AIM: Estimation of Fe(II) in Mohr’s salt solution using standard KMnO₄ solution via Redox titration

**Theory:** Titrations in which a reducing agent is titrated against an oxidizing agent or vice versa are called Redox titration. In a redox reaction if one substance is oxidized the other is reduced. Oxidation is defined as the process in which loss of electron from the element takes place and reduction is a process where electrons are accepted by the element or the ion. The reagent which undergoes reduction is an oxidizing agent and the reagent which undergoes oxidation is a reducing agent. The oxidation and reduction are complementary to one another and takes place simultaneously.

The equivalent weight of an oxidizing and reducing agent can be obtained by dividing molecular weight of the compound by the total number of electrons that are gained or lost in a reaction per molecule of the substance.

\[
\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- = \text{Mn}^{2+} + 4\text{H}_2\text{O}
\]

Therefore, equivalent weight of KMnO₄ = (Molecular weight of KMnO₄)/ 5

Similarly, for the oxidation of Fe^{2+} → Fe^{3+} ion

\[
\text{Fe}^{2+} - \text{e}^- = \text{Fe}^{3+}
\]

Therefore, equivalent weight of Ferrous salt = (Molecular weight of Ferrous salt)/1

In this redox titration under experiment KMnO₄ oxidizes ferrous ion of the salt to ferric ion in acidic medium and itself reduces to colorless manganous (Mn^{2+}) ion.

\[
\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- = \text{Mn}^{2+} + 4\text{H}_2\text{O}
\]

\[
[\text{Fe}^{2+} - \text{e}^- = \text{Fe}^{3+}] \times 5
\]

\[
\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} = \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \quad \text{(Ionic equation)}
\]

The actual equation is:

\[
2\text{KMnO}_4 + 10\text{FeSO}_4 + 8\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}
\]

As the change in colour in acid – base indicator depends on the pH of the reaction mixture, the change in colour of the indicator in redox titration depends upon the electrode potential of the system. Therefore, a redox indicator has to be chosen in such a way that its potential lies within that of the system. In this titration, KMnO₄, the oxidizing agent is the self indicator as it is strongly coloured (purple) and decolorizes after
reduction. Potassium permanganate is purple in its oxidized form (MnO$_4^-$) but its reduced form (Mn$^{2+}$) is colorless in acidic medium.

\[
\text{MnO}_4^- + 8\text{H}^+ + 5\text{e} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}
\]

(purple) (colorless)

As, the titration proceeds, the MnO$_4^-$ will converted to Mn$^{2+}$ and simultaneously Fe$^{2+}$ will converted to Fe$^{3+}$. When whole of the reducing agent (Fe$^{2+}$) will consumed, the oxidizing agent (MnO$_4^-$) cannot be reduced, then the addition even one drop of KMnO$_4$ solution given its colour to the solution. This indicates the end point of the titration.

**Apparatus:** Burette, pipette, conical flask, burette stand and clamp

**Chemicals:** KMnO$_4$, H$_2$SO$_4$, Mohr’s salt [(NH$_4$)$_2$SO$_4$, FeSO$_4$, 6H$_2$O].

**Procedure:**

1. Primary standard Mohr’s salt solution was provided.
2. Secondary standard KMnO$_4$ and unknown Fe(II) solution was provided.
3. **Standardization of KMnO$_4$ solution by standard Mohr’s salt solution:** Pipette out 20 mL of standard Mohr’s salt solution into a 100 mL conical flask, add 20 mL of dilute H$_2$SO$_4$ (1:8 V/V). Titrate with standard KMnO$_4$ solution from the burette with constant stirring till the first permanent pink color develops in the solution. Repeat thrice.
4. **Estimation of Fe (II) in the given solution:** Pipette out 20 mL of unknown Fe(II) solution in a 100 mL conical flask, add 20 mL of dilute H$_2$SO$_4$ (1:8 V/V). Titrate with standard KMnO$_4$ solution of known strength till the first permanent pink color develops throughout the whole mass of the solution. Take minimum 3 readings.
Observations and Calculations:

Strength of standard Mohr’s salt solution (S1) = 0.01(N)

Table 1: Standardization of KMnO₄ solution

<table>
<thead>
<tr>
<th>Entry</th>
<th>Volume of Mohr’s salt (mL) (V₁)</th>
<th>Burette Reading (mL)</th>
<th>Volume of KMnO₄ required (mL)</th>
<th>Mean volume of KMnO₄ required (mL) (V₂)</th>
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<td>Initial</td>
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Therefore, strength of KMnO₄ (S₂) can be calculated as follows:

\[ V₁S₁ = V₂S₂ \]

\[ S₂ = \frac{V₁S₁}{V₂} \text{ (N)} \]

Table 2: Unknown Mohr’s salt with KMnO₄ solution.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Volume of unknown Mohr’s salt (mL)</th>
<th>Burette Reading (mL)</th>
<th>Volume of KMnO₄ required (mL)</th>
<th>Mean volume of KMnO₄ required (mL) (V’)</th>
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1000 mL of 1(N) KMnO₄ solution = 1 equivalent of Fe = 56 g of Fe

V’ mL of S₂(N) KMnO₄ solution = 0.056 x V’ x S₂ g of Fe

20 mL solution contains (0.056 x V’ x S₂) g of Fe

1000 mL solution contains (0.056 x V’ x S₂ x 50) g of Fe

Therefore, Fe present in the solution = (0.056 x V’ x S₂ x 50) g/L

= A g/L (say)

Result can also be expressed in terms of Mohr’s salt in g/L.

56 g of Fe present in 392 g of Mohr’s salt

A g of Fe present in (392 x A)/56 g of Mohr’s salt

Therefore, amount of Fe(II) in A g/L

and amount of Mohr’s salt is (392 x A)/56 g/L
**Discussion:-**

i) Potassium permanganate (KMnO₄) is a strong oxidizing agent in acid medium. Sulphuric acid is the most suitable acid as it has no action upon permanganate in dilute solution.

ii) With dilute HCl, there is a probability that some amount of permanganate may be consumed in the formation of Cl₂ gas and thus interfere the estimation.

\[
2\text{MnO}_4^- + 10\text{Cl}^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8\text{H}_2\text{O}
\]

iii) HNO₃ cannot be used as it itself is a strong oxidizing agent and may oxidize the reducing agent, thereby may cause error in estimation.

**Precaution:-**

i) All the glass apparatus should be washed thoroughly with distilled water before use.

ii) Burette and pipette should be rinsed with the solution to be taken in it.

iii) There should not be any leakage in the burette.

iv) KMnO₄ solution should be kept in dark.

v) KMnO₄ solution should not be filtered through filter paper, it should be taken by decantation.

vi) Freshly prepared KMnO₄ should be used.

vii) H₂SO₄ should be added in excess otherwise brown precipitate of MnO₂ may appear.

viii) The titration (conical flask) should be placed on white paper or board to identify properly the color change at the end point.