CHAPTER 08

REDOX REACTIONS-1

1. Oxidation

Oxidation is defined as the addition of oxygen/electronegative element to a substance or removal of hydrogen/ electropositive element from a substance.

For example

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$
$$2H_2S(g) + O_2(g) \longrightarrow 2S(s) + 2H_2O(l)$$
$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$$

2. Reduction

Reduction is defined as the removal of oxygen/electronegative element from a substance or addition of hydrogen or electropositive element to a substance.
For example,

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$
(Removal of oxygen from mercuric oxide)

$$2FeCl_3(aq) + H_2(g) \longrightarrow 2FeCl_2(aq) + 2HCl(aq)$$
(removal of electronegative element, chlorine from ferric chloride)

$$CH_2 = CH_2(g) + H_2(g) \longrightarrow C_2H_6(g)$$
(addition of hydrogen)

3. Redox Reactions (electronic concept)

A few examples of redox reaction on the basis of electronic concept are given below: According to electronic concept every redox reaction consists of two steps known as half reactions.

(i) Oxidation reaction: Half reactions that involve loss of electrons are called oxidation reactions.

(ii) Reduction reaction: Half reactions that involve gain of electrons are called reduction reactions.

(iii) Oxidising agent/Oxidants: Oxidant or oxidising agent is a chemical substance which can accept one or more electrons and causes oxidation of some other species. In other words, the oxidation number of oxidant decreases in a redox reaction.

Important Oxidants Molecules of most electronegative elements such as O_2, O_3, halogens. Compounds having element in its highest oxidation state e.g.,$K_2Cr_2O_7$, $KMnO_4$, $HClO_4$, H_2SO_4, $KClO_3$, $Ce(SO_4)_2$.Oxides of metals and non-metals such as MgO, CrO_3, CO_2, etc.

(iv) Reducing agent/Reductants: Reductant or reducing agent is a chemical substance which can give one or more electrons and causes reduction of some other species. In other words, the oxidation number of reductant increases in a redox reaction.

Important Reductants

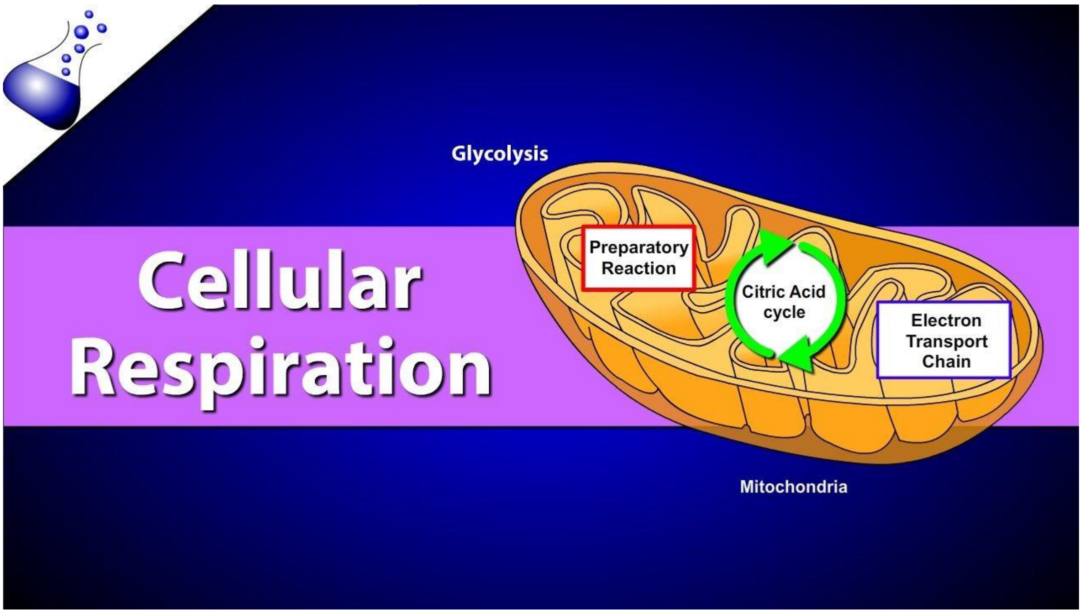
All metals such as Na, AI, Zn, etc., and some non – metals, e.g., C, S. P, H_2, etc.
Metallic hydrides like NaH , LiH , KH, CaH_2 etc

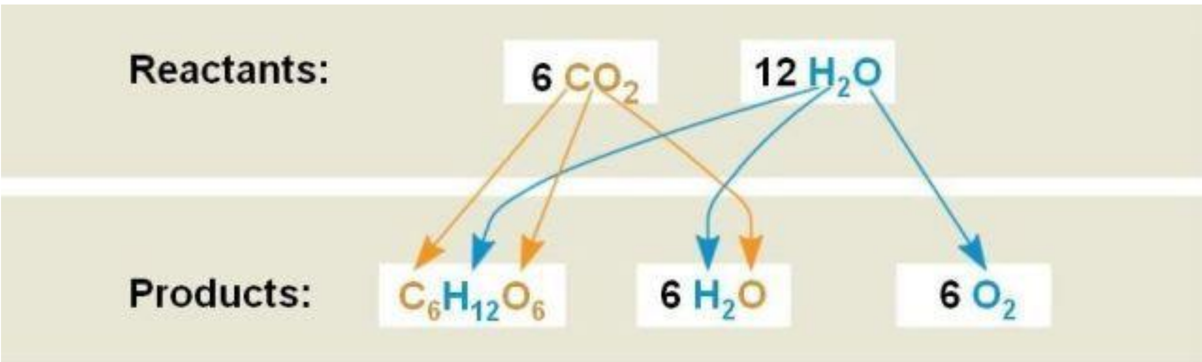
4. Examples of Redox Reactions from our Environment

➢ Respiration

Cellular respiration which is the ultimate source of energy in human beings encompasses a series of redox reactions. So, the food that we consume is converted into energy by redox reactions only.

During the process of respiration, the carbon-dioxide is reduced whereas the water is oxidised to form oxygen.





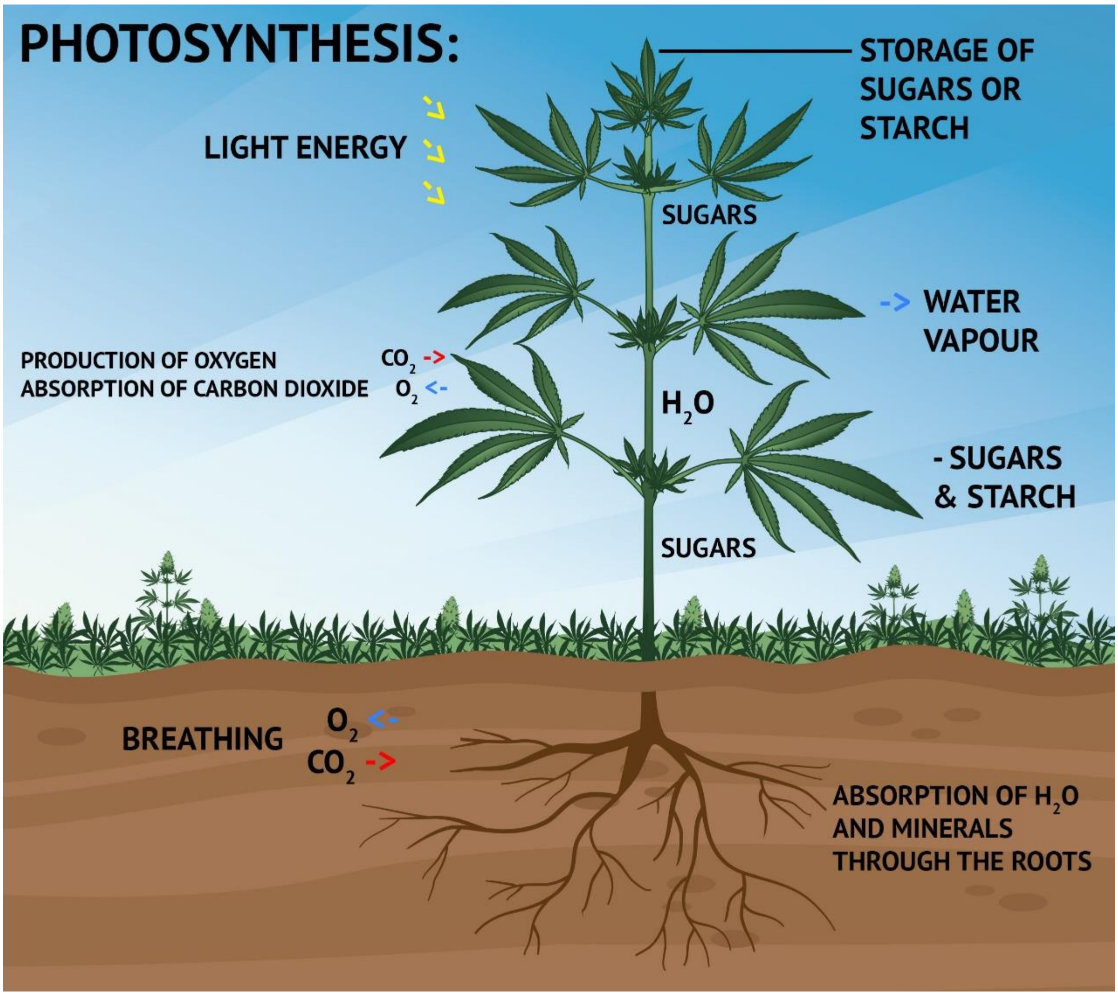
$$6\,CO_2 + 12\,H_2O + \text{Light energy} \rightarrow C_6H_{12}O_6 + 6\,O_2 + 6\,H_2O$$

Combustion

Combustion forms the classic example of redox reactions in real-life. However, whenever we talk about combustion, we usually view it as a physical change than a chemical one. The burning of organic material and combustion of hydrocarbons in fossil fuels form yet another important example of redox reactions. During the process of combustion, the oxygen present in the atmosphere is being reduced whereas the compound which is being burned is undergoing oxidation.

➢ Photosynthesis

The process of photosynthesis takes place in the leaves of the plants. What happens is that carbon dioxide and water combine in the presence of sunlight to release oxygen and glucose. The glucose which is formed in the whole process of photosynthesis is used to fuel the metabolic reactions of the plants. In photosynthesis, water is oxidised and carbon dioxide is reduced.



Corrosion

The process of corrosion forms yet another example of redox reactions in everyday life.

On contact with a metal, say, an iron door, some of the oxygen atoms present in water oxidise iron (or the metal) and, thereby, lead to the generation of free hydrogen ions. The hydrogen ions generated combine with oxygen to yield water, and the whole cycle begins once again.

- **Rusting**

The exposure of iron (or an alloy of iron) to oxygen in the presence of moisture leads to the formation of rust. Oxygen is a very good oxidizing agent whereas iron is a reducing agent. Therefore, the iron atom readily gives up electrons when exposed to oxygen.

The chemical reaction is given by:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

The oxidation state of iron is further increased by the oxygen atom when water is present.

$$4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O^{2-}$$

Now, the following acid-base reactions occur between the iron cations and the water molecules.

$$Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+$$

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

The hydroxides of iron are also formed from the direct reaction between the iron cations and hydroxide ions.

$$O_2 + H_2O + 4e^- \rightarrow 4OH^-$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$$

The resulting hydroxides of iron now undergo dehydration to yield the iron oxides that constitute rust.

5. Oxidation Number

It is the oxidation state of an element in a compound which is the charge assigned to an atom of a compound is equal to the number of electrons in the valence shell of an atom that are gained or lost completely or to a large extent by that atom while forming a bond in a compound.

6. Rules for Assigning Oxidation Numbers

(i) The oxidation number of an element in its elementary form is zero.
For example, H_2, O_2, N_2 etc. have oxidation number equal to zero.
(ii) In a single monoatomic ion, the oxidation number is equal to the charge on the ion.
For example, Na^+ ion has oxidation number of +1 and Mg^{2+} ion has +2.
(iii) Oxygen has oxidation number -2 in its compounds. However, there are some exceptions.
Compounds such as peroxides. Na_2O_2, H_2O_2
oxidation number of oxygen = – 1 In OF_2
O.N. of oxygen = +2 O_2F_2
O.N. of oxygen = +1
(iv) In non-metallic compounds of hydrogen like HCl, H_2S, H_2O oxidation number of hydrogen = + 1 but in metal hydrides oxidation number of hydrogen = -1
[LiH, NaH, CaH_2 etc.]
(v) In compounds of metals and non-metals metals have positive oxidation number while non-metals have negative oxidation number. For example, In NaCl. Na has +1 oxidation number while chlorine has -1.
(vi) If in a compound there are two non-metallic atoms the atoms with high electronegativity is assigned negative oxidation number while other atoms have positive oxidation number.
(vii) The algebraic sum of the oxidation number of all atoms in a compound is equal to zero.
(viii) In poly atomic ion the sum of the oxidation no. of all the atoms in the ion is equal to the net charge on the ion.

For example, in $(CO_3)^{2-}$Sum of carbon atoms and three oxygen atoms is equal to -2.
Fluorine (F_2) is so highly reactive non-metal that it displaces oxygen from water.

$$2\overset{+1}{H_2}\overset{-2}{O}(aq) + 2\overset{0}{F_2}(g) \longrightarrow 4\overset{+1}{H}\overset{-1}{F}(g) + \overset{0}{O_2}(g)$$

7. Fractional Oxidation Numbers

Elements as such do not have any fractional oxidation numbers. When the same element are involved in different bonding in a species, their actual oxidation states are whole numbers but an average of these is fractional.

For example, In C_3O_2

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

The average O.N. of carbon atoms $= \dfrac{(2+2+0)}{3} = \dfrac{4}{3}$.

Fractional O.N. of a particular element can be calculated only if we know about the structure of the compound or in which it is present.