CHAPTER 11

OXIDATION AND REDUCTION (Redox Reactions)

Several chemical reactions involve transfer of electrons from one chemical substance to another. These electron-transfer reactions are termed **oxidation-reduction** or **redox reactions.** Redox reactions play a vital role in our daily life. These reactions are accompanied by energy changes in the form of heat, light, electricity, etc. Generation of electricity in batteries, production of heat energy by burning chemical substances, extraction of metals such as sodium, aluminium, iron, etc., manufacture of a number of useful products such as caustic soda, potassium permanganate, etc.; electrodeposition or electroplating are common examples of redox reactions. Before we discuss the application of redox reactions in the production of electricity in different cells and the electrolysis phenomenon, it will be proper to study first the basic concepts of oxidation-reduction. The present chapter deals with the basic fundamentals of oxidation-reduction.

11.1 MOLECULAR AND IONIC EQUATIONS

Consider the reaction between solutions of ferric chloride and stannous chloride. When they are mixed, ferrous chloride and stannic chloride are formed. The chemical change can be represented by the following equation:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

The reactants and products have been written in molecular forms; thus, the equation is termed as **molecular equation.** Since, the reactants and products involved in the chemical change are ionic compounds, these will be present in the form of ions in the solution. So, the above chemical change can be written in the following manner also:

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

or $$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

The ferric ions combine with stannous ions to form ferrous ions and stannic ions. This is an **ionic equation** for the above chemical change.

Ionic equations represent chemical changes in terms of ions which actually undergo reaction. The ions which do not undergo any electronic change during a chemical change are termed **spectator ions.** The spectator ions are not included in the final balanced equations.

The rules to be followed for writing ionic equations are:

(i) All soluble ionic compounds involved in a chemical change are expressed in ionic symbols and covalent substances are written in molecular form. H_2O, NH_3, NO_2, NO, SO_2, CO, CO_2, etc., are expressed in molecular form.

(ii) The ionic compound which is highly insoluble is expressed in molecular form.

(iii) The ions which are common and equal in number on both sides, *i.e.*, spectator ions, are cancelled.

(iv) Besides the atoms, the ionic charges must also be balanced on both the sides.

SOME SOLVED EXAMPLES

Example 1. *Write the following equation in ionic form.*

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

Solution: In this equation HCl and $MnCl_2$ are ionic in nature. Writing these compounds in ionic form,

$$MnO_2 + 4H^+ + 4Cl^- = Mn^{2+} + 2Cl^- + 2H_2O + Cl_2$$

$2Cl^-$ ions are common on both sides; so these are cancelled. The desired ionic equation reduces to,

$$MnO_2 + 4H^+ + 2Cl^- = Mn^{2+} + 2H_2O + Cl_2$$

Example 2. *Represent the following equation in ionic form.*

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 7H_2O + K_2SO_4$$

Solution: In this equation except H_2O, all are ionic in nature. Representing these compounds in ionic forms,

$$2K^+ + Cr_2O_7^{2-} + 14H^+ + 7SO_4^{2-} + 6Fe^{2+} + 6SO_4^{2-} \longrightarrow$$

$$6Fe^{3+} + 9SO_4^{2-} + 2Cr^{3+} + 3SO_4^{2-} + 2K^+ + SO_4^{2-} + 7H_2O$$

$2K^+$ ions and $13SO_4^{2-}$ ions are common on both sides, so these are cancelled. The desired ionic equation reduces to,

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

Total charges are equal on both sides; thus, the balanced ionic equation is the same as above.

Example 3. *Write the balanced ionic equation for the reaction of sodium bicarbonate with sulphuric acid.*

Solution: The molecular equation for the chemical change is:

$$NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$

$NaHCO_3$, H_2SO_4 and Na_2SO_4 are ionic compounds; so these are written in ionic forms.

$$Na^+ + HCO_3^- + 2H^+ + SO_4^{2-} \longrightarrow 2Na^+ + SO_4^{2-} + H_2O + CO_2$$

Na^+ and SO_4^{2-} ions are spectator ions; hence these shall not appear in the final equation.

$$HCO_3^- + 2H^+ \longrightarrow H_2O + CO_2$$

To make equal charges on both sides, HCO_3^- should have a coefficient 2.

$$2HCO_3^- + 2H^+ \longrightarrow H_2O + CO_2$$

In order to balance the hydrogen and carbon on both sides, the molecules of H_2O and CO_2 should have a coefficient 2 respectively.

$$2HCO_3^- + 2H^+ = 2H_2O + 2CO_2$$

or $$HCO_3^- + H^+ = H_2O + CO_2$$

This is the balanced ionic equation.

Example 4. *Write the following ionic equation in the molecular form if the reactants are chlorides.*

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

Solution: For writing the reactants in molecular forms, the requisite number of chloride ions are added.

$$\underbrace{2Fe^{3+} + 6Cl^-}_{} + \underbrace{Sn^{2+} + 2Cl^-}_{}$$

or $$2FeCl_3 + SnCl_2$$

Similarly $8Cl^-$ ions are added on RHS to neutralise the charges.

$$\underbrace{2Fe^{2+} + 4Cl^-}_{} + \underbrace{Sn^{4+} + 4Cl^-}_{}$$

or $$2FeCl_2 + SnCl_4$$

Thus, the balanced molecular equation is

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

11.2 OXIDATION AND REDUCTION

Early Ideas of Oxidation and Reduction: The term oxidation was first used to describe chemical reactions in which oxygen was added to an element or a compound. The phenomenon of combustion was the earliest example of oxidation. Later on the term oxidation was extended to describe many more reactions which occurred without the use of even oxygen.

Oxidation is a process which involves:

(a) Addition of oxygen:

$2Mg + O_2^* = 2MgO$ (Oxidation of magnesium)

$S + O_2^* = SO_2$ (Oxidation of sulphur)

$2CO + O_2^* = 2CO_2$ (Oxidation of carbon monoxide)

$Na_2SO_3 + H_2O_2^* = Na_2SO_4 + H_2O$ (Oxidation of sodium sulphite)

(b) Removal of hydrogen:

$H_2S + Cl_2^* = 2HCl + S$ (Oxidation of hydrogen sulphide)

$4HI + O_2^* = 2H_2O + 2I_2$ (Oxidation of hydrogen iodide)

$4HCl + MnO_2^* = MnCl_2 + 2H_2O + Cl_2$ (Oxidation of hydrogen chloride)

(c) Addition of an electronegative element:

$Fe + S^* = FeS$ (Oxidation of iron)

$SnCl_2 + Cl_2^* = SnCl_4$ (Oxidation of stannous chloride)

$2Fe + 3F_2^* = 2FeF_3$ (Oxidation of iron)

(d) Removal of an electropositive element:

$2KI + H_2O_2^* = 2KOH + I_2$ (Oxidation of potassium iodide)

$2K_2MnO_4 + Cl_2^* = 2KCl + 2KMnO_4$ (Oxidation of potassium manganate)

$2KI + Cl_2^* = 2KCl + I_2$ (Oxidation of potassium iodide)

A substance which brings oxidation is known as **oxidising agent.** The substances marked with asterisk sign (*) in above equations are oxidising agents.

Reduction is just the reverse of oxidation.

Reduction is a process which involves:

(a) Removal of oxygen:

$CuO + C^* = Cu + CO$ (Reduction of cupric oxide)

$\underset{\text{Steam}}{H_2O} + \underset{\text{Coke}}{C^*} = \underbrace{CO + H_2}_{\text{Water gas}}$ (Reduction of water)

$Fe_3O_4 + 4H_2^* = 3Fe + 4H_2O$ (Reduction of magnetic oxide)

(b) Addition of hydrogen:

$Cl_2 + H_2^* = 2HCl$ (Reduction of chlorine)

$S + H_2^* = H_2S$ (Reduction of sulphur)

$C_2H_4 + H_2^* = C_2H_6$ (Reduction of ethene)

(c) Removal of an electronegative element:

$2HgCl_2 + SnCl_2^* = Hg_2Cl_2 + SnCl_4$ (Reduction of mercuric chloride)

$$2FeCl_3 + H_2^* = 2FeCl_2 + 2HCl \text{ (Reduction of ferric chloride)}$$

$$2FeCl_3 + H_2S^* = 2FeCl_2 + 2HCl + S$$

(Reduction of ferric chloride)

(d) Addition of an electropositive element:

$$HgCl_2 + Hg^* = Hg_2Cl_2 \text{ (Reduction of mercuric chloride)}$$

$$CuCl_2 + Cu^* = Cu_2Cl_2 \quad \text{(Reduction of cupric chloride)}$$

The substance which brings reduction is known as **reducing agent.** The substances marked with asterisk sign (*) in the above equations are reducing agents.

A substance, which undergoes oxidation, acts as a reducing agent while a substance, which undergoes reduction, acts as an oxidising agent.

Mg, S, Cu, Na_2SO_3, H_2S, HI, H_2, C, KI are reducing agents, while O_2, Cl_2, F_2, H_2O_2, MnO_2, $FeCl_3$, $CuCl_2$, Fe_3O_4, CuO, etc., are oxidising agents in the above examples.

All oxidation and reduction reactions are complimentary of one another and occur simultaneously, one cannot take place without the other. No single oxidation and no single reduction process is known. The simultaneous oxidation and reduction reactions are generally termed as redox reactions.

e.g., $$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

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

In above example iron undergoes reduction from +3 to +2 and tin undergoes oxidation from +2 to +4.

Redox reactions are divided into two main types:

(i) Intermolecular redox: In such redox reactions, one molecule of reactant is oxidised whereas molecule of other reactant is reduced.

e.g., $$NO_3^- + H_2S + H_2O + H^+ \longrightarrow NH_4^+ + HSO_4^-$$

Oxidised

Reduced

(ii) Intramolecular redox: One atom of a molecule is oxidised and other atom of same molecule is reduced then it is intramolecular redox reaction.

e.g., $$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$$

11.3 MODERN CONCEPT OF OXIDATION AND REDUCTION

According to the modern concept, loss of electrons is oxidation whereas gain of electrons is reduction.

Examples of oxidation reactions are:

$$Na \longrightarrow Na^+ + e$$

$$Zn \longrightarrow Zn^{2+} + 2e$$

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

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e$$

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e$$

$$[Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + e$$

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

Examples of reduction reactions are:

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

$$S + 2e \longrightarrow S^{2-}$$

$$Cu^{2+} + 2e \longrightarrow Cu$$

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

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

$$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O$$

Oxidation and reduction can be represented in a general way as shown below :

Loss of electrons $\longrightarrow$ Oxidation

$-e \quad -e \quad -e \quad -e \quad -e \quad -e \quad -e \quad -e$

$\overset{4-}{M} \quad \overset{3-}{M} \quad \overset{2-}{M} \quad \overset{1-}{M} \quad \overset{0}{M} \quad \overset{1+}{M} \quad \overset{2+}{M} \quad \overset{3+}{M} \quad \overset{4+}{M}$

$+e \quad +e \quad +e \quad +e \quad +e \quad +e \quad +e \quad +e$

Reduction $\longleftarrow$ Gain of electrons

In a redox process the valency of the involved species changes. The valency of a reducing agent increases while the valency of an oxidising agent decreases in a redox reaction. The valency of a free element is taken as zero.

Increase in valency $\longrightarrow$ Oxidation

$$-4, -3, -2, -1, 0, +1, +2, +3, +4$$

Reduction $\longleftarrow$ Decrease in valency

When there is no change in valency it means there is no oxidation or reduction, *e.g.*, in

$$\left.\begin{array}{l} BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl \\ BaSO_4 \longrightarrow Ba^{2+} + SO_4^{2-} \end{array}\right\} \text{(No change in valency)}$$

Conclusions

(i) Oxidation is a process in which one or more electrons are lost or valency of the element increases.

(ii) Reduction is a process in which one or more electrons are gained or valency of the element decreases.

(iii) Oxidising agent is a material which can gain one or more electrons, *i.e.*, valency decreases.

(iv) Reducing agent is a material which can lose one or more electrons, *i.e.*, valency increases.

(v) Redox reaction involves two half reactions, one involving loss of electron or electrons (oxidation) and the other involving gain of electron or electrons (reduction).

Examples:

$-2e$ Oxidation

1. $$2Hg^{2+} + Sn^{2+} \longrightarrow Hg_2^{2+} + Sn^{4+}$$

$+2e$ Reduction

+ 2e
Reduction

2. $$Sn^{2+} + 2Fe^{3+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

− 2e
Oxidation

+ 2e
Reduction

3. $$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

− 2e
Oxidation

11.4 ION-ELECTRON METHOD FOR BALANCING REDOX REACTIONS

The method for balancing redox reactions by ion electron method was developed by **Jette** and **LaMev** in 1927. It involves the following steps:

(i) Write down the redox reaction in ionic form.

(ii) Split the redox reaction into two half reactions, one for oxidation and the other for reduction.

(iii) Balance each half reaction for the number of atoms of each element. For this purpose:

(a) Balance the atoms other than H and O for each half reaction using simple multiples.

(b) Add water molecules to the side deficient in oxygen and H^+ to the side deficient in hydrogen. This is done in acidic or neutral solutions.

(c) In alkaline solution, for each excess of oxygen, add one water molecule to the same side and two OH^- ions to the other side. If hydrogen is still unbalanced, add one OH^- ion for each excess hydrogen on the same side and one water molecule to the other side.

(iv) Add electrons to the side deficient in electrons as to equalise the charge on both sides.

(v) Multiply one or both the half reactions by a suitable number so that the number of electrons become equal in both the equations.

(vi) Add the two balanced half reactions and cancel any term common to both sides.

The following solved problems illustrate the various steps of ion electron method:

Example 5. *Balance the following equations by ion electron method.*

(a) $FeCl_3 + H_2S \longrightarrow FeCl_2 + HCl + S$

(b) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$

(c) $KI + Cl_2 \longrightarrow KCl + I_2$

(d) $MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2$

(e) $H_2S + HNO_3 \longrightarrow H_2SO_4 + NO_2 + H_2O$

Solution: (a) $FeCl_3 + H_2S \longrightarrow FeCl_2 + HCl + S$

Ionic equation, $Fe^{3+} + H_2S \longrightarrow Fe^{2+} + H^+ + S$

1st step. Splitting the redox reaction into two half reactions,

$$\underset{\text{(Oxidation half reaction)}}{H_2S \longrightarrow 2H^+ + S} \qquad \underset{\text{(Reduction half reaction)}}{Fe^{3+} \longrightarrow Fe^{2+}}$$

2nd step. Adding electrons to the side deficient in electrons,

$$H_2S \longrightarrow 2H^+ + S + 2e$$
$$Fe^{3+} + e \longrightarrow Fe^{2+}$$

3rd step. Balancing electrons in both the half reactions,

$$H_2S \longrightarrow 2H^+ + S + 2e$$
$$2Fe^{3+} + 2e \longrightarrow 2Fe^{2+}$$

4th step. Adding both the half reactions,

$$H_2S + 2Fe^{3+} \longrightarrow 2H^+ + S + 2Fe^{2+}$$

Converting it into molecular form,

$$H_2S + 2Fe^{3+} + 6Cl^- \longrightarrow 2H^+ + 2Cl^- + S + 2Fe^{2+} + 4Cl^-$$

or $$H_2S + 2FeCl_3 \longrightarrow 2HCl + S + 2FeCl_2$$

(b) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$

Ionic equation,

$$Cu + H^+ + NO_3^- \longrightarrow Cu^{2+} + NO + H_2O$$

1st step. Splitting into two half reactions,

$$\underset{\text{(Oxidation half reaction)}}{Cu \longrightarrow Cu^{2+}} \; ; \quad \underset{\text{(Reduction half reaction)}}{NO_3^- + H^+ \rightarrow NO + H_2O}$$

2nd step. Adding H^+ ions to the side deficient in hydrogen,

$$Cu \longrightarrow Cu^{2+}; \quad NO_3^- + 4H^+ \longrightarrow NO + 2H_2O$$

3rd step. Adding electrons to the side deficient in electrons,

$$Cu \longrightarrow Cu^{2+} + 2e; \; NO_3^- + 4H^+ + 3e \longrightarrow NO + 2H_2O$$

4th step. Balancing electrons in both half reactions,

$$3Cu \longrightarrow 3Cu^{2+} + 6e; \; 2NO_3^- + 8H^+ + 6e \longrightarrow 2NO + 4H_2O$$

5th step. Adding both the half reactions,

$$3Cu + 2NO_3^- + 8H^+ \longrightarrow 3Cu^{2+} + 2NO + 4H_2O$$

Converting it into molecular form,

$$3Cu + 2NO_3^- + 8H^+ + 6NO_3^- \longrightarrow 3Cu^{2+} + 6NO_3^- + 2NO + 4H_2O$$

or $$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

(c) $KI + Cl_2 \longrightarrow KCl + I_2$

Ionic equation, $I^- + Cl_2 \longrightarrow Cl^- + I_2$

Splitting into two half reactions,

$$\underset{\text{(Oxidation)}}{I^- \longrightarrow I_2} \; ; \qquad \underset{\text{(Reduction)}}{Cl_2 \longrightarrow Cl^-}$$

Making number of atoms equal,

$$2I^- \longrightarrow I_2 ; \qquad Cl_2 \longrightarrow 2Cl^-$$

Adding electrons to the sides deficient in electrons,

$$2I^- \longrightarrow I_2 + 2e; \quad Cl_2 + 2e \longrightarrow 2Cl^-.$$

Adding both the half reactions,

$$2I^- + Cl_2 \longrightarrow I_2 + 2Cl^-$$

Converting it into molecular form,

$$2K^+ + 2I^- + Cl_2 \longrightarrow I_2 + 2Cl^- + 2K^+$$

or $$2KI + Cl_2 \longrightarrow I_2 + 2KCl$$

(d) $MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2$

Ionic equation,

$$MnO_2 + H^+ + Cl^- \longrightarrow Mn^{2+} + H_2O + Cl_2$$

1st step. Splitting into two half reactions,

$$\underset{\text{(Oxidation half reaction)}}{Cl^- \longrightarrow Cl_2} \quad ; \quad \underset{\text{(Reduction half reaction)}}{MnO_2 + H^+ \longrightarrow Mn^{2+} + H_2O}$$

2nd step. Adding H^+ ions to the side deficient in hydrogen,

$$Cl^- \longrightarrow Cl_2 \quad ; \quad MnO_2 + 4H^+ \longrightarrow Mn^{2+} + 2H_2O$$

3rd step. Making atoms equal on both sides,

$$2Cl^- \longrightarrow Cl_2 ; \quad MnO_2 + 4H^+ \longrightarrow Mn^{2+} + 2H_2O$$

4th step. Adding electrons to the side deficient in electrons,

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

$$MnO_2 + 4H^+ + 2e \longrightarrow Mn^{2+} + 2H_2O$$

5th step. Adding both the half reactions,

$$2Cl^- + MnO_2 + 4H^+ \longrightarrow Cl_2 + Mn^{2+} + 2H_2O$$

Converting it into molecular form,

$$MnO_2 + 2Cl^- + 4H^+ + 2Cl^- \rightarrow Cl_2 + Mn^{2+} + 2Cl^- + 2H_2O$$

or $$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

(e) $H_2S + HNO_3 \longrightarrow H_2SO_4 + NO_2 + H_2O$

Ionic equation,

$$H_2S + NO_3^- \longrightarrow NO_2 + H_2O$$

1st step. Splitting into two half reactions,

$$\underset{\text{(Oxidation half reaction)}}{H_2S \longrightarrow SO_4^{2-}} \quad ; \quad \underset{\text{(Reduction half reaction)}}{NO_3^- \longrightarrow NO_2 + H_2O}$$

2nd step. Add water to the side deficient in oxygen,

$$H_2S + 4H_2O \longrightarrow SO_4^{2-} + 10H^+$$

3rd step. Add H^+ ions to the side deficient in hydrogen,

$$NO_3^- + 2H^+ \longrightarrow NO_2 + H_2O$$

4th step. Add electrons to the side deficient in electrons,

$$H_2S + 4H_2O \longrightarrow SO_4^{2-} + 10H^+ + 8e$$

$$NO_3^- + 2H^+ + e \longrightarrow NO_2 + H_2O$$

5th step. Balancing electrons in both the half reactions,

$$H_2S + 4H_2O \longrightarrow SO_4^{2-} + 10H^+ + 8e$$

$$[NO_3^- + 2H^+ + e \longrightarrow NO_2 + H_2O] \times 8$$

6th step. Adding both the half reactions,

$$H_2S + 4H_2O + 8NO_3^- + 6H^+ \longrightarrow SO_4^{2-} + 8NO_2 + 8H_2O$$

or $$H_2S + 8NO_3^- + 6H^+ \longrightarrow SO_4^{2-} + 8NO_2 + 4H_2O$$

Converting it into molecular form,

$$H_2S + 8HNO_3 \longrightarrow H_2SO_4 + 8NO_2 + 4H_2O$$

Example 6. *Balance the following equations by ion electron method:*

(a) $MnO_4^- + Fe^{2+} + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$

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

(c) $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow Cr^{3+} + I_2 + H_2O$

(d) $Cr_2O_7^{2-} + SO_2 + H^+ \longrightarrow Cr^{3+} + HSO_4^- + H_2O$

(e) $I_2 + OH^- \longrightarrow IO_3^- + I^- + H_2O$

(f) $Cl_2 + IO_3^- + OH^- \longrightarrow IO_4^- + Cl^- + H_2O$

Solution:

(a) $MnO_4^- + Fe^{2+} + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$

1st step. Splitting into two half reactions,

$$\underset{\text{(Reduction half reaction)}}{MnO_4^- + H^+ \longrightarrow Mn^{2+} + H_2O} \; ; \quad \underset{\text{(Oxidation half reaction)}}{Fe^{2+} \longrightarrow Fe^{3+}}$$

2nd step. Adding hydrogen ions to the side deficient in hydrogen,

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

3rd step. Adding electrons to the sides deficient in electrons,

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

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

4th step. Balancing electrons in both half reactions,

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

$$5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e$$

5th step. Adding both the half reactions,

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

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

Splitting into two half reactions,

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

Balanced as in Question (a),

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

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

Balancing electrons in both half reactions,

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

$$5[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e]$$

Adding both the half reactions,

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

(c) $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow Cr^{3+} + I_2 + H_2O$

1st step. Splitting into two half reactions,

$$\underset{\text{(Reduction half reaction)}}{Cr_2O_7^{2-} + H^+ \longrightarrow Cr^{3+} + H_2O} \qquad \underset{\text{(Oxidation half reaction)}}{I^- \longrightarrow I_2}$$

2nd step. Adding hydrogen ions to the side deficient in hydrogen,

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

3rd step. Making atoms equal on both sides,

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O \ ; \ 2I^- \longrightarrow I_2$$

4th step. Adding electrons to the sides deficient in electrons,

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

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

5th step. Balancing electrons,

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

$$3[2I^- \longrightarrow I_2 + 2e]$$

6th step. Adding both the half reactions,

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

(d) $Cr_2O_7^{2-} + SO_2 + H^+ \longrightarrow Cr^{3+} + HSO_4^- + H_2O$

1st step. Splitting into two half reactions,

$$\underset{\text{(Reduction half reaction)}}{Cr_2O_7^{2-} + H^+ \longrightarrow Cr^{3+} + H_2O}; \quad \underset{\text{(Oxidation half reaction)}}{SO_2 \longrightarrow HSO_4^-}$$

2nd step. Adding H^+ ions to side deficient in hydrogen,

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

3rd step. Adding water to the side deficient in oxygen,

$$SO_2 + 2H_2O \longrightarrow HSO_4^- + 3H^+$$

4th step. Making atoms equal on both sides,

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

5th step. Adding electrons to the sides deficient in electrons,

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

$$SO_2 + 2H_2O \longrightarrow HSO_4^- + 3H^+ + 2e$$

6th step. Balancing electrons in both the half reactions,

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

$$[SO_2 + 2H_2O \longrightarrow HSO_4^- + 3H^+ + 2e] \times 3$$

7th step. Adding both the half reactions,

$$Cr_2O_7^{2-} + 5H^+ + 3SO_2 \longrightarrow 2Cr^{3+} + 3HSO_4^- + H_2O$$

(e) $I_2 + OH^- \longrightarrow IO_3^- + I^- + H_2O$

1st step. Splitting into two half reactions,

$$\underset{\text{(Oxidation half reaction)}}{I_2 + OH^- \longrightarrow IO_3^- + H_2O}; \quad \underset{\text{(Reduction half reaction)}}{I_2 \longrightarrow I^-}$$

2nd step. Adding OH^- ions,

$$I_2 + 12OH^- \longrightarrow 2IO_3^- + 6H_2O$$

3rd step. Adding electrons to the sides deficient in electrons,

$$I_2 + 12OH^- \longrightarrow 2IO_3^- + 6H_2O + 10e; \ I_2 + 2e \longrightarrow 2I^-$$

4th step. Balancing electrons in both the half reactions,

$$I_2 + 12OH^- \longrightarrow 2IO_3^- + 6H_2O + 10e$$

$$5[I_2 + 2e^- \longrightarrow 2I^-]$$

5th step. Adding both the half reactions,

$$6I_2 + 12OH^- \longrightarrow 2IO_3^- + 10I^- + 6H_2O$$

Dividing by 2,

$$3I_2 + 6OH^- \longrightarrow IO_3^- + 5I^- + 3H_2O$$

(f) $Cl_2 + IO_3^- + OH^- \longrightarrow IO_4^- + Cl^- + H_2O$

1st step. Splitting into two half reactions,

$$\underset{\text{(Oxidation half reaction)}}{IO_3^- + OH^- \longrightarrow IO_4^- + H_2O}; \quad \underset{\text{(Reduction half reaction)}}{Cl_2 \longrightarrow Cl^-}$$

2nd step. Adding QH $^-$ ions,

$$IO_3^- + 2OH^- \longrightarrow IO_4^- + H_2O$$

3rd step. Adding electrons to the sides deficient in electrons,

$$IO_3^- + 2OH^- \longrightarrow IO_4^- + H_2O + 2e$$

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

4th step. Adding both the half reactions,

$$IO_3^- + 2OH^- + Cl_2 \longrightarrow IO_4^- + 2Cl^- + H_2O$$

11.5 OXIDATION NUMBER (Oxidation State)

It is defined as **the charge (real or imaginary) which an atom appears to have when it is in combination.** In the case of electrovalent compounds, the oxidation number of an element or radical is the same as the charge on the ion. This is the real charge and is developed by the loss and gain of electron or electrons. For example, in the electrovalent compound, sodium chloride (NaCl), the charge on sodium and chlorine is +1 and –1, respectively. The charges have been developed by the transfer of one electron from Na-atom to Cl-atom. Thus, in NaCl ($Na^+ Cl^-$), the oxidation number of sodium is +1 and that of chlorine is –1.

The oxidation numbers of atoms in covalent compounds can be derived by assigning the electrons of each bond to the more electronegative atom of the bonded atoms. For a molecule of HCl both the electrons of the covalent bond are assigned to the chlorine atom since it is more electronegative than hydrogen.

$$H \times \overset{\circ\circ}{\underset{\circ\circ}{\mathrm{Cl}}} \,{}^{\circ}_{\circ}$$

Thus, chlorine atom has one more electron than the neutral chlorine atom which brings one unit negative charge on chlorine. The oxidation number of chlorine in this compound is –1. The hydrogen atom has lost the only electron possessed by it, thus acquiring one unit positive charge. The oxidation number of hydrogen is, therefore, +1 in this compound. In the case of covalent bond between two identical atoms, *i.e.*, electronegativity difference is zero, the bonding electrons are shared equally between the bonded atoms, *i.e.*, no charge is developed on any of the atoms. Thus, the oxidation numbers of both chlorine atoms are zero in the molecule of chlorine.

$$\underset{7\text{ electrons}}{\overset{\circ\circ}{\underset{\circ\circ}{\mathrm{Cl}}}} \quad \underset{7\text{ electrons}}{\overset{\circ\circ}{\underset{\circ\circ}{\mathrm{Cl}}}} \quad \left[\begin{array}{l}\text{In neutral chlorine atom,}\\ \text{7 electrons are present}\\ \text{in the valency shell}\end{array}\right]$$

Counting of electrons in this fashion is not convenient in many molecules and therefore the following operational rules are followed which are helpful and convenient in determining the oxidation numbers:

(i) The oxidation number (Ox.no.) of an atom in free elements is zero, no matter how complicated the molecule is, hydrogen in H_2, sulphur in S_8, phosphorus in P_4, oxygen in O_2 or O_3, all have zero value of oxidation numbers.

(ii) The fluorine, which is the most electronegative element, has oxidation number –1 in all of its compounds.

(iii) Oxidation number of oxygen is –2 in all compounds except in peroxides, superoxides and oxygen fluorides. In peroxides (O_2^{2-}), oxygen has oxidation number –1; in superoxides (O_2^-), oxygen has oxidation number $-1/2$; and in OF_2, the oxygen has an oxidation number +2.

(iv) The oxidation number of hydrogen is +1 in all of its compounds except in metallic hydrides like NaH, BaH_2, etc. Hydrogen is in –1 oxidation state in these hydrides.

(v) The oxidation number of an ion is equal to the electrical charge present on it.

(vi) The oxidation number of IA elements (Li, Na, K, Rb, Cs and Fr) is +1 and the oxidation number of IIA elements (Be, Mg, Ca, Sr, Ba and Ra) is +2.

(vii) For complex ions, the algebraic sum of oxidation numbers of all the atoms is equal to the net charge on the ion.

(viii) In the case of neutral molecules, the algebraic sum of the oxidation numbers of all the atoms present in the molecule is zero.

The following solved examples illustrate the application of the above rules for finding out the oxidation number of an element in particular species:

Example 7. *What is the oxidation number of Mn in $KMnO_4$ and of S in $Na_2S_2O_3$?*

Solution: Let the Ox.no. of Mn in $KMnO_4$ be x.

We know that, Ox. no. of K = +1

Ox. no. of O = – 2

$$\begin{array}{llcccccl}
\text{So,} & \text{Ox. no. K} & + & \text{Ox. no. Mn} & + & 4(\text{Ox. no. O}) & = 0 \\
\text{or} & +1 & + & x & + & 4(-2) & = 0 \\
\text{or} & +1 & + & x & - & 8 & = 0 \\
\text{or} & & & x = +8-1 = +7 & & &
\end{array}$$

Hence, Ox.no. of Mn in $KMnO_4$ is +7.

Similarly, for S in $Na_2S_2O_3$,

$$2(\text{Ox. no. Na}) + 2(\text{Ox. no. S}) + 3(\text{Ox. no. O}) = 0$$

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

$$x = +2$$

Hence, Ox.no. of S in $Na_2S_2O_3$ = + 2.

Example 8. *What is the oxidation number of Cr in $K_2Cr_2O_7$?* (Ranchi 1996)

Solution: Let the Ox.no. of Cr in $K_2Cr_2O_7$ be x.

We know that, Ox.no. of K = + 1

Ox. no. of O = – 2

$$\begin{array}{llcccccl}
\text{So,} & 2(\text{Ox. no. K}) & + & 2(\text{Ox. no. Cr}) & + & 7(\text{Ox. no. O}) & = 0 \\
 & 2(+1) & + & 2(x) & + & 7(-2) & = 0 \\
\text{or} & +2 & + & 2x & - & 14 & = 0 \\
\text{or} & & & 2x = +14-2 = +12 & & & \\
\text{or} & & & x = +\dfrac{12}{2} = +6 & & &
\end{array}$$

Hence, oxidation number of Cr in $K_2Cr_2O_7$ is +6.

Example 9. *What is the oxidation number of Fe in $K_4Fe(CN)_6$?*

Solution: Let the oxidation number of Fe be x.

We know that, Ox.no. of K = +1

Ox. no. of $(CN)^-$ = –1

$$\begin{array}{llcccccl}
\text{So,} & 4(\text{Ox. no. K}) & + & \text{Ox. no. Fe} & + & 6(\text{Ox. no. CN}^-) & = 0 \\
 & 4(+1) & + & x & + & 6(-1) & = 0 \\
\text{or} & +4 & + & x & - & 6 & = 0 \\
\text{or} & & & x = +6-4 = +2 & & &
\end{array}$$

The oxidation number of iron in $K_4Fe(CN)_6$ is +2.

Example 10. *Find the oxidation number of*

(a) S in SO_4^{2-} ion *(b) S in HSO_3^- ion*

(c) Pt in $(PtCl_6)^{2-}$ ion *(d) Mn in $(MnO_4)^-$ ion*

Solution: (a) Let the oxidation number of S be x.

We know that, Ox.no. of O = – 2

$$\begin{array}{llcccl}
\text{So,} & \text{Ox. no. S} & + & 4(\text{Ox. no. O}) & = -2 \\
\text{or} & x & + & 4(-2) & = -2 \\
\text{or} & x & - & 8 & = -2 \\
\text{or} & & x = +8-2 = +6 & &
\end{array}$$

The oxidation number of S in SO_4^{2-} ion is +6.

(b) Let the oxidation number of S be x in HSO_3^- ion.

We know that, Ox.no. of H = + 1

Ox. no. of O = – 2

So, $\quad$ Ox. no. H + Ox. no. S + 3(Ox. no. O) = −1

$$+1 + x + 3(-2) = -1$$

or $\quad +1 + x - 6 = -1$

or $\quad x - 5 = -1$

or $\quad x = +5 - 1 = +4$

The oxidation number of S in HSO_3^- ion is + 4.

(c) Let oxidation number of Pt be x.

We know that Ox.no. of Cl = −1.

So, $\quad$ Ox. no. Pt + 6(Ox. no. Cl) = −2

$$x + 6(-1) = -2$$

or $\quad x - 6 = -2$

or $\quad x = +6 - 2 = +4$

The oxidation number of Pt in $[Pt(Cl)_6]^{2-}$ ion is + 4.

(d) Let oxidation number of Mn be x.

We know that, Ox.no. of O = −2.

So, $\quad$ Ox. no. Mn + 4(Ox. no. O) = −1

$$x + 4(-2) = -1$$

or $\quad x - 8 = -1$

or $\quad x = +8 - 1 = +7$

The oxidation number of Mn in $[MnO_4]^-$ ion is +7.

Example 11. *Which compound amongst the following has the highest oxidation number for Mn?*

$KMnO_4$, K_2MnO_4, MnO_2 and Mn_2O_3.

Solution:

		Ox.no. of Mn
$KMnO_4$	$+1 + x - 8 = 0$, $x = +7$	+7
K_2MnO_4	$+2 + x - 8 = 0$, $x = +6$	+6
MnO_2	$x - 4 = 0$, $x = +4$	+4
Mn_2O_3	$2x - 6 = 0$, $x = +3$	+3

Thus, the highest oxidation number for Mn is in $KMnO_4$.

Sometimes, oxidation numbers have such values which at first sight appear strange. For example, the oxidation number of carbon in cane sugar ($C_{12}H_{22}O_{11}$), glucose ($C_6H_{12}O_6$), dichloromethane, etc., is zero.

Cane sugar ($C_{12}H_{22}O_{11}$)

$$12 \times x + 22 \times 1 + 11(-2) = 0$$
$$12x + 22 - 22 = 0$$
So, $x = 0$

Glucose ($C_6H_{12}O_6$)

$$6 \times x + 12 \times 1 + 6(-2) = 0$$
$$6x + 12 - 12 = 0$$
So, $x = 0$

Dichloromethane (CH_2Cl_2)

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

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. Oxidation state of S in SO_4^{2-}: [BCECE (Medical) 2005]

(a) +6 (b) +3
(c) +2 (d) −2

[**Ans.** (a)]

[**Hint:** Let oxidation state of S is x.

$\therefore \quad x + 4(-2) = -2$

$x = +6$]

2. Arrange the following in the increasing order of oxidation state of Mn: (JCECE 2004)

(i) Mn^{2+} (ii) MnO_2 (iii) $KMnO_4$ (iv) K_2MnO_4

(a) (i) > (ii) > (iii) > (iv) (b) (i) < (ii) < (iv) < (iii)
(c) (ii) < (iii) < (i) < (iv) (d) (iii) < (i) < (iv) < (ii)

[**Ans.** (b)]

[**Hint:** $\underset{(+2)}{Mn^{2+}} < \underset{(+4)}{MnO_2} < \underset{(+6)}{K_2MnO_4} < \underset{(+7)}{KMnO_4}$]

3. Which of the following has least oxidation state of Fe? (JCECE 2004)

(a) $K_3[Fe(OH)_6]$
(b) $K_2[FeO_4]$
(c) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
(d) $[Fe(CN)_6]^{3-}$

[**Ans.** (c)]

[**Hint:** In mohr salt $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, oxidation state of iron is +2 which is least.

$K_3[Fe(OH)_6]$	$+3 + x - 6 = 0$	$x = +3$
$K_2[FeO_4]$	$+2 + x - 8 = 0$	$x = +6$
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	**+2 state** in $FeSO_4$ $(x - 2 = 0)$	
$Fe(CN)_6^{3-}$	$x - 6 = -3$	$x = +3$]

4. Oxidation state of carbon in HCOOH will be:

(a) +1 (b) +2 (c) −4 (d) 0

[**Ans.** (b)]

[**Hint:** Let the oxidation state of carbon be x.

$$2 + x - 4 = 0$$
$$x = 2]$$

5. Oxidation states of chlorine in $HClO_4$ and $HClO_3$ are:

(a) +4, +3 (b) +7, +5 (c) +3, +4 (d) +5, +7

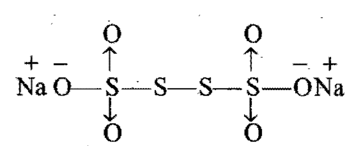
[**Ans.** (b)]

[**Hint:** $HClO_4$: $+1 + x - 8 = 0$, $x = +7$

$HClO_3$: $+1 + x - 6 = 0$, $x = +5$]

11.6 SPECIAL EXAMPLES OF OXIDATION STATE DETERMINATION

1. Oxidation state of sulphur in $Na_2S_4O_6$: It is only average oxidation number of sulphur. Let us see the structure of $Na_2S_4O_6$.



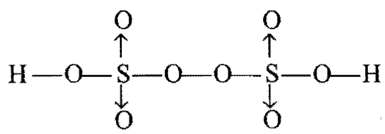
From the structure, it is clear that the sulphur atoms acting as donor atoms have +5 oxidation number (each). On the other hand, the sulphur atom involved in pure covalent bond formation has zero oxidation number.

2. Oxidation number of sulphur in $(CH_3)_2SO$ (dimethyl sulphoxide): Here, oxidation number $O = -2$, oxidation number of each CH_3 group is +1.

$$\therefore \quad +2 + x - 2 = 0 \text{ or } x = 0$$

Thus, sulphur lies in zero oxidation state.

3. Oxidation number of sulphur in perdisulphuric acid $H_2S_2O_8$: It may be done only when the structure is drawn.



Oxidation number of S = x; oxidation number of H = +1; oxidation number of oxygen in peroxo linkage = −1; oxidation number of other six oxygen atoms = −2 each.

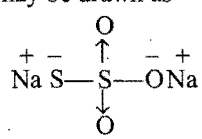
$$\therefore \quad +2 + (-12) + 2x - 2 = 0$$

$$\therefore \quad x = +6 \qquad \text{(oxidation number of sulphur)}$$

4. Oxidation number of sulphur in hypo, $Na_2S_2O_3$: Let the average oxidation number of sulphur be 'x'.

$$\therefore \quad +2 + 2x - 6 = 0 \quad \therefore \quad x = +2$$

Structure of hypo may be drawn as—



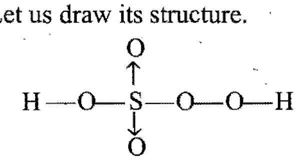
Here, the two sulphur atoms have different oxidation states:

(i) Oxidation number of donor sulphur atom is +5. It gives up four electrons in coordination and one electron in covalent bond formation with oxygen.

(ii) Sulphur, bonded with Na, lies in −1 state since one electron of Na lies towards the sulphur. Electrons of S—S bond are equally shared between two sulphur atoms.

Thus +5 and −1 are two oxidation states of the two sulphur atoms.

5. Oxidation number of sulphur in peroxo monosulphuric acid (H_2SO_5): Let us draw its structure.



Here, we have to consider Ox.no. of H = +1

Ox.no. of oxygen in peroxo linkage = −1

Ox. no. of rest of oxygen = −2

$$\therefore \quad +2 + x - 6 - 2 = 0 \text{ or } x = +6$$

Thus, sulphur in H_2SO_5 lies in +6 oxidation state.

6. Fe in its oxides, FeO, Fe_2O_3 and Fe_3O_4:

In FeO $\longrightarrow x - 2 = 0, x = +2$

In $Fe_2O_3 \longrightarrow 2x - 6 = 0, x = +3$

In $Fe_3O_4 \longrightarrow 3x - 8 = 0, x = +8/3$ (fractional)

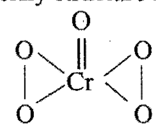
Here, in Fe_3O_4, oxidation number is the average of those in FeO and Fe_2O_3.

$$FeO + Fe_2O_3 = Fe_3O_4$$

Average oxidation number of Fe in

$$Fe_3O_4 = \frac{+2 + 2(+3)}{3} = +\frac{8}{3}$$

7. Oxidation state of chromium in CrO_5: CrO_5 has butterfly structure having two peroxo bonds



Peroxo oxygen has (−1) oxidation state.

Let oxidation state of chromium be 'x'.

$$x + 4(-1) + (-2) = 0$$

$$x = +6$$

8. Oxidation state of chlorine in bleaching powder: Bleaching powder has two chlorine atoms having different oxidation states.

Ca^{2+}	$(OCl)^-$	Cl^-
	(hypochloride ion)	(chloride ion)
	Chlorine in +1 state	Chlorine in −1 state

9. Fractional values of oxidation numbers are possible as in $Na_2S_4O_6$, Fe_3O_4, N_3H, etc.

$Na_2S_4O_6$

$$2 \times 1 + 4x + 6(-2) = 0$$
$$2 + 4x - 12 = 0$$
$$4x = +10$$
$$x = +\frac{10}{4} = +2.5$$

Oxidation number of S is + 2.5

Fe_3O_4

$$3 \times x + 4(-2) = 0$$
$$3x - 8 = 0$$
$$3x = 8$$
$$x = +\frac{8}{3} \text{ or } +2\frac{2}{3}$$

Oxidation number of iron is $+2\frac{2}{3}$

N_3H

$$3x + 1 = 0$$
$$3x = -1$$
$$x = -1/3$$

Oxidation number of nitrogen is −1/3

10. Oxidation state of carbon and nitrogen in HCN and HNC: We should take into consideration the following fundamental aspects of bonding while counting the oxidation state of covalently bonded molecules:

(a) Single covalent bond contributes one unit for oxidation number.

(b) Negative oxidation number is assigned to more electronegative atom and positive oxidation number to less electronegative atom.

(c) Coordinate bond is represented by an arrow from donor atom to acceptor atom.

$$\underset{\text{Donor}}{A} \longrightarrow \underset{\text{Acceptor}}{B}$$

If donor atom is less electronegative and acceptor is more, then + 2 state is given to donor and –2 state is given to acceptor.

But it should be noted that if the donor is more electronegative than the acceptor, then contribution of coordinate bond for both atoms regarding oxidation state is neglected, *e.g.*,

(i) $$H—C\equiv N$$

$$+1+a-3=0$$

$$a=+2$$

Carbon is in +2 state and nitrogen is in – 3 state. Each bond contributes –1 state to more electronegative atom.

(ii) $$H—N\equiv C$$

Oxidation state of H = + 1

Oxidation state of nitrogen = (–1) + (–2) + (0) = – 3

Covalent bond with hydrogen contributes (–1) and covalent bond with carbon contributes (–2) and there is zero contribution of coordinate bond. Let the oxidation state of carbon be 'x'.

$$+1-3+x=0;\ x=+2$$

11. $Fe_{0.94}O$ (Oxidation state of iron is to be determined):

$$0.94x-2=0$$

$$x=2/0.94=200/94$$

12. $NH_2—NH_2$ (Oxidation state of nitrogen is to be determined):

$$2x+4=0$$

$$x=-2$$

13. KI_3 (Oxidation state of iodine is to be determined):

$$+1+3x=0$$

$$x=-1/3$$

KI_3 is mixture of $\overset{+1}{K}\,\overset{-1}{I}$ and $\overset{0}{I_2}$. Thus, two iodine atoms lie in zero state and one lies in –1 state.

14. $Na_2[Fe(CN)_5NO]$: In iron complex NO lies in NO^+ state; thus oxidation state of 'Fe' may be determined as:

$$+2+x-5+1=0$$

$$x=+2$$

15. $[Fe(NO)(H_2O)_5]SO_4$:

$$x+1+5(0)-2=0$$

$$x=+1$$

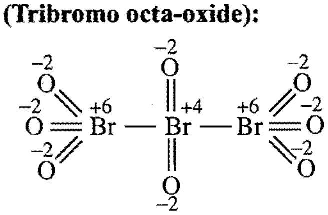
16. NOCl or $Cl—N=O$:

Oxidation state of chlorine = – 1

Oxidation state of oxygen = – 2

Thus, Oxidation state of nitrogen

17. Br_3O_8 (Tribromo octa-oxide):



$$\text{Average oxidation state}=\frac{(+6)+(4)+(+6)}{3}=\frac{16}{3}$$

18. C_3O_2 (Carbon sub-oxide):

$$\overset{-2}{O}=\overset{+2}{C}=\overset{0}{C}=\overset{+2}{C}=\overset{-2}{O}$$

$$\text{Average oxidation state}=\frac{+4}{3}.$$

11.7 OXIDATION NUMBERS (States) IN DIFFERENT TYPES OF ELEMENTS

Zero group elements have zero oxidation number (state) as they do not show chemical activity while other elements have at least two oxidation states: zero when they exist in free state and positive or negative when they exist in compounds. Many elements show different oxidation states in different compounds. In the case of representative elements, the highest positive oxidation number (state) of an element is the same as its group number while the highest negative oxidation state is equal to (8 – group number) with negative sign with a few exceptions.

(i) Alkali metals (IA) show uniformly +1 oxidation state, as they have ns^1 configuration and have only a tendency to lose this electron.

(ii) Alkaline earth metals (IIA) show a common oxidation state of +2 as they have ns^2 configuration.

(iii) Elements of group IIIA have ns^2np^1 outer shell configuration, suggesting +1 and +3 oxidation states corresponding to use of np or $ns\,np$ electrons.

(iv) Elements of group IVA have ns^2np^2 outer shell configuration. They show oxidation states +4 (maximum) and – 4 (minimum). However, Sn and Pb show either +2 or +4 oxidation states being metallic in nature.

(v) VB elements have outer shell configuration ns^2np^3. They show oxidation states between +5 and –3.

(vi) The elements of VIA (with the exception of oxygen) show maximum oxidation state +6 and minimum oxidation state –2.

(vii) The elements of VIIA (with the exception of fluorine) show maximum +7 and minimum –1 oxidation state.

(viii) Transition metals exhibit a large number of oxidation states due to involvement of $(n-1)\,d$ electrons besides ns electrons.

The most common oxidation states of the representative elements are shown in the following table:

Group	Outer shell configuration	Common oxidation numbers (states) except zero in free state
IA	ns^1	+ 1
IIA	ns^2	+ 2
IIIA	ns^2np^1	+ 3, + 1
IVA	ns^2np^2	+ 4, + 3, + 2, + 1, – 1, – 2, – 3, – 4
VA	ns^2np^3	+ 5, + 3, + 1, – 1, – 3
VIA	ns^2np^4	+ 6, + 4, + 2, – 2
VIIA	ns^2np^5	+ 7, + 5, + 3, + 1, – 1

11.8 VALENCY AND OXIDATION NUMBER

Valency of an element means the power or capacity of the element to combine with other elements. The valency of an element is numerically equal to the number of hydrogen atoms or chlorine atoms or twice the number of oxygen atoms that combine with one atom of that element. It is also equal to the number of electrons lost or accepted or shared by the atom of an element. In every case valency of an element is a pure number and has no plus or minus sign associated with it, while oxidation number (state) is an arbitrary number which can have positive, negative, zero or even fractional value. For example, in the following compounds of carbon, the oxidation number varies from – 4 to + 4 but valency of carbon is 4 in all the compounds:

Compound	CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
Ox.no. of carbon	-4	-2	0	$+2$	$+4$

Thus, valency and oxidation number concepts are different. In some cases (mainly in the case of electrovalent compounds), valency and oxidation number are the same but in other cases they may have different values. Points of difference between the two have been tabulated below:

Valency	Oxidation number
1. It is the combining capacity of the element. No plus or minus sign is attached to it.	Ox.no. is the charge (real or imaginary) present on the atom of the element when it is in combination. It may have plus or minus sign.
2. Valency of an element is usually fixed.	Ox.no. of an element may have different values. It depends on the nature of the compound in which it is present.
3. Valency is always a whole number.	Ox.no. of the element may be a whole number or fractional.
4. Valency of the element is never zero except of noble gases.	Ox.no. of the element may be zero.

Term	Oxidation number
Oxidation	Increases
Reduction	Decreases
Oxidising agent	Decreases
Reducing agent	Increases

Example 12. *In the following reactions, identify the species oxidised, the species reduced, the oxidising agent and the reducing agent:*

(a) $4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2$

(b) $SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2$

(c) $2H^+ + Mg = Mg^{2+} + H_2$

(d) $H_2SO_4 + 2H_2S = 3S + 3H_2O$

Solution: (a) $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$

Writing the oxidation numbers on various atoms,

$$\overset{+4\ -2}{MnO_2} + \overset{+1\ -1}{4HCl} = \overset{+2\ -1}{MnCl_2} + \overset{0}{Cl_2} + \overset{+1\ -2}{2H_2O}$$

Ox.no. of Mn changes from +4 to +2, *i.e.*, decrease in oxidation number. MnO_2 is thus reduced. It acts as an oxidising agent. Ox.no. of Cl changes from –1 to 0, *i.e.*, increase in oxidation number. HCl is thus oxidised. It acts as a reducing agent.

(b) $SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2$

Writing the oxidation numbers on various atoms,

$$\overset{+2\ -1}{SnCl_2} + \overset{+3\ -1}{2FeCl_3} = \overset{+4\ -1}{SnCl_4} + \overset{+2\ -1}{2FeCl_2}$$

Ox.no. of Sn changes from +2 to +4, *i.e.*, increase in oxidation number. $SnCl_2$ is thus oxidised or it acts as a reducing agent.

Ox.no. of Fe changes from +3 to +2, *i.e.*, decrease in oxidation number. $FeCl_3$ is thus reduced or it acts as an oxidising agent.

(c) $Mg + 2H^+ \longrightarrow Mg^{2+} + H_2$

Writing oxidation numbers of various atoms,

Decrease

$$\overset{0}{Mg} + \overset{+1}{2H^+} \longrightarrow \overset{(+2)}{Mg^{2+}} + \overset{0}{H_2}$$

Increase

Mg is oxidised, *i.e.*, it acts as a reducing agent. H^+ is reduced, *i.e.*, it acts as an oxidising agent.

(d) $H_2SO_3 + 2H_2S = 3S + 3H_2O$

Writing oxidation numbers on various atoms,

Increase

$$\overset{+1\ +4-2}{H_2SO_3} + \overset{+1\ -2}{2H_2S} \longrightarrow \overset{0}{3S} + \overset{+1\ -2}{3H_2O}$$

Decrease

H_2SO_3 is reduced, *i.e.*, it acts as oxidising agent. H_2S is Oxidised, *i.e.*, it acts as reducing agent.

Example 13. *Which one of the following reactions is a redox reaction?*

(a) $CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$

(b) $Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2NaCl$

(c) $SO_2 + H_2O \longrightarrow H_2SO_3$

(d) $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

Solution: The reaction in which change in oxidation numbers of some of the atoms takes place is termed as a redox reaction.

(a) $\overset{+2+6-2}{CuSO_4} + \overset{-3+1}{4NH_3} \longrightarrow \overset{+2\ -3-1}{[Cu(NH_3)_4]}\overset{+6-2}{SO_4}$

No change in oxidation number of any of the atoms.

(b) $\overset{+1\ +6\ -2}{Na_2SO_4} + \overset{+2\ -1}{BaCl_2} \longrightarrow \overset{+2\ +6-2}{BaSO_4} + \overset{+1\ -1}{2NaCl}$

No change in oxidation number of any one of the atoms.

(c) $\overset{+4-2}{SO_2} + \overset{+1\ -2}{H_2O} \longrightarrow \overset{+1\ +4-2}{H_2SO_3}$

No change in oxidation number of any one of the atoms.

(d) $\overset{+2+6-2}{2CuSO_4} + \overset{+1-1}{4KI} \longrightarrow \overset{+1\ -1}{Cu_2I_2} + \overset{+1\ +6-2}{2K_2SO_4} + \overset{0}{I_2}$

Oxidation number of Cu decreases from +2 to +1 and oxidation number of iodine increases from −1 to 0.

Thus, out of the above four reactions, the reaction (d) is a redox reaction.

Example 14. *Explain why HNO_3 acts only as oxidising agent while HNO_2 can act both as a reducing agent and an oxidising agent?*

Solution: Nitrogen can have oxidation numbers from −3 to +5. The oxidation number of nitrogen in HNO_3 is +5. Thus, increase in oxidation number beyond +5 cannot occur. Hence, HNO_3 cannot act as reducing agent. The oxidation number of nitrogen in HNO_3 can only decrease; thus it acts as an oxidising agent. In HNO_2, the oxidation number of nitrogen is +3. Thus, it can increase or decrease within the range −3 to +5. Hence, it can act as an oxidising as well as a reducing agent.

11.9 BALANCING OXIDATION-REDUCTION REACTIONS BY OXIDATION NUMBER METHOD

In a balanced redox reaction, total increase in oxidation number must be equal to the total decrease in oxidation number. This equivalence provides the basis for balancing redox reactions. This method is applicable to both molecular and ionic equations. The general procedure involves the following steps:

(i) Write the skeleton equation (if not given, frame it) representing the chemical change.

(ii) Assign oxidation numbers to the atoms in the equation and find out which atoms are undergoing oxidation and reduction. Write separate equations for the atoms undergoing oxidation and reduction.

(iii) Find the change in oxidation number in each equation. Make the change equal in both the equations by multiplying with suitable integers. Add both the equations.

(iv) Complete the balancing by inspection. First balance those substances which have undergone change in oxidation number and then other atoms except hydrogen and oxygen. Finally balance hydrogen and oxygen by putting H_2O molecules wherever needed.
The final balanced equation should be checked to ensure that there are as many atoms of each element on the right as there are on the left.

(v) In ionic equations the net charges on both sides of the equation must be exactly the same. Use H^+ ion/ions in acidic reactions and OH^- ion/ions in basic reactions to balance the charge and number of hydrogen and oxygen atoms.

The following examples illustrate the above rules:

Example 15. *Balance the following equation by oxidation number method:*

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

Solution: Writing the oxidation numbers of all the atoms.

$$\overset{0}{Cu} + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \longrightarrow \overset{+2}{Cu}(\overset{+5}{N}\overset{-2}{O_3})_2 + \overset{+4}{N}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}$$

Change in Ox.no. has occurred in copper and nitrogen.

$$\overset{0}{Cu} \longrightarrow \overset{+2}{Cu}(NO_3)_2 \quad \text{... (i)}$$

$$H\overset{+5}{N}O_3 \longrightarrow \overset{+4}{N}O_2 \quad \text{... (ii)}$$

Increase in Ox.no. of copper = 2 units per molecule Cu

Decrease in Ox. no. of nitrogen = 1 unit per molecule HNO_3

To make increase and decrease equal, eq. (ii) is multiplied by 2.

$$Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

Balancing nitrate ions, hydrogen and oxygen, the following equation is obtained:

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

This is the balanced equation.

SOME SOLVED EXAMPLES

Example 16. *Balance the following equation by oxidation number method:*

$$K_2Cr_2O_7 + FeSO_4 + H_2SO_4 = Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

Solution: Writing oxidation numbers of all the atoms.

$$\overset{+2}{K_2}\overset{+6}{Cr_2}\overset{-2}{O_7} + \overset{+2}{Fe}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4} = \overset{+3}{Cr_2}(\overset{+6}{S}\overset{-2}{O_4})_3 + \overset{+3}{Fe_2}(\overset{+6}{S}\overset{-2}{O_4})_3 + \overset{+1}{K_2}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{-2}{O}$$

Change in Ox.no. has occurred in chromium and iron.

$$K_2\overset{+6}{Cr_2}O_7 \longrightarrow \overset{+3}{Cr_2}(SO_4)_3 \quad \text{... (i)}$$

$$\overset{+2}{Fe}SO_4 \longrightarrow \overset{+3}{Fe_2}(SO_4)_3 \quad \text{... (ii)}$$

Decrease in Ox.no. of Cr per molecule

$$= (2 \times 6 - 2 \times 3) = 6 \text{ units}$$

Increase in Ox. no. of Fe per molecule = 1 unit

Hence, eq. (ii) should be multiplied by 6,

$$K_2Cr_2O_7 + 6FeSO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3$$

To balance sulphate ions and potassium ions, 7 molecules of H_2SO_4 are needed.

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4$$

To balance hydrogen and oxygen, $7H_2O$ should be added on RHS. Hence, balanced equation is,

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

Example 17. *Balance the following equation by oxidation number method:*

$$K_2Cr_2O_7 + HCl \longrightarrow KCl + CrCl_3 + H_2O + Cl_2$$

Solution: Writing the oxidation numbers of all the atoms.

$$\overset{+1}{K_2}\overset{+6}{Cr_2}\overset{-2}{O_7} + \overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+1}{K}\overset{-1}{Cl} + \overset{+3}{Cr}\overset{-1}{Cl_3} + \overset{+1}{H_2}\overset{-2}{O} + \overset{0}{Cl_2}$$

The Ox.no. of Cr has decreased while that of chlorine has increased.

$$K_2\overset{+6}{Cr_2}O_7 \longrightarrow 2\overset{+3}{Cr}Cl_3 \quad \text{... (i)}$$

$$H\overset{-1}{Cl} \longrightarrow \overset{0}{Cl} \quad \text{... (ii)}$$

Decrease in Ox.no. of Cr = 6 units per molecule $K_2Cr_2O_7$

Increase in Ox. no. of Cl = 1 unit per molecule HCl

Eq. (ii) is multiplied by 6.

$$K_2Cr_2O_7 + 6HCl \longrightarrow 2CrCl_3 + 3Cl_2$$

To balance chlorine and potassium, 14 molecules of HCl are required.

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2CrCl_3 + 3Cl_2 + 2KCl$$

To balance hydrogen and oxygen, $7H_2O$ are added to RHS. Hence, the balanced equation is,

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

Example 18. *Balance the following equation by oxidation number method:*

$$NaIO_3 + NaHSO_3 \longrightarrow Na_2SO_4 + NaHSO_4 + I_2 + H_2O$$

Solution: Writing oxidation numbers of all the atoms.

$$\overset{+1}{Na}\,\overset{+5}{I}\,\overset{-2}{O_3} + \overset{+1}{Na}\,\overset{+1}{H}\,\overset{+4}{S}\,\overset{-2}{O_3} \longrightarrow \overset{+1}{Na_2}\,\overset{+6}{S}\,\overset{-2}{O_4} + \overset{+1}{Na}\,\overset{+1}{H}\,\overset{+6}{S}\,\overset{-2}{O_4} + \overset{0}{I_2} + \overset{+1}{H_2}\overset{-2}{O}$$

The oxidation no. of I has decreased while that of S has increased.

$$Na\overset{+5}{I}O_3 \longrightarrow \overset{0}{I} \qquad \text{... (i)}$$

$$NaH\overset{+4}{S}O_3 \longrightarrow NaH\overset{+6}{S}O_4 \qquad \text{... (ii)}$$

Decrease in Ox.no. of I = 5 units per molecule $NaIO_3$

Increase in Ox.no. of S = 2 units per molecule $NaHSO_3$

Eq. (i) is multiplied by 2 and eq. (ii) is multiplied by 5 as to make decrease and increase equal.

$$2NaIO_3 + 5NaHSO_3 \longrightarrow I_2 + 3NaHSO_4 + 2Na_2SO_4$$

To balance hydrogen and oxygen, one H_2O molecule should be added on RHS. Hence, the balanced equation is

$$2NaIO_3 + 5NaHSO_3 \rightarrow I_2 + 3NaHSO_4 + 2Na_2SO_4 + H_2O$$

Example 19. *Balance the following equation by oxidation number method:*

$$I_2 + NaOH \longrightarrow NaIO_3 + NaI + H_2O$$

Solution: Writing oxidation numbers of all the atoms,

$$\overset{0}{I_2} + \overset{+1}{Na}\overset{-2}{O}\overset{+1}{H} \longrightarrow \overset{+1}{Na}\overset{+5}{I}\overset{-2}{O_3} + \overset{+1}{Na}\overset{-1}{I} + \overset{+1}{H_2}\overset{-2}{O}$$

The Ox.no. of iodine has increased as well as decreased.

$$\overset{0}{I} \longrightarrow Na\overset{+5}{I}O_3 \qquad \text{... (i)}$$

$$\overset{0}{I} \longrightarrow Na\overset{-1}{I} \qquad \text{... (ii)}$$

Increase in Ox.no. of I = 5 units per I atom

Decrease in Ox.no. of I = 1 unit per I atom

Eq. (ii) should be multiplied by 5 as to make increase and decrease equal.

$$3I_2 \longrightarrow NaIO_3 + 5NaI$$

To balance Na, 6 molecules of NaOH should be added on LHS.

$$3I_2 + 6NaOH \longrightarrow NaIO_3 + 5NaI$$

To balance hydrogen and oxygen, $3H_2O$ should be added on RHS. Hence, the balanced equation is

$$3I_2 + 6NaOH \longrightarrow NaIO_3 + 5NaI + 3H_2O$$

Example 20. *Balance the following equation by oxidation number method:*

$$PbS + H_2O_2 \longrightarrow PbSO_4 + H_2O$$

Solution: Writing oxidation numbers of all the atoms,

$$\overset{+2}{Pb}\,\overset{-2}{S} + \overset{+1}{H_2}\overset{-1}{O_2} \longrightarrow \overset{+2}{Pb}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{-2}{O}$$

The oxidation number of S has increased and O has decreased.

$$Pb\overset{-2}{S} \longrightarrow Pb\overset{+6}{S}O_4 \qquad \text{... (i)}$$

$$H_2\overset{-1}{O_2} \longrightarrow H_2\overset{-2}{O} \qquad \text{... (ii)}$$

Increase in Ox.no. of S = 8 units per PbS molecule

Decrease in Ox.no. of O = 1 unit per $\frac{1}{2}H_2O_2$ molecule

= 2 units per H_2O_2 molecule

Multiplying eq. (ii) by 4 as to make increase and decrease equal.

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

This is the balanced equation.

Example 21. *Balance the following equation by oxidation number method:*

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

Solution: Writing oxidation numbers of all the atoms,

$$\overset{0}{Zn} + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \longrightarrow \overset{+2}{Zn}(\overset{+5}{N}\overset{-2}{O_3})_2 + \overset{-3}{N}\overset{+1}{H_4}\overset{+5}{N}\overset{-2}{O_3} + \overset{+1}{H_2}\overset{-2}{O}$$

The oxidation numbers of Zn and N have changed.

$$\overset{0}{Zn} \longrightarrow \overset{+2}{Zn}(NO_3)_2 \qquad \text{... (i)}$$

$$H\overset{+5}{N}O_3 \longrightarrow \overset{-3}{N}H_4NO_3 \qquad \text{... (ii)}$$

Increase in Ox.no. of Zn = 2 units per Zn atom

Decrease in Ox.no. of N = 8 units per HNO_3 molecule

Eq. (i) should be multiplied by 4

$$4Zn + HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3$$

To balance nitrogen, 9 molecules of HNO_3 should be added on LHS.

To balance hydrogen and oxygen, $3H_2O$ molecules should be added on RHS. Hence, the balanced equation is

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Example 22. *Balance the following equation by oxidation number method:*

$$HgS + HCl + HNO_3 \longrightarrow H_2HgCl_4 + NO + S + H_2O$$

Solution: Writing the oxidation numbers of the atoms.

$$\overset{+2}{Hg}\overset{-2}{S} + \overset{+1}{H}\overset{-1}{Cl} + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \longrightarrow \overset{+1}{H_2}\overset{+2}{Hg}\overset{-1}{Cl_4} + \overset{+2}{N}\overset{-2}{O} + \overset{0}{S} + \overset{+1}{H_2}\overset{-2}{O}$$

The oxidation numbers of S and N have changed.

$$Hg\overset{-2}{S} \longrightarrow \overset{0}{S} \qquad \text{... (i)}$$

$$H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{N}O \qquad \text{... (ii)}$$

Increase in Ox.no. of S = 2 units per HgS molecule

Decrease in Ox. no. of N = 3 units per HNO_3 molecule

Multiplying eq. (i) by 3 and eq. (ii) by 2 as to make increase and decrease equal

$$3HgS + 2HNO_3 \longrightarrow 3S + 2NO$$

Balancing Hg and chlorine,

$$3HgS + 2HNO_3 + 12HCl \longrightarrow 3H_2HgCl_4 + 3S + 2NO$$

To balance hydrogen and oxygen, $4H_2O$ molecules are added on RHS. Hence, the balanced equation is

$$3HgS + 2HNO_3 + 12HCl \rightarrow 3H_2HgCl_4 + 3S + 2NO + 4H_2O$$

Example 23. *Balance the following equation by oxidation number method:*

$$Cl_2 + IO_3^- + OH^- \longrightarrow IO_4^- + Cl^- + H_2O$$

Solution: Writing oxidation numbers of all atoms,

$$\overset{0}{Cl_2} + \overset{+5-2}{IO_3^-} + \overset{-2\ +1}{OH^-} \longrightarrow \overset{+7-2}{IO_4^-} + \overset{-1}{Cl^-} + \overset{+1\ -2}{H_2O}$$

Oxidation numbers of Cl and I have changed.

$$\overset{0}{Cl_2} \longrightarrow \overset{-1}{2Cl^-} \quad \text{... (i)}$$

$$\overset{+5}{IO_3^-} \longrightarrow \overset{+7}{IO_4^-} \quad \text{... (ii)}$$

Decrease in Ox.no. of Cl = 2 units per Cl_2 molecule

Increase in Ox. no. of I = 2 units per IO_3^- molecule

$$Cl_2 + IO_3^- \longrightarrow IO_4^- + 2Cl^-$$

To balance oxygen $2OH^-$ ions be added on LHS and one H_2O molecule on RHS. Hence, the balanced equation is

$$Cl_2 + IO_3^- + 2OH^- \longrightarrow IO_4^- + 2Cl^- + H_2O$$

Example 24. *Balance the following equation by oxidation number method:*

$$Al + KMnO_4 + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + K_2SO_4 + MnSO_4 + H_2O$$

Solution: Writing oxidation numbers of all atoms,

$$\overset{0}{Al} + \overset{+1\ +7-2}{KMnO_4} + \overset{+1\ +6-2}{H_2SO_4} \longrightarrow \overset{+3\ +6-2}{Al_2(SO_4)_3} + \overset{+1\ +6-2}{K_2SO_4} + \overset{+2+6-2}{MnSO_4} + \overset{+1\ -2}{H_2O}$$

The oxidation numbers of Al and Mn have changed

$$\overset{0}{Al} \longrightarrow \overset{+3}{Al_2(SO_4)_3} \quad \text{... (i)}$$

$$\overset{+7}{KMnO_4} \longrightarrow \overset{+2}{MnSO_4} \quad \text{... (ii)}$$

Increase in Ox.no. of Al = 3 units per Al atom

= 6 units per $Al_2(SO_4)_3$ molecule

Decrease in Ox. no. of Mn = 5 units per $KMnO_4$ molecule

Multiply eq. (i) by 10 and eq. (ii) by 6 as to make increase and decrease equal

$$10Al + 6KMnO_4 \longrightarrow 5Al_2(SO_4)_3 + 6MnSO_4 + 3K_2SO_4$$

To balance SO_4^{2-} ions, $24H_2SO_4$ molecules be added on LHS.

$$10Al + 6KMnO_4 + 24H_2SO_4 \longrightarrow 5Al_2(SO_4)_3 + 6MnSO_4 + 3K_2SO_4$$

To balance hydrogen and oxygen, 24 H_2O molecules be added on RHS. Hence, the balanced equation is

$$10Al + 6KMnO_4 + 24H_2SO_4 \longrightarrow 5Al_2(SO_4)_3 + 6MnSO_4 + 3K_2SO_4 + 24H_2O$$

11.10 DISPROPORTIONATION AND OXIDATION-REDUCTION

One and the same substance may act simultaneously as an oxidising agent and as a reducing agent with the result that a part of it gets oxidised to a higher state and rest of it is reduced to lower state of oxidation. Such a reaction, in which a substance undergoes simultaneous oxidation and reduction is called disproportionation and the substance is said to **disproportionate.**

The following are some of the examples of disproportionation:

Increase

(a) $\overset{-1}{H_2O_2} + \overset{-1}{H_2O_2} \longrightarrow \overset{-2}{H_2O} + \overset{0}{O_2}$

Decrease

Decrease

(b) $\overset{+5}{4KClO_3} \longrightarrow \overset{+7}{3KClO_4} + \overset{-1}{KCl}$

Increase

Decrease

(c) $\overset{0}{4P} + 3NaOH + 3H_2O \longrightarrow \overset{+1}{3NaH_2PO_2} + \overset{-3}{PH_3}$

Increase

Decrease

(d) $\overset{0}{3Cl_2} + \underset{\text{(conc.)}}{6NaOH} \xrightarrow{\text{Hot}} \overset{-1}{5NaCl} + \overset{+5}{NaClO_3} + 3H_2O$

Increase

(e) Oxidation state of chlorine lies between –1 to +7; thus out of ClO^-, ClO_2^-, ClO_3^-, ClO_4^-; ClO_4^- does not undergo disproportionation because in this oxidation state of chlorine is highest, *i.e.*, +7. Disproportionation of the other oxoanions are:

$$\overset{+1}{3ClO^-} \longrightarrow \overset{-1}{2Cl} + \overset{+5}{ClO_3^-}$$

$$\overset{+3}{6ClO_2^-} \longrightarrow \overset{+5}{4ClO_3^-} + \overset{-1}{2Cl^-}$$

$$\overset{+5}{4ClO_3^-} \longrightarrow \overset{-1}{Cl^-} + \overset{+7}{3ClO_4^-}$$

Equivalent mass of substance undergoing disproportionation can be calculated by n-factor method:

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{n\text{-factor}}$$

$$n\text{-factor} = \frac{n_1 \times n_2}{n_1 + n_2}$$

Example :

$n = 2$ (loss of two electron)

$$3\overset{+1}{H_3PO_2} \longrightarrow \overset{-3}{PH_3} + 2\overset{+3}{H_3PO_3}$$

$n = 4$ (gain of four electrons)

$$n\text{-factor} = \frac{4 \times 2}{4 + 2} = \frac{4}{3}$$

$$\text{Equivalent mass of } H_3PO_2 = \frac{\text{Molecular mass}}{n\text{-factor}}$$

$$= \frac{m}{4/3} = \frac{3m}{4}$$

11.11 AUTOXIDATION

Turpentine and numerous other unsaturated compounds, phosphorus and certain metals like Zn and Pb can absorb oxygen from the air in presence of water. The water is oxidised to hydrogen peroxide. This phenomenon of formation of H_2O_2 by the oxidation of H_2O is known as **autoxidation.** The substance such as turpentine or phosphorus or lead which can activate the oxygen is called **activator.** The activator is supposed to first combine with oxygen to form an addition compound, which acts as an **autoxidator** and reacts with water or some other acceptor so as to oxidise the latter. For example:

$$\underset{\text{(Activator)}}{Pb} + O_2 \longrightarrow \underset{\text{(Autoxidator)}}{PbO_2}$$

$$PbO_2 + \underset{\text{(Acceptor)}}{H_2O} \longrightarrow PbO + H_2O_2$$

The turpentine or other unsaturated compounds which act as activators are supposed to take-up oxygen molecule at the double bond position to form unstable peroxide called moloxide, which then gives up the oxygen to water molecule or any other acceptor.

$$RCH{=}CHR + O_2 \longrightarrow \begin{matrix} RHC & — & CHR \\ | & & | \\ O & — & O \end{matrix}$$

$$\begin{matrix} RHC & — & CHR \\ | & & | \\ O & — & O \end{matrix} + 2H_2O \longrightarrow RCH{=}CHR + 2H_2O_2$$

$$2KI + H_2O_2 \longrightarrow 2KOH + I_2$$

The evolution of iodine from KI solution in presence of turpentine can be confirmed with starch solution which turns blue.

With this concept, the phenomenon of induced oxidation can also be explained. Na_2SO_3 solution is oxidised by air but Na_3AsO_3 solution is not oxidised by air. If mixture of both is taken, it is observed that both are oxidised. This is induced oxidation.

$$Na_2SO_3 + O_2 \longrightarrow \underset{\text{Moloxide}}{Na_2SO_5}$$

$$Na_2SO_5 + Na_3AsO_3 \longrightarrow Na_3AsO_4 + Na_2SO_4$$

$$\overline{Na_2SO_3 + Na_3AsO_3 + O_2 \longrightarrow Na_2SO_4 + Na_3AsO_4}$$

11.12 FORMAL CHARGE

In polyatomic molecule or ion the net charge is possessed by the ion or molecule as a whole and not by particular atom. For certain purpose formal charge (F.C.) is assigned to each atom.

Formal charge (F.C.) on an atom in a Lewis structure = Total number of valence electrons in the free atom (V) − Total number of non-bonding (lone pair) electrons (N) − $\frac{1}{2}$ × Total number of bonding (shared electrons) (B)

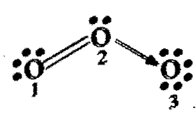
The formal charge of atom in a polyatomic ion/molecule is defined as:

$$\text{F.C.} = V - N - \frac{1}{2}B$$

The formal charge is the difference between the number of valence electrons in an isolated (i.e., free) atom and the number of electrons assigned to that atom, in its dot structure.

Let us calculate formal charge on each atom of ozone:

Formal charge at oxygen number 1



$$V = 6, N = 4, B = 4$$

$$\text{F.C.} = V - N - \frac{1}{2}B$$

$$= 6 - 4 - \frac{1}{2} \times 4 = 0$$

Formal charge at oxygen number 2

$$V = 6, N = 2, B = 6$$

$$\text{F.C.} = V - N - \frac{1}{2}B$$

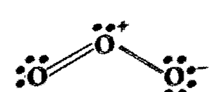
$$= 6 - 2 - \frac{1}{2} \times 6 = 1$$

Formal charge at oxygen number 3

$$V = 6, N = 6, B = 2$$

$$\text{F.C.} = 6 - 6 - \frac{1}{2} \times 2 = -1$$

On the basis of formal charge, the structure of ozone may be drawn as,



we must note that formal charges do not indicate real charge separation within the molecule.

Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a compound. The lowest energy structure means the structure with the smallest formal charges on each atom of the compound. Formal charge is based on the concept that electron pairs are shared equally by neighbouring atoms.

Note: (1) A Lewis dot structure for a molecule is preferable when all formal charges are zero.

(2) In a dot structure adjacent formal charges should be zero or of opposite sign.

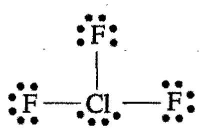
(3) Among the several Lewis dot structure for same species, the structure with negative formal charges on more electronegative atom is preferred.

Let us consider thiocyanate:

	Formal charges N	C	S	Total
Structure I ($:\ddot{N}=C=\ddot{S}:$)$^-$	−1	0	0	−1
Structure II ($:\ddot{C}=N=\ddot{S}:$)$^-$	+1	−2	0	−1
Structure III ($:\ddot{C}=S=\ddot{N}:$)$^-$	−1	−2	+2	−1

Structure III will be correct structure because each atom has non-zero formal charge in the lowest energy state.

Some illustrations of formal charge calculation:

1. 

Formal charge at chlorine:

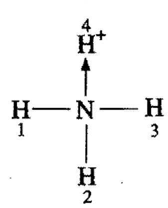
$$V = 7, N = 4, B = 6$$

$$\text{F.C.} = 7 - 4 - \frac{1}{2} \times 6 = 0$$

Formal charge at fluorine:

$$V = 7, N = 6, B = 2$$

$$\text{F.C.} = 7 - 6 - \frac{1}{2} \times 2 = 0$$

2. 

Formal charge at nitrogen:

$$V = 5, N = 0, B = 8$$

$$\text{F.C.} = 5 - 0 - \frac{1}{2} \times 8 = +1$$

Formal charge at hydrogens 1,2,3:

$$V = 1, N = 0, B = 2$$

$$\text{F.C.} = V - N - \frac{1}{2} \times B$$

$$= 1 - 0 - \frac{1}{2} \times 2 = 0$$

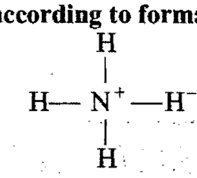
Formal charge at hydrogen number 4:

$$V = 0, N = 0, B = 2$$

$$\text{F.C.} = V - N - \frac{1}{2} \times B$$

$$= 0 - 0 - \frac{1}{2} \times 2 = -1$$

The, structure according to formal charge:



11.13 STOCK NOTATION

In the compounds of metals, the oxidation number is represented by the Roman numeral, placed in parenthesis, after the symbol of the metal in the molecular formula. For example:

(i) Cu_2O (Cuprous oxide, oxidation state of copper = +1); its stock notation will be Cu_2(I)O.

(ii) CuO (Cupric oxide, oxidation state of copper = +2); its stock notation will be Cu(II)O.

The stock notation is not used in case of compounds formed by non-metals.

Stock Notation of Some Compounds

Formula of compound	Chemical name of compound	Oxidation state of metal	Stock notation
$HAuCl_4$	Chloroauric acid	Au (+3)	HAu (III) Cl_4
Tl_2O	Thallous oxide	Tl (+1)	Tl_2 (I) O
FeO	Ferrous oxide	Fe (+2)	Fe (II) O
Fe_2O_3	Ferric oxide	Fe (+3)	Fe_2 (III) O_3
Cr_2O_3	Chromic oxide	Cr (+3)	Cr_2 (III) O_3
CuI	Cuprous iodide	Cu (+1)	Cu (I) I
MnO	Mangnese oxide	Mn (+2)	Mn (II) O
MnO_2	Mangnese dioxide	Mn (+4)	Mn (IV) O_2
$K_2Cr_2O_7$	Potassium dichromate	Cr (+6)	Kr Cr_2 (VI) O_7
$KMnO_4$	Potassium permanganate	Mn (+7)	K Mn (VII) O_4
V_2O_5	Vanadium pentoxide	V (+5)	V_2 (V) O_5
$FeSO_4$	Ferrous sulphate	Fe (+2)	Fe_2 (II) SO_4
$Fe_2(SO_4)_3$	Ferric sulphate	Fe (+3)	Fe_2 (III) $(SO_4)_3$
$CuCl_2$	Cupric chloride	Cu (+2)	Cu (II) Cl_2

11.14 STOICHIOMETRY OF REDOX REACTIONS IN SOLUTIONS

Calculations based on chemical equations are known as stoichiometry. A chemical equation is the symbolic representation of a chemical change. It gives the following informations used in solving the numerical problems based on a chemical equation:

(i) It gives the number of moles of the reactants and the products involved in the reaction.

(ii) It gives relative masses of the reactants and products.

(iii) It gives volume of the gaseous reactants and products.

Problems based on chemical equations have also been dealt in Chapter-1. In this section, we will deal with redox reactions only. In the stoichiometry of redox reactions, the chemical equations must be balanced.

Example 25. *Balance the following chemical equation:*

$$H_2O_2 + O_3 \longrightarrow H_2O + O_2$$

Indicating the changes in oxidation numbers of oxygen, find the equivalent weight of H_2O_2 for this reaction. **(West Bengal 2005)**

Solution: $\overset{-1}{H_2O_2} + \overset{0}{O_3} \xrightarrow[\text{Oxidised}]{} \overset{-2}{H_2O} + \overset{0}{O_2}$

Balanced equation will be:

$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

Equivalent mass of $H_2O_2 = \frac{34}{2} = 17$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Molecular and ionic equations: When the reactants and products involved in a chemical change are written in molecular forms in the chemical equation, it is termed as molecular equation. The chemical changes when represented in terms of ions which actually undergo reaction are called ionic equations. The ions which do not undergo any change and equal in number in both reactants and products are termed spectator ions and are not included in the final balanced equations.

$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$ (Molecular equation)

$Ag^+ + Cl^- \longrightarrow AgCl$ (Ionic equation)

[NO_3^- and Na^+ ions are spectator ions.]

2. Oxidation and reduction: Oxidation is a process which involves either of the following:

(i) addition of oxygen,
(ii) removal of hydrogen,
(iii) addition of an electronegative element or group,
(iv) removal of an electropositive element or group,
(v) increase in the valency of an electropositive element,
(vi) loss of one or more electrons by an atom or an ion or a molecule.

Reduction is just reverse of oxidation. It is a process which involves either of the following:

(i) removal of oxygen,
(ii) addition of hydrogen,
(iii) removal of an electronegative element or group,
(iv) addition of an electropositive element or group,
(v) decrease in the valency of electropositive element,
(vi) gain of one or more electrons by an atom or an ion or a molecule.

A substance which undergoes oxidation or gets oxidised acts as a **reducing agent** while a substance which undergoes reduction or gets reduced acts as an **oxidising agent.**

All oxidation-reduction reactions are complimentary of one another and occur simultaneously. Oxidation-reduction reaction is termed **redox reaction.** The word "redox" includes **red + ox; red** means reduction and **ox** means oxidation. In redox reaction one substance undergoes oxidation and the other substance undergoes reduction, *i.e.*, the reaction between a reducing agent and an oxidising agent is termed as redox reaction.

Any material which is capable of accepting electron or electrons acts as an oxidising agent and the material which loses electron or electrons acts as reducing agents.

Loss of electrons → Oxidation

$-e \quad -e \quad -e \quad -e \quad -e \quad -e \quad -e \quad -e$

$\overset{-4}{M} \quad \overset{-3}{M} \quad \overset{-2}{M} \quad \overset{-1}{M} \quad \overset{0}{M} \quad \overset{+1}{M} \quad \overset{+2}{M} \quad \overset{+3}{M} \quad \overset{+4}{M}$

$+e \quad +e \quad +e \quad +e \quad +e \quad +e \quad +e \quad +e$

Reduction ← Gain of electrons

3. Ion electron method for balancing redox reaction: The following steps are followed:

(i) Ionic equation of redox reaction is first written.

(ii) The ionic reaction is split into two half reactions, one for oxidation and the other for reduction.

(iii) Each half reaction is balanced for the number of atoms of each element. For this purpose: (a) First of all atoms other than H and O for each half reaction are balanced using simple multiples. (b) In acidic and neutral mediums, H ions are added to the side deficient in hydrogen and water molecules to the side deficient in oxygen. (c) In alkaline medium, for each excess of oxygen atom, one water molecule is added to the same side and two OH^- ions to the other side. If hydrogen is still unbalanced, one OH^- ion is added for each excess of hydrogen on the same side and one water molecule to the other side.

(iv) Electrons are added to the side deficient in electrons as to equalise the charges on both sides of the half reactions.

(v) Electrons are made equal in both the half reactions by multiplying one or both the half reactions by a suitable number.

(vi) Both the balanced half reactions are added and any term common to both sides is cancelled.

4. Oxidation number or oxidation state: It is defined as the charge (real or imaginary) which an atom appears to have when it is in combination. In the case of electrovalent compounds, the oxidation number of an element or radical is the same as the charge on the ion. The following rules are followed in ascertaining the oxidation number in any type of compounds:

(i) The oxidation number of an atom in free elements is zero no matter how complicated the molecule is.
(ii) The oxidation number of fluorine is always –1.
(iii) The oxidation number of oxygen is –2 in all compounds except in peroxides, super oxides and oxygen fluorides.
(iv) The oxidation number of hydrogen is +1 in all of its compounds except in metallic hydrides. In metallic hydrides, oxidation number of hydrogen is –1.
(v) The oxidation number of an ion is equal to the electrical charge present on it.
(vi) The oxidation number of alkali metals is +1 and that of alkaline earth metals is +2.
(vii) For complex ions, the algebraic sum of oxidation no. of all the atoms is equal to the net charge on the ion.
(viii) In the case of neutral molecules, the algebraic sum of the oxidation numbers of all the atoms present in the molecules is zero.

Oxidation numbers are quite arbitrary. The values may be positive, negative, zero and even fractional. Many elements show different oxidation numbers in different compounds. In the case of representative elements, the highest oxidation number of an element is the same as its group number while highest negative oxidation number is equal to (8-group number) with negative sign with a few exceptions.

IA elements	+1	VA elements	–3 to +5
IIA elements	+2	VIA elements	–2 to +6
IIIA elements	+3, +1	VIIA elements	–1 to +7
IVA elements	–4 to +4		

The valency and oxidation number concepts are different. In some cases (electrovalent compounds), valency and oxidation number are the same but in other cases they have different values. Valency of an element is usually fixed while oxidation number may have different values.

5. Oxidation and reduction in terms of change in oxidation numbers: Oxidation and reduction are defined on the basis of change in oxidation number.

Oxidation is a process in which an atom undergoes algebraic increase in oxidation number and reduction is a process in which an atom undergoes algebraic decrease in oxidation number. In an oxidising agent, there is always decrease in oxidation number and in reducing agent, there is always increase in oxidation number.

6. Balancing oxidation-reduction reactions by oxidation number method:

(i) The skeleton equation of the chemical change is written.
(ii) Oxidation numbers are assigned to atoms in the equation. The atoms in which change in oxidation number has taken place are selected and two half reactions involving oxidation and reduction are selected.
(iii) Change in oxidation numbers in both the equations is made equal by multiplying with suitable integers and then both the equations are added.
(iv) First of all, those substances are balanced which have undergone change in oxidation number and then other atoms except hydrogen and oxygen. Finally hydrogen and oxygen are balanced.

In ionic equations, the net charges on both sides are made equal. H^+ ions in acidic reactions and OH^- ions in basic reactions are used to balance the charge and number of hydrogen and oxygen atoms.

7. Autoxidation: Certain materials such as turpentine, olefinic compounds, phosphorus, metals like zinc and lead, etc., can absorb oxygen from the air in presence of water and the water is converted to hydrogen peroxide. This phenomenon of formation of H_2O_2 by oxidation of H_2O is known as **autoxidation.** The material which absorbs oxygen and activates it, is called the **activator.** The addition compound of activator and oxygen is termed **autoxidator.** This reacts with water or some other acceptor so as to oxidise the latter.

8. Disproportionation: One and the same substance may act simultaneously as an oxidising agent and as a reducing agent with the result that a part of it gets oxidised and rest of it is reduced. This nature of the change is termed **disproportionation.**

Questions

1. Matrix-Match Type Questions

[A] Match the Column-I with Column-II:

Column-I (Compound)	Column-II (Oxidation state)
(a) CrO_5	(p) +6
(b) H_2SO_4	(q) +1
(c) $CaOCl_2$	(r) −1
(d) $(CH_3)_2SO$	(s) 0

[B] Match the Column-I with Column-II:

Column-I (Redox process)	Column-II (n-factor for underlined species)
(a) $\underline{As_2S_3} \rightarrow AsO_3^- + SO_4^{2-}$	(p) 28
(b) $\underline{I_2} \rightarrow I^- + IO_3^-$	(q) 4/3
(c) $\underline{H_3PO_2} \rightarrow PH_3 + 2H_3PO_3$	(r) 1
(d) $\underline{H_3PO_2} + NaOH \rightarrow NaH_2PO_2 + H_2O$	(s) 5/3

[C] Match the Column-I with Column-II:

Column-I (Compound)	Column-II (Oxidation state of nitrogen)
(a) Mg_3N_2	(p) −1
(b) NO	(q) +2
(c) $(N_2H_5)_2SO_4$	(r) −2
(d) NH_2OH	(s) −3

[D] Match the Column-I with Column-II:

Column-I (Compound)	Column-II (Oxidation state of)
(a) CrO_5	(p) Oxygen is −2
(b) $Na_2S_2O_3$	(q) Oxygen is −1
(c) H_2SO_5	(r) Sulphur is +6
(d) $H_2S_2O_7$	(s) Sulphur is +2

[E] Match the Column-I with Column-II:

Column-I	Column-II
(a) $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$	(p) Intermolecular redox reaction
(b) $PbO_2 + H_2O \rightarrow PbO + H_2O_2$	(q) Disproportionation
(c) $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$	(r) Intramolecular redox reaction
(d) $Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$	(s) Metal displacement

2. Indicate which of the substance/ion in the following reactions is an oxidising agent and which is a reducing agent?

(i) $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

(ii) $2Mg + SO_2 \longrightarrow 2MgO + S$

(iii) $2SO_2 + O_2 \longrightarrow 2SO_3$

(iv) $Ca + Cl_2 \longrightarrow CaCl_2$

(v) $Sn^{2+} + 2Hg^{2+} \longrightarrow Hg_2^{2+} + Sn^{4+}$

(vi) $2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$

(vii) $2I^- + H_2O_2 \longrightarrow 2OH^- + I_2$

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

(ix) $SO_2 + 2HNO_3 \longrightarrow H_2SO_4 + 2NO_2$

(x) $SO_2 + Cl_2 + 2H_2O \longrightarrow 2HCl + H_2SO_4$

3. Which substance/ion is oxidised and which substance/ion is reduced in the following reactions?

(i) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

(ii) $H_2S + 2FeCl_3 \longrightarrow 2FeCl_2 + 2HCl + S$

(iii) $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

(iv) $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$

(v) $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

(vi) $3N_2H_4 + 2BrO_3^- \longrightarrow 3N_2 + 2Br^- + 6H_2O$

(vii) $Cl_2 + SO_3^{2-} + H_2O \longrightarrow 2Cl^- + SO_4^{2-} + 2H^+$

(viii) $2I^- + Cl_2 \longrightarrow 2Cl^- + I_2$

4. Arrange the following in the order of:

(a) increasing oxidation number of iodine:
I_2, HI, HIO_4, ICl

(b) increasing oxidation number of chlorine:
Cl_2O_7, Cl_2O, HCl, ClF_3, Cl_2

(c) increasing oxidation number of nitrogen:
NH_3, N_3H, N_2O, NO, N_2O_5

5. Find the oxidation number of :

(i) I in KIO_3

(ii) P in NaH_2PO_4

(iii) P in $P_2O_7^{4-}$

(iv) Fe in $[Fe(CN)_6]^{4-}$

(v) Ni in $[Ni(CN)_6]^{4-}$

(vi) S in $H_2S_2O_8$

(vii) N in NO_3^-

(viii) S in S_2Cl_2

(ix) P in $Mg_2P_2O_7$

(x) Cr in $K_2Cr_2O_7$ (Ranchi 1996)

(xi) Mn in MnO_4^-

(xii) Pt in $[PtCl_6]^{2-}$

(xiii) P in PH_4^+

(xiv) C in $C_{12}H_{22}O_{11}$

(xv) Fe in $Na_2[Fe(CN)_5NO]$

(xvi) Cr in $(NH_4)_2Cr_2O_7$

(xvii) V in $Rb_4Na[HV_{10}O_{28}]$

(xviii) Xe in $BaXeO_6$

(xix) Cl in $Ca(ClO_2)_2$

(xx) Ni in $Ni(CO)_4$

6. (a) Which compound among the following has the lowest oxidation number of Mn?
$KMnO_4$, K_2MnO_4, MnO_2 and Mn_2O_3
(b) Which compound among the following has the highest oxidation number of P?
PH_3, H_3PO_2, PCl_3, H_3PO_4
(c) Which compound among the following has the zero oxidation state of carbon?
CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4
(d) Which compound among the following has the lowest oxidation number of chlorine?
$HClO_4$, $HOCl$, ClF_3, $HClO_3$, HCl

Short Answer Type

7. Balance the following equations by ion electron method:

(i) $MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$ (acidic medium)

(ii) $MnO_4^- + SnO_2^{2-} + H_2O \longrightarrow MnO_2 + SnO_3^{2-} + OH^-$ (alkaline medium)

(iii) $Cu + NO_3^- + 8H^+ \longrightarrow Cu(NO_3)_2 + NO + H_2O$ (acidic medium)

(iv) $Cl_2 + IO_3^- + OH^- \longrightarrow IO_4^- + Cl^- + H_2O$ (alkaline medium)

(v) $I_2 + NaOH \longrightarrow NaIO_3 + NaI + H_2O$ (alkaline medium)

(vi) $Zn + NO_3^- + OH^- \longrightarrow ZnO_2^{2-} + NH_3 + H_2O$ (alkaline medium)

(vii) $Cr(OH)_3 + ClO^- + OH^- \longrightarrow CrO_4^{2-} + Cl^- + H_2O$

[Hint: Half reactions

$$[Cr(OH)_3 + 5OH^- \longrightarrow CrO_4^{2-} + 4H_2O + 3e] \times 2$$
$$[ClO^- + H_2O + 2e \longrightarrow Cl^- + 2OH^-] \times 3$$
$$2Cr(OH)_3 + 4OH^- + 3ClO^- \longrightarrow 2CrO_4^{2-} + 3Cl^- + 5H_2O \text{]}$$

(viii) $As_2S_3 + NO_3^- + H^+ + H_2O \longrightarrow H_3AsO_4 + NO + S$

[Hint: Half reactions

$$[As_2S_3 + 8H_2O \longrightarrow 2H_3AsO_4 + 3S + 10H^+ + 10e] \times 3$$
$$[NO_3^- + 4H^+ + 3e \longrightarrow NO + 2H_2O] \times 10$$
$$3As_2S_3 + 4H_2O + 10NO_3^- + 10H^+ \longrightarrow 6H_3AsO_4 + 9S + 10NO \text{]}$$

(ix) $Zn + H^+ + NO_3^- \longrightarrow Zn^{2+} + NH_4^+ + H_2O$

(x) $P_4 + OH^- + H_2O \longrightarrow H_2PO_2^- + PH_3$

[Hint: Half reactions

$$[P_4 + 8OH^- \longrightarrow 4H_2PO_2^- + 4e] \times 3$$
$$P_4 + 12H_2O + 12e \longrightarrow 4PH_3 + 12OH^-$$
$$4P_4 + 12OH^- + 12H_2O \longrightarrow 12H_2PO_2^- + 4PH_3$$

or $\quad P_4 + 3OH^- + 3H_2O \longrightarrow 3H_2PO_2^- + PH_3$]

(xi) $HgS + Cl^- + H^+ + NO_3^- \longrightarrow HgCl_4^{2-} + S + NO + H_2O$

[Hint: Half reactions

$$[HgS + 4Cl^- \longrightarrow HgCl_4^{2-} + S + 2e] \times 3$$
$$[NO_3^- + 4H^+ + 3e \longrightarrow NO + 2H_2O] \times 2$$
$$3HgS + 12Cl^- + 2NO_3^- + 8H^+ \longrightarrow 3HgCl_4^{2-} + 3S + 2NO + 4H_2O \text{]}$$

(xii) $Co^{2+} + NO_2^- + H^+ \longrightarrow Co^{3+} + NO + H_2O$

(xiii) $CrI_3 + H_2O_2 + OH^- \longrightarrow CrO_4^{2-} + IO_4^- + H_2O$

[Hint: Half reactions

$$[CrI_3 + 32OH^- \longrightarrow CrO_4^{2-} + 3IO_4^- + 16H_2O + 27e] \times 2$$
$$[H_2O_2 + 2e \longrightarrow 2OH^-] \times 27$$
$$2CrI_3 + 27H_2O_2 + 10OH^- \longrightarrow 2CrO_4^{2-} + 6IO_4^{2-} + 32H_2O \text{]}$$

(xiv) $MnO_4^- + H^+ + H_2O_2 \longrightarrow Mn^{2+} + H_2O + O_2$

[Hint: Half reactions

$$[MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[H_2O_2 \longrightarrow 2H^+ + O_2 + 2e] \times 5$$
$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2 \text{]}$$

(xv) $C_2H_5OH + I_2 + OH^- \longrightarrow CHI_3 + HCO_2^- + I^- + H_2O$

[Hint: Half reactions

$$[C_2H_5OH + \tfrac{3}{2}I_2 + 6OH^- \longrightarrow CHI_3 + HCO_2^- + 5H_2O + 5e] \times 2$$
$$[I_2 + 2e \longrightarrow 2I^-] \times 5$$
$$2C_2H_5OH + 8I_2 + 12OH^- \longrightarrow 2CHI_3 + 2HCO_2^- + 10I^- + 10H_2O$$

or $\quad C_2H_5OH + 4I_2 + 6OH^- \longrightarrow CHI_3 + HCO_2^- + 5I^- + 5H_2O$]

(xvi) $Cr_2O_7^{2-} + H^+ + C_2O_4^{2-} \longrightarrow Cr^{3+} + CO_2 + H_2O$

(xvii) $Ag^+ + AsH_3 + H_2O \longrightarrow H_3AsO_3 + H^+ + Ag$

(xviii) $MnO_2 + OH^- + O_2 \longrightarrow MnO_4^{2-} + H_2O$

[Hint: Half reactions

$$[MnO_2 + 4OH^- \longrightarrow MnO_4^{2-} + 2H_2O + 2e] \times 2$$
$$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$$
$$2MnO_2 + 4OH^- + O_2 \longrightarrow 2MnO_4^{2-} + 2H_2O \text{]}$$

8. Balance the following equations by oxidation number method.

(i) $CO + Fe_3O_4 \longrightarrow FeO + CO_2$

(ii) $H_2O_2 + ClO_2 + OH^- \longrightarrow Cl^- + O_2 + H_2O$

(iii) $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow Cr^{3+} + I_2 + H_2O$

(iv) $Cr_2O_7^{2-} + HNO_2 + H^+ \longrightarrow Cr^{3+} + NO_3^- + H_2O$

(v) $KI + H_2SO_4 \longrightarrow K_2SO_4 + I_2 + SO_2 + H_2O$

(vi) $HgS + HCl + HNO_3 \longrightarrow H_2HgI_4 + NO + S + H_2O$

(vii) $[Fe(CN)_6]^{3-} + N_2H_4 + OH^- \rightarrow [Fe(CN)_6]^{4-} + N_2 + H_2O$

[Hint: Two half reactions

$$[\overset{+3}{Fe}(CN)_6]^{3-} \longrightarrow [\overset{+2}{Fe}(CN)_6]^{4-}$$

(change in Ox.no. per Fe atom = −1)

$$\overset{-2}{N_2}H_4 \longrightarrow \overset{0}{N_2}$$

(change in Ox.no. per N atom = +2)

Total increase = $2 \times (+2) = +4$

$$4[Fe(CN)_6]^{3-} + N_2H_4 \longrightarrow 4[Fe(CN)_6]^{4-} + N_2$$
$$[4Fe(CN)_6]^{3-} + N_2H_4 + 4OH^- \longrightarrow 4[Fe(CN)_6]^{4-} + N_2 + 4H_2O]$$

(viii) $MnO_4^{2-} + H^+ \longrightarrow MnO_2 + MnO_4^- + H_2O$ (IIT 1994)

[Hint:
$$\overset{VI}{MnO_4^{2-}} \longrightarrow \overset{IV}{MnO_2}$$
$$[\overset{VI}{MnO_4^{2-}} \longrightarrow \overset{VII}{MnO_4^-}] \times 2$$
$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O]$$

(ix) $HNO_3 + Cu_2O \longrightarrow Cu(NO_3)_2 + NO + H_2O$

(x) $AuCl_4^- + Sn^{2+} + H^+ \longrightarrow Sn^{4+} + AuCl + HCl$

(xi) $S + OH^- \longrightarrow S^{2-} + S_2O_3^{2-}$

[**Hint:** $\overset{0}{S} \longrightarrow S^{2-}$ (decrease of 2)

$2\overset{0}{S} \longrightarrow S_2O_3^{2-}$ (increase of 2 per S atom)]

(xii) $NaClO_3 + KI + HCl \longrightarrow NaCl + KCl + I_2 + H_2O$

(xiii) $PbCrO_4 + H_2SO_4 + FeSO_4 \longrightarrow Fe_2(SO_4)_3 + PbSO_4 + Cr_2(SO_4)_3 + H_2O$

(xiv) $As + HNO_3 \longrightarrow H_3AsO_4 + NO_2 + H_2O$

(xv) $Fe_2(SO_4)_3 + H_2SO_3 + H_2O \longrightarrow FeSO_4 + H_2SO_4$

(xvi) $C_6H_{12}O_6 + H_2SO_4 \longrightarrow CO_2 + SO_2 + H_2O$

9. Balance the following equations:

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

(ii) $P_2H_4 \longrightarrow PH_3 + P_4H_2$

[**Hint:** $3 \times [P_2H_4 + 2H^+ + 2e \longrightarrow 2PH_3]$

$2P_2H_4 \longrightarrow P_4H_2 + 6H^+ + 6e$

$5P_2H_4 \longrightarrow 6PH_3 + P_4H_2$]

(iii) $Na_2HAsO_3 + KBrO_3 + HCl \longrightarrow NaCl + KBr + H_3AsO_4$

[**Hint:** $[HAsO_3^{2-} + H_2O \longrightarrow H_3AsO_4 + 2e] \times 3$

$BrO_3^- + 6H^+ + 6e \longrightarrow Br^- + 3H_2O$

$3HAsO_3^{2-} + BrO_3^- + 6H^+ + 3H_2O \longrightarrow 3H_3AsO_4 + Br^- + 3H_2O$

or $3Na_2HAsO_3 + KBrO_3 + 6HCl \longrightarrow 3H_3AsO_4 + KBr + 6NaCl$]

(iv) $FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$

[**Hint:** Both iron and sulphur in FeS_2 undergo a change in oxidation state.

Increase

$\overset{+2\,-1}{FeS_2} \longrightarrow \overset{+3}{Fe} + 2\overset{+4}{SO_2}$ Total increase = 10 + 1 = 11

Increase 5 × 2 = 10

$O_2^0 \longrightarrow 2O^{2-}$ Total decrease = 2 × 2 = 4]

(v) $As_2S_5 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO_2 + H_2O$

Increase 5 × 8 = 40

[**Hint:** $\overset{-2}{As_2S_5} + \overset{+5}{HNO_3} \longrightarrow \overset{+6}{H_2SO_4} + \overset{+4}{NO_2}$]

Decrease 1 × 1 = 1

(vi) $MnO + PbO_2 + HNO_3 \longrightarrow HMnO_4 + Pb(NO_3)_2 + H_2O$

(vii) $P + NaOH + H_2O \longrightarrow NaH_2PO_2 + PH_3$

Increase 1 × 1 = 1

[**Hint:** $\overset{0}{P} \longrightarrow \overset{+1}{NaH_2PO_2} + \overset{-3}{PH_3}$]

Decrease 1 × 3 = 3

(viii) $KClO_3 + H_2SO_4 \longrightarrow KHSO_4 + O_2 + ClO_2 + H_2O$

[**Hint:** $[ClO_3^- + 2H^+ + e \longrightarrow ClO_2 + H_2O] \times 2$

$2ClO_3^- \longrightarrow 2ClO_2 + O_2 + 2e$

$4ClO_3^- + 4H^+ \longrightarrow 4ClO_2 + O_2 + 2H_2O$

or $4KClO_3 + 4H_2SO_4 \longrightarrow 4KHSO_4 + 4ClO_2 + O_2 + 2H_2O$]

(ix) $Ag + KCN + O_2 + H_2O \longrightarrow KAg(CN)_2 + KOH$

[**Hint:** $[Ag + 2CN^- \longrightarrow [Ag(CN)_2]^- + e] \times 4$

$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$]

(x) $Ca(OCl)_2 + KI + HCl \longrightarrow CaCl_2 + I_2 + KCl + H_2O$

[**Hint:** $OCl^- + 2H^+ + 2e \longrightarrow Cl^- + H_2O$

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

$OCl^- + 2H^+ + 2I^- \longrightarrow Cl^- + I_2 + H_2O$

or $2OCl^- + 4H^+ \longrightarrow 2Cl^- + 2I_2 + 2H_2O$]

10. Calculate the oxidation state of underlined:

(a) $Ba_2\underline{Xe}O_2$ (b) $\underline{Ba}Cl_2$ (c) $\underline{C_{12}}H_{22}O_{11}$ (d) $\underline{I}F_7$

(e) $Na_2[\underline{Fe}(CN)_5NO]$ (f) $\underline{Ru}O_4$ (g) $K_2\underline{Ta}F_7$ (h) $Na_2\underline{Mo}O_4$

(i) $\underline{U_2}O_7^{4-}$ (j) C in diamond.

11. Give the oxidation state of underlined:

(a) $\underline{Fe_3}O_4$ (b) $Ca\underline{OCl_2}$ (c) $\underline{NH_4}NO_3$

(d) $NH_4\underline{N}O_2$ (e) $K\underline{O_2}$ (f) $H_2\underline{S}O_5$

(g) $(CH_3)_2\underline{S}O$ (h) $H_2\underline{S_2}O_8$ (i) $Na_2\underline{S_2}O_3$

(j) $Na_2\underline{S_4}O_6$ (k) $\underline{Cr}O_5$ (l) $\underline{Co}SeO_4$

12. Balance the following equations by ion electron method:

(a) $Zn + BrO_4^- + OH^- + H_2O \longrightarrow [Zn(OH)_4]^{2-} + Br^-$

(b) $MnO_4^{2-} + H_2O \longrightarrow MnO_4^- + OH^- + MnO_2$

(c) $Fe(CN)_6^{4-} + H^+ + MnO_4^- \longrightarrow Fe^{3+} + CO_2 + NO_3^- + Mn^{2+}$

(d) $Cu_3P + Cr_2O_7^{2-} \longrightarrow Cu^{2+} + H_3PO_4 + Cr^{3+}$ (acid medium)

(e) $Hg_2(CN)_2 + Ce^{4+} \longrightarrow CO_3^{2-} + NO_3^- + Hg(OH)_2 + Ce^{3+}$ (basic medium)

(f) $K_3Fe(CN)_6 + Cr_2O_3 + KOH \longrightarrow K_4Fe(CN)_6 + K_2CrO_4 + H_2O$ (basic medium)

(g) $Na_2HAsO_3 + KBrO_3 + HCl \longrightarrow NaCl + KBr + H_3AsO_4$

13. Calculate the oxidation state of vanadium in the following complex compound: $Rb_4Na[HV_{10}O_{28}]$

14. (a) Arrange the following compounds in increasing order of oxidation number of manganese:

$MnCl_2, MnO_2, KMnO_4, K_2MnO_4$

(b) Indicate valency and oxidation states of carbon in the following compounds:

$CH_4, CH_3Cl, CH_2Cl_2, CHCl_3, CCl_4$

15. Complete and balance the following compounds:

(a) Acidic solution of Fe^{2+} ion gives a brown ring when it comes in contact with NO_3^- ion. Complete the following reactions of this process:

$[Fe(H_2O)_6]^{2+} + NO_3^- + H^+ \longrightarrow ..... + [Fe(H_2O)_6]^{3+} + H_2O$

$[Fe(H_2O)_6]^{2+}\; ..... \longrightarrow ..... + H_2O$

(b) $Ca_5(PO_4)_3F + H_2SO_4 + H_2O \xrightarrow{Heat} ..... + 5CaS \cdot 2H_2O + ...$

(c) $Sn + 2KOH + 4H_2O \longrightarrow ..... + ...$ (IIT 1994)

(d) $AlBr_3 + K_2Cr_2O_7 + H_3PO_4 \longrightarrow K_3PO_4 + AlPO_4 + ... + ...$

(e) $K_2Cr_2O_7 + HCl \longrightarrow KCl + ... + ... + H_2O$ (IIT 1992)

(f) $Ag^+ + AsH_3 \longrightarrow H_3AsO_3 + H^+ + ...$

16. Arrange following ions in increasing order of oxidation number of sulphur: $S_4O_6^{2-}, HS^-, HSO_4^-, S_2O_8^{2-}, S_2O_3^{2-}, SO_3^{2-}$

17. Determine equivalent weight of underlined species:

(a) $NH_4NO_3 \longrightarrow N_2O + 3H_2O$

(b) $\underline{3MnO_2} + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$

(c) $2HS^- + \underline{4HSO_3^-} \longrightarrow 3S_2O_3^{2-} + 3H_2O$

(d) $3Cl_2 + 6NaOH \longrightarrow 5NaCl + \underline{NaClO_3} + 3H_2O$

(e) $\underline{K_2Cr_2O_7} + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$

18. Which of the following structures is accurate on the basis of formal charge?

(a) $H{-}C\equiv N\colon$; (b) $H{-}N\equiv C\colon$

[Hint: (a) $H{-}C\equiv N\colon$

$$\text{F.C.} = V - N - \frac{1}{2}B$$

F.C. at 'H' $= 1 - 0 - \frac{1}{2} \times 2 = 0$

F.C. at 'C' $= 4 - 0 - \frac{1}{2} \times 8 = 0$

F.C. at 'N' $= 5 - 2 - \frac{1}{2} \times 6 = 0$

(b) $H{-}N\equiv C\colon$

F.C. at 'H' $= 1 - 0 - \frac{1}{2} \times 2 = 0$

F.C. at 'N' $= 5 - 0 - \frac{1}{2} \times 8 = +1$

F.C. at 'C' $= 4 - 2 - \frac{1}{2} \times 6 = -1$

Structure (a) having zero formal charges at each atom will be accurate.]

19. On the basis of formal charge select the most plausible structure:

(a) H_2NOH or H_2ONH (b) SCN^- or CNS^- or CSN^-

(c) $[\colon\ddot{N}=N=\ddot{N}\colon]^-$ or $[\colon\underset{\cdot\cdot}{\ddot{N}}-N\equiv N\colon]^-$

(d) NOCl or ONCl

Answers

1. [A] (a — p); (b — p); (c — q, r); (d — s)

[B] (a — p); (b — s); (c — q); (d — r)

[C] (a — s); (b — q); (c — s); (d — p)

[D] (a — p, q); (b — p, s); (c — p, q, r); (d — p, r)

[E] (a — r); (b — p); (c — p, s); (d — q)

2.

	Oxidising agent	Reducing agent
(i)	$FeCl_3$	$SnCl_2$
(ii)	SO_2	Mg
(iii)	O_2	SO_2
(iv)	Cl_2	Ca
(v)	Hg^{2+}	Sn^{2+}
(vi)	Cu^{2+}	I^-
(vii)	H_2O_2	I^-
(viii)	SO_2	H_2S
(ix)	HNO_3	SO_2
(x)	Cl_2	SO_2

3.

	Oxidised	Reduced
(i)	PbS	H_2O_2
(ii)	H_2S	$FeCl_3$
(iii)	HCl	MnO_2
(iv)	$SnCl_2$	$FeCl_3$
(v)	$C_2O_4^{2-}$	MnO_4^-
(vi)	N_2H_4	BrO_3^-
(vii)	SO_3^{2-}	Cl_2
(viii)	I^-	Cl_2

4. (a) HI(−1), I_2(0), ICl(+1), HIO_4(+7)

(b) HCl(−1), Cl_2(0), Cl_2O(+1), ClF_3(+3), Cl_2O_7 (+7)

(c) NH_3(−3), N_3H(−1/3), N_2O(+1), NO(+2), N_2O_5(+5).

5. (i) +5 (ii) +5 (iii) +5 (iv) +2 (v) +2 (vi) +6 (one peroxo linkage is present) (vii) +5 (viii) +1 (ix) +5 (x) +6 (xi) +7 (xii) +4 (xiii) −3 (xiv) 0 (zero)(xv) +3 (xvi) +6 (xvii) +5 (xviii) +8 (xix) +3 (xx) 0 (zero).

6. (a) Mn_2O_3 (b) H_3PO_4 (c) CH_2Cl_2 (d) HCl.

7. (i) $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(ii) $2MnO_4^- + 3SnO_2^{2+} + H_2O \longrightarrow 2MnO_2 + 3SnO_3^{2-} + 2OH^-$

(iii) $3Cu + 2NO_3^- + 8H^+ \longrightarrow 3Cu^{2+} + 2NO + 4H_2O$

(iv) $Cl_2 + IO_3^- + 2OH^- \longrightarrow IO_4^- + 2Cl^- + H_2O$

(v) $3I_2 + 6NaOH \longrightarrow NaIO_3 + 5NaI + 3H_2O$

(vi) $4Zn + NO_3^- + 7OH^- \longrightarrow 4ZnO_2^{2-} + NH_3 + 2H_2O$

(ix) $4Zn + NO_3^- + 10H^+ \longrightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$

(xii) $CO^{2+} + NO_2^- + 2H^+ \longrightarrow CO^{3+} + NO + H_2O$

(xvi) $Cr_2O_7^{2-} + 14H^+ + 3C_2O_4^{2-} \longrightarrow 2Cr^{3+} + 7H_2O + 6CO_2$

(xvii) $AsH_3 + 3H_2O + 6Ag^+ \longrightarrow H_3AsO_3 + 6H^+ + 6Ag$

8. (i) $CO + Fe_3O_4 \longrightarrow 3FeO + CO_2$

(ii) $5H_2O_2 + 2ClO_2 + 2OH^- \longrightarrow 2Cl^- + 5O_2 + 6H_2O$

(iii) $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

(iv) $Cr_2O_7^{2-} + 3HNO_2 + 5H^+ \longrightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$

(v) $2KI + 2H_2SO_4 \longrightarrow K_2SO_4 + I_2 + SO_2 + 2H_2O$

(vi) $3HgS + 12HCl + 2HNO_3 \longrightarrow 3H_2HgCl_4 + 2NO + 3S + 4H_2O$

(ix) $3Cu_2O + 14HNO_3 \longrightarrow 6Cu(NO_3)_2 + 2NO + 7H_2O$

(x) $AuCl_4^- + Sn^{2+} + 3H^+ \longrightarrow AuCl + Sn^{4+} + 3HCl$

(xi) $4S + 6OH^- \longrightarrow 2S^{2-} + S_2O_3^{2-} + 3H_2O$

(xii) $NaClO_3 + 6KI + 6HCl \longrightarrow NaCl + 6KCl + 3I_2 + 3H_2O$

(xiii) $2PbCrO_4 + 6FeSO_4 + 8H_2SO_4 \longrightarrow 2PbSO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 8H_2O$

(xiv) $As + 5HNO_3 \longrightarrow H_3AsO_4 + 5NO_2 + H_2O$

(xv) $Fe_2(SO_4)_3 + H_2SO_3 + H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$

(xvi) $C_6H_{12}O_6 + 12H_2SO_4 \longrightarrow 6CO_2 + 12SO_2 + 18H_2O$

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

(iv) $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

(v) $As_2S_5 + 40HNO_3 \longrightarrow 5H_2SO_4 + 2H_3AsO_4 + 40NO_2 + 12H_2O$

(vi) $2MnO + 5PbO_2 + 10HNO_3 \longrightarrow 2HMnO_4 + 5Pb(NO_3)_2 + 4H_2O$

(vii) $4P + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$

(ix) $4Ag + 8KCN + O_2 + 2H_2O \longrightarrow 4KAg(CN)_2 + 4KOH$

(x) $Ca(OCl)_2 + 4KI + 4HCl \longrightarrow CaCl_2 + 4KCl + 2I_2 + 2H_2O$

10. (a) 0 (b) +2 (c) 0 (d) +7 (e) 3 (f) +8 (g) +5 (h) +2 (i) +5 (j) 0

OBJECTIVE QUESTIONS

Set–1 : Questions with single correct answer

1. Oxidation is defined as:
(a) loss of electrons (b) gain of electrons
(c) gain of protons (d) loss of protons

2. A reducing agent is a substance which can:
(a) accept electrons (b) donate electrons
(c) accept protons (d) donate protons

3. A redox reaction is:
(a) proton transfer reaction (b) ion combination reaction
(c) a reaction in solution (d) electron transfer reaction

4. Which of the following is not a redox reaction?
(a) Burning of candle (b) Rusting of iron
(c) Dissolving a salt in water (d) Dissolving Zn in dil. H_2SO_4

5. The reaction, $H_2S + H_2O_2 = S + 2H_2O$ manifests:
(a) oxidising action of H_2O_2 (b) reducing nature of H_2O_2
(c) acidic nature of H_2O_2 (d) alkaline nature of H_2O_2

6. The oxidation number of Fe in $K_4Fe(CN)_6$ is: (CBSE 1993; KCET 2008)
(a) + 6 (b) + 4 (c) + 3 (d) + 2

7. In $Ni(CO)_4$, the oxidation state of Ni is:
(a) 4 (b) zero (c) 2 (d) 8

8. Pick the group which does not contain a neutral oxide : (ISAT 2010)
(a) $NO_2, P_4O_{10}, Al_2O_3, NO$ (b) MgO, N_2O_5, SO_3, N_2O
(c) CO_2, SO_3, CaO, XeO_3 (d) $CO, SiO_2, SnO_2, Na_2O_3$

9. Magnesium reacts with acids producing hydrogen and corresponding magnesium salts. In such reactions Mg undergoes:
(a) reduction
(b) oxidation
(c) neither oxidation nor reduction
(d) simple dissolution

10. When P reacts with caustic soda, the products are PH_3 and NaH_2PO_2. The reaction is an example of:
(a) oxidation
(b) reduction
(c) both oxidation and reduction
(d) neutralisation

11. Which of the following reactions is not a redox reaction ? [PET (Raj.) 2008]
(a) $Ag^+ + Cl^- \longrightarrow AgCl$
(b) $Zn(s) + Cu^{2+}(aq.) \longrightarrow Zn^{2+}(aq.) + Cu(s)$
(c) $2Mg(s) + O_2(g) \longrightarrow 2MgO$
(d) $FeO + C \longrightarrow Fe + CO$

12. Which of the following is not a redox change?
(a) $2H_2S + SO_2 = 2H_2O + 3S$
(b) $2BaO + O_2 = 2BaO_2$
(c) $BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$
(d) $2KClO_3 = 2KCl + 3O_2$

13. The conversion of $K_2Cr_2O_7$ into $Cr_2(SO_4)_3$ is a process of:
(a) oxidation (b) reduction
(c) decomposition (d) substitution

14. In the reaction, $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$, I_2 acts as:
(a) reducing agent
(b) oxidising agent
(c) oxidising as well as reducing agent
(d) none of the above

15. The most common oxidation state of oxygen is –2. This is best explained as due to:
(a) 2 electrons in the outermost shell
(b) 4 electrons in the outermost shell
(c) 6 electrons in the outermost shell
(d) 8 electrons in the outermost shell

16. Select the compound in which chlorine shows oxidation state + 7:
(a) $HClO_4$ (b) $HClO_3$ (c) $HClO_2$ (d) $HClO$

17. Which one of the following is a reducing agent?
(a) Ozone (b) Chlorine (c) $FeCl_3$ (d) Na_2SO_3

18. The oxidation number of nitrogen in NH_2OH is:
(a) zero (b) +1 (c) –1 (d) –2

19. HBr and HI reduce sulphuric acid. HCl can reduce $KMnO_4$ and HF can reduce:
(a) H_2SO_4 (b) $KMnO_4$
(c) $K_2Cr_2O_7$ (d) none of these

20. One mole of N_2H_4 loses 10 moles of electrons to form a new compound Y. Assuming that all nitrogen appear in the new compound, what is the oxidation state of nitrogen? (There is no change in the oxidation state of hydrogen.)
(a) –1 (b) –3 (c) +3 (d) +5

21. The brown ring complex compound is formulated as $[Fe(H_2O)_5(NO)]SO_4$. The oxidation state of iron is: (CET Karnataka 2009)
(a) +1 (b) +2 (c) +3 (d) zero

22. A solution of sodium metal in liquid ammonia is strongly reducing due to the presence of :
(a) sodium atoms (b) sodium hydroxide
(c) sodium amide (d) solvated electrons

23. In which of the following compounds, iron has an oxidation state of +3? (DPMT 2009)

(a) $Fe(NO_3)_2$
(b) FeC_2O_4
(c) $[Fe(H_2O)_6]Cl_3$
(d) $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$

24. When $KMnO_4$ is reduced with oxalic acid in acidic solution, the oxidation number of Mn changes from:
(a) 7 to 2 (b) 7 to 4 (c) 7 to 6 (d) 6 to 2

25. In which of the following reactions the underlined substance is oxidised?
(a) $3Mg + \underline{N_2} + Mg_3N_2$ (b) $2KI + \underline{Br_2} = 2KBr + I_2$
(c) $\underline{CuO} + \overline{H_2} = Cu + H_2O$ (d) $\underline{CO} + \overline{Cl_2} = COCl_2$

26. Of the following elements, which one has the same oxidation state in all of its compounds?
(a) Hydrogen (b) Fluorine (c) Carbon (d) Oxygen

27. When tin(IV) chloride is treated with excess of conc. hydrochloric acid, the complex ion $(SnCl_6)^{2-}$ is formed. The oxidation state of tin in this complex ion is:
(a) +4 (b) zero (c) −2 (d) −4

28. In the following reaction,
$$3Br_2 + 6CO_3^{2-} + 3H_2O = 5Br^- + BrO_3^- + 6HCO_3^-$$
[PMT (MP) 1997]
(a) bromine is oxidised, carbonate is reduced
(b) bromine is reduced, carbonate is oxidised
(c) bromine is neither reduced nor oxidised
(d) bromine is reduced as well as oxidised

29. If an element is in its lowest oxidation state, under proper conditions, it can act as:
(a) a reducing agent
(b) an oxidising agent
(c) oxidising as well as reducing agent
(d) neither oxidising nor reducing agent

30. The oxidation state of phosphorus varies from:
(a) −1 to +1 (b) −3 to +3
(c) −3 to +5 (d) −5 to +1

31. In which of the following reactions no change in valency occurs?
(a) $SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$
(b) $2Na + O_2 \longrightarrow Na_2O_2$
(c) $Cl_2 + 2NaOH \longrightarrow NaClO + NaCl + H_2O$
(d) $AgNO_3 + KCl \longrightarrow AgCl + KNO_3$

32. When SO_2 is passed through an acidified solution of $K_2Cr_2O_7$, then chromium sulphate is formed. Change in oxidation state of Cr is from: (KCET 2008)
(a) +4 to +2 (b) +6 to +3
(c) +7 to +2 (d) +5 to +3

33. In a reaction,
$2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + H_2O + SO_2$, H_2SO_4 acts as:
(a) reducing agent (b) oxidising agent
(c) dehydrate (d) none of these

34. Oxidation number of iodine varies from:
(a) −1 to +1 (b) −1 to +7 (c) +3 to +5 (d) −1 to +5

35. Oxidation number of fluorine in F_2O is:
(a) +1 (b) +2 (c) −1 (d) −2

36. In the compounds $KMnO_4$ and $K_2Cr_2O_7$, the highest oxidation state is of the element:
(a) potassium (b) chromium (c) oxygen (d) manganese

37. In a reaction, the oxidation number of an element becomes zero from −1. It is a case of:
(a) oxidation
(b) reduction
(c) neither oxidation nor reduction
(d) both oxidation and reduction

38. $Cl_2 + H_2S \longrightarrow 2HCl + S$,
In the above reaction, oxidation state of chlorine changes from: [PET (Raj.) 2008]
(a) zero to −1 (b) 1 to zero
(c) zero to 1 (d) remains unchanged

39. During electrolysis the reaction at anode is:
(a) oxidation (b) reduction
(c) decomposition (d) none of these

40. Which of the following is a mild oxidising agent?
(a) Ag_2O (b) $KMnO_4$ (c) $K_2Cr_2O_7$ (d) Cl_2

41. The common oxidation state of alkali metals in the combined state is:
(a) +1 (b) +2 (c) −1 (d) −2

42. Carbon is in highest oxidation state in:
(a) CH_3Cl (b) CCl_4 (c) $CHCl_3$ (d) CH_2Cl_2

43. The oxidation number and covalency of sulphur in S_8 is:
(a) +2, 0 (b) 0, 2 (c) 0, 8 (d) 6, 2

44. Addition of iron or zinc to copper sulphate causes precipitation of copper owing to the:
(a) reduction of Cu^{2+} (b) oxidation of Cu^{2+}
(c) hydrolysis of $CuSO_4$ (d) ionisation of $CuSO_4$

45. In a reaction,
$$H_2O\,(\text{steam}) + C\,(\text{glowing}) = CO + H_2$$
(a) H_2O is the reducing agent
(b) H_2O is the oxidising agent
(c) carbon is the oxidising agent
(d) oxidation-reduction does not occur

46. The oxidation numbers of C in CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 are respectively:
(a) + 4, + 2, 0, −2, −4 (b) + 2, + 4, 0, −4, −2
(c) −4, −2, 0, + 2, + 4 (d) −2, −4, 0, + 4, + 2

47. Which of the following statements is correct?
(a) Oxidation of a substance is followed by reduction of another
(b) Reduction of a substance is followed by oxidation of another
(c) Oxidation and reduction are complementary reactions
(d) It is not necessary that both oxidation and reduction should take place in the same reaction

48. Reduction never involves:
(a) gain of electrons
(b) decrease in oxidation number
(c) loss of electrons
(d) decrease in valency of electropositive component

49. In which of the following reactions has the underlined substance been reduced?
(a) $\underline{\text{Carbon monoxide}}$ + copper oxide $\longrightarrow$ carbon dioxide + copper
(b) $\underline{\text{Copper oxide}}$ + hydrochloric acid $\longrightarrow$ copper chloride + water

(c) Hydrogen + iron oxide $\longrightarrow$ iron + water
(d) Steam + iron $\longrightarrow$ iron oxide + hydrogen

50. In which of the following reactions, the underlined element has decreased its oxidation number during the reaction?
(a) $\underline{Fe} + CuSO_4 \longrightarrow Cu + FeSO_4$
(b) $\underline{H_2} + Cl_2 \longrightarrow 2HCl$
(c) $\underline{C} + H_2O \longrightarrow CO + H_2$
(d) $\underline{MnO_2} + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

51. If three electrons are lost by a metal ion, M^{3+}, its final oxidation number would be:
(a) zero (b) + 6
(c) + 2 (d) + 4

52. Select the compound in which chlorine is assigned the oxidation number +5:
(a) $HClO_4$ (b) $HClO_2$ (c) $HClO_3$ (d) HCl

53. In the alumino thermic process, aluminium acts as:
(a) an oxidising agent (b) a flux
(c) a reducing agent (d) a solder

54. The strongest reducing agent is:
(a) K (b) Ca (c) Al (d) Zn

55. In the reaction; $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$; Zn undergoes:
(a) oxidation (b) reduction
(c) simple dissolution (d) double decomposition

56. Phosphorus has the oxidation state of +3 in:
(a) ortho phosphoric acid (b) phosphorus acid
(c) meta phosphoric acid (d) pyrophosphoric acid

57. Oxidation number of P in PO_4^{3-}, of S in SO_4^{2-} and that of Cr in $Cr_2O_7^{2-}$ are respectively: [CBSE (PMT) 2009]
(a) –3, +6 and +6 (b) +5, +6 and +6
(c) +3, +6 and +5 (d) +5, +3 and +6

58. The conversion of PbO into $Pb(NO_3)_2$ involves:
(a) oxidation
(b) reduction
(c) neither oxidation nor reduction
(d) both oxidation and reduction

59. The highest state of Mn is shown in:
(a) K_2MnO_4 (b) $KMnO_4$ (c) MnO_2 (d) Mn_2O_3

60. In which one of the following changes, there is transfer of five electrons?
(a) $MnO_4^- \longrightarrow Mn^{2+}$ (b) $CrO_4^{2-} \longrightarrow Cr^{3+}$
(c) $MnO_4^- \longrightarrow MnO_2$ (d) $Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$

61. The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is: (IIT 1990)
(a) + 3 (b) + 2 (c) + 1 (d) –1

62. The oxidation state of the most electronegative element in the products of the reaction between BaO_2 and H_2SO_4 are: (IIT 1991)
(a) 0 and –1 (b) –1 and –2
(c) –2 and 0 (d) –2 and + 1

63. In the reaction, $4Fe + 3O_2 \longrightarrow 4Fe^{3+} + 6O^{2-}$ which of the following statements is incorrect? (MLNR 1991)
(a) It is a redox reaction
(b) Metallic iron is a reducing agent
(c) Fe^{3+} is an oxidising agent
(d) Metallic iron is reduced to Fe^{2+}

64. Which of the following halide ions is easiest to oxidise?
(a) F^- (b) Cl^- (c) Br^- (d) I^-

65. In the reaction of sodium thiosulphate with I_2 in aqueous medium the equivalent weight of sodium thiosulphate is equal to: [JEE (WB) 2010]
(a) molar mass of sodium thiosulphate
(b) the average molar masses of $Na_2S_2O_3$ and I_2
(c) half the molar mass of sodium thiosulphate
(d) twice of molar mass of sodium thiosulphate

66. The oxidation number of chlorine in HOCl is:
(a) –1 (b) zero (c) + 1 (d) + 2

67. In the reaction, $Cl_2 + OH^- \longrightarrow Cl^- + ClO_4^- + H_2O$, chlorine is:
(a) oxidised
(b) reduced
(c) oxidised as well as reduced
(d) neither oxidised nor reduced

68. The oxidation number of arsenic atom in H_3AsO_4 is:
(a) –1 (b) –3 (c) + 3 (d) + 5

69. In which of the following reactions, hydrogen is acting as an oxidising agent?
(a) With iodine to give hydrogen iodide
(b) With lithium to give lithium hydride
(c) With nitrogen to give ammonia
(d) With sulphur to give hydrogen sulphide

70. In acid medium, the reaction, $MnO_4^- \longrightarrow Mn^{2+}$ is:
(a) oxidation by 3 electrons (b) reduction by 3 electrons
(c) oxidation by 5 electrons (d) reduction by 5 electrons

71. 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 equation are: (IIT 1992)

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

72. The oxidation number of Pt in $[Pt(C_2H_4)Cl_3]^-$ is: (MLNR 1993)
(a) + 1 (b) + 2 (c) + 3 (d) + 4

73. Oxidation number of P in $Mg_2P_2O_7$ is:
(a) + 3 (b) + 2 (c) + 5 (d) –3

74. The oxidation number of phosphorus in PO_4^{3-}, P_4O_{10} and $P_2O_7^{4-}$ is: (CPMT 1992)
(a) + 5 (b) + 3 (c) –3 (d) + 2

75. The oxidation state of Cr in $K_2Cr_2O_7$ is: [CEE (Bihar) 1992; AFMC 1993]
(a) + 7 (b) + 6 (c) + 3 (d) + 2

76. Bromine reacts with hot aqueous alkali to give bromide and

bromate. What is the change that is brought about in oxidation state of bromine to bromate?
(a) –1 to + 5 (b) 0 to + 5
(c) –1 to + 7 (d) None of these

77. Which one of the following leads to redox reaction?
(a) $AgNO_3 + HCl$ (b) $KOH + HCl$
(c) $KI + Cl_2$ (d) $NH_3 + HCl$

78. Oxidation number of 'S' in $Na_2S_4O_6$ is: (CBSE 1993)
(a) + 0.5 (b) 2.5 (c) + 4 (d) + 6

79. Which one of the following is not a redox reaction? (AIIMS 1993)
(a) $CaCO_3 \longrightarrow CaO + CO_2$
(b) $2H_2 + O_2 \longrightarrow 2H_2O$
(c) $Na + H_2O \longrightarrow NaOH + \frac{1}{2}H_2$
(d) $MnCl_3 \longrightarrow MnCl_2 + \frac{1}{2}Cl_2$

80. The oxidation number of nitrogen in NO_3^- is:
(a) –1 (b) + 2 (c) + 3 (d) + 5

81. Oxygen has an oxidation state of + 2 in:
(a) H_2O_2 (b) OF_2 (c) SO_2 (d) H_2O

82. When iron is rusted, it is:
(a) oxidised (b) reduced
(c) evaporated (d) decomposed

83. An element, which never has a positive oxidation state in any of its compounds, is:
(a) boron (b) oxygen
(c) chlorine (d) fluorine

84. Starch iodide paper is used to test for the presence of:
(a) iodine (b) iodide ion
(c) oxidising agent (d) reducing agent

85. Which of the acid possesses oxidising, reducing and complex forming properties?
(a) HNO_3 (b) H_2SO_4 (c) HCl (d) HNO_2

86. Which substance is serving as a reducing agent in the following reaction?
$14H^+ + Cr_2O_7^{2-} + 3Ni \longrightarrow 2Cr^{3+} + 7H_2O + 3Ni^{2+}$ (CBSE 1994)
(a) H_2O (b) Ni (c) H^+ (d) $Cr_2O_7^{2-}$

87. The oxidation state of iodine in $H_4IO_6^-$ is:
(a) +7 (b) –1 (c) + 5 (d) +1

88. Oxidation number of N in NH_4NO_3 is: [PMT (Raj.) 1993]
(a) –3 (b) + 5 (c) –3 and +5 (d) +3 and –5

89. The element, which shows minimum oxidation number in its compounds, is: [PET (Raj.) 1992]
(a) Fe (b) Mn (c) Ca (d) K

90. In which of the following compounds, the oxidation number of iodine is fractional? [PET (Raj.) 1992]
(a) IF_7 (b) I_3^- (c) IF_5 (d) IF_3

91. The missing term in the following equation is:
$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + \ldots$$
(a) Sn^{4+} (b) Sn^{3+} (c) Sn^{2+} (d) Sn^+

92. A compound contains atoms A, B and C. The oxidation number of A is + 2, of B is + 5 and of C is –2. The possible formula of the compound is:
(a) ABC_2 (b) $B_2(AC_3)_2$
(c) $A_3(BC_4)_2$ (d) $A_3(B_4C)_2$

93. The correct set of oxidation numbers of nitrogen in ammonium nitrate is: [PET (Raj.) 2007]
(a) – 3, + 3 (b) – 1, + 1 (c) + 1, – 1 (d) – 3, + 5

94. In which of the following pairs, the oxidation states of sulphur and chromium are same? [PET (Raj.) 2007]
(a) SO_3^{2-}, CrO_4^{2-} (b) SO_3, CrO_4^{2-}
(c) SO_2, CrO_4^{2-} (d) $SO_2, Cr_2O_7^{2-}$

95. For the redox reaction, $HgCl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$, the correct coefficients of reactants for the balanced equation are:
(a) 1, 1 (b) 1, 2
(c) 2, 2 (d) 2, 1

96. The value of n in the following equation is:
$$Cr_2O_7^{2-} + 14H^+ + nFe^{2+} \longrightarrow 2Cr^{3+} + nFe^{3+} + 7H_2O$$
[PET (MP) 2008]
(a) 2 (b) 3 (c) 7 (d) 6

97. In the reaction, $8Al + 3Fe_3O_4 \longrightarrow 4Al_2O_3 + 9Fe$, the number of electrons transferred from reductant to oxidant is:
(a) 8 (b) 4 (c) 16 (d) 24
[**Hint:** $8Al \longrightarrow 8Al^{3+} + 24e$
$9Fe^{8/3+} + 24e \longrightarrow 9Fe$]

98. Which of the following examples does not represent disproportionation?
(a) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$
(b) $2H_2O_2 \longrightarrow 2H_2O + O_2$
(c) $4KClO_3 \longrightarrow 3KClO_4 + KCl$
(d) $3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

99. Why is the following reaction is not possible?
$$Cr_2O_7^{2-} + Fe^{3+} + H^+ \longrightarrow \ldots + \ldots + \ldots$$
(a) Both $Cr_2O_7^{2-}$ and Fe^{3+} are reducing agents
(b) Both $Cr_2O_7^{2-}$ and Fe^{3+} are oxidising agents
(c) $Cr_2O_7^{2-}$ is a strong oxidising agent while Fe^{3+} is a weak oxidising agent
(d) The solution is acidic in nature

100. Which one of the following statements is not correct?
(a) Oxidation number of S in $(NH_4)_2S_2O_8$ is + 6
(b) Oxidation number of Os in OsO_4 is + 8
(c) Oxidation number of S in H_2SO_5 is + 8
(d) Oxidation number of O in KO_2 is $-\frac{1}{2}$

101. The oxide which cannot act as a reducing agent, is: (CBSE 1995)
(a) SO_2 (b) NO_2
(c) CO_2 (d) ClO_2

102. Coordination number and oxidation number of Cr in $K_3Cr(C_2O_4)_3$ are respectively: (CBSE 1995)
(a) 4 and + 2 (b) 6 and + 3 (c) 3 and –3 (d) 3 and 0

103. In the following reaction,

$$4P + 3KOH + 3H_2O \longrightarrow 3KH_2PO_2 + PH_3$$

(a) P is oxidised only
(b) P is reduced only
(c) P is oxidised as well as reduced
(d) none of the above

104. Which reaction does not involve either oxidation nor reduction?

(a) $VO^{2+} \longrightarrow V_2O_3$ (b) $Na \longrightarrow Na^+$
(c) $CrO_4^{2-} \longrightarrow Cr_2O_7^{2-}$ (d) $Zn^{2+} \longrightarrow Zn$

105. In which of the following processes is nitrogen oxidised?

(a) $NH_4^+ \longrightarrow N_2$ (b) $NO_3^- \longrightarrow NO$
(c) $NO_2 \longrightarrow NO_2^-$ (d) $NO_3 \longrightarrow NH_4^+$

106. It is found that V forms a double salt isomorphous with Mohr's salt. The oxidation number of V in this compound is:

(a) + 3 (b) + 2 (c) + 4 (d) − 4

107. How many moles of electrons are involved in the reduction of one mole of MnO_4^- ion in alkaline medium to MnO_3^- ?

(a) 2 (b) 1 (c) 3 (d) 4

108. One mole of N_2H_4 loses 10 moles of electrons to form a new compound *Y*. Assuming that all nitrogen appears in the new compound, what is the oxidation number of nitrogen in *Y* (there is no change in the oxidation state of hydrogen)?

(a) −3 (b) + 3 (c) + 5 (d) + 1

109. Oxidation number of C in HNC is:

(a) + 2 (b) −3 (c) + 3 (d) zero

110. Oxidation number of Fe in $Fe_{0.94}O$ is:

(a) 200 (b) 200/94 (c) 94/200 (d) none of these

111. Oxidation number of Fe in $Na_2[Fe(CN)_5NO]$ is:

(a) + 2 (b) + 1 (c) + 3 (d) −2

112. Oxidation number of Cl in $CaOCl_2$ is:

(a) −1 and + 1 (b) + 2
(c) −2 (d) none of these

113. Equivalent weight of FeC_2O_4 in the change,

$FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2$ is:

(a) $M/3$ (b) $M/6$ (c) $M/2$ (d) $M/1$

114. Oxidation state of Fe in Fe_3O_8 is: (CBSE 1999)

(a) 3/2 (b) 4/5 (c) 5/4 (d) 8/3

115. In which of the following compounds transition metal has zero oxidation state? (CBSE 1999)

(a) CrO_5 (b) Fe_3O_4 (c) $FeSO_4$ (d) $Fe(CO)_5$

116. The oxidation number of sulphur in S_8, S_2F_2 and H_2S respectively are: (IIT 1999)

(a) 0, +1 and −2 (b) +2, +1 and −2
(c) 0, +1 and +2 (d) −2, +1 and −2

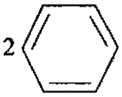
117. The reaction, $3ClO^-(aq.) \rightarrow ClO_3^-(aq.) + 2Cl^-(aq.)$ is an example of: [IIT (S) 2000]

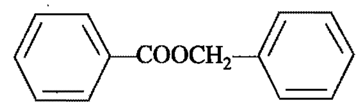
(a) oxidation reaction
(b) reduction reaction
(c) disproportionation reaction
(d) decomposition reaction

118. The oxidation state of 'S' in $H_2S_2O_8$ is: [PET (MP) 2002; RPMT 2007]

(a) +2 (b) +4 (c) +6 (d) +7

119. Which is not a disproportionation reaction?

(a) 2  CHO $\xrightarrow{Al\,(OC_2H_5)_3}$



(b) $\begin{array}{c} CHO \\ | \\ COOH \end{array} + OH^- \longrightarrow \begin{array}{c} CH_2OH \\ | \\ COO^- \end{array} + \begin{array}{c} COO^- \\ | \\ COO^- \end{array}$

(c) $NaH + H_2O \longrightarrow NaOH + H_2$
(d) All of the above

120. Which of the following is a disproportionation reaction?

(a) $Cu_2O + 2H^+ \longrightarrow Cu + Cu^{2+} + H_2O$
(b) $2CrO_4^2 + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$
(c) $CaCO_3 + 2H^+ \longrightarrow Ca^{2+} + H_2O + CO_2$
(d) $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

121. When $KMnO_4$ acts as an oxidising agent and ultimately forms MnO_4^{2-}, MnO_2, Mn_2O_3 and Mn^{2+}, then the number of electrons transferred in each case respectively is: (AIEEE 2002)

(a) 4, 3, 1, 5 (b) 1, 5, 3, 7
(c) 1, 3, 4, 5 (d) 3, 5, 7, 1

122. Which of the following is a redox reaction: (AIEEE 2002)

(a) $NaCl + KNO_3 \longrightarrow NaNO_3 + KCl$
(b) $CaC_2O_4 + 2HCl \longrightarrow CaCl_2 + H_2C_2O_4$
(c) $Mg(OH)_2 + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_4OH$
(d) $Zn + 2AgCN \longrightarrow 2Ag + Zn(CN)_2$

123. For the decolourisation of 1 mole of $KMnO_4$, the no. of moles of H_2O_2 required is: (AIIMS 2004)

(a) $\frac{1}{2}$ (b) $\frac{3}{2}$ (c) $\frac{5}{2}$ (d) $\frac{7}{2}$

124. In H_2O_2, the oxidation state of oxygen is: (CPMT 2000)

(a) −2 (b) −1 (c) 0 (d) − 4

125. The reaction of $KMnO_4$ and HCl results in:

(a) oxidation of Mn in $KMnO_4$ and production of Cl_2
(b) reduction of Mn in $KMnO_4$ and production of H_2
(c) oxidation of Mn in $KMnO_4$ and production of H_2
(d) reduction of Mn in $KMnO_4$ and production of Cl_2

126. Consider the following reaction,

$$5H_2O_2 + xClO_2 + 2OH^- \longrightarrow xCl^- + yO_2 + 6H_2O$$

The reaction is balanced if:

(a) $x = 5, y = 2$ (b) $x = 2, y = 5$
(c) $x = 4, y = 10$ (d) $x = 5, y = 5$

127. In the chemical reaction,

$$Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-$$

(a) water is oxidised (b) electrons are reduced
(c) silver is oxidised (d) silver is reduced
(e) hydrogen is reduced

128. The reaction, $2H_2O(l) \rightarrow 4H^+(aq.) + O_2(g) + 4e^-$ is:
(a) a redox reaction (b) a hydrolysis reaction
(c) a solvolysis reaction (d) an oscillatory reaction
(e) an acid catalyst reaction

129. Which of the following molecules can act as an oxidising agent as well as a reducing agent?
(a) H_2S (b) SO_3 (c) H_2O_2 (d) F_2
(e) H_2SO_4

130. Which of the following is not a reducing agent?
(a) SO_2 (b) H_2O_2 (c) CO_2 (d) NO_2

131. Equivalent mass of oxidising agent in the reaction,
$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O \quad \text{is:}$$
(a) 32 (b) 64 (c) 16 (d) 8

132. A, B and C are three elements forming part of a compound in oxidation states of +2, +5 and –2 respectively. What could be the compound?
(a) $A_2(BC)_2$ (b) $A_2(BC_4)_3$ (c) $A_3(BC_4)_2$ (d) ABC

133. Among the following, identify the species with an atom in +6 oxidation state:
(a) MnO_4^- (b) $Cr(CN)_6^{3-}$ (c) NiF_6^{2-} (d) CrO_2Cl_2

134. On reduction of $KMnO_4$ by oxalic acid in acidic medium, the oxidation number of Mn changes. What is the magnitude of this change?
(a) 7 to 2 (b) 6 to 2 (c) 5 to 2 (d) 7 to 4

135. The oxidation number of iron in Fe_3O_4 is:
(a) +2 (b) +3 (c) 8/3 (d) 2/3

136. Number of moles of $K_2Cr_2O_7$ reduced by one mole of Sn^{2+} ions is:
(a) 1/3 (b) 3 (c) 1/6 (d) 6

137. In standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry the equivalent weight of $K_2Cr_2O_7$ is:
(a) molecular weight /2 (b) molecular weight /6
(c) molecular weight /3 (d) same as molecular weight

138. In the balanced chemical reaction,
$$IO_3^- + aI^- + bH^+ \longrightarrow cH_2O + dI_2$$
a, b, c and d respectively correspond to: (AIIMS 2005; AMU 2009)
(a) 5, 6, 3, 3 (b) 5, 3, 6, 3 (c) 3, 5, 3, 6 (d) 5, 6, 5, 5
[Hint: The balanced equation will be:
$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O]$$

139. In alkaline medium ClO_2 oxidises to H_2O_2 and O_2 and itself gets reduced to Cl^-. How many moles of H_2O_2 are oxidised by 1 mole of ClO_2? (PET 2005)
(a) 1 (b) 1.5 (c) 2.5 (d) 3.5
(e) 5
[Hint: The balanced chemical equation is:
$$2ClO_2 + 5H_2O_2 + 2OH^- \longrightarrow 2Cl^- + 5O_2 + 6H_2O$$
$$2 \text{ mol } ClO_2 \equiv 5 \text{ mol } H_2O_2$$
$$\therefore \quad 1 \text{ mol } ClO_2 \equiv 2.5 \text{ mol } H_2O_2]$$

140. Oxidation number of xenon in $XeOF_2$ is: [CET (J&K) 2005]
(a) zero (b) 2
(c) 4 (d) 3

141. The oxidation number of cobalt in $K[Co(CO)_4]$ is:
(a) +1 (b) +3 (c) –1 (d) –3

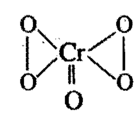
142. The oxidation state of iodine in IPO_4 is: [JEE (Orissa) 2005]
(a) +1 (b) +3
(c) +5 (d) +7
[Hint: Let oxidation state of iodine be x
$x - 3 = 0, \; x = +3,$
$\because PO_4^{3-}$ has combined oxidation number –3.]

143. The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is:
(a) +3 (b) +2
(c) +1 (d) 0

144. Nitrogen forms a variety of compounds in all oxidation states ranging from: [PMT (Himachal) 2006]
(a) –3 to +5 (b) –3 to +3
(c) –3 to +4 (d) –3 to +6

145. In alkaline medium, H_2O_2 reacts with Fe^{3+} and Mn^{2+} separately to give: [JEE (Orissa) 2006]
(a) Fe^{4+} and Mn^{4+} (b) Fe^{2+} and Mn^{2+}
(c) Fe^{2+} and Mn^{4+} (d) Fe^{4+} and Mn^{2+}
[Hint: $2K_3[\overset{3+}{Fe}(CN)_6] + 2KOH + 2H_2O_2 \longrightarrow$
$2K_4[\overset{2+}{Fe}(CN)_6] + 2H_2O + O_2$
$$\overset{2+}{Mn}SO_4 + H_2O_2 \longrightarrow \overset{4+}{Mn}O_2 + H_2SO_4]$$

146. CrO_5 has structure as shown,



The oxidation number of chromium in the above compound is: [PMT (Kerala) 2006; JEE (Orissa) 2008]
(a) +4 (b) +5 (c) +6 (d) +10 (e) 0

147. Which of the following chemical reactions depicts the oxidising behaviour of H_2SO_4? (AIEEE 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) $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

148. The oxidation numbers of the sulphur atoms in peroxymonosulphuric acid (H_2SO_5) and peroxydisulphuric acid ($H_2S_2O_8$) are respectively : [JEE (J & K) 2009]
(a) +8 and +7 (b) +3 and +3
(c) +6 and +6 (d) +4 and +6

149. When phosphorus reacts with caustic soda, the products are PH_3 and NaH_2PO_2. This reaction is an example of: [BHU (Mains) 2007]
(a) oxidation (b) reduction
(c) disproportionation (d) none of these

150. When hydrogen peroxide is added to acidified potassium dichromate, a blue colour is produced due to formation of: [PET (Kerala) 2007]
(a) CrO_3 (b) Cr_2O_3 (c) CrO_5 (d) CrO_4^{2-}
(e) $Cr_2O_7^{2-}$

[**Hint:** $K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + H_2Cr_2O_7$

$[H_2O_2 \longrightarrow H_2O + (O)]4$

$H_2Cr_2O_7 + 4(O) \longrightarrow 2CrO_5 + H_2O$

$K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow 2CrO_5 + K_2SO_4 + 5H_2O$]

151. Number of moles of MnO_4^- required to oxidise one mole of ferrous oxalate completely in acid medium will be :

(a) 7.5 moles (b) 0.2 moles (c) 0.6 moles (d) 0.4 moles [CBSE-PMT (Pre) 2008]

[**Hint:** $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2$

Number of moles of MnO_4^- required to oxidise one mole of oxalate $= \frac{2}{5} = 0.4$]

152. Oxidation number of iodine in IO_3^-, IO_4^-, KI and I_2 respectively are : [PMT (Kerala) 2008]

(a) $-1, -1, 0, +1$ (b) $+3, +5, +7, 0$

(c) $+5, +7, -1, 0$ (d) $-1, -5, -1, 0$

(e) $-2, -5, -1, 0$

153. In the redox reaction :

$x\,KMnO_4 + y\,NH_3 \rightarrow KNO_3 + MnO_2 + KOH + H_2O$ (DPMT 2009)

(a) $x = 4, y = 6$ (b) $x = 3, y = 8$

(c) $x = 8, y = 6$ (d) $x = 8, y = 3$

[**Hint :** Balanced equation is :

$8KMnO_4 + 3NH_3 \longrightarrow 8MnO_2 + 3KNO_3 + 5KOH + 2H_2O$]

154. The reaction :

$3ClO^- \longrightarrow ClO_3^- + 2Cl^-$ is an example of : (SCRA 2009)

(a) oxidation reaction

(b) reduction reaction

(c) disproportionation reaction

(d) decomposition reaction

155. Which of the following species will not exhibit disproportionation reaction? [AMU (Engg.) 2009]

(a) ClO^- (b) ClO_2^-

(c) ClO_3^- (d) ClO_4^-

156. Which of the following shows nitrogen with its increasing order of oxidation number ? [PMT (Kerala) 2010]

(a) $NO < N_2O < NO_2 < NO_3^- < NH_4^+$

(b) $NH_4^+ < N_2O < NO_2 < NO_3^- < NO$

(c) $NH_4^+ < N_2O < NO < NO_2 < NO_3^-$

(d) $NH_4^+ < NO < N_2O < NO_2 < NO_3^-$

157. Oxidation states of P in $H_4P_2O_5, H_4P_2O_6, H_4P_2O_7$ are respectively : (AIPMT 2010)

(a) +3, +5, +4 (b) +5, +3, +4

(c) +5, +4, +3 (d) +3, +4, +5

Assertion-Reason TYPE QUESTIONS

Set–1

The questions given below consist of an '**Assertion**' **(A)** and '**Reason**' **(R)**. Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct, and (R) is the correct explanation of (A).

(b) If both (A) and (R) are correct, but (R) is not the correct explanation of (A).

(c) If (A) is correct, but (R) is incorrect.

(d) If (A) is incorrect, but (R) is correct.

1. (A) In aqueous solution, SO_2 reacts with H_2S liberating sulphur.

(R) SO_2 is an effective reducing agent.

2. (A) Fluorine acts as a stronger reducing agent than oxygen.

(R) Fluorine is more electronegative.

3. (A) $PbCl_2$ is more stable than $PbCl_4$.

(R) $PbCl_4$ is a powerful oxidising agent.

4. (A) Among halogens fluorine is the.

(R) Fluorine is the most electronegative element.

5. (A) In the reaction between potassium permanganate and potassium iodide, potassium permanganate act as oxidising agent.

(R) Oxidation state of manganese changes from +2 to +7 during the reaction.

Set–2

The questions given below consist of two statements each as '**Assertion**'**(A)** and '**Reason**' **(R)**. While answering these questions you are required to choose any one of the following four:

(a) If both (A) and (R) are true, and (R) is the correct explanation of (A).

(b) If both (A) and (R) are true, but (R) is not the correct explanation of (A).

(c) If (A) is true, but (R) is false.

(d) If (A) and (R) are both false.

1. (A) Identification of cathode and anode is done with the help of thermometer.

(R) Higher is the value of reduction potential, greater would be its reducing power. (AIIMS 1999)

2. (A) Zinc reacts with H_2SO_4 to give H_2 gas but copper does not.

(R) Zinc has higher reduction potential than copper.

3. (A) Absolute electrode potential can be easily measured by using vacuum tube voltmeter.

(R) Oxidation or reduction cannot take place alone.

4. (A) Sulphur dioxide and chlorine are both bleaching agents.

(R) Both are reducing agents. (AIIMS 1994)

5. (A) Hydrogen peroxide acts only as oxidising agent. $(H_2O_2 \longrightarrow H_2O + O)$

(R) All peroxides behave as the oxidising agent only.

6. (A) $HClO_4$ is stronger acid than $HClO_3$.
   (R) Oxidation state of Cl in $HClO_4$ is +VII and in $HClO_3$; it is +V.
7. (A) Oxidation number of Ni in $Ni(CO)_4$ is taken zero.
   (R) The oxidation number of CO has been taken to be zero.
8. (A) Oxidation state of 'H' is +1 in CuH_2 and is −1 in CaH_2.
   (R) Ca is stronger electropositive than hydrogen.
9. (A) Iodine shows oxidation state of +1 and +3 in the compounds ICl and ICl_3 respectively.
   (R) Iodine coming below the halogens F, Cl and Br in the halogen group of elements in the periodic table shows a higher degree of electropositive nature. (SCRA 2007)

Answers : OBJECTIVE QUESTIONS

1. (a)	2. (b)	3. (d)	4. (c)	5. (a)	6. (d)	7. (b)	8. (c)
9. (b)	10. (c)	11. (a)	12. (c)	13. (b)	14. (b)	15. (c)	16. (a)
17. (d)	18. (c)	19. (d)	20. (c)	21. (b)	22. (d)	23. (c)	24. (a)
25. (d)	26. (b)	27. (a)	28. (d)	29. (a)	30. (c)	31. (d)	32. (b)
33. (b)	34. (b)	35. (c)	36. (d)	37. (a)	38. (a)	39. (a)	40. (a)
41. (a)	42. (b)	43. (b)	44. (a)	45. (b)	46. (c)	47. (c)	48. (c)
49. (d)	50. (d)	51. (b)	52. (c)	53. (c)	54. (a)	55. (a)	56. (b)
57. (b)	58. (c)	59. (b)	60. (a)	61. (c)	62. (b)	63. (d)	64. (d)
65. (a)	66. (c)	67. (c)	68. (d)	69. (b)	70. (d)	71. (a)	72. (b)
73. (c)	74. (a)	75. (b)	76. (b)	77. (c)	78. (b)	79. (a)	80. (d)
81. (b)	82. (a)	83. (d)	84. (c)	85. (d)	86. (b)	87. (a)	88. (c)
89. (d)	90. (b)	91. (a)	92. (c)	93. (d)	94. (b)	95. (c)	96. (d)
97. (d)	98. (a)	99. (b)	100. (c)	101. (c)	102. (b)	103. (c)	104. (c)
105. (a)	106. (b)	107. (a)	108. (b)	109. (a)	110. (b)	111. (a)	112. (a)
113. (d)	114. (d)	115. (d)	116. (a)	117. (c)	118. (c)	119. (c)	120. (a)
121. (c)	122. (c)	123. (c)	124. (b)	125. (d)	126. (b)	127. (d)	128. (a)
129. (c)	130. (c)	131. (c)	132. (c)	133. (d)	134. (a)	135. (c)	136. (a)
137. (b)	138. (a)	139. (c)	140. (c)	141. (c)	142. (b)	143. (a)	144. (a)
145. (c)	146. (c)	147. (a)	148. (c)	149. (c)	150. (c)	151. (d)	152. (c)
153. (d)	154. (c)	155. (d)	156. (c)	157. (d)			

Answers : ASSERTION-REASON TYPE QUESTIONS

- **Set–1**

1. (b)	2. (b)	3. (b)	4. (b)	5. (c)

- **Set–2**

1. (d)	2. (c)	3. (d)	4. (c)	5. (d)	6. (b)	7. (a)	8. (a)
9. (a)							

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

1. Oxidation states of carbon atoms in diamond and graphite are:
(a) +2, +4 (b) +4, +2 (c) – 4, 4 (d) zero, zero

2. Oxidation state(s) of chlorine in $CaOCl_2$ (bleaching powder) is/are:
(a) +1 and –1 (b) +1 only
(c) –1 only (d) none of these

3. Oxidation number of sulphur in S_8, S_2F_2 and H_2S are:
(a) +2, 0, +2 (b) 0, +1, –2 (c) –2, 0, +2 (d) 0, +1, +2

4. The reaction, $H_2S + H_2O_2 \longrightarrow 2H_2O + S$, shows:
(a) acidic nature of H_2O_2 (b) reducing nature of H_2O_2
(c) oxidising action of H_2O_2 (d) alkaline nature of H_2O_2

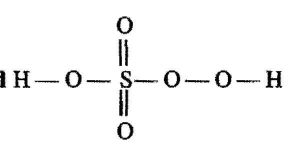
5. For the redox reaction,
$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O,$$
the correct coefficients of the reactants for the balanced reaction are:

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	5	16
(b)	16	3	12
(c)	15	16	12
(d)	2	16	5

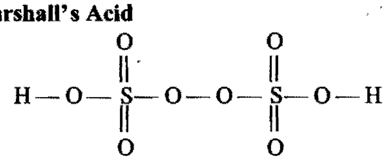
6. Number of moles of $K_2Cr_2O_7$ that can be reduced by 1 mole of Sn^{2+} ions is:
(a) $\frac{1}{3}$ (b) $\frac{3}{2}$ (c) $\frac{5}{6}$ (d) $\frac{6}{5}$
[**Hint:** Balanced equation is:
$$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 3Sn^{4+}$$
1 mole of $Sn^{2+} \equiv \frac{1}{3}$ mole of $Cr_2O_7^{2-}$]

7. The reaction, $3ClO^-(aq.) \longrightarrow ClO_3^-(aq.) + 2Cl^-(aq.)$, is an example of:
(a) reduction reaction
(b) oxidation reaction
(c) disproportionation reaction
(d) spallation reaction

8. The oxidation states of sulphur in Caro's and Marshall's acid are:
(a) +6, +6 (b) +4, +6 (c) +6, –6 (d) +6, +4
[**Hint:**

H_2SO_5 **Caro's Acid**  (+6) State

$H_2S_2O_8$ **Marshall's Acid**

 (+6) State

Both these acids have peroxy link.]

9. Which among the following compounds have +6 state with the metal atoms?
(a) $[Fe(CN)_6]^{4-}$ (b) $[Fe(CN)_6]^{3-}$
(c) $[Cr(CN)_6]^{3-}$ (d) CrO_2Cl_2

10. The oxidation number of nitrogen atoms in NH_4NO_3 are:
(a) +3, +3 (b) +3, –3 (c) –3, +5 (d) –5, +3
[**Hint:** $NH_4NO_3 \rightleftharpoons NH_4^+ + NO_3^-$
NH_4^+ $x + 4 = +1$
$x = -3$
NO_3^- $x - 6 = -1$
$x = +5$]

11. In the chemical reaction,
$$K_2Cr_2O_7 + xH_2SO_4 + ySO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + zH_2O$$
the values 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) $x = 2, y = 2, z = 2$

12. In which of the following pairs both members contain peroxy linkage?
(a) $H_2S_2O_8, H_4P_2O_6$ (b) $H_2SO_5, H_4P_2O_7$
(c) $H_2TiO_4, H_4P_2O_8$ (d) S_3O_9, P_4O_7

13. Which of the following agents is the most oxidising?
(a) O_3 (b) $KMnO_4$ (c) H_2O_2 (d) $K_2Cr_2O_7$

14. When methane is burnt in oxygen to produce CO_2 and H_2O, the oxidation number changes by:
(a) –8 (b) zero (c) +8 (d) +4
[**Hint:** $\overset{-4}{C}H_4 + 2O_2 \longrightarrow \overset{+4-4}{C}O_2 + 2H_2O$
Oxidation number change $= +4 - (-4) = +8$]

15. Which of the following has been arranged in order of increasing oxidation number of nitrogen?
(a) $NH_3 < N_2O_5 < NO < N_2$
(b) $NO_2^+ < NO_3^- < NO_2^- < N_3^-$
(c) $NH_4^+ < N_2H_4 < NH_2OH < N_2O$
(d) $NO_2 < NaN_3 < NH_4^+ < N_2O$

16. In the ethylene molecule the two carbon atoms have the oxidation numbers:
(a) –1, –1 (b) –2, –2 (c) –1, –2 (d) +2, –2

17. In which of the following coordination compounds do the transition metals have an oxidation number of +6?
(a) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (b) $[Fe(CO)_5]$
(c) $[(H_2O)_5Cr—O—Cr(H_2O)_5]^{4+}$
(d) $K_2[Cr(CN)_2O_2(O_2)NH_3]$

18. In the redox reaction:
$$xMnO + yPbO_2 + zHNO_3 \longrightarrow HMnO_4 + Pb(NO_3)_2 + H_2O$$
(a) $x = 2, y = 5, z = 10$ (b) $x = 2, y = 7, z = 8$
(c) $x = 2, y = 5, z = 8$ (d) $x = 2, y = 5, z = 5$

19. In the redox reaction:

$xKMnO_4 + yNH_3 \longrightarrow KNO_3 + MnO_2 + KOH + H_2O$

(a) $x = 4,\ y = 6$ (b) $x = 8,\ y = 3$
(c) $x = 8,\ y = 6$ (d) $x = 3,\ y = 8$

20. In the ionic equation:

$xCH_3CH_2OH + yI_2 + zOH^- \longrightarrow CHI_3 + HCO_2^- + I^- + H_2O$

(a) $x = 1,\ y = 4,\ z = 6$ (b) $x = 1,\ y = 6,\ z = 4$
(c) $x = 1,\ y = 8,\ z = 12$ (d) $x = 1,\ y = 8,\ z = 8$

21. The oxidation number of Cr is +6 in:
(a) $FeCr_2O_4$ (b) $KCrO_3Cl$ (c) CrO_5 (d) $[Cr(OH)_4]^-$

22. The oxidation number of carbon is zero in:
(a) HCHO (b) CH_2Cl_2 (c) $C_6H_{12}O_6$ (d) $C_{12}H_{22}O_{11}$

23. Which of the following have been arranged in order of decreasing oxidation number of sulphur?
(a) $H_2S_2O_7 > Na_2S_4O_6 > Na_2S_2O_3 > S_8$
(b) $SO^{2+} > SO_4^{2-} > SO_3^{2-} > HSO_4^-$
(c) $H_2SO_5 > H_2SO_3 > SCl_2 > H_2S$
(d) $H_2SO_4 > SO_2 > H_2S > H_2S_2O_8$

24. Oxidation number of carboxylic carbon atom in CH_3COOH is:
(a) +2 (b) +4 (c) +1 (d) +3

25. Which among the following are autoredox reactions?
(a) $P_4 + OH^- \longrightarrow H_2PO_4^- + PH_3$
(b) $S_2O_3^{2-} \longrightarrow SO_4^{2-} + S$
(c) $H_2O_2 \longrightarrow H_2O + O_2$
(d) $AgCl + NH_3 \longrightarrow [Ag(NH_3)_2]Cl$

26. Oxidation state of nitrogen is incorrectly given for: **[PMT (Pb.) 2006]**

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

27. Oxidation number of C in HNC is:
(a) +2 (b) −3
(c) +3 (d) zero

[**Hint:** HNC
$+1 - 3 + x = 0$
$x = +2$]

28. Which of the following groups of molecules act both as oxidising agent as well as reducing agent?
(a) $KMnO_4, O_3, SO_3$ (b) $HClO_4, HNO_2, H_2O_2$
(c) HNO_2, SO_2, H_2O_2 (d) HNO_3, SO_2, H_2SO_4

29. Match the List-I with List-II and select the correct answer from the given Codes:

List-I (Compound)	List-II (Oxidation state of nitrogen)
A. N_2O_5	(i) −2
B. NaN_3	(ii) +5
C. NO	(iii) −1/3
D. N_2H_4	(iv) +2

Codes:	A	B	C	D
(a)	(ii)	(iii)	(iv)	(i)
(b)	(i)	(ii)	(iii)	(iv)
(c)	(iv)	(i)	(ii)	(iii)
(d)	(iii)	(i)	(iv)	(ii)

30. The oxidation state of molybdenum in its oxo complex species $[Mo_2O_4(C_2H_4)_2(H_2O_2)]^{2-}$ is:
(a) 2 (b) 3 (c) 4 (d) 5

31. $KMnO_4$ is a strong oxidising agent in acid medium. To provide acid medium, H_2SO_4 is used instead of HCl. This is because: **[PMT (Kerala) 2007]**
(a) H_2SO_4 is a stronger acid than HCl
(b) HCl is oxidised by $KMnO_4$ to Cl_2
(c) H_2SO_4 is a dibasic acid
(d) rate is faster in the presence of H_2SO_4
(e) only H_2SO_4 is completely ionized

32. Which of the following oxides cannot work as a reducing agent? **[PET (Raj.) 2006]**
(a) CO_2 (b) NO_2 (c) SO_2 (d) ClO_2

33. The coordination number and oxidation state of Cr in $K_3[Cr(C_2O_4)_3]$ are respectively: **[PET (Raj.) 2006]**
(a) 3 and +3 (b) 2 and 0
(c) 6 and +3 (d) 4 and +2

34. The reaction, $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$ is an example of : **[JEE (Orissa) 2008]**
(a) disproportionation reaction
(b) neutralisation reaction
(c) double decomposition reaction
(d) pyrolytic reaction

35. Balance the following equation and choose the correct value of sum of coefficients of the products :

$$CS_2 + Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$

(a) 5 (b) 3 (c) 6 (d) 2

36. 6×10^{-3} mole $K_2Cr_2O_7$ reacts completely with 9×10^{-3} mole X^{n+} to give XO_3^- and Cr^{3+}. The value of 'n' is :
(a) 1 (b) 2 (c) 3 (d) 5

37. Hydrazine reacts with KIO_3 in presence of HCl as;

$$N_2H_4 + IO_3^- + 2H^+ + Cl^- \longrightarrow ICl + N_2 + 3H_2O$$

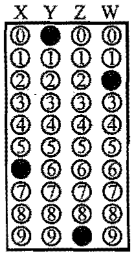
The equivalent masses of N_2H_4 and KIO_3 respectively are :
(a) 8, 87 (b) 8, 35.6 (c) 16, 53.5 (d) 8, 53.5

Answers

1. (d)	**2.** (a)	**3.** (b)	**4.** (c)	**5.** (a)	**6.** (a)	**7.** (c)	**8.** (a)
9. (d)	**10.** (c)	**11.** (a)	**12.** (c)	**13.** (a)	**14.** (c)	**15.** (c)	**16.** (b)
17. (d)	**18.** (a)	**19.** (b)	**20.** (a)	**21.** (b, c)	**22.** (a, b, c, d)	**23.** (a, c)	**24.** (d)
25. (a, b, c)	**26.** (c)	**27.** (a)	**28.** (c)	**29.** (a)	**30.** (b)	**31.** (b)	**32.** (a)
33. (c)	**34.** (a)	**35.** (d)	**36.** (a)	**37.** (d)			

Integer Answer TYPE QUESTIONS

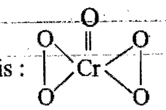
This section contains 9 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



1. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 is: **(IIT 2009)**

   [**Hint :** $4KOH + 2MnO_2 + O_2 \longrightarrow 2K_2\overset{+2\ +6\ -8}{MnO_4} + 2H_2O$]

2. How many peroxy links are there in CrO_5?

   [**Hint :** Structure of CrO_5 is : 

   There are two peroxy links in this molecule.]

3. How many moles of electrons are involved in the conversion of 1 mol $Cr_2O_7^{2-}$ into Cr^{3+} ion?

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

4. In the following reaction, hydrazine is oxidised to N_2

   $$N_2H_4 + OH^- \longrightarrow N_2 + H_2O + e^-$$

   The equivalent mass of N_2H_4 (hydrazine) is:

5. Nitrobenzene ($C_6H_5NO_2$) can be reduced to aniline ($C_6H_5NH_2$) by electrolytic reduction; the equivalent mass of nitrobenzene will be equal to $\left(\frac{\text{molecular mass}}{n}\right)$. The value of n is:

   [**Hint :** $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6[H] \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$]

6. How many sulphur atoms in $Na_2S_4O_6$ have zero oxidation state?

7. 6×10^{-3} mole $K_2Cr_2O_7$ reacts completely with 9×10^{-3} mole x^{n+} to give XO_3^- and Cr^{3+}. The value of n is:

8. The sum of oxidation number of nitrogen in NH_4NO_3 is :

9. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is: **(IIT 2010)**

   [**Hint :** $Si_6O_{18}^{-12}$ is a cyclic silicate. The value of n will be '3' to balance the charge $Be_nAl_2Si_6O_{18}$

   $$2n + 6 - 12 = 0$$
   $$n = 3]$$

Answers

1. (6) 2. (2) 3. (6) 4. (8) 5. (6) 6. (2) 7. (1) 8. (2)
9. (3)

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

Valency and oxidation number are different for an element. Valency of carbon is generally 4, however, the oxidation state may be $-4, -2, 0, +2, -1$, etc. In the compounds containing carbon, hydrogen and oxygen, the oxidation number of carbon can be calculated as:

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

where, n_H, n_O and n_C are number of respective atoms.

Answer the following questions:

1. Which of the following compounds have zero oxidation state at carbon?
   (a) $C_6H_{12}O_6$ (b) HCOOH (c) HCHO (d) CH_4
2. Which of the following oxides of carbon has fractional oxidation state?
   (a) Carbon monoxide (b) Carbon dioxide
   (c) Carbon suboxide (d) All of these
3. Which of the following compounds of carbon has highest oxidation state?
   (a) CH_4 (b) CH_3OH (c) CH_2O (d) HCOOH
4. Oxidation state of carbon in diamond is:
   (a) zero (b) +1 (c) −1 (d) +2
5. In which of the following compounds, the valency of carbon is two?
   (a) Carbenes (b) Allenes (c) Alkenes (d) Ketenes

Passage 2

Oxidation and reduction process involves the transaction of electrons. Loss of electrons is oxidation and the gain of electrons is reduction. It is thus obvious that in a redox reaction, the oxidant is reduced by accepting the electrons and the reductant is oxidised by losing electrons. The reactions in which a species disproportionates into two oxidation states (lower and higher) are called disproportionation reactions. In electrochemical cells, redox reaction is involved, i.e., oxidation takes place at anode and reduction at cathode.

Answer the following questions:

1. The reaction,
   $$Cl_2 \longrightarrow Cl^- + ClO_3^-$$
   is:
   (a) oxidation
   (b) reduction
   (c) disproportionation
   (d) neither oxidation nor reduction
2. Select the correct statement:
   (a) oxidation takes place at anode in electrochemical cell
   (b) reduction takes place at cathode in electrolytic cell
   (c) oxidation takes place at cathode in electrolytic cell
   (d) all are correct
3. In the reaction:
   $$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$
   (a) I_2 is a reducing agent (b) I_2 is an oxidising agent
   (c) $S_2O_3^{2-}$ is a reducing agent (d) $S_2O_3^{2-}$ is an oxidising agent
4. Determine the change in oxidation number of sulphur in H_2S and SO_2 respectively in the following reaction:
   $$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$
   (a) 0, +2 (b) +2, −4 (c) −2, +2 (d) +4, 0
5. Which of the following reactions is/are correctly indicated?

	Oxidant		Reductant		
(a)	HNO_3	+ Cu	$\longrightarrow$	$Cu^{2+} + NO_2$
(b)	$2Zn$	$+ O_2$	$\longrightarrow$	ZnO
(c)	Cl_2	$+ 2Br^-$	$\longrightarrow$	$2Cl^- + Br_2$
(d)	$4Cl_2$	$+ CH_4$	$\longrightarrow$	$CCl_4 + 4HCl$

Passage 3

Redox reactions are of three types:
(i) Intermolecular redox reactions,
(ii) Intramolecular redox reactions,
(iii) Auto redox reactions
OR
Disproportionation reactions.
Redox reactions are divided into two main types:
(i) Chemical redox reactions,
(ii) Electrochemical redox reactions which either produce or consume electricity.
Oxidation and reduction process takes place in a reaction simultaneously.

Answer the following questions:

1. Which of the following is a redox reaction?
   (a) $NaCl + KNO_3 \longrightarrow NaNO_3 + KCl$
   (b) $CaC_2O_4 + 2HCl \longrightarrow CaCl_2 + H_2C_2O_4$
   (c) $Mg(OH)_2 + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_4OH$
   (d) $Zn + 2AgCN \longrightarrow 2Ag + Zn(CN)_2$
2. Select the intramolecular redox reaction(s) among the following:
   (a) $2KClO_3 \longrightarrow 2KCl + 3O_2$
   (b) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$
   (c) $Cl_2 \longrightarrow Cl^- + ClO_3^-$
   (d) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$
3. In which of the following reactions, H_2O_2 acts as reducing agent?
   (a) $Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$
   (b) $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$
   (c) $HCHO + H_2O_2 \longrightarrow HCOOH + H_2O$
   (d) $PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$
4. Which among the following acts as oxidising as well as reducing agent?
   (a) HNO_2 (b) HNO_3 (c) H_2SO_4 (d) $KMnO_4$
5. The value of x in the following reaction,
   $$MnO_4^- + 8H^+ + xe \longrightarrow Mn^{2+} + 4H_2O \text{ is:}$$
   (a) 5 (b) 10 (c) 2 (d) 3

Passage 1.	1. (a, c)	2. (c)	3. (d)	4. (a)	5. (a)
Passage 2.	1. (c)	2. (a, b)	3. (b, c)	4. (b)	5. (a, c, d)
Passage 3.	1. (d)	2. (a, b, d)	3. (a, b, d)	4. (a)	5. (a)

SELF ASSESSMENT

ASSIGNMENT NO. 11

SECTION-I

Straight Objective Type Questions

This section contains 8 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. In the reaction:

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$ **[PET (MP) 2007]**

(a) oxidation of iodide into iodine takes place
(b) reduction of iodine into iodide takes place
(c) both oxidation and reduction of iodine takes place
(d) none of the above

2. The oxidation state of chromium in chromium trioxide is: **[CET (J&K) 2007]**

(a) +3 (b) +4 (c) +5 (d) +6

3. For the reaction between $KMnO_4$ and H_2O_2, the number of electrons transferred per mol of H_2O_2 is:

(a) one (b) two
(c) three (d) four

4. In the ionic equation,

$$BiO_3^- + 6H^+ + xe^- \longrightarrow Bi^{3+} + 3H_2O$$

the value of x is:

(a) 6 (b) 2
(c) 4 (d) 3

5. In $[Cr(O_2)(NH_3)_4H_2O]Cl_2$, oxidation number of Cr is +3, then oxygen will be in the form:

(a) dioxo (b) peroxo
(c) superoxo (d) oxo

6. In the reaction, $CrO_5 + SnCl_2 \longrightarrow CrO_4^{2-} + SnCl_4$, the element undergoing oxidation and reduction respectively are:

(a) Cr, Sn (b) Sn, Cr
(c) Sn, O (d) Cl, C

7. Equivalent mass of $KMnO_4$ in acidic, basic and neutral are in the ratio of:

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

8. A compound of Xe and F is found to have 53.5% Xe. What is the oxidation number of Xe in this compound?

(a) −4 (b) 0
(c) +4 (d) +6

SECTION-II

Multiple Answers Type Objective Questions

9. Peroxide ions are present in:

(a) H_2O_2 (b) BaO_2
(c) OF_2 (d) $H_2S_2O_8$

10. The metals undergoing disproportionation are:

(a) Sn (b) Na (c) Cu (d) Ca

11. The non-metals undergoing disproportionation are:

(a) P_4 (b) Cl_2 (c) I_2 (d) F

12. Which of the following can act as oxidising as well as reducing agent?

(a) O_3 (b) HNO_3 (c) SO_2 (d) H_2O_2

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

(a) −1 (b) +1 (c) −2 (d) +2

14. Select those species that can function both as oxidising and also as reducing agent: **[BHU (Mains) 2010]**

(a) KI (b) KI_3 (c) I_2 (d) H_2O_2

15. The species that contain peroxide ions are: **[BHU (Mains) 2010]**

(a) PbO_2 (b) H_2O_2 (c) SrO_2 (d) BaO_2

SECTION-III

Assertion-Reason Type Questions

This section contains 4 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

16. **Statement-1:** Spectator ions are the species that are present in the solution but do not take part in the reaction.

Because

Statement-2: The phenomena of formation of H_2O_2 by the oxidation of H_2O is known as auto-oxidation.

[**Hint:** $Zn + 2H^+ + 2Cl^- \longrightarrow Zn^{2+} + 2Cl^- + H_2$. Here, Cl^- ion is spectator ion.]

17. Statement-1: Oxidation number of carbon in HCN is + 2.

Because

Statement-2: Carbon always shows an oxidation state of + 4.

18. Statement-1: Bromide ion acts as a reducing agent in the reaction,

$$2MnO_4^- + Br^- + H_2O \longrightarrow 2MnO_2 + BrO_3^- + 2OH^-.$$

Because

Statement-2: Oxidation number of bromine increases from – 1 to + 5.

19. Statement-1: Oxidation number of carbon in HCHO is zero.

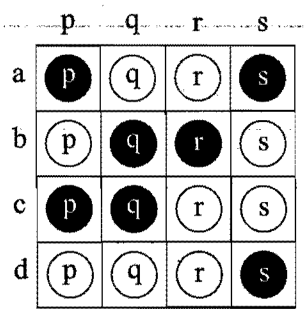
Because

Statement-2: HCHO is a covalent organic compound.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:



If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled 4 × 4 matrix should be as follows:

20. Match the Column-I with Column-II:

Column-I (Chemical species)	Column-II (Oxidation number of sulphur)
(a) S	(p) + 6
(b) H_2S	(q) + 1
(c) S_2Cl_2	(r) 0
(d) $H_2S_2O_8$	(s) – 2

21. Match the Column-I with Column-II:

Column-I (Compound)	Column-II (Oxidation state of sulphur)
(a) Sulphurus acid (H_2SO_3)	(p) + 5
(b) Peroxy mono sulphuric acid (H_2SO_5)	(q) + 3
(c) Dithionic acid ($H_2S_2O_6$)	(r) + 6
(d) Dithionous acid ($H_2S_2O_4$)	(s) + 4

22. Match the Column-I with Column-II:

Column-I	Column-II
(a) $O_2^- \longrightarrow O_2 + O_2^{2-}$	(p) Redox reaction
(b) $CrO_4^{2-} + H^+ \longrightarrow$	(q) One of the products has trigonal planar structure
(c) $MnO_4^- + NO_2^- + H^+ \longrightarrow$	(r) dimeric bridged tetrahedral metal ion
(d) $NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	(s) disproportionation

Answers

1. (a)	**2.** (d)	**3.** (c)	**4.** (b)	**5.** (c)	**6.** (c)	**7.** (d)	**8.** (d)
9. (a, b, d)	**10.** (a, c)	**11.** (a, b, c)	**12.** (c, d)	**13.** (a, b)	**14.** (b, c, d)	**15.** (b, c, d)	**16.** (b)
17. (c)	**18.** (a)	**19.** (b)	**20.** (a-r) (b-s) (c-q) (d-p)		**21.** (a-s) (b-r) (c-p) (d-q)		
22. (a-p,s) (b-r) (c-p,q) (d-p)							