Estimation of Cu(II) using sodium thiosulphate solution (Iodometrically)

BSc. (H) Physics
Semester-III
GE: Chemistry

Aim: Estimation of Cu(II) using sodium thiosulphate solution (iodometrically)

Oxidation-Reduction (Redox) Reactions:

- Reaction involving change of oxidation number or transfer of electrons among the reacting substances.
- The standard solutions are either oxidising or reducing agents.
- The principal oxidising agents are $KMnO_4$, $K_2Cr_2O_7$, $Ce(SO_4)_2$, I_2, KIO_3, and $KBrO_3$.
- Frequently used reducing agents are Fe(II) and Sn(II) compounds, $Na_2S_2O_3$, As_2O_3, $Hg_2(NO_3)_2$, VCl_2 or VSO_4, $CrCl_2$ or $CrSO_4$ & $TiCl_3$ or $Ti_2(SO_4)_3$.

$$\mathbf{2MnO_4^- + 5H_2C_2O_4 + 6H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2}$$

(Pink) (Colourless)

$$\mathbf{2MnO_4^- + 10Fe^{2+} + 16H^+ \longrightarrow 2Mn^{2+} + 10Fe^{3+} + 8H}$$

(Pink) (Colourless)

$$\mathbf{Cr_2O_7 2- + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O}$$

(Orange) (Green)

$$\mathbf{CuSO_4 + 4KI \longrightarrow Cu_2I_2 + K_2SO_4 +}$$

(Blue) (White ppt)

$$\mathbf{2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI}$$

(Sod. Thiosulphate) (Sod. Tetrathionate)

Iodine Titration

- ❖ The redox titration involving iodine directly or indirectly as an oxidizing agent are called iodine titrations.

Iodimetric Titrations: Titrations with a standard solution of iodine.

<u>Applications of Iodimetric Titrations</u>:

- ★ Determination of $S_2O_3^{2-}$
- ★ Determination of SO_3^{2-}
- ★ Determination of AsO_3^{3-}
- ★ Determination of $SnCl_2$

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

$$Na_2SO_3 + I_2 + H_2O \longrightarrow Na_2SO_4 + 2HI$$

$$Na_3AsO_3 + I_2 + H_2O \longrightarrow Na_3AsO_4 + 2HI$$

<u>Iodometric Titrations</u>: Iodine titrations in which some oxidizing agent liberate I_2 from an I- solution and then liberated I_2 is titrated with a standard solution of reducing agent.

Applications of Iodometric Titrations

Estimation of $CuSO_4$, $K_2Cr_2O_7$, $KMnO_4$, Fe^{3+}, H_2O_2, Br_2, Cl_2 etc.

$$\underset{\text{(Blue)}}{CuSO_4} + 4KI \longrightarrow \underset{\text{(White ppt)}}{Cu_2I_2} + K_2SO_4 + I_2$$

$$\underset{\text{(Sod. Thiosulphate)}}{2Na_2S_2O_3} + I_2 \longrightarrow \underset{\text{(Sod. Tetrathionate}}{Na_2S_4O_6} + 2NaI$$

$$\underset{\text{Orange}}{K_2Cr_2O_7} + 4H_2SO_4 \longrightarrow \underset{\text{Green}}{Cr_2(SO_4)_3} + K_2SO_4 + 4H_2O + 3O$$

$$6KI + 3H_2SO_4 + 3O \longrightarrow 3K_2SO_4 + 3H_2O + 3I_2$$

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

DETECTION OF THE END POINT:

- In this titration a solution of starch is used as indicator.
- Starch reacts with iodine in the presence of iodide to form an intensely blue-colored complex, which is visible at very low concentrations of iodine.
- The color sensitivity decreases with increasing temperature of the solution.
- It cannot be used in a strongly acid medium because hydrolysis of the starch occurs.
- The great merit of starch is that it is inexpensive.

Disadvantages of Starch

- It is insoluble in cold water.
- Instability of suspensions in water
- It gives a water-insoluble complex with iodine, the formation of which precludes the addition of the indicator early in the titration (for this reason, in titrations of iodine, the starch solution should not be added until just prior to the end point when the colour begins to fade).
- There is sometimes a 'drift' end point, which is marked when the solutions are dilute.

Preparation and Use of Starch Solution:

- Make a paste of 0.1 g of soluble starch with a little water, and pour the paste, with constant stirring, into 100 mL of boiling water, and boil for 1 minute. Allow the solution to cool and add 2-3 g of potassium iodide. Keep the solution in a stoppered bottle.
- Only freshly prepared starch solution should be used.
- The same volume of starch solution should always be added in a titration.
- In the titration of iodine, starch must not be added until just before the end point is reached.
- Apart from the fact that the fading of the iodine colour is a good indication of the approach at the end point, if the starch solution is added when the iodine concentration is high, some iodine may remain adsorbed even at the end point.

The Starch-Iodine Complex

- Numerous analytical procedures are based on redox titrations involving iodine.
- Starch is the indicator of choice for these procedures because it forms an intense blue complex with iodine.
- Starch is not a redox indicator; it responds specifically to the presence of I_2, not to a change in redox potential.
- The active fraction of starch is amylose, a polymer of the sugar -D-glucose. Small molecules can fit into the center of the coiled, helical polymer.
- In the presence of starch, iodine forms I_6 chains inside the amylose helix and the color turns dark blue.

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- Starch is readily biodegraded, so it should be freshly prepared.
- A hydrolysis product of starch is glucose, which is a reducing agent. Therefore, partially hydrolyzed starch solution can be a source of error in a redox titration.

Preparation of Sodium thiosulphate Solution

- Sodium thiosulphate ($Na_2S_2O_3.5H_2O$) is readily obtainable in a state of high purity, but there is always some uncertainty as to the exact water content because of the efflorescent nature of the salt and for other reasons. The substance is therefore unsuitable as a primary standard. It is a reducing agent by virtue of the half-cell reaction:

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-}$$

Recommendations for the Preparation of Sod. Thiosulphate:

- Prepare the solution with recently boiled distilled water.
- Add 3 drops of chloroform, this improves the keeping qualities of the solution.
- Avoid exposure to light, as this tends to hasten the decomposition.

Standardisation of Sod. Thiosulphate Solution:

- The standardisation of thiosulphate solutions may be done with potassium iodate, potassium dichromate, copper and iodine as primary standards, or with potassium permanganate or cerium(lV) sulphate as secondary standards

Estimation of Cu(II) from Copper sulphate solution

Pipette 10.0 mL of $CuSO_4$ solution into a 250 mL conical flask then add a few drops of dilute sodium carbonate solution until a faint permanent precipitate remains, and this is removed by means of a drop or two of acetic acid. Then 0.25 g KI (or 2 mL of a 10 per cent solution) is added and titrate the liberated iodine with standard solution of sod. thiosulphate until the brown color of iodine fades, then add 0.4 mL of starch solution, and continue the addition of the thiosulphate solution until the blue colour commences to fade. Then add about 0.25 g of potassium thiocyanate or ammonium thiocyanate, preferably as a 10 per cent aqueous solution: the blue colour will instantly become more intense. Complete the titration as quickly as possible. The precipitate possesses a pale pink colour, and a distinct permanent end point is readily obtained

Experiment

Aim: To estimate the strength in g/L of a given copper sulphate solution being provided with an approx. N/30 sod. thiosulphate (hypo) solution.

Theory:

Step 1: $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

$2Cu^{2+} + 2I^- \longrightarrow 2Cu^+ + I_2$

or $2I^-(aq.) \longrightarrow I_2 + 2e^-$

$2Cu^{2+} + 2e^- \longrightarrow 2Cu^+$

Step 2: $I_2 + I^- \rightleftharpoons I_3^-$

(Water Insoluble) **(Water soluble)**

Step 3: $\text{Starch} + I_3^- \longrightarrow \text{Starch-}I_3$ **(Starch-triiodide complex)**

(Colourless) **(Dark Blue)**

Step 4: $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

Note:

Why starch is added just before the end point?

The starch is not added at the beginning of the titration when the iodine concentration is high. Instead, it is added just before the end point when the dilute iodine color becomes pale yellow.

There are two reasons for such timing:

First reason is that the iodine–starch complex is only slowly dissociated, and a diffuse endpoint would result if a large amount of the iodine were adsorbed on the starch.

The second reason is that most iodometric titrations are performed in strongly acid medium and the starch has a tendency to hydrolyze in acid solution.

Starch-iodine complexation is temperature dependent. At 50 ^{0}C, the color is only one-tenth as intense as at 25 ^{0}C. If maximum sensitivity is required, cooling in ice water is recommended. Organic solvents decrease the affinity of iodine for starch and markedly reduce the utility of the indicator.

Why KSCN or NH_4SCN is added?

When copper(II) is titrated iodometrically, the end point is diffuse unless thiocyanate ion is added. This is due adsorption of I_2 on the surface of the cuprous iodide precipitate and only slowly reacts with the thiosulfate titrant. The thiocyanate coats the precipitate with CuSCN and displaces the iodine from the surface. The potassium thiocyanate should be added near the end point since it is slowly oxidized by iodine to sulfate. The pH must be buffered to around 3. If it is too high, copper(II) hydrolyzes and cupric hydroxide will precipitate. If it is too low, air oxidation of iodide becomes appreciable because it is catalyzed in the presence of copper.

References

Quantitative Chemical Analysis: D.C. Harris
Vogel’s Quantitative Chemical Analysis