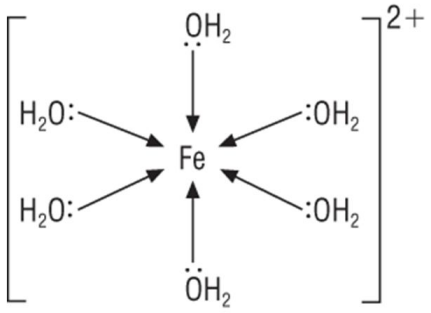
Exp No :08

Name of the Experiment: Determination of Ferrous (Iron) (Fe) Content in a Solution with Standard Potassium Permanganate ($KMnO_4$) Solution [REDOX Titration]

1. Theory

Iron is widely used in various industries, including steel production, pharmaceuticals, water treatment, and food manufacturing. Determining the iron content is neccesary to ensure the quality and purity of the final products in industries. For example, in the steel industry, the iron content directly affects the mechanical and physical properties of the steel. The presence of excessive irons in soil water leads to discoloration, foul taste, and corrosion in pipes. Therefore, monitoring of iron levels is necessary to assess the quality of drinking water and to ensure the safety and usability of natural waters in industries.

Complex ion $[Fe(H_2O)_6]^{2+}$



On laboratory scale, iron concentration is generally determined using redox titration method. In redox titrations, a reducing agent is titrated against the oxidising agent or vice versa. The reaction between the analyte and the titrant involves a transfer of electrons, resulting in a change in their oxidation states. In this experiment, Ammonium Iron(II) sulfate, or **Mohr's Salt** (named after German scientist Karl Friedrich Mohr) is used as the source of iron. Mohr salt is an inorganic light green coloured crystalline salt with the formula **$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$** containing two different cations of Fe^{2+} and NH_4^+. It is classified as a double salt of ferrous sulfateand ammonium sulfate. Like the other ferrous sulfate salts, ferrous ammonium sulfate dissolves in water to give the aquo complex $[Fe(H_2O)_6]^{2+}$, which has a octahedral molecular geometry. The amount of ferrous ion (Fe^{2+}) in the solution can be determined by a redox titration with standard potassium permanganate ($KMnO_4$).

Concerning the titration, Mohr's salt acts as a reducing agent and the $KMnO_4$ acts as an oxidizing agent. Here, $KMnO_4$ oxidized the ferrous ions to ferric ions (Fe^{3+}) and reduced to manganese dioxide (MnO_2). The experiment is performed in acidic solution as $KMnO_4$ acts as an excellent oxidizing agent in acidic environment. It is worth noting that $KMnO_4$ can act as a self-indicator in this redox titration. The characteristic color change of $KMnO_4$ from purple to pink owing to its change in oxidation state can be used to determine the endpoint of the titration without using any additional external indicator.

Initially, the secondary standard reagent, potassium permanganate solution need to standardized with the help of a standard oxalic acid solution, which is a primary standard substance. Oxalic acid reacts with acidified potassium permanganate in the following ways.

Reduction Half reaction: $2\ KMnO_4 + 3\ H_2SO_4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 3\ H_2O + 5\ [O]$

Oxidation Half reaction: $5\ (COOH)_2 + 5\ [O] \rightarrow 5\ H_2O + 10\ CO_2\uparrow$

Overall reaction: $2\ KMnO_4 + 5\ H_2C_2O_4 + 8\ H_2SO_4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 5\ H_2SO_4 + 10\ CO_2 + 8\ H_2O$

Here, the concentration of the analyte is calculated based on the stoichiometry of the balanced redox equation and the volume and concentration of the titrant used. From the stoichiometry, it is seen that two mole of oxalic acid reacts with five moles of potassium permanganate, i.e.,

$$\mathbf{2\ mol\ KMnO_4 \equiv 5\ mol\ H_2C_2O_4}$$

On next phase, the standardized $KMnO_4$ will be used to determine the content of iron in Mohr's salt. The reactions regarding the ferrous sulphate with acidified $KMnO_4$ are given below-

Reduction Half Reaction: $\mathbf{2\ KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 3\ H_2O + 5[O]}$

Oxidation Half Reaction:

$$\mathbf{[2(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + 2\ (NH_3)_2SO_4 + 13H_2O] \times 5}$$

Overall Reaction:

$$\mathbf{2\ KMnO_4 + 8\ H_2SO_4 + 10\ (NH_4)_2Fe(SO_4)_2 \cdot 6H_2O \rightarrow K_2SO_4 + 2\ MnSO_4 + 5\ Fe_2(SO_4)_3 + 10\ (NH_3)_2SO_4 + 68\ H_2O}$$

The simplified and ionic equations of the reactions are,

$$\mathbf{MnO_4^- + 8H^+ + 5\ e^- (Reduction) \rightarrow Mn^{2+} + 4\ H_2O}$$

$$\mathbf{[\ Fe^{2+}\ (Oxidation) \rightarrow\ Fe^{3+} + e^-] \times 5}$$

$$\mathbf{2MnO_4^- + 8H^+ + 5\ Fe^{2+} \rightarrow 2Fe^{3+} + Mn^{2+} + 4\ H_2O}$$

The concentration of the iron is calculated based on the stoichiometry of the balanced redox equation and the volume and concentration of the titrant used. From the balanced equation, it can be seen that 2 mole of $KMnO_4$ reacts with 5 moles of ferrous ions (Fe^2).

$$\mathbf{2\ mol\ KMno_4 \equiv 5\ mol\ Fe^{2+}}$$

Using the stoichiometry, the concentration of iron will be determined using redox titration method.

2. Apparatus

Volumetric flask (100 mL), Conical flask (250 mL), Burette, Pipette (10 mL), Funnel, Thermometer, Tripod stand, Burner, Wash bottle, Iron stand etc.

3. Chemicals

- Mohr`s Salt [$FeSO_4.\ (NH_4)_2SO_4.6H_2O$]
- Oxalic Acid Dihydrate ($C_2H_2O_4.2H_2O$)
- Potassium Permanganate ($KMnO_4$)
- Sulphuric Acid (H_2SO_4)

4. Phase

The experiment will be done in two phases

a. Standardization of potassium permanganate solution with standard oxalic acid solution.

b. Determination of Fe content in Mohr's Salts using standard potassium permanganate solution

a. <u>Standardization of potassium permanganate ($KMnO_4$) solution:</u>

- **<u>Preparation of 0.1 N oxalic acid solution</u>**:

To prepare 0.1 N 100 mL $C_2H_2O_4.2H_2O$ solution, weigh out the required amount (calculate by yourself) of $C_2H_2O_4.2H_2O$ and transfer into a 100 mL volumetric flask, dissolve it properly and make up to the mark by adding distilled water.

Strength of prepared $\mathbf{C_2H_2O_4}$ Solution= $\frac{wt.taken}{wt.¿}$ *be taken ¿* × 0.1 N

= N

- **<u>Standardization Procedure:</u>**

1. Rinse the burette with potassium permanganate ($KMnO_4$) solution and fill it.
2. Pipette out 10 mL oxalic acid di-hydrate ($C_2H_2O_4.2H_2O$) solution in a conical flask.
3. Dilute the solution up to 100 mL with distilled water.
4. Add 10 mL (3.0 N) sulphuric acid (H_2SO_4) in the solution.
5. Heat the mixture up to 60 ºC temperature before titrating with potassium permanganate (Check the temp. using thermometer).
6. Note down the initial reading before starting the titration.
7. Slowly titrate the oxalic acid solution with potassium permanganate ($KMnO_4$) solution and simultaneously while swirling the solution in the flask gently.
8. The purple colour of $KMnO_4$ disappears when it added to oxalic acid solution. The appearance of permanent pink colour will indicate the end point of titration, i.e., the complete oxidation of oxalic acid.

Table for standardization of $KMnO_4$

Number of Observation	Volume of $C_2H_2O_4$ solution, V_1 (mL)	Volume of $KMnO_4$ Solution				Remarks
		IBR (mL)	FBR (mL)	Diff. (mL)	Mean Volume, V_2 (mL)	
1.						
2.						
3.						
4.						

N.B.: IBR = Initial Burette Reading, FBR = Final Burette Reading

- **Calculation**: $S_2 = V_1S_1/V_2$

  = ---------- N solution

  = N

Where,

V_1 (Volume of $C_2H_2O_4$ solution) = mL

S_1 (Strength of $C_2H_2O_4$ solution) = N

V_2 (Volume of $KMnO_4$ solution) = mL

S_2 (Strength of $KMnO_4$ solution) = ?

Strength of 0.1 N Potassium permanganate ($KMnO_4$) is .....Y.....N

b. Determination of Fe content in Mohr's Salts

1) Take 10 mL of supplied Mohr`s salt [$FeSO_4.(NH_4)_2SO_4.6H_2O$] solution in a conical flask.

2) Dilute up to 100 mL with distilled water.

3) Add 10 mL (3.0 N) sulphuric acid (H_2SO_4).

4) Slowly titrate the ferrous solution with "**Y**" N potassium permanganate ($KMnO_4$) solutions.

5) Purple color of $KMnO_4$ disappears slowly and at the end point pink colour appears.

Table for determination Fe^{2+} content

Number of Observation	Volume of Mohr Salt (mL)	Volume of Potassium permanganate ($KMnO_4$)				Remarks
		IBR (mL)	FBR (mL)	Diff(mL)	Mean	
1						
2						
3						

- **Calculation**:

1000 mL of 1 N $KMnO_4$ can consume 55.84 gms of Fe^{2+}

1 mL of 1 N ,, ,, 55.84 / 1000 gms of Fe^{2+}

X mL of **Y N** ,, ,, (**55.84 × X × Y) / 1000**gms of Fe^{2+}

= **p** gms of Fe^{2+}

*[Here **X** and **Y** are the Vol and Strength of $KMnO_4$]*

10 mL Mohr`s Salt [$FeSO_4.(NH_4)_2SO_4.6H_2O$] solution contain **p** gms of Fe^{2+}

1 mL ,, ,, ,, **p**/10gms of Fe^{2+}

100 mL ,, ,, ,, **p** × 100 /10 gms of Fe^{2+}

= gms of Fe^{2+}

5. Result

The amount of **Ferrous (Iron)** in 100 mL supplied in Mohr Salt **[$FeSO_4.(NH_4)_2SO_4.6H_2O$]** solution is ..... gms

6. % of error

[(Std result ~ Obs result) / Std result] × 100

= %

7. Discussion

[Write down your ***Observation, Assumption, Perception, Limitations, Safety Considerations, and Possible source of Error*** regarding the experiment]

8. Key Points

a. Molecular formulae of Mohr's Salt and its hydrolysis reaction
b. Definition of double salt with example
c. Oxidizing agent and Reducing agent with examples
d. Self-Indicator
e. Why Mohr's Salt is used in determining Fe content but not other iorn salts?
f. Stability of ferrous and ferric ions.