Chapter 05

REDOX REACTIONS

1. OXIDATION & REDUCTION

Let us do a comparative study of oxidation and reduction

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

2. OXIDATION NUMBER

It is an imaginary or apparent charge developed over atom of an element when it goes from its elemental free state to combined state in molecules.

It is calculated on basis of an arbitrary set of rules.

It is a relative charge in a particular bonded state.

In order to keep track of electron-shifts in chemical reactions involving formation of compounds, a more practical method of using oxidation number has been developed.

In this method, it is always assumed that there is a complete transfer of electron from a less electronegative atom to a more electronegative atom.

2.1 Rules Governing Oxidation Number

- The following rules are helpful in calculating oxidation number of the elements in their different compounds. it is to be remembered that the basis of these rule is the electronegativity of the element.

- **Fluorine Atom**

  Fluorine is most electronegative atom (known). It always has oxidation number 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 –1/2

(iii) ozonide (e.g. KO_3) is –1/3

(iv) in 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 atoms (Cl, Br, I) have oxidation number equal to –1.

  But if halogen atom is attached with a 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.

(c) Aluminium always has +3 oxidation number

NOTE

Metal may have negative or zero 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 oxidation numbers of atoms of all elements in a molecule is zero.
- Sum of the oxidation numbers of atoms of all elements in an ion is equal to the charge on the ion.
- If the group number of an element in modern periodic table is n, then its oxidation number may vary from

  (n – 10) to (n – 18) (but it is mainly applicable for p-block elements)

  e.g. N-atom belongs to 15th group in the periodic table, therefore as per rule, its oxidation number may vary from

  $-3 \text{ to } +5 \left(\overset{-3}{N}H_3, \overset{+2}{N}O, \overset{+3}{N}_2O_3, \overset{+4}{N}O_2, \overset{+5}{N}_2O_5 \right)$
- The maximum possible oxidation number of any element in a compound is never more than the number of electrons in valence shell. (but it is mainly applicable for p-block elements)

3. CALCULATION OF AVERAGE OXIDATION NUMBER

Example

Calculate oxidation number of underlined element :

(a) $Na_2\underline{S}_2O_3$ (b) $Na_2\underline{S}_4O_6$

Sol.

(a) Let oxidation number of S-atom is x. Now work accordingly with the rules given before.

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

$x = +2$

(b) Let oxidation number of S-atom is x

$\therefore (+1) \times 2 + (x) \times 4 + (-2) \times 6 = 0$

$x = +2.5$

- It is important to note here that $Na_2S_2O_3$ have two S-atoms and there are four S-atom in $Na_2S_4O_6$. However none of the sulphur atoms in both the compounds have +2 or + 2.5 oxidation number, it is the average of oxidation number, which reside on each sulphur atom. Therefore, we should work to calculate the individual oxidation number of each sulphur atom in these compounds.

4. CALCULATION OF INDIVIDUAL OXIDATION NUMBER

It is important to note that to calculate individual oxidation number of the element in its compound one should know the structure of the compound and use the following guidelines.

Formula :

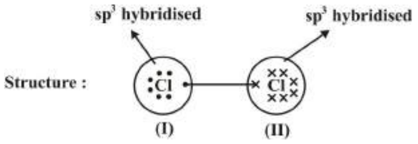
Oxidation Number = Number of electrons in the valence shell - Number of electrons taken up after bonding

Guidelines : It is based on electronegativity of elements.

1. If there is a bond between similar type of atom and each atom has same type of hybridisation, then bonded pair electrons are equally shared by each element.

Example

Calculate oxidation number of each Cl-atom in Cl_2 molecule



I. Number of electrons in the valence shell = 7

Number of electrons taken up after bonding = 7.

$\therefore$ oxidation number = 7 – 7 = 0.

II. similarly, oxidation number = 7 – 7 = 0

2. If there is a bond between different type of atoms :

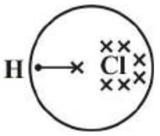
   e.g. A – B (if B is more electronegative than A)

   Then after bonding, bonded pair of electrons are counted with B-atom

Example

Calculate oxidation number of each atom in HCl molecule

Structure :



NOTE

Electron of H-atom is now counted with Cl-atom, because Cl-atom is more electronegative than H-atom

- H : Number of electrons in the valence shell = 1

  Number of electrons taken up after bonding = 0

  Oxidation number of H = 1 – 0 = + 1
- Cl : Number of electrons in the valence shell = 7

  Number of electrons taken up after bonding = 8

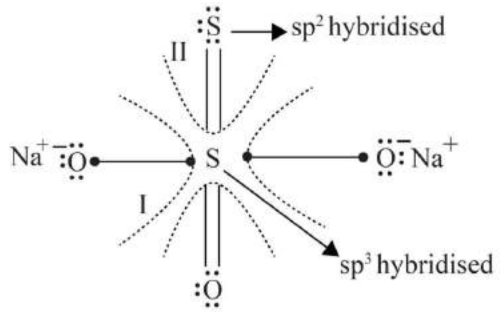
  Oxidation number of Cl = 7 – 8 = –1

Example

Calculate individual oxidation number of each S-atom in $Na_2S_2O_3$ (sodium thiosulphate) with the help of its structure.

Sol.

Structure :



NOTE

I (central S-atom) is sp^3 hybridised (25% s-character) and II (terminal S-atom) is sp^2 hybridised (33% s-character). Therefore, terminal sulphur atom is more electronegative than central sulphur atom. Now, the shared pair of electrons are counted with terminal S-atom.

- $\therefore$ I, S-atom : Number of electrons in the valence shell = 6

  Number of electrons left after bonding = 0

  Oxidation number of central S-atom = 6 – 0 = +6
- II, S-atom : Number of electrons in the valence shell = 6

  Number of electrons left after bonding = 8

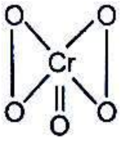
  Oxidation number of terminal S-atom = 6 – 8 = – 2

  Now, you can also calculate Average Oxidation number of

  $S = \frac{6+(-2)}{2} = +2$ (as we have calculated before)

4.1 Miscellaneous Examples

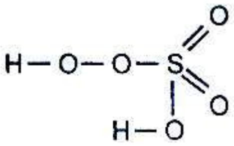
In order to determine the exact or individual oxidation number we need to take help from the structures of the molecules. Some special cases are discussed as follows :

- 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 oxidation number of Cr is x.

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

$\therefore$ Oxidation number of Cr = +6

- The structure of H_2SO_5 is 

From the structure, it is evident that in H_2SO_5, there is one peroxide linkage, two sulphur-oxygen double bonds and one OH group. Let the oxidation number of S = x.

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

or $x + 2 - 8$ or $x - 6 = 0$ or $x = 6$

$\therefore$ Oxidation number of S in H_2SO_5 is + 6

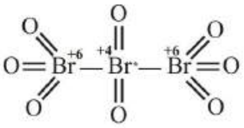
5. PARADOX OF FRACTIONAL OXIDATION NUMBER

Fractional oxidation number is the average of oxidation state of all atoms of element under examination and the structural parameters reveal that the atoms of element for whom fractional oxidation state is realised a 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 different 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.

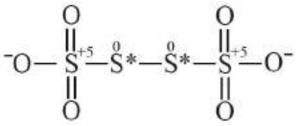
  $$O = \overset{+2}{C} = \overset{0}{C}^{*} = \overset{+2}{C} = O$$

  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 $S_4O_6^{2-}$, average oxidation number of S is + 2.5, whereas the reality being + 5, 0*, 0* and +5 oxidation number respectively for respective sulphur atoms.



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

In general, the conclusion is that the idea of fractional oxidation state should be taken with care and the reality is revealed by the structures only.

6. OXIDISING AND REDUCING AGENT

- **Oxidising Agent or Oxidant**

  Oxidising agents are those compounds which can oxidise others and reduce itself during the chemical reaction. Those reagents in which for an element, oxidation number decreases or which undergoes gain of 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.

- **Reducing Agent or Reductant**

  Reducing agents are those compounds which can reduce other and oxidise itself during the chemical reaction. Those reagents in which for an element, oxidation number increases or which undergoes loss of electrons in a redox reaction are termed as reductants.

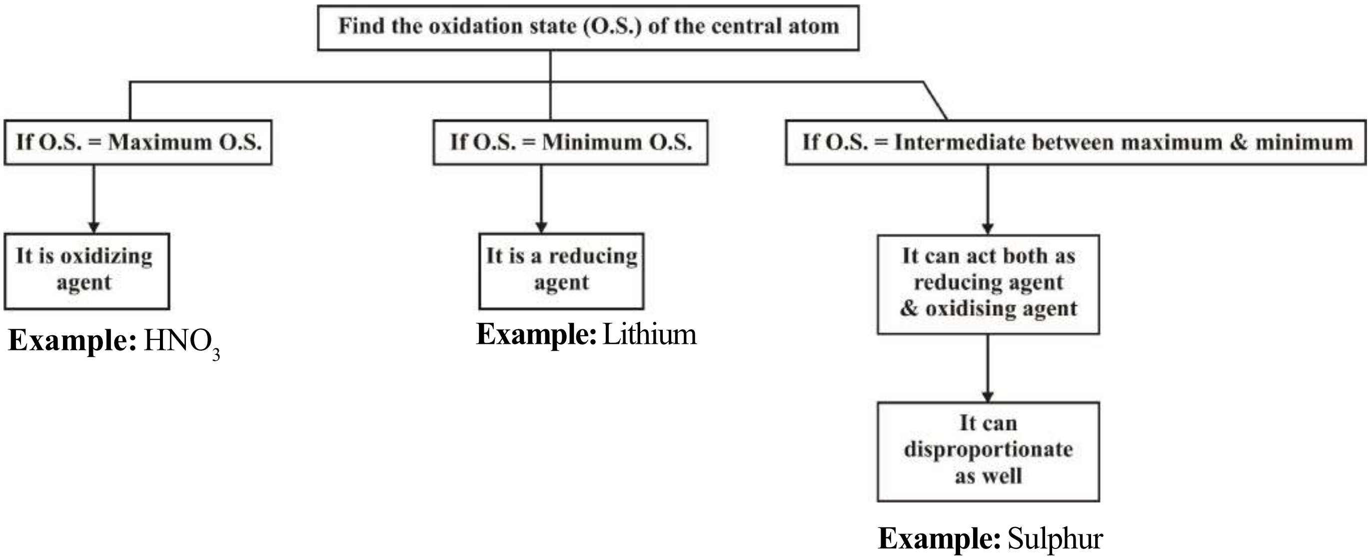
  e.g. KI, $Na_2S_2O_3$ etc are the powerful reducing agents.

NOTE

There are some compounds also which can work both as oxidising agent and reducing agent

e.g. H_2O_2, NO_2^-

How to Identify whether a particular substance is an Oxidising or a Reducing Agent



7. REDOX REACTION

A reaction in which oxidation and reduction simultaneously take place is called a redox reaction. In all redox reactions, the total increase in oxidation number must be equal to the total decrease in oxidation number.

e.g.

$$10\overset{+2}{Fe}SO_4 + 2K\overset{+5}{Mn}O_4 + 8H_2SO_4 \longrightarrow$$

$$5\overset{+3}{Fe}_2(SO_4)_3 + 2\overset{+2}{Mn}SO_4 + K_2SO_4 + 8H_2O$$

7.1 Disproportionation Reaction

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

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. For **Example**

$$2H_2\overset{(-1)}{O}_2(aq) \rightarrow 2H_2\overset{(-2)}{O}(l) + \overset{(0)}{O}_2(g)$$

$$\overset{(0)}{S}_8(s) + 12OH^-(aq) \longrightarrow$$

$$4\overset{(-2)}{S^{2-}}(aq) + 2\overset{(+2)}{S}_2O_3^{2-}(aq) + 6H_2O(l)$$

$$\overset{(0)}{Cl}_2(g) + 2OH^-(aq) \longrightarrow \overset{(+1)}{Cl}O^-(aq) + \overset{(-1)}{Cl^-}(aq) + H_2O(l)$$

Consider the Following Reations

(a) $2KClO_3 \longrightarrow 2KCl + 3O_2$

$KClO_3$ plays a role of oxidant and reductant both. Here, Cl present in $KClO_3$ is reduced and O present in $KClO_3$ is oxidized. Since same element is not oxidized and reduced, so it is not a disproportionation reaction, although it looks like one.

(b) $\overset{-3}{N}H_3\overset{+3}{N}O_2 \rightarrow \overset{0}{N}_2 + 2H_2O$

Nirogen in this compound has -3 and +3 oxidation number, which is not a definite value. So it is not a disporportionation reaction. It is an example of comproportionation reaction, which is a class of redox reaction in which an element from two different oxidation state gets converted into a single oxidation state.

(c) $4K\overset{+5}{Cl}O_3 \longrightarrow 3K\overset{+7}{Cl}O_4 + K\overset{-1}{Cl}$

It is a case of disproportionation reaction and Cl atom is disproportionating.

List of Some Important Disproportionation Reactions

1. $H_2O_2 \longrightarrow H_2O + O_2$
2. $X_2 + OH^-(dil.) \longrightarrow X^- + XO^- \ (X = Cl, Br, I)$
3. $X_2 + OH^-(conc.) \longrightarrow X^- + XO_3^-$

   F_2 does not undergo disproportionation as it is the most electronegative element.

   $F_2 + NaOH(dil.) \longrightarrow F^- + OF_2$

   $F_2 + NaOH(conc.) \longrightarrow F^- + O_2$
4. $(CN)_2 + OH^- \longrightarrow CN^- + OCN^-$
5. $P_4 + OH^- \longrightarrow PH_3 + H_2PO_2^-$
6. $S_8 + OH^- \longrightarrow S^{2-} + S_2O_3^{2-}$
7. $MnO_4^{2-} \longrightarrow MnO_4^- + MnO_2$
8. $NH_2OH \longrightarrow N_2O + NH_3$

   $NH_2OH \longrightarrow N_2 + NH_3$
9. Oxyacids of Phosphorus (+1, +3 oxidation number)

   $H_3PO_2 \longrightarrow PH_3 + H_3PO_3$

   $H_3PO_3 \longrightarrow PH_3 + H_3PO_4$
10. Oxyacids of Chlorine (Halogens) (+1, +3, +5 Oxidation number)

    $ClO^- \longrightarrow Cl^- + ClO_2^-$

    $ClO_2^- \longrightarrow Cl^- + ClO_3^-$

    $ClO_3^- \longrightarrow Cl^- + ClO_4^-$
11. $HNO_2 \longrightarrow NO + HNO_3$

- 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 reaction.

$$\overset{-1}{I^-} + \overset{+5}{I}O_3^- + H^+ \longrightarrow \overset{0}{I}_2 + H_2O$$

8. BALANCING OF REDOX REACTIONS

All balanced equations must satisfy two criteria.

1. **Atom balance (Mass Balance) :**

   There should be the same number of atoms of each kind on reactant and product side.

2. **Charge Balance :**

   The sum of actual charges on both sides of the equation must be equal.

   There are two methods for balancing the redox equations

1. Oxidation – number change method
2. Ion electron method or half cell method

- Since First method is not very much fruitful for the balancing of redox reactions, students are advised to use second method (Ion electron method) to balance the redox reactions

8. 1 Ion Electron Method

By this method redox equations are balanced in two different medium.

(a) Acidic medium (b) Basic medium

- **Balancing in Acidic Medium**

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

Example

Balance the following redox reaction :

$FeSO_4 + KMnO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + H_2O + K_2SO_4$

Sol.

Step-I :

Assign the oxidation number to each element present in the reaction

$$\overset{+2}{Fe}\,\overset{+6\,-2}{SO_4} + \overset{+1}{K}\,\overset{+7}{Mn}\overset{-2}{O_4} + \overset{+1}{H_2}\,\overset{+6\,-2}{SO_4} \longrightarrow \overset{+3}{Fe_2}\,(\overset{+6\,-2}{SO_4})_3 + \overset{+2}{Mn}\,\overset{+6\,-2}{SO_4} + \overset{+1}{H_2}\overset{-2}{O}$$

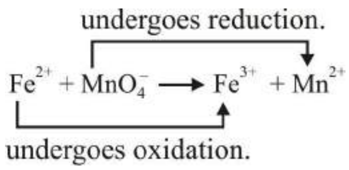
Step II :

Now convert the reaction in Ionic form by eliminating the elements or species, which are not undergoing either oxidation or reduction.

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

Step III :

Now identify the oxidation/reduction occuring in the reaction



Step IV :

Spilt the Ionic reaction in two half, one for oxidation and other for reduction.

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

Step V :

Balance the atom other than oxygen and hydrogen atom in both half reactions

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

Fe & Mn atoms are balanced on 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 :

Equation (i) & (ii) are balanced atomwise. Now balance both equations chargewise. To balance the charge, add electrons to the electrically positive side.

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

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

Step VIII :

The number of electrons gained and lost in each half-reaction are equalised by multiplying both the half reactions with a suitable factor and finally the half reactions are added to give the overall balanced reaction.

Here, we multiply equation (1) by 5 and (2) by 1 and add them :

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

$$5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O \quad ....(2)\times 1$$

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

(Here, at his stage, you will get balanced redox reaction in Ionic form)

Step IX :

Now convert the ionic reaction into molecular form by adding the elements or species, which are removed in step (2).

Now, by some manipulation, you will get :

or

$$5\,FeSO_4 + KMnO_4 + 4H_2SO_4 \longrightarrow \frac{5}{2}Fe_2\,(SO_4)_3 + MnSO_4 + 4H_2O + \frac{1}{2}K_2SO_4$$

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

- **Balancing in Basic Medium**

  In this case, except step VI, all the steps are same. We can understand it by the following **Example**

Example

Balance the following redox reaction in basic medium :

$$ClO^- + CrO_2^- + OH^- \longrightarrow Cl^- + CrO_4^{2-} + H_2O$$

Sol. By using upto step V, we will get :

$$\overset{+1}{ClO^-} \xrightarrow{\text{Reduction}} Cl^- \quad \Big| \quad \overset{+3}{CrO_2^-} \xrightarrow{\text{Oxidation}} \overset{+6}{CrO_4^{2-}}$$

Now, students are advised to follow step VI to balance 'O' and 'H' atom.

$$2H^+ + ClO^- \longrightarrow Cl^- + H_2O \;\mid\; 2H_2O + CrO_2^- + 4H^+ + CrO_4^{-2}$$

Now, since we are balancing in basic medium, therefore add as many as OH^- on both side of equation as there are H^+ ions in the equation.

$$2OH^- + 2H^+ + ClO^- \to Cl^- + H_2O + 2OH^-$$

Finally you will get

$$H_2O + ClO^- \to Cl^- + 2OH^- \quad ....(i)$$

$$4OH^- + 2H_2O + CrO_2^- \to CrO_4^{2-} + 4H^+ + 4OH^-$$

Finally you will get

$$4OH^- + CrO_2^- \to CrO_4^{2-} + 2H_2O \quad ....(ii)$$

Now see equation (i) and (ii) in which O and H atoms are balanced by OH^- and H_2O

Now from step VIII

$$2e^- + H_2O + ClO^- \to Cl^- + 2OH^- \qquad ....(i)\times 3$$

$$4OH^- + CrO_2^- \to CrO_4^{2-} + 2H_2O + 3e^- \qquad ....(ii)\times 2$$

$$\text{Adding : } 3ClO^- + 2CrO_2^- + 2OH^- \to 3Cl^- + 2CrO_4^{2-} + H_2O$$

9. CONCEPT OF EQUIVALENTS

9.1 Equivalent Mass of Element

Number of parts by mass of an element which reacts or displaces from a compound 1.008 parts by mass of hydrogen, 8 parts by mass of oxygen and 35.5 parts by mass of chlorine, is known as the equivalent weight of the element.

e.g. $2Mg + O_2 \longrightarrow 2MgO$

48g 32g

12g 8g

$\because$ 32g of O_2 reacts with 48 g of Mg

$$\therefore\ 8\text{ g of }O_2 = \frac{48\times 8}{32} = 12g$$

$\therefore$ Equivalent weight of Mg $= 12$

Similarly, $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

65.5 g 32.75

$$\therefore\ \text{Equivalent weight of Zn} = \frac{65.5}{2} = 32.75g$$

$$Al \;+\; \frac{3}{2}Cl_2 \longrightarrow AlCl_3$$

$$27\text{ g} \qquad \frac{3}{2}\times 71\text{ g}$$

$\because$ 111.5 g chlorine reacts with 27 g of Al.

$$\therefore\ 35.59\text{ chlorine reacts with } \frac{27\times 35.5}{111.5} = 9.0\text{ g of Al}$$

$$\therefore\ \text{Equivalent weight of aluminium} = \frac{27}{3} = 9.0$$

As we can see from the above examples that equivalent weight is the ratio of atomic weight and a factor (say n-factor or valency factor) which is in above three cases is their respective valencies.

Equivalent Weight (E) :

In general, Eq. wt. (E) =

$$\frac{\text{Atomic weight or molecular weight}}{\text{valency factor (v.f)}} = \frac{\text{Mol. wt.}}{\text{n} - \text{factor}} = \frac{\text{M}}{\text{x}}$$

$$\text{Number of Equivalents} = \frac{\text{mass of species}}{\text{eq. wt. of that species}}$$

For a solution, Number of equivalents = N_1V_1, where N is the normality and V is the volume in litres

- Equivalent mass is a pure number which, when expressed in gram, is called gram equivalent mass.
- The equivalent mass of substance may have different values under different conditions.
- There is no hard and fast rule that equivalent weight will be always less than the molecular mass.

9.2 Valency Factor Calculation

- **For Elements :**

  Valency factor = valency of the element.

- **For Acids :**

  Valency factor = number of replaceable H^+ ions per acid molecule

Example

	NaOH,	KOH
Sol. v.f. →	1	1
Eq. wt.	$\frac{M}{1}$	$\frac{M}{1}$

- Bases may be defined as the substances in which OH group is/are directly attached with group I elements (Li, Na, K, Rb, Cs), group II elements (Be, Mg, Ca, Ba) or group III elements (Al, Ga, In, Tl), transition metals, non-metallic cations like PH_4^+, NH_4^+ etc.
- **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 replaceble H^+ or OH^- than actually replaced in reaction.
- **v. f.** for base is the number of H^+ ion from the acid replaced by each molecule of the base

Example

$$\underset{\text{Base}}{2NaOH} + \underset{\text{Acid}}{H_2SO_4} \longrightarrow Na_2SO_4 + 2H_2O$$

Sol. Valency factor of base = 1

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

- **v. f.** for acid is the number of OH^- replaced from the base by each molecule of acid

Example

$$\underset{\text{Base}}{NaOH} + \underset{\text{Acid}}{H_2SO_4} \longrightarrow NaHSO_4 + H_2O$$

Sol. Valency factor of acid = 1

Here, one of molecule of H_2SO_4 replaced one OH^- from NaOH. Therefore, valency factor for H_2SO_4 is one

$$\therefore \text{Eq. wt. of } H_2SO_4 = \frac{\text{Mol. wt}}{1}$$

- **Salts :**

(a) **In Non-Reacting Condition**

- **Valency factor =** Total number of positive charge or negative charge present in the compound.

Example

		Na_2CO_3	$Fe_2(SO_4)_3$	$FeSO_4.7H_2O$
Sol.	v.f. =	2	$2 \times 3 = 6$	2
	Eq. wt.	$\frac{M}{2}$	$\frac{M}{6}$	$\frac{M}{2}$

(b) **In Reacting Condition**

Example

$$\underset{\text{Base}}{Na_2CO_3} + \underset{\text{Acid}}{HCl} \longrightarrow NaHCO_3 + NaCl$$

Sol. It is an acid base reaction, therefore valency factor for Na_2CO_3 is one while in non-reacting condition, it will be two.

(c) **Equivalent Weight of Oxidising / Reducing Agents in a Redox Reaction**

In case of redox change, **v.f.** = Total change in oxidation number per molecule.

Example

$$KMnO_4 + H_2O_2 \longrightarrow Mn^{2+} + O_2$$

Sol. Mn in $KMnO_4$ is going from +7 to +2, so change in oxidation number per molecule of $KMnO_4$ is 5. So the valency factor of $KMnO_4$ is 5 and equivalent weight is $\frac{M}{5}$.

10. NORMALITY

Normality of a solution is defined as the number of equivalents of solute present in one litre (1000 mL) solution.

Let V mL of a solution is prepared by dissolving W g of solute of equivalent weight E in water.

- Number of equivalents of solute $= \frac{W}{E}$

  VmL of solution contain $\frac{W}{E}$ equivalents of solute

  $\therefore$ 1000 mL solution will contain $\frac{W \times 1000}{E \times V}$ equivalents of solute.

- **Normality (N)** $= \frac{W \times 1000}{E \times V}$
- **Normality (N) = Molarity × Valency factor**

  $N \times V\,(\text{in mL}) = M \times V\,(\text{in mL}) \times n$

  or

- milliequivalents = millimoles × n

Example

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

Sol : **Normality (N)** $= \frac{W \times 1000}{E \times V}$

Here $W = 15.8$ g, $V = 50$ mL

$$E = \frac{\text{molar mass of } KMnO_4}{\text{Valency factor}} = 158/5 = 31.6$$

So, normality = 10 N

Example

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

Sol : Normality = Molarity × valency factor $= 5 \times 6 = 30$ N

11. LAW OF EQUIVALENCE

The law states that one equivalent of an element combine with one equivalent of the other. In a chemical reaction, equivalents and milli equivalents of reactants react in equal amount to give same number of equivalents or milli equivalents of products separately.

Accordingly

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

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

(ii) In a compound M_xN_y

meq of M_xN_y = meq of M = meq of N

Example

Find the number of moles of $KMnO_4$ needed to oxidise one mole Cu_2S in acidic medium.

The reaction is

$$KMnO_4 + Cu_2S \longrightarrow Mn^{2+} + Cu^{2+} + SO_2$$

Sol. From law of equivalence,

equivalents of Cu_2S = equivalents of $KMnO_4$

moles of Cu_2S × v.f. = moles of $KMnO_4$ × v.f.

1 × 8 = moles of $KMnO_4$ × 5 $\Rightarrow$ moles of $KMnO_4$ = 8/5

($\therefore$ v.f. of Cu_2S = 2 (2 – 1) + 1 (4 – (–2)) = 8 and v.f. of $KMnO_4$ = 1 (7 – 2) = 5)

Example

The number of moles of oxalate ions oxidized by one mole of MnO_4^- ion in acidic medium are :

(a) $\frac{5}{2}$ (b) $\frac{2}{5}$

(c) $\frac{3}{5}$ (d) $\frac{5}{3}$

Sol. $$\underset{+7}{MnO_4^-} + \underset{+3}{C_2O_4^{2-}} \rightleftharpoons \underset{+2}{Mn^{+2}} + \underset{+4}{2CO_2}$$

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

x (mole) × 2 = 1 × 5

($\therefore$ v.f. of $C_2O_4^{2-}$ = 2 (4 – 3) = 2

and v.f. of MnO_4^- = 1 (7 – 2) = 5.

$x = \frac{5}{2}$ mole of $C_2O_4^{2-}$ ions.

Example

How many millilitres of 0.02 M $KMnO_4$ solution would be required to exactly titrate 25 mL of 0.2 M $Fe(NO_3)_2$ solution in acidic medium ?

Sol. **Method -1 : Mole Concept Method**

Starting with 25 mL of 0.2 M Fe^{2+}, we can write :

Millimoles of $Fe^{2+} = 25 \times 0.2$ .... (1)

and in volume V (in milliliters) of the $KMnO_4$,

Millimoles of $MnO_4^- = V\,(0.02)$ .... (2)

The balanced reaction is :

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

This requires that at the equivalent point,

$$\frac{\text{m.moles of } MnO_4^-}{1} = \frac{\text{m.moles of } Fe^{2+}}{5}$$

$$\therefore \frac{V(0.02)}{1} = \frac{(25)\,(0.2)}{5} \text{ (from (1) \& (2))}$$

$\therefore V = 50$ mL.

Method -2 : Equivalent Method

At the equivalence point,

milliequivalents of MnO_4^- = milliequivalents of Fe^{2+}

$$M_1 \times vf_1 \times V_1 = M_2 \times vf_2 \times V_2$$

$$0.02 \times 5 \times V_1 = 0.2 \times 1 \times 25$$

$$(\because MnO_4^- \to Mn^{2+};\ v.f. = 5,\ \ Fe^{2+} \to Fe^{3+};\ v.f. = 1)$$

$\therefore V_1 = 50$ mL.

12 TITRATIONS

Titration is procedure for determining the concentration of a solution by allowing a carefully measured volume to react with a standard solution of another substance, whose concentration is known.

Standard Solution - It is a solution whose concentration is known and is taken in burette. It is also called **Titrant.**

There are two type of **titrants :**

- **Primary Titrants/Standard -** These reagents can be accurately weighed and their solutions are not to be standardised before use.

  Ex : Oxalic acid, $K_2Cr_2O_7$, $AgNO_3$, $CuSO_4$, ferrous ammonium sulphate, hypo etc.

- **Secondardy Titrants/Standard :** These reagents cannot be accurately weighed and their solutions are to be standardised before use.

  Ex : NaOH, KOH, HCl, H_2SO_4, I_2, $KMnO_4$, etc.

Titrate : Solution consisting of substance to be estimated, generally taken in a beaker.

Equivalence Point : It is the point when number of equivalents of titrant added becomes equal to number of equivalents of titrate.

At Equivalence Point :

$$n_1V_1M_1 = n_2V_2M_2$$

Indicator : An auxiliary substance added for physical detection of completion of titration at equivalence point. It generally show colour change on completion of titration.

Types of Titrations :

- Acid-base titrations (to be studied in Ionic equilibrium)
- Redox Titrations

12. 1 Some Common Redox Titrations

12.1.1 Permanganate Titrations

- $KMnO_4$ is generally used as oxidising agent in acidic medium, generally provided by dilute H_2SO_4.
- $KMnO_4$ works as self indicator persistent pink color is indication of end point.
- Mainly used for estimation of Fe^{2+}, oxalic acid, oxalates, H_2O_2 etc.

Example

Write the balanced reaction of titration of $KMnO_4$ Vs oxalic acid in presence of H_2SO_4.

Sol. Reaction :

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

Redox Changes $2C^{3+} \longrightarrow 2C^{4+} + 2e^- \quad \left(E_{H_2C_2O_4} = \frac{M}{2}\right)$

$$5e^- + Mn^{7+} \longrightarrow Mn^{2+} \quad \left(E_{KMnO_4} = \frac{M}{5}\right)$$

Indicator : $KMnO_4$ acts as self indicator.

Example

Write the balanced reaction of titration of $KMnO_4$ Vs ferrous ammonium sulphate in presence of H_2SO_4.

Sol. Reaction :

$$2KMnO_4 + 10\,[FeSO_4\,(NH_4)_2SO_4.6H_2O] + 8H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 10(NH_4)_2\,SO_4 + K_2SO_4 + 2MnSO_4 + 68H_2O$$

Redox Changes : $Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad \left(E_{FeSO_4} = \frac{M}{1}\right)$

$$Mn^{7+} + 5e^- \longrightarrow Mn^{2+} \quad \left(E_{KMnO_4} = \frac{M}{5}\right)$$

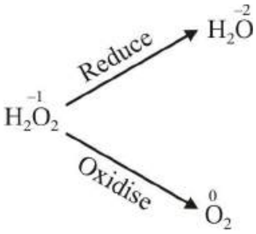
Indicator : $KMnO_4$ acts as self indicator.

Redox Titrations : (Excluding Iodometric/Iodimetric titrations)

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

13. HYDROGEN PEROXIDE (H_2O_2)

H_2O_2 can behave both like oxidising and reducing agent in both the mediums (acidic and basic).



- **Oxidising Agent :** ($H_2O_2 \rightarrow H_2O$)

  (a) **Acidic Medium :** $2e^- + 2H^+ + H_2O_2 \longrightarrow 2H_2O$

  $v.f = 2$

  (b) **Basic Medium :** $2e^- + H_2O_2 \longrightarrow 2OH^-$

  $v.f = 2$

- **Reducing Agent : ($H_2O_2 \rightarrow O_2$)**

  (a) **Acidic Medium :** $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$

  $v.f = 2$

  (b) **Basic Medium :**

  $2OH^- + H_2O_2 \longrightarrow O_2 + 2H_2O + 2e^-$

  $v.f = 2$

NOTE

Valency factor of H_2O_2 is always equal to 2.

Volume Strength of H_2O_2 : Strength of H_2O_2 is represented as 10V, 20V, 30V etc.

20VH_2O_2 means **one litre** of this sample of H_2O_2 on decomposition gives **20L of O_2** gas of **STP.**

Decomposition of H_2O_2 is given as :

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

1 mole $\quad \frac{1}{2} \times 22.4$ L O_2 at STP

$= 34g \quad = 11.2$ L O_2 at STP

To obtain 11.2 litre O_2 at STP, at least 34 g H_2O_2 must be decomposed.

For 20 L O_2, we should decompose atleast $\frac{34}{11.2} \times 20$ g H_2O_2

$\therefore$ 1L solution of H_2O_2 contains $\frac{34}{11.2} \times 20$ g H_2O_2

$\therefore$ 1L solution of H_2O_2 contains $\frac{34}{11.2} \times \frac{20}{17}$ equivalents of H_2O_2

$$(E_{H_2O_2} = \frac{M}{2} = \frac{34}{2} = 17)$$

$$\text{Nomality of } H_2O_2 = \frac{34}{11.2} \times \frac{20}{17} = \frac{20}{5.6}$$

- **Normality of H_2O_2 (N)** $= \dfrac{\text{Volume strength of } H_2O_2}{5.6}$

$$\because \; M_{H_2O_2} = \frac{N_{H_2O_2}}{v.f.} = \frac{N_{H_2O_2}}{2}$$

- **Molarity of H_2O_2 (M)** $= \dfrac{\text{Volume strength of } H_2O_2}{11.2}$

Strength (in g/L) : Denoted by S

Strength = Molarity × Mol. wt = Molarity × 34

Strength = Normality × Eq. weight = Normality × 17

Example

20 mL of H_2O_2 after acidification with dilute H_2SO_4 required 30 mL of $\frac{N}{12}$ $KMnO_4$ for complete oxidation. Final the strength of H_2O_2 solution. [Molar mass of H_2O_2 = 34]

Sol. meq. of $KMnO_4$ = meq. of H_2O_2

$$30 \times \frac{1}{12} = 20 \times N'$$

$$N' = \frac{30}{12 \times 20} = \frac{1}{8}N$$

$$\therefore \text{strength} = N' \times \text{equivalent mass} = \frac{1}{8} \times 17 = 2.12 \text{ g/L.}$$

14. HARDNESS OF WATER

Temporary Hardness - due to bicarbonates of Ca & Mg.

(a) Boiling : Soluble salts converts to insoluble salt during boiling which forms ppt and can easily removed by filtration.

$$Mg(HCO_3)_2 \xrightarrow{Boil} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

$Mg(OH)_2$ is precipitated because of high solubility product of $Mg(OH)_2$ as compared to that of $MgCO_3$

$$Ca(HCO_3)_2 \xrightarrow{Boil} CaCO_3 \downarrow CO_2 \uparrow + H_2O$$

Filtrate is soft water.

(b) Clark's method (calcium hydroxide/lime water method) :

$$Ca(HCO_3)_2 + Ca(OH)_2 \text{ (calculated amount)}$$
$$\rightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \text{ (calculated amount)}$$
$$\rightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$$

Permanent Hardness - due to chlorides & sulphates of Ca & Mg. There are some method by which we can soften the water sample.

(a) Addition of washing soda (sodium carbonate) : It reacts with chloride and sulphate of Mg^{2+} and Ca^{2+} to precipitate out as $MgCO_3$ and $CaCO_3$.

$$MCl_2 + Na_2CO_3 \rightarrow MCO_3 \downarrow + 2\,NaCl\,(M = Mg/Ca)$$

$$MSO_4 + Na_2CO_3 \rightarrow MCO_3 \downarrow + Na_2SO_4\,(M = Mg/Ca)$$

Parts Per Million (ppm)

When the solute is present in very less amount, then this concentration term is used. It is defined as the number of parts of the solute present in every 1 million parts of the solution. ppm can both be in terms of mass or in terms of moles. If nothing has been specified, we take ppm to be in terms of mass. Hence, a 100 ppm solution means that 100 g of solute is present in every 1000000g of solution.

$$ppm_A = \frac{\text{mass of A}}{\text{Total mass}} \times 10^6 = \text{mass fraction} \times 10^6$$

14.1 Measurement of Hardness

Hardness is measured in terms of ppm (parts per million) of $CaCO_3$ or equivalent to it.

$$\text{Hardness in ppm} = \frac{\text{mass of } CaCO_3}{\text{Total mass of solution}} \times 10^6$$

Example

0.00012% $MgSO_4$ and 0.000111% $CaCl_2$ is present in ater. What is the measured hardness of water and millimoles of washing soda required to purify water 1000 L water ?

Sol. Basis of calculation = 100 g hard water

$$MgSO_4 = 0.00012g = \frac{0.00012}{120} \text{ mole}$$

$$CaCl_2 = 0.000111g = \frac{0.000111}{111} \text{ mole}$$

$\therefore$ equivalent moles of $CaCO_3$ =

$$\left(\frac{0.00012}{120} + \frac{0.000111}{111}\right) \text{mole}$$

$\therefore$ mass of $CaCO_3$ =

$$\left(\frac{0.00012}{120} + \frac{0.000111}{111}\right) \times 100 = 2 \times 10^{-4} \text{ g}$$

Hardness (in terms of ppm of $CaCO_3$) =

$$\frac{2 \times 10^{-4}}{100} \times 10^6 = 2 \text{ ppm}$$

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

$$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na_2SO_4$$

$\therefore$ Required Na_2CO_3 for 100g of water =

$$\left(\frac{0.00012}{120} + \frac{0.000111}{111}\right) \text{mole}$$

$$= 2 \times 10^{-6} \text{ mole}$$

$\therefore$ Required Na_2CO_3 for 1000 litre water =

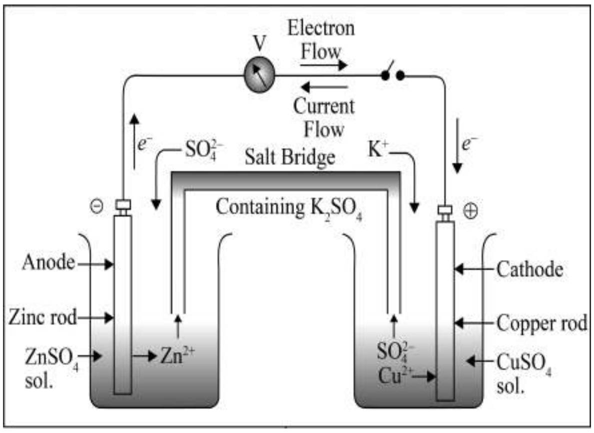
$$\frac{2 \times 10^{-6}}{100} \times 10^6 = \frac{2}{100} \text{ mole} \quad (\because d = 1g/mL)$$

$$= \frac{20}{1000} \text{ mole} = 20 \text{ m mole}$$

15. ELECTROCHEMICAL CELL

It is a device which converts chemcial energy produced in an indriect redoc reaction into electrical energy.

Redox couple is defined as a combination of the oxidised and reduced froms of the same substance taking part in an oxidation or reduction half reaction.



Representation of an electrochemcial cell

$$Zn\,|\,Zn^{2+}(C_1)\,||\,Cu^{2+}(C_2)\,|\,Cu$$

$$\text{At anode : } Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

$$\text{At cathode : } Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

15.1 Important Generalisation

Oxidation occurs at the anode while reduction occurs at the cathode.

Anode acts as the negative pole while cathode acts as the positve pole.

Electrons flow from anode to cathode in the external circuit while current flows from cathode to anode.

Chemcial energy of the redox reaction occuring in the galvic cell is converted into electrical energy.

16. ELECTRODE POTENTIAL

The tendency of an electrode to lose or gain electrons.

If the concetration of electrolytes is taken as unity (1 mol L^{-1}) or if any gas appears in the electrode reaction, it is taken at 1 atm presure and temoerature is taken as 298 K, then the electrode potentials is called standard electrode potential (E^o)

By convertion, the standrad electrode potential (E^o) of hydrogen electrode is 0.00 volt.

A negative E^o means that the H^+ / H_2 couple.

A positive E^o means that the redox couple is a weaker reducing agent than the H^+ / H_2 couple.

The electrode potential is termed as oxidation potential if the electrode loses electrons and is called the reduction potential if the electrode gains electrons.

16.1 Electromotive Series

A list of oxidising agents, arranged in decreasing order of their strength is called the activity or electromotive or electrochemical series.

Standard Reduction Potentials in Aqueous Solutions at 25°C

Oxidizing Agent				Reducing Agent	Reduction Potential (V)
F_2	+	$2e^-$	→	$2F^-$	2.87
H_2O_2	+	$2H^+ + 2e^-$	→	$2H_2O$	1.78
MnO_4^-	+	$8H^+ + 5e^-$	→	$Mn^{2+} + 4H_2O$	1.51
Au^{3+}	+	$3e^-$	→	Au	1.50
Cl_2	+	$2e^-$	→	$2Cl^-$	1.36
O_2	+	$4H^+ + 4e^-$	→	$2H_2O$	1.23
$Cr2O_7^{2-}$	+	$14H^+ + 6e^-$	→	$2Cr^{3+} + 7H_2O$	1.23
Br_2	+	$2e^-$	→	$2Br^-$	1.07
NO_3^-	+	$4H^+ + 3e^-$	→	$NO + 2H_2O$	0.96
Ag^+	+	e^-	→	Ag	0.80
I_2	+	$2e^-$	→	$2I^-$	0.54
Cu^+	+	e^-	→	Cu	0.52
O_2	+	$2H_2O + 4e^-$	→	$4OH^-$	0.40
Cu^{2+}	+	$2e^-$	→	Cu	0.34
$2H_3O^+$	+	$2e^-$	→	$H_2 + 2H_2O$	0.00
Pb^{2+}	+	$2e^-$	→	Pb	–0.13
Sn^{2+}	+	$2e^-$	→	Sn	–0.14
Ni^{2+}	+	$2e^-$	→	Ni	–0.26
Fe^{2+}	+	$2e^-$	→	Fe	–0.45
Cr^{3+}	+	$2e^-$	→	Cr	–0.74
Zn^{2+}	+	$2e^-$	→	Zn	–0.76
$2H_2O$	+	$2e^-$	→	$H_2 + 2OH^-$	–0.83
Mn^{2+}	+	$2e^-$	→	Mn	–1.19
Al^{3+}	+	$3e^-$	→	Al	–1.66
Mg^{2+}	+	$2e^-$	→	Mg	–2.37
Na^+	+	e^-	→	Na	–2.71
Ca^{2+}	+	$2e^-$	→	Ca	–2.87
Ba^{2+}	+	$2e^-$	→	Ba	–2.91
K^+	+	e^-	→	K	–2.93
Li^+	+	e^-	→	Li	–3.04

Increasing Strength of Oxidizing Agent ↑

Increasing Strength of Reducing Agent ↓

16.2 Application

To compare the relative strength of oxidising and reducing agents.

Comparison of reactivity of metals.

To predict whether a metal willl liberate hydrogen from the aqueous solution of acids or not.

SUMMARY

- Oxidation is a process which involves loss of electrons or increase in oxidation number.
- Reduction is a process which involves gain of electrons or decrease in oxidation number.
- Oxidation agent is a substance which accepts one or more electrons or its oxidation number decreases.
- Reducing agent is a substance which loses one or more electrons or its oxidation number increases.
- Oxidation and Reduction always occur side by side.

Oxidation Number :

- Oxidation numnber is the charge which an atom appears to have when all other atoms ar removed from it as ions.

  For elementary state, O.N is zero.

  e.g., He(O.N. = 0), H_2 (O.N. = 0), S_n (O.N. = 0)
- Oxidation number of hydrogen is +1 except in hydrides NaH, LiH, CaH_2 (-1).
- Oxidation number of oxygen is always -2 except in peroxides, H_2O, N_2O_2 (-1)

  in superpxodes KO_2 (-1/2)

  in OF_2 (+2)

  O_2F_2 (+1)
- Combination reaction

  $$2Mg + O_2 \rightarrow 2MgO$$
- Decomposition reaction

  $$2KClO_3 \rightarrow 2KCl + 3O_2$$
- Displacement reaction

  $$CuSO_4 + Zn \rightarrow Cu + ZnSO_4$$

  $$Sn + 2HCl \rightarrow SnCl_2 + H_2$$

  $$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$
- Disporpotionation reactions

  The reactions in which the oxidation number of an element both increases and decreases.

  e.g., $2H_2O_2 \rightarrow 2H_2O + O_2$

  In this case the oxidation number of O decreases from -1 to -2 (in H_2O) and increases from -1 to 0 (in O_2)

  $$Cl_2 + 2OH^- \rightarrow OCl^- + Cl^- + H_2O$$

  O.N. of Cl increases from 0 to +1 (in OCl^-) and decreases from 0 to -1 (in Cl^-).

  $3ClO^- \rightarrow ClO_3^- + 2Cl^-$ is also a disproportionation reaction because O.N. of Cl increase from +1 (in ClO^-) to +5 (in ClO_3^-) and decrease from +1 to -1 (in Cl^-).

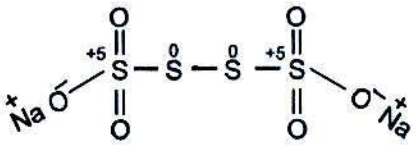
  Oxidation and reduction reactions can be balanced by oxidation number method and half reaction method.

SOLVED EXAMPLES

Example – 1

Calculate individual oxidation number of each S-atom in $Na_2S_4O_6$ (sodium tetrathionate) with the help of its structure.

Sol.



Example – 2

Find the average and individual oxidation number of Fe & Pb in Fe_3O_4 & Pb_3O_4, which are mixed oxides.

Sol. (i) Fe_3O_4 is mixture of FeO & Fe_2O_3 in 1 : 1 ratio

so, individual oxidation number of Fe = +2 & +3

& average oxidation number $= \dfrac{1(+2) + 2\,(+3)}{3} = 8/3$

(ii) Pb_3O_4 is a mixture of PbO & PbO_2 in 2 : 1 molar ratio so, individual oxidation number of Pb are +2 & +4 &

average oxidation number of Pb $= \dfrac{2(+2) + 1\,(+4)}{3} = 8/3$

Example – 3

Balance the following equations :

(a) $H_2O_2 + MnO_4^- \longrightarrow Mn^{+2} + O_2$ (acidic medium)

(b) $Zn + HNO_3$ (dil) $\longrightarrow Zn(NO_3)_2 + H_2O + NH_4NO_3$

(c) $CrI_3 + KOH + Cl_2 \longrightarrow K_2CrO_4 + KIO_4 + KCl + H_2O$

(d) $P_2H_4 \longrightarrow PH_3 + P_4$

(e) $Ca_3(PO_4)_2 + SiO_2 + C \longrightarrow CaSiO_3 + P_4 + CO$

Sol. (a) $6H^+ + 5H_2O_2 + 2MnO_4^- \longrightarrow 2Mn^{+2} + 5O_2 + 8H_2O$

(b) $4Zn + 10HNO_3(\text{dil}) \longrightarrow$
$4Zn\,(NO_3)_2 + 3H_2O + NH_4NO_3$

(c) $2CrI_3 + 64KOH + 27Cl_2 \longrightarrow 2K_2CrO_4 + 6KIO_4$
$+ 54KCl + 32H_2O$

(d) $6P_2H_4 \longrightarrow 8PH_3 + P_4$

(e) $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow$
$6CaSiO_3 + P_4 + 10CO$

Example – 4

Calculate the normality of a solution obtained by mixing 50 mL of 5M solution of $K_2Cr_2O_7$ and 50 mL of 2 M $K_2Cr_2O_7$ in acidic medium.

Sol. v.f. of $K_2Cr_2O_7 = 6$

so $N_f = \dfrac{N_1V_1 + N_2V_2}{V_1 + V_2}$

$= \dfrac{5 \times 6 \times 50 + 2 \times 6 \times 50}{50 + 50} = 21\,N$

Example – 5

Calculate the normality of a solution containing 13.4 g of sodium oxalate in 100 mL **Sol.**

Sol. Normality $= \dfrac{\text{wt. in g / eq. wt}}{\text{vol of solution in litre}}$

Here, eq. wt. of $Na_2C_2O_4 = 134/2 = 67$

so $N = \dfrac{13.4/67}{100/1000} = 2N$

Example – 6

The number of moles of ferrous oxalate oxidised by one mole of $KMnO_4$ in acidic medium is :

(a) $\dfrac{5}{2}$ (b) $\dfrac{2}{5}$ (c) $\dfrac{3}{5}$ (d) $\dfrac{5}{3}$

Ans. (d)

Sol. $\underset{+2}{Fe}\underset{+3}{C_2}O_4 + K\underset{+7}{Mn}O_4 \rightarrow \underset{+2}{Mn^{+2}} + \underset{+3}{Fe^{+3}} + \underset{+4}{C}O_2$

Eq. of FeC_2O_4 = Eq. of $KMnO_4$

moles of $FeC_2O_4 \times 3$ = moles of $KMnO_4 \times 5$

so, moles of $FeC_2O_4 = 5/3$

Example – 7

How many moles of $KMnO_4$ are needed to oxidise a mixture of 1 mole of each $FeSO_4$ & FeC_2O_4 in acidic medium ?

(a) $\frac{4}{5}$ (b) $\frac{5}{4}$ (c) $\frac{3}{4}$ (d) $\frac{5}{3}$

Ans. (a)

Sol. Balanced equations are :

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

$$6KMnO_4 + 10FeC_2O_4 + 24H_2SO_4 \rightarrow$$
$$3K_2SO_4 + 6MnSO_4 + 5Fe_2(SO_4)_3 + 20CO_2 + 24H_2O$$

Eq. of $KMnO_4$ = Eq. of $FeSO_4$ + Eq. of FeC_2O_4

moles of $KMnO_4 \times 5$ = moles of $FeSO_4 \times 1$ + moles of $FeC_2O_4 \times 3$

$\therefore$ moles of $KMnO_4 = 4/5$

Example – 8

A fresh H_2O_2 solution is labelled 11.2 V. This solution has the same concentration as a solution which is :

(a) 3.4 % (w/w) (b) 3.4% (v/v) (c) 3.4% (w/v)
(d) None of these

Ans. (c)

Sol. Molarity of $H_2O_2 = \frac{\text{vol. strength}}{11.2} = \frac{11.2}{11.2} = 1$

Now, $\%\,(w/v) = \frac{\text{wt. of solute in g}}{\text{wt. of solution in mL}} \times 100$

$= \text{Molarity} \times \text{Mol. wt. of solute} \times \frac{1}{10}$

$= 1 \times 34 \times \frac{1}{10} = 3.4\%$

Example – 9

100 mL each of 1N H_2O_2 and 11.2 V H_2O_2 solution are mixed, then the final solution is equivalent to :

(a) 3 M H_2O_2 solution

(b) 0.5 N H_2O_2 solution

(c) 25.5 g/L H_2O_2 solution

(d) 2.55 g/L H_2O_2

Ans. (c)

Sol. $N_{\text{final}} = \frac{N_1V_1 + N_2V_2}{V_1 + V_2} = \frac{1 \times 100 + \left(\frac{11.2}{5.6}\right) \times 100}{100 + 100} = 3/2 = 1.5N$

So, $\text{Molarity} = \frac{\text{Normality}}{\text{v.f.}} = \frac{1.5}{2} = 0.75\text{ M}$

Strength of solution in g/L = Molarity × Mol. wt. = 0.75 × 34 = 25.5 g/L

Example – 10

Consider the elements: Cs, Ne, I and F

(a) Identify the element that exhibits only negative oxidation state.

(b) Identify the element that exhibits only positive oxidation state.

(c) Identify the element that exhibits both positive and negative oxidation states.

(d) Identify the element which exhibits neither the negative nor does the positive oxidation state.

Sol. (a) Fluorine is only element in the periodic table that shows always only negative oxidation state of –1.

(b) Cesium is the metal and it shows positive oxidation state of +1.

(c) Iodine is nonmetal but it will show both positive and negative oxidation states.

(d) Neon is noble gas and it oxidation sate is zero due to stable noble gas configuration.

Example – 11

Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess of chlorine is removed by treating with sulphur dioxide. Present a balanced equation for this redox change taking place in water.

Sol. Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess of chlorine is removed by treating with sulphur dioxide due to the formation of two acids like H_2SO_4 and HCl.

The balanced equation:

$$Cl_2 + SO_2 \rightarrow SO_4^{-2} + Cl^{-1}$$

Reduction half reaction

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

Oxidation half reaction:

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$

Balanced, reaction:

$$Cl_2 + SO_2 + 2H_2O \rightarrow 2Cl^- + SO_4^{2-} + 4H^+$$

Example – 12

The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+}, MnO_2, and H^+ ion. Write a balanced ionic equation for the reaction.

Sol. The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+}, MnO_2, and H^+ ion. Let us write the reaction: $Mn^{3+}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + MnO_{2(s)} + H^+_{(aq)}$

The oxidation half equation by balancing the electrons and charge are: $Mn^{3+}_{(aq)} \rightarrow MnO_{2(aq)} + 4H^+_{(aq)} + e^-$

Now balance the O atoms and H^+ ions by adding water molecules,

$$Mn^{3+}_{(aq)} + 2H_2O_{(l)} \rightarrow MnO_{2(s)} + 4H^+_{(aq)} + e^- \quad .....(i)$$

On the other hand, the reduction half equation by balancing the electrons are: $Mn^{3+}_{(aq)} + e^- \rightarrow Mn^{2+}_{(aq)} \quad .....(ii)$

Combine the both equation (i) and (ii) by adding as:

$$2Mn^{3+}_{(aq)} + 2H_2O_{(l)} \rightarrow MnO_{2(s)} + 2Mn^{2+}_{(aq)} + 4H^+_{(aq)}$$

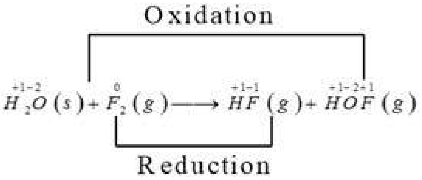
Example – 13

Fluorine reacts with ice and results in the change:

$$H_2O(s) + F_2(g) \rightarrow HF(g) + HOF(g)$$

Justify that this reaction is a redox reaction.

Sol. Let's write the oxidation number of each atom involved in the given reaction:



Oxidation number of F increases from 0 to +1 in HOF and the oxidation number decreases from 0 to –1 in HF. F is oxidized as well as reduced. So that the given reaction is a redox reaction.

Example – 14

While sulphur dioxide and hydrogen peroxide can act as oxidising as well as reducing agents in their reactions, ozone and nitric acid act only as oxidants. Why?

Sol. Sulphur dioxide and hydrogen peroxide can act as oxidizing as well as reducing agents in their reactions because of the range of the oxidation states of the elements.

The Sulphur range is +6 to -2. In case of SO_2 the Sulphur oxidation state is +4. It has a chance to oxidized as well as reduced. That's why SO_2 can act as an oxidising as well as a reducing agent. The oxygen range is 0 to -2. In case of H_2O_2 the oxygen oxidation state is -1. It has a chance to oxidized as well as reduced. That's why H_2O_2 can act as an oxidising as well as a reducing agent.

In case of ozone and nitric acid, the oxygen and nitrogen can only decrease the oxidation state only. Hence, ozone and HNO_3 acts only as an oxidant.

Example – 15

The compound AgF_2 is an unstable compound. However, if formed, the compound acts as a very strong oxidizing agent. Why?

Sol. The stable oxidation state of silver is +1. Compound AgF_2 is an unstable compound. However, if formed, the compound acts as a very strong oxidizing agent due to convert into its stable oxidation state.

Example – 16

Write the formulae for the following compounds:

(a) Mercury(II) chloride

(b) Nickel(II) sulphate

(c) Tin(IV) oxide

(d) Thallium(I) sulphate

(e) Iron(III) sulphate

(f) Chromium(III) oxide

Sol. (a) Mercury (II) chloride: $HgCl_2$

(b) Nickel (II) sulphate: $NiSO_4$

(c) Tin (IV) oxide: SnO_2

(d) Thallium (I) sulphate: Tl_2SO_4

(e) Iron (III) sulphate: $Fe_2(SO_4)_3$

(f) Chromium (III) oxide: Cr_2O_3

Example – 17

Out of aluminium and silver vessel, which one will be more suitable to store 1 M HCl solution and why ?

$$E^o_{Al^{3+}|Al} = -1.66V, E^o_{Ag^+|Ag} = +0.80V.$$

Sol. Since reduction potential of silver is more than that of hydrogen $\left(E^o_{H^+|H_2}, Pt = 0\right)$, silver vessel will be suitable to store 1M HCl. On the other hand, $E^o_{Al^{3+}|Al}$ is less than that of hydrogen $\left(E^o_{H^+|H_2}, Pt\right)$ so that hydrogen will be liberated if stored in aluminium vessel.

Example – 18

40.05 mL of 1.0 M Ce^{+4} are required to titrate 20.0 mL of 1.0 mL of 1.0 M Sn^{2+} to Sn^{4+}. What is the oxidation state of cerium in the reduction product ?

Sol. The reaction occurring are :

$$Ce^{4+} + ne^- \rightarrow Ce^{(4-n)+}$$

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$$

To balance the equations, (the no. of electrons lost = no. of electrons gained) multiply eq. (i) by 2 and eq. (ii) by n and add

$$2Ce^{4+} + nSn^{2+} \rightarrow Ce^{(4-n)+} + Sn^{4+}$$

Moles of Ce^{4+} in 40.05 mL of 1.0 M solution,

$$= \frac{1.0}{1000} \times 40.05 = 40.05 \times 10^{-3}\,\text{mol}$$

Now 2 mol of Ce^{4+} will oxidise n mole of Sn^{2+}

40.05×10^{-3} mol of Ce^{4+} will oxidise Sn^{2+}

$$\frac{n}{2} \times 40.05 \times 10^{-3}\,\text{mol} = 20.02n \times 10^{-3}\,\text{mol}$$

But moles of in 20.0 mL of 1.0 M solution

$$= \frac{1.0}{1000} \times 20.0 = 20.0 \times 10^{-3}\,\text{mol}$$

$$\therefore 20.02n \times 10^{-3}\,\text{mol} = 20.0 \times 10^{-3}\,\text{mol}$$

$$\therefore n = 1$$

Hence 1 mol of electrons are required in the reduction of each mol of ion.

$$\therefore \quad Ce^{4+} + e^- \rightarrow Ce^{3+}$$

Ce^{3+} is the reduction product.

Example – 19

The degree of hardness of a given sample of hard water is 60 ppm. If the entire hardness is due to $MgSO_4$, how much of $MgSO_4$ is present per kilogram of hard water ?

Sol. Degree of hardness of water = 60 ppm

Since degree of hardness is the number of parts of calcium carbonate or equivalent to calcium and magnesium salts present in a million parts of water by mass,

$\therefore 10^6$ g of water contain 60 g of

Now 1 mol of $CaCO_3$ = 1 mol of $MgSO_4$

100 g of $CaCO_3$ = 120 g of $MgSO_4$

$$10^6 \text{ g of water contain } MgSO_4 = \frac{60 \times 120}{100} = 72\text{g}$$

$$10^3 \text{ g of water will contain } MgSO_4 = \frac{72}{10^6} \times 10^3 = 0.072\text{g}$$

$\therefore$ 1 kg of water contains $MgSO_4$ = 72 mg

Example – 20

Refer to the periodic table given in your book and now answer the following questions:

Select the possible non-metals that can show disproportionation reaction.

Sol. In disproportionation reactions, one of the reacting substances always contains an element that can exist in at least three oxidation states.

Phosphorous(P_4), Chlorine (Cl), Iodine(I), and sulphur (S_8) can show disproportionation reactions. Disproportionation are those reactions in which the atom of same element is simultaneously oxidized as well as reduced. Manganese (Mn), Chromium(Cr) and Copper(Cu), can show disproportionation reactions. Disproportionation are those reactions in which the atom of same element is simultaneously oxidized as well as reduced.

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

Concept of Oxidation and Reduction

1. Which of the following behaves as both oxidising and reducing agents?

(a) H_2SO_4 (b) SO_2
(c) H_2S (d) HNO_3

2. The compound that can work both as an oxidising as well as a reducing agent is :

(a) $KMnO_4$ (b) H_2O_2
(c) $Fe_2(SO_4)_3$ (d) $K_2Cr_2O_7$

3. Which of the following is not a redox reaction?

(a) $CaCO_3 \rightarrow CaO + CO_2$
(b) $O_2 + 2H_2 \rightarrow 2H_2O$
(c) $Na + H_2O \rightarrow NaOH + 1/2\ H_2$
(d) $MnCl_3 \rightarrow MnCl_2 + 1/2\ Cl_2$

4. Which substance serves as reducing agents in the following reaction?

$14H^+ + Cr_2O_7^{2-} + 3Ni \rightarrow 2Cr^{3+} + 7\,H_2O + 3Ni^{2+}$

(a) H_2O (b) Ni
(c) H^+ (d) $Cr_2O_7^{2-}$

5. Which of the following reactions depicts the oxidising property of SO_2?

(a) $SO_2 + H_2O \longrightarrow H_2SO_3$
(b) $2H_2S + SO_2 \longrightarrow 3S + 2H_2O$
(c) $Cl_2 + SO_2 \longrightarrow SO_2Cl_2$
(d) $2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+$

6. Nitric oxide acts as a reducing agent in the reaction

(a) $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$
(b) $2NO + 3I_2 + 4H_2O \longrightarrow 2NO_3^- + 6I^- + 8H^+$
(c) $2NO + H_2SO_3 \longrightarrow N_2O + H_2SO_4$
(d) $2NO + H_2S \longrightarrow N_2O + S + H_2O$

Oxidation Number

7. The oxidation stae of osmium (Os) in OsO_4 is

(a) +7 (b) +5
(c) +4 (d) +8

8. Oxidation number of nitrogen in $(NH_4)_2SO_4$ is

(a) – 1/3 (b) – 1
(c) + 1 (d) – 3

9. The oxidation number of Phosphorus in $Mg_2P_2O_7$ is :

(a) + 3 (b) + 2
(c) + 5 (d) – 3

10. In which of the following compounds, nitrogen has an oxidation state of – 1?

(a) N_2O (b) NO_2^-
(c) NH_2OH (d) N_2H_4

11. A metal ion M^{3+} loses 3 electrons, its oxidation number will be :

(a) + 3 (b) + 6
(c) 0 (d) – 3

12. In which of the following reactions is there a change in the oxidation number of nitrogen atom?

(a) $2\,NO_2 \rightarrow N_2O_4$
(b) $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
(c) $N_2O_5 + H_2O \rightarrow 2HNO_3$
(d) None of these

13. When SO_2 is passed through an acidified solution of potassium dichromate the oxidation state of S changes from:

(a) + 4 to 0 (b) + 4 to + 2
(c) + 4 to + 6 (d) + 6 to + 4

14. Oxidation state of nitrogen is correctly given for

Compound	**Oxidation state**
(a) $[Co(NH_3)_5Cl]Cl_2$	0
(b) NH_2OH	+ 1
(c) $(N_2H_5)_2SO_4$	+ 2
(d) Mg_3N_2	– 3

15. The oxidation state of chromium in $Cr(CO)_6$ is :

(a) 0　(b) + 2

(c) – 2　(d) + 6

16. In which of the following pairs, there is greatest difference in the oxidation number of the underlined elements?

(a) $\underline{N}O_2$ and $\underline{N}_2O_4$　(b) $\underline{P}_2O_5$ and $\underline{P}_4O_{10}$

(c) $\underline{N}_2O$ and $\underline{N}O$　(d) $\underline{S}O_2$ and $\underline{S}O_3$

17. In which of the compounds does manganese exhibit highest oxidation number?

(a) MnO_2　(b) Mn_3O_4

(c) K_2MnO_4　(d) $MnSO_4$

18. Which of the following elements has least oxidation number?

(a) $Ni(CN)_4$　(b) $Ni(CO)_4$

(c) Fe_2O_3　(d) SF_6

19. The oxidation number of sulphur in S_8, S_2F_2, H_2S respectively are :

(a) 0, + 1 and –2　(b) + 2, + 1 and –2

(c) 0, + 1 and + 2　(d) –2, + 1 and – 2

Types & Balancing of Redox Reactions

20. In which of the following reactions, there is no change in valency?

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

(b) $SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$

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

(d) $2BaO + O_2 \longrightarrow 2BaO_2$

21. Which of the following is a disproportionation reaction ?

(a) $Cu_2O + 2H^{\oplus} \longrightarrow Cu + Cu^{2+} + H_2O$

(b) $2CrO_4^{2-} + 2H^{\oplus} \longrightarrow Cr_2O_7^{2-} + H_2O$

(c) $CaCO_3 + 2H^{\oplus} \longrightarrow Ca^{2+} + H_2O + CO_2$

(d) $Cr_2O_7^{2-} + 2\overset{\ominus}{O}H \longrightarrow 2CrO_4^{2-} + H_2O$

22. For the redox reaction,

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

23. What is the coefficient of oxalate ion in the following reaction?

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

(a) 4　(b) 2

(c) 3　(d) 5

24. In the equation

$NO_2^{\ominus} + H_2O \longrightarrow NO_3^{\ominus} + 2H^{\oplus} + ne^-$

n stands for

(a) 1　(b) 2

(c) 3　(d) 4

25. For the redox reaction $MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$, The correct stoichiometric coefficients of MnO_4^-, $C_2O_4^{2-}$ and H^+ are respectively:

(a) 2,5,16　(b) 16,5,2

(c) 5,16,2　(d) 2,16,5

26. In the chemical reaction, $K_2Cr_2O_7 + XH_2SO_4 + YSO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + ZH_2O$, X, Y and Z are

(a) 1,3,1　(b) 4,1,4

(c) 3,2,3　(d) 2,1,2

27. In the chemical reaction,

$K_2Cr_2O_7 + xH_2SO_4 + ySO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + zH_2O$

x, y and z are

(a) 1, 3, 1　(b) 4, 1, 4

(c) 3, 2, 3　(d) 2, 1, 2

28. In the balanced chemical reaction

$IO_3^{\ominus} + aI^{\ominus} + bH^{\ominus} \longrightarrow cH_2O + dI_2$

a, b, c and d respectively, correspond to

(a) 5, 6, 3, 3　(b) 5, 3, 6, 3

(c) 3, 5, 3, 6　(d) 5, 6, 5, 5

29. In the chemical reaction,

$K_2Cr_2O_7 + xH_2SO_4 + ySO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + zH_2O$

x, y and z are

(a) 1, 3, 1　(b) 4, 1, 4

(c) 3, 2, 3　(d) 2, 1, 2

30. How many moles of $MnO_4^{\ominus}$ ion will react with 1 mol of ferrous oxalate in acidic medium ?

(a) $\frac{1}{5}$ (b) $\frac{2}{5}$

(c) $\frac{3}{5}$ (d) $\frac{5}{3}$

Redox Reactions and Electrode Processes

31. Which of the following statement is correct for a galvanic cell ?

(a) Reduction occurs at cathode

(b) Oxidation occurs at anode

(c) Electrons flow from anode to cathode

(d) All the statements are correct

32. The correct order of reactivity of K, Mg, Zn and Cu with water according to the electrochemical series is

(a) $K > Mg > Zn > Cu$ (b) $Mg > Zn > Cu > K$

(c) $K > Zn > Mg > Cu$ (d) $Cu > Zn > Mg > K$

33. Consider the following standard reduction potentials:

$$Ca^{2+} + 2e^- \rightleftharpoons Ca;\ E^\circ = -2.76\ V$$

$$Pb^{2+} + 2e^- \rightleftharpoons Pb;\ E^\circ = -0.13\ V$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu;\ E^\circ = 0.34\ V$$

$$Hg_2^{2+} + 2e^- \rightleftharpoons Hg;\ E^\circ = 0.80\ V$$

$$Pt^{2+} + 2e^- \rightleftharpoons Pt;\ E^\circ = 1.20\ V$$

Which of the following metals is the strongest reducing agent?

(a) Ca (b) Pb

(c) Cu (d) Hg

34. Consider the following electrodes potentials:

(a) $V^{2+} + 2e^- \rightarrow V;\ E^\circ = -1.18 V$

(b) $Cu^{2+} + e^- \rightarrow Cu^+;\ E^\circ = 0.15 V$

(c) $2H^+ + 2e^- \rightarrow H_2;\ E^\circ = 0.00 V$

(d) $Mg^{2+} + 2e^- \rightarrow Mg;\ E^\circ = -2.37\ V$

Based on the above data, state which of the following is the strongest reducing agent ?

35. The standard reduction potentials at 298 K are given against each of the following half cell reactions :

I. $E^{\ominus}_{Zn^{2+}|Zn} = -0.76 V$ II. $E^{\ominus}_{Cr^{3+}|Cr} = -0.74 V$

III. $E^{\ominus}_{H^{\oplus}|H_2} = 0.00 V$ IV. $E^{\ominus}_{Fe^{3+}|Fe^{+2}} = +0.77 V$

Based on the above data, state which of the following is the strongest reducing agent ?

(a) Zn (b) Cr

(c) H_2 (d) Fe

Equivalent Concept

36. In the reaction $VO + Fe_2O_3 \rightarrow FeO + V_2O_5$ the eq. wt. of V_2O_5 is equal to its

(a) mol. wt. (b) mol. wt./8

(c) mol. wt./6 (d) none of these

37. The eq. wt. of K_2CrO_4 as an oxidising agent in acid medium is

(a) mol. wt./2 (b) $\frac{2 \times \text{mol. wt.}}{3}$

(c) $\frac{\text{mol. wt.}}{3}$ (d) $\frac{\text{mol. wt.}}{6}$

38. In the conversion $NH_2OH \rightarrow N_2O$, the equivalent weight of NH_2OH will be :

(a)M/4 (b)M/2

(c)M/5 (d)M/1

(M = molecular weight of NH_2OH)

39. 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

40. M is molecular weight of $KMnO_4$. The equivalent weight of $KMnO_4$ when it is converted into K_2MnO_4 is :

(a) M (b) M/3

(c) M/5 (d) M/7

41. The equivalent mass of oxidising agent in the following reaction is

$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$

(a) 32 (b) 64

(c) 16 (d) 8

42. In the following reaction :

$$NO_3^{\ominus} + As_2S_3 + H_2O \longrightarrow AsO_4^{3-} + NO + SO_4^{2-} + H^{\oplus}$$

the equivalent weight of As_2S_3 (with molecular weight M) is:

(a) $\frac{3M}{28}$ (b) $\frac{M}{4}$

(c) $\frac{M}{24}$ (d) $\frac{M}{28}$

43. Equivalent weight of H_3PO_2 (molecular weight = M) when it disproportionates into PH_3 and H_3PO_3 is

(a) M (b) $\frac{M}{2}$

(c) $\frac{M}{4}$ (d) $\frac{3M}{4}$

44. Equivalent weight of $MnO_4^{\ominus}$ in acidic, neutral and basic media are in ratio of :

(a) 3 : 5 : 15 (b) 5 : 3 : 1

(c) 5 : 1 : 13 (d) 3 : 15 : 5

45. K_2CrO_4 oxidises KI in the presence of HCl to I_2. The equivalent weight of the K_2CrO_4 is

(a) $\frac{Mw}{2}$ (b) $Mw \times \frac{2}{3}$

(c) $\frac{Mw}{3}$ (d) $\frac{Mw}{6}$

46. The equivalent weight of $MnSO_4$ is half its molecular weight when it is converted to

(a) Mn_2O_3 (b) MnO_2

(c) $MnO_4^{\ominus}$ (d) MnO_4^{2-}

Redox Titrations

47. If equal volumes of 0.1 M $KMnO_4$ and 0.1 M $K_2Cr_2O_7$ solutions are allowed to oxidise Fe^{2+} to Fe^{3+} in acidic medium, then Fe^{2+} will be oxidised :

(a) More by $KMnO_4$ (b) More by $K_2Cr_2O_7$

(c) Equal in both cases (d) Cannot be determined.

48. Volume V_1 mL of 0.1M $K_2Cr_2O_7$ 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) 2/5 V_1 (b) 5/2 V_1

(c) 113 V_1 (d) Can not be determined

49. 80 mL of $KMnO_4$ solution reacts with 3.4 g of $Na_2C_2O_4.2H_2O$ in acidic medium. The molarity of the $KMnO_4$ solution is

(a) 0.5 M (b) 0.1 M

(c) 5 M (d) 1 M

50. What weight of $NaHSO_3$ is required to react with 100 mL of solution containing 0.33 g of $NaIO_3$ according to the following reaction

$$IO_3^{\ominus} + HSO_3^{\ominus} \longrightarrow I^{\ominus} + SO_4^{2-}$$

(a) 0.52 g (b) 5.2 g

(c) 1.04 g (d) 10.4 g

51. What volume of 0.05 M $K_2Cr_2O_7$ in acidic medium is needed for complete oxidation of 200 mL of 0.6 M FeC_2O_4 solution?

(a) 1.2 mL (b) 1.2 L

(c) 120 mL (d) 800 mL

52. KI reacts with H_2SO_4 producing I_2 and H_2S. The volume of 0.2 M H_2SO_4 required to produce 0.1 mol of H_2S is

(a) 4 L (b) 2.5 L

(c) 3.8 L (d) 5 L

Volume Strength of Hydrogen Peroxide

53. 34 g of H_2O_2 is present in 1120 mL of solution. This solution is called

(a) 10 vol solution (b) 20 vol solution

(c) 34 vol solution (d) 32 vol solution

54. A 5.0 mL solution of H_2O_2 liberates 1.27 g of iodine from an acidified KI solution. The percentage strength of H_2O_2 is

(a) 11.2 (b) 5.6

(c) 1.7 (d) 3.4

55. The volume strength of 1.5 N H_2O_2 solution is

(a) 4.8 (b) 8.4

(c) 3.0 (d) 8.0

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTIONS

1. MnO_4^- is a good oxidising agent in different medium changing to

$$MnO_4^- \longrightarrow \begin{cases} Mn^{2+} \\ MnO_4^{2-} \\ MnO_2 \\ Mn_2O_3 \end{cases}$$

Changes in oxidation number respectively, are **(2002)**

(a) 1, 3, 4, 5 (b) 5, 4, 3, 2

(c) 5, 1, 3, 4 (d) 2, 6, 4, 3

2. Oxidation number of Cl in $CaOCl_2$ (bleaching powder) is **(2002)**

(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^-

3. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is **(2005)**

(a) +3 (b) +2

(c) +6 (d) +4

4. The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is **(2005)**

(a) 0 (b) +1

(c) +2 (d) +3

5. Which of the following chemical reactions depicts the oxidising behaviour of H_2SO_4? **(2006)**

(a) $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$

(b) $Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$

(c) $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

(d) $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

6. Consider the following reaction,

$$xMnO_4^- + yC_2O_4^{2-} + zH^+ \rightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2}H_2O$$

The values of x, y and z in the reaction are, respectively **(2013)**

(a) 5, 2 and 16 (b) 2, 5 and 8

(c) 2, 5 and 16 (d) 5, 2 and 8

7. Given, $E^o_{Cr^{3+}/Cr} = -0.74$ V; $E^o_{MnO_4^-/Mn^{2+}} = 1.51$V

$E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V; $E^o_{Cl/Cl^-} = 1.36$V

Based on the data given above strongest oxidising agent will be **(2013)**

(a) Cl (b) Cr^{3+}

(c) Mn^{2+} (d) MnO_4^-

8. Consider the reaction :

$$H_2SO_{3(aq)} + Sn^{4+}_{(aq)} + H_2O_{(\ell)} \rightarrow Sn^{2+}_{(aq)} + HSO^-_{4(aq)} + 3H^+_{(aq)}$$

Which of the following statements is correct? **(Online 2014 SET-4)**

(a) H_2SO_3 is the reducing agent because it undergoes recuction

(b) Sn^{4+} is the reducing agent because it undergoes oxidation

(c) H_2SO_3 is the reducing agent because it undergoes oxidation

(d) Sn^{4+} is the oxidizing agent because it undergoes oxidation

9. How many electrons are involved in the following redox reaction ?

$$Cr_2O_7^{2-} + Fe^{2+} + C_2O_4^{2-} \rightarrow Cr^3 + Fe^{3+} + CO_2$$

(Unbalanced) **(Online 2014 SET-4)**

(a) 3 (b)4

(c) 5 (d) 6

10. What is the oxidation number of sulphur in $Na_2S_4O_6$? **(Online 2016 SET-1)**

(a) 2/3 (b) 3/2

(c) 3/5 (d) 5/2

11. The value of n in

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

(Online 2017 SET-1)

(a) 5 (b) 4

(c) 2 (d) 3

12. Which of the following reactions is an example of a redox reaction ? **(2017)**

(a) $XeF_2 + PF_5 \rightarrow [XeF]^+ PF_6^-$

(b) $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

(c) $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

(d) $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

13. In KO_2, the nature of oxygen species and the oxidation state of oxygen atom are, respectively : **(Online 2018 SET-2)**

(a) Oxide and -2

(b) Superoxide and $-\frac{1}{2}$

(c) Peroxide and

(d) Superoxide and -1

14. The chemical nature of hydrogen peroxide is: **(10-01-2019 Shift - 1)**

(a) Oxidising agent in acidic medium, but not in basic medium.

(b) Reducing agent in basic medium, but not in acidic medium.

(c) Oxidising and reducing agent in acidic medium, but not in basic medium

(d) Oxidising and reducing agent in both acidic and basic medium.

15. In the reaction of oxalate with permanganate in acidic medium, the number of electrons involved in producing one molecule of CO_2 is **(10-01-2019 Shift - 2)**

(a) 1 (b) 10

(c) 2 (d) 5

16. An example of a disproportionation reaction is: **(12-04-2019 Shift - 1)**

(a) $2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

(b) $2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$

(c) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

(d) $2CuBr \rightarrow CuBr_2 + Cu$

17. The oxidation states of nitrogen in NO, NO_2, N_2O and NO_3^- are in the order of : **(18-03-2021 Shift - 2)**

(a) $NO_3^- > NO_2 > NO > N_2O$

(b) $N_2O > NO_2 > NO > NO_3^-$

(c) $NO > NO_2 > N_2O > NO_3^-$

(d) $NO_2 > NO_3^- > NO > N_2O$

18. The species given below that does NOT show disproportionation reaction is : **(20-07-2021 Shift - 1)**

(a) BrO_4^- (b) BrO^-

(c) BrO_2^- (d) BrO_3^-

19. The correct order of following 3d metal oxides, according to their oxidation number is : **(25-07-2021 Shift - 1)**

(A) CrO_3 (B) Fe_2O_3 (C) MnO_2 (D) V_2O_5 (E) Cu_2O

(a) (D) > (A) > (B) > (C) > (E)

(b) (A) > (C) > (D) > (B) > (E)

(c) (A) > (D) > (C) > (B) > (E)

(d) (C) > (A) > (D) > (E) > (B)

20. Identify the process in which change in the oxidation state is five : **(25-07-2021 Shift - 2)**

(a) $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$ (b) $MnO_4^- \rightarrow Mn^{2+}$

(c) $CrO_4^{2-} \rightarrow Cr^{3+}$ (d) $C_2O_4^{2-} \rightarrow 2CO_2$

21. The oxidation states of 'P' in $H_4P_2O_7$, $H_4P_2O_5$ and $H_4P_2O_6$ respectively, are : **(10-01-2019 Shift - 2)**

(a) 7, 5 and 6 (b) 5, 4 and 3

(c) 5, 3 and 4 (d) 6, 4 and 5

22. In which one of the following sets all species show disproportionation reaction? **(31-08-2021 Shift - 2)**

(a) ClO_2^-, F_2, MnO_4^- and $Cr_2O_7^{2-}$

(b) $Cr_2O_7^{2-}, MnO_4^-, ClO_2^-$ and Cl_2

(c) MnO_2, ClO_2^-, Cl_2 and Mn^{3+}

(d) $ClO_4^-, MnO_4^-, ClO_2^-$ and F_2

23. The exact volumes of 1 M NaOH solution required to neutralise 50 mL of 1 M H_3PO_3 solution and 100 mL of 2 M H_3PO_2 solution, respectively, are : **(16-03-2021 Shift - 2)**

(a) 100 mL and 100 mL (b) 100 mL and 50 mL

(c) 100 mL and 200 mL (d) 50 mL and 50 mL

Numerical Value Type Questions

24. The reaction of sulphur in alkaline medium is given below :

$$S_{8(s)} + aOH^-_{aq} \rightarrow bS^{2-}_{(aq)} + cS^{2-}_{(aq)} + cS_2O^-_{3(aq)} + dH_2O_{(l)}$$

The values of 'a' is ________. (Integer answer)

(24-02-2021 Shift-1)

25. In basic medium CrO_4^{2-} oxidises $S_2O_3^{2-}$ to form SO_4^{2-} and itself changes into $Cr(OH)_4$. The volume of 0.154 M CrO_4^{2-} required to react with 40 mL of 0.25 M $S_2O_3^{2-}$ is _____ mL. (Rounded-off to the nearest integer) **(25-02-2021 Shift-1)**

26. 0.4 g mixture of NaOH, Na_2CO_3 and some inert impurities was first titrated with $\frac{N}{10}HCl$ using phenolphthalein as an indicator, 17.5 mL of HCl was required at the end point. After this methyl orange was added and titrated. 1.5 mL of same HCl was required for the next end point.The weight percentage of Na_2CO_3 in the mixture is _______. (Rounded-off to the nearest integer) **(25-02-2021 Shift-1)**

27. Consider titration of NaOH solution versus 1.25 M oxalic acid solution. At the end point following burette readings were obtained.

(i) 4.5 mL (ii) 4.5 mL

(iii) 4.4 mL (iv) 4.4 mL (v) 4.4 mL

If the volume of oxalic acid taken was 10.0 mL then the molarity of the NaOH solution is _______ M. (Rounded-off the nearest integer) **(25-02-2021 Shift - 1)**

28. Consider the following reaction

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O, E^\circ = 1.51V$$

The quantity of electricity required in Faraday to reduce five moles of MnO_4^- is _____ . **(26-02-2021 Shift - 1)**

29. Dichromate ion is treated with base, the oxidation number of Cr in the product formed is **(26-02-2021 Shift - 1)**

30. $2MnO_4^- + bC_2O_4^{2-} + cH^+ \rightarrow xMn^{2+} + yCO_2 + zH_2O$

If the above equation is balanced with integer coefficients, the value of c is ________. (Round off to the Nearest Integer) **(16-03-2021 Shift-1)**

31. 15 mL of aqueous solution of Fe^{2+} in acidic medium completely reacted with 20 mL of 0.03 M aqueous $Cr_2O_7^{2-}$.

The molarity of the Fe^{2+} solution is .... × 10^{-2} M. (Round off to the Nearest Integer) **(17-03-2021 Shift-1)**

32. 10.0 mL of Na_2CO_3 solution is titrated 0.2 M HCl solution. The following titre values wer obtained in 5 readings : 4.8 mL, 4.9 mL, 5.0 mL, 5.0 mL and 5.0 mL.

Based on these readings, and convention of titrimetric estimation the concentration of Na_2CO_3 solution is .... mM. (Round off to the Nearest Integer). **(18-03-2021 Shift - 2)**

33. When 10 mL of an aqueous solution of Fe^{2+} ion was titrated in the presence of dil. H_2SO_4 using diphenylamine indicator, 15 mL of 0.02 M solution of $K_2Cr_2O_7$ was required to get the end point. The molarity of the solution containing Fe^{2+} ions is x × 10^{-2} M. The value of x is _________. (Nearest Integer) **(25-07-2021 Shift - 1)**

34. 10.0 mL of 0.05 M $KMnO_4$ solution was consumd in a titration with 10.0 mL of given oxalic acid dihydrate solution. The strength of given oxalic acid solution is ...... × 10^{-2} g/L. (Round off to the narest integer) **(25-07-2021 Shift - 1)**

35. When 10 mL of an aqueous solution of $KMnO_4$ was titrated in acidic medium, equal volume of 0.1 M of an aqueous solution of ferrous sulphate was required for complete discharge of colour. The strength of $KMnO_4$ in grams per litre is _______ × 10^{-2}. (Nearest integer)

[Atomic mass of K = 39, Mn = 55, O = 16]

(27-08-2021 Shift - 1)

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

Objective Questions I [Only One Correct Option]

1. In the reaction, $2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$

(a) $FeCl_3$ acts as an oxidizing agent

(b) Both H_2S and $FeCl_3$ are oxidized

(c) $FeCl_3$ is oxidised while H_2S is reduced

(d) H_2S acts as an oxidizing agent

2. When $KMnO_4$ reacts with acidified $FeSO_4$

(a) Only $FeSO_4$ is oxidised

(b) Only $KMnO_4$ is oxidised

(c) $FeSO_4$ is oxidised and $KMnO_4$ is reduced

(d) None of the above

3. The oxidation number of cobalt in $K_3[Co(NO_2)_6]$ is

(a) 0
(b) +4

(c) +3
(d) +6

4. For the redox reaction,

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

the correct coefficients of the reactions for the balanced reaction are respectively MnO_4^-, $C_2O_4^-$, H^+ :

(a) 2, 5, 16
(b) 16, 3, 12

(c) 15, 16, 12
(d) 2, 16, 5

5. In the reaction between SO_2 and O_3, the equivalent weight of ozone is :

(a) The same as its molecular weight

(b) Half the molecular weight

(c) One – third of the molecular weight

(d) One – fourth of the molecular weight

6. In the reaction, $8Al + 3Fe_3O_4 \rightarrow 4Al_2O_3 + 9Fe$, the number of electrons transferred from reductant to oxidant is:

(a) 8
(b) 4

(c) 7
(d) 24

7. If $Sn^{2+} + 2e^- \rightarrow Sn; \quad E^o = -0.14\,V$

$Sn^{4+} + 2e^- \rightarrow Sn^{2+}; \quad E^o = +0.13\,V$ then:

(a) Sn^{2+} will disproportionates to Sn^{4+} and Sn

(b) Sn^{2+} is stable and it will not disproportionate

(c) Sn^{4+} is easily reduced to Sn

(d) none of the above

8. A bottle of H_2O_2 is labelled as 10 vol H_2O_2. 112 mL of this solution of H_2O_2 is titrated against 0.04 M acidified solution of $KMnO_4$. The volume of $KMnO_4$ in litre is

(a) 1 L
(b) 2 L

(c) 3 L
(d) 4 L

9. Which of the following is a redox reaction?

(a) H_2SO_4 with NaOH

(b) In atmosphere, O_3 from O_2 by lightning

(c) Nitrogen oxides from nitrogen and oxygen by lightning

(d) Evaporation of H_2O

10. Phosphorus has the oxidation state of + 3 in

(a) Phosphorous acid

(b) Orthophosphoric

(c) Hypophosphorous acid

(d) Metaphosphoric acid

11. In a chemical reaction

$$K_2Cr_2O_7 + xH_2SO_4 + ySO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + zH_2O;$$

the value of x, y and z respectively are:

(a) $x = 1, y = 3, z = 1$
(b) $x = 4, y = 1, z = 4$

(c) $x = 3, y = 2, z = 1$
(d) $x = 2, y = 2, z = 1$

12. 1 mole of equimolar mixture of ferric oxalate and ferrous oxalate will require x mole of $KMnO_4$ in acidic medium for complete oxidation, x is:

(a) 0.5 mole
(b) 0.9 mole

(c) 1.2 mole
(d) 4.5 mole

13. 20 mL of 0.2 M NaOH (aq) solution is mixed with 35 mL of 0.1 M NaOH (aq) solution and the resultant solution is diluted to 100 mL. 40 mL of this diluted solution reacted with 10% impure sample of oxalic acid ($H_2C_2O_4$). The weight of impure sample is:

(a) 0.15 gram
(b) 0.135 gram

(c) 0.59 gram
(d) None of these

14. 32 g of a sample of $FeSO_4.7H_2O$ were dissolved in dilute sulphuric acid and water and its volume was made up to 1 litre, 25 mL of this solution required 20 mL of 0.02 M $KMnO_4$ solution for complete oxidation. Calculate the weight % of $FeSO_4.7H_2O$ in the sample.

(a) 34.75
(b) 69.5

(c) 89.5
(d) None of these

15. 125 mL of 63% (w/v) $H_2C_2O_4 \cdot 2H_2O$ solution is made to react with 125 mL of a 40% (w/v) NaOH solution. The resulting solution is : (ignoring hydrolysis of ions)

(a) Neutral (b) Acidic

(c) Strongly acidic (d) Alkaline

16. An element A in a compound ABD has oxidation number –n. It is oxidised by $Cr_2O_7^{2-}$ in acidic medium. In the experiment, 1.68×10^{-3} moles of $K_2Cr_2O_7$ were used for 3.36×10^{-3} moles of ABD. The new oxidation number of A after oxidation is :

(a) 3 (b) 3 – n

(c) n –3 (d) + n

17. Which of the following solutions will exactly oxidize 25 mL of an acid solution of 0.1 M iron (II) oxalate :

(a) 10 mL of 0.25 M $KMnO_4$

(b) 25 mL of 0.2 M $KMnO_4$

(c) 25 mL of 0.6 M $KMnO_4$

(d) 15 mL of 0.1 M $KMnO_4$

18. In the reaction of sodium thiosulphate with I_2 in aqueous medium the equivalent weight of sodium thiosulphate is equal to:

(a) molar mass of sodium thiosulphate

(b) the average molar masses of $Na_2S_2O_3$ and I_2

(c) half the molar masss of sodium thiosulphate

(d) twice of molar mass of sodium thiosulphate

19. Based on the following information arrange four metals A, B, C and D in order of decreasing ability to act as reducing agents:

(I) Only A, B and C react with 1 M HCl to give H_2 (g)

(II) When C is added to solutions of the other metal ions, metallic B and D are formed

(III) Metal C does not reduce A^{n+}.

(a) C > A > B > D (b) C > A > D > B

(c) A > C > D > B (d) A > C > B > D

20. A mixture of FeO and Fe_2O_3 is completely reacted with 100 mL of 0.25 M acidified $KMnO_4$ solution. The resultant solution was then titrated with Zn dust which converted Fe^{3+} of the solution of Fe^{2+}. The Fe^{2+} required 1000 mL of 0.10 M $K_2Cr_2O_7$ solution. Find out the weight % Fe_2O_3 in the mixture.

(a) 80.85 (b) 19.15

(c) 50 (d) 89.41

Objective Questions II

[One or more than one correct option]

21. Which of the following can act both as an oxidising as well as reducing agent :

(a) HNO_2 (b) H_2O_2

(c) H_2S (d) SO_2

22. In an electrochemical cell, a salt bridge is used:

(a) to avoid mechanical contact of electrolyte solution in cathodic and anodic half-cell

(b) to maintain electrical neutrality in the cell

(c) to avoid liquid junction potential

(d) to mix the solution of anodic and cathodic half-cell

23. Which of the following reactions do not involve oxidation or reduction:

(a) $2\,Rb + 2H_2O \longrightarrow 2\,RbOH + H_2$

(b) $2CuI_2 \longrightarrow 2\,CuI + I_2$

(c) $NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2\,O$

(d) $4\,KCN + Fe(CN)_2 \longrightarrow K_4[Fe(CN)_6]$

24. When Cl_2 reacts with aqeous NaOH in cold condition then oxidation number of chlorine changes from 0 to:

(a) -1 (b) +1

(c) -2 (d) +2

25. In the reaction

$$I_2 + C_2H_5OH + \bar{O}H \rightarrow CHI_3 + HCOO^- + H_2O + I^-$$

which of the following statements is/are correct?

(a) The coefficients of $\bar{O}H$ and I^- in the given in balanced equation are, respectively, 6 and 5.

(b) The coefficients of $\bar{O}H$ and I^- in the given balanced equation are, respectively, 5 and 6.

(c) C_2H_5OH is oxidised to CHI_3 and $HCOO^-$

(d) The number of electrons in the conversion of C_2H_5OH to CHI_3 and $HCOO^-$ is 8.

26. When a equimolar mixture of Cu_2S and CuS is titrated with $Ba(MnO_4)_2$ in acidic medium, the final product's contains Cu^{2+}, SO_2 and Mn^{2+}. If the mol. wt. of Cu_2S, CuS and $Ba(MnO_4)_2$ are M_1, M_2 and M_3 respectively then:

(a) eq. wt. of Cu_2S is $\frac{M_1}{8}$

(b) eq. wt. of CuS is $\frac{M_2}{6}$

(c) eq. wt. of $Ba(MnO_4)_2$ is $\frac{M_3}{5}$

(d) Cu_2S and CuS both have same equivalents in mixture

27. Identify the correct statements with reference to the given reaction, $P_4 + 3OH^- + H_2O \rightarrow PH_3 + 3H_2PO_2^-$

(a) Phosphorus is undergoing reduction only

(b) Phosphorus is undergoing oxidation only

(c) Phosphorus is undergoing oxidation as well as reduction.

(d) Hydrogen is undergoing neither oxidation nor reduction

28. 25 mL of 0.5 M H_2O_2 solution is added to 50 mL of 0.2 M $KMnO_4$ in acid solution. Which of the following statements is false :

(a) 0.010 mole of oxygen gas is liberated.

(b) 0.005 mole of $KMnO_4$ is left.

(c) 0.030 g of oxygen gas is evolved.

(d) 0.0025 mole H_2O_2 does not react with $KMnO_4$.

29. In the following reaction : $Cr(OH)_3 + OH^- + IO_3^- \rightarrow CrO_4^{2-} + H_2O + I^-$

(a) IO_3^- is oxidising agent

(b) $Cr(OH)_3$ is oxidised

(c) $6e^-$ are being taken per iodine atom

(d) None of these

30. 500 mL of a 0.05 M Mohr salt solution required the same volume of permanganate solution for complete oxidation. Which of the followings is (are) true regarding the above redox reaction?

(a) The molarity of $KMnO_4$ must be 0.01 M if the medium is acidic

(b) The molarity of $KMnO_4$ must be 1 M if the medium is basic.

(c) The medium has no role to play in redox reaction.

(d) In the above reaction Fe(II) is oxidized to Fe(III) irrespective of medium.

31. Given that, $E^\circ_{Ni^{2+}/Ni} = -0.25V, E^\circ_{Cu^{2+}/Cu} = +0.34V$

$E^\circ_{Ag^{2+}/Ag} = +0.80\,V,\ E^\circ_{Zn^{2+}/Zn} = -0.76\ V$

Which of the following redox processes will not take place in specified direction?

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

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

(c) $Cu(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$

(d) $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

Numerical Value Type Questions

32. In the reaction : $Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow Na_2SO_4 + H_2SO_4 + 8HCl$, the equivalent weight of $Na_2S_2O_3$ will be : (M = molecular weight of $Na_2S_2O_3$)

33. It requires 40 mL of 1 M Ce^{4+} to titrate 20 mL of 1M Sn^{2+} to Sn^{4+}. What is the oxidation state of the Cerium in the product?

34. Oxidation number of chlorine in $NOClO_4$ is ....

35. In the redox reaction,

$xNO_3^- + y\ As_2S_3 + zH_2O \rightarrow AsO_4^{3-} + NO + SO_4^{2-} + H^+$

What is the value of $\frac{x}{z}$?

36. A volume of 12.5 mL of 0.05 M SeO_2 reacts with 25mL of 0.1M $CrSO_4$ which is oxidised to Cr^{3+}. To what oxidation state was the selenium converted by the reaction?

37. 20 mL of H_2O_2 after acidification with dilute H_2SO_4 required 30 mL of N/12 $KMnO_4$ for complete oxidation. The strength of H_2O_2 solution is in g/L : [Molar mass of H_2O_2 = 34]

38. A sample of 28 mL of H_2O_2 (aq) solution required 10 mL of 0.1 $KMnO_4$ (aq) solution for complete reaction in acidic medium. What is the volume strength of H_2O_2?

Assertion Reason

(A) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

(B) If both Assertion and Reason are true but Reason is not the correct explanation of Assertion.

(C) If Assertion is true but Reason is false.

(D) If Assertion is false but Reason is true.

39. **Assertion (A) :** KO_2 is superoxide.

Reason (R) : Oxidation state of oxygen of KO_2 is – 2.

(a) A (b) B

(c) C (d) D

40. **Assertion (A) :** MnO_2 can act as an oxidizing agent as well as reducing agent.

Reason (R) : Oxidation state of Mn lies between highest and lowest oxidation state.

(a) A (b) B

(c) C (d) D

41. **Assertion (A) :** F_2 does not undergo disproportionation reactions.

Reason (R) : Fluorine shows only 0 and – 1 oxidation states.

(a) A (b) B

(c) C (d) D

42. **Assertion (A) :** White phosphorous reacts with aqueous caustic soda to form PH_3 and NaH_2PO_2 . It is disproportionation reaction.

Reason (R) : In the reaction of disproportionation, same substance is oxidised as well as reduced simultaneously.

(a) A (b) B

(c) C (d) D

43. **Assertion (A) :** If 1.50 mol of $KMnO_4$ is required for oxidation in acidic medium, 2.50 mol of $KMnO_4$ would be required for same oxidation but in basic medium.

Reason (R) : In acidic medium, oxidation state of Mn changes from +7 to +2, while is basic medium , it changes from +7 to +4.

(a) A (b) B

(c) C (d) D

Match the following

Each questions has two columns. Four options are given representing matching elements from Column-I and Column-II. Only one of these four options corresponds to a correct matching, for each question.

44.

Column - I **(Redox reaction)**	**Column - II** **(molar ratio of reducing to oxidising agent)**
(A) $ClO^- + Fe(OH)_2 \rightarrow Cl^- + Fe(OH)_3$	(p) 3 : 2
(B) $Cr_2O_7^{2-} + FeC_2O_4 \rightarrow Cr^{3+} + CO_2 + Fe^{3+}$	(q) 2 : 1
(C) $H_2O_2 + Cr(OH)_3 \rightarrow CrO_4^{2-} + H_2O$	(r) 1 : 3
(D) $N_2H_4 + Cu(OH)_2 \rightarrow N_2O + Cu$	(s) 2 : 3
(E) $MnO_4^- + C_2O_4^{2-} \rightarrow MnO_2 + CO_2$	

45. Match the reaction in column 1 with the coefficients x and y given in column II.

Column - I **(Reaction)**	**Column - II** **(The coefficients of x and y are)**
(A) $xCu + yHNO_3 \rightarrow Cu(NO_3)_2 + NO + NO_2 + H_2O$	(p) 2 and 6
(B) $xKI + yBaCrO_4 \xrightarrow{H^{\oplus}} I_2 + CrCl_3$	(q) 6 and 2
(C) $xAs_2S_3 + yNO_3^- \rightarrow AsO_4^{3-} + NO + SO_4^{2-}$	(r) 3 and 28
(D) $4P + 3OH^- + 3H_2O \rightarrow xPH_3 + yH_2PO_2$	(s) 1 and 3
(E) $xKI + yH_2SO_4 \rightarrow I_2 + H_2S + K_2SO_4$	(t) 8 and 5

46.

Column - I	**Column - II**
(A) $\text{Eq. wt.} = \dfrac{\text{Molecular weight}}{33}$	(p) When CrI_3 oxidises into $Cr_2O_7^{2-}$ and IO_4^-
(B) $\text{Eq. wt.} = \dfrac{\text{Molecular weight}}{27}$	(q) When $Fe(SCN)_2$ oxidises into Fe^{3+}, SO_4^{2-}, CO_3^{2-}, and NO_3^-
(C) $\text{Eq. wt.} = \dfrac{\text{Molecular weight}}{28}$	**(r)** When NH_4SCN oxidizes into SO_4^{2-}, CO_3^{2-} and NO_3^-
(D) $\text{Eq. wt.} = \dfrac{\text{Molecular weight}}{24}$	**(s)** When As_2S_3 oxidises into AsO_3^- and SO_4^{2-}

47.

Column - I	**Column - II**
(A) $\underline{P_2H_4} \rightarrow PH_3 + P_4H_2$	(p) $E = \dfrac{3M}{4}$
(B) $\underline{I_2} \rightarrow I^- + IO_3^-$	(q) $E = \dfrac{3M}{5}$
(C) $MnO_4^- + Mn^{2+} + H_2O \rightarrow \underline{Mn_3O_4} + H^+$	(r) $E = \dfrac{15M}{26}$
(D) $\underline{H_3PO_2} \rightarrow PH_3 + H_3PO_3$	(s) $E = \dfrac{5M}{6}$

Paragraph type questions

Use the following passage, solve Q.48 to Q.50

Passage

The valency of carbon is generally 4, but its oxidation state may be -4, -2, 0, 2, -1 etc. In the compounds containing C, H and O, the oxidation number of C is calculated as

$$\text{Oxidation number of C} = \frac{2n_O - n_H}{n_C}$$

where n_O, n_H, n_C are the number of oxygen, hydrogen, and carbon atoms, respectively.

48. In which of the following compounds is the oxidation state of C a fraction?

(a) CO
(b) CO_2
(c) Carbon suboxide
(d) All

49. In which of the following compounds the oxidation state of C is 2?

(a) Ketenes
(b) Alkenes
(c) Allenes
(d) Carbenes

50. In which of the following compounds is the oxidation state of C highest?

(a) HCOOH
(b) HCHO
(c) CH_3OH
(d) CH_4

Use the following passage, solve Q.51 to Q.53

Passage

$$\textbf{Equivalent weight} = \frac{\text{Molecular weight / Atomic weight}}{\text{n} - \text{factor}}$$

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 reciprocal 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 : $KMnO_4\ (n = 5) \rightarrow Mn^{2+}$
2. In neutral medium : $KMnO_4\ (n = 3) \rightarrow Mn^{2+}$
3. In basic medium : $KMnO_4\ (n = 1) \rightarrow Mn^{6+}$

Example 2

$$FeC_2O_4 \rightarrow Fe^{3+} + 2CO_2$$

Total no. of moles of e^- lost by 1 mole of FeC_2O_4

$= 1 + 1 \times 2 \Rightarrow 3$

$\therefore$ n-factor of $FeC_2O_4 = 3$

51. n-factor of $Ba(MnO_4)_2$ in acidic medium is

(a) 2
(b) 6
(c) 10
(d) None of these

52. For the reaction,

$$H_3PO_2 + NaOH \rightarrow NaH_2PO_2 + H_2O$$

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

53. For the reaction, $Fe_{0.95}O$ (molar mass: M) $\rightarrow Fe_2O_3$. 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

Use the following passage, solve Q.54 to Q.55

Passage

The next two questions deal with an experiment. An unknown metal 'X' is found to react spontaneously with 1.0M solution of $CuSO_4$ plating out Cu(s). X does not react with a solution of 1.0M $Zn(NO_3)_2$. The half-reactions for these metals are:

$$X^{2+}(aq) + 2e^- \longrightarrow X(s)$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu$$

$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn$$

54. What is the correct order for listing the metals according to decreasing strength as reducing agent ?

(a) X, Cu, Zn
(b) Cu, Zn, X
(c) Cu, X, Zn
(d) Zn, X, Cu

55. Another metal Y displaces Cu^{2+} from its aqueous solution but can't displace Zn^{2+} from its aqueous solution. Which of the following statements regarding X and Y is correct?

(a) X is stronger reducing agent than Y
(b) X is weaker reducing agent than Y
(c) Both X and Y are weaker reducing agents than Cu
(d) X can be either stronger or weaker reducing agent than Y.

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTIONS

Objective Questions I [Only one correct option]

1. The equivalent weight of $MnSO_4$ is half of its molecular weight when it converts to **(1988)**

(a) Mn_2O_3 (b) MnO_2

(c) MnO_4^- (d) MnO_4^{2-}

2. The volume strength of 1.5 N H_2O_2 is **(1990)**

(a) 4.8 (b) 8.4

(c) 3.0 (d) 8.0

3. 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

(1992)

MnO_4^-	$C_2O_4^{2-}$	H^+
(a) 2	5	16
(b) 16	5	2
(c) 5	16	2
(d) 2	16	5

4. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution **(1997)**

(a) $\frac{2}{5}$ (b) $\frac{3}{5}$

(c) $\frac{4}{5}$ (d) 1

5. The number of moles of $KMnO_4$ that will be needed to react completely with one mole of ferrous oxalate in acidic medium is **(1997)**

(a) $\frac{2}{5}$ (b) $\frac{3}{5}$

(c) $\frac{4}{5}$ (d) 1

6. The normality of 0.3 M phosphorus acid (H_3PO_3) is **(1999)**

(a) 0.1 (b) 0.9

(c) 0.3 (d) 0.6

7. The oxidation number of sulphur in S_8, S_2F_2, H_2S respectively, are **(1999)**

(a) 0, +1 and -2 (b) +2, +1 and -2

(c) 0, +1 and +2 (d) -2, +1 and -2

8. Among the following, the species in which the oxidation number of an element is +6 **(2000)**

(a) MnO_4^- (b) $Cr(CN)_6^{3-}$

(c) NiF_6^{2-} (d) CrO_2Cl_2

9. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralize 10 mL of this solution is **(2000)**

(a) 40 mL (b) 20 mL

(c) 10 mL (d) 4 mL

10. The reaction, $3ClO(aq)^- \longrightarrow ClO_3(aq)^- + 2Cl(aq)^-$ is an example of **(2001)**

(a) oxidation reaction

(b) reduction reaction

(c) disproportionate reaction

(d) decomposition reaction

11. In the standardization of $Na_2S_2O_3$ and $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is **(2000)**

(a) (molecular weight)/2

(b) (molecular weight)/6

(c) (molecular weight)/3

(d) same as molecular weight

12. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is **(2007)**

(a) 3 (b) 4

(c) 5 (d) 6

13. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen ? **(2012)**

(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

14. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type; the oxidation states of phosphorus in phosphine and the other product are respectively (2013)

(a) redox reaction; –3 and – 5

(b) redox reaction; 3 and + 5

(c) disproportionation reaction; –3 and +5

(d) disproportionation reaction; –3 and + 3

15. For the reaction : (2016)

$$I^- + ClO_3^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2$$

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.

16. The order of the oxidation state of the phosphorus atom in $H_3PO_2, H_3PO_4, H_3PO_3,$ and $H_4P_2O_6$ is (2017)

(a) $H_3PO_3 > H_3PO_2 > H_3PO_4 > H_4P_2O_6$

(b) $H_3PO_4 > H_3PO_2 > H_3PO_3 > H_4P_2O_6$

(c) $H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$

(d) $H_3PO_2 > H_3PO_3 > H_4P_2O_6 > H_3PO_4$

Assertion Reason

(a) Assertion is true; Reason is true; Reason is the correct explanation of Assertion.

(b) Assertion is true; Reason is true; Reason is not the correct explanation of Assertion.

(c) Assertion is true; Reason is false.

(d) Assertion is false; Reason is true.

17. **Assertion (A):** In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume required at the equivalence point is twice that of the acid required using phenolphthalein indicator.

Reason(R) : Two moles of HCl are required for the complete neutralization of one mole of Na_2CO_3. (1991)

(a) A (b) B

(c) C (d) D

Fill in the Blank

18. The compound $YBa_2Cu_3O_7$, which shows super conductivity, has copper in oxidation state................. Assume that the rare earth element yttrium is in its usual +3 oxidation state. (1994)

Numerical Value Type Questions

19. A student performs a titration with different burettes and finds titre values of 25.2 mL, 25.25 mL, and 25.0 mL. number of significant figures in the average titre value is (2010)

20. Among the following, the number of elements showing only one non-zero oxidation state is O, Cl, F, N, P, Sn, Tl, Na, Ti (2010)

21. The difference in the oxidation numbers of the two types of sulphur atoms in $Na_2S_4O_6$ is (2011)

Subjective Type Questions

22. The density of a 3 M sodium thiosulphate solution ($Na_2S_2O_3$) is 1.25 g per mL. Calculate (i) the percentage by weight of sodium thiosulphate (ii) the mole fraction of sodium thiosulphate and (iii) the molalities of Na^+ and $S_2O_3^{2-}$ ions. (1983)

23. 4.08 g of a mixture of BaO and unknown carbonate MCO_3 was heated strongly. The residue weighed 3.64 g. This was dissolved in 100 mL of 1 N HCl. The excess acid required 16 mL of 2.5 N NaOH solution for complete neutralization. Identify the metal M. (1983)

24. 2.68×10^{-3} moles of a solution containing an ion A^{n+} require 1.61×10^{-3} moles of MnO_4^- for the oxidation of A^{n+} to AO_3^- in acidic medium. What is the value of n? (1984)

25. A sample of hydrazine sulphate ($N_2H_6SO_4$) was dissolved in 100 mL of water, 10 mL of this solution was reacted with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ion formed was estimated and it, required 20 mL of M/50 potassium permanganate solution. Estimate the amount of hydrazine sulphate in one litre of the solution (1984)

Reaction:

$$4Fe^{3+} + N_2H_4 \rightarrow N_2 + 4Fe^{2+} + 4H^+$$

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

26. 5 mL of 8 N nitric acid, 4.8 mL of 5 N hydrochloric acid and a certain volume of 17 M sulphuric acid are mixed together and made up to 2 L. 30 mL of this acid mixture exactly neutralise 42.9 mL of sodium carbonate solution containing one gram of $Na_2CO_3.10H_2O$ in 100 mL of water. Calculate the amount in gram of the sulphate ions in solution. (1985)

27. An equal volume of a reducing agent is titrated separately with 1M $KMnO_4$ in acid, neutral and alkaline medium. The volumes of $KMnO_4$ required are 20 mL in acid, 33.3 mL in neutral and 100 mL in alkaline media. Find out the oxidation state of mangnese in each reduction product. Give the balanced equations for all the three half reaction. Find out the volume of 1M $K_2Cr_2O_7$ consumed, if the same volume of the reducing agent is titrated in acid medium. **(1989)**

28. An organic compound X on analysis gives 24.24 per cent carbon and 4.04 per cent hydrogen. Further, sodium extract of 1.0 g of X gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound X may be represented by two isomeric structures Y and Z. Y on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound while Z on similar treatment gives ethanal. Find out the molecular formula of X and gives the structure of Y and Z. **(1989)**

29. A mixture of $H_2C_2O_4$ (oxalic acid) and $NaHC_2O_4$ weighing 2.02 g was dissolved in water and the solution made up to one litre. Ten millilitres of the solution required 3.0 mL of 0.1 N sodium hydroxide solution for complete neutralization. In another experiment, 10.0 mL of the same solution, in hot dilute sulphuric acid medium, required 4.0 mL of 0.1 N potassium permanganate solution for complete reaction. Calculate the amount of $H_2C_2O_4$ and $NaHC_2O_4$ in the mixture. **(1990)**

30. A solution of 0.2 g of a compound containing Cu^{2+} and $C_2O_4^{2-}$ ions on titration with 0.02 M $KMnO_4$ in presence of H_2SO_4 consumes 22.6 mL of the oxidant. The resultant solution is neutralized with Na_2CO_3 , acidified with dilute acetic acid and treated with excess KI. The liberated iodine requires 11.3 mL of 0.05 M $Na_2S_2O_3$ solution for complete reduction. Find out the mole ratio of Cu^{2+} to $C_2O_4^{2-}$ in the compound. Write down the balanced redox reactions involved in the above titrations. **(1991)**

31. A 1.0 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made up to 100.0 mL. An aliquot of 25.0 mL of this solution requires for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration. **(1991)**

32. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is gently heated till the evolution of CO_2 gases. The volume of CO_2 at 750 mm Hg pressure and at 298 K is measured to be 123.9 mL. A 1.5 g of the same sample requires 150 mL of (M/10) HCl for complete neutralization. Calculate the percentage composition of the components of the mixture. **(1992)**

33. One gram of commercial $AgNO_3$ is dissolved in 50 mL of water. It is treated with 50 mL of a KI solution. The silver iodide thus precipitated is filtered off. Excess of KI in the filtrate is titrated with (M/10) KIO_3 solution in presence of 6 M HCl till all I^- ions are converted into ICl. It requires 50 mL of (M/10) KIO_3 solution. 20 mL of the same stock solution of KI requires 30 mL of (M/10) KIO_3 under similar conditions. Calculate the percentage of $AgNO_3$ in the sample.

Reaction :

$KIO_3 + 2KI + 6HCl \rightarrow 3ICl + 3KCl + 3H_2O$ **(1992)**

34. A 5.0 cm³ solution of H_2O 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 **(1995)**

35. A 20.0 cm³ mixture of CO, CH_4 and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be 13.0 cm³. A further contraction of 14.0 cm³ occurs when the residual gas is treated with KOH solution. Find out the composition of the gaseous mixture in terms of volume percentage. **(1995)**

36. 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 liberation of idoine. The resulting solution is diluted to 100 mL. A 20 mL of the dilute solution requires 11.0 mL of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 mL of the dilute solution, after complete extraction of the iodine required 12.80 mL of 0.25 M $KMnO_4$ solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+}. Calculate the percentage of Fe_2O_3 and Fe_3O_4 in the original sample. **(1996)**

37. To a 25 mL H_2O_2 solution, excess of acidified solution of potassium iodide was added. The iodine liberated required 20 mL of 0.3 N sodium thiosulphate solution. Calculate the volume strength of H_2O_2 solution. **(1997)**

38. An aqueous solution containing 0.10 g KIO_3 (formula weight = 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 decolourise the blue starch-iodine complex.Calculate the molarity of the sodium thiosulphate solution. **(1998)**

39. How many millilitres of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper (II) carbonate ? **(1999)**

40. 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 the $KMnO_4$ solution is just decolourised 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 balanced equation involved in the reactions and calculate the molarity of H_2O_2. **(2001)**

41. Calculate the amount of calcium oxide required when it reacts with 852 g of P_4O_{10}. **(2005)**

42. To measure the quantity of $MnCl_2$ dissolved in an aqueous solution, it was completely converted to $KMnO_4$ using thereaction.

$$MnCl_2 + K_2S_2O_8 + H_2O \rightarrow KMnO_4 + H_2SO_4 + HCl$$

(equation not balanced).

Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 mg) was added in portions till the colour of the permanganate ion disappeared. The quantity of $MnCl_2$ (in mg) present in the initial solution is_______. **(2018)**

43. The amount of water produced (in g) in the oxidation of 1 mole of rhombic sulphur by conc. HNO_3 to a compound with the highest oxidation state of sulphur is______(Given data: molar mass of water = 18g mol^{-1}) **(2019)**

44. 5.00 mL of 0.10 M oxalic acid solution taken in a conical flask is titrated NaOH from a burette using phenolphthalein indicator. The volume of NaOH required for the appearance of permament faint pink colour is tabulated below for five experiments. What is the concentration, in molarity, of the NaOH solution? **(2020)**

Exp. No.	Vol. of NaOH (mL)
1	12.5
2	10.5
3	9.0
4	9.0
5	9.0

45. In the chemical reaction between stoichiometric quantities of $KMnO_4$ and Kl in weakly basic solution, what is the number of moles of I_2 released for 4 moles of $KMnO_4$ consumed? **(2020)**

Answer Key

CHAPTER -5 | REDOX REACTION

EXERCISE - 1 :
BASIC OBJECTIVE QUESTIONS

1. (b) **2.** (b) **3.** (a) **4.** (b) **5.** (b)
6. (b) **7.** (d) **8.** (d) **9.** (c) **10.** (c)
11. (b) **12.** (d) **13.** (c) **14.** (d) **15.** (a)
16. (d) **17.** (c) **18.** (b) **19.** (a) **20.** (c)
21. (a) **22.** (a) **23.** (d) **24.** (b) **25.** (a)
26. (a) **27.** (a) **28.** (a) **29.** (a) **30.** (c)
31. (d) **32.** (a) **33.** (a) **34.** (d) **35.** (a)
36. (c) **37.** (c) **38.** (b) **39.** (c) **40.** (a)
41. (c) **42.** (d) **43.** (d) **44.** (a) **45.** (c)
46. (b) **47.** (b) **48.** (a) **49.** (b) **50.** (a)
51. (b) **52.** (b) **53.** (a) **54.** (d) **55.** (b)

EXERCISE - 2 :
PREVIOUS YEAR JEE MAINS QUESTIONS

1. (c) **2.** (d) **3.** (a) **4.** (d) **5.** (a)
6. (c) **7.** (d) **8.** (c) **9.** (d) **10.** (d)
11. (a) **12.** (d) **13.** (b) **14.** (d) **15.** (a)
16. (d) **17.** (a) **18.** (a) **19.** (c) **20.** (b)
21. (c) **22.** (c) **23.** (c) **24.** (12.00) **25.** (173.0)
26. (4.00) **27.** (6.00) **28.** (25.0) **29.** (6.00) **30.** (16.0)
31. (24.0) **32.** (50.0) **33.** (18.0) **34.** (1575.0) **35.** (316.0)

EXERCISE - 3 :
ADVANCED OBJECTIVE QUESTIONS

1. (a) **2.** (c) **3.** (c) **4.** (a) **5.** (b)
6. (d) **7.** (b) **8.** (a) **9.** (c) **10.** (a)
11. (a) **12.** (b) **13.** (a) **14.** (b) **15.** (a)
16. (b) **17.** (d) **18.** (a) **19.** (d) **20.** (a)
21. (a,b,d) **22.** (a,b,c) **23.** (c,d) **24.** (a,b)
25. (a,c,d) **26.** (a,b) **27.** (c,d) **28.** (a,c,d)
29. (a,b,c) **30.** (a,d) **31.** (a,c) **32.** (M/8)
33. (+3) **34.** (7.00) **35.** (7.00) **36.** (.00) **37.** (2g/L)
38. (1.00) **39.** (c) **40.** (a) **41.** (a) **42.** (a)
43. (a)
44. ($A \to q; B \to q; C \to r; D \to s; E \to p$)
45. ($A \to p; B \to q; C \to r; D \to s; E \to t$)
46. ($A \to q; B \to p; C \to s; D \to r$)
47. ($A \to s; B \to q; C \to r; D \to p$) **48.** (c) **49.** (d)
50. (a) **51.** (c) **52.** (a) **53.** (a) **54.** (d)
55. (d)

EXERCISE - 4 :
PREVIOUS YEAR JEE ADVANCED QUESTIONS

1. (b) **2.** (b) **3.** (a) **4.** (a) **5.** (b)
6. (d) **7.** (a) **8.** (d) **9.** (a) **10.** (c)
11. (b) **12.** (d) **13.** (b) **14.** (c) **15.** (a,b,d)
16. (c) **17.** (b) **18.** (7/3) **19.** (3.00) **20.** (2.00)
21. (5.00)
22. ($i \to 37.92; ii \to 0.065; iii \to 7.73 \text{ and } 3.86$)
24. (2) **25.** (6.5g/L) **26.** (6.5g)
27. (16.67 mL) **29.** (1.12g) **30.** (1:2)
31. (1.04×10^{21}) **32.** (26.5%) **33.** (85%)
34. (4.48%) **35.** (50%, 20%, 30%)
36. (49.33%, 34.8%) **37.** (1.33V) **38.** (0.06)
39. (8.1 mL) **40.** (0.1 M) **41.** (1008 gm)
42. (126.00) **43.** (288.00) **44.** (0.11)
45. (6.00)