Redox Reactions

The reactions that involve oxidation and reduction as its two half reactions are called redox reactions.

1. **Classical Idea of Redox Reactions:**

   According to classical concepts, oxidation and reduction are defined as the process that involve:

   Oxidation

   (*i*) Addition of oxygen
   (*ii*) Addition of electronegative element
   (*iii*) Removal of hydrogen
   (*iv*) Removal of electropositive element

   Reduction

   (*i*) Removal of oxygen
   (*ii*) Removal of electronegative element
   (*iii*) Addition of hydrogen
   (*iv*) Addition of electropositive element

2. **Oxidising and Reducing Agents** In a redox reaction, the substance which oxidises the other or which itself undergo reduction is called the oxidising agent. The substance that reduces the other and itself undergo oxidation is called the reducing agent.

3. **Redox Reactions in Terms of Electron Transfer** Because of simultaneous loss and gain of electrons in oxidation reduction processes, the redox reactions, (or the oxidation-reduction reactions) are also called electron transfer reactions.

4. **Oxidising and Reducing Agents in Terms of Electron Transfer**
   Oxidation Loss of electron(s) by any species.
   Reduction Gain of electron(s) by any species.
   Oxidising agent Acceptor of electron(s).
   Reducing agent Donor of electron(s).

5. **Oxidation Number** Oxidation number is defined as "the charge that an atom of the element possesses in its ion or appear to have when present in the combined state with other atoms."

6. **Rules for Calculating Oxidation Number** *These rules are given below*:

Rule 1 The oxidation number of an atom in its free or elementary state or in any of its allotropes is zero. e.g. The oxidation state of H in H_2, S in S_8, P in P_4.

Rule 2 In case of ions having only one kind of atoms, the oxidation number of each atom is equal to charge present on the ion. e.g. In case of Na^+, Mg^{2+}, Fe^{3+}, Cl^- and O^{2-}, the oxidation state is respectively + 1, + 2, + 3, − 1, − 2.

Rule 3 The oxidation state of alkali metals in all their compounds is always + 1. Similarly, in case of alkaline earth metals, it is always + 2. For aluminium, oxidation state is always + 3.

Rule 4 The oxidation state (O.S) of oxygen in most of its compounds is − 2, with an exception of peroxides and superoxides in which the oxidation state of oxygen is respectively − 1 and − 1/2.

Rule 5 The oxidation state of hydrogen is generally + 1 with an exception of metallic hydrides like NaH, CaH_2 etc. In these hydrides, oxidation state of hydrogen is −1.

Rule 6 The oxidation state of fluorine in all of its compounds is always − 1. Other halogens (i.e. chlorine, bromine and iodine) also exhibit − 1 oxidation state but it is not always true. In case of oxoacids and oxoanions, halogens (except fluorine) exhibit positive oxidation state.

Rule 7 The algebraic sum of the oxidation numbers of all the atoms present in a compound must be equal to zero.

Rule 8 In case of polyatomic ions, the algebraic sum of oxidation number of all the atoms present in the ion must be equal to the charge on the ion. e.g. in case of carbonate ion (CO_3^{2-}), it is equal to − 2.

7. **Paradox of Fractional Oxidation Number**

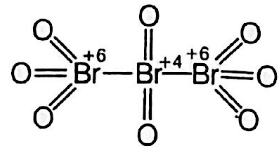
- In C_3O_2, the oxidation state of central C atom is 0.

$$\text{Thus,}\quad \overset{-2}{O}=\overset{+2}{C}=\overset{0}{C}=\overset{+2}{C}=\overset{-2}{O}$$

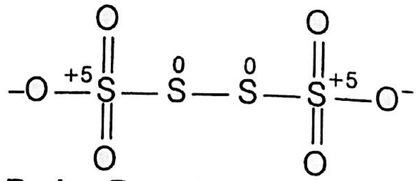
and the average of oxidation states of 3 C atoms in

$$C_3O_2 = \frac{2+2+0}{3} = \frac{4}{3}$$

- Average O.S of Br in Br_3O_8 is 16/3 while the oxidation states of three Br atoms are + 6, + 4 and + 6 as shown below:



- The average O.S of the four S-atoms in $S_4O_6^{2-}$ is 2.5 while the actual O.S of the four S-atoms are +5, 0, 0 and +5 as shown below:



8. **Types of Redox Reactions** *The redox reactions can be classified into following types:*

(*i*) **Combination reactions** The reactions in which two or more atoms or molecules combine together to give only a single compound are called combination reactions.

(*ii*) **Decomposition reactions** These are just opposite to the combination reactions.

(*iii*) **Displacement reactions** These are the reactions in which an atom (or ion) displaces the ion (or atom) of another element from a compound. These reactions can be represented as

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

Depending upon the nature of element displaced, these reactions can be classified into two categories.

(a) **Metal displacement reactions** In which metal is displaced.

$$\underset{\substack{\text{Copper}\\\text{sulphate}\\\text{(Oxidant)}}}{CuSO_4(aq)} + \underset{\substack{\text{Zinc}\\\text{(Reductant)}}}{Zn(s)} \longrightarrow \underset{\text{Copper}}{Cu(s)} + \underset{\text{Zinc sulphate}}{ZnSO_4(aq)}$$

(b) **Non-metal displacement reactions** In which non-metal is displaced.

$$\underset{\substack{\text{Sodium}\\\text{(Reductant)}}}{2Na(s)} + \underset{\text{Oxidant}}{+\,2H_2O(l)} \longrightarrow \underset{\substack{\text{Sodium}\\\text{hydroxide}}}{2NaOH(aq)} + \underset{\text{Hydrogen}}{H_2(g)}$$

(*iv*) **Disproportionation reactions** These are a special kind of redox reactions in which the same element undergoes oxidation as well as reduction.

9. **Balancing of Redox Reactions**

(*i*) **Ion electron method** The method involves the following steps:

(a) Write redox reaction in ionic form.

(b) Split redox reaction into oxidation half and reduction half reactions. Balance atoms of each half reactions by using simple multiples. For balancing H and O, add H^+ ion and H_2O to the appropriate sides, similarly add OH^- and H_2O to the appropriate sides. Balance the charge on both the sides and multiply one or both half reactions by suitable number to equalise number of electrons in both equations. Add the two balance half reactions and cancel common terms.

(ii) **Oxidation number method** The method involves the following steps:

(a) Assign oxidation number to the atoms in the equation and write separate equations for atoms undergoing oxidation and reduction.

(b) Find the change in oxidation number in each equation and make the change equal in both the equations by multiplying with suitable integers. After adding both the equations complete the balancing (by balancing H and O).

10. Redox Titrations In redox titrations, the strength of a reductant/oxidant is determined by titrating it with standard solution of oxidant/reductant using a redox sensitive indicator.

11. Terminology Used in Electrode Processes

(*i*) **Electrodes** A metal rod or strip dipped in its own salt solution is called an electrode.

(*ii*) **Anode** The electrode at which oxidation, i.e. loss of electrons from the metal takes place is called the anode.

(*iii*) **Cathode** It is the electrode at which reduction, i.e. gain of electrons by the metal ion occurs.

(*iv*) **Redox couple** The combination of the oxidised and reduced forms of a substance taking part in an oxidation or reduction half reaction is called the redox couple.

(*v*) **Electrode potential** The potential associated with an electrode is known as the electrode potential. It is represented by the symbol E.

(*vi*) **Standard electrode potential** The potential of an electrode in which the concentration of each species taking part in the electrode reaction is unity. If any gas is involved in the electrode reaction, its pressure is taken as 1 atmosphere and temperature is maintained at 298 K is called the standard electrode potential. It is represented by $E°$.

12. Electrochemical Cell It is a technique which is used to convert chemical energy into electrical energy. Daniell or voltaic cell is an important example of this cell.

Representation of an electrochemical cell

Reactions involved in a Daniell cell :

Anode half reaction (oxidation)

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

Cathode half reaction (reduction)

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

Thus, the Daniell cell is represented as

$$\underbrace{Zn | Zn^{2+}}_{\text{Anode}} \quad \underbrace{||}_{\text{Salt bridge}} \quad \underbrace{Cu^{2+} | Cu}_{\text{Cathode}}$$

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = E^{\circ}_{red} + E^{\circ}_{oxi}$$