A Text Book of Chemistry -Semester III

substance is called as reducing agent (reductant) i.e. reducing agent losses electron and itself oxidized to higher valency state.

The oxidizing agents are potassium permanganate, potassium dichromate, potassium iodate, ceric salts and I_2 solution etc. The reducing agents are sodium oxalate, oxalic acid Ferrous sulphate, ferrous ammonium sulphate (Mohr's Salt) etc.

Electrode potential measures the electron releasing tendency of a redox system. electrode potential of redox system can be determined by the combination of two half cells. One half cell which release electron (oxidation) and other half cell which gain electron (reduction)

2.15 Important oxidation- reduction titration reagent

a) Potassium permagnate (KMnO4)

Potassium permagnate (KMnO₄) is most useful oxidizing agent. The colour of KMnO₄ solution is pink. In order to prepare 1M solution KMnO₄, 158 g KMnO₄ dissolve while 31.6 g KMnO₄ dissolve to prepare 1N solution.

Equivalent weight of KMnO₄ =
$$\frac{\text{Molecular weight of KMnO_4}}{\text{Number of }e^{-} \text{ accepted by one molecule of oxidising agent}}$$
$$= \frac{158}{5}$$

Potassium permagnate widely used in acidic medium. In acidic medium, manganese in KMnO₄ reduces from Mn⁺⁷ to Mn⁺². The chemical reaction of KMnO₄ in acidic medium represented as follow,

$$2K_{(+7)}^{2KMnO_4} + 3H_2SO_4 \rightarrow K_2SO_4 + 2M_2SO_4 + 3H_2O + 5[O]$$

Among the mineral acids HCl, HNO₃ and H₂SO₄, only H₂SO₄ is most suitable for use with potassium permanganate. Potassium permanganate cannot be used with HCl because of its reducing action and cannot be used with HNO₃ because HNO₃ is itself oxidizing agent. The redox titration with KMnO₄ can be performed using reducing agent like FeSO₄, oxalic acid, etc.

The reaction with FeSO₄ is

 $2KMnO_4 + 10 FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O_4$ The reaction with oxalic acid is Ferric sulphate

 $2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O_4$

In redox titration with KMnO₄, colour changes from pink to colourless due to formation of colourless K_2SO_4 and $2MnSO_4$. The advantage of potassium permanganate is that it itself act as an indicator. The following are drawbacks of its,

- i) Its solution protected from sunlight.
- ii) It is less stable in alkaline and acidic medium. iii) It cannot be used as a primary standard.

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b) Potassium dichromate (K₂Cr₂O₇)

Potassium Dichromate is strong oxidizing agent and more useful than KMnO4. Potassium dichromate is a salt of chromic acid K Cr₂O₇. The chemical reaction of Potassium dichromate in acidic solution gives three atoms of oxygen.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

The ionic reaction represented as

 $\operatorname{Cr}_{2} \operatorname{O}_{7}^{2^{-}} + 14 \operatorname{H}^{+} + 6e^{-} \longrightarrow 2 \operatorname{Cr}_{(+3)}^{3^{+}} + 7 \operatorname{H}_{2} \operatorname{O}_{(+3)}$

During reaction of potassium dichromate in acidic solution, a molecule of potassium dichromate gain 6 election and oxidation state of chromium reduces from +6 to +3.

Equivalent wt. of $K_2Cr_2O_7 = \frac{\text{Molecular wt. of } K_2Cr_2O_7}{6}$ $=\frac{294}{6}=49$

The acidic solution of $K_2Cr_2O_7$ with Ferrous ammonium sulphate (Mohr's salt) undergo following chemical reaction.

 $K_2Cr_2O_7 + 6 \text{ FeSO}_4 + 7 \text{ H}_2SO_4 \longrightarrow K_2SO_4 + Cr_2 (SO_4)_3 + 7 \text{ H}_2O + 3\text{Fe}_2 (SO_4)_3$

Potassium dichromate solution is stable towards light and used as a primary standard.

c) lodine (l₂) solution

Iodine is mild oxidizing agent and oxidizes ions such as thiosulphate(S₂O₃²⁻), sulphite $(S0_3^{2-})$, arsenite (ASO₃³⁻) and Ferrous ions quantitatively in neutral or moderately acid solution. There are two types of titration involving iodine namely iodimetry and iodometry.

 $I_2 + 2e^- \rightarrow 2I^-$

i) lodimetry: The titration in which standard iodine solution is used as oxidant and directly treated with a reducing agent is known as lodimetry. It includes the determination of thiosulphate, sulphilite, arsenites, etc.

The reactions involved are

 $I_2 + 2S_2O_3^{2} \rightarrow S_4O_6^{2} + 2I^{-1}$ $I_2 + SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2I^ I_2$ +AsO₃³⁻ + H₂O \rightarrow AsO₄³⁻ + 2H⁺ + 2I⁻

II) lodometry: The titration in which lodine is liberated by oxidation of an iodine ion (usually potassium iodide) by a strong oxidizing agent in neutral or slightly acidic solution.

 $Cr_2O_7 + 6I^+ + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$ $2MnO_4^{-} + 10I^{-} + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$ $Br_2 + 2I^- \longrightarrow 2Br^+ + I_2$

lodine is involved in an equivalent amount and is titrated with a standardized solution of a reducing agent, generally sodium thiosulphate.