato), which gives intense blue colour with I₂. It is probably that the straight chain takes a spiral form on reaction with I₂ and produces intense blue colour. The one with branched chain is called amylopectin and from purple-red colour complex with I₂.

A solution of iodine in aqueous iodide has a dark yellow colour. So the colourless solution of the I₂ can itself serve as the indication for the end point (i.e., iodine can itself acts as indicator). But the end point can be more easily detectable by using the starch solution. Starch reacts with I₂ to form an intensely blue-colored complex, which is visible even in low concentration (~2 x 10⁻² M). This colour sensitivity decreases with increase in temp, external solvents (e.g., ethanol) and strong acid.

Note 4: Avoid vigorous shaking to eliminate any possibility of liberation of I₂ gas out of the solution.

Note 5: Avoid exposing the solution to direct sunlight since it accelerate the rate of aerial oxidation of I⁻ as follows:



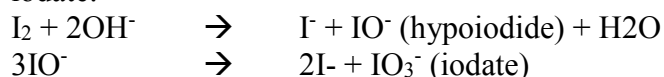
Note 6: Starch solution should be added in the titration mixture when the colour of the solution fades from dark yellow to light yellow (straw colour). If the starch is added when the concentration of I₂ is high (like at the beginning of the titration), starch will make a

permanent blue-coloured adsorbed complex with iodine. This colour will remain even it reaches the end point of the titration and hence will produce wrong result.

Note 7: The only advantage of using starch solution is that it is inexpensive. There are some disadvantages like i) starch is insoluble in cold water. ii) starch solution (colloid) cannot be kept prepared for long time (unstable). iii) it produces permanent blue colour complex when the concentration of I₂ is high. That is why it should be added just prior to the end point. iv) When the solution is diluted, the end point is difficult to determine. These disadvantages can mostly be overcome by choosing sodium starch glycollate instead of potato starch.

Note 8: Wait for 10 sec to confirm that colour change is stable.

Note 9: For accurate result, the solution should be acidic, preferably pH 4 –5.5. If the pH is more than 8, (i.e., basic medium) the I₂ reacts with hydroxide and produce iodide and iodate:



Note 10: Preparation of CuSO₄ solution: Weigh the appropriate amount of CuSO₄.5H₂O crystals. Dissolve in appropriate amount of distilled water. Small amount of acetic acid must be added to check the hydrolysis (for 250ml N/30 CuSO₄ solution, about 5ml of acetic acid is added).

Experiment no. 4:

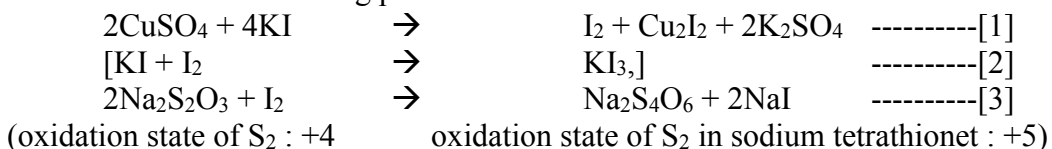
Objective: To determine the amount of copper (in g/L) in the given sample solution of copper sulphate (bottle no. XY) by supplied sodium thiosulphate (hypo) solution as an intermediate solution. Provided a known strength standard copper sulphate solution (4.5000 g/L).

Equivalent wt. of copper: 63.54

Equivalent wt. of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$): 249.68

Theory: The strength of copper sulphate solution is determined by iodometric method (Note 1). When KI is added to the solution of copper sulphate, an equivalent amount of I_2 is liberated along with the formation white precipitate (of cuprous iodide, Cu_2I_2). This free iodine (I_2), which remains in solution as $[\text{KI}_3]$ complex (Note 2) is then titrated with sodium thiosulphate solution using starch as indicator (Note 3). At the end point of the titration, the blue colour (due to formation of starch – iodine complex) of the solution will disappear and a white precipitate of the Cu_2I_2 will remain in conical.

The reactions that are taking place are:



Procedure:

(a) *Standardization of hypo solution with the help of known strength standard copper sulphate solution*

Burette was rinsed and filled up to the zero mark with hypo solution. 10ml of supplied known strength copper sulphate solution was pipetted out in a clean conical flask. 5ml of 5% KI solution was added in that conical flask and mixed well (Note 4). The solution was kept for 1-2min. (Note 5). The solution became dark yellow due to the liberated I_2 which remains in the solution as KI_3 complex; stabilization of I_2 in water solution (eqn. 1). The liberated I_2 was titrated with hypo solution added from the burette. The dark yellow colour was faded slowly on addition of hypo solution. When the solution become light yellow (straw colour), 2-3 drops of freshly prepared starch solution (Note 6) was added as indicator (Note 7). The solution become deep blue in colour due to the formation of iodo-starch complex. Hypo solution was added further drop wise with constant stirring until the blue colour disappears (Note 8) and white precipitate of Cu_2I_2 remains. This was the end point of the titration. Burette reading was recorded. The titration was repeated until concordant readings were obtained.

(b) *Determination of the strength of given unknown copper sulphate solution:* The same procedure was repeated for the unknown strength copper sulphate solution and readings were recorded.

Observation and Calculations:

Weight of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ salt dissolved in distilled water: 4.5000 g/L

Normality of the solution, $N_1 = 4.5000 / 249.68$

a) Titration of copper sulphate solution with unknown strength hypo solution:

Sl. No.	Vol. of copper sulphate solution taken (V_1)	Burette readings (ml)		Vol. of hypo soln. needed (ml)
		Initial	Final	
1.	10ml			
2.				
3.				
4.				

Concordant reading:ml (V_2)

b) Titration of with *unknown* strength of copper sulphate solution with the hypo solution:

Sl. No.	Vol. of copper sulphate solution taken (V_3)	Burette readings (ml)		Vol. of hypo soln. needed (ml)
		Initial	Final	
1.	10ml			
2.				
3.				
4.				

Concordant reading:ml (V_4)

Since, 1gram-equivalent wt. of copper sulphate \equiv 1gram-equivalent wt. of sodium thiosulphate

$$N_1 \times V_1 = N_2 \times V_2$$
$$N_2 = (4.5000 / 249.68 \times 10) / V_2 \quad (\text{where, } N_2 \text{ is the strength of hypo sol.})$$

For unknown copper sulphate solution:

$N_3 \times V_3 = N_2 \times V_4$ (where, N_3 is the strength of unknown strength copper sulphate solution.)

$$N_3 = (N_2 \times V_4) / 10$$

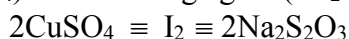
Hence, amount of copper in the unknown strength copper sulphate solution = $N_3 \times \text{eq. wt. of copper (g/L)}$

$$= N_3 \times 63.54 \text{ g/L}$$

Result: The amount of copper in the supplied unknown (Bottle no. XY) strength copper sulphate solution wasg/L

NOTES:

Note 1: In this redox titration, iodine was used indirectly as an oxidizing agent and is called iodometric titration. Oxidizing agent, CuSO_4 , liberates iodine from KI and that iodine was titrated with sodium thiosulphate solution (reducing agent). The amount of iodine liberated from iodide (i.e., KI) is equivalent to the quantity of the oxidizing agent (CuSO_4) and reducing agent ($\text{Na}_2\text{S}_2\text{O}_3$) present.

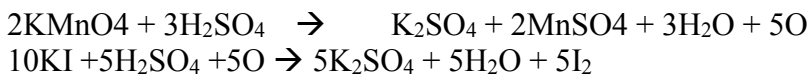
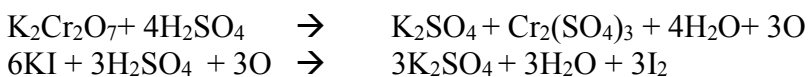


On the other hand, when the standard iodine solution is *directly* titrated by a reducing agent (such as sodium thiosulphate), then the titration is called as iodimetry titration. These two types of titration are also called iodine titration.

Examples of other oxidizing and reducing agents:

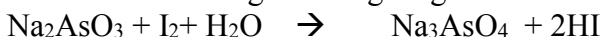
$\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 (oxidizing agents)

Reactions involving these oxidizing reagents:



Arsenites, sulphites and stannous chloride (reducing agents)

Reactions involving reducing reagent:



Note 2: I_2 (iodine) is volatile at room temperature and is not completely soluble in water. To keep the produced I_2 in solution, *excess* KI is added which makes $[\text{KI}_3]$ complex (eqn.) and thus stabilizes the I_2 in solution. This $[\text{KI}_3]$ is a weak complex and readily liberate I_2 which reacts with the reducing agent (e.g., thiosulphate).





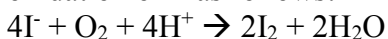
The amount of the KI added is actually more than the exact amount necessary to reduce Cu^{2+} (i.e., CuSO_4) to Cu^{1+} (i.e., Cu_2I_2): 5% KI means 0.30N. 5ml 0.30N KI (eq. wt. 167) solution when added in 10ml 0.03N CuSO_4 (generally the strength of the supplied CuSO_4 solution), strength of KI solution becomes (5ml x 0.3N = 15ml x X) 0.1N. On the other hand, normality of 0.03N CuSO_4 in reaction mixture is 0.02N (10ml x 0.03N = 15ml x X). So the KI is added 5 times in excess.

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A solution of iodine in aqueous iodide has a dark yellow colour. So the colourless solution of the I_2 can itself serve as the indication for the end point (i.e., iodine can itself acts as indicator). But the end point can be more easily detectable by using the starch solution. Starch reacts with I_2 to form an intensely blue-coloured complex, which is visible even in low concentration ($\sim 2 \times 10^{-2}$ M). This colour sensitivity decreases with increase in temp, external solvents (e.g., ethanol) and strong acid.

Note 4: Avoid vigorous shaking to reduce any possibility of liberation of I_2 out of the solution.

Note 5: Avoid exposing the solution to direct sunlight since it accelerate the rate of aerial oxidation of I^- as follows:

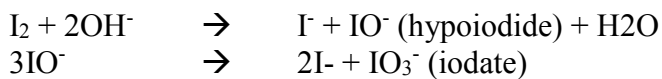


Note 6: Starch solution should be added in the titration mixture when the colour of the solution fades from dark yellow to light yellow (straw colour). If the starch is added when the concentration of I_2 is high (like at the beginning of the titration), starch will make a *permanent* blue-coloured adsorption complex with iodine. This colour will remain even it reaches the end point of the titration and hence will produce wrong result.

Note 7: The only advantage of using starch solution is that it is inexpensive. There are some disadvantages like i) starch is insoluble in cold water. ii) starch solution (colloid) cannot be kept prepared for long time (unstable). iii) it produces permanent blue colour complex when the concentration of I_2 is high. That is why it should be added just prior to the end point. iv) When the solution is diluted, the end point is difficult to determine. These disadvantages can mostly be overcome by choosing sodium starch glycollate instead of potato starch.

Note 8: Wait for 10 sec to confirm that colour change is stable.

Note 9: For accurate result, the solution should be acidic, preferably pH 4 –5.5. If the pH is more than 8, (i.e., basic medium) the I_2 reacts with hydroxide and produce iodide and iodate:



Note 10: Preparation of CuSO₄ solution: Weigh the appropriate amount of CuSO₄.5H₂O crystals. Dissolve in appropriate amount of distilled water. Small amount of acetic acid must be added to check the hydrolysis (for 250ml N/30 CuSO₄ solution, about 5ml of acetic acid is added).

Questionnaires on Iodometric titration:

1. What are 'iodometric', 'iodimetric', 'iodine' titrations?
2. Explain the roles of CuSO₄, N₂S₂O₃ and KI in your experiment. Write down the reactions involved.
3. Why is KI added '*in excess*'?
4. What is the preferred pH range for doing this titration?
5. Explain the reasons for the appearance of dark yellow, straw, blue and white color in different stages of your titration.
6. Why is Starch added in the later stage of titration (instead of at the beginning of the titration)?
7. Why it is necessary to use '*freshly*' prepared starch solution?
8. What are advantages and disadvantages of using starch solution as indicator?
9. How to prepare CuSO₄ solution?
10. Why should you avoid 'vigorous shaking' and exposure to direct sunlight'?