Oxidation – Reduction Titrations

What are Redox titrations? Define oxidation & reduction.

Ans: Redox Titrations: These are the titrations in which substance to be determined is either oxidized or reduced by means of a solution with which the titration is done.

Oxidation & Reduction:

Oxidation: According to older concept; oxidation is defined as addition of oxygen.

Eg: $C + O_2 \rightarrow CO_2$

$2Mg + O_2 \rightarrow 2\ MgO$

Reduction: According to older concept; reduction is defined as removal of oxygen by use of Hydrogen.

Eg: $CuO + H_2 \xrightarrow{\text{Hot}} Cu + H_2O$

According to newer concept:

Oxidation involves an increase in valency.

Eg: $\underset{+2}{FeSO_4} \xrightarrow{\text{oxidation}} \underset{+3}{Fe_2(SO_4)_3}$ Valency of Fe increases from +2 to +3

Reduction involves decrease in valency

Eg: $\underset{+3}{Fe_2(SO_4)_3} \xrightarrow{\text{Reduction}} \underset{+2}{FeSO_4}$ Valency of Fe decreases from 3 to 2

Explain Redox Reactions/Concept of Redox reactions

Ans: Redox Reactions involve electron transfer during the process. Taking the following example the redox reactions can be explained as follows:

$$2FeCl_3 + SnCl_2 \longrightarrow 2\ FeCl_2 + SnCl_4 \qquad (1)$$

in terms of ions the above equation can be written as

$$2Fe^{3+} + 6\ Cl^- + Sn^{++} + 2Cl^- \rightarrow 2Fe^{2+} + 4\ Cl^- + Sn^{4+} + 4Cl^-$$

Or, $2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$ (2)

Or, partial ionic equation can be written as

$$2Fe^{3+} \xrightarrow{\text{Reduction}} 2\,Fe^{2+} \quad (3)$$

$$Sn^{2+} \xrightarrow{\text{Oxidation}} Sn^{4+} \quad (4)$$

Equations must be balanced not only with regard to number & kind of atoms; but also electrically, i.e. the net electric charge on each side must be the same.
Therefore, Equation (3) can be balanced by adding one electron to left hand side.

i.e. $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ (a)

& eq. (4) can be balanced by adding 2 e^- on right hand side

i.e. $Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$ (b)

or $2Fe^{3+} + 2e^- \rightleftharpoons 2Fe^{2+}$ (a')

$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$ (b')

Adding a' & b'

$2Fe^{3+} + Sn^{2+} + 2e^- \rightleftharpoons 2Fe^{2+} + Sn^{4+} + 2\,e^-$

Cancel e^- of both the sides.

Therefore, Net Equation obtained is :

$2Fe^{3+} + Sn^{2+} \rightleftharpoons 2Fe^{2+} + Sn^{4+}$

Explain Reduction of $KMnO_4$ by $Fe(II)SO_4$ in presence of H_2SO_4.

Ans: The first partial equation (Reduction) is as follows.

$MnO_4^- \longrightarrow Mn^{2+}$

To balance it atomically, 8H atoms are added.

$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

To balance electrically 5e- are required on left hand side

i.e. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

Second partial equation (i.e. Oxidation) is as follows:

$$Fe^{2+} \longrightarrow Fe^{3+}$$

To balance electrically electrons (e^-) must be added on right hand side.

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$

But, gain & loss of electrons (e^-) must be equal. One MnO_4^- ion uses $5e^-$ & one Fe^{2+} ion liberates one electron.

$\therefore$ Two partial equations apply in ratio of 1: 5

$$\therefore \quad MnO_4^- + 8H^+ + 5\cancel{e} \rightleftharpoons Mn^{2+} + 4H_2O$$
$$5(Fe^{2+} \rightleftharpoons Fe^{3+} + \cancel{e^-})$$

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

Explain Interaction of $K_2Cr_2O_7$ & KI in presence of dil. H_2SO_4

Ans: The first partial equation is written as:

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

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

To balance electrically 6 electrons are added to left hand side

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

& 2nd partial equation is written as:

$$I^- \longrightarrow I_2$$

$$2\,I^- \longrightarrow I_2$$

$$2I^- \rightleftharpoons I_2 + 2\,e^-$$

One dichromate ion uses $6\ e^-$ & Two I^- (iodide) ions liberates $2e^-$; hence the two partial equations apply in ration 1: 3.

$$\therefore Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$$
$$3\,(2\,I^- \rightleftharpoons I_2 + 2\,e^-)$$

$$Cr_2O_7^{2-} + 14H^+ + 6\,I^- + \cancel{6e^-} \rightleftharpoons 2Cr^{3+} + 3I_2 + 7H_2O + \cancel{6e^-}$$

Define equivalent of oxidant/reductant.

Ans: Equivalent of an oxidant or a reductant is defined as mole divided by number of electrons, which one mole of the substance gains or looses in the reaction.

for eg. $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4\ H_2O$

Equivalent = MnO_4^- / 5 OR Equivalent of $KMnO_4$ / 5

eg. $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$

Equivalent = $Cr_2O_7^{2-}$ / 6 OR Equivalent of $K_2Cr_2O_7$ / 6

Define Oxidation Number.

Ans: Oxidation number of an element is the number, which when applied to that element in a particular compound; indicates the amount of oxidation or reduction which is required to convert one atom of element from the Free State to that in the compound. If oxidation is important to effect the change, oxidation number is positive. If Reduction is important to effect the change, oxidation number is negative.

what are the rules to determine oxidation number?

Ans: Following are the rules to determine oxidation number.

(i) Oxidation no. of free or uncombined element is zero.

(ii) Oxidation no. of H (except in hydrides) has a value of +1.

(iii) Oxidation no. of O (except in peroxides) is -2

(iv) Oxidation no. of metal in combination (except in Hydrides) is +ve.

(v) Oxidation no. of a radical or ion is that of its electrovalency with the correct sign attached i.e. is equal to its electrical charge.

(vi) Oxidation no. of a compound is always zero, and is determined by sum of oxidation no. of individual atom, each multiplied by no. of atom of that element in molecule.

Calculate the equivalent of an oxidizing agent.

Ans: Equivalent of an oxidizing agent is determined by change in oxidation number which the reduced element experiences.

Ex. Reduction of $KMnO_4$ in presence of dil. H_2SO_4 to Mn (II) salt

$$\underset{+1\ +7\ -8}{K\ MnO_4} \xrightarrow{H_2SO_4} \underset{+2\ +6\ -8}{Mn\ SO_4}$$

Change in oxidation number of Mn is from +7 to +2 i.e. by 5 units

Equivalent of $KMnO_4$ is therefore; 1/5 mole.

$\therefore$ Equivalent wt. of $KMnO_4$ = Mol. Wt. of $KMnO_4$ / 5

Calculate the equivalent of potassium dichromate.

$$\underset{+2\ +12\ -14}{K_2Cr_2O_7} \longrightarrow \underset{+6\ \ -6}{Cr_2(SO_4)_3}$$

Change in oxidation number of two atoms of Cr is from +12 to +6 i.e. by 6 units

$\therefore$ Equivalent wt. of $K_2Cr_2O_7$ = Mol. Wt. of $K_2Cr_2O_7$ / 6

Calculate the equivalent of $FeSO_4$. (Equivalent of Reducing agent)

Ans. Equivalent of reducing agent is determined by change in oxidation number which the oxidized element suffers.

Eg.
$$2(\overset{+2\ \ -2}{FeSO_4}) \longrightarrow \overset{+6\ \ -6}{Fe_2(SO_4)_3}$$

The Change in oxidation number is from +2 to +3 per atom of Fe or by one unit

$\therefore$ Equivalent wt. of $FeSO_4$ = Mol. Wt. of $FeSO_4$ / 1

Eg. Oxidation of $H_2C_2O_4 \longrightarrow CO_2 + H_2O$

$$\underset{+2\ +6\ -8}{H_2C_2O_4} \longrightarrow 2\underset{+4\ -4}{CO_2}$$

For 2 C atoms, the charge on R.H.S. would be +8.
Therefore, change in oxidation no. of Carbon will be +6 to + 8 i.e. by 2 units.
$\therefore$ Equivalent wt. of oxalic acid = Mol. Wt. / 2