

CHAPTER - 04

REDOX REACTION

I. Classical concept

A) Oxidation :

Addition of O_2 : $2Mg + O_2 \longrightarrow 2MgO$

Addition of electronegative element : $Mg + Cl_2 \longrightarrow MgCl_2$

Removal of H_2 : $Zn + 2HCl \longrightarrow ZnCl_2 + H_2$

Removal of electropositive element : $2NaI + H_2O_2 \longrightarrow 2NaOH + I_2$

B) Reduction

Addition of Hydrogen : $H_2 + Cl_2 \longrightarrow 2HCl$

Addition of electropositive element : $CuCl_2 + Cu \longrightarrow Cu_2Cl_2$

Removal of O_2 : $Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe$

Removal of electronegative element : $2FeCl_3 + H_2 \longrightarrow 2FeCl_2 + 2HCl$

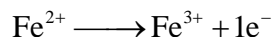
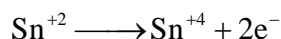
II. Electron transfer concept of oxidation and reduction

OXIDATION

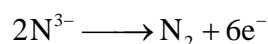
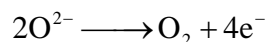
The reaction in which an atom or an element or an ion or molecule loses electrons is called oxidation

1. Neutral atom : $Na \longrightarrow Na^+ + 1e^-$; $Mg \longrightarrow Mg^{2+} + 2e^-$

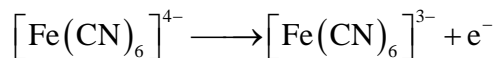
2. Cation : When a cation loses electrons. There is an increase in positive charge.



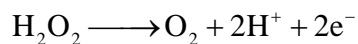
3. Anion : When an anion loses electron equal to its negative charge, it gets converted to a neutral atom.



4. **Complex anion** : When a complex anion loses electron, its negative charge decreases.



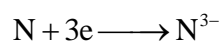
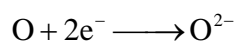
5. When a molecule loses electrons, it breaks up into its constituents



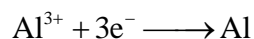
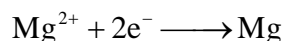
REDUCTION

The reaction in which an element or an atom or an ion or a molecule accepts electrons, is called reduction.

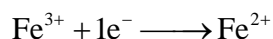
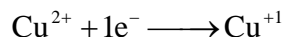
1. **Neutral atom** : When a neutral element or atom accepts electrons, it gets converted into an anion.



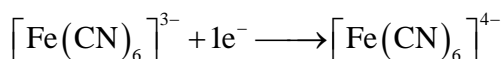
2. **Cation** : When a cation accepts electrons equal to its charge, it gets converted into a neutral atom.



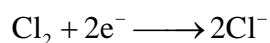
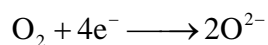
3. Similarly, when a cation accepts electrons then, its positive charge decreases.



4. **Anion** : When an anion accepts electrons, its negative charge increases.



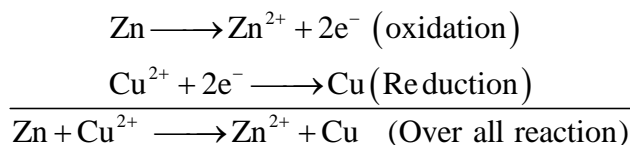
5. **Molecule** : When a molecule accepts electron, it is a reduction reaction.



Oxidation	: loss of electrons by any species
Reduction	: Gain of electrons by any species
Oxidising agent	: Acceptor of electrons
Reducing agent	: Donor of electron

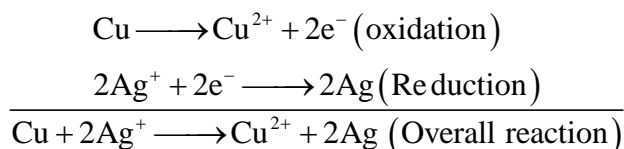
Competitive Electron Transfer Reactions

Dip zinc rod in copper nitrate solution taken in a beaker A and a copper rod in silver nitrate solution in another beaker B. After few minutes we can see that in beaker A, zinc rod partially dissolves and its surface is coated with metallic copper. The blue colour of CuSO_4 solution takes and finally it becomes colourless. This is due to the following reaction taking place in beaker A.



In this reaction Zn acts as a reducing agent and Cu^{2+} acts as an oxidising agent.

In beaker B copper rod dissolves partially and its surface is coated with metallic silver from silver nitrate solution, the solution develops blue colour due to the formation of Cu^{2+} ions.



Conclusion : In the above reactions, Zn releases electrons to copper and copper releases electrons to Ag and electron releasing tendency of them is in the order $\text{Zn} > \text{Cu} > \text{Ag}$. These types of reactions are called competitive electron transfer reaction.

Oxidation number : Oxidation number is the charge present on the atom of the element when it is in combination

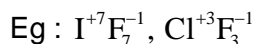
Rules for assigning oxidation number

- Oxidation state of any element in the free state is zero.
For example : The oxidation state of H, P, S, O, Fe and Br in H_2 , P_4 , S_8 , O_2 , Fe and Br_2 , respectively is equal to zero.
- In all hydrogen compounds the oxidation number per atom of hydrogen is taken to be +1. The exception occurs when hydrogen forms compounds with strong metals [metallic hydrides].
For example : KH, NaH, MgH_2 , CaH_2 etc. In all of these, the oxidation state of hydrogen is -1.
- Oxidation number of oxygen is -2 in most of its compounds.

Exceptions :

- In peroxides oxidation number of oxygen is -1. Eg : H_2O_2 , BaO_2 , SrO_2
 - In superoxides oxidation state of oxygen is -1/2. Eg : KO_2 , RbO_2
 - In OF_2 oxidation number of oxygen is +2
 - In O_2F_2 oxidation number of oxygen is +1
- Oxidation number of halogens in halides is always -1
 - Oxidation number of fluorine is always -1
 - Oxidation number of alkali metal is always +1
 - Oxidation number of alkaline earth metal is always +2

8. In inter halogen compounds the more electronegative atom of the two halogens gets the oxidation number of -1 .

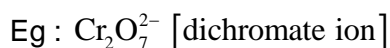


9. The algebraic sum of all the oxidation numbers of elements in a compound is equal to zero.



Oxidation number of K + Oxidation number of Mn + 4 (Oxidation number of oxygen) = 0

10. The algebraic sum of all the oxidation numbers of elements in a radical is equal to net charge on the radical.



$2 \times \text{oxidation number of Cr} + 7 \times \text{oxidation number of O} = 2$

11. Variable oxidation number is most commonly shown by transition elements as well as by p-block elements.

Transition elements

Fe : +2, +3

Cu : +1, +2

Mn : +1, +2, +3, +4, +5, +6, +7

Ni : +2, +4

Co : +2, +3

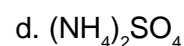
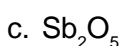
p-Block elements

As : +3, +5

Sb : +3, +5

Sn : +2, +4

1. Calculate the oxidation number of all atoms in the following compounds and ions:



- a. In PbSO_4 or $\text{Pb}^{2+}(\text{SO}_4)^{2-}$

Oxidation number of Pb = +2

Oxidation number of each O atom = -2

Let oxidation number of S = x

$$\therefore +2 + x + 4(-2) = 0 \Rightarrow 2 + x - 8 = 0 \Rightarrow x = +6$$

Hence, oxidation number of S in PbSO_4 = +6

- b. In CrO_4^{2-}

Oxidation number of each O atom = -2

Let oxidation number of Cr = x

$$x + 4(-2) = -2 \Rightarrow x - 8 = -2 \Rightarrow x = 6$$

Hence, oxidation number of Cr in CrO_4^{2-} = +6

c. In Sb_2O_5

Oxidation number of each O atom = -2

Let oxidation number of Sb = x

$$2x + 5(-2) = 0 \Rightarrow 2x - 10 = 0 \Rightarrow x = +5$$

Hence, oxidation number of Sb in $\text{Sb}_2\text{O}_5 = +5$ **d. In $(\text{NH}_4)_2\text{SO}_4$ or $(\text{NH}_4^+)_2\text{SO}_4^{2-}$** Let oxidation number of N in $\text{NH}_4^+ = x$

Oxidation number of each H atom = +1

$$x + 4(+1) = +1 \text{ (Taking } \text{NH}_4^+)$$

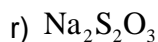
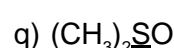
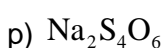
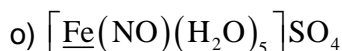
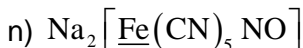
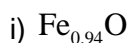
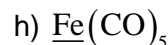
$$x = -3$$

Hence, oxidation number of N in $(\text{NH}_4)_2\text{SO}_4 = -3$ and oxidation number of each O atom = -2

Let oxidation number of S = x

$$\therefore x + 4(-2) + 2 \text{ (taking } \text{SO}_4^{2-})$$

$$x - 8 = -2 \Rightarrow \text{or } x = 6$$

Hence, oxidation number of S in $(\text{NH}_4)_2\text{SO}_4 = 6$ **1. Determine the oxidation number of following underlined elements:**

a) $\underline{\text{HCN}}$: The evaluation cannot be made directly in some cases, eg. HCN, by using rules proposed earlier as we have no rule for the evaluation of the oxidation number of both N and C. In all such cases, evaluation of oxidation number should be made using indirect concept or using fundamentals by which following rules have been formed.

i. Each covalently bond contributes one unit for oxidation number.

ii. Covalency bonded atoms with less electronegativity acquire positive oxidation number whereas other atoms with more electronegativity acquire negative oxidation number

iii. In case of a coordinate bond, give +2 value for oxidation number to the atom from which coordinate bond is directed to a more electronegative atom.

If coordinate bond is directed from a more electronegative to a less electronegative atom, then neglect the contribution of coordinate bond for both atoms in which coordinate bond exists.

Thus, $\text{H}-\text{C}\equiv\text{N}$

Three bonds on N atom implies more electronegative $1 + a + 3(-1) = 0$

Oxidation number of N = $3(-1) = -3$

Oxidation number of C, $a = +2$

b. $\text{H}\underline{\text{N}}\text{C} : \text{H}-\text{C}\equiv\text{N}$

Oxidation number of H = +1

Oxidation number of N

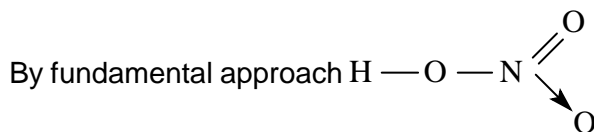
$$= [-2 + (-1) + 0] = -3$$

[For covalent bond with C] [For covalent bond with C] [No contribution for coordinate bond]

According to fundamental concept = -3

$$\therefore 1 + (-3) + a = 0 \Rightarrow a = +2$$

c. $\text{H}\underline{\text{N}}\text{O}_3$: By rules, $1 + a + 3(-2) = 0 \Rightarrow a = +5$



Oxidation number of H = +1

Oxidation number of N

$$= +1 + (+2) + (2) = +5$$

[Covalent bond with O] [Two covalent bond with O; N being less electronegative than O] [coordinate bond]

d. $\text{K}\underline{\text{O}}_2$: A superoxide of K

Oxidation number of K = +1

Oxidation number of O = a

$$1 + 2(a) = 0 \text{ and } a = -1/2$$

e. $\underline{\text{Fe}_3\text{O}_4} : 3(a + b(-2)) = 0 \Rightarrow a = +8/3$

Fe_3O_4 is a mixed oxide of $\text{FeO} \cdot \text{Fe}_2\text{O}_3$

Therefore, Fe has two oxidation numbers +2 and +3, respectively. However, factually speaking, oxidation number in Fe_3O_4 is an average of two values, ie. +2 and +3

Therefore, average oxidation number = $\frac{+2 + (\times 3)}{3} = +\frac{8}{3}$

f. $\underline{\text{KI}_3} : 1 + 3(a) = 0 \Rightarrow a = -1/3$

Since KI_3 is $\text{KI} + \text{I}_2$, therefore, I has two oxidation numbers -1 and 0, respectively.

However, oxidation number of I in KI_3 is an average of two values -1 and 0.

Therefore, average oxidation number = $\frac{-1 + 2(0)}{3} = -\frac{1}{3}$

g. $\underline{\text{N}_3\text{H}} : 3(a) + 1 = 0 \Rightarrow a = -1/3$

h. $\underline{\text{Fe}(\text{CO})_5} : \text{Sum of oxidation number of CO} = 0; \therefore a + 5(0) = 0 \Rightarrow a = 200/94$

i. $\underline{\text{Fe}_{0.94}\text{O}} : 0.94(a) + (-2) = 0 \Rightarrow a = 200/94$

j. $\underline{\text{NH}_2\text{NH}_2} : \text{Both N have same nature, therefore each N has oxidation number } -2.$

k. $\underline{\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}}$

Oxidation number of Fe = a

Sum of oxidation number for $(\text{NH}_4)_2\text{SO}_4 = 0$

Sum of oxidation number of $\text{H}_2\text{O} = 0$

Sum of oxidation number of $\text{SO}_4^{2-} = -2$

$\therefore a + (-2) + 0 + 6(0) = 0 \Rightarrow a = +2$

l. $\underline{\text{NOCl}} : \text{Cl} - \text{N} = \text{O} \text{ or use } \text{NO}^{\oplus}\text{Cl}^{\ominus}$

Oxidation number of N = +1 (for covalent bond with Cl)

Oxidation number of N = +2 (for two covalent bonds with O)

Therefore, oxidation number of N in $\text{NOCl} = +3$

m. $\underline{\text{NOClO}_4} : \text{The compound may be written as } \text{NO}^+ \text{ClO}_4^{\ominus} \text{ for } \text{ClO}_4^{\ominus}$

For ClO_4^{\ominus} , let the oxidation number of Cl = a

$\therefore a + 4(-2) = -1 \Rightarrow a = +7$

n. $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$: NO in iron complex has NO^{\oplus} nature

$$\therefore 2 \times 1 + [a + 5(-1) + (+1)] = 0$$

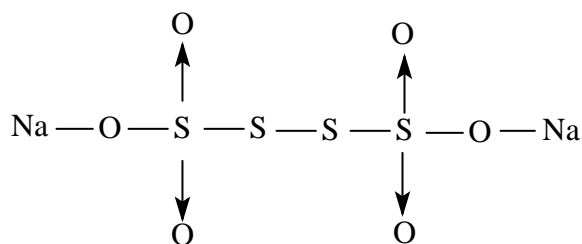
$$\therefore a = +2$$

o. $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]\text{SO}_4$: $a + 1 + 5 \times 0 + (-2) = 0 \Rightarrow a = +1$

p. $\text{Na}_2\text{S}_4\text{O}_6$: $2(+1) + 4a + 6(-2) = 0$

$$\therefore a = +5/2$$

Here also, this value is the average oxidation number of S. The structure of $\text{Na}_2\text{S}_4\text{O}_6$ is



Thus, oxidation number of each S atom forming coordinate bond is +5, whereas oxidation number of each S atom involved in pure covalent bonding is zero. Therefore, average oxidation number

$$= \frac{+5 + 5 + 0 + 0}{4} = +\frac{5}{2}$$

q. $(\text{CH}_3)_2\text{SO}$ or Dimethyl sulphoxide

Oxidation number of $\text{CH}_3 = +1$

Oxidation number of O = -2

$$\therefore 2(+1) + a + (-2) = 0 \Rightarrow a = 0$$

r. CaOCl_2 : In bleaching powder, two Cl atoms are as $\text{Ca}(\text{OCl})\text{Cl}$, i.e., one as Cl having oxidation number -1 and other as OCl^{\ominus} having oxidation number +1

OXIDATION STATE OF OXYGEN IN DIFFERENT FORMS

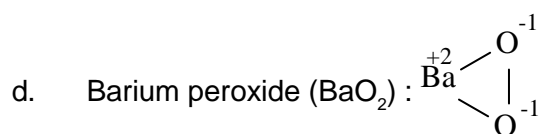
1. Oxidation state of oxygen in Peroxides and Peracides: Oxidation state (oxidation number) of oxygen in peroxides ($-\text{O}-\text{O}-$), eg: H_2O_2 , and peroxyacids is -1.

For example:

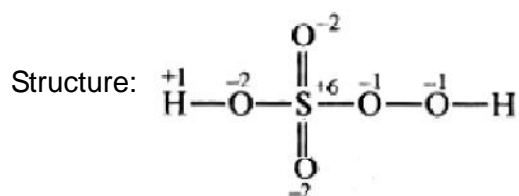
a. Hydrogen peroxide (H_2O_2): $\text{H}^{\overset{+1}{}}-\text{O}^{\overset{-1}{}}-\text{O}^{\overset{-1}{}}-\text{H}^{\overset{+1}{}}$

b. Sodium peroxide (Na_2O_2): $\text{Na}^{\overset{+1}{}}-\text{O}^{\overset{-1}{}}-\text{O}^{\overset{-1}{}}-\text{Na}^{\overset{+1}{}}$

c. Strontium peroxide (SrO_2): $\text{Sr}^{\overset{+2}{}} \begin{array}{l} \nearrow \text{O}^{\overset{-1}{}} \\ \searrow \text{O}^{\overset{-1}{}} \end{array}$



- e. Peroxosulphuric acid or peroxy sulphuric acid or permonooxo sulphuric acid or persulphuric acid or Caro's acid (H_2SO_5)



- i. Calculation of oxidation state of S in H_2SO_5 and their anions:

Two oxygen in peroxide bond are in -1 oxidation state $= -1 \times 2 = -2$

Three oxygen in -2 oxidation state $= -2 \times 3 = -6$

$$\therefore \text{H}_2\text{SO}_5 = 2 + x - 2 - 6 = 0 \Rightarrow x = 6$$

Oxidation number of S = $+6$

- ii. HSO_5^\ominus (monohydroperoxo sulphate ion)

$$\text{HSO}_5^\ominus = 1 + x - 2 - 6 = -1 \Rightarrow x = 6$$

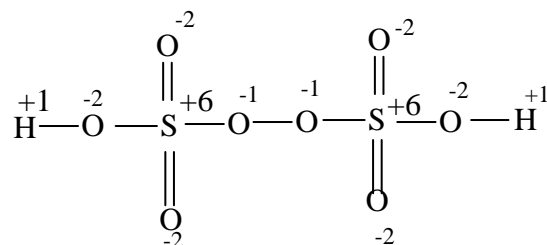
Oxidation number of S = 6

- iii. SO_5^{2-} (peroxosulphate ion)

$$\text{SO}_5^{2-} = x - 2 - 6 = -2 \Rightarrow x = 6$$

- f. Peroxodisulphuric acid or peroxydisulphuric acid or permonooxodisulphuric acid or per disulphuric acid or Marshall's acid ($\text{H}_2\text{S}_2\text{O}_8$):

Structure



- i. Oxide state and oxidation number of S in $\text{H}_2\text{S}_2\text{O}_8$ and their anions:

Two oxygen in peroxide bond are in -1 oxidation state $= -1 \times 2 = -2$

Six oxygen in $\text{H}_2\text{S}_2\text{O}_8$ are in -2 oxidation state $= -2 \times 6 = -12$

$$\therefore \text{H}_2\text{S}_2\text{O}_8 : 2 + 2x - 2 - 12 = 0; \quad 2x = 12 \Rightarrow x = 6$$

Oxidation number of S in $\text{H}_2\text{S}_2\text{O}_8 = +6$

ii. Monohydroperoxodisulphate ion or hydro-persulphate ion $\left(\text{HS}_2\text{O}_8^\ominus\right)$

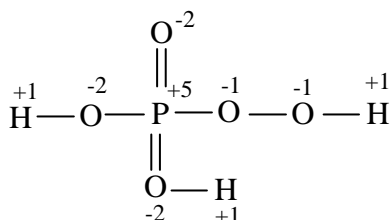
$$1 + 2x - 2 - 12 = -1$$

$$2x = 12 \Rightarrow x = 6$$

Oxidation number of S in $\text{S}_2\text{O}_8^{2-} = +6$

g. Peroxophosphoric acid or peroxyphosphoric acid or permonooxophosphoric acid or perphosphoric acid $(\text{H}_3\text{PO})_5$:

Structures:



h. Oxidation state (oxidation number) of P in H_3PO_5 and their anions:

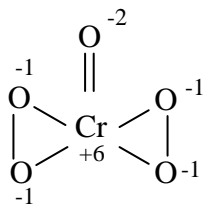
Two oxygen in peroxide bond are in -1 oxidation state $= -1 \times 2 = -2$

Three oxygen in H_3PO_5 PO_5 are in -2 oxidation state $= -2 \times 3 = -6$

$$\text{H}_3\text{PO}_5 = 3 + x - 2 - 6 = 0 \Rightarrow x = 5$$

Oxidation number of P = $+5$

i. Chromium pentaoxide (butterfly structure) (CrO_5) :



Oxidation state (oxidation number) of Cr in CrO_5 : There are two peroxide ($-\text{O}-\text{O}-$) bonds in CrO_5 . For oxygen in two peroxide bond are in -1 oxidation state $= -1 \times 4 = -4$

One oxygen in CrO_5 is in -2 oxidation state $= -2 \times 1 = -2$

$$\therefore \text{CrO}_5 = x - 4 - 2 = 0 \Rightarrow x = +6$$

Oxidation number of Cr = $+6$

Oxidation state of oxygen in superoxides

Oxidation number of oxygen in superoxides is $-1/2$, eg. in $\overset{+2}{K}\overset{-1/2}{O_2}$ (potassium superoxides) and $\overset{+1}{Rb}\overset{-1/2}{O_2}$ (Rubidium superoxide)

Oxidation state of oxygen, when it is bonded to fluorine

In such compounds, eg., oxygen difluoride $\left(\overset{+2}{O}\overset{-1}{F_2}\right)$ and dioxygen difluoride $\left(\overset{+1}{O_2}\overset{-1}{F_2}\right)$, the oxygen is assigned an oxidation number of +2 and +1 respectively. The number assigned to oxygen depends upon the bonding state of oxygen but this number should be a positive figure only.

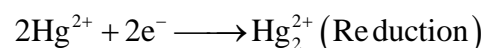
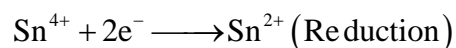
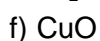
STOCK NOTATION

The oxidation number state of a metal in a compound is sometimes represented by Stock notation given by German chemist Alfred Stock. In this notation, the oxidation number is expressed by a roman numeral such as I, II, III, IV, V, VI, VII etc, indicating the oxidation state of the metal within parenthesis after the symbol or name of the metal.

For example, nitrogen forms five oxides, ie. N_2O , NO , NO_2 , N_2O_4 and N_2O_5 having the oxidation number +1, +2, +4, +4 and +5, respectively. Therefore, according to stock notation, they are represented as $N_2(I)O$, $N(II)O$, $N(IV)O_2$, $N_2(IV)O_4$, and $N_2(V)O_5$, respectively.

Similarly, aurous chloride and auric chloride are written as $Au(I)Cl$ and $Au(III)Cl_3$. Similarly, stannous chloride and stannic chloride are written as $Sn(II)Cl_2$ and $Sn(IV)Cl_4$, respectively. This change in oxidation state explains whether the species is present in oxidised or reduced form.

Thus, $Sn(II)Cl_2$ is the reduced form of $Sn(IV)Cl_4$. Similarly, $Hg_2(I)Cl_2$ is the reduced form of $Hg(II)Cl_2$.

**3. Using stock notations, represent the following compounds:**

	Compound	Stock notation	Name of the compound
a	$\overset{+1}{\text{H}} \overset{+3}{\text{Au}} \overset{1 \times 4}{\text{Br}_4}$	Hau(III) Br ₄	Hydroauric bromide
b	$\overset{+1 \times 2}{\text{Tl}_2} \overset{-2}{\text{O}}$	Tl ₂ (I)O	Thallous oxide
c	$\overset{+2}{\text{Fe}} \overset{-2}{\text{O}}$	Fe(II) O	Ferrous oxide
d	$\overset{+3 \times 2}{\text{Fe}_2} \overset{-2 \times 3}{\text{O}_3}$	Fe ₂ (III) O ₃	Ferric oxide
e	$\overset{+1}{\text{Cu}} \overset{-1}{\text{Br}}$	Cu(I)Br	Cuprous bromide
f	$\overset{+2}{\text{Cu}} \overset{-2}{\text{O}}$	Cu(II)Br	Cupric oxide
g	$\overset{+2}{\text{Mn}} \overset{-2}{\text{O}}$	Mn(II)O	Manganese oxide
h	$\overset{+4}{\text{Mn}} \overset{-2 \times 2}{\text{O}_2}$	Mn(IV)O ₂	Manganese dioxide

Difference between valency and oxidation number (these two terms have different meanings as explained below)

	Oxidation number	Valency
1	Oxidation number is the residual charge left on the atom when other atoms are removed as ions	It is the combining capacity of an element. It is also defined as the number of H atoms or twice the number of O atoms with which an atom of the element reacts.
2	It can be zero, eg., oxidation number of C in CH_2Br_2 is zero	It cannot be zero
3	It refers to the charge, which can be positive or negative, eg: in CuCl_2 , the oxidation number of Cu is +2 and that of Cl is -1	It is only a number and it is not assigned as positive or negative. For example, in CuCl_2 , the valency of Cu is 2 and that of Cl is 1
4	It can have fractional value, eg:- oxidation number of S in $\text{K}_2\text{S}_2\text{O}_8$ is +5/2	It is always a whole number, since atoms always combine in simple whole numbers.
5	Oxidation number of an element can be different in different compounds, eg:- oxidation number of C in CH_4 , C_2H_6 , CH_3Br , C_2H_2 , CH_2Br_2 , CCl_4 and CHBr_3 are -4, -3, -2, -1, 0, +4 and +2 respectively	It is fixed in all its compounds, eg:- the valency of C is 4 in all its compounds, such as CH_4 , C_2H_6 , CH_3Br , C_2H_2 , CH_2Br_2 , CCl_4 and CHBr_3 .

FRACTIONAL OXIDATION STATE

Fractional oxidation state is the average oxidation state of the element and the structural parameters show that the element whose oxidation state is determined is present in different oxidation state.

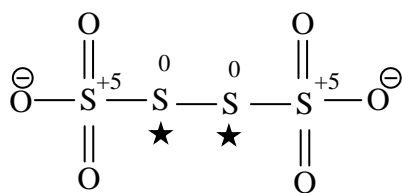
Structures and oxidation numbers of the species $\text{S}_4\text{O}_6^{2-}$ (tetrathionate ion), C_3O_2 (carbon suboxide), and Br_3O_8 (tribromooctaoxide) show the following bonding situations.

a. $\text{S}_4\text{O}_6^{2-}$ ($4x - 12 = -2$, $x = 2.5$)

Oxidation number of S = 2.5

Structures:

Structure

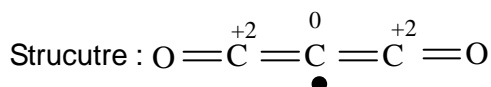


The element marked with asterisk in each species is showing different oxidation state (oxidation number) from the rest of the atoms of the same element in each of the species.

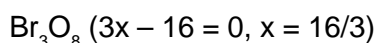
In the species $S_4O_6^{2-}$, each of the two extreme S atoms shows oxidation state of +5 and the middle S atom as 0. The average of oxidation numbers of the four sulphur atoms is 2.5, whereas the reality being +5, 0, 0 and +5 oxidation number, respectively, for each sulphur.

b. C_3O_2 ($3x - 4 = 0$, $x = 4/3$)

Oxidation number of C = 4.3

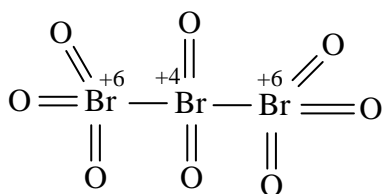


In C_3O_2 , two terminal carbon atoms are present in +2 oxidation state each, whereas the third C atom (middle carbon) is in zero oxidation state and the average is 4/3.



Oxidation number of Br = 16/3

Structures:

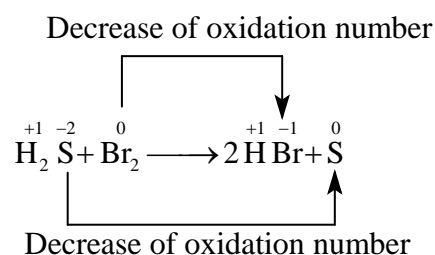


In Br_3O_8 , each of the two terminal Br atoms is present in +6 oxidation state and the middle Br atom is present in +4 oxidation state. The average that is different from reality is 16/3.

Therefore, in general, the fractional oxidation state reality is revealed by the structures only. It is concluded that fractional oxidation state is the average oxidation number only. This proves that the element in that particular species is present in more than one whole number oxidation states.

III. Oxidation and reduction in terms of oxidation number

Oxidation is defined as a chemical process in which oxidation number of the element increases. On the other hand, reduction is defined as the chemical process in which oxidation number of the element decreases. For example, let us consider the reaction between hydrogen sulphide and bromine to give Hydrogen bromide and sulphur.

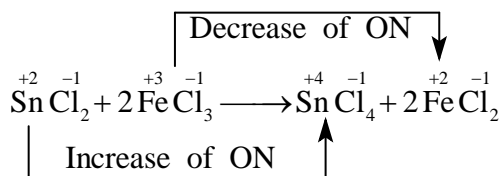


In the above example, the oxidation number of bromine decreases from 0 to -1, thus it is reduced. The oxidation number of 's' increases from -2 to 0. Hence, H_2S is oxidised. Let us now define the reducing and oxidising agents in the light of the concept of oxidation number.

Oxidising agent : is a substance which undergoes increase in the oxidation number of one or more of its elements.

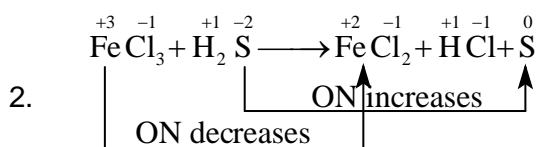
In the above example, H_2S is reducing agent while Br_2 is oxidising agent.

Example : Identify the oxidising agent and reducing agent in the following reaction.



Oxidising agent - FeCl_3

Reducing agent - SnCl_2



Oxidising agent - FeCl_3

Reducing agent - H_2S

Important oxidising agents.

1. Molecule made up of electronegative elements. Eg : O_2 , O_3 , X_2 (Halogens)
Note : Fluorine is the strongest oxidant
2. Compounds containing an element which is the highest oxidation state.
Eg : KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Cr}_2\text{O}_7$, CrO_3 , H_2SO_4 , HNO_3 , FeCl_3 etc
3. Oxides of elements
Eg: MgO , CuO , CrO_3 , CO_2 , P_4O_{10} etc.

Important reducing agents:-

1. **Metals** : Eg- Na, Zn, Fe, Al etc
2. **Few non metals** : Eg - C, H_2 , S etc
3. **Hydracids** - HBr, HI, H_2S etc
4. Few compounds containing an element in the lower oxidation state.
Eg: FeCl_2 , FeSO_4 , SnCl_2 , Cu_2O
5. Metallic hydrides Eg : NaH, LiH etc
6. Organic compounds like HCOOH and $(\text{COOH})_2$

Substances which acts as oxidising as well as reducing agents

H_2O_2 , SO_2 , H_2SO_3 , HNO_2 , NaNO_2 , Na_2SO_3 etc.

Tips for the identification of oxidising and reducing agents:

If an element is in its highest possible oxidation state in a compound, the compound can function as an oxidising agent.

Eg: KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, HNO_3 , H_2SO_4 , HClO_4 etc

If an element is in its lowest possible oxidation state in a compound, the compound can function only as a reducing agent.

Eg: H_2O_2 , H_2SO_3 , HNO_2 , SO_2 etc.

Highly electronegative element is in its highest oxidation state in a compound, that compound can function as powerful oxidising agent.

Eg: KClO_4 , KClO_3 , KBrO_3 , KIO_3 etc.

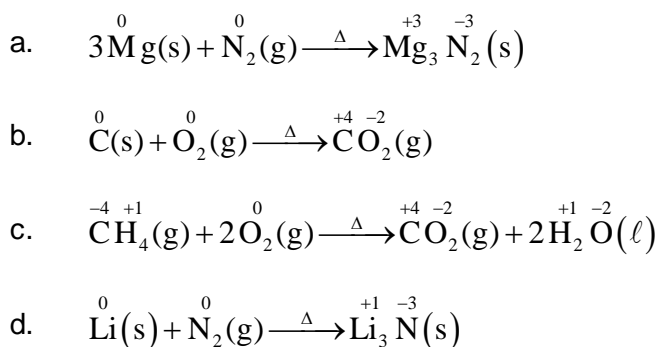
An electronegative element is in its lowest possible oxidation state in a compound or in a free state, it can function as powerful reducing agent.

Eg : I^- , Br^- , N^{3-} etc.

TYPES OF REDOX REACTIONS

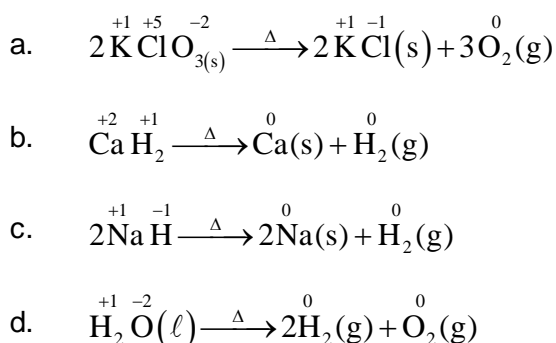
- Combination Reactions :** A reaction in which two atoms or molecules combine together to form a third molecule is called a combination reaction. For example $\text{A} + \text{B} \longrightarrow \text{C}$.

Either A or B both A and B must be in the elemental form for such a reaction to be a redox reaction. All combustion reactions in which elemental oxygen is used and all other reactions that involve elements other than oxygen are redox reactions. For example.



In reaction (c), there is no change in the oxidation number of hydrogen.

- Decomposition Reactions :** Decomposition reactions are those in which when a molecule breaks down to form two or more components, at least one of them must be in the elemental state. Thus, decomposition reactions are reverse of combination reactions. For example:



- Displacement Reactions :** A reaction in which an atom or ion in a compound is replaced by an atom or ion of another element is called a displacement reaction. It may be denoted as: $\text{X} + \text{YZ} \longrightarrow \text{XZ} + \text{Y}$

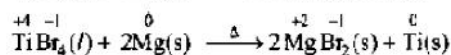
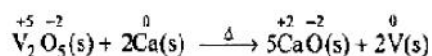
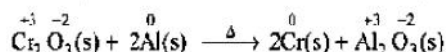
Types of displacement reactions

These are two types :

a. Metal displacement reactions**b. Nonmetal displacement reactions**

- a. Metal displacement reactions :** In these reactions, a metal in the compound is displaced by some other metal in the uncombined or elemental state. These reactions are used in metallurgical processes in which pure metals are obtained from their compounds in ores.

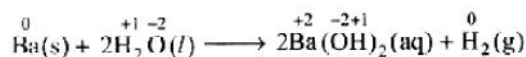
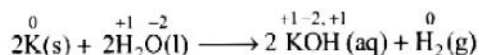
For example :



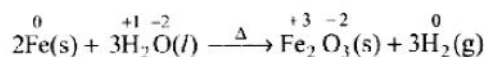
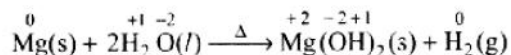
In all the above cases, the reducing metal is a better reducing agent than the one that is being reduced, which shows more capability to lose electrons as compared to the one that is reduced.

- a. Non-metal displacement reactions :** In these reactions, a metal or nonmetal displaces another nonmetal from its compound. These nonmetal displacement redox reactions include hydrogen displacement and the rarely occurring reaction involving oxygen or halogens displacement.

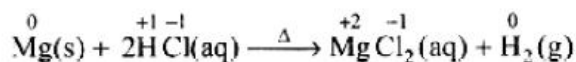
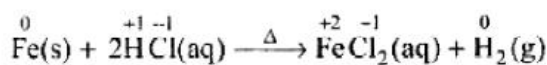
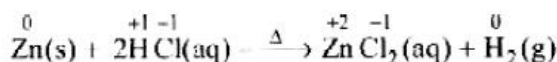
- i. All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) which are very good reductants displace hydrogen from cold water, for example,



- ii. Less reactive metals such as Mg and Fe react with steam to produce dihydrogen gas, for example,



- iii. Many metals, including those which do not react with cold water, displace dihydrogen from acids, for example,



The reactions of Zn and Mg with HCl are used in the preparation of dihydrogen gas in the laboratory.

Reactivity of Metals

The reactivity of metals is determined by the rate of evolution of H_2 by metals from H_2O and aqueous acids, for example, Na reacts with water at the fastest rate, Mg reacts slowly, Fe reacts at the slowest rate while Ag, and Au do not react at all.

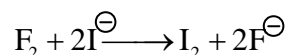
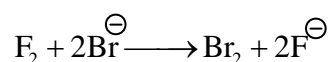
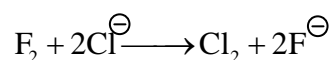
Order of reducing activity : $\text{Zn} > \text{Cu} > \text{Ag}$

Reactivity of Nonmetals

The nonmetals, such as halogens, have a tendency to accept electrons, therefore, their reactivity depends upon their oxidising power.

Order of decreasing oxidising power of halogens is : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

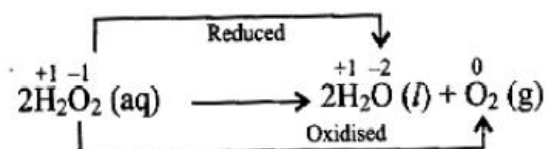
Thus F_2 is the strongest oxidising agent; it displaces Cl_2 , Br_2 and I_2 from the solutions of their respective ions (Cl^- , Br^- and I^-). F_2 is very reactive so it displaces O_2 from H_2O , for example:



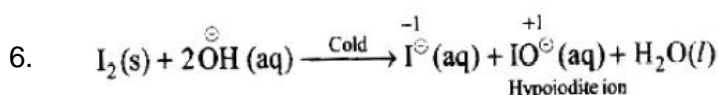
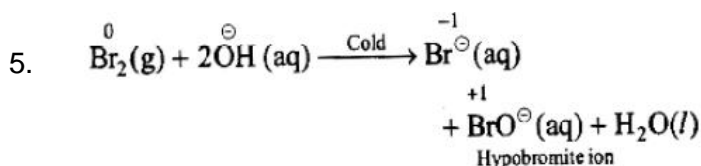
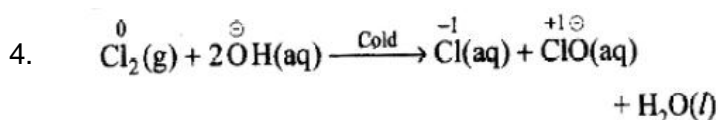
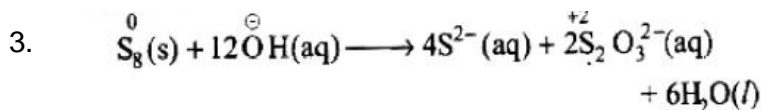
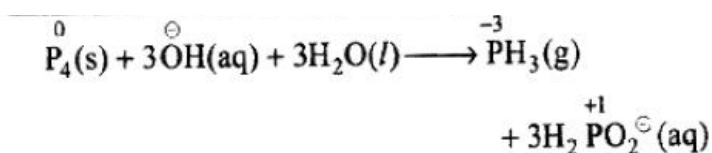
Disproportionation reactions : In a disproportionation reaction, an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances in a disproportionation reaction always contains an element that can exist in at least three oxidation states. The element in the form of reacting substances is in the intermediate oxidation state, and both lower and higher oxidation states of that element are formed in the reaction.

For examples

- Decomposition of H_2O_2 (hydrogen peroxide) to H_2O and O_2 . In H_2O_2 , -1 oxidation state of O is converted to zero oxidation state in O_2 and decreases to -2 oxidation state in H_2O



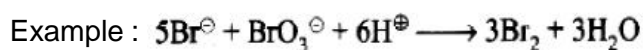
2. Phosphorous, sulphur and chloride undergo disproportionation in the basic medium as given below:



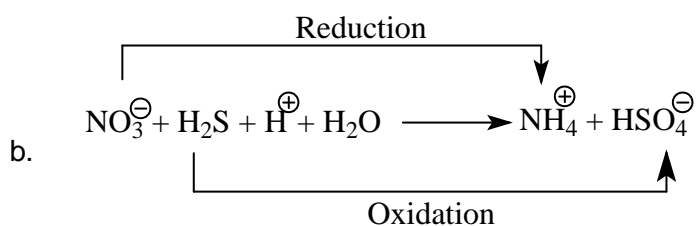
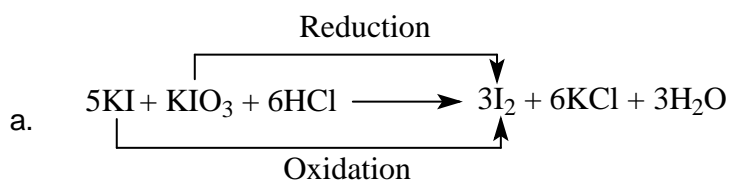
Fluorine does not show a disproportionation reaction since it is the most electronegative element, therefore it cannot exhibit any positive oxidation state. The reaction of fluorine takes place as follows

Comproportionation Reaction : Conproportionation reaction is the reverse of disproportionation reaction.

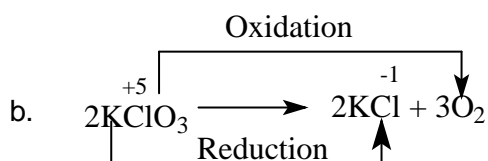
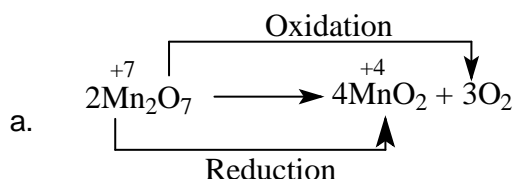
For example, Br^- and BrO_3^- in acidic medium undergoes oxidation and reduction respectively to give Br_2 .



Intermolecular redox reaction : It is similar to redox in which one molecule is oxidised and other molecule is reduced. For example,



Intramolecular Redox reaction : In this reaction one atom of a molecule is oxidised and another is reduced. For example,



BALANCING OF REDOX REACTIONS

Two methods are commonly used for balancing chemical equations involving redox reactions. The first method is based on the change in the oxidation number of the oxidant and the reductant (oxidation number method) and the second method is based on splitting the redox reaction into two half reactions, one involving oxidation and the other involving reduction (ion-electron method)

a. Oxidation number method

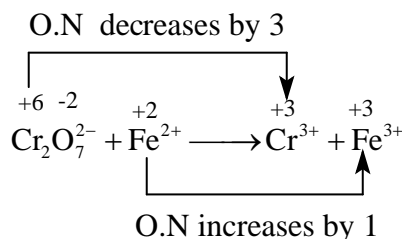
The various steps involved are:

- Write the skeletal equation for all the known reactants and products of the reaction
- Indicate the oxidation number of all the atoms in each compound in the skeletal equation and ignore the atoms or groups in which there is no change of oxidation number. Now identify the atoms undergoing change in their oxidation number.
- Calculate the increase or decrease in the oxidation number per atom and then for the whole molecule in which it occurs. If these are not equal then multiply by suitable coefficients so that these become equal.
- Balancing the chemical equation with respect to all atoms except H and O.
Finally balance with respect to H and O atoms. For balancing oxygen atoms and water molecules to the side deficient in it. Balancing of hydrogen atoms will depend on the medium (acidic or basic) as explained below.
 - If the reaction is in an acidic medium then the deficiency in hydrogen atoms can be made up by adding H^+ ions on the side that is deficient in it.
 - If the reaction is in a basic medium the deficiency in hydrogen atoms can be made up by adding water molecules on the deficient side and adding equal number of OH^- ions on the other side of the equation.

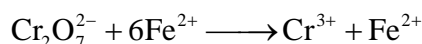
Finally, the equation is balanced by cancelling common species present on both sides of the equation.

1. Dichromate ion in aqueous acidic medium reacts with ferrous ion to give ferric and chromic ions. Write the balanced chemical equation corresponding to the reaction.?

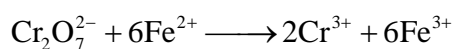
- i. The skeletal equation is $\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} \longrightarrow \text{Cr}^{3+} + \text{Fe}^{3+}$
- ii. Write the oxidation number of each atom.



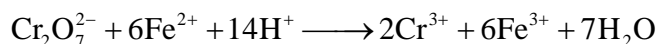
- iii. The oxidation number of Cr in chromate ion is +6 and it changes to +3 in Cr^{3+} and the oxidation number of Fe^{2+} is +2 and changes to +3 in Fe^{3+} . Therefore chromate ion acts as the oxidant and Fe^{2+} acts as the reductant. The oxidation number of chromium atom decreases by 3 and for dichromate ion containing two chromium ions, the total decrease is 6. The oxidation number of iron increases by 1. In order to equalise the increase and decrease in oxidation number of the oxidant and reductant, we must multiply Fe^{2+} by 6.



- iv. Now balancing all elements on both sides except O and H we get



- v. H_2O molecules to the RHS.

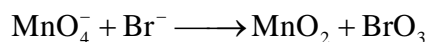


Thus, the balanced equation is $\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$

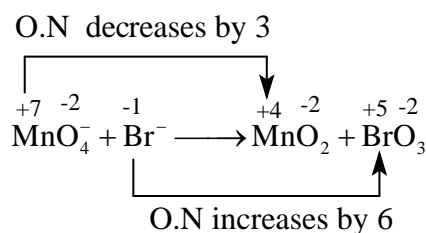
Thus, the balanced equation is $\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$

2. Permanganate ion reacts with bromide ion in basic medium to give manganese dioxide and bromate ion. Write the balanced chemical equation for the reaction.

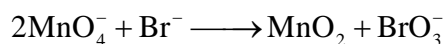
- i. The skeletal equation is



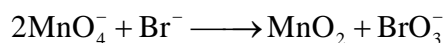
- ii. Write the oxidation number of each atom.



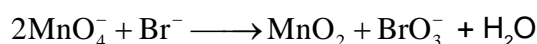
- iii. The oxidation number of Mn decreases from +7 to +4 and Br increases from -1 to +5. Therefore permanganate ion acts as the oxidant and Br^- acts as the reductant. In order to have equal increase in oxidation number of reductant and decrease in the oxidation number of oxidant, we should multiply permanganate ion by 2.



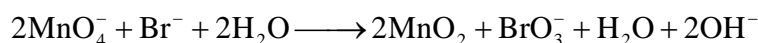
- iv. Balance all atoms other than H and O on both sides.



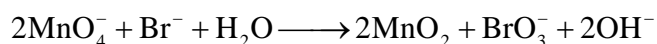
- v. Now balancing for oxygen atoms we add one H_2O molecule on RHS



- vi. As the reaction takes place in basic medium for balancing for 2H atom, we add 2 water molecules on LHS and two OH^- ions on RHS.



Cancel one water molecule from both sides. We get the balanced chemical equation as



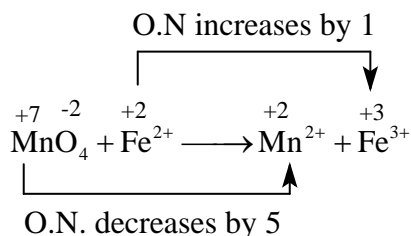
B. Ion-electron method (Half reaction method)

In this method first of all identify the oxidant and the reductant in the skeletal equation and then split the redox reaction into two half reactions corresponding to oxidation and reduction. The balancing of the equation is carried out systematically in various steps discussed below.

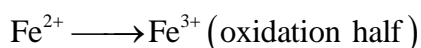
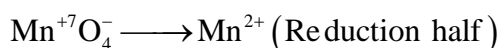
- Indicate the oxidation number of each atom involved in the reaction. Identify the elements which undergo a change in the oxidation number.
- Divide the skeletal redox equation into two half reactions, oxidation half and reduction half. In each half reaction balance the atoms which undergo the change in oxidation number.
- Add electrons to the side to make up for the difference in oxidation number in each half reaction.
- Balance oxygen atom by adding proper number of H_2O molecules to the side which is falling short of O atoms in each half reaction.
- In the acidic medium, H atoms are balanced by adding H^+ ions to the side deficient in H atoms. However, in the basic medium, H atoms are balanced by adding H_2O molecules equal in number to the deficiency of H atoms and equal number of OH^- ions are included in the opposite side of the equation.
- Multiply the half reaction equations by appropriate coefficients so that the number of electrons involved in both the equations is same. Add the two equations and cancel the electrons and other common species on both sides.

1. Permanganate ion reacts with ferrous ion in acidic medium to give Fe^{3+} and Mn^{2+} ions. Write balanced chemical equation for the reaction?

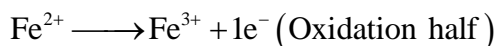
- i. Write the oxidation number of each element in the skeletal equation.



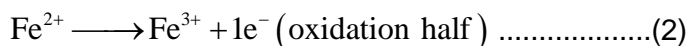
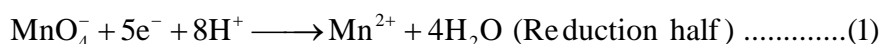
- ii. Since the oxidation number of Mn decreases from +7 to +2 and the oxidation number of Fe increases from +2 to +3, permanganate ion is reduced and ferrous ion is oxidised. Therefore we can write the half reactions as



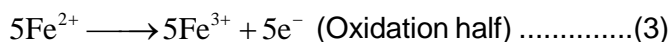
- iii. Add sufficient number of electrons to the half reaction.



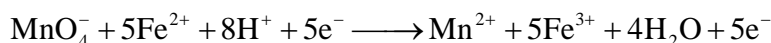
- iv. It can be seen that the half reactions are always balanced with respect to other atoms and now balancing with respect to oxygen atoms by adding water molecules and for hydrogen by adding H^+ ions (acidic medium) we get



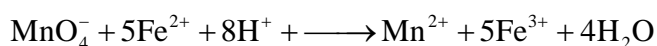
- v. To balance the number of electrons lost in equation (2) and gained in equation (1), multiply equation (2) by 5.



- vi. Add equation (1) to (3)

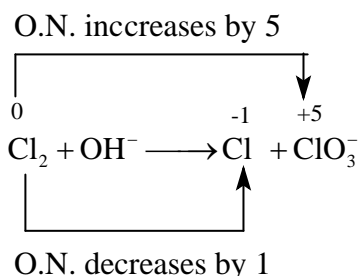


\therefore The balanced chemical equation is



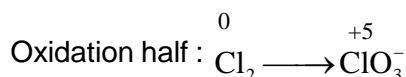
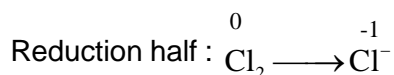
2. **Balance the following equation in basic medium.** $\text{Cl}_2 + \text{OH}^- \longrightarrow \text{Cl}^- + \text{ClO}_3^-$

- i. Write the oxidation number of each element in the skeletal equation

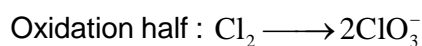
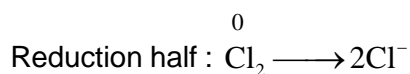


- ii. It can be seen that Cl atom has oxidation number 0 in chlorine gas while in chloride ion it is -1 and in chlorate ion it is $+5$. ie, chlorine undergoes both oxidation and reduction.

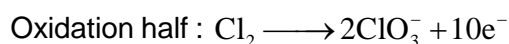
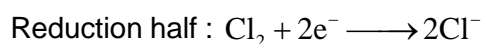
\therefore the two half reactions are



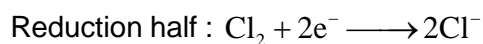
- iii. Balance all atoms other than O and H



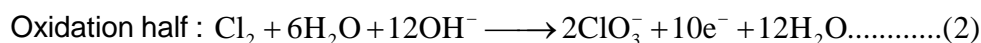
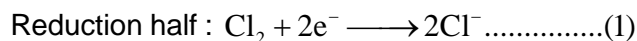
- iv. Add sufficient number of electrons to the half reactions



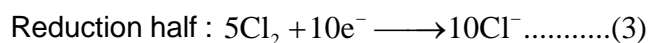
- v. Balance O atoms by adding water molecules on the deficient side



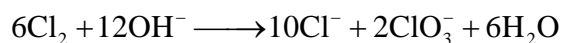
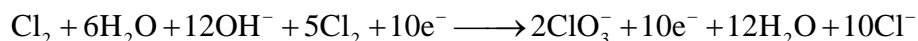
- vi. The reaction takes place in alkaline medium and for balancing of hydrogen atoms add water molecules on the deficient side and equal number of OH^- ions on the opposite side.



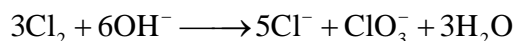
- vii. To balance the number of electron lost in equation (2) and gained in equation (1), multiply equation (1) by 5.



viii. Add equation (2) to (3)



The above equation is balanced but does not have the simplest coefficients. Thus, divide both sides by 2.



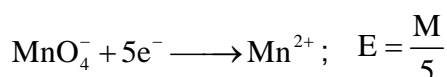
EQUIVALENT WEIGHT OF OXIDANT AND REDUCTANT

Equivalent weight of oxidant

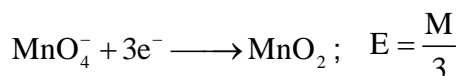
$$E_{\text{oxidant}} = \frac{\text{molar mass}}{\text{Number of electron gained by one molecule}}$$

1. Eg : Equivalent weight of KMnO_4

Equivalent weight of KMnO_4 in acidic medium

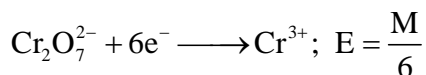


Equivalent weight of KMnO_4 in basic or neutral medium



Equivalent weight of KMnO_4 in strong basic medium $\text{MnO}_4^- + \text{e}^- \longrightarrow \text{MnO}_4^{2-}; \quad E = \frac{M}{1}$
(Permanganate ion) (Manganate ion)

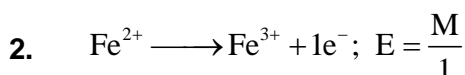
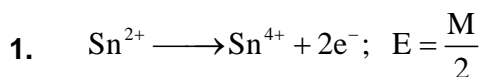
2. Eg : Equivalent weight potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in acidic as well as basic medium



Equivalent weight of reductant

$$E_{\text{reductant}} = \frac{\text{molecular mass}}{\text{No. of electron lost by one molecule}}$$

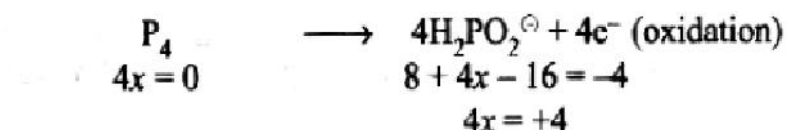
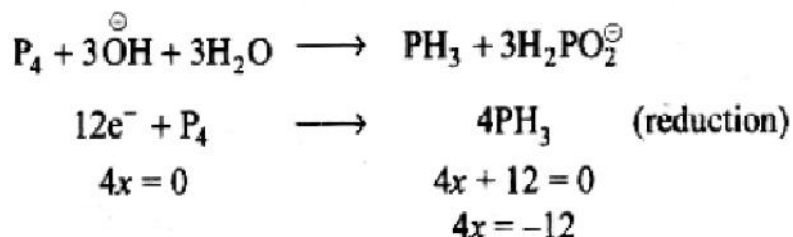
Examples:



Equivalent weight of the element or compound in disproportionation reaction

Equivalent weight is the sum of the equivalent weights in oxidation and reduction reaction, i.e. $(M/n_1 + M/n_2)$, where M is the molecular mass of the compound and n_1 and n_2 are the number of electrons in oxidation and reduction reactions, respectively.

For example, the equivalent weight of P_4 in the disproportionation reaction shown below is:



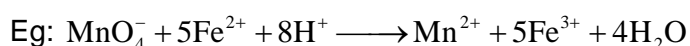
$$Ew = \left(\frac{M}{4} + \frac{M}{12} \right) = \left(\frac{31 \times 4}{4} + \frac{31 \times 4}{12} \right) = \left(31 + \frac{31}{3} \right) = 41.33$$

REDOX REACTIONS AS THE BASIS FOR TITRATIONS

Redox titrations can be performed in the same manner as acid-base titrations by titrating one reagent with the other. The end point is detected with the help of a redox indicator which changes colour on oxidation or reduction. In some cases, such as oxidation by permanganate ions, the reactant itself undergoes colour change and functions as an indicator. The usage of indicators in redox titration is illustrated below.

i. Permanganometric titrations

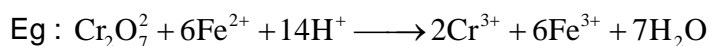
It involves the use of potassium permanganate ($KMnO_4$) as oxidising agent and reducing agents such as ferrous salts, oxalate ions, oxalic acid etc in acidic medium.



Here permanganate ion (MnO_4^-) acts as the self indicator. The visible end point is achieved when the last trace of reductant is oxidised and the first lasting lineage of pink colour appears.

ii. Dichrometric titrations

In this, the oxidising agent is potassium dichromate ($K_2Cr_2O_7$) in acidic medium.



Here $Cr_2O_7^{2-}$ is not a self indicator. In dichrometric titrations, diphenylamine is used as indicator, which is oxidised to blue colour at the end point by $Cr_2O_7^{2-}$ ions.

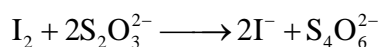
iii. Iodimetric and Iodometric titrations

Iodimetric titrations

Iodimetry is concerned with the titrations using a standard solution of iodine while iodometry deals with the titration of iodine liberated in chemical reactions. Starch is used as indicator. Starch reacts

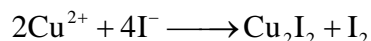
with iodine in presence of iodide to form a blue complex. This is a very sensitive colour reaction.

Iodimetric titrations involve the direct use of iodine as oxidising agent and thiosulphates, sulphates, arsenates etc as reducing agents.

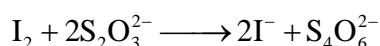


Iodometric titrations

These titrations involve the indirect use of iodine for estimation of oxidising agents like KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, CuSO_4 , etc. Which oxidises I^- ions to I_2 .



Iodine thus obtained is titrated against sodium thiosulphate solution.

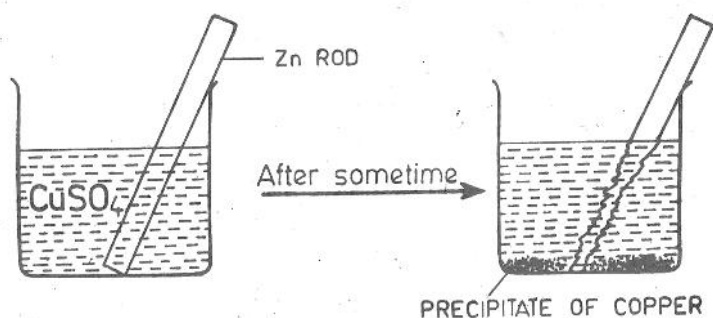


On addition of starch after the liberation of iodine from the reaction of Cu^{2+} ions on iodide ions, an intense blue colour appears. This colour disappears when iodine is consumed by the thiosulphate ions. Thus, the end point can easily be determined.

REDOX REACTIONS AND ELECTROCHEMICAL CELLS

In aqueous solutions, the spontaneous redox reactions can be carried out directly as well as indirectly. The energy liberated during the direct and indirect redox reactions appear in different forms. Let us discuss briefly, the direct and indirect redox reactions.

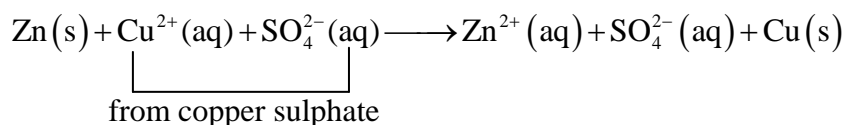
- DIRECT REDOX REACTIONS : A redox reaction in which oxidation and reduction takes place in the same vessel is called direct redox reaction.** In such reactions, the transference of electrons from reducing agent to oxidising agent occurs over a very short distance (generally within the molecular diameters). For example, if a zinc rod is immersed in copper sulphate solution taken in a beaker, a spontaneous reaction takes place and the following observations are made:



- Zinc rod starts dissolving and loses its mass gradually.
- The blue colour of CuSO_4 solution slowly fades
- A reddish brown precipitate of copper settles down at the bottom of the beaker
- The reaction is exothermic, i.e., it takes place with the evolution of heat
- The solution remains electrically neutral

vi. The reaction does not continue indefinitely but stops after some time.

The overall reaction taking place in the beaker may be represented as:



Discarding the common SO_4^{2-} ions. $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$

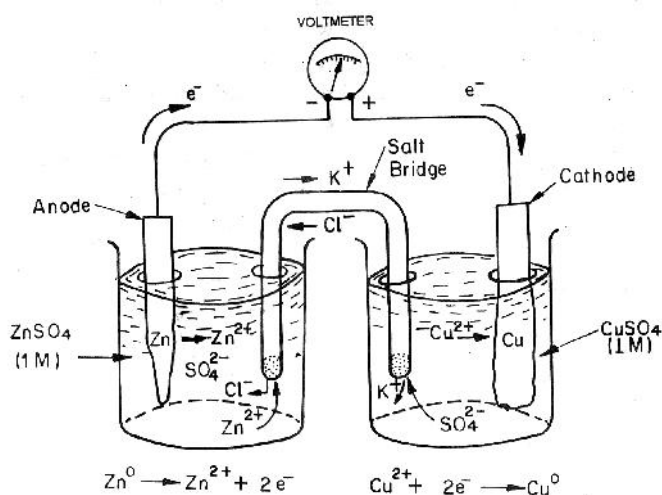
INDIRECT REDOX REACTIONS AND ELECTROCHEMICAL CELLS

The redox reactions in which oxidation and reduction take place in different vessels are called indirect redox reactions. In such reactions, the transference of electrons between reducing agent and oxidising agent takes place indirectly through the conducting wires. The arrangement for carrying out the indirect redox reaction is referred to as electrochemical cells.

Electrochemical cell or Galvanic cell : An electrochemical cell is a device in which chemical energy is converted into electrical energy. These are also called galvanic cells or voltaic cells after the names of Luigi Galvani and Alessandro Volta respectively who were among the first few to conduct experiments on conversion of chemical energy into electrical energy.

In order to understand as to how the indirect redox reaction is used to produce electrical energy let us consider one of the simplest electrochemical cells involving reaction between zinc and copper sulphate (Daniell cell).

Daniell cell is a simplest form of galvanic cell, a zinc rod is placed in ZnSO_4 solution and a copper rod is placed in CuSO_4 solution in two separate beakers. The two metallic rods which act as electrodes are connected by a conducting wire through a voltmeter. The two solutions are joined by the inverted U-tube known as salt bridge. The tube is filled with aqueous solution of some electrolyte such as KCl , KNO_3 or NH_4Cl to which gelatin or agar-agar has been added to convert it into semi-solid paste. A schematic diagram of this cell has been shown in figure.

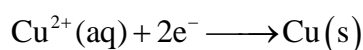


Observations

- There is a deflection in the voltmeter which indicates the flow of electrons through the connecting wires.
- The direction of deflection indicates the flow of conventional current from copper to zinc indicating that copper is +ve terminal and zinc is -ve terminal.
- The zinc rod loses mass whereas the copper rod gains mass.
- The concentration of zinc sulphate solution increases and that of copper sulphate solution decreases.
- The solutions in the two beakers remain electrically neutral throughout.
- the reaction as well as the flow of electrons stops after some time.

Now let us explain the above observations in terms of working of cell. Zinc atoms undergo oxidation and are oxidised to Zn^{2+} ions, by losing electrons. $\text{Zn(s)} \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$

The electrons liberated during oxidation are pushed through the connecting wire to copper rod where these are picked up by Cu^{2+} ions, which get reduced to copper atoms. The copper atoms as formed get deposited on the copper rod. That is why copper rod gains weight.



The overall reaction taking place in the cell is : $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$

The electrode at which oxidation takes place is called anode and that at which reduction takes place is called cathode. In the above electro-chemical cell oxidation occurs at the zinc rod, therefore, zinc is anode and reduction occurs at the copper rod, hence, copper is cathode. It may be noted that anode electrode constitutes -ve terminal and the cathode electrode constitutes +ve terminal of the cell.

By convention, the direction of flow of current is from +ve terminal to -ve terminal which is opposite to the flow of electrons.

Function of salts bridge : In the electrochemical cell a salt bridge serves two very important functions:

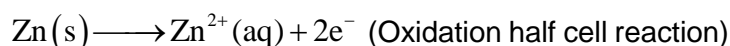
- It allows the flow of current by completing the circuit
- It maintains electrical neutrality

It may be explained as follows:

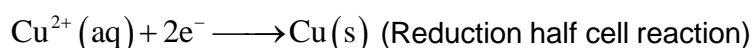
The transference of electrons from zinc anode to copper cathode leads to development of a net positive charge around the anode due to formation of Zn^{2+} ions and net negative charge around the cathode due to deposition of Cu^{2+} ions as Cu(s) on the 'cathode'. The positive charge accumulated around the anode will prevent electrons to flow from it and the negative charge (due to excess of SO_4^{2-} ions) collected around the cathode will prevent the acceptance of electrons from the anode. As the transference of electrons stops, no current will flow. The salt bridge comes to the aid and restores electrical neutrality of the solutions in the two compartments. It contains a concentrated solution of an inert electrolyte, the ions of which are not involved in electrochemical reactions. The anions (Cl^{-}) of the electrolyte migrate to the anode compartment and cations. (i.e. K^{+} ions) migrate to the cathode compartment so that the solutions in these compartments become neutral and the flow of electron continues. Thus, the salt bridge helps to prevent the accumulation of charges and maintains the flow of current.

HALF CELL AND HALF CELL REACTIONS

It has been pointed out that oxidation and reduction in the electrochemical cell take place in different vessels. These two parts of the electrochemical cell are called half cells and reactions taking place in them are called half cell reactions. The half cell in which oxidation takes place is called oxidation half cell and the reaction taking place in it is oxidation half cell reaction. Similarly, the half cell in which reduction takes place is called reduction half cell and the reaction taking place in it is called reduction half cell reaction. For example, the half cell reactions in zinc-copper sulphate cell are:



Similarly, copper electrode and copper sulphate solution constitute reduction half cell.

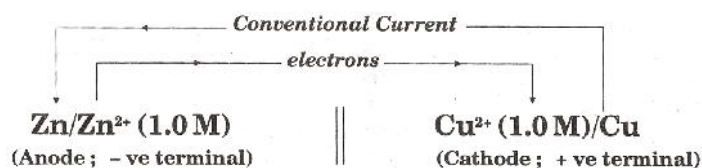


Representation of Galvanic cell

The electrochemical cell can be represented briefly according to certain universally accepted conventions as described below:

1. The half cell is usually represented as M/M^{n+} or M^{n+}/M where M represent the symbol of the element and M^{n+} represents its cation in electrolyte. The line(/) represents the interface between the two phases (may be solid/liquid or liquid/solid/gas). The concentration of electrolyte may also be mentioned in brackets.

Therefore Galvanic cell is represented as



Electrode potential (E)

Electrode potential is a measure of the tendency of an electrode to gain or lose electrons. When it is dipped in its own solution. The tendency of an electrode to loss electrons is called oxidation potential (E_{oxi}). The tendency of an electrode to gain electrons is called reduction potential (E_{red}). Oxidation potential is numerically equal to reduction potential but opposite sign. According to IUPAC convention, the reduction potential alone is called electrode potential.

EMF of the cell (E_{cell})

The difference in the electrode potentials of the two electrodes of the cell is termed as electromotive force. (E_{cell} or Cell voltage). Mathematically, it can be expressed as

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

Since in the representation of a cell cathode is written on right hand side and anode on left hand side, therefore, EMF of a cell is also sometimes written as

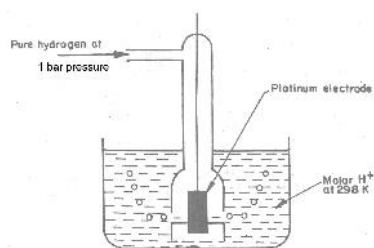
$$\text{EMF} = E_{\text{right}} - E_{\text{left}} = E_{\text{R}} - E_{\text{L}}$$

Standard and Electrode Potential (E^0)

The electrode potential under standard conditions (298 K temperature, 1 bar pressure, and 1M concentration) is called Standard Electrode Potential.

Standard Hydrogen Electrode (SHE)

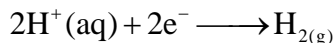
SHE hydrogen electrode consists of a platinum wire sealed into a glass tube and carrying a platinum foil at one end. The platinum foil is coated with finely divided platinum. This electrode is placed in beaker containing an aqueous solution of some acid (HCl) having one molar concentration of H^+ ions. Hydrogen gas at one atmospheric pressure is continuously bubbled through the solution at a temperature of 298 K. The oxidation or reduction in the SHE takes place at platinum foil.



When SHE acts as anode, oxidation will take place at it as $H_{2(g)} \longrightarrow 2H^+(aq) + 2e^-$

In such a case it is represented as $Pt, \frac{1}{2}H_2 / H^+ (1M)$

When SHE acts as cathode, reduction will take place at it as



In this case it is represented as $H^+ (1M) / \frac{1}{2}H_2, Pt$. Pt here, is an inert electrode.

The electrode potentials of other electrodes are determined by coupling them with SHE. The electrode potential of an electrode determined relative to the standard hydrogen electrode under standard conditions is called standard electrode potential. It is represented as E^0 . The standard conditions are 1M concentration of ions in the solution, 298 K temperature and 1 atmospheric pressure.

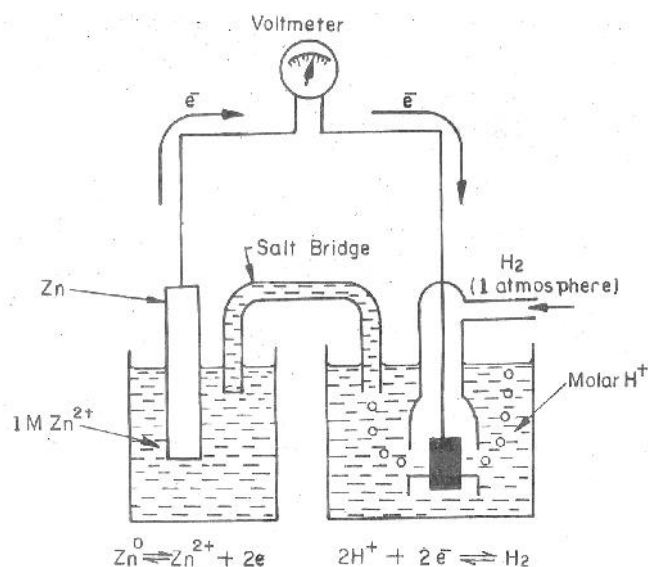
MEASUREMENT OF STANDARD ELECTRODE POTENTIALS

In order to determine the standard electrode potential of an electrode, the electrode in standard conditions is connected to standard hydrogen electrode to constitute a cell. If the electrode forms the negative terminal of the cell, it is allotted negative electrode potential and if it forms the positive terminal of the cell, it is allotted a positive value of electrode potential. The potential difference between the electrodes is determined with the help of voltmeter (or more correctly by potentiometer). At the same time, direction of flow of current is also observed which gives the idea of direction of flow of electrons. Electron flow occurs from anode to cathode whereas current flows from cathode to anode.

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

Knowing the E_{cell}^0 and electrode potential of one of the electrodes (SHE), the electrode potential of the other electrode can be calculated.

For example, in order to find out standard electrode potential of zinc electrode, zinc electrode containing 1M concentration of Zn^{2+} ions is connected to SHE as shown in figure.



The voltmeter reading shows the potential difference E_{cell}^0 of 0.76 volt and direction of conventional current is observed to be from SHE to zinc. This implies that zinc electrode acts as anode and SHE acts as cathode.

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = E_{2\text{H}^+/\text{H}_2}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0$$

$$0.76 = 0 - E_{\text{Zn}^{2+}/\text{Zn}}^0$$

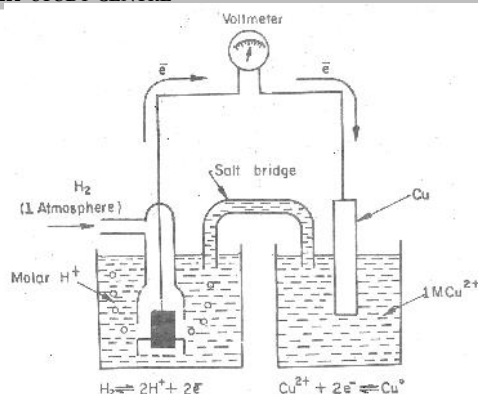
$$E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ volts}$$

Similarly, when standard copper electrode is coupled with SHE, the voltmeter reading shows as potential difference (E_{cell}^0) of 0.34 volt. The direction of flow of conventional current is from copper to SHE. This means that, in this cell copper acts as cathode and SHE acts as anode.

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{2\text{H}^+/\text{H}_2}^0$$

$$0.34 = E_{\text{Cu}^{2+}/\text{Cu}}^0 - 0$$

$$E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34 \text{ volts}$$



ELECTROCHEMICAL SERIES

The arrangement of various elements in order of increasing values of standard reduction potentials is called electrochemical series or activity series.

Standard Electrode (Reduction) Potentials at 298 K (Electro-chemical Series)

Electrode	Half-cell reaction (reduction)	E° (volts)
Li^+/Li	$\text{Li}^+ + \text{e}^- \longrightarrow \text{Li}$	-3.05
M^+/M (M = K, Rb or Cs)	$\text{M}^+ + \text{e}^- \longrightarrow \text{M}$	-2.93
Ba^{2+}/Ba	$\text{Ba}^{2+} + 2\text{e}^- \longrightarrow \text{Ba}$	-2.90
Ca^{2+}/Ca	$\text{Ca}^{2+} + 2\text{e}^- \longrightarrow \text{Ca}$	-2.87
Na^+/Na	$\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$	-2.71
Mg^{2+}/Mg	$\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$	-2.38
Be^{2+}/Be	$\text{Be}^{2+} + 2\text{e}^- \longrightarrow \text{Be}$	-1.70
Al^{3+}/Al	$\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$	-1.66
Zn^{2+}/Zn	$\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$	-0.76
Cr^{3+}/Cr	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$	-0.74
Fe^{2+}/Fe	$\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}$	-0.44
Cd^{2+}/Cd	$\text{Cd}^{2+} + 2\text{e}^- \longrightarrow \text{Cd}$	-0.40
Co^{2+}/Co	$\text{Co}^{2+} + 2\text{e}^- \longrightarrow \text{Co}$	-0.28
Ni^{2+}/Ni	$\text{Ni}^{2+} + 2\text{e}^- \longrightarrow \text{Ni}$	-0.25
Sn^{2+}/Sn	$\text{Sn}^{2+} + 2\text{e}^- \longrightarrow \text{Sn}$	-0.14
Pb^{2+}/Pb	$\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$	-0.13
$\text{H}^+/\frac{1}{2}\text{H}_2$ (SHE)	$\text{H}^+ + \text{e}^- \longrightarrow \frac{1}{2}\text{H}_2$	-0.00
$\text{Sn}^{4+}/\text{Sn}^{2+}$	$\text{Sn}^{4+} + 2\text{e}^- \longrightarrow \text{Sn}^{2+}$	+0.15
Cu^{2+}/Cu	$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$	+0.34
$\frac{1}{2}\text{I}_2/\text{I}^-$	$\frac{1}{2}\text{I}_2 + \text{e}^- \longrightarrow \text{I}^-$	+0.54
$\text{Fe}^{3+}/\text{Fe}^{2+}$	$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$	+0.77
Ag^+/Ag	$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	+0.80
$\frac{1}{2}\text{Br}_2/\text{Br}^-$	$\frac{1}{2}\text{Br}_2 + \text{e}^- \longrightarrow \text{Br}^-$	+1.07
$\frac{1}{2}\text{Cl}_2/\text{Cl}^-$	$\frac{1}{2}\text{Cl}_2 + \text{e}^- \longrightarrow \text{Cl}^-$	+1.36
Au^{3+}/Au	$\text{Au}^{3+} + 3\text{e}^- \longrightarrow \text{Au}$	+1.50
$\frac{1}{2}\text{F}_2/\text{F}^-$	$\frac{1}{2}\text{F}_2 + \text{e}^- \longrightarrow \text{F}^-$	+2.87

Applications of the electrochemical series

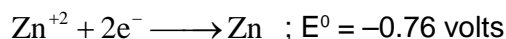
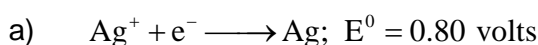
1. Calculation of the standard EMF of the cell, From the electrochemical series, the standard reduction potentials of electrodes are found out. The electrode with higher reduction potential is taken as cathode and other as anode. From this EMF of the cell is calculated as

$$EMF^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

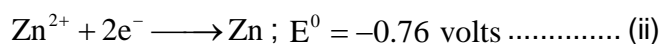
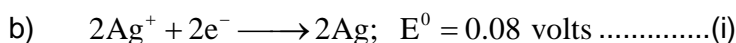
- Qn. Calculate the EMF of the given cell, also write the overall cell reaction.

$Zn | Zn^{2+} (1M) || Ag^+ (1M) | Ag$. Standard reduction potential for Zn^{2+} / Zn is -0.76 volts and for Ag^+ / Ag is 0.80 volts.

Solutions : It is clear from the cell, that silver electrode acts as a cathode and zinc electrode acts as anode:

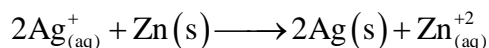


Multiply the first equation by 2 so as to equalise the number of electrons



$$EMF = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = 0.80 - (-0.76) = 1.56 \text{ volts.}$$

The overall cell reaction can be obtained to subtracting equation (ii) from equation (i).

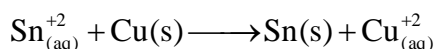


2. **Comparison of the reactivities of metals.**: The metal having smaller reduction potential can displace metals having larger reduction potential from the solutions of their salts. In other words, the metal occupying higher position in the series can displace the metals lying below it from the solutions of their salts. For example, zinc lies above copper in the series and hence, it can displace copper from copper sulphate solution. Copper cannot displace zinc from zinc sulphate solution because it lies below zinc in the series and hence, it is less reactive.
3. **Predicting the feasibility of a redox reactions.** With the help of electromotive series we can predict whether a given redox reaction will take place or not. From the given equation the substances undergoing oxidation and reduction are identified. The substance undergoing oxidation will act as anode and the substance undergoing reduction will act as a cathode. The EMF of this hypothetical cell is calculated as under:

$$EMF = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

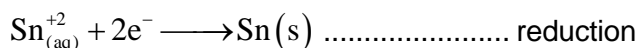
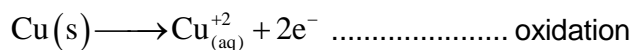
If EMF comes out to be positive the given redox reaction will take place and if EMF comes out to be negative the given redox reaction will not take place.

Qn. Predict whether the following redox reaction is feasible or not under standard conditions:



Given that $E_{\text{Sn}^{+2}/\text{Sn}}^0 = -0.136$ volts and $E_{\text{Cu}^{+2}/\text{Cu}}^0 = 0.34$ volts

Solution : The above reaction can be split into two half reactions as given below:



Since at copper electrode oxidation takes place so it acts as anode and at tin electrode reduction takes place so it acts as cathode.

$$\text{EMF} = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = E_{\text{Sn}^{+2}/\text{Sn}}^0 - E_{\text{Cu}^{+2}/\text{Cu}}^0 = -0.136 - 0.34 = -0.476 \text{ volts}$$

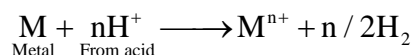
Since the value of EMF comes out to be negative, the given reaction is not feasible.

4. To compare oxidising and reducing powers of elements

Electrochemical series helps to identify a good oxidising agent or reducing agent. All the substance appearing on the top of the electrochemical series are a good reducing agent. ie, they have negative value of standard reduction potential. Whereas those appearing on the bottom of the electro chemical series are a good oxidising agent. That is they have positive value of standard reduction potential. For example fluorine electrode with a standard reduction potential value of +2.87 V is a strong oxidising agent and Li^+ with standard reduction potential value of -3.05 V is a strong reducing agent.

5. To predict the reaction of a metal with dilute acids to liberate hydrogen gas.

Some metals like Fe, Zn react with dil.acids like HCl, H_2SO_4 to liberate H_2 gas while some metals like Cu, Ag do not liberate H_2 gas with dil.HCl, dil. H_2SO_4 . A prediction about capacity of a given metal to produce H_2 gas by its reaction with dilute acids can be easily made from the knowledge of electromotive series. Chemical reaction between metal and acid can be represented, in general as



For the above reaction to occur, the E_{red}^0 of metal (M^{n+}/M) must be lower than that of hydrogen. Hence, it can be concluded that metals which lie above hydrogen in the electromotive series can reduce H^+ ions to hydrogen and hence, liberate hydrogen gas on reaction with dil acids. In other words, metals having negative reduction potentials can displace hydrogen from acids. For example,

zinc ($E_{\text{Zn}^{+2}/\text{Zn}}^0 = -0.76$ volt) lies above hydrogen in the series and hence, it can displace hydrogen

from dilute acids, whereas copper ($E_{\text{Cu}^{+2}/\text{Cu}}^0 = +0.34$ volts) which is lying below hydrogen in the series cannot displace hydrogen from acids.