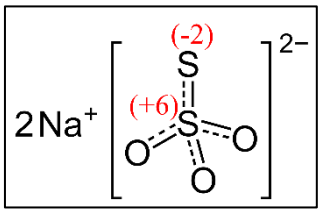
Experiment No.	

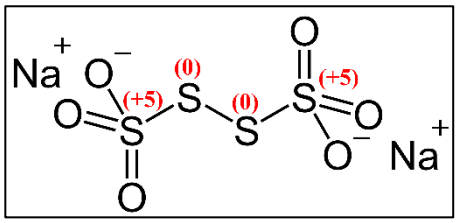
Objective: To determine the strength (in g/L) of the given unknown strength sodium thiosulphate (hypo) solution by a known strength (5.0000 g/L) standard copper sulphate solution.
Equivalent wt. of sodium thiosulphate ($Na_2S_2O_3.5H_2O$): 248.18 g
Equivalent wt. of copper sulphate ($CuSO_4.5H_2O$): 249.68 g

Theory: The strength of sodium thiosulphate (hypo) solution is determined by iodometric method. When KI is added to the solution of copper sulphate, an equivalent amount of I_2 is liberated along with the formation of white cuprous iodide (Cu_2I_2). This *free* iodine I_2, which remains in solution as potassium triiodide [KI_3] complex is then titrated with sodium thiosulphate solution using starch as indicator. At the end point of the titration, the blue colour (due to the formation of starch – iodine complex) of solution will disappear and a white precipitate of the Cu_2I_2 will remain in conical flask.
The reactions that are taking place are:

$2CuSO_4 + 4KI \rightarrow I_2 + Cu_2I_2 + 2K_2SO_4$ ----------[1]
$[KI + I_2 \rightleftharpoons KI_3]$ ----------[2]
$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$ ----------[3]

(oxidation state of S : +4 oxidation state of S in sodium tetrathionet : +5)





Procedure:

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

Observation and Calculations:

Weight of $CuSO_4.5H_2O$ salt dissolved in distilled water: 5.0000 g/L

Normality of the solution, $N_1 = \frac{5}{249.68}$

Titration of copper sulphate solution with the hypo solution of unknown strength:

Sl. No.	Vol. of copper sulphate solution taken (V_1) (ml)	Burette readings (ml)		Vol. of hypo soln. needed (ml)	Concordant reading (V_2) (ml)
		Initial	Final		
1	10	0.0			
2	10	0.0			
3	10	0.0			

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

$$N_1V_1 = N_2V_2$$

$$N_2 = \frac{5}{249.68} \times \frac{10}{V_2}$$

(where, N_2 is the strength of hypo sol.)

Hence, strength of the unknown hypo solution = N_2 x eq. wt. of sodium thiosulphate (g/L)

$$= \frac{5}{249.68} \times \frac{10}{V_2} \times 248.18 \text{ g/L}$$

Result: The strength of the supplied sodium thiosulphate (hypo) solution was found to be …….g/L.

Note 1: 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. This is an indirect method of iodine titration, and is known as iodometric titration.
On the other hand, when a standard iodine solution is *directly* titrated by a reducing agent (such as sodium thiosulphate), then the titration is called as iodimetric titration. These two types of titration are also called iodine titration.

Examples of other oxidizing and reducing agents:
$K_2Cr_2O_7$, $KMnO_4$ (oxidizing agents)
Arsenites, sulphites and stannous chloride (reducing agents)

Reactions involving oxidizing reagents:

$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$
$6KI + 3H_2SO_4 + 3O \rightarrow 3K_2SO_4 + 3H_2O + 3I_2$

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$

$10KI + 5H_2SO_4 + 5O \rightarrow 5K_2SO_4 + 5H_2O + 5I_2$

Reactions involving reducing reagent:
$Na_2AsO_3 + I_2 + H_2O \rightarrow Na_3AsO_4 + 2HI$

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 $[KI_3]$ complex and thus stabilizes in solution. This $[KI_3]$ is a weak complex and readily liberate I_2 which reacts with the reducing agent (e.g., thiosulphate).

$KI + I_2 \rightarrow KI_3$

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

This amount of KI is 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 0.30 N. 5 ml 0.30 N KI (eq. wt. 167) solution when added in 10 ml 0.03 N $CuSO_4$ solution), strength of KI solution becomes (5 ml x 0.3N = 15 ml x X)=0.1N. On the other hand, normality of 0.03N $CuSO_4$ in reaction mixture is 0.02N (10 ml x 0.03N = 15 ml x X). So the KI is added about 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 I_2. It is probably that the straight chain takes a spiral form on reaction with I_2 and produces intense blue colour. The one with branched chain is called amylopectin and from purple-red colour complex with I_2.
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 from an intense blue colour complex, which is visible even in low concentration (~2×10^{-2} M). This colour sensitivity decreases with an increase in temp, external solvents (e.g., ethanol) and strong acid.

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

Note 5: Avoid exposing the solution to direct sunlight since it accelerates the rate of aerial oxidation of I^- as follows:
$4I^- + O_2 + 4H^+ \rightarrow 2I_2 + 2H_2O$

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 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 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 glycolate 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:

$I2 + 2OH^- \rightarrow I^- + IO^-$ (hypoiodide) + H_2O

$3IO^- \rightarrow 2I- + IO3^-$ (iodate)

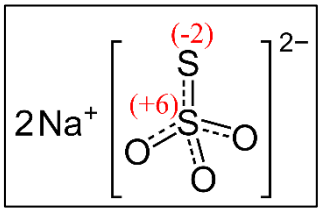
Note 10: Preparation of $CuSO_4$ solution: Weigh the appropriate amount of $CuSO_4.5H_2O$ crystals. Dissolve in appropriate amount of distilled water. A small amount of acetic acid must be added to check the hydrolysis (for 250 ml N/30 $CuSO_4$ solution, about 5 ml of acetic acid is added).

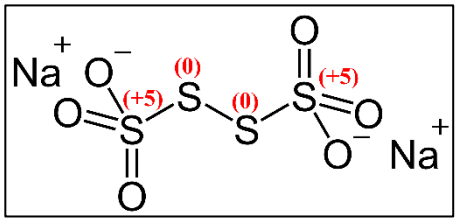
Experiment No.	

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). [Just for example. Check on the day of experiment.]
Equivalent wt. of copper: 63.54 g
Equivalent wt. of cupper sulphate ($CuSO4.\ 5H_2O$): 249.68

Theory: The strength of sodium thiosulphate (hypo) solution is determined by iodometric method. When KI is added to the solution of copper sulphate, an equivalent amount of I_2 is liberated along with the formation of white cuprous iodide (Cu_2I_2). This *free* iodine I_2, which remains in solution as potassium triiodide [KI_3] complex is then titrated with sodium thiosulphate solution using starch as indicator. At the end point of the titration, the blue colour (due to the formation of starch – iodine complex) of solution will disappear and a white precipitate of the Cu_2I_2 will remain in conical flask.
The reactions that are taking place are:

$2CuSO_4 + 4KI \rightarrow I_2 + Cu_2I_2 + 2K_2SO_4$ ----------[1]
$[KI + I_2 \rightleftharpoons KI_3]$ ----------[2]
$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$ ----------[3]
(oxidation state of S : +4 oxidation state of S in sodium tetrathionet : +5)





Procedure:

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

1. A burette was rinsed and was filled up to the zero mark with hypo solution.
2. 10 ml of supplied and of known strength of copper sulphate solution was pipetted out in a clean conical flask.
3. 5 ml of 5% KI solution was added in that conical flask and mixed well. The solution was kept for 1-2 min. The solution became dark yellow due to the liberated I_2 which remains in the solution as KI_3 complex.

4. The iodine was titrated with hypo solution added from the burette. The dark yellow colour faded slowly on addition of hypo solution. When the solution become light yellow (straw colour), 2-3 drops of freshly prepared starch solution was added as an indicator. The solution turned deep blue in colour due to the formation of iodo- starch complex.

5. Hypo solution was added further drop wise with constant stirring until the blue colour disappears and white precipitate of Cu_2I_2 remains. This was the end point of the titration.

The burette reading was recorded.

6. The titration was repeated until concordant readings were obtained.

(b) Determination of the strength of the 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 $CuSO_4.5H_2O$ 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 the supplied hypo solution:

Sl. No.	Vol. of copper sulphate solution taken (V_1) (ml)	Burette readings (ml)		Vol. of hypo soln. needed (ml)	Concordant reading (V_2) (ml)
		Initial	Final		
1	10	0.0			
2	10	0.0			
3	10	0.0			

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

Sl. No.	Vol. of copper sulphate solution taken (V_3) (ml)	Burette readings (ml)		Vol. of hypo soln. needed (ml)	Concordant reading (V_4) (ml)
		Initial	Final		
1	10	0.0			
2	10	0.0			
3	10	0.0			

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

$$N_1 \times V_1 = N_2 \times V_2$$

$$N_2 = \frac{5}{249.68} \times \frac{10}{V_2}$$

(where, N_2 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 x eq. wt. of copper (g/L)

$= N_3 \times 63.54$ g/L

Hence, amount of copper sulphate in the unknown strength copper sulphate solution = N3 x eq. wt. of copper sulphate (g/L)

$= N_3 \times 249.68$ g/L

Result: The amount of **copper** in the supplied copper sulphate solution was found to be…….g/L

The amount of **copper sulphate** in the supplied copper sulphate solution was found to be…….g/L

Some important questions related to iodometry

- What are ‘iodometric’, ‘iodimetric’, ‘iodine’ titrations?
- Explain the roles of $CuSO_4$, $Na_2S_2O_3$ and KI in your experiment. Write down the reactions involved.
- Why is KI added ‘in excess’?
- What is the preferred pH range for performing this titration?
- Explain the reasons for the appearance of dark yellow, straw, blue and white color in different stages of your titration.
- Why is starch added in the later stage and not in the beginning of the titration?
- Why is it necessary to use a ‘freshly’ prepared solution of starch?
- What are the advantages and disadvantages of using starch solution as indicator?
- How to prepare a standard copper sulphate solution?
- Why should you avoid the titration mixture to undergo vigorous shaking and to be exposed to direct sunlight?