# REDOX & EQUIVALENT CONCEPTS (STOCHIOMETRY-II)

## 1. OXIDATION & REDUCTION

Let us do a comparative study of oxidation and Reduction ;

| | **Oxidation** | | **Reduction** |
|---|---|---|---|
| (1) | Addition of oxygen | (i) | Removal of oxygen |
| **e.g.** | $2Mg + O_2 \rightarrow 2MgO$ | **e.g.** | $CuO + C \rightarrow Cu + CO$ |
| (2) | Removal of Hydrogen | (ii) | Addition of Hydrogen |
| **e.g.** | $H_2S + Cl_2 \rightarrow 2HCl + S$ | **e.g.** | $S + H_2 \rightarrow H_2S$ |
| (3) | Increase in positive charge | (iii) | Decrease in positive charge |
| **e.g.** | $Fe^{2+} \rightarrow Fe^{3+} + e^-$ | **e.g.** | $Fe^{3+} + e \rightarrow Fe^{2+}$ |
| (4) | Increase in oxidation number | (iv) | Decrease in oxidation number |
| | $\overset{(+2)}{SnCl_2} \rightarrow \overset{(+4)}{SnCl_4}$ | | $\overset{(+7)}{MnO_4^-} \rightarrow \overset{(+2)}{Mn^{2+}}$ |
| (5) | Removal of electron | (v) | Addition of electron |
| **e.g.** | $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$ | **e.g.** | $Fe^{3+} + e^- \rightarrow Fe^{2+}$ |

## 2. Oxidation Number :

- It is an imaginary or apparent charge gained by an element when it goes from its elemental free state to combined state in molecules.
- It is calculated on basis of a arbitrary set of rules.
- It is a relative charge in a particular bonded state.

### 2.1 Rules governing oxidation number :

The following rules are helpful in calculating oxidation number of the elements in their different compounds. It is remember that the basis of these rule is the electronegativity of the element.

- **Fluorine atom :**

  Fluorine is most electronegativity atom (known). It always has oxidation no. equal to –1 in all its compounds.

- **Oxygen atom :**

  In general and as well as in its oxides, oxygen atom has oxidation number equal to –2.

**In case of :**
(i) peroxide (e.g. $H_2O_2$, $Na_2O_2$) is $-1$
(ii) super oxide (e.g. $KO_2$) is $-\frac{1}{2}$
(iii) ozonide ($KO_3$) is $-\frac{1}{3}$
(iv) oxygen fluoride $OF_2$ is $+2$ & in $O_2F_2$ is $+1$

- **Hydrogen atom :**

  In general, H atom has oxidation number equal to +1. But in metallic hydrides (e.g. NaH, KH) it is –1.

- **Halogen atom :**

  In general, all halogen atom (Cl, Br, I) has oxidation number equal to –1.

  But if halogen atom is attached with an more electronegative atom than halogen atom then it will show positive oxidation numbers.

e.g. $K\overset{+5}{Cl}O_3$ $H\overset{+5}{I}O_3$ $H\overset{+7}{Cl}O_4$ $K\overset{+5}{Br}O_3$

- **Metals :**

  (a) Alkali metal (Li, Na, K, Rb, ..........) always have oxidation number +1.

  (b) Alkaline earth metal (Be, Mg, Ca ........) always have oxidation number +2.

**Note :** Metal may have positive or zero oxidation number.

(c) Aluminium always have +3 oxidation number

- Oxidation number of an element in free state or in allotropic forms is always zero.

e.g. $\overset{0}{O_2},\overset{0}{S_8},\overset{0}{P_4},\overset{0}{O_3}$

- Sum of the charges of elements in a molecule is zero.
- Sum of the charges of all elements in an ions is equal to the charge on the ion.
- If the group no. of an element in periodic table is n then its oxidation number may vary from n to n – 8 (but it is mainly applicable in p-block elements)

e.g. N-atom belongs to v group in the periodic table therefore as per rule its oxidation number may vary from

–3 to +5 $(\overset{-3}{N}H_3,\overset{+2}{N}O,\overset{+3}{N_2}O_3,\overset{+4}{N}O_2,\overset{+5}{N_2}O_5)$

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***Ex.1 Calculate oxidation number of underlined element $Na_2S_2O_3$ :***

**Sol.** Let oxidation number of S-atom is x. Now work accordingly with the rules given before.

$(+1) \times 2 + (x) \times 2 + (-2) \times 3 = 0$

$x = +2$

***Ex.2 $Na_2S_4O_6$ :***

**Sol.** Let oxidation number of S-atom is x

$(+1) \times 2 + (x) \times 2 + (-2) \times 6 = 0$

$x = +2.5$

- It's important to note here that $Na_2S_2O_3$ have two S-atom and there are four S-atom in $Na_2S_4O_6$ but sulphur atom in both the compound have +2 or +2.5 oxidation number, it is the average charge (O. No.) Which reside on each sulphur atom therefore we should work to calculate the individual oxidation number of each sulphur atom in these compound.

***Ex.3 Calculate the O.S. of all the atoms in the following species :***

***(i) $ClO^-$, (ii) $NO_2^-$, (iii) $NO_3^-$ (iv) $CCl_4$ (v) $K_2CrO_4$ and (vi) $KMnO_4$***

**Sol.** (i) In $ClO^-$, the net charge on the species is –1 and therefore the sum of the oxidation states of Cl and O must be equal to –1. Oxygen will have an O.S. of –2 and if the O.S. of Cl is assumed to be 'x' then x – 2 should be equal to –1.

x is + 1

(ii) $NO_2^-$ : $(2 \times -2) + x = -1$ (where 'x' is O.S. of N)

$\therefore x = +3$

(iii) $NO_3^-$ : $x + (3 \times -2) = -1$ (where 'x' is O.S. of N)

$x = +5$

(iv) In $CCl_4$, Cl has an O.S. of –1

$x + 4 \times -1 = 0$

$\therefore x = +4$ (where 'x' is O.S. of C)

(v) $K_2CrO_4$ : K has O.S. of +1 and O has O.S. of –2 and let Cr has O.S. 'x' then, $2 \times +1 + x + 4 \times -2 = 0$

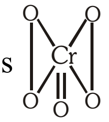
$\therefore x = +6$

(vi) $KMnO_4$ : $+1 + x + (4 \times -2) = 0$

$\therefore x = +7$ (where x is O.S. of Mn).

## 2.2 MISCELLANEOUS EXAMPLES

In order to determine the exact or individual oxidation number we need to take help from the structures of the molecules. Some special cases are discussed as follows :

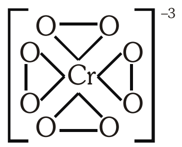
- The structure of $CrO_5$ is 

From the structure it is evident that in $CrO_5$ there are two peroxide linkages and one double bond.

The contribution of each peroxide linkage is –2. Let the O.N. of Cr is x.

$\therefore$ $x + (-2)2 + (-2) = 0$ or $x = 6$

$\therefore$ O.N. of Cr = +6 **Ans.**

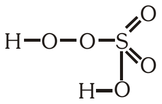
$K_3CrO_8$ 

From the structure it is evident that in $CrO_8^{-3}$ there are four peroxide linkages.

The contribution of each peroxide linkage is –2. Let the O.N. of Cr is x.

$\therefore$ $x + (-2)4 = -3$ or $x = +5$

$\therefore$ O.N. of Cr = +5 **Ans.**

- The strcuture of $H_2SO_5$ is 

From the structure, it is evident that in $H_2SO_5$. there are one peroxide linkage, two sulphur - oxygen double bond and one OH group. Let the O.N. of S = x.

∴ $+1 - 2 + x + (-2)\,2 + (-2) + 1 = 0$

or $x + 2 - 8 = 0$

or $x - 6 = 0$

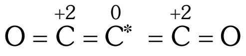
or $x = 6$

∴ O.N. of S in $H_2SO_5$ is +6 **Ans**

## 2.3 PARADOX OF FRACTIONAL OXIDATION NUMBER

Fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is actually present in different oxidation states. Structure of the species $C_3O_2$, $Br_3O_8$ and $S_4O_6^{2-}$ reveal the following bonding situations.

- The element marked with asterisk in each species is exhibiting the different oxidation state (oxidation number) from rest of the atoms of the same element in each of the species. This reveals that in $C_3O_2$, two carbon atoms are present in +2 oxidation state each whereas the third one is present in zero oxidation state and the average is 4/3. However the realistic picture is +2 for two terminal carbons and zero for the middle carbon.

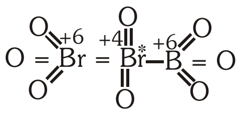


$$O = \overset{+2}{C} = \overset{0}{C^*} = \overset{+2}{C} = O$$

Structure of $C_3O_2$

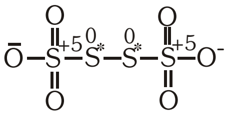
(Carbon suboxide)

- Likewise in $Br_3O_8$, each of the two terminal bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality is 16/3.



Structure of $Br_3O_8$ (tribromooctaoxide)

- In the same fashion, in the species $S_4O_6^{2-}$, is 2.5, whereas the reality being +5,0,0 and +5 oxidation number respectively for each sulphur.



Structure of $S_4O_6^{2-}$ (tetrathionate ion)

## 3.1 OXIDISING AND REDUCING AGENT

### 3.1 Oxidising agent or Oxidant :

Oxidising agents are those compound which can oxidise others and reduced itself during the chemical reaction. Those reagents whose O.N. decrease or which gain electrons in a redox reaction are termed as oxidants

e.g. $KMnO_4$, $K_2Cr_2O_7$, $HNO_3$, conc. $H_2SO_4$ etc, are powerful oxidising agents.

### 3.1 Reducing agent or Reductant :

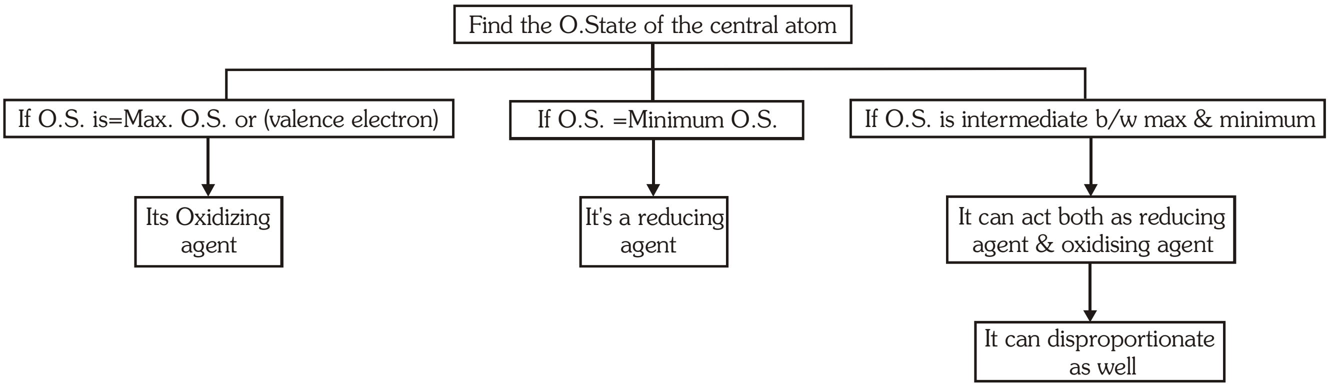
Redusing agents are those compound which can reduce others and oxidise itself during the chemical reaction. Those reagents whose O.N. increase or which loses electrons in a redox reaction are termed as reductants.

e.g. KI, $Na_2S_2O_3$ are powerful reducing agents.

**Note :** There are some compounds also which can work both oxidising agent and reducing agent.

e.g. $H_2O_2$, $NO_2^-$

## 3.3 HOW TO IDENTIFY WHETHER A PARTICULAR SUBSTANCE IS AN OXIDISING OR REDUCING AGENT



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***Ex.4. Identify the species undergoing oxidation and reduction***

*(i)* $\underbrace{N_2 + \overbrace{H_2 \longrightarrow NH_3}^{(O)}}_{(R)}$

*(ii)* $\underbrace{Zn + \overbrace{HCl \longrightarrow ZnCl_2 + H_2}^{(R)}}_{(O)}$

(R)

*(iii)* $Mg + O_2 \longrightarrow MgO$

(O)

*(iv)* $Zn + NaOH \longrightarrow Na_2ZnO_2 + H_2$

(R)

(R)

*(v)* $H_2SO_4 + Mg \longrightarrow MgSO_4 + SO_2 + H_2O$

(O)

*(vi)* $H_2SO_4 + NaOH \longrightarrow Na_2SO_4 + H_2O$

*Neither O & R*

(R)

*(vii)* $Cl_2 + NaOH \longrightarrow NaCl + NaClO_3 + H_2O$

(O)

(R)

*(viii)* $FeCl_3 + SnCl_2 \longrightarrow FeCl_2 + SnCl_4$

(O)

*(ix)* $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

*No oxidation and no reduction.*

## 4 REDOX REACTION

A reaction in which oxidation and reduction simultaneously take place.

In all redox reactions the total increase in oxidation number must equal the total decrease in oxidation number.

e.g. $10\overset{+2}{Fe}SO_4 + 2K\overset{+7}{Mn}O_4 + 8H_2SO_4 \longrightarrow 5\overset{+3}{Fe_2}(SO_4)_3 + 2\overset{+2}{Mn}SO_4 + K_2SO_4 + 8H_2O$

## 5. TYPE OF REACTION

### 5.1 Combination Reactions :

When two or more element combine to form compound then such reaction are redox reaction.

For example

$$A + B \longrightarrow C$$

(a) $3\overset{0}{Mg}(s) + \overset{0}{N_2}(g) \xrightarrow{\Delta} \overset{+2}{Mg_3}\overset{-3}{N_2}(s)$

(b) $\overset{0}{C}(s) + \overset{0}{O_2}(g) \xrightarrow{\Delta} \overset{+4}{C}\overset{-2}{O_2}(g)$

(c) $\overset{-4}{C}\overset{+1}{H_4}(g) + 2\overset{0}{O_2}(g) \xrightarrow{\Delta} \overset{+4}{C}\overset{-2}{O_2}(g) + 2\overset{+1}{H_2}\overset{-2}{O}(\ell)$

(d) $\overset{0}{Li}(s) + \overset{0}{N_2}(g) \xrightarrow{\Delta} \overset{+1}{Li_3}\overset{-3}{N}(s)$

In reaction (c), there is no change in the oxidation number of hydrogen.

### 5.2 Decomposition Reactions :

Decomposition reactions are opposite of combination. Decomposition reactions are those in which when a molecule breaks down to form two or more components, at least one of them must be in the elemental state. For example :

(a) $2\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O_3}(s)\xrightarrow{\Delta}2\overset{+1}{M}\overset{-1}{Cl}(s)+3\overset{0}{O_2}(g)$

(b) $\overset{+2}{Ca}\overset{-1}{H_2}\xrightarrow{\Delta}\overset{0}{Ca}(s)+\overset{0}{H_2}(g)$

(c) $2\overset{+1}{Na}\overset{-1}{H}(s)\xrightarrow{\Delta}2\overset{0}{Na}(s)+\overset{0}{H_2}(g)$

(d) $\overset{+1}{H_2}\overset{-2}{O}(\ell)\xrightarrow{\Delta}2\overset{0}{H_2}(g)+\overset{0}{O_2}(g)$

Exception :

$$\overset{+2}{Ca}\overset{+4}{C}\overset{-2}{O_3}(s)\xrightarrow{\Delta}\overset{+2}{Ca}\overset{-2}{O}(s)+\overset{+4}{C}\overset{-2}{O}{}_2(g)$$

### 5.3 Displacement Reactions :

A reaction in which an atom or iron in a compund is replaced by an atom or ion of another element is called a displacement reaction. It may be denoted as :

$$X+YZ\longrightarrow XZ+Y$$

### 5.4 Disproportionations reactions :

A redox reaction in which a same element present in a particular compound in a definite oxidation state is oxidized as well as reduced simultaneously is a disproportionation reactions.

Disproportionation reactions are a special type of redox reactions. One of the reactants in a disproportionation reaction always contains **an element that can exist in at least three oxidation states.** The element in the form of reacting substance is in the intermediate oxidation state and both higher and lower oxidation states of that element are formed in the reaction.

$$2\overset{+1}{H_2}\overset{-1}{O_2}(aq)\longrightarrow H_2O(\ell)+O_2(g)$$

$$\overset{0}{S_8}(s)+12OH^-(aq)\longrightarrow 4\overset{-2}{S}{}^{2-}(aq)+2\overset{+2}{S_2}O_3^{2-}(aq)+6H_2O(\ell)$$

$$\overset{0}{Cl_2}(g)+2OH^-(aq)\longrightarrow \overset{+1}{Cl}O^-(aq)+\overset{-1}{Cl^-}(aq)+H_2O(\ell)$$

- **Consider following reactions :**

(a) $2KClO_3=2KCl+3O_2$

$KClO_3$ plays a role of oxidant and reductant both. Because same element is not oxidised and reduced. Here, Cl present in $KClO_3$ is reduced and O present in $KClO_3$ is oxidized. So **its not a disproportion reaction** although it looks like one.

(b) $NH_4NO_2\longrightarrow N_2+2H_2O$

Nitrogen in this compound has –3 and +3 oxidation number so it is not a definite value, so its not a disproportion reaction. Its a example of **comproportionation reaction** which is a class of redox reaction in which a element from two different oxidation state gets converted into a single oxidation state.

(c) $4KClO_3 \longrightarrow 3KClO_4 + KCl$

Its a case of disproportionation reaction in which Cl is the atom disproportionating.

- **List of some important disproportionation reaction :**

1. $H_2O_2 \longrightarrow H_2O + O_2$
2. $X_2 + OH^- \text{ (dil.)} \longrightarrow X^- + XO^-$
3. $X_2 + OH^- \text{ (conc.)} \longrightarrow X^- + XO_3^-$

**$F_2$ does not (can not) undergo disproportionation as it is the most electronegative element.**

$F_2 + NaOH \text{ (dil)} \longrightarrow F^- + OF_2$

$F_2 + NaOH \text{ concentration (dil)} \longrightarrow F^- + O_2$

- Reverse of disproportionation is called Comproportionation. In some of the disproportionation reactions by changing the medium (from acidic to basic or reverse) the reaction goes in backward direction and can be taken as an example of Comproportionation.

$$I^- + IO_3^- + H^+ \longrightarrow I_2 + H_2O \text{ (acidic)}$$

## 6. BALANCING OF REDOX REACTION

All balanced equations must satisfy two criteria

**1. Atom balance (mass balance) :**

That is there should be the same number of atoms of each kind in reactant and products side.

**2. Charge balance :**

That is the sum of actual charges on both side of the equation must be equal

There are two methods for balancing the redox equations

(a) Oxidation - number change method

(b) Ion electron method or half cell method

**(a) Oxidation number change method :**

This method was given by Jonson. In a balanced redox reaction, total increase in oxidation number must be equal to total decreases in oxidation number. This equivalence provides the basis for balancing redox reactions.

The general procedure involves the following steps :

(i) Select the atom in oxidising agent whose oxidation number decreases and indicate the gain of electrons.

(ii) Select the atom in reducing agent whose oxidation number increases and write the loss of electrons.

(iii) Now cross multiply i.e. multiply oxidising agent by the number of loss of electrons and reducing agent by number of gain of electrons.

(iv) Balance the number of atoms on both sides whose oxidation numbers change in the reaction.

(v) In order to balance oxygen atoms, add $H_2O$ molecules to the side deficient in oxygen. Then balance the number of H atoms by adding $H^+$ ions in the hydrogen.

***Ex.5 Write the skeleton equation for each of the following processes and balance them by ion electron method :***

***(i) Permagnet ion oxidizes oxalate ions in acidic medium to carbon dioxide and gets reduced itself to $Mn^{2+}$ ions.***

***(ii) Chlorine reacts with base to form chlorate ion, chloride ion and water in acidic medium.***

**Sol.** (i) The skeleton equation for the process :

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

◆ **Step (1)** : Indicating oxidation number :

$$\overset{+7}{Mn}\overset{-2}{O}_4^- + \overset{+3}{C}_2O_4^{2-} \longrightarrow Mn^{2+} + \overset{+4}{C}\overset{-2}{O}_2 + \overset{+1}{H}_2\overset{-2}{O}$$

◆ **Step (2)** : Writing oxidation and reduction half reaction :

$\overset{+3}{C}_2O_4^{2-} \longrightarrow 2\overset{+4}{C}O_2$ (Oxidation half)

$\overset{+7}{Mn}O_4^- \longrightarrow Mn^{2+}$ (Reduction half)

◆ **Step (3)** : Adding electrons to make the difference in O.N.

$$\overset{+3}{C}_2O_4^{2-} \longrightarrow 2\overset{+4}{C}O_2 + 2e^-$$

$$\overset{+7}{Mn}O_4^- + 5e^- \longrightarrow Mn^{2+}$$

◆ **Step (4)** : Balancing 'O' atom by adding $H_2O$ molecules

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

$$MnO_4^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

◆ **Step (5)** : Balancing H atom by adding $H^+$ ions

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

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

◆ **Step (6)** : Multiply the oxidation half reaction by 2 and reduction half reaction by 5 to equalize the electrons lost and gained and add the two half reactions.

$$\begin{array}{l} [C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5 \\ [MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O] \times 2 \\ \hline 2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O \end{array}$$

(ii) The skeleton equation for the given process :

$$Cl_2 + OH^- \longrightarrow Cl^- + ClO_3^- + H_2O$$

◆ **Step (1) :** Indicate the oxidation number of each atom

$$\overset{0}{Cl}_2 + \overset{-2}{O}H^- \longrightarrow Cl^- + \overset{+5}{Cl}O_3^- + \overset{+1}{H}_2\overset{-2}{O}$$

Thus, chlorine is the only element which undergoes the change in oxidation number. It decreases its oxidation number from 0 to 1 and also increases its oxidation number from 0 to 5.

- **Step (2) :** Write the oxidation and reduction half reactions

$\overset{0}{Cl_2} \longrightarrow 2\,\overset{+5}{Cl}O_3^-$ (Oxidation half)

$\overset{0}{Cl_2} \longrightarrow 2Cl^-$ (Reduction half)

- **Step (3) :** Add electrons to make up for the difference in O.N.

$\overset{0}{Cl_2} \longrightarrow 2\,\overset{+5}{Cl}O_3^- + 10e^-$

$\overset{0}{Cl_2} + 2e^- \longrightarrow 2Cl^-$

- **Step (4) :** Balance O atoms by adding $H_2O$ molecules

$Cl_2 + 6H_2O \longrightarrow 2(ClO_3)^- + 10e^-$

$Cl_2 + 2e^- \longrightarrow Cl^-$

- **Step (5) :** Since medium is basic, balance H atoms by adding $H_2O$ molecules to the side falling short of H atoms and equal number of $OH^-$ ions to the other side.

$Cl_2 + 6H_2O + 12OH^- \longrightarrow 2ClO_3^- + 10e^- + 12H_2O$

$Cl_2 + 2e^- \longrightarrow 2Cl^-$

- **Step (6) :** Multiply the reduction half reaction by 5 and add two half reactions.

$Cl_2 + 5H_2O + 2OH^- \longrightarrow 2ClO_3^- + 10e^- + 12H_2O$

$[Cl_2 + 2e^- \longrightarrow 2Cl^-] \times 5$

$Cl_2 + 5Cl_2 + 12OH^- \longrightarrow 2ClO_3^- + 10Cl^- + 6H_2O$

or, $6Cl_2 + 12OH^- \longrightarrow 2ClO_3^- + 10Cl^- + 6H_2O$

or, $3Cl_2 + 6OH^- \longrightarrow ClO_3^- + 5Cl^- + 3H_2O$

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***Ex.6 Balance the following chemical reaction by oxidation number method and write their skeleton equation :***

***(i) The nitrate ions in acidic medium oxidize magnesium to $Mg^{2+}$ ions but itself gets reduced to nitrous oxide.***

**Sol.** (i) The skeleton equation for the given process is

$Mg + NO_3^- \longrightarrow Mg^{2+} + N_2O + H_2O$

- **Step (1) :** $\overset{0}{Mg} + (\overset{+5}{N}\overset{-2}{O_3})^- \longrightarrow Mg^{2+} + \overset{+1}{N_2}\overset{-2}{O} + \overset{+1}{H_2}\overset{-2}{O}$

Multiply $NO_3^-$ by 2 to equalize N atoms

- **Step (2) :** O.N. increases by 2 per Mg atom

$$\overset{0}{Mg} + \underbrace{2NO_3^- \longrightarrow Mg^{2+} + \overset{+1}{N_2}O}_{4 \times 2 = 8} + H_2O$$

O.N. decreases by 4 per N atom

- **Step (3) :** Equalize increase/decrease in O.N. by multiplying Mg by 4 and $2NO_3^-$ by 1.

  $4Mg + 2NO_3^- \longrightarrow Mg^{2+} + N_2O + H_2O$

- **Step (4) :** Balance atoms other than O and H

  $4Mg + 2NO_3^- \longrightarrow 4Mg^{2+} + N_2O + H_2O$

- **Step (5) :** Balance O atoms

  $4Mg + 2NO_3^- \longrightarrow 4Mg^{2+} + N_2O + H_2O + 4H_2O$

- **Step (6) :** Balance H atoms as is done in acidic medium.

  $4Mg + 2NO_3^- + 10H^+ \longrightarrow 4Mg^{2+} + N_2O + 5H_2O$

**(b) Ion electron method or half cell method :**

By this method redox equation are balanced in two different medium

(a) Acidic medium (b) Basic medium

- **Balancing in acidic medium**

  Students are advised to follow the following steps to balance the redox reactions by ion electron method in acidic medium.

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***Ex.7 Balance the following redox reaction.***

$$FeSO_4 + KMnO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + H_2O$$

**Sol : Step-I** assign the oxidation No. to each elements present in the reaction.

$$\overset{+2\;+6\;-2}{Fe\,S\,O_4} + \overset{+1\;+7\;-2}{KMnO_4} + \overset{+1\;+6\;-2}{H_2SO_4} \longrightarrow \overset{+3\;\;+6\;-2}{Fe_2(SO_4)_3} + \overset{+2\;+6\;-2}{MnS\,O_4} + \overset{+1\;-2}{H_2O}$$

**Step-II** Now convert the reaction in ionic form by eliminating the elements or species which are not going either oxidation or reduction

$$Fe^{2+} + \overset{+7}{Mn}O_4^- \longrightarrow Fe^{3+} + Mn^{2+}$$

**Step-III** Now identify the oxidation / reduction occurring into the reaction.

undergoes reduction

$$Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$$

undergoes oxidation

**Step-IV** Split the ionic reaction in two half one for oxidation and other for reduction

$$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} \;\Big|\; MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+}$$

**Step-V** Balance the atom other than oxygen and hydrogen atom in both half reactions

$$Fe^{2+} \rightarrow Fe^{3+} \;\Big|\; MnO_4^- \rightarrow Mn^{2+}$$

Fe & Mn atom are balanced in both side.

**Step-VI** Now balance O & H atom by $H_2O$ & $H^+$ respectively by the following way for one excess oxygen atom add one $H_2O$ on the other side and two $H^+$ on the same side.

$Fe^{2+} \longrightarrow Fe^{3+}$ (no oxygen atom) ..........(i)

$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$ .........(ii)

**Step VII** Now see equation (i) & (ii) is balanced atomwise. Now balance both equations chargewise to balance the charge add electrons to the electrically positive side.

$$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} + e^- \qquad ..........(1)$$

$$5e^- + 8H^+ + MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+} + 4H_2O \qquad ..........(2)$$

**Step VIII** The number of electrons gained and lost in each half-reaction are equalised by multiply suitable factor in both the half reaction and finally the half reactions are added to give the over all balanced reaction.

Here we multiply equation (i) by 5 and (ii) by one

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \qquad .............(1) \times 5$$

$$5e^- + 8H^+ + MnO_4^- \rightarrow M^{2+} + 4H_2O \qquad .............(2) \times 1$$

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

(Here at this stage you will get balanced redox reaction in ionic form)

**Step IX** Now convert the ionic reaction in to molecular form by adding the elements or species which are removed instep (II).

Now by some manipulation you will get

$$5\,FeSO_4 + KMnO_4 + 4H_2SO_4 \rightarrow \frac{5}{2}\,Fe_2(SO_4)_3 + MnSO_4 + 4H_2O \qquad \text{or}$$

$$10\,FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O + K_2SO_4$$

---

## 7. Equivalent weight (E) :

$$\text{Eq. wt (E)} = \frac{\text{Molecular weight}}{\text{valency factor (v.f)}} = \frac{\text{Mol. wt.}}{\text{n} - \text{factor}}$$

$$\text{no of Equivalents} = \frac{\text{mass of a sample}}{\text{eq. wt. of that species}}$$

- Equivalent mass is a pure number when expressed in gram, it is called gram equivalent mass.
- The equivalent mass of substance may have different values under different conditions.

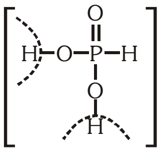
## 8. Valency factor calculation :

- **For Acids :**

  valence factor = number of replaceable $H^+$ ions

**Solved Examples :**

**Ex :** HCl, $H_2SO_4$ $H_3PO_4$ $H_3PO_3$



{see there are only two replaceable $H^+$ ions}

| | | | | |
|---|---|---|---|---|
| **Sol :** valence→ factor | 1 | 2 (assume 100% dissociation) | 3 | 2 |
| Eq.wt.→ | $\frac{M}{1}$ | $\frac{M}{2}$ | $\frac{M}{3}$ | $\frac{M}{2}$ |

**Self practice problems :**

**1.** Find the valence factor for following acids

(i) $CH_3COOH$ (ii) $NaH_2PO_4$ (iii) $H_3BO_3$

**Answers :**

**1.** (i) 1 (ii) 2 (iii) 1

---

## 8.2 For Base :

v.f. = number of replicable $OH^-$ ions

**Solved Examples :**

**Ex :** NaOH KOH

**Sol :** v.f.→ 1 1

E.→ $\frac{M}{1}$ $\frac{M}{1}$

**Self practice problems :**

**1.** Find the valence factor for following bases

(i) $Ca(OH)_2$ (ii) CsOH (iii) $Al(OH)_3$

**Answers :**

**1.** (i) 2 (ii) 1 (iii) 3

### 8.3 Acid - base reaction :

In case of acid base reaction, the valence factor is the actual number of $H^+$ or $OH^-$ replaced in the reaction. The acid or base may contain more number of replaceable $H^+$ or $OH^-$ than actually replaced in reaction.

v.f. for base is the number of $H^+$ ion form the acid replaced by per molecule of the base.

---

***Ex.9*** $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

***Base Acid***

**Sol :** valency factor of base = 1

valency factor of acid = 2

Here two molecule of NaOH replaced $2H^+$ ion from the $H_2SO_4$ therefore per molecule of NaOH replaced only one $H^+$ ion of acid so v.f. = 1

- v.f. for acid is number of $OH^-$ replaced for the base by per molecule of acid

***Ex.10*** $NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$

***Base Acid***

**Sol :** valence factor of acid = 1

here one of molecule of $H_3PO_4$ replaced one $OH^-$ from NaOH therefore v.f. for $H_3PO_4$ is = 1

$$E = \frac{\text{mol. wt. of } H_3PO_4}{1}$$

***Ex.11*** $2NaOH + H_3PO_4 \rightarrow Na_2HPO_4 + 2H_2O$

***Base Acid***

**Sol :** valence factor of acid = 2

here one of molecule of $H_3PO_4$ replaced two $OH^-$ from NaOH therefore v.f. for $H_3PO_4$ is = 2

$$E = \frac{\text{mol. wt. of } H_3PO_4}{2}$$

***Ex.12*** $Al(OH)_3 + HCl \rightarrow Al(OH)_2Cl + H_2O$

***Base Acid***

**Sol :** valence factor of base = 1

here one of molecule of $Al(OH)_3$ replaced one $H^+$ from HCl therefore v.f. for $Al(OH)_3$ is = 1

$$E = \frac{\text{mol. wt. of } Al(OH)_3}{1}$$

---

### 8.4 For Salts :

v.f. = Total number of positive charge or negative charge present into the compound.

**Solved Examples :**

| ***Ex.13*** | $Na_2CO_3$ | $Fe_2(SO_4)_3(2Fe^{3+} + 3SO_4^{2-})$ | $FeSO_4.7H_2O$ |
|---|---|---|---|
| **Sol :** V.f. | 2 | $2 \times 3 = 6$ | 2 |
| E. | $\frac{M}{2}$ | $\frac{M}{6}$ | $\frac{M}{2}$ |

---

### 8.5 Eq. wt. of oxidising / reducing agents in redox reaction :

The equivalent weight of an oxidising agent is that weight which accepts one mole electron in a chemical reaction.

(a) Equivalent wt. of an oxidant (get reduced)

$$= \frac{\text{Mol.wt.}}{\text{No. of electrons gained by one mole}}$$

***Ex.14 In acidic medium***

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

***Eq. wt. of*** $K_2Cr_2O_7 = \frac{\text{Mol. wt of } K_2Cr_2O_7}{6} = \frac{\text{Mol. wt.}}{6}$

**Note :** [6 in denominator indicates that 6 electrons were gained by $Cr_2O_7^{2-}$ as it is clear from the given balanced equation]

(b) Similarly equivalent wt. of a reductant (gets oxidised)

$$= \frac{\text{Mol. wt.}}{\text{No. of electrons lost by one mole}}$$

***Ex.15*** ***In acidic medium,***

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

***Here, Total electrons lost = 2***

***So, eq. wt.*** $= \dfrac{\text{Mol. wt.}}{2}$

***(c)*** ***In different condition a compound may have different equivalent weights. Because, it depends upon the number of electrons gained or lost by that compound in that reaction.***

**Ex.15** (i) $MnO_4^- \longrightarrow Mn^{2+}$ (acidic medium)

(+7) (+2)

Here 5 electrons are taken so eq. wt. = $\dfrac{\text{Mol.wt.of } KMnO_4}{5} = \dfrac{158}{5} = 31.6$

(ii) $MnO_4^- \longrightarrow Mn^{+4}$ (neutral medium)

(+7) (+4)

Here, only 3 electrons are gained, so eq. wt. = $\dfrac{\text{Mol.wt.of } KMnO_4}{3} = \dfrac{158}{3} = 52.7$

(iii) $MnO_4^- \longrightarrow MnO_4^{-2}$ (alkaline medium)

(+7) (+6)

Here, only one electron is gained, so eq. wt. = $\dfrac{\text{Mol.wt.of } KMnO_4}{1} = 158$

**Note :** It is important to note that $KMnO_4$ acts as an oxidant in every medium although with different strength which follows the order.

acidic medium > neutral medium > alkaline medium

***Ex.16*** $2S_2O_3^{--} \longrightarrow S_4O_6^{--} + 2e^-$

***(Reducing agent)***

***equivalent weight of*** $S_2O_3^{--} = \dfrac{2M}{2} = M$

---

◆ **Questions based on Equivalent weight :**

**1.** Molecular weight of $KMnO_4$ in acidic medium and neutral medium will be respectively :

(A) 7 × equivalent wt. and 2 × equivalent wt. (B) 5 × equivalent wt. and 3 × equivalent wt.

(C) 4 × equivalent wt. and 5 × equivalent wt. (D) 2 × equivalent wt. and 4 × equivalent wt.

**2.** In acidic medium, equivalent weight of $K_2Cr_2O_7$ (Mol. wt. = M) is –

(A) M/3 (B) M/4 (C) M/6 (D) M/2

**Answers :**

**(1)** B **(2)** A **(3)** C

## 9. NORMALITY

Normality of solution is defined as the number of equivalent of solute present in one litre (1000 mL) solutions. Let a solution is prepared by dissolving W g of solute of eq. wt. E in V mL water.

- No. of equivalent of solute = $\frac{W}{E}$
- V mL of solution have $\frac{W}{E}$ equivalent of solute
- 1000 mL solution have $\frac{W \times 1000}{E \times VmL}$
- **Normality (N) =** $\frac{W \times 1000}{E \times VmL}$
- **Normality (N) = Molarity × Valence factor**

Normality (N) = molarity × Valence factor (n)

**or** N × V (in mL) = M × V (in mL) × n

**or** milli equivalents = millimoles × n

## 10. LAW OF EQUIVALENCE

The law states that one equivalent of an element combine with one equivalent of the other, and in a chemical reaction equivalent and mill equivalent of reactants react in equal amount to give same no. of equivalent or milli equivalents of products separately.

**According :**

(i) $aA + bB \rightarrow mM + nN$

m.eq of A = m.eq of B = m.eq of M = m.eq of N

(ii) In a compound $M_xN_y$

m.eq of $M_xN_y$ = m.eq of M = m.eq of N

---

***Ex.17 The number of moles of oxalate ions oxidized by one mole of $MnO_4^-$ ion in acidic medium.***

*(A)* $\frac{5}{2}$ *(B)* $\frac{2}{5}$ *(C)* $\frac{3}{5}$ *(D)* $\frac{5}{3}$

**Sol :** Equivalents of $C_2O_4^{2-}$ = equivalents of $MnO_4^-$

x (mole) × 2 = 1 × 5

$x = \frac{5}{2}$

***Ex.18 What volume of 6 M HCl and 2 M HCl should be mixed to get two litre of 3 M HCl ?***

**Sol.** Let, the volume of 6 M HCl required to obtain 2 L of 3M HCl = x L

$\therefore$ Volume of 2 M HCl required = (2 – x) L

$M_1V_1 \quad + \quad M_2V_2 \quad = \quad M_3V_3$

6M HCl 2M HCl 3M HCl

$6 \times (x) + 2 \times (2 - x) = 3 \times 2$

$\Rightarrow 6x + 4 - 6x = 6 \Rightarrow 4x = 2$

$\therefore\ x = 0.5$ L

Hence, volume of 6 M HCl required = 0.5 L

Volume of 2M HCl required = 1.5 L

***Ex.19 In a reaction vessel, 1.184 g of NaOH is required to be added for completing the reaction. How many millilitre of 0.15 M NaOH should be added for this requirement ?***

**Sol.** Amount of NaOH present in 1000 mL of 0.15 M NaOH = 0.15 × 40 = 6 g

$\therefore$ 1 mL of this solution contain NaOH $= \frac{6}{1000} \times 10^{-3}$ g

$\therefore$ 1.184 g of NaOH will be present in $= \frac{1}{6 \times 10^{-3}} \times 1.184 = 197.33$ mL

***Ex.20 What weight of $Na_2CO_3$ of 85% purity would be required to prepare 45.6 mL of 0.235N $H_2SO_4$***

**Sol.** Meq. of $Na_2CO_3$ = Meq. of $H_2SO_4$ = 45.6 × 0.235

$$\therefore \quad \frac{W_{Na_2CO_3}}{E_{Na_2CO_3}} \times 1000 = 45.6 \times 0.235$$

$$\Rightarrow \quad \frac{W_{Na_2CO_3}}{106/2} \times 1000 = 45.6 \times 0.235$$

$$\therefore \quad W_{Na_2CO_3} = 0.5679 \text{ g}$$

For 85 g of pure $Na_2CO_3$, weighed sample = 100 g

$\therefore$ For 0.5679 g of pure $Na_2CO_3$, weighed sample $= \frac{100}{85} \times 0.5679$

$= 0.6681$ g

---

## 10.1 Drawbacks of Equivalent concept :

(i) Since equivalent weight of a substance for example oxidising or reducing agent may be variable hence it is better to use mole concept.

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

$\therefore$ Eq. wt of $MnO_4^- = \frac{MnO_4^-(\text{mol.wt.})}{5}$

e.g. $3e^- + 2H_2O + MnO_4^- \rightarrow MnO_2 + 4OH^-$

$\therefore$ Eq. wt. of $MnO_4^- = \frac{MnO_4^-}{3}$

**Thus the no. of equivalents of $MnO_4^-$ will be different in the above two cases but no. of moles will be same.**

(ii) **Normality of any solution depends on reaction while molarity does not.**

For example.

Consider 0.1 mol $KMnO_4$ dissolved in water to make 1L solution. Molarity of this solution is 0.1 M. However, its normality is not fixed. It will depend upon the reaction in which $KMnO_4$ participates, e.g. If $KMnO_4$ forms $Mn^{2+}$, normality = 0.1 × 5 = 0.5 N. This same sample of $KMnO_4$, if employed in a reaction giving $MnO_2$ as product (Mn in +4 state) will have normality 0.1 × 3 = 0.3 N.

(iii) **The concept of equivalents is handy, but it should be used with care.** One must never equate equivalents in a sequence which involves same element in more than two oxidation states. Consider an example $KIO_3$ reacts with KI to liberate iodine and liberated iodine is titrated with standard hypo solution, The reaction are

(i) $IO_3^- + I^- \longrightarrow I_2$

(ii) $I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + I^-$

meq of hypo = meq of $I_2$ = meq of $IO_3^-$ + meq of $I^-$

$\because IO_3^-$ react with $I^- \Rightarrow$ meq of $IO_3^-$ = meq of $I^-$

◆ meq of hypo = 2 × meq of $IO_3^-$

This is wrong. Note that $I_2$ formed by (i) have v.f. = 5/3 & reacted in equation (ii) have v.f. = 2.

$\because$ v.f. of $I_2$ in both the equation are different therefore we cannot equate m.eq is sequence. In this type of case students are advised to use mole concept.

---

***Ex.21 How many milliliters of 0.02000 M $KMnO_4$ solution would be required to exactly titrate 25.00 mL of 0.2000 M $Fe(NO_3)_2$ solution.***

**Sol : Method - 1 : Mole concept method**

Starting with 25.00 mL of 0.2000M$Fe^{2+}$, we can write.

Millimoles of $Fe^{2+}$ = 25.00 × 0.2000

and in volume V (in milliliters of the $MnO_4^-$)

Millimoles of $MnO_4^-$ = V (0.02000)

The balanced reaction is :

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

This requires that at the equivalent point,

$$\frac{V(0.02000)}{1} = \frac{(25.00)(0.2000)}{5} \qquad V = 50.00\text{ mL}$$

**Method - 2 : Equivalent Method :**

Equivalents of $MnO_4^-$ = 5 × moles of $MnO_4^-$

Normality $MnO_4^-$ = 5 × molarity of $MnO_4^-$

For $Fe^{2+}$, moles and equivalents are equal, At the equivalence point,

Equivalents of $MnO_4^-$ = Equivalents of $Fe^{2+}$

or $V_{MnO_4^-} \times$ Normality of $MnO_4^-$

$= V_{Fe^{2+}} \times$ Normality of $Fe^{2+}$

For 0.02000 M $MnO_4^-$ solution

Normality of $MnO_4^-$ = (5) (0.02000) = 0.1 N and for 0.2000 M $Fe^{2+}$ solution

Normality of $Fe^{2+}$ = 0.2000 N $\quad V_{MnO_4^-} = (25.00\text{ mL})\left(\dfrac{0.2000}{0.1000}\right) = 50.00\,\text{mL}$

## 10.2 FOR ACID-BASE (NEUTRALIZATION REACTION) OR REDOX REACTION

$N_1V_1 = N_2V_2$ is always true.

But $M_1V_1 = M_2V_2$ (may or may not be true )

But $M_1 \times n_1 \times V_1 = M_2 \times n_2 \times V_2$ (always true where n terms represent n-factor).

## 10.3 SOME OXIDIZING AGENTS/REDUCING AGENTS WITH EQ. WT.

| **Species** | **Changed to** | **Reaction** | **Electrons exchanged or change in O.N.** | **Eq. wt.** |
|---|---|---|---|---|
| $MnO_4^-$(O.A.) | $Mn^{+2}$<br>in acidic medium | $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ | 5 | $E = \dfrac{M}{5}$ |
| $MnO_4^-$(O.A.) | $MnO_2$<br>in neutral medium | $MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$ | 3 | $E = \dfrac{M}{3}$ |
| $MnO_4^-$(O.A.) | $MnO_4^{2-}$<br>in basic medium | $MnO_4^- + e^- \longrightarrow MnO_4^{2-}$ | 1 | $E = \dfrac{M}{1}$ |
| $Cr_2O_7^{2-}$(O.A.) | $Cr^{3+}$<br>in acidic medium | $CrO_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ | 6 | $E = \dfrac{M}{6}$ |
| $MnO_2$(O.A.) | $Mn^{2+}$<br>in acidic medium | $MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$ | 2 | $E = \dfrac{M}{2}$ |
| $Cl_2$(O.A.)<br>in bleaching powder | $Cl^-$ | $Cl_2 + 2e^- \longrightarrow 2Cl^-$ | 2 | $E = \dfrac{M}{2}$ |
| $CuSO_4$(O.A.)<br>in iodometric titration | $Cu^+$ | $Cu^{2+} + e^- \longrightarrow Cu^+$ | 1 | $E = \dfrac{M}{1}$ |
| $S_2O_3^{2-}$ (R.A.) | $S_4O_6^{2-}$ | $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$ | 2<br>(for two molecules) | $E = \dfrac{2M}{2} = M$ |
| $H_2O_2$(O.A.) | $H_2O$ | $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$ | 2 | $E = \dfrac{M}{2}$ |
| $H_2O_2$(R.A.) | $O_2$ | $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$ (O.N. of oxygen in $H_2O_2$ is –1 per atom) | 2 | $E = \dfrac{M}{2}$ |
| $Fe^{2+}$(R.A.) | $Fe^{3+}$ | $Fe^{2+} \longrightarrow Fe^{3+} + e^-$ | 1 | $E = \dfrac{M}{1}$ |

**Ex.22** ***To find the n-factor in the following chemical changes.***

*(i)* $KMnO_4 \xrightarrow{H^+} Mn^{2+}$ *(ii)* $KMnO_4 \xrightarrow{H_2O} Mn^{4+}$

*(iii)* $KMnO_4 \xrightarrow{OH^-} Mn^{6+}$ *(iv)* $K_2Cr_2O_7 \xrightarrow{H^+} Cr^{3+}$

*(v)* $C_2O_4^{2-} \rightarrow CO_2$ *(vi)* $FeSO_4 \rightarrow Fe_2O_3$

*(vii)* $Fe_2O_3 \rightarrow FeSO_4$

**Sol.** (i) In this reaction, $KMnO_4$ which is an oxidizing agent, itself gets reduced to $Mn^{2+}$ under acidic conditions.

$n = |1 \times (+7) - 1 \times (+2)| = 5$

(ii) In this reaction, $KMnO_4$ gets reduced to $Mn^{4+}$ under neutral or slightly (weakly) basic conditions.

$n = |1 \times (+7) - 1 \times (+4)| = 3$

(iii) In this reaction, $KMnO_4$ gets reduced to $Mn^{6+}$ under basic conditions.

$n = |1 \times (+7) - 1 \times (+6)| = 1$

(iv) In this reaction, $K_2Cr_2O_7$ which acts as an oxidizing agent reduced to $Cr^{3+}$ under acidic conditions. (It does not react under basic conditions.)

$n = |2 \times (+6) - 2 \times (+3)| = 6$

(v) In this reaction, $C_2O_4^{2-}$ (oxalate ion) gets oxidized to $CO_2$ when it is reacted with an oxidizing agent.

$n = |2 \times (+3) - 2 \times (+4)| = 2$

(vi) In this reaction, ferrous ions get oxidized to ferric ions.

$n = |1 \times (+2) - 1 \times (+3)| = 1$

(vi) In this reaction, ferric ions are getting reduced to ferrous ions.

$n = |2 \times (+3) - 2 \times (+2)| = 2$

**Ex.23** ***Calculate the molar ratio in which the following two substances would react ?***

***$Ba_3(PO_4)_2$ and $AlCl_3$***

**Sol.** n-factor of $Ba_3(PO_4)_2 = 3 \times (+2) = 6 = n_1$

While n-factor of $AlCl_3 = 1 \times (+3) = 3 = n_2$

$$\frac{n_1}{n_2} = \frac{6}{3} \qquad \text{If} \qquad \frac{n_1}{n_2} = \frac{x}{y}$$

Molar ratio $= \frac{y}{x}$ (inverse of equivalent ratio)

∴ Molar ratio in which $Ba_3(PO_4)_2$ and $AlCl_3$ will react = 3 : 6 = 1 : 2

## 10.4 APPLICATIONS OF THE LAW OF EQUIVALENCE

### 10.4.1 Simple Titration

In this, we can find the concentration of unknown solution by reacting it with solution of known concentration (standard solution).

For example, let there be a solution of substance A of unknown concentration. We are given solution of another substance B whose concentration is known ($N_1$). We take a certain known volume of A in a flask ($V_2$) and then we add B to A slowly till all the A is consumed by B (this can be known with the help of indicators). Let us, assume that the volume of B consumed is $V_1$. According to the law of equivalence, the number of g equivalents of B at the end point.

$\therefore N_1V_1 = N_2V_2$, where $N_2$ is the conc. of A.

From this we can calculate the value of $N_2$.

**Ex.24** ***1.20 g sample of $Na_2CO_3$ and $K_2CO_3$ was dissolved in water to form 100 mL of a Solution. 20 mL of this solution required 40 mL of 0.1 N HCl for complete neutralization. Calculate the weight of $Na_2CO_3$ in the mixture. If another 20 mL of this solution is treated with excess of $BaCl_2$ what will be the weight of the precipitate ?***

**Sol.** Let, weight of $Na_2CO_3$ = x g

Weight of $K_2CO_3$ = y g

$\therefore x + y = 1.20$ g ............(i)

For neutralization reaction of 100 mL

Meq. of $Na_2CO_3$ + Meq. of $K_2CO_3$ = Meq. of HCl

$$\Rightarrow \frac{x}{106} \times 2 \times 1000 + \frac{y}{138} \times 2 \times 1000 = \frac{40 \times 0.1 \times 100}{20}$$

$\therefore 69x + 53y = 73.14$ .............(ii)

From Eqs. (i) and (ii), we get

x = 0.5962 g

y = 0.604 g

Solution of $Na_2CO_3$ and $K_2CO_3$ gives ppt. of $BaCO_3$ with $BaCl_2$

(Meq. of $Na_2CO_3$ + Meq. of $K_2CO_3$) in 20 mL = Meq. of $BaCO_3$

$\Rightarrow$ Meq. of HCl for 20 mL mixture = Meq. of $BaCO_3$

$\Rightarrow$ Meq. of $BaCO_3 = 40 \times 0.1 = 4$

$$\frac{W_{BaCO_3}}{M_{BaCO_3}} \times 1000 = 40 \times 0.1 = 4$$

$$\frac{W_{BaCO_3}}{197} \times 2 \times 1000 = 4$$

$\therefore W_{BaCO_3} = 0.394$ g

---

## 10.4.2 BACK TITRATION

Back titration is used to calculate % purity of a sample. Let us assume that we are given an impure solid substance C weighing w gs and we are asked to calculate the percentage of pure C in the sample. We will assume that the impurities are inert. We are provided with two solutions A and B, where the concentration of B is known ($N_1$) and that of A is not known. This type of titration will work only if the following condition is satisfied, i.e. the nature of compounds A, B and C should be such that A and B can react with each other. A and C can react with each other but the product of A and C should not react with B.

Now, we take a certain volume of A in a flask ( the g equivalents of A taken should be ≥ g equivalents of C in the sample and this can be done by taking A in excess). Now, we perform a simple titration using B. Let us assume that the volume of B used is $V_1$. In another beaker, we again take the solution of A in the same volume as taken earlier. Now, C is added to this and after the reaction is completed, the solution is being titrated with B. Let us assume that the volume of B used up is $V_2$. Gram equivalents of B used in the first titration = $N_1V_1$.

$\therefore$ gm. equivalents of A initially $= N_1V_1$

gm. equivalents of B used in the second titration $= N_1V_2$

$\therefore$ gm. equivalents of A left in excess after reacting with C $= N_1V_2$

gm. equivalents of A that reacted with C $= N_1V_1 - N_1V_2$

If the n-factor of C is x, then the moles of pure C $= \dfrac{N_1V_1 - N_1V_2}{x}$

$\therefore$ The weight of C $= \dfrac{N_1V_1 - N_1V_2}{x} \times$ Molecular weight of C

$\therefore$ Percentage of C $= \dfrac{N_1V_1 - N_1V_2}{x} \times \dfrac{\text{Molecular wt. of C}}{w} \times 100$

## ❑ SOME REDOX TITRATIONS (EXCLUDING IODOMETRIC / IODIMETRIC)

| Estimation of | By titrating with | Reactions | Relation between O.A. and R.A. |
|---|---|---|---|
| $Fe^{2+}$ | $MnO_4^-$ | $Fe^{2+} \longrightarrow Fe^{3+} + e^-$<br>$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ | $5Fe^{2+} \equiv MnO_4^-$<br>Eq. wt. $Fe^{2+} = M/1$<br>Eq. wt. $MnO_4^- = M/5$ |
| $Fe^{2+}$ | $Cr_2O_7^{2-}$ | $Fe^{2+} \longrightarrow Fe^{3+} + e^-$<br>$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ | $6Fe^{2+} \equiv Cr_2O_7^{2-}$<br>Eq. wt. $Cr_2O_7^{2-} = M/6$ |
| $C_2O_4^{2-}$ | $MnO_4^-$ | $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$<br>$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$ | $5C_2O_4^{2-} \equiv 2MnO_4^-$<br>Eq. wt. $C_2O_4^{2-} = M/2$<br>Eq. wt. $MnO_4^- = M/5$ |
| $H_2O_2$ | $MnO_4^-$ | $H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$<br>$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ | $5H_2O_2 \equiv 2MnO_4^-$<br>Eq. wt. $H_2O_2 = M/2$<br>Eq. wt. $MnO_4^- = M/5$ |
| $As_2O_3$ | $MnO_4^-$ | $As_2O_3 + 5H_2O \rightarrow 2AsO_4^{3-} + 10H^+ + 4e^-$ | Eq. wt. $As_2O_3 = M/4$ |
| $AsO_3^{3-}$ | $BrO_3^-$ | $AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$<br>$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$ | Eq. wt. $AsO_3^{3-} = M/2$<br>Eq. wt. $BrO_3^- = M/6$ |

### 10.4.3 Iodometric and Iodimetric Titration :

The reduction of free iodine to iodide ions and oxidation of iodide ions to free iodine occurs in these titrations.

$I_2 + 2e^- \longrightarrow 2I^-$ (reduction)

$2I^- \longrightarrow I_2 + 2e^-$ (oxidation)

These are divided into two types :

**(i) Iodometic Titration :**

In iodometric titrations, an oxidizing agent is allowed to react in neutral medium or in acidic medium with excess of potassium iodide to liberate free iodine.

$$KI + \text{oxidizing agent} \longrightarrow I_2$$

Free iodine is titrated against a standard reducing agent usually with sodium thiosulphate. Halogen, dichromates, cupric ion, peroxides etc., can be estimated by this method.

$$I_2 + 2NaS_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

$$K_4Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 3I_2$$

**(ii) Iodimetric Titration**

These are the titrations in which free iodine is used as it is difficult to prepare the solution of iodine (volatile and less soluble in water), it is dissolved in KI solution :

$$KI + I_2 \longrightarrow KI_3 \text{ (Potassium triiodide)}$$

This solution is first standardized before using with the standard solution of substance such as sulphite, thiosulphate, arsenite etc, are estimated.

In iodimetric and iodometric titration, starch solution is used as an indicator. Starch solution gives blue or violet colour with free iodine. At the end point, the blue or violet colour disappears when iodine is completely changed to iodide.

## ❑ SOME IODOMETRIC TITRATIONS (TITRATING SOLUTIONS IS $Na_2S_2O_3.5H_2O$)

| Estimation of | Reaction | Relation between O.A. and R.A. |
|---|---|---|
| $I_2$ | $I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$<br>or<br>$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$ | $I_2 = 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $Na_2S_2O_3$ = M/1 |
| $CuSO_4$ | $2CuSO_4 + 4KI \longrightarrow 2Cu_2I_2 + 2K_2SO_4 + I_2$<br>$Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$<br>(White ppt.) | $2CuSO_4 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $CuSO_4$ = M/1 |
| $CaOCl_2$ | $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$<br>$Cl_2 + 2KI \longrightarrow 2KCl + I_2$<br>$CaOCl_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$ | Eq. wt. of $CaOCl_2$ = M/2 |
| $MnO_2$ | $MnO_2 + 4HCl(conc) \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$<br>$Cl_2 + 2KI \longrightarrow 2KCl + I_2$<br>or<br>$MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + Cl_2$<br>$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$ | $MnO_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $MnO_2$ = M/2 |
| $IO_3^-$ | $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$ | $IO_3^- \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$<br>Eq. wt. of $IO_3^-$ = M/6 |
| $H_2O_2$ | $H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$ | $H_2O_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $H_2O_2$ = M/2 |
| $Cl_2$ | $Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$ | $Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$<br>Eq. wt. of $Cl_2$ = M/2 |
| $O_3$ | $O_3 + 6I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$ | $O_3 \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$<br>Eq. wt. of $O_3$ = M/6 |
| $Cr_2O_7^{2-}$ | $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$ | $Cr_2O_7^{2-} \equiv 3I_2 \equiv 6I$<br>Eq. wt. of $Cr_2O_7^{2-}$ |
| $MnO_4^-$ | $2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2MnO_4^- + 5I_2 + 8H_2O$ | $2MnO_4^- \equiv 5I_2 \equiv 10I$<br>Eq. wt. of $MnO_4^-$ = M/5 |
| $BrO_3^-$ | $BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$ | $BrO_3^- \equiv 3I_2 \equiv I_2$<br>Eq. wt. of $BrO_3^-$ = M/6 |
| As(V) | $H_3AsO_4 + 2I^- + 2H^+ \longrightarrow H_3AsO_3 + H_2O + I_2$ | $H_3AsO_4 \equiv I_2 \equiv 2I$<br>Eq. wt. of $H_3AsO_4$ = M/2 |

## ❑ SOME IODIMETRIC TITRATION (TITRATING SOLUTIONS IS $I_2$ IN KI)

| Estimation of | Reaction | Relation between O.A. and R.A. |
|---|---|---|
| $H_2S$<br>(in acidic medium) | $H_2S + I_2 \longrightarrow S + 2I^- + 2H^+$ | $H_2S \equiv I_2 \equiv 2I$<br>Eq. wt. of $H_2S = M/2$ |
| $SO_3^{2-}$<br>(in acidic medium) | $SO_3^{2-} + I_2 + H_2O \longrightarrow SO_3^{2-} + 2I^- + 2H^+$ | $SO_3^{2-} \equiv I_2 \equiv 2I$<br>Eq. wt. of $SO_3^{2-} = M/2$ |
| $Sn^{2+}$<br>(in acidic medium) | $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$ | $Sn^{2+} \equiv I_2 \equiv 2I$<br>Eq. wt. of $Sn^{2+} = M/2$ |
| As(III) (at pH = 8) | $H_2AsO_3^- + I_2 + H_2O \longrightarrow$<br>$HAsO_4^{2-} + 2I^- + 2H^+$ | $H_2AsO_3^- \equiv I_2 \equiv 2I$<br>Eq. wt. of $H_2AsO_3^- = M/2$ |
| $N_2H_4$ | $N_2H_4 + 2I_2 \longrightarrow N_2 + 4H^+ + 4I^-$ | $N_2H_4 \equiv 2I_2 \equiv 4I$<br>Eq. wt. of $N_2H_4 = M/4$ |

## 11. Hardness of water :

**Hard water** does not give lather with soap. Water free from soluble salts of calcium and magnesium is called **Soft water**. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out Ca/Mg stearate.

$$2C_{17}H_{35}COONa(aq) + M^{2+}(aq) \rightarrow (C_{17}H_{35}COO)_2M \downarrow + 2Na^+(aq);\ \text{M is Ca/Mg}$$

**Hardness of water is of two types**

(a) Temporary Hardness

(b) Permanent Hardness

**Temporary Hardness :-**

This is due to presence of bicarbonate of calcium and magnesium. Rain water dissolves a small quantities of $CO_2$ from the atmospher forming a very dilute solution of carbonic acid.

This water attacks Ca and Mg carbonate in any rock

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

Temporary hardness in water is easily removed by boiling, as the bicarbonates decomposes readily and the insoluble carbonates are precipitated.

$$Ca(HCO_3)_2 \xrightarrow{\text{Boil}} \underset{\text{(Insoluble)}}{CaCO_3} + H_2O + CO_2$$

$$Mg(HCO_3)_2 \xrightarrow{\text{Boil}} \underset{\text{(Insoluble)}}{MgCO_3} + H_2O + CO_2$$

Temporarily hardness can also be removed by clark's process which involves the addition of slaked lime Ca(OH)

$$Ca(HCO_3)_2 + Ca(OH)_2 \xrightarrow{\text{Boil}} \underset{\text{(Insoluble)}}{2CaCO_3} + 2H_2O$$

**Permanent Hardness :-** Permanent hardness is due to presence of sulphates and chlorides of both calcium and magnesium. This type of hardness cannot be removed by boiling or by $Ca(OH)_2$;. Substance used to remove the hardness of water are known as water softener. This various water softeners are -

**(i)** **Washing soda :-** It removes both the temporary and permanent hardness by converting soluble Ca and Mg compounds into insoluble Carbonates.

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

$$\mathrm{C\ aSO_4} + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

$$Ca(HCO_3)_2 + Na_2CO_3 \longrightarrow \underset{\text{(Insoluble)}}{CaCO_3} + \underset{\text{(Insoluble)}}{NaHCO_3}$$

**(ii)** **Permutit:** Permutit is technical name given to certain hydrated silicates of aluminium and sodium.or sodium alumunium orthosilicate or sodium zeolite.

**Example :** $Na_2\,Al_2\,Si_2\,O_8\,xH_2O$.

$$Na_2\,Al_2\,Si_2\,O_8\,xH_20 + Ca^{+2} \longrightarrow Ca\,Al_2\,Si_2\,O_8\,xH_2O + 2Na^{\oplus}$$

$$Na_2\,Al_2\,Si_2\,O_8\,xH_2O + Mg^{+2} \longrightarrow Mg\,Al_2\,Si_2\,O_8\,xH_2O + 2Na^{\oplus}$$

These ions can be re-exchanged by treating it with brine (NaCl) solution.

$$Ca\,Al_2\,Si_2\,O_8\,xH_2O + 2NaCl \longrightarrow Na_2\,Al_2\,Si_2\,O_8\,xH_2O + CaCl_2$$

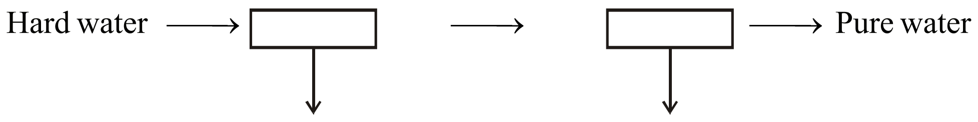
This method is useful for the removal of both temporary and permanent hardness of water.

**(iii)** **CALGON:** The complex salt of metaphosphoric acid, sodium hexametaphosphate $(Na_4(PO_3)_6$ is called Calgon. It is represented as $Na_2[Na_4(PO_3)_6]$.

$$2CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + Na_2SO_4$$

$$2MgSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Mg_2(PO_3)_6] + Na_2SO_4$$

**(iv)** **Ion exchange Resins:-** Ion exchange resins are the most popular water softener thease days. This resins are synthetic substance. The cation exchanger consists of granular insoluble organic acid resins having giant molecules with $-SO_3H$ or -COOH groups while the anion exchanges contains giant organic molecules with basic groups derived from amine. Ion exchange resins removes all soluble mineral from water.



| | |
|---|---|
| Cation exchanger<br>Remove cation like<br>$Na^+$, $Mg^{2+}$ or $Ca^{2+}$<br>and furnish $H^+$ | Cation exchanger<br>Remove anion like<br>$SO_4^{2-}$, $Cl^-$ or $NO_3^+$<br>and furnish $OH^-$ |

$$H^+ + OH^- \longrightarrow H_2O$$

$$Ca^{2+} + RH_2 \longrightarrow R_2Ca + 2H^+$$

The water coming from cation exchanger is acidic due to H®. This water is then passed through another bed containing anion exchanger. This exchanger removes anion like $Cl^-$, $SO_4^{2-}$, $NO_3$ by exchanging with OH– ions.

**Reaction at Cation exchanger :**

$$Ca^{+2} + RH_2 \longrightarrow R_2Ca + 2H^{\oplus}$$

$$Mg^{+2} + RH_2 \longrightarrow R_2Mg + 2H^{\oplus}$$

**Reaction at Anion exchanger :**

$$R.(OH)_2 + Cl^- \longrightarrow RC1_2 + OH^-$$

$$R.(OH)_2 + SO_4^{2-} \longrightarrow RSO_4 + OH^-$$

**NOTE :** Degree of Hardness of water is measured in terms of ppm of $CaCO_3$ which is defined as number of parts of $CaCO_3$ by mass present in one million parts by mass of water whose equivalent is equal to the gram equivalent of various calcium & magnesium salts.

For **example** consider the sample of hard water which is found to contain 36 mg of $MgSO_4$ per kg of water.

gm equivalent of $CaCO_3$ = gm eq. of $MgSO_4$

$$\frac{W_{CaCO_3}}{100} \times 2 = \frac{36 \times 10^{-3}}{120} \times 2$$

$W_{CaCO_3} = 3 \times 10^{-2}$gm

degree of hardness = ppm of $CaCO_3 = \frac{3 \times 10^{-2}}{1000} \times 10^6 = 30$

## 12. GLOSSARY

**Aliquot.** A portion of the whole, usually a simple fraction. A portion of a sample withdraw from a volumetric flask with a pipet is called an aliquot.

**Analytical concentration.** The total number of moles per litre of a solute regardless of any reactions that might occur when the solute dissolves. Used synonymously with formality.

**Equivalent.** The amount of a substance which furnishes or reacts with 1 mol of $H^+$ (acid-base), 1 mol of electrons (redox), or 1 mol of a univalent cation (precipitation and complex formation).

**Equivalent weight.** The weight in grams of one equivalent of a substance.

**Equivalence point.** The point in a titration where the number of equivalents of titrant is the same as the number of equivalents of analyte.

**End point.** The point in a titration where an indicator changes color.

**Formula weight.** The number of formula weights of all the atoms in the chemical formula of a substance.

**Formality.** The number of formula weights of solute per litre of solution; synonymous with analytical concentration.

**Indicator.** A chemical substance which exhibits different colors in the presence of excess analyte or titrant.

**Normality.** The number of equivalents of solute per litre of solution.

**Primary standard.** A substance available in a pure form or state of known purity which is used in standardizing a solution.

**Standardization.** The process by which the concentration of a solution is accurately ascertained.

**Standard solution.** A solution whose concentration has been accurately determined.

**Titrant.** The reagent (a standard solution) which is added from a buret to react with the analyte.

## *SOME MORE SOLVED EXAMPLES*

**Ex.25** A 3.00 g sample containing $Fe_3O_4$, $Fe_2O_3$ and an inert impure substance, is treated with excess of KI solution in presence of dilute $H_2SO_4$. The entire iron is converted into $Fe^{2+}$ along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the diluted solution require 11 mL of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 mL of diluted solution after complete extraction of the iodine requires 12.80 mL of 0.25 $KMnO_4$ solution in dilute $H_2SO_4$ medium for the oxidation of $Fe^{2+}$. Calculate the percentages of $Fe_2O_3$ and $Fe_3O_4$ in the original sample.

**Sol.** Let number of moles of $Fe_3O_4$ is 'a' and no. of moles of $Fe_2O_3$ is 'b' in 3 gram sample.

Now, 'a' moles $Fe_3O_4$ means (a moles $Fe_2O_3$ + a mole of FeO)

So, in sample (a + b) moles $Fe_2O_3$ and 'a' mole FeO present.

$$Fe_2O_3 + KI + \xrightarrow{H_2SO_4} FeSO_4 + I_2 + K_2SO_4 + H_2O$$

No. of gram equivalent of $Fe_2O_3$ = no. of gram equivalent of $I_2$

$$n_{Fe_2O_3} \times n_{f(Fe_2O_3)} = n_{I_2} \times n_{f(I_2)}$$

$$(a + b) \times 2 = n_{I_2} \times 2$$

$$n_{I_2} = (a + b) \text{ moles.}$$

Now, solution is diluted to 100 ml

$$\text{So, } [I_2] = \frac{n}{V_{\text{litre}}} = \frac{(a+b)}{100/1000} = 10(a+b)$$

$$[Fe^{2+}] = \left(\frac{n(Fe^{2+})}{V_{\text{litre}}}\right) = \frac{(3a+2b)}{100/1000} = 10(3a + 2b)$$

Now 20 ml of this solution titrated with 11 ml, 0.5 M $Na_2S_2O_3$

$$I_2 + Na_2S_2O_3 \rightarrow NaI + Na_2S_4O_6$$

No. of gram equivalent of $I_2$ = no. of gram equivalent of $Na_2S_2O_3$

$$(N \times V)_{I_2} = (N \times V)_{Na_2S_2O_3}$$

$$(M \times n_f \times V)_{I_2} = (M \times n_f \times V)_{Na_2S_2O_3}$$

$$10\,(a + b) \times 2 \times 20 = 0.5 \times 1 \times 11$$

$$a + b = \frac{11}{800} \qquad \text{...... (i)}$$

50 ml of solution after extraction of $I_2$ allowed to oxidation of $Fe^{2+}$ by 12.80 ml, 0.25 M $KMnO_4$.

$Fe^{2+} + KMnO_4 + H_2SO_4 \rightarrow Fe^{3+} + MnSO_4 + K_2SO_4 + H_2O$

no. of gram equivalent of $Fe^{2+}$ = no. of gram equivalent of $KMnO_4$.

$(M \times n_f \times V)_{Fe^{2+}} = (M \times n_f \times V)_{KMnO4}$

$10(3a + 2b) \times 1 \times 50 = 0.25 \times 5 \times 12.80$

$3a + 2b = \frac{16}{500}$ .....(ii)

By (i) & (ii)

a = 0.0045 moles

b = 0.00925 moles

$$\text{so } \% \ Fe_2O_3 = \frac{Wt(Fe_2O_3)}{\text{Total wt.}} \times 100 = \frac{b \times 160}{3} \times 100 = \frac{0.00925 \times 160}{3} \times 100 = 49.33\%.$$

$$\% \ Fe_2O_3 = \frac{Wt(Fe_2O_3)}{\text{Total wt.}} \times 100 = \frac{a \times 232}{3} \times 100 = \frac{0.0045 \times 232}{3} \times 100 = 34.8\,\%$$

**Ex.26** Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KMnO_4$ (20 mL) acidified with dilute $H_2SO_4$. The same volume of $KMnO_4$ solution is just decolorized by 10 mL of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated $MnO_2$. The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute $H_2SO_4$. Write the equations involved in the reactions and calculate the molarity of $H_2O_2$.

**Sol.** Let molarity of $H_2O_2$ solution is $M_1$

20 ml, $M_1$ molar $H_2O_2$ react with 20 ml $KMnO_4$ in $H_2SO_4$ solution

$H_2O_2 + KMnO_4 + H_2SO_4 \rightarrow MnSO_4 + K_2SO_4 + H_2O + O_2$

no. of gram equivalent of $H_2O_2$ = no. of gram equivalent of $KMnO_4$

$(M \times n_f \times V)_{H_2O_2} = (M \times n_f \times V)_{KMnO_4}$

$M_1 \times 2 \times 20 = M_{KMnO_4} \times 5 \times 20$ .......(i)

20 ml $KMnO_4$ decolourise by 10 ml $MnSO_4$ in neutral medium.

$KMnO_4 + MnSO_4 + H_2O \rightarrow MnO_2 + H_2SO_4 + KHSO_4$

no. of gram equivalent of $KMnO_4$ = no. of gram equivalent of $MnO_2$

$M_{KMnO_4} \times 3 \times 20\text{ml}$ = no. of gram equivalent of $MnO_2$

$M_{KMnO_4} \times 3 \times 20 \times 10^{-3} = n_{MnO_2} \times 6/5$ ......(ii)

and obtained $MnO_2$ dissolved in 10 ml, 0.2 M $Na_2C_2O_4$

$MnO_2 + Na_2C_2O_4 + H_2SO_4 \rightarrow MnSO_4 + CO_2 + Na_2SO_4 + H_2O$

no. of gram equivalent of $MnO_2$ = no. of gram equivalent of $Na_2C_2O_4$

$n_{MnO_2} \times 2 = 0.2 \times 2 \times 10 \times 10^{-3}$

$n_{MnO_2} = 2\times10^{-3}$ moles .......(iii)

From equaiton (ii)

$$M_{KMnO_4} \times 3 \times 20 \times 10^{-3} = 2 \times 10^{-3} \times \frac{6}{5}$$

$$M_{KMnO_4} = \frac{2}{50}$$

From equation (1)

$$M_1 \times 2 \times 20 = \frac{2}{50}\times5\times20$$

$M_1 = 0.1M$

**Ex.27** One litre of a mixture of $O_2$ and $O_3$ ($O_3 \longrightarrow O_2 + O^{2-}$) at 1 atm and 273 K was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 ml of M/10 sodium thiosulphate solution for titration. What is the percent of ozone in the mixture ? Ultraviolet radiation of wave length 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture ?

**Sol.** Let in 1 litre mixture x litre is $O_2$ and y litre is $O_3$ at NTP

excess KI reduce $O_3$ into $O_2$ and $O^{2-}$

$KI + O_3 + H_2O \rightarrow I_2 + O_2 + KOH$

no. of gram equivalent of $O_3$ = no. of gram equivalent of $I_2$

$(n \times n_f)_{O_3} = (n \times n_f)_{I_2}$

$$\frac{y}{22.4}\times2 = n_{I_2} \times 2$$

$$n_{I_2} = \frac{y}{22.4} \qquad ......(1)$$

Now, released $I_2$ required 40 ml , $\frac{1}{10}$M $Na_2S_2O_3$

$I_2 + Na_2S_2O_3 \rightarrow NaI + Na_2S_4O_6$

No. of gram equivalent of $I_2$ = no. of gram equivalent of $Na_2S_2O_3$

$$n_{I_2} \times 2 = \frac{1}{10} \times 1 \times 40 \times 10^{-3}$$

$n_{I_2} = 2 \times 10^{-3}$ moles

Now from equation (1)

$$\frac{y}{22.4} = 2\times10^{-3}$$

$y = (44.8 \times 10^{-3})$ litre = 0.0448 litre

$x = 1 - y = 1 - 0.0448 = 0.9552$ litre

$$\% \text{ (by wt)} = \frac{wt(O_3)}{wt.(total)} \times 100$$

$$= \frac{n(O_3) \times 48}{n(O_3) \times 48 + n(O_2) \times 32} \times 100$$

$$= \frac{\frac{y}{22.4} \times 48}{\frac{y}{22.4} \times 48 + \frac{x}{22.4} \times 32} \times 100$$

$$= \frac{3y}{3y + 2x} \times 100$$

$$= \frac{3 \times 0.0448}{3 \times 0.048 + 2 \times 0.9552} \times 100$$

$$= \frac{0.1344}{2.0448} \times 100 = 6.57\ \%$$

One photon required for breaking of one $O_3$ bond in to $O_2$ & O

$$O_3 \xrightarrow{hv} O_2 + O$$

So. no. of photon required = no. of $O_3$ bonds break

= no. of $O_3$ molecules

$$= n_{O_3} \times N_A = \frac{0.0448}{22.4} \times 6 \times 10^{23}$$

$= 1.2 \times 10^{21}$ photons.

**Ex.28** A mixture of FeO and $Fe_2O_3$ is reacted with acidified $KMnO_4$ solution having a concentration of 2/5 M, 100 mL of which was used. The solution was then titrated with Zn dust which converted $Fe^{3+}$ of the solution to $Fe^{2+}$. The $Fe^{2+}$ required 1000 mL of 2/15 M $K_2Cr_2O_7$ solution. Find the % by mol of FeO and $Fe_2O_3$.

**Sol.** Let no. of moles of FeO is x millimoles & $Fe_2O_3$ is y millimoles in mixture.

$FeO + KMnO_4 + H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$

no. of milligram equivalent of FeO = no. of milli gram equivalent of $KMnO_4$.

$$x \times 1 = \frac{2}{5} \times 5 \times 100$$

x = 200 m moles.

Zn - dust convert all $Fe^{3+}$ to $Fe^{2+}$

So no. of millimoles of $Fe^{2+}$ in solution is = (x + 2y).

$Fe^{2+} + K_2Cr_2O_7 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe^{3+} + K_2SO_4 + H_2O$

no. of milli gram equivalent of $Fe^{2+}$ = no. of milligram equivalent of $K_2Cr_2O_7$

$$(x + 2y) \times 1 = \frac{2}{15} \times 6 \times 1000$$

$$(200 + 2y) = \frac{2}{15} \times 1000$$

y = 300 millimoles.

$$\% \text{ FeO (by moles)} = \frac{x}{x+y} \times 100 = \frac{200}{500} \times 100 = 40\%$$

% $Fe_2O_3$ (by moles) = 60%

**Ex.29** A substance of crude copper is boiled in $H_2SO_4$ till all the copper has reacted. The impurities are inert to the acid. The $SO_2$ liberated in the action is passed into 100 mL of 0.4 M acidified $KMnO_4$($SO_2 \rightarrow SO_4^{-2}$) The solution of $KMnO_4$ after passage of $SO_2$ is allowed to react with oxalic acid and requires 25 mL of 1 M oxalic acid. If the purity of copper is 95.25%, what was the weight of the sample.

**Sol.** let given sample is w gram and no. of moles of Cu in given sample is x millimoles.

$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

x millimoles x millimoles

$SO_2 + KMnO_4 + H_2SO_4 \rightarrow MnSO_4 + H_2O + SO_3 + K_2SO_4$

no. of milligram eq. of $SO_2$ = no. of milli gram eq. of $KMnO_4$

x × 2 = no. of gram eq. of $KMnO_4$

left $KMnO_4$ reduced by $H_2C_2O_4$

$KMnO_4 + H_2SO_4 + H_2C_2O_4 \rightarrow MnSO_4 + CO_2 + H_2O + K_2SO_4$

no. of milligram eq. of $KMnO_4$(left)

= no. of mill gram equ. of $H_2C_2O_4$

= 1 × 2 × 25

So, total milligram eq. of $KMnO_4$ = milligram eq. of $SO_2$ + milligram eq. of $H_2C_2O_4$

$0.4 \times 5 \times 100 = x \times 2 + 1 \times 2 \times 25$

x = 75 millimoles

wt(Cu) = 95.25% of W

$$75 \times 10^{-3} \times 63.5 = \frac{95.25}{100} \times W$$

$\Rightarrow$ W = 5 gram.

**Ex.30** $H_2O_2$ is reduced rapidly by $Sn^{2+}$, the products being $Sn^{4+}$ and water. $H_2O_2$ decomposes slowly at room temperature to yield $O_2$ and water. Calculate the volume of $O_2$ produced at 273 K and 1.00 atm when 200 g of 10.0 % by mass $H_2O_2$ in water is treated with 88.2 mL of 1 M $Sn^{2+}$ and then the mixture is allowed to stand until no further reaction occurs.

**Sol.** Let x millimoles of $H_2O_2$ react with 1M, 88.2 ml $Sn^{2+}$

$H_2O_2 + Sn^{2+} \rightarrow Sn^{4+} + H_2O$

no. of milligram equivalent of $H_2O_2$

= no. of milligram eq. of $Sn^{2+}$

$x_{\text{millimole}} \times 2 = 1 \times 2 \times 88.2$

x = 88.2 millimoles

Total given moles of $H_2O_2$ is

$$n_{\text{total}} = \frac{W(H_2O_2)}{34} = \frac{10\%\text{ of } 200\text{ gram}}{34}$$

$$= \frac{20}{34}\text{ moles}$$

= 0.5882 moles

= 588.2 millimoles.

so. no. of moles of $H_2O_2$ that decomposed to $O_2$

= 588.2 – 88.2

= 500 millimoles

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

$$n(O_2)\text{ released} = \frac{1}{2} \times 500 = 250\text{ millimoles}$$

$V_{O_2}$ (at 1atm, 273 K) = $250 \times 10^{-3} \times 22.4 = 5.6$ litre.

**Ex.31** 0.84 g iron ore containing x percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required x ml of a dichromatic solution for oxidizing the iron content to ferric state. Calculate the normality of dichromatic solution.

**Sol.** Let Normality of $K_2Cr_2O_7$ solution is N

$Fe^{2+} + K_2Cr_2O_7 + H^+ \rightarrow Fe^{3+} + Cr^{3+} + H_2O$

no. of gram eq. of $Fe^{2+}$ = no. of gram eq. of $K_2Cr_2O_7$

$$n_{Fe^{2+}} \times 1 = N \times x \times 10^{-3}$$

$$\frac{W_{Fe^{2+}}}{56} \times 1 = N \times x \times 10^{-3}$$

$$\frac{\frac{x}{100} \times 0.84}{56} \times 1 = N \times x \times 10^{-3}$$

N = 0.15

**Ex.32** 5 g of pyrolusite (impure $MnO_2$) were heated with conc. HCl and $Cl_2$ evolved was pssed through excess of KI solution. The iodine liberated required 40 mL of N/10 hypo solution. Find the % of $MnO_2$ in the pyrolusite.

**Sol.** Let moles of $MnO_2$ in 5 gram sample is x.

$MnO_2 + HCl \rightarrow MnCl_2 + Cl_2 + H_2O$

no. of gram eq. of $MnO_2$ = no. of gram equivalent of $Cl_2$

$x \times 2 = n_{(Cl_2)} \times 2$

$x = n_{(Cl_2)}$

so $n_{I_2} = n_{Cl_2} = x$

evolved $Cl_2$ passes through KI that released $I_2$

$Cl_2 \quad + \quad 2\,KI \rightarrow \quad I_2 \quad + \quad 2KCl$

x moles x moles

Evaled $I_2$ required 40 ml , $\frac{N}{10}$ $Na_2S_3O_3$

$I_2 \quad + \quad 2Na_2S_2O_3 \quad \rightarrow \quad 2NaI \quad + \quad Na_2S_4O_6$

no. of gram equivalent of $I_2$ = no. of gram equivalent of hypo

$$x \times 2 = \frac{1}{10} \times 40 \times 10^{-3}$$

$x = 2 \times 10^{-3}$ moles

$$\% \ MnO_2 = \frac{\text{wt.}(MnO_2)}{\text{total wt.}} \times 100$$

$$= \frac{x \times 87}{5} \times 100 = \frac{2 \times 10^{-3} \times 87}{5} \times 100$$

= 3.48 %

**Ex.33** A 458 g sample containing $Mn_3O_4$ was dissolved and all manganese was converted to $Mn^{2+}$. In the presence of fluoride ion, $Mn^{2+}$ is titrated with 3 lit of $KMnO_4$ solution (which was 1.25 N against oxalate in acidic medium), both reactants being converted to a complex of Mn(III) , What was the % of $Mn_3O_4$ in the sample ?

**Sol.** $KMnO_4 + H_2C_2O_4 + H_2SO_4 \rightarrow CO_2 + MnSO_4 + K_2SO_4 + H_2O$

3 litre, M molar

Normality ($KMnO_4$) = Molarity × $n_f$

1.25 = M × 5

M = 0.25

Let x moles of $Mn_3O_4$ present in 458 gram sample

$Mn_3O_4 \rightarrow 3Mn^{2+}$

xmole 3xmoles

$Mn^{2+} + KMnO_4 \rightarrow Mn^{3+}$

no. of gram eq. of $Mn^{2+}$ = no. of gram eq. $KMnO_4$

$3x \times 1 = (M \times n_f \times V)_{KMnO_4}$

$3x \times 1 = 0.25 \times 4 \times 3$

x = 1 moles

$$\%\ Mn_3O_4\ (\text{by wt}) = \frac{w(Mn_3O_4)}{w_{total}} \times 100$$

$$= \frac{1 \times 229}{458} \times 100 = 50\%$$

**Ex.34** 80 gm of a sample of Anhydrous $CuSO_4$ was dissolved in water and made to 250 mL. 25 mL of this solution after taking usual precaution was treated with a little excess of KI solution. A white ppt. of $Cu_2I_2$ and iodine was evolved. The iodine so evolved required 40 mL of 1 M hypo solution. What is the approximate purity of $CuSO_4$ solution.

**[Mol. wt. of $CuSO_4$ = 160]**

**Sol.** Let 80 gram sample contains x moles of $CuSO_4$ that desolve in 250 ml solution

So 25 ml solution contain (x/10) moles $CuSO_4$

$CuSO_4 \ + \ KI \ \rightarrow \ Cu_2I_2 \ + \ I_2$

no. of gram eq. of $CuSO_4$ = no. of gram eq. of $I_2$

$$\frac{x}{10} \times 1 = n_{(I_2)} \times 2$$

$$n_{(I_2)} = \frac{x}{20}$$

Evalved $I_2$ required 40 ml, 1M hypo solution

$I_2 + Na_2S_2O_3 \rightarrow NaI + Na_2S_4O_6$

no. of gram eq. of $I_2$ = no. of gram eq. of hypo

$n(I_2) \times 2 = 1 \times 1 \times 40 \times 10^{-3}$

$$\frac{x}{20} \times 2 = 40 \times 10^{-3}$$

$x = 40 \times 10^{-2}$ moles

$$\%\ CuSO_4\ (\text{by mass}) = \frac{wt(CuSO_4)}{wt\ total} \times 100$$

$$= \frac{40 \times 10^{-2} \times 160}{80} \times 100 = 80\%$$

## *EXERCISE # S-I*

### *OXIDATION NUMBER*

**1.** Calculate oxidation number of underlines elements in the following compounds

(a) $H_2\underline{S}_2O_7$ (b) $H_4\underline{P}_2O_7$ (c) $\underline{S}_2O_3^{2-}$ (d) $\underline{C}H_4$

(e) $\underline{C}Cl_4$ (f) $Ca\underline{O}_2$ (g) $\underline{Z}nO_2^{2-}$ (h) $\underline{Cr}O_2Cl_2$

(i) $Ca(\underline{Cl}O_2)_2$

**RR0001**

**2.** Classify each of the following unbalanced half–reactions as either an oxidation or a reduction :

(a) $O_2(g) \longrightarrow OH^-(aq)$ (b) $H_2O_2(aq) \longrightarrow O_2(g)$

(c) $MnO_4^-(aq) \longrightarrow MnO_4^{2-}(aq)$ (d) $CH_3OH(aq) \longrightarrow CH_2O(aq)$

**RR0002**

**3.** Identify the oxidant and reductant in the following reactions :

(a) $Zn(s) + \frac{1}{2}O_2(g) \longrightarrow ZnO(s)$

(b) $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

(c) $10H^+(aq) + 4Zn(s) + NO_3^-(aq) \longrightarrow 4Zn^{2+}(aq) + NH_4^+(aq) + 3H_2O(\ell)$

**RR0003**

### *BALANCING OF REDOX*

**4.** Balance the following redox reactions by oxidation number method :

(i) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$ (Acidic medium) **RR0004**

(ii) $Br_2 + H_2O_2 \longrightarrow BrO_3^- + H_2O$ (Acidic medium) **RR0005**

(iii) $MnO_4^- + Fe^{+2} \longrightarrow Mn^{+2} + Fe^{+3}$ (Acidic medium) **RR0006**

(iv) $MnO_2 + Cl^- \longrightarrow Mn^{+2} + Cl_2 + H_2O$ (Acidic medium) **RR0007**

(v) $ClO^- + CrO_2^- \xrightarrow{OH^-} Cl^- + CrO_4^{2-} + H_2O$ (Basic medium) **RR0008**

**5.** Balance the following redox reactions by half-reaction method (Ion electron method):

(i) $MnO_4^-(aq) + I^-(aq) \longrightarrow MnO_2(s) + I_2(s)$ (in basic medium) **RR0009**

(ii) $MnO_4^-(aq) + SO_2(g) \longrightarrow Mn^{2+}(aq) + HSO_4^-(aq)$ (in acidic solution) **RR0010**

(iii) $H_2O_2(aq) + Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + H_2O(l)$ (in acidic solution) **RR0011**

(iv) $Cr_2O_7^{2-}(aq.) + SO_2(g) \longrightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$ (in acidic solution) **RR0012**

**6.** Find the valence factor for the following acid/bases -

| | | |
|---|---|---|
| (1) $CH_3COOH$ | (2) $NaH_2PO_4$ | (3) $H_3BO_3$ |
| (4) $NaOH$ | (5) $Ca(OH)_2$ | (6) $CsOH$ |

**RR0013**

**7.** Find the n-factor of underlined species in the following non redox reaction.

(1) $NaOH + \underline{H_3PO_4} \longrightarrow NaH_2PO_4 + H_2O$

(2) $NaOH + \underline{H_2SO_4} \longrightarrow NaHSO_4 + H_2O$

(3) $\underline{Ca(OH)_2} + HCl \longrightarrow Ca(OH)Cl + H_2O$

(4) $\underline{Na_2CO_3} + HCl \longrightarrow NaHCO_3 + NaCl$

(5) $\underline{\mathbf{Na_2CO_3}} + HCl \longrightarrow NaCl + H_2O + CO_2$

**RR0014**

**8.** What will be the equivalent wt. of $H_3PO_4$ in each of the reaction.

$H_3PO_4 + OH^- \longrightarrow H_2PO_4^- + H_2O$

$H_3PO_4 + 2OH^- \longrightarrow HPO_4^{2-} + 2H_2O$

$H_3PO_4 + 3OH^- \longrightarrow PO_4^{3-} + 3H_2O$

**RR0015**

**9.** What is the equivalent weight of $HNO_3$ in following reaction ?

$HNO_3 + H_2S \longrightarrow H_2O + NO + S$

**RR0016**

**10.** Find out the equivalent weight of the underlined species in the following reaction :

(i) $\underline{ClO_3^-} + Fe^{2+} + H^+ \longrightarrow Cl^- + Fe^{3+} + H_2O$

(ii) $CuO + \underline{NH_3} \longrightarrow Cu + N_2 + H_2O$

**RR0017**

**11.** Find out the $n_{factor}$ of $(NH_4)_2Cr_2O_7$ in the following decomposition reaction.

$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2(g) + H_2O$

**RR0018**

**12.** Find out the $n_{factor}$ of $IO_3^-$ in the following disproportination reaction.

$I_2 \xrightarrow{OH^-} IO_3^- + I^-$

**RR0019**

## ACID BASE TITRATION

**13.** How many millilitre of 0.5 M $H_2SO_4$ are needed to dissolve 0.5 g of copper II carbonate ?**[JEE 1999]**

**RR0020**

**14.** An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is : **[JEE 2001]**

**RR0021**

**15.** Calculate volume of 1N $H_3PO_4$ required to react with 20 ml 2N $Ca(OH)_2$ solution

**RR0022**

**16.** Calculate volume of 1N $H_2SO_4$ required to react with 20 ml 1 M $Al(OH)_3$ solution

**RR0023**

**17.** Calculate volume of 0.4 M NaOH required to react with following mixture

HCl(1 mol) + $H_2SO_4$ (2 mol)

**RR0024**

**18.** Calculate volume of 0.2 M $H_2SO_4$ required to react with following mixture

NaOH(1 mol) + $Ca(OH)_2$ (2 mol)

**RR0025**

**19.** How many litre of 0.1N HCl are required to react completely with 19 gm mixture of $Na_2CO_3$ and $NaHCO_3$ containing equimolar amount of two ?

**RR0026**

**20.** $H_3PO_4$ is a tri basic acid and one of its salt is $NaH_2PO_4$. What volume in ml of 1 M NaOH solution should be added to 12 g of $NaH_2PO_4$ to convert it into $Na_3PO_4$ ?

**RR0027**

### *REDOX TITRATION*

**21.** Calculate the normality of a solution containing 50 mL of 5 M solution of $K_2Cr_2O_7$ in acidic medium.

**RR0028**

**22.** A 5.0 $cm^3$ solution of $H_2O_2$ liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of $H_2O_2$ solution in terms of volume strength at STP. **[JEE' 1995]**

**RR0029**

**23.** Calculate the normality of a solution containing 15.8 g of $KMnO_4$ in 50 mL acidic solution.

**RR0030**

**24.** 20 mL of $H_2O_2$ after acidification with dil $H_2SO_4$ required 30 mL of $\frac{N}{12}$ $KMnO_4$ for complete oxidation. The strength of $H_2O_2$ solution is [Molar mass of $H_2O_2$ = 34]

**RR0031**

**25.** It required 40 ml of 1 M $Ce^{4+}$ to titrate 20 ml of 1 M $Sn^{2+}$ to $Sn^{4+}$. What is the oxidation state of cerium in the product.

**RR0032**

**26.** A volume of 10.0 ml of 1 M $SeO_2$ reacted with exactly 20 ml of 2 M $CrSO_4$. In the reaction, $Cr^{2+}$ was oxidized to $Cr^{3+}$. To what oxidation state was selenium converted by the reaction.

**RR0033**

**27.** Potassium acid oxalate $K_2C_2O_4 . 3H_2C_2O_4 . 4H_2O$ can be oxidized by $MnO_4^-$ in acid medium. Calculate the volume of 0.1 M $KMnO_4$ reacting in acid solution with 5.08 gm of the acid oxalate.

**RR0034**

**28.** A 1 g sample of $H_2O_2$ solution containing x% $H_2O_2$ by mass requires x cm$^3$ of a $KMnO_4$ solution for complete oxidation under acidic condition. Calculate the normality of $KMnO_4$ solution.

**RR0035**

**29.** Metallic tin in the presence of HCl is oxidized by $K_2Cr_2O_7$ to stannic shloride, $SnCl_4$. What volume of deci-normal dichromate solution would be reduced by 11.9 gm of tin [Sn = 119]

**RR0036**

**30.** Calculate the number of millimoles of $K_2Cr_2O_7$ which will completely react with 40 ml 0.1 MKI Solution.

**RR0037**

**31.** Find the number of moles of $KMnO_4$ needed to oxidise one mole $Cu_2S$ in acidic medium. The reaction is : $Cu_2S + KMnO_4 \longrightarrow Cu^{2+} + Mn^{2+} + SO_2$

**RR0038**

**32.** 0.4 M $KMnO_4$ solution completely reacts with 0.05 M $FeSO_4$ solution under acidic conditions. The volume of $FeSO_4$ used is 50 mL. What volume of $KMnO_4$ was used ?

**RR0039**

### *BACK TITRATION*

**33.** 50 gm of a sample of $Ca(OH)_2$ is dissolved in 50 ml of 0.5 N HCl solution. The excess of HCl was titrated with 0.3N – NaOH. The volume of NaOH used was 20cc. Calculate % purity of $Ca(OH)_2$

**RR0040**

**34.** 10 g $CaCO_3$ were dissolved in 250 ml of 1 M HCl. What volume of 2 M KOH would be required to neutralise excess HCl.

**RR0041**

**35.** 20 g of a sample of $Ba(OH)_2$ is dissolved in 10 mL of 0.5 N HCl solution : The excess of HCl was titrated with 0.1 N NaOH. The volume of NaOH used was 20 cc. Calculate the percentage of $Ba(OH)_2$ in the sample. (Ba = 137)

**RR0042**

**36.** To 50 L of 0.2 N NaOH, 2.5 L of 2N HCl and 15 L of 0.1 N $FeCl_3$ solutions are added. What weight of $Fe_2O_3$ can be obtained from the precipitate? Also report the normality of NaOH left in resultant solution :

**RR0043**

### *Hardness of water*

**37.** Softening of hard water by using sodium aluminium silicate (zeolite) is due to -
Adsorption of ......... and .........ions of hard water, replacing ............ ions

**RR0044**

**38.** One litre of a sample of hard water contains 10 mg of $CaCl_2$ & 9.5 mg of $MgCl_2$. What is degree of hardness in terms of ppm of $CaCO_3$

**RR0045**

## *EXERCISE # S-II*

**1.** Find out the oxidation number of the underlined elements in the following compounds:

(a) $Na_2\underline{S}_4O_6$ (b) $\underline{C}_3O_2$ (c) $K\underline{I}_3$ (d) $\underline{Fe}_3O_4$

**RR0046**

(e) $\underline{C}H_3\underline{C}H_2OH$ (f) $\underline{C}H_3\underline{C}OOH$ (g) $\underline{Br}_3O_8$ (h) $CaO\underline{Cl}_2$

**RR0047**

(i) $\underline{Fe}\underline{S_2}$ (j) $\underline{O}F_2$ (k) $H\underline{O}F$ (l) $\underline{O_2}^+$

**RR0048**

(m) $\underline{O_2}^-$ (n) $C_6H_5\underline{C}HO$ (o) $C_6H_5\underline{N}O_2$ (p) $C_6H_5\underline{N}H_2$

**RR0049**

(q) $(\underline{C}N)_2$ (r) $\underline{C}N^-$ (s) $\underline{C}NO^-$

**RR0050**

**2.** Calculate oxidation number of underlines elements in the following compounds

(a) $K[\,\underline{Co}(C_2O_4)_2.(NH_3)_2]$ (b) $K\underline{Al}(\underline{S}O_4)_2.12H_2O$

(c) $[\underline{Fe}(CN)_6]^{4-}$ (d) $\underline{Fe}_{0.93}O$

**RR0051**

(e) $H_2\underline{S}_2O_8$ (f) $\underline{Cr}O_{\underline{5}}$

(g) $H_2\underline{S}O_5$ (h) $K_3\underline{Cr}O_8$

**RR0052**

(r) $Na_2[\underline{Fe}(CN)_5NO^+]$ (s) $\underline{Cr}(CN)_6^{3-}$

**RR0053**

**3.** Balance the following redox reactions by half-reaction method

(i) $KMnO_4$(aq.) + $FeC_2O_4$(aq.) + $H_2SO_4$ (aq.) $\longrightarrow$
$MnSO_4$ (aq.) + $Fe_2(SO_4)_3$ (aq.) + $CO_2$(g) + $H_2O$(*l*) (Acidic medium)

**RR0054**

(ii) $P_4$(s) + $OH^-$(aq.) $\longrightarrow$ $PH_3$(aq) + $HPO_2^-$ (aq.) (Basic medium)

**RR0055**

(iii) $I_2$(s) + NaOH(aq.) $\longrightarrow$ NaI (aq.) + $NaIO_3$(aq.) + $H_2O$(*l*) (Basic medium)

**RR0056**

(iv) $HNO_2$(aq.) $\rightarrow$ $NO_3^-$ + NO(g) (acidic medium)

**RR0057**

(v) $IO_3^- + I^- + H^+ \rightarrow I_2 + H_2O$ (acidic medium)

**RR0058**

(vi) $Cu_2S + MnO_4^- + H^+ \rightarrow Cu^{2+} + Mn^{2+} + SO_2$ (Acidic medium)

**RR0059**

(vii) HCHO (*l*) + $2[Ag(NH_3)_2]^+$(aq.) + $3OH^-$(aq.) $\rightarrow$ 2Ag(s) + $HCOO^-$(aq.) + $4NH_3$(aq.) + $2H_2O$(*l*)
(basic medium)

**RR0060**

**4.** A solution containing 4.2g of KOH and $Ca(OH)_2$ is neutralized by an acid. It consumes 0.1 equivalent of acid, calculate the percentage composition of the sample.

**RR0061**

**5.** Calculate volume of 0.4 M $KMnO_4$ required to react with following in acidic medium

$$KHC_2O_4(1\text{ mol}) + H_2C_2O_4(2\text{ mol})$$

**RR0062**

**6.** Calculate volume of 0.4 M NaOH required to react with following mixture.

$$KHC_2O_4(1\text{ mole}) + H_2C_2O_4(2\text{ mol})$$

**RR0063**

**7.** Calculate volume of 0.2 M $KMnO_4$ required to react with following mixture in acidic medium.

$$KHC_2O_4\ (128\text{ gm}) + H_2C_2O_4\ (180\text{ gm})$$

**RR0064**

**8.** 520 gm mixture of $Fe_2O_3$ and FeO reacts completely with 158 gm $KMnO_4$ in acidic medium Calculate the mole % of $Fe_2O_3$ in mixture.

**RR0065**

**9.** Calculate the millimoles of $Br_2$ produced when 10 ml of 0.1 M $BrO_3^-$ reacts with excess of $Br^-$.

**RR0066**

**10.** One gm of impure sodium carbonate is dissolved in water and the solution is made up to 250 ml. To 50 ml of this made up solution, 50 ml of 0.1N – HCl is added and the mix after shaking well required 10 ml of 0.16 N – NaOH solution for complete titration. Calculate the % purity of the sample.

**RR0067**

**11.** 100 ml sample of hard water containing only $Ca^{2+}$ hardness is passed through a column of cation exchange resin ($H^+$ – resin). The water coming out the column require 20 ml of 0.02M NaOH for its titration. What is hardness of water as ppm of $Ca^{2+}$

**RR0068**

**12.** 3.55 g sample of bleaching powder suspended in $H_2O$ was treated with enough acetic acid and KI solution. Iodine thus liberated required 80 mL of 0.2 M hypo for titration. Calculate the % of available chlorine.

**RR0069**

**13.** 3.2 g of pyrolusite ($MnO_2$) was treated with 50 mL of 0.5 M oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 mL in a flask. 25 mL of this solution when treated with 0.02 M $KMnO_4$ required 32 mL of the solution : Find the % of $MnO_2$ in the sample.

**RR0070**

**14.**. Mg can reduce $NO_3^-$ to $NH_3$ in basic medium.

$NO_3^- + Mg (s) + H_2O \rightarrow Mg (OH)_2 (s) + OH^- (aq.) + NH_3(g)$

A 25.0 mL sample of $NO_3^-$ solution was treated with Mg. The $NH_3$ (g) was passed into 100 mL of 0.15 N HCl. The excess of HCl required 32.10 mL of 0.10 N NaOH for neutralization. What was the molarity of $NO_3^-$ ions in the original sample ?

**RR0071**

**15.** A mixture of $H_2SO_4$ and $H_2C_2O_4$ (oxalic acid) and some inert impurity weighing 3.185 g was dissolved in water and the solution made up to 1 litre, 10 mL of this solution required 3 mL of 0.1 N NaOH for complete neutralization. In another experiment 100 mL of the same solution in hot condition required 4 mL of 0.02M $KMnO_4$ solution for complete reaction. The wt. % of $H_2SO_4$ in the mixture was :-

**RR0072**

**16.** An aqueous solution containing 0.10 g $KIO_3$ (formula wt. 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated $I_2$ consumed 45.0 mL of thiosulphate solution to decolourise the blue starch – iodine complex. Calculate the molarity of the sodium thiosulphate solution. **[JEE 1998]**

**RR0073**

## EXERCISE # O-I

**1.** The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is :

(A) +3 (B) +2 (C) +1 (D) –1

**RR0074**

**2.** The oxidation states of the most electronegative element in the products of the reaction of $BaO_2$ with dilute $H_2SO_4$.

(A) 0 and –1 (B) –1 and –2 (C) –2 and 0 (D) –2 and +2

**RR0075**

**3.** In the coordination compound, $K_4[Ni(CN)_6]$, the oxidation state of nickel is **[AIEEE-03]**

(A) +1 (B) +2 (C) –1 (D) 0

**RR0076**

**4.** The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is - **[AIEEE-05]**

(A) +2 (B) +3 (C) 0 (D) +1

**RR0077**

**5.** Oxidation number of Cl in $CaOCl_2$ (bleaching powder is ) **[AIEEE-02]**

(A) Zero, since it contains $Cl_2$ (B) –1, since it contains $Cl^-$

(C) +1, since it contains $ClO^-$ (D) +1 and –1 since it contains $ClO^-$ and $Cl^-$

**RR0078**

**6.** The oxidation number of sulphur in $S_8$, $S_2F_2$ and $H_2S$ respectively are :

(A) 0, +1 and –2 (B) +2, +1 and –2

(C) 0, +1 and +2 (D) –2, +1 and –2

**RR0079**

**7.** The incorrect order of decreasing oxidation number of S in compounds is :-

(A) $H_2S_2O_7 > Na_2S_4O_6 > Na_2S_2O_3 > S_8$ (B) $H_2SO_5 > H_2SO_3 > SCl_2 > H_2S$

(C) $SO_3 > SO_2 > S_8 > H_2S$ (D) $H_2SO_4 > SO_2 > H_2S > H_2S_2O_8$

**RR0080**

**8.** Which of the following is a redox **[AIEEE-02]**

(A) $2NaAg(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2Ag$

(B) $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$

(C) $N_2O_5 + H_2O \longrightarrow 2HNO_3$

(D) $AgNO_3 + KI \longrightarrow AgI + KNO_3$

**RR0081**

**9.** Which reaction does not represent autoredox or disproportionation :-

(A) $Cl_2 + OH^- \longrightarrow Cl^- + ClO_3^- + H_2O$

(B) $2H_2O_2 \longrightarrow H_2O + O_2$

(C) $2Cu^+ \longrightarrow Cu^{+2} + Cu$

(D) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$

**RR0082**

**10**. Which of the following is not a redox reaction?

(A) $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$ (B) $2BaO + O_2 \rightarrow 2BaO_2$

(C) $2KClO_3 \rightarrow 2KCl + 3O_2$ (D) $SO_2 + 2H_2S \rightarrow 2H_2O + 3S$

**RR0083**

**11.** $H_2O_2$ acts as a reducing agent in:

(A) $FeCl_2 + HCl + H_2O_2 \longrightarrow FeCl_3 + H_2O$

(B) $Cl_2 + H_2O_2 \longrightarrow HCl + O_2$

(C) $HI + H_2O_2 \longrightarrow I_2 + H_2O$

(D) $H_2SO_3 + H_2O_2 \longrightarrow H_2SO_4 + H_2O$

**RR0084**

**12.** Match List-I (Compounds) with List-II (Oxidation states of nitrogen) and select answer using the codes given below the lists :-

| | **List-I** | | **List-II** |
|---|---|---|---|
| (a) | $NaN_3$ | 1. | +5 |
| (B) | $N_2H_2$ | 2. | +2 |
| (C) | NO | 3. | –1/3 |
| (D) | $N_2O_5$ | 4. | –1 |

| **Code :** | (a) | (B) | (C) | (D) |
|---|---|---|---|---|
| (A) | 3 | 4 | 2 | 1 |
| (B) | 4 | 3 | 2 | 1 |
| (C) | 3 | 4 | 1 | 2 |
| (D) | 4 | 3 | 1 | 2 |

**RR0085**

**13.** $MnO_4^-$ is good oxidising agent in different medium changing to - **[AIEEE-02]**

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

$\longrightarrow MnO_4^{2-}$

$\longrightarrow MnO_2$

$\longrightarrow Mn_2O_3$

Changes in oxidation number respectively are -

(A) 1, 3, 4, 5 (B) 5, 4, 3, 2 (C) 5, 1, 3, 4 (D) 2, 6, 4, 3

**RR0086**

**14.** In the reaction,

$xHI + yHNO_3 \longrightarrow NO + I_2 + H_2O$

(A) x = 3, y = 2 (B) x = 2, y = 3 (C) x = 6, y = 2 (D) x = 6, y = 1

**RR0087**

**15.** The number of electrons to balance the following equation :-

$NO_3^- + 4H^+ + e^- \rightarrow 2H_2O + NO$ is

(A) 5 (B) 4 (C) 3 (D) 2

**RR0088**

**16.** Number of moles of electrons taken up when 1 mole of $NO_3^-$ ions is reduced to 1 mole of $NH_2OH$ is

(A) 2 (B) 4 (C) 5 (D) 6

**RR0089**

**17.** For the redox reaction,

$$MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$$

the correct coefficients of the reactants for the balanced reaction are :

| | $MnO_4^-$ | $C_2O_4^{2-}$ | $H^+$ |
|---|---|---|---|
| (A) | 2 | 5 | 16 |
| (B) | 16 | 5 | 2 |
| (C) | 5 | 16 | 2 |
| (D) | 2 | 16 | 5 |

**RR0090**

**18.** In a redox reaction, the equivalent weight of $HNO_2$ is found to be 23.5. The reaction products might contain

(A) $NO_2$ (B) NO (C) $NH_3$ (D) $HNO_3$

**RR0091**

**19.** When $N_2$ is converted into $NH_3$, the equivalent weight of nitrogen will be :

(A) 1.67 (B) 2.67 (C) 3.67 (D) 4.67

**RR0092**

**20.** The equivalent mass of $MnSO_4$ is half its molecular mass when it is converted to : **[JEE 1998]**

(A) $Mn_2O_3$ (B) $MnO_2$ (C) $MnO_4^-$ (D) $MnO_4^{2-}$

**RR0093**

**21.** When $KBrO_3$ ion reacts with $Br^-$ ion in acid solution $Br_2$ is liberated.The equivalent weight of $KBrO_3$ in this reaction is

(A) M/8 (B) M/3 (C) M/5 (D) M/6

**RR0094**

**22.** In the reaction $CrO_5 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + H_2O + O_2$ one mole of $CrO_5$ will liberate how many moles of $O_2$ :-

(A) 5/2 (B) 5/4 (C) 9/2 (D) 7/4

**RR0095**

**23.** A solution of $KMnO_4$ is reduced to $MnO_2$. The normality of solution is 0.6. The molarity is :

(A) 1.8M (B) 0.6M (C) 0.1M (D) 0.2M

**RR0096**

**24.** The normality of 0.3 M phosphorus acid ($H_3PO_3$) is :

(A) 0.1 (B) 0.9 (C) 0.3 (D) 0.6

**RR0097**

**25.** 0.52 g of a dibasic acid required 100 mL of 0.2 N NaOH for complete neutralization. The equivalent weight of acid is

(A) 26 (B) 52 (C) 104 (D) 156

**RR0098**

**26.** What is the equivalent weight of $H_2SO_4$ in the reaction ?

$$H_2SO_4 + NaI \rightarrow Na_2SO_4 + I_2 + H_2S + H_2O$$

(A) 12.25 (B) 49 (C) 61.25 (D) None of these

**RR0099**

**27.** 125 mL of 63% (w/v) $H_2C_2O_4 . 2H_2O$ is made to react with 125 mL of a 40% (w/v) NaOH solution. The resulting solution is :-

(A) neutral (B) acidic (C) strongly acidic (D) alkaline

**RR0100**

**28.** The mass of oxalic acid crystals ($H_2C_2O_4 . 2H_2O$) required to prepare 50 mL of a 0.2 N solution is :-

(A) 4.5 g (B) 6.3 g (C) 0.63 g (D) 0.45 g

**RR0101**

**29.** If 25 mL of a $H_2SO_4$ solution reacts completely with 1.06 g of pure $Na_2CO_3$, what is the normality of this acid solution :

(A) 1 N (B) 0.5 N (C) 1.8 N (D) 0.8 N

**RR0102**

**30.** The number of moles of $KMnO_4$ that will be required to react with 2 mol of ferrous oxalate is

(A) $\frac{6}{5}$ (B) $\frac{2}{5}$ (C) $\frac{4}{5}$ (D) 1

**RR0103**

**31.** The oxidation state of chromium in the final product formed by the reaction between Kl and acidified potassium dichromate solution is - **[AIEEE-05]**

(A) +6 (B) +4 (C) +3 (D) +2

**RR0104**

**32.** The number of mole of $KMnO_4$ that will need to react completely with one mole ferrous oxalate in acidic solution is : **[JEE 1997]**

(A) 2/5 (B) 3/5 (C) 4/5 (D) 1

**RR0105**

**33.** The number of mole of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is : **[JEE 1997]**

(A) 2/5 (B) 3/5 (C) 4/5 (D) 1

**RR0106**

**34.** What volume of 0.1 M $KMnO_4$ is needed to oxidize 100 mg of $FeC_2O_4$ in acid solution ?

(A) 4.1 mL (B) 8.2 mL (C) 10.2 mL (D) 4.6 mL

**RR0107**

**35.** What volume of 6 M $HNO_3$ is needed to oxidize 8 g of $Fe^{2+}$ to $Fe^{3+}$, $HNO_3$ gets converted to NO?

(A) 8 mL (B) 7.936 mL (C) 32 mL (D) 64 mL

**RR0108**

**36.** The minimum quantity of $H_2S$ needed to precipitate 63.5 g of $Cu^{2+}$ will be nearly.

(A) 63.5 g (B) 31.75 g (C) 34 g (D) 2.0 g

**RR0109**

**37.** The volume of 1.5 M$H_3PO_4$ solution required to neutralize exactly 90 mL of a 0.5 M Ba $(OH)_2$ solution is :-

(A) 10 mL (B) 30 mL (C) 20 mL (D) 60 mL

**RR0110**

**38.** Hydrogen peroxide in aqueous solution decomposes on warming to give oxygen according to the equation

$$2H_2O_2\,(aq) \longrightarrow 2H_2O\,(\ell) + O_2\,(g)$$

Under conditions where 1 mole of gas occupies 24 $dm^3$. 100 $cm^3$ of XM solution of $H_2O_2$ produces 3 $dm^3$ of $O_2$. Thus X is :-

(A) 2.5 (B) 1 (C) 0.5 (D) 0.25

**RR0111**

**39.** A mixture of $NaHC_2O_4$ and $KHC_2O_4 \cdot H_2C_2O_4$ required equal volumes of 0.2 N $KMnO_4$ and 0.12 N NaOH separately. What is the molar ratio of $NaHC_2O_4$ and $KHC_2O_4 \cdot H_2C_2O_4$ in the mixture ?

(A) 6 : 1 (B) (C) 1 : 3 (D) none

**RR0112**

**40.** Volume $V_1$ mL of 0.1 M$K_2Cr_2O_7$ is needed for complete oxidation of 0.678 g $N_2H_4$ in acidic medium. The volume of 0.3 M $KMnO_4$ needed for same oxidation in acidic medium will be :-

(A) $\frac{2}{5}V_1$ (B) $\frac{5}{2}V_1$ (C) 113 $V_1$ (D) can't say

**RR0113**

**41.** $As_2O_3$ is oxidised to $H_3AsO_4$ by $KMnO_4$ in acidic medium. Volume of 0.02M $KMnO_4$ required for this purpose by 1mmol of $As_2O_3$ will be

(A) 10 mL (B) 20 mL (C) 40 mL (D) 80 mL

**RR0114**

**42.** When ozone is passed through dry KOH, $KO_3$ is obtained and $O_2$ is liberated. In this reaction __________ is oxidised and _________ is reduced.

(A) hydrogen, oxygen
(B) potassium, oxygen
(C) oxygen, oxygen
(D) oxygen, hydrogen

**RR0115**

**43.** 100 ml of 0.1M $NaAl(OH)_2CO_3$ is neutralised by 0.25 N HCl to form NaCl, $AlCl_3$ and $CO_2$. Volume of HCl required is

(A) 10 mL
(B) 40 mL
(C) 100mL
(D) 160 mL

**RR0116**

**44.** x mmol of $XeF_4$ quantitatively oxidized KI to $I_2$ and liberated Xe, alongwith formation of KF. This iodine required 20 ml of decinormal hypo solution for exact titration. The value of x is

(A) 0.5
(B) 1.0
(C) 2.0
(D) 5.0

**RR0117**

**45.** Temporary hardness is due to $HCO_3^-$ of $Mg^{2+}$ and $Ca^{2+}$. It is removed by addition of CaO.

$$Ca(HCO_3)_2 + CaO \rightarrow 2CaCO_3 + H_2O$$

Mass of CaO required to precipitate 2 g $CaCO_3$ is :-

(A) 2.00
(B) 0.56 g
(C) 0.28 g
(D) 1.12 g

**RR0118**

**46.** 0.3 g of an oxalate salt was dissolved in 100 mL solution. The solution required 90 mL of N/20 $KMnO_4$ for complete oxidation. The % of oxalate ion in salt is :-

(A) 33%
(B) 66%
(C) 70%
(D) 40%

**RR0119**

## *EXERCISE # O-II*

**1.** If 10 g of $V_2O_5$ is dissolved in acid and is reduced to $V^{2+}$ by zinc metal, how many mole $I_2$ could be reduced by the resulting solution if it is further oxidised to $VO^{2+}$ ions ?

**[Assume no change in state of $Zn^{2+}$ ions] (V = 51, O = 16, I = 127) :**

(A) 0.11 mole of $I_2$ (B) 0.22 mole of $I_2$ (C) 0.055 mole of $I_2$ (D) 0.44 mole of $I_2$

**RR0120**

**2.** The number of moles of $Cr_2O_7^{2-}$ needed to oxidize 0.136 equivalents of $N_2H_5^+$ by the reaction $N_2H_5^+ + Cr_2O_7^{2-} \rightarrow N_2 + Cr^{3+} + H_2O$ is

(A) 0.136 (B) 0.068 (C) 0.0227 (D) 0.272

**RR0121**

**3.** Dichloroacetic acid ($CHCl_2COOH$) is oxidized to $CO_2$, $H_2O$ and $Cl_2$ by 600 meq of an oxidizing agent. Same amount of acid can neutralize how many moles of ammonia to form ammonium dichloroacetate?

(A) 0.0167 (B) 0.1 (C) 0.3 (D) 0.6

**RR0122**

**4.** $HNO_3$ oxidises $NH_4^+$ ions to nitrogen and itself gets reduced to $NO_2$. The moles of $HNO_3$ required by 1 mol of $(NH_4)_2SO_4$ is :-

(A) 4 (B) 5 (C) 6 (D) 2

**RR0123**

**5.** During the disproportionation of iodine to iodide and iodate ions, the ratio of iodate and iodide ions formed in alkaline medium is :-

(A) 1 : 5 (B) 5 : 1 (C) 3 : 1 (D) 1 : 3

**RR0124**

**6.** When arsenic sulphide is boiled with NaOH, sodium arsenite and sodium thioarsenite are formed

$x\,As_2S_3 + y\,NaOH \longrightarrow Na_3AsO_3 + x\,Na_3AsS_3 + \frac{y}{2}\,H_2O$. What are the values of x and y ?

(A) 1, 6 (B) 2, 8 (C) 2, 6 (D) 1, 4

**RR0125**

**7.** 35 mL sample of hydrogen peroxide gives of 500 mL of $O_2$ at 27°C and 1 atm pressure. Volume strength of $H_2O_2$ sample will be :-

(A) 10 volume (B) 13 volumes (C) 11 volume (D) 12 volume

**RR0126**

**8.** An element A in a compound ABD has oxidation number $A^{n-}$. It is oxidised by $Cr_2O_7^{2-}$ in acid medium. In the experiment $1.68 \times 10^{-3}$ moles of $K_2Cr_2O_7$ were used for $3.26 \times 10^{-3}$ moles of ABD. The new oxidation number of A after oxidation is :-

(A) 3 (B) 3 – n (C) n – 3 (D) +n3

**RR0127**

**9.** 50g of pure $CaCO_3$ is heated to liberate $CO_2$. Liberated $CO_2$ required 0.4 mol of moist ammonia to yield only $(NH_4)_2CO_3$. Find the volume of $CO_2$ liberated at STP adding excess dil. HCl to this heated residue.

(A) zero (B) 4.42 L (C) 6.81 L (D) 6.72 L

**RR0128**

**10.** For the reaction

$I^- + ClO_3^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2$

The correct statement(s) in the balanced equation is / are :

(A) Stoichiometric coefficient of $HSO_4^-$ is 6

(B) Iodide is oxidized

(C) Sulphur is reduced

(D) $H_2O$ is one of the products

**RR0129**

**11.** A sample of $KMnO_4$ solution required 50 ml when titrated against 3 mmol of oxalic acid. The normality of same solution in reaction with alkaline $H_2O_2$ is

(A) 0.120 N (B) 0.060 N (C) 0.072 N (D) 0.036 N

**RR0130**

**Assertion Reason Type**

**12.** **Statement–1 :-** Moles of $KMnO_4$ required for oxidation of $Fe^{2+}$ in acidic and basic medium will be different.

**Statement–2 :-** Final oxidation state to which $Mn^{7+}$ will be reduced will be different in case of acidic and basic medium.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

**RR0131**

**13.** **Statement–1 :-** Mass of a particular substance that combine with 8 gm of oxygen is said to be equivalent weight of substance.

**Statement–2 :-** x gm of metal gave y gm of its oxide, so equivalent weight of metal is $\left(\frac{x}{y-x}\right)\times 8$

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

**RR0132**

**14.** **Statement–1 :-** Degree of hardness of water is measured in terms of ppm of $CaCO_3$.

**Statement–2 :-** If water contains 120 ppm of $MgSO_4$, and 2ppm NaCl, its hardness in terms of $CaCO_3 > 100$ ppm.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

**RR0133**

**MATCH THE COLUMN**

**15.**

| **Column-I** | **Column-II** |
|---|---|
| (A) $\underline{P_2H_4} \longrightarrow PH_3 + P_4H_2$ | (p) $E = \frac{3M}{4}$ |
| (B) $\underline{I_2} \longrightarrow I^- + IO_3^-$ | (q) $E = \frac{3M}{5}$ |
| (C) $MnO_4^- + Mn^{2+} + H_2O \longrightarrow \underline{Mn_3O_4} + H^+$ | (r) $E = \frac{15M}{26}$ |
| (D) $\underline{H_3PO_2} \longrightarrow PH_3 + H_3PO_3$ | (s) $E = \frac{5M}{6}$ |

**RR0134**

**Paragraph for Q.16 to Q.19**

$$\text{Equivalent weight} = \frac{\text{Molecular weight / Atomic weight}}{\text{n – factor}}$$

n-factor is very important in redox as well as non-redox reactions. With the help of n-factor we can predicts the molar ratio of the reactant species taking part in reactions. The reaciprocal of n-factor's ratio of the reactants is the molar ratio of the reactants.

In general n-factor of acid/base is number of moles of $H^+$ /$OH^-$ furnished per mole of acid/base. n-factor of a reactant is no. of moles of electrons lost or gained per mole of reactant.

**Example 1 :**

1. In acidic medium : $KMnO_4$ (n = 5) $\longrightarrow Mn^{2+}$
2. In neutral medium : $KMnO_4$ (n = 3) $\longrightarrow Mn^{2+}$
3. In basic medium : $KMnO_4$ (n = 1) $\longrightarrow Mn^{6+}$

**Example 2 :** $FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2$

Total no. of moles of $e^-$ lost by 1 mole of $FeC_2O_4 = 1 + 1 \times 2 \Rightarrow 3$

$\therefore$ n-factor of $FeC_2O_4 = 3$

**16.** n-factor of $Ba(MnO_4)_2$ in acidic medium is :

(A) 2 (B) 6 (C) 10 (D) none of these

**RR0135**

**17.** For the reaction,

$$H_3PO_2 + NaOH \longrightarrow NaH_2PO_2 + H_2O$$

What is the equivalent weight of $H_3PO_2$ ? (mol. wt. is M)

(A) M (B) M/2 (C) M/3 (D) none of these

**RR0136**

**18.** For the reaction, $Fe_{0.95}O$ (molar mass : M) $\longrightarrow Fe_2O_3$. What is the eq. wt. of $Fe_{0.95}O$ ?

(A) $\frac{M}{0.85}$ (B) $\frac{M}{0.95}$ (C) $\frac{M}{0.8075}$ (D) none of these

**RR0137**

**19.** In the reaction, $xVO + yFe_2O_3 \longrightarrow FeO + V_2O_5$. What is the value of x and y respectively ?

(A) 1, 1 (B) 2, 3 (C) 3, 2 (D) none of these

**RR0138**

**Table type question :**

| **Column-I**<br>**(1 mole of each oxidizing) agent is taken)** | **Column-II**<br>**(oxidation number** | **Column-III**<br>**(Reducing agents)** |
|---|---|---|
| (A) $KMnO_4$ (acidic) | (P) O.N of Mn = 4 | (1) 3 mole of $FeSO_4$ |
| (B) $KMnO_4$ (neutral) | (Q) O.N of Mn = 7 | (2) 0.5 mole of $I_2$ changes to $HIO_3$ |
| (C) $MnO_2$ (acidic) | (R) O.N of Cr = 6 | (3) 1 mole of $K_2C_2O_4$ |
| (D) $K_2CrO_4$ (acidic) | (S) O.N of Cr = 7 | (4) 1.5 mole $K_2SO_3$ |

**20.** Which of the following is correct

(A) A ; P ; 2 (B) A ; Q ; 4 (C) B ; Q ; 1 (D) B ; Q ; 3

**RR0139**

**21.** Which of the following is correct

(A) A ; Q ; 3 (B) C ; P ; 3 (C) C ; P ; 4 (D) C ; Q ; 1

**RR0139**

**22.** Which of the following is correct

(A) D ; R ; 1 (B) D ; R ; 2 (C) D ; S ; 1 (D) D ; R ; 4

**RR0139**

## EXERCISE # J-MAINS

**1.** Given : **[JEE(Main-online)-2013]**

$X\ Na_2HAsO_3 + Y\ NaBrO_3 + ZHCl \rightarrow NaBr + H_3AsO_4 + NaCl$

The values of X, Y and Z in the above redox reaction are respectively :

(1) 2, 1, 3 (2) 3, 1, 6 (3) 2, 1, 2 (4) 3, 1, 4

**RR0140**

**2.** Consider the following reaction : **[JEE(Main)-2013]**

$$xMnO_4^- + yC_2O_4^{2-} + zH^+ \rightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2}H_2O$$

The values of x, y and z in the reaction are respectively :-

(1) 5,2 and 16 (2) 2,5 and 8 (3) 2, 5 and 16 (4) 5,2 and 8

**RR0141**

**3.** How many electrons are involved in the following redox reaction ? **[JEE(Main-online)-2014]**

$Cr_2O_7^{2-} + Fe^{2+} + C_2O_4^{2-} \rightarrow Cr^{3+} + Fe^{3+} + CO_2$ (Unbalanced)

(1) 3 (2) 4 (3) 5 (4) 6

**RR0142**

**4.** Consider the reaction **[JEE(Main-online)-2014]**

$$H_2SO_{3(aq)} + Sn^{4+}_{(aq)} + H_2O_{(l)} \rightarrow Sn^{2+}_{(aq)} + HSO^-_{4(aq)} + 3H^+_{(aq)}$$

Which of the following statements is correct?

(1) $H_2SO_3$ is the reducing agent because it undergoes oxidation

(2) $H_2SO_3$ is the reducing agent because it undergoes reduction

(3) $Sn^{4+}$ is the reducing agent because it undergoes oxidation

(4) $Sn^{4+}$ is the oxidizing agent because it undergoes oxidation

**RR0143**

**5.** In which of the following reaction $H_2O_2$ acts as a reducing agent ? **[JEE(Main)-2014]**

(a) $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (b) $H_2O_2 - 2e^- \rightarrow O_2 + 2H^+$

(c) $H_2O_2 + 2e^- \rightarrow 2OH^-$ (d) $H_2O_2 + 2OH^- - 2e^- \rightarrow O_2 + 2H_2O$

(1) (a), (c) (2) (b), (d) (3) (a), (b) (4) (c), (d)

**RR0144**

**6.** The molecular formula of a commercial resin used for exchanging ions in water softening is $C_8H_7SO_3Na$ (Mol. w.t 206). What would be the maximum uptake of $Ca^{2+}$ ions by the resin when expressed in mole per gram resin ? **[JEE(Main)-2015]**

(1) $\frac{2}{309}$ (2) $\frac{1}{412}$ (3) $\frac{1}{103}$ (4) $\frac{1}{206}$

**RR0145**

**7.** The volume of 0.1N dibasic acid sufficient to neutralize 1 g of a base that furnishes 0.04 mole of $OH^-$ in aqueous solution is : **[JEE(Main)-OnLine-2016]**

(1) 400 mL (2) 200 mL (3) 600 mL (4) 800 mL

**RR0146**

**8.** Which of the following reactions is an example of a redox reaction ? **[JEE(Main)-2017]**

(1) $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$ (2) $XeF_2 + PF_5 \rightarrow [XeF]^+PF_6^-$

(3) $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$ (4) $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

**RR0147**

**9.** In which of the following reaction, hydrogen peroxide acts as an oxidizing agent ?

(1) $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$ **[JEE(Main)-OnLine-2017]**

(2) $HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$

(3) $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$

(4) $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$

**RR0148**

**10.** In $KO_2$, the nature of oxygen species and the oxidation state of oxygen atom are, respectively

(1) Superoxide and –1/2 (2) Oxide and –2 **[JEE(Main)-OnLine-2018]**

(3) Peroxide and –1/2 (4) Superoxide and –1

**RR0150**

**11.** In the reaction of oxalate with permaganate in acidic medium, the number of electrons involved in producing one molecule of $CO_2$ is : **[JEE(Main)-(Jan.)-2019]**

(1) 10 (2) 2 (3) 1 (4) 5

**RR0151**

**12.** The chemical nature of hydrogen preoxide is :- **[JEE(Main)-(Jan.)-2019]**

(1) Oxidising and reducing agent in acidic medium, but not in basic medium.

(2) Oxidising and reducing agent in both acidic and basic medium

(3) Reducing agent in basic medium, but not in acidic medium

(4) Oxidising agent in acidic medium, but not in basic medium.

**RR0152**

**13.** The hardness of a water sample (in terms of equivalents of $CaCO_3$) containing $10^{-3}$ M $CaSO_4$ is : (molar mass of $CaSO_4$ = 136 g $mol^{-1}$) **[JEE(Main)-(Jan.)-2019]**

(1) 100 ppm (2) 50 ppm (3) 10 ppm (4) 90 ppm

**RR0153**

**14.** 50 mL of 0.5 M oxalic acid is needed to neutralize 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is : **[JEE(Main)-(Jan.)-2019]**

(1) 4 g (2) 2 g (3) 8 g (4) 1 g

**RR0154**

**15.** In order to oxidise a mixture one mole of each of $FeC_2O_4$, $Fe_2(C_2O_4)_3$, $FeSO_4$ and $Fe_2(SO_4)_3$ in acidic medium , the number of moles of $KMnO_4$ required is - **[JEE(Main)-(April)-2019]**

(1) 3 (2) 2 (3) 1 (4) 1.5

**RR0155**

**16.** The correct order of the oxidation states of nitrogen in NO, $N_2O$, $NO_2$ and $N_2O_3$ is :

(1) $NO_2 < N_2O_3 < NO < N_2O$

(2) $NO_2 < NO < N_2O_3 < N_2O$

(3) $N_2O < N_2O_3 < NO < NO_2$

(4) $N_2O < NO < N_2O_3 < NO_2$ **[JEE(Main)-(April)-2019]**

**RR0156**

**17.** An example of a disproportionation reaction is : **[JEE(Main)-(April)-2019]**

(1) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$ (2) $2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

(3) $2CuBr \rightarrow CuBr_2 + Cu$ (4) $2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$

**RR0158**

**18.** 100 mL of a water sample contains 0.81 g of calcium bicarbonate and 0.73 of magnesium bicarbonate. The hardness of this water sample expressed in terms of equivalents of $CaCO_3$ is:
(molar mass of calcium bicarbonate is 162 g $mol^{-1}$ and magnesium bicarbonate is 146 $gmol^{-1}$)

(1) 1,000 ppm (2) 10,000 ppm **[JEE(Main)-(April)-2019]**

(3) 100 ppm (4) 5,000 ppm

**RR0159**

**19.** 25 ml of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution?

**[JEE(Main)-(Jan)-2019]**

(1) 25 mL (2) 50 mL (3) 12.5 mL (4) 75 mL

**RR0160**

**20.** Oxidation number of potassium in $K_2O$, $K_2O_2$ and $KO_2$ , respectively, is : **[JEE(Main)-(Jan)-2020]**

(1) +1, +4 and +2 (2) +1, +2 and +4

(3) +1, +1 and +1 (4) +2 , +1 and $+\frac{1}{2}$

**RR0167**

**21.** The compound that cannot act both as oxidising and reducing agent is :**[JEE(Main)-(Jan)-2020]**

(1) $H_2O_2$ (2) $H_2SO_3$ (3) $HNO_2$ (4) $H_3PO_4$

**RR0168**

**22.** The hardness of a water sample containing $10^{-3}$ M $MgSO_4$ expressed as $CaCO_3$ equivalents (in ppm) is ______. **[JEE(Main)-(Jan)-2020]**

**(molar mass of $MgSO_4$ is 120.37 g/mol)**

**RR0169**

## *EXERCISE # J-ADVANCED*

**1.** Reduction of the metal centre in aqueous permanganate ion involves - **[JEE-2011]**

(A) 3 electrons in neutral medium (B) 5 electrons in neutral medium

(C) 3 electrons in alkaline medium (D) 5 electrons in acidic medium

**RR0161**

**2.** Reaction of $Br_2$ with $Na_2CO_3$ in aqueous solution gives sodium bromide and sodium bromate with evolution of $CO_2$ gas. The number of sodium bromide molecules involved in the balanced chemical equation is. **[JEE- 2011]**

**RR0162**

**3.** Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen-

(A) $HNO_3$, NO, $NH_4Cl$, $N_2$ (B) $HNO_3$, NO, $N_2$, $NH_4Cl$

(C) $HNO_3$, $NH_4Cl$, NO, $N_2$ (D) NO, $HNO_3$, $NH_4Cl$, $N_2$ **[JEE- 2012]**

**RR0163**

**4.** 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is **[JEE- 2012]**

(A) 0.48 M (B) 0.96 M (C) 0.24 M (D) 0.024 M

**RR0164**

**5.** In neutral or faintly alkaline solution, 8 moles permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product. the magnitude of X is**[JEE- 2016]**

**RR0165**

**6.** To measure the quantity of $MnCl_2$ dissolved in an aqueous solution, it was completely converted to $KMnO_4$ using the reaction, **[JEE- 2018]**

$MnCl_2 + K_2S_2O_8 + H_2O \rightarrow KMnO_4 + H_2SO_4 + HCl$ (equation not balanced).

Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 g) was added in portions till the colour of the permanganate ion disappeard. The quantity of $MnCl_2$ (in mg) present in the initial solution is _____.

**(Atomic weights in g mol$^{-1}$ : Mn = 55, Cl = 35.5)**

**RR0166**

# ANSWER-KEY

## *EXERCISE # S-I*

**1.** (a) +6 (b) +5 (c) +2 (d) –4
(e) +4 (f) –1 (g) +2 (h) +6
(i) +3

**2.** (a) Reduction (b) Oxidation
(c) Reduction (d) Oxidation

**3.** (a) Oxidant : $O_2$ ; Reductant : Zn
(b) Oxidant : $H^+$ ; Reductant : Zn
(c) Oxidant : $NO_3^-$ ; Reductant : Zn

**4.** (i) $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
(ii) $Br_2 + 5H_2O_2 \longrightarrow 2BrO_3^- + 4H_2O + 2H^+$
(iii) $MnO_4^- + 5Fe^{+2} + 8H^+ \longrightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$
(iv) $MnO_2 + 2Cl^- + 4H^+ \longrightarrow Mn^{+2} + Cl_2 + 2H_2O$
(v) $3ClO^- + 2CrO_2^- + 2OH^- \longrightarrow 3Cl^- + 2CrO_4^{2-} + H_2O$

**5.** (i) $2MnO_4^- + 6I^- + 4H_2O \longrightarrow 2MnO_2 + 3l_2 + 8OH^-$
(ii) $H^+ + 2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5HSO_4^-$
(iii) $2Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O$
(iv) $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$

**6.** Ans. (1) 1 (2) 2 , 1 (3) 1
(4) 1 (5) 2 (6) 1

**7.** (1) 1 (2) 1 (3) 1 (4) 1 (5) 2

**8.** 98, 49, 32.67
**9.** Ans.21
**10.** Ans. (i) $\frac{83.5}{6}$ ; (ii) $\frac{17}{3}$
**11.** Ans. 6
**12.** Ans.5
**13.** Ans.(8.097 mL)
**14.** Ans.(40)
**15.** Ans.40 ml
**16.** Ans.60 ml
**17.** Ans.12.5 L
**18.** Ans.12.5 L
**19.** Ans. V = 3 lit.
**20.** Ans. 200 mL
**21.** Ans. 30 N
**22.** Ans.(4.48)
**23.** Ans. 10 N
**24.** Ans.2.12 g/L
**25.** Ans.+ 3
**26.** Ans.Zero
**27.** Ans.V = 160 ml
**28.** Ans.0.588 N
**29.** Ans.4 lit.
**30.** Ans. $\frac{2}{3}$
**31.** Ans. 8/5
**32.** Ans. 1.25 mL
**33.** Ans.1.406%
**34.** Ans.V = 25 mL
**35.** Ans.1.28%
**36.** Ans.40 g , 0.0518N
**37.** Ans.($Ca^{2+}$ , $Mg^{2+}$, $Na^+$)
**38.** Ans.(19.09)

## *EXERCISE # S-II*

**1.** (a) +2.5 (b) +4/3 (c) –1/3 (d) +8/3
(e) –3, –1 (f) –2, +2 (g) +16/3 (h) 0
(i) +2, –1 (j) +2 (k) 0 (l) +1/2
(m) –1/2 (n) +1 (o) +3 (p) –3
(q) +3 (r) +2 (s) +4

**2.** (a) +3 (b) +3, +6 (c) +2 (d) $+\frac{200}{93}$
(e) +6 (f) +6 (g) +6 (h) +5
(r) +2 (s) +3

**3.** (i) $6KMnO_4$(aq.) + $10FeC_2O_4$(aq.) + $24H_2SO_4$ (aq.) $\longrightarrow$
$6MnSO_4$ (aq.) + $5Fe_2(SO_4)_3$ (aq.) + $20CO_2$(g) + $3K_2SO_4$ + $24H_2O$(*l*)

(ii) $5P_4$(s) + $12OH^-$(aq.) + $12H_2O \longrightarrow 8PH_3$(aq) + $12HPO_2^-$ (aq.)

(iii) $3I_2$(s) + 6NaOH(aq.) $\longrightarrow$ 5NaI (aq.) + $NaIO_3$(aq.) + $3H_2O$(*l*)

(iv) $3HNO_2$(aq.) $\rightarrow NO_3^- + H^+ + 2NO$(g) + $H_2O$

(v) $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

(vi) $5Cu_2S + 8MnO_4^- + 44H^+ \rightarrow 10Cu^{2+} + 5O_2 + 8Mn^{2+} + 22\,H_2O$

(vii) HCHO (*l*) + $[Ag(NH_3)_2]^+$ (aq.) + $2OH^-$ (aq.) $\rightarrow$ Ag(s) + $2NH_3$(aq.) + $HCOO^-$(aq.) + $H_2O$(*l*)

**4.** KOH = 35%, $Ca(OH)_2$ = 65%

**5.** Ans. 3 *l*
**6.** Ans. 12.5 *l*
**7.** Ans. 6 *l*
**8.** Ans. 16.66%
**9.** Ans. 3
**10.** Ans. 90.1%
**11.** Ans. (80)
**12.** Ans. 16%
**13.** Ans. 24.46%
**14.** Ans. 0.47
**15.** Ans. (40)
**16.** Ans. (0.0626 M)

## *EXERCISE # O-I*

**1.** Ans. (C)
**2.** Ans. (B)
**3.** Ans. (B)
**4.** Ans. (B)
**5.** Ans. (D)
**6.** Ans. (A)
**7.** Ans. (D)
**8.** Ans. (A)
**9.** Ans. (D)
**10.** Ans. (A)
**11.** Ans. (B)
**12.** Ans. (A)
**13.** Ans. (C)
**14.** Ans. (C)
**15.** Ans. (C)
**16.** Ans. (D)
**17.** Ans. (A)
**18.** Ans. (D)
**19.** Ans. (D)
**20.** Ans. (B)
**21.** Ans. (C)
**22.** Ans. (D)
**23.** Ans. (D)
**24.** Ans. (D)
**25.** Ans. (A)
**26.** Ans. (C)
**27.** Ans. (D)
**28.** Ans. (C)
**29.** Ans. (D)
**30.** Ans. (A)
**31.** Ans. (C)
**32.** Ans. (B)
**33.** Ans. (A)
**34.** Ans. (A)
**35.** Ans. (B)
**36.** Ans. (C)
**37.** Ans. (C)
**38.** Ans. (A)
**39.** Ans. (D)
**40.** Ans. (A)
**41.** Ans. (C)
**42.** Ans. (C)
**43.** Ans. (D)
**44.** Ans. (A)
**45.** Ans. (B)
**46.** Ans. (B)

## EXERCISE # O-II

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1.** | **Ans. (A)** | **2.** | **Ans. (C)** | **3.** | **Ans. (B)** | **4.** | **Ans. (C)** |
| **5.** | **Ans. (A)** | **6.** | **Ans. (A)** | **7.** | **Ans. (B)** | **8.** | **Ans. (B)** |
| **9.** | **Ans. (C)** | **10.** | **Ans. (A,B,D)** | **11.** | **Ans. (C)** | **12.** | **Ans. (A)** |
| **13.** | **Ans. (B)** | **14.** | **Ans. (C)** | **15.** | **(A) → s ; (B) → q ; (C) → r ; (D) → p** | | |
| **16.** | **Ans. (C)** | **17.** | **Ans. (A)** | **18.** | **Ans. (A)** | **19.** | **Ans. (B)** |
| **20.** | **Ans. (C)** | **21.** | **Ans. (B)** | **22.** | **Ans. (A,D)** | | |

## EXERCISE # J-MAINS

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1.** | **Ans. (2)** | **2.** | **Ans. (3)** | **3.** | **Ans. (4)** | **4.** | **Ans. (1)** |
| **5.** | **Ans. (2)** | **6.** | **Ans. (2)** | **7.** | **Ans. (1)** | **8.** | **Ans. (1)** |
| **9.** | **Ans. (3)** | **10.** | **Ans. (1)** | **11.** | **Ans. (3)** | **12.** | **Ans. (2)** |
| **13.** | **Ans. (1)** | **14.** | **Ans. (1)** | **15.** | **Ans. (2)** | **16.** | **Ans. (4)** |
| **17.** | **Ans. (3)** | **18.** | **Ans. (2)** | **19.** | **Ans. (1)** | **20.** | **Ans. (3)** |
| **21.** | **Ans. (4)** | **22.** | **Ans. (100)** | | | | |

## EXERCISE # J-ADVANCED

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1.** | **Ans. (A,C,D)** | **2.** | **Ans. (5)** | **3.** | **Ans. (B)** | **4.** | **Ans. (C)** |
| **5.** | **Ans. (6)** | **6.** | **Ans. (126)** | | | | |