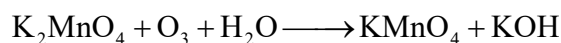
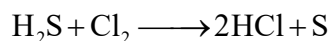
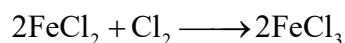
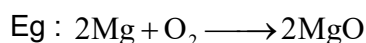


## CHAPTER - 05

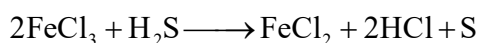
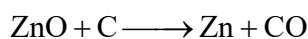
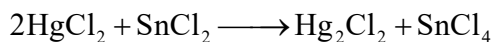
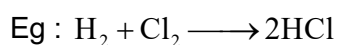
# REDOX REACTIONS

### EARLIER CONCEPT OF OXIDATION

Oxidation is the process of addition of oxygen or any electronegative element or group or removal of hydrogen or any electropositive element or group.

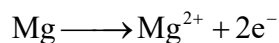
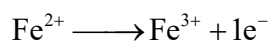
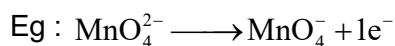


Reduction is the process of addition of hydrogen or any electropositive element or group or removal of oxygen or any electronegative element or group.



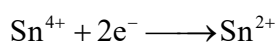
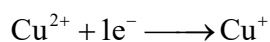
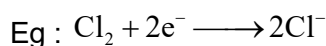
### ELECTRONIC CONCEPT

According to the electronic concept, oxidation involves loss of electrons or removal of electrons.



Here  $\text{MnO}_4^{2-}$ ,  $\text{Fe}^{2+}$  and  $\text{Mg}$  are donating electrons (electron donor) and are called Reducing agents.

∴ Reducing agent is electron donor or we can say that reducing agents are getting oxidised. Similarly reduction involves gain of electrons or addition of electrons.



$\text{Cl}_2$ ,  $\text{Sn}^{4+}$  and  $\text{Cu}^{2+}$  are accepting electrons and are called oxidising agents.

∴ Oxidising agent is electron acceptor. Hence oxidising agents are getting reduced. We have another concept for oxidation and reduction, called oxidation number concept.

### **Oxidation Number concept**

Oxidation number is the number of electrons lost or gained when an atom in the free state changes to the combined state.

**OR**

It is the positive or negative charge allotted to each atom in a compound assuming all the bonds are ionic bonds.

In  $\text{FeCl}_3$ , the oxidation number of iron is +3 and that of chlorine is -1.

Eg :  $\overset{+3}{\text{Fe}}\overset{-1}{\text{Cl}}_3$ ,  $\overset{+1}{\text{H}}\overset{+5}{\text{N}}\overset{-2}{\text{O}}_3$ ,  $\overset{+1}{\text{Na}}_2\overset{+4}{\text{C}}\overset{-2}{\text{O}}_3$  etc

It is also called oxidation state.

### **Rules for oxidation number**

1. The oxidation number of all elements in free state is zero

Eg : O.N of H atom in  $\text{H}_2 = 0$

O.N of O atom in  $\text{O}_3 = 0$

O.N of P atom in  $\text{P}_4 = 0$

O.N of S atom in  $\text{S}_8 = 0$

2. The oxidation number of hydrogen is +1 in usual compounds and -1 in metallic hydrides (ionic hydrides)

Eg :  $\overset{+1}{\text{N}}\text{H}_3$ ,  $\overset{+1}{\text{C}}\text{H}_4$ ,  $\overset{+1}{\text{H}}_2\text{O}$ ,  $\overset{+1}{\text{H}}_2\text{SO}_4$ ,  $\text{NaH}^{-1}$ ,  $\text{CaH}_2^{-1}$

3. The oxidation number of oxygen is -2 in usual compounds, ( $\text{SO}_3^{-2}$ ,  $\text{P}_2\text{O}_5^{-2}$ ,  $\text{Cl}_2\text{O}_7^{-2}$ ,  $\text{HClO}_4^{-2}$ )

-1 in peroxides, ( $\text{H}_2\text{O}_2^{-1}$ ,  $\text{BaO}_2^{-1}$ ) and  $-\frac{1}{2}$  in superoxides ( $\text{KO}_2^{-1/2}$ )

Oxygen has positive oxidation in oxyfluorides.

( $\overset{+1}{\text{O}}_2\text{F}_2$ ,  $\overset{+2}{\text{O}}\text{F}_2$ )

4. Fluorine is the most electronegative element with -1 oxidation state.
5. In compounds, the O.N. of Group I metals is +1 and that of Group-II metals is +2.

$\overset{+1}{\text{Na}}_2\text{SO}_4$ ,  $\overset{+1}{\text{K}}_2\text{CO}_3$

$\overset{+2}{\text{Ba}}\text{Cl}_2$ ,  $\overset{+2}{\text{Sr}}\text{SO}_4$ ,  $\overset{+2}{\text{Mg}}\text{CO}_3$

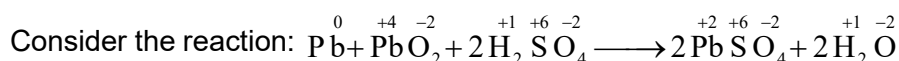
6. The O.N. of a compound is zero and that of an ion is equal to the charge on the ion
7.
  - 1) The algebraic sum of O.N. of all atoms in a neutral compound is zero
  - 2) The algebraic sum of O.N. of all atoms in an ion is equal to the charge on the ion
8. O.N. of covalent bond
  - 1) Each covalent bond contributes one unit for O.N
  - 2) Covalently bonded atoms with less electronegativity acquire positive O.N. While other atom with more electronegativity acquire negative O.N.
9. O.N. of co-ordinate bond

1) Give +2 value of O.N. to the atom from which coordinate bond is directed to a more electronegative atom. +2 to donor atom and -2 to acceptor atom.

2) If co-ordinate bond is directed from a more electronegative atom to a less electronegative atom, contribution of coordinate bond is neglected.

### Oxidation/Reduction in terms of O.N

Oxidation is the process in which O.N. increases. Reduction is the process in which O.N. decreases.



The O.N. of Pb increases from 0 to +2  $\therefore$  Pb is oxidised to  $\text{PbSO}_4$ .

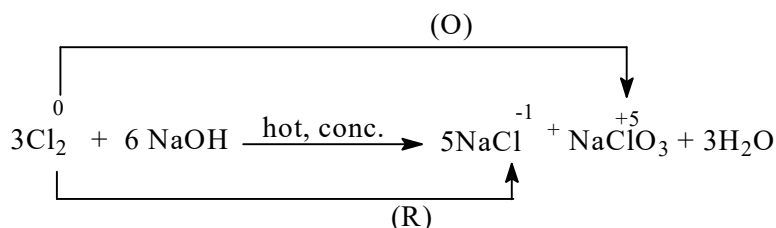
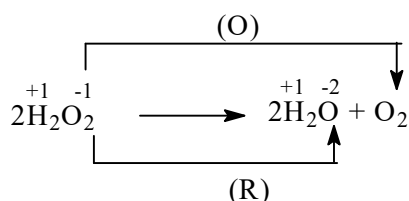
The O.N. of Pb in  $\text{PbO}_2$  decreases from +4 to +2.  $\therefore$   $\text{PbO}_2$  is reduced to  $\text{PbSO}_4$ . Such reactions in which oxidation and reduction occur simultaneously is called a Redox reaction.

Here Pb is the reducing agent and  $\text{PbO}_2$  is the oxidising agent.

Neutralisation reactions and precipitation reactions are not redox reactions because there is no change in oxidation number.

### 3. **Disproportionation reaction**

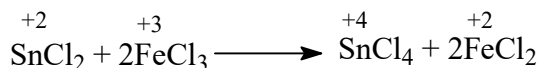
The same element in the same oxidation state is simultaneously oxidised and reduced.



### Reducing agent and oxidising agent

Reducing agent is an electron donor. Hence after oxidation, the O.N. of the reducing agent increases.

Oxidising agent is electron acceptor. Hence after reduction, the oxidation number of oxidising agent decreases.



Here  $\text{SnCl}_2$  is the reducing agent and  $\text{FeCl}_3$  is the oxidising agent.

### **Exercise :**

Determine the oxidation number of

1) P in  $\text{NaH}_2\text{PO}_2$

Let O.N. of P = x

$$\therefore 1 + 2 + x - 4 = 0; \therefore x = +1$$

$$\begin{aligned}
 2) \quad & \text{Cr in } \text{Cr}_2\text{O}_7^{2-} \\
 & 2x - 14 = -2 \\
 & 2x = 12 \\
 & \therefore x = +6
 \end{aligned}$$

### RANGE FOR OXIDATION NUMBER

There is a range for oxidation number

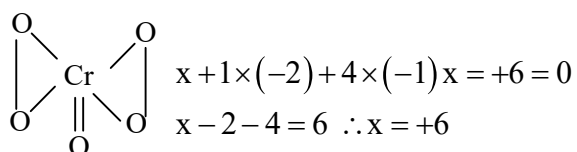
Element	Oxidation number	Range
S	-2, 0, +1, +4, +6	-2 to +6
N	-3, -2, -1, -1/3, 0, +1, +2, +3, +4, +5	-3 to +5
Cl	-1, 0, +1, +3, +4, +5, +7	-1 to +7
H	-1, +1	-
P	-3, 0, +1, +3, +5	-3 to +5
O	-2, -1, -1/2, 0, +1, +2	-2 to +2
C	-4, -3, -2, -1, 0, +2, +3, +4	-4 to +4
Cr	+3, +6	-
Mn	+2, +8/3, +3, +4, +6, +7	+2 to +7
Si	-4, +4	-
Fe	+8/3, +2, +3	-
Os	+8	-
Xe	+6	-

### Exceptional cases of evaluation of oxidation numbers

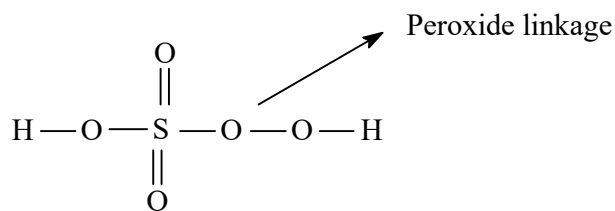
The oxidation number is evaluated based on the structure using the concept of chemical bonding.

1.  $\text{CrO}_5$  (chromium pentoxide or blue per chromate)

By usual method, the oxidation of Cr is +10. But the maximum oxidation of Cr is +6 only. (Cr has only  $5e^-$  in 3d orbitals and  $1e^-$  in 4s orbital). This is because 4, oxygen atoms are in peroxide linkage.

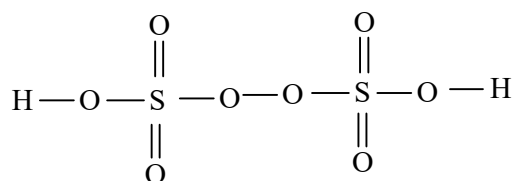


2. S in  $\text{H}_2\text{SO}_5$  (Peroxomonosulphuric acid, Caro's acid)



$$2 \times (+1) + x + 3 \times (-2) + 2 \times (-1) = 0; \therefore x = +6$$

3. S in  $\text{H}_2\text{S}_2\text{O}_8$  (Peroxi disulphuric acid, Marshall's acid). It is also has a peroxide linkage



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

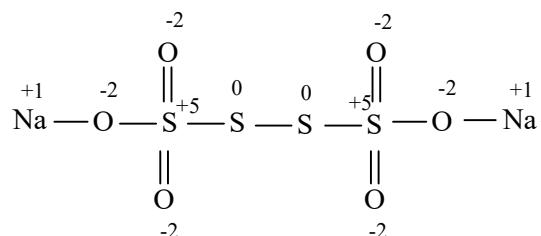
(for H)                      (for S)                      (for O)                      (for O-O)

$$\therefore 2x = +12 \text{ or } x = +6$$

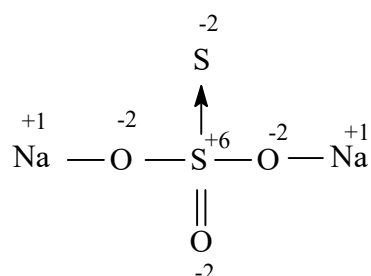
4. S in  $\text{Na}_2\text{S}_4\text{O}_6$  (Sodium tetra thionate)

$$2 + 4x - 12 = 0 \therefore 4x = 10; \therefore x = \frac{+10}{4} = 2.5$$

Fraction : average O.N

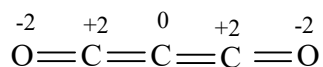


5. S in  $\text{Na}_2\text{S}_2\text{O}_3$  (Sodium thiosulphate)

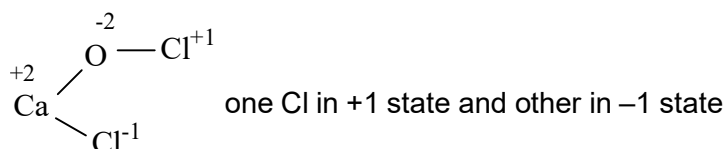


The donor S atom is in +6 and acceptor S atom in -2

6. C in  $C_3O_2$

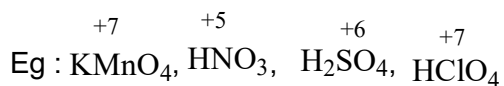


7. Cl in  $CaOCl_2$  (Bleaching powder)

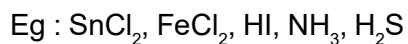


### To predict whether the compound is oxidising agent or reducing agent

1. If the central atom of the compound is in the highest oxidation state, it will act only as oxidising agent.



2. If the central atom is in the lowest oxidation state, it will act only as reducing agent.



3. If the central atom is in an intermediate oxidation state, it will act as both oxidising agent and reducing agent



### EQUIVALENT WEIGHT

Equivalent weight of a substance (oxidant or reductant) is equal to molecular weight divided by number of electrons lost or gained by one molecule of a substance in a redox reaction.

$$\text{Eq. wt. of O.A.} = \frac{\text{Molecular weight}}{\text{No. of } e^- \text{ gained by one molecule (n - factor or valence factor)}}$$

$$\text{Eq. wt. of R.A.} = \frac{\text{Molecular weight}}{\text{No. of } e^- \text{ lost by one molecule (n - factor or valence factor)}}$$

## BALANCING OF REDOX REACTIONS

### I. Ion-electron method (half reaction method)

- i. Write down the reaction in ionic form.
- ii. Split it into 2 half reactions (oxidation and reduction)

#### iii. To balance each half reaction

- a. Balance the other atom except H and O
- b. Balance the O.N. by adding  $e^-$
- c. Balance the charge by adding  $H^+$  for reactions in acidic medium and  $OH^-$  for reactions in basic medium
- d. Balance H and O by adding  $H_2O$  molecules.
- iv. Make the no. of electrons equal in both half reactions.
- v. Add the 2 balanced half reactions and cancel the common term if any

### II. Oxidation number method

- i. Write down the reaction in ionic form, and mark the oxidation and reduction
- ii. Make the number of atoms equal other than H and O
- iii. Find the increase in O.N. and decrease in O.N.
- iv. Make the increase and decrease equal. (by multiplication with suitable integer)
- v. Balance charge by adding  $H^+$  for reactions in acid medium and  $OH^-$  for reactions in basic medium.
- vi. Balance H and O by adding  $H_2O$  molecules.

## REDOX TITRATIONS

Titration between oxidising agent and reducing agent

### I. Permanganometry

$KMnO_4$  is used as O.A. (in acidic medium)  $H_2C_2O_4$  (oxalic acid) or Mohr's salt is the R.A.  $KMnO_4$  itself acts as a self indicator. End point is the appearance of a permanent pale pink colour.

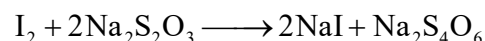
### II. Dichrometry

$K_2Cr_2O_7$  is used as O.A. (in acidic medium)  $FeSO_4$  is the R.A.

External indicator : Potassium ferricyanide . At the end point the prussian blue colour changes.

### III. Iodimetry

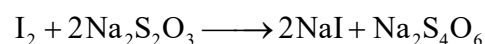
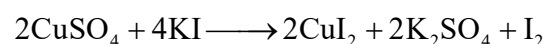
Estimation of a R.A. using standard  $I_2$  solution is called iodimetry.



Starch is used as indicator. At the end point the blue colour disappears.

### IV. Iodometry

Here  $I_2$  is produced by a reaction between O.A. and KI solution. The  $I_2$  liberated is titrated against  $Na_2S_2O_3$  solution using starch as indicator.



By this method, the O.A. can be estimated.

## CHAPTER - 06

# CHEMICAL THERMODYNAMICS

The branch of chemistry which deals with the study of different forms of energy and their interconversions is called thermodynamics.

### BASICS OF THERMODYNAMICS

#### System and surroundings

The part of the universe under our experimental observation is called the system. The remaining part which exchanges energy and matter with the system is called the surrounding.

Thus system + surroundings  $\rightarrow$  universe

The system is separated from surroundings by real or imaginary boundaries.

If the physical properties and chemical compositions are the same throughout the system, the system is called homogeneous. Otherwise the system is heterogeneous.

#### Different types of systems

1. **Open system** : A system which can exchange energy and matter with the surroundings is called an open system.  
Eg : Hot water placed in an open beaker
2. **Closed system** : A system which can exchange only energy but not matter with the surroundings is called a closed system.  
Eg : Hot water placed in a closed beaker.
3. **Isolated system** : A system which can exchange neither energy nor matter with the surroundings is called an isolated system.  
Eg : Hot water placed in a thermoflask

### MACROSCOPIC PROPERTIES OF A SYSTEM

The properties which arise due to the bulk behaviour of matter in the system are called macroscopic properties.

Eg : Mass, Volume, Energy etc.

1. **Extensive properties** : The properties which depend upon the amount of substance present in the system are called extensive properties. Eg : Mass, Volume, Energy etc.
2. **Intensive properties** : The properties which are independent of the amount of substance present in the system and depend only on the nature of the substance are called intensive properties.