Oxidation-Reduction Titrations or Redox Titrations

The titration based on oxidation and reduction reaction between the titrant and analyte is called Redox titration. Oxidation is the process of the addition of oxygen or removal of hydrogen/electron and reduction involves the process of addition of hydrogen/electrons or removal of oxygen. Oxidizing agents are substances that gain one or more electrons and are reduced. Reducing agents are substances that lose one or more electrons and are oxidized. That is, oxidizing agents are electron acceptors, and reducing agents are electron donors.

In redox systems, the titration method can be adopted to determine the strength of a reductant/oxidant using a redox sensitive indicator. Redox titrations involving potassium permanganate are called permanganometric titrations. In these reactions, MnO_4^- ions acts as the self indicator.

Redox reaction can also be a basis of titration. We know that redox reaction are a combination of two reactions; oxidation and reduction reaction. The oxidation reaction involves increment in the oxidation state whereas in a reduction, the oxidation number of reactant molecules reduces by certain numbers. The substance that oxidised is known as **reducing agent**. On the contrary, the substance that reduces is known as an **oxidising agent** in the redox reaction.

Redox Reaction

Redox reaction is just like an acid-base reactions. An acid can show its acidic properties in the presence of base only. Like acid-base reaction, redox reactions are concerned with the transfer of electrons between species.

One compound has to give electron and oxidizes and another compound has to accept electron. Hence redox reaction is a combination of oxidation-reduction reaction. Each reaction by itself is known a **"half-reaction"** and whole reaction is called as redox reaction. For example,

$$\mathbf{Cu\ (s) \rightarrow\rightarrow Cu^{2}+ + 2\ e^{-}}$$

This is oxidation half-reaction which implies that copper get oxidized to copper (ii) ion. Here copper is a reducing agent. Another half reaction is reduction half reaction; in which two silver ions accept two electrons to form silver atom. Here Ag+ is the oxidizing agent.

$$\mathbf{2\ Ag^{+}\ (aq) + 2\ e^{-} \rightarrow\rightarrow 2\ Ag\ (s)}$$

Now combination of these two half reaction gives redox reaction.

$$Cu(s) \rightarrow Cu^{2+}\ (aq) + 2e^{-}$$
$$2Ag^{+}\ (aq) + 2e^{-} \rightarrow 2Ag(s)$$

$$Cu(s) + 2Ag^{+}(aq) + 2e^{-} \rightarrow Cu^{2+}(aq) + 2Ag(s) + 2e^{-}$$

or

$$Cu(s) + 2Ag^{+}\ (aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

The best example of redox titration is the determination of iron by using potassium permanganate or potassium dichromate as standard solution, where dichromate reacts with iron yielding Fe^{3+} and Cr^{3+}.

The reaction involves oxidation of ferrous ion and reduction of dichromate ion to chromium (iii) ion.

$6\ Fe^{2+} = 6\ Fe^{3+} + 6\ e$ (Oxidation half reaction)

(reduction half reaction) $6\ e^- + 14\ H^+ + Cr_2O_7^{2-} = 2\ Cr^{3+} + 7\ H_2O$

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

The redox titration of any substance by using permanganate solution consists of following steps.

Preparation of Permanganate Solutions

For the preparation of stock solution of permanganate solution, the weighing amount of the material is dissolved in an appropriate volume of distilled water.
The resulting solution is then heated to boiling for an hour and then filtered. The filtrate solution is used as primary standard solution.

Standardization of Permanganate Solutions

Sodium oxalate or arsenic (III) oxide can be used for the standardization of solution. The equilibrium redox reaction of sodium oxalate and permanganate solution is as follows;

$2MnO_4^- + 5\ C_2O_4^{2-} + 16\ H^+ \rightarrow\rightarrow 2Mn^{2+} + 10\ CO_2 + 8H_2O$

While primary standard arsenic(III)oxide is soluble in alkali yielding the arsenate.

$As_2O_3 + 4OH^- \rightarrow\rightarrow 2\ HAsO_3^{2-} + H_2O$

This arsenate further reduces the permanganate in acidic solution and form AsO_4^{3-} and Mn^{2+} . Potassium iodide or iodate is used as a catalyst for this reaction.

$As\ O_3^{3-} \rightarrow\rightarrow As\ O_4^{3-}$

$5\ (H_2O + AsO_3^{3-} \rightarrow\rightarrow AsO_4^{3-} + 2\ H^+ + 2\ e)$

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

$5\ AsO_3^{3-} + 2\ MnO_4^- + 6\ H^+ \rightarrow\rightarrow 5\ AsO_4^{3-} + 2\ Mn^{2+} + 3\ H_2O$

Calculations Involving Redox Systems

The equivalent weight of given unknown substance involved in Redox reactions will be,

Equivalent weight

= Molecular weightnumber of e involvedMolecular weightnumber of e involved

The relation between equivalent weight and concentration is termed called normality, N, where

N = Number of equivalents L Numberofequivalents L

The relation between normality and molarity is

Normality = Molarity x number of electrons involve in reaction

Some Redox titration involves iodine as an oxidizing agent. If standard iodine is used for the oxidation of a reducing agent (analyte), the method is termed as iodimetry. On the other hand, the indirect presence of iodine in titration in a Redox reaction is called iodometry.

Iodine formed a complex ion (triiodide ion) with iodide ion solution.

$$I_2 + I^- = I_3^-$$

Here this tri-iodide ion acts as an oxidizing agent and involved in both type of redox titration.

Reducing Agents Used in Titrations Involving Iodine

Usually Sodium thiosulfate ($Na_2S_2O_3$) also known as hypo is used as a reducing agent in redox titration involving iodine.

The reaction between iodine and thiosulfate is as follows;

$$\mathbf{I_2 + 2\ S_2O_3^{2-} \rightarrow\rightarrow 2\ I^- + S_4O_6^{2-}}$$

Since I_2 is present as the tri-iodide in aqueous solutions containing iodide , hence reaction can be written as ;

$$\mathbf{I_3^- + 2\ S_2O_3^{2-} \rightarrow\rightarrow 3\ I^- + S_4O_6^{2-}}$$

Because if the presence of water of hydration, sodium thiosulfate cannot be used as a primary standard. Hence reaction takes place in acidic solution and in presence of excess iodide.

$$\mathbf{IO_3^- + 5\ I^- + 6\ H^+ \rightarrow\rightarrow 3\ I_2 + 3\ H_2O}$$

Potassium dichromate solution is also used for standardization of thiosulfate in acidic solution, with excess iodide ion;

$$\mathbf{Cr_2O_7^{2-} + 6\ I^- + 14\ H^+ \rightarrow\rightarrow 2\ Cr^{3+} + 3\ I_2 + 7\ H_2O}$$

Indicators Involved in Iodine Method

Since starch can form a complex with iodine, it is one of best and easily available indicator for this redox titration.

Iodometry

In the Iodometry, this is based on the oxidation of iodide into iodine. Iodometry is used for determine the amount of oxidizing agents. The amount of oxidizing agent is determined by titration of iodine with thio sulfate. Starch is used as indicator. The end point detection is based on the formation of **blue starch complex.**

Iodometric titration (oxidation of iodide) is done in two steps.

First step

The first step is done by the reaction between the oxidizing agents ($KMnO_4$, $K_2Cr_2O_7$, $CuSO_4$, peroxides etc) and KI (excess) in neutral or in weak acidic medium. Thus the iodine is quickly liberated.

$$\mathbf{KI + Oxidizing\ agent \rightarrow\rightarrow I_2\ (or)}$$
$$\mathbf{2I^- \rightarrow\rightarrow I_2 + 2e^-}$$

$$\mathbf{K_2Cr_2O_7 + 6KI + 7H_2SO_4 \rightarrow\rightarrow Cr_2\ (SO_4)_3 + 4K_2\ SO_4 + 7H_2O + 3I_2}$$

Second step

In this step, the liberated iodine (in first step) is titrated with standard solution of sodium thiosulfate. Starch is used as indicator. At the end point, the blue or violet color of starch indicator disappears due to change of iodine to iodide. So the titration in which liberated iodine (from potassium iodide) is titrated with a standard solution of sodium thiosulfate is known as iodometric titration. Thus the chemical reaction is

$$\mathbf{I_2 + Na_2S_2O_3 \rightarrow\rightarrow 2NaI + Na_2S_2O_4}$$
$$\mathbf{Or}$$
$$\mathbf{2S_2O_3^{2-} + I_2 \rightarrow\rightarrow S_4O_6^{2-} + 2I^-}$$

This is the principle reaction which shows the reduction of iodine. Thus the halogens, oxy halogens, cupric ions, peroxides, sulfur dioxide in food industry etc can be measured by this method. Iodometric tit rations are completed in a weak acid medium due to decomposition of thiosulphate to S_2. The pH of iodine solution should be < 8.5 because iodine disproportionate at basic pH.

Iodimetry

- In the method of Iodimetry, an analyte (a reducing agent) is titrated with a standard iodine solution.
- The free iodine solution is used in Iodimetry titration.
- The formation of free iodine solution is very difficult because iodine is less soluble in water.
- So the solution of iodine is made with the use of KI.
- This is used as standard solution.
- The standardization of this solution is needed before taking in use.
- The chemical reaction between KI and iodine is given below

$$\mathbf{KI + I_2 \rightarrow\rightarrow KI_3}$$

- Thus, in an Iodimetric titrations, the iodine is directly used as an oxidizing agent in neutral or slightly acidic medium and starch is used as indicator.
- The thiosulfate, sulfites, arsenite etc are used as reducing agents.

The chemical reaction can be written as

$$\mathbf{2S_2O_3^{2-}\ (thiosulphate) + I_2 \rightarrow\rightarrow S_4O_6^{2-}\ (tetra\ thionate) + 2I^-}$$

$$\mathbf{I_2 + SO_3^{2-}\ (sulfite) + H_2O \rightarrow\rightarrow 2I^- + SO_4^{2-}\ (sulfate) + 2H^+}$$

Difference between Iodometry and Iodimetry

Iodometry	**Iodimetry**
In Iodometry, liberated iodine is titrated with standard solution of thio sulphate.	In Iodimetry, an analyte is directly titrated with the iodine solution.
It is an indirect method because iodine is not directly used in titration.	It is a direct method.
This is especially used to determine the amount of oxidizing agent.	Iodimetry is used for reducing agent.

A **redox indicator** (also called an **oxidation-reduction indicator**) is an indicator which undergoes a definite color change at a specific electrode potential.

The requirement for fast and reversible color change means that the oxidation-reduction equilibrium for an indicator redox system needs to be established very quickly. Therefore only a few classes of organic redox systems can be used for indicator purposes.

There are two common types of redox indicators:

- metal-organic complexes (Ex. phenanthroline)
- true organic redox systems (Ex. Methylene blue)

Sometimes colored inorganic oxidants or reductants (Ex. Potassium manganate, Potassium dichromate) are also *incorrectly* called redox indicators. They can’t be classified as **true** redox indicators because of their **irreversibility**.