

Oxidation Reduction

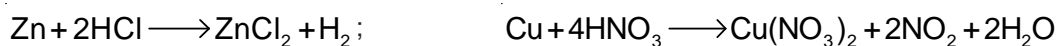
1. OXIDATION AND REDUCTION

1.1 OLD CONCEPT OF OXIDATION

(a) Oxidation is a chemical reaction in which oxygen is added



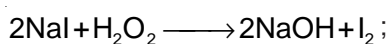
(b) Hydrogen is removed i.e. hydrogen becomes less



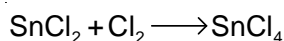
(c) Electronegative element is added



(d) Electropositive element is removed



(e) Valency of electropositive element increases



1.2 OLD CONCEPT OF REDUCTION

(a) Hydrogen is added. For example



(b) Oxygen is lost. For example



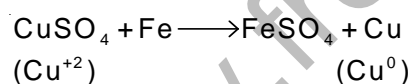
(c) Electropositive element is added. For example



(d) Electronegative element is removed. For example



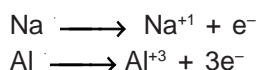
(e) Valency of electropositive element decreases. For example



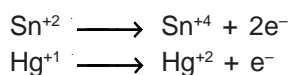
1.3 MODERN CONCEPT OF OXIDATION

The reaction in which an element or an atom or an ion or molecule loses electron is called **oxidation**. de electronation is oxidation.

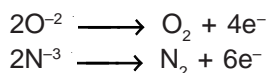
(a) **Neutral atom** : When a neutral atom loses electron, it gets converted to a positive ion.



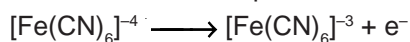
(b) **Cation** : When a cation loses electron, there is an increase in its positive charge.



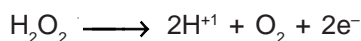
(c) **Anion** : When an anion loses electron equal to its negative charge, it gets converted to a neutral atom.



- (d) **Complex Anion** : When a complex anion loses electron, its negative charge decreases.



- (e) **Molecule** : When a molecule loses electrons, it breaks up into its constituents.



Therefore in oxidation reactions–

- (i) Positive charge increases and negative charge decreases
- (ii) Oxidation number increases

1.4 MODERN CONCEPT OF REDUCTION

The reaction in which an element or an atom or an ion (positive or negative) or a molecule accepts electron, is called **reduction**. Electronation is reduction.

- (a) **Neutral Atom** : When a neutral element or atom accepts electron, it gets converted into an anion.



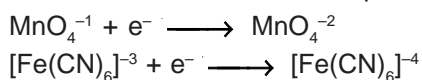
- (b) **Cation** : When a cation accepts electron equal to its charge, it gets converted into a neutral atom.



- (c) Similarly, when a cation accepts less electrons than its charge, its positive charge decreases. For example



- (d) **Anion** : When an anion accepts electron, its negative charge increases.



- (e) **Molecule** : When a molecule accepts electron, it is a reduction reaction.



Therefore in reduction reactions–

- (i) Positive charge decreases and negative charge increases
- (ii) Oxidation number decreases

2. OXIDANTS

- (i) Molecules of most electronegative elements e.g. O_2 , O_3 , halogens
- (ii) Compounds having either of an element (under lined) in their highest oxidation state e.g. KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , HNO_3 , FeCl_3 , HgCl_2 , KClO_3 , NaNO_3 etc.
- (iii) Oxides of metals and non metals e.g. MgO , CaO , CrO_3 , H_2O_2 , CO_2 , SO_3 , etc.

3. REDUCTANTS

- (i) All metals e.g. Na, Al, Zn etc.
- (ii) Some non metals e.g. C, S, P, H_2 etc.
- (iii) Halogen acids e.g. HI, HBr, HCl.
- (iv) Metallic hydrides e.g. NaH, LiH, CaH_2 etc.
- (v) Compounds having either of an element (under lined) in their lowest oxidation state e.g. FeCl_2 , FeSO_4 , Hg_2Cl_2 , SnCl_2 , Cu_2O etc.
- (vi) Some organic compounds e.g. HCOOH, Aldehydes, Oxalic acid, Tartaric acid etc.

4. REDOX REACTIONS

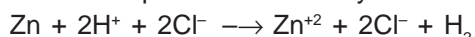
Redox reactions are the chemical reactions which involve both oxidation as well as reduction simultaneously. In fact, oxidation and reduction go hand in hand. The redox reactions are of two types :

(i) Direct redox and (ii) Indirect redox reactions.

When chemical reactions are carried out then some of the species may lose electrons whereas some other may gain electrons. The concept of electron transfer can easily explain in the redox reactions in the case of ionic substances. However, for covalent compounds we use a new term oxidation number to explain oxidation and reduction or redox reactions. Before discussing in detail, some other terms frequently being used are:

5. SPECTATOR IONS

Species that are present in the solution but not take part in the reaction and are also omitted while writing the net ionic reaction are called spectator ions or bystander ions.



In this reaction ions are omitted and are called as spectator ions and appear on the reactant as well as product side.

6. TYPES OF REDOX REACTION

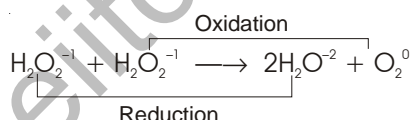
6.1 AUTOXIDATION

Turpentine, Phosphorous and metals like Zn and Pb can absorb oxygen from air in the presence of water. The water oxidized to hydrogen peroxide. The phenomena of formation of H_2SO_4 by the oxidation of H_2O is known as autoxidation.



6.2 DISPROPORTIONATION

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



7. OXIDATION NUMBER

- The definition :** Oxidation number of an element in a particular compound represents the number of electrons lost or gained by an element during its change from free state into that compound or Oxidation number of an element in a particular compound represents the extent of oxidation or reduction of an element during its change from free state into that compound.
- Oxidation number is given positive sign if electrons are lost.
Oxidation number is given negative sign if electrons are gained.
- Oxidation number represents real charge in case of ionic compounds, however, in covalent compounds it represents for imaginary charge.
- It is the residual charge which an atom appears to have when other atom are withdrawn from the molecules as ions by containing electrons with more electronegative atoms.

7.1 THE RULE FOR DERIVING OXIDATION NUMBER

Following arbitrary rules have been adopted to derive Oxidation Number of elements on the basis of periodic properties of elements.

- In uncombined state or free state, Oxidation Number of an element is zero.
- In combined state Oxidation Number of

- a. F is always -1 .
- b. O is -2 ; In peroxides ($-O-O-$) it is -1 and in superoxide $-1/2$. However in F_2O , it is $+2$.
- c. H is 1 ; In ionic hydrides it is -1 .
- d. metals is always positive.
- e. alkali metals (IA e.g. Li, Na, K, Rb, Cs, Fr) is always $+1$.
- f. alkaline earth metals (IIA e.g. Be, Mg, Ca, Sr, Ba, Ra) is always $+2$.
- g. halogens in halides is always -1 .
- h. sulphur in sulphides in always -2 .
3. The algebraic sum of all the Oxidation Number of elements in a compound is equal to zero. e.g. K_2MnO_4
 $2 \times$ Oxidation Number of K + Oxidation Number of Mn + 4 (Oxidation Number of O) = 0
4. The algebraic sum of all the Oxidation Numbers of elements in a radical is equal to net charge on that radical
 e.g. $C_2O_4^{2-}$. $2 \times$ Oxidation Number of C + 4 (Oxidation Number of O) = -2 .
5. Oxidation Number can be zero, +ve, -ve, integer or fraction.
6. Maximum Oxidation Number of an element is (except O & F) = Group Number.
 Minimum Oxidation Number of an element is (except metals) = Group Number -8 .

Note : Group number in Mendeleef's modern periodic table.

7. The most common oxidation states of some representative elements are given below.
8. 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 ($+7$, $+6$, $+5$, $+4$, $+3$, $+2$, $+1$) etc.
p-block elements : As ($+3$ & $+5$); Sb ($+3$ & $+5$), Sn ($+2$ & $+4$) etc.

Group	Outer shell configuration	Common Oxidation Number
I gp	ns^1	0, +1
II gp	ns^2	0, +2
III gp	$ns^2 np^1$	0, +1, +3
IV gp	$ns^2 np^2$	0, ± 1 , ± 2 , ± 3 , ± 4
V gp	$ns^2 np^3$	0, ± 1 , ± 3 , +5
VI gp	$ns^2 np^4$	0, ± 2 , +4, +6
VII gp	$ns^2 np^5$	0, ± 1 , +3, +5, +7
Zero gp	$ns^2 np^6$	0 (usually)

EXCEPTIONS

- (i) Oxidation Number of Cl in Cl_2O is $+1$, because Cl acts as an electropositive element in this.
- (ii) Oxidation Number of Cl in ClF_3 = $+3$
- (iii) Oxidation Number of Cl in $KClO_3$ = $+5$
- (iv) Oxidation Number of I in IF_7 = $+7$
- (v) Oxidation Number of I in IF_5 = $+5$

7.1.1 OXIDATION NUMBER OF RADICALS

Oxidation Number of radicals is equal to charge present on them. For example,

- (i) Oxidation Number of sulphite (SO_3^{-2}), sulphate (SO_4^{-2}), thiosulphate ($S_2O_3^{-2}$), oxalate ($C_2O_4^{-2}$), carbonate (CO_3^{-2}), sulphide (S^{-2}) is equal to charge (-2) present on each of them.
- (ii) Oxidation Number of each of the anions, Cl^{-1} , Br^{-1} , I^{-1} , NO_3^{-1} , CN^{-1} , OH^{-1} , SCN^{-1} , CH_3COO^{-1} and HCO_3^{-1} is -1 .
- (iii) Oxidation Number of each of the anions. PO_4^{-3} , BO_3^{-3} , AsO_4^{-3} . (Arsenate) and AsO_3^{-3} (Arsenite) is -3 .
- (iv) Oxidation Number of each of the cations, CH_3^+ , NH_4^+ , Na^+ , K^+ is $+1$.
- (v) Oxidation Number of each of the cations, Ca^{+2} , Mg^{+2} , Sr^{+2} and Fe^{+2} is $+2$.
- (vi) Oxidation Number of Al in $[Al(H_2O)_6]^{+3}$ is $+3$.

7.1.2 S ELEMENT

- | | | | | |
|----|-------------------------------------|-----------------------|----------------|---------|
| 1. | S in H ₂ S | 2(1) + x = 0 | +2 + x = 0 | x = - 2 |
| 2. | S in SO ₂ | x + 2(-2) = 0 | x - 4 = 0 | x = + 4 |
| 3. | S in SO ₄ ⁻² | x + 4(-2) = -2 | x - 8 = - 2 | x = + 6 |
| 4. | S in SO ₃ ⁻² | x + 3(-2) = -2 | x - 6 = - 2 | x = + 4 |
| 5. | S in SF ₆ | x + 6(-1) = 0 | x - 6 = 0 | x = + 6 |
| 6. | S in H ₂ SO ₃ | 2(-1) + x + 3(-2) = 0 | +2 + x - 6 = 0 | x = + 4 |
| 7. | S in As ₂ S ₃ | 2(3) + 3x = 0 | 6 + 3x = 0 | x = - 2 |

7.1.3 P ELEMENT

- | | | | | |
|----|--|-----------------------------|----------------------|------------------|
| 1. | Oxidation number of P in P ₄ | = 0 | | |
| 2. | P in PO ₄ ⁻³ | x + 4(-2) = -3 | x - 8 = - 3, | x = + 5 |
| 3. | P in NaHPO ₂ | 1(1) + 1(1) + 2(-2) = 0 | +1 + 1 + x - 4 = 0, | x = +2 |
| 4. | P in H ₃ PO ₃ | 3(+1) + x + 3(-2) = 0 | + 3 + x - 6 = 0, | x = + 3 |
| 5. | P in Na ₂ HPO ₄ | 2(1) + 1(1) + x + 4(-2) = 0 | + 2 + 1 + x - 8 = 0, | x = + 5 |
| 6. | P in Mg ₂ P ₂ O ₇ | 2(2) + 2x + 7(-2) = 0 | + 4 + 2x - 14 = 0, | 2x = 10, x = + 5 |

7.1.4 OXIDATION NUMBER OF Cr IN ITS VARIOUS COMPOUNDS

- | | | | | |
|-----|--|------------------|---------|---------|
| 1. | Cr in CrO : | x - 2 = 0, | x = + 2 | |
| 2. | Cr in Cr ₂ O ₃ : | 2x - 6 = 0, | x = + 3 | |
| 3. | Cr in CrSO ₄ : | x - 2 = 0, | x = + 2 | |
| 4. | Cr in Cr ₂ (SO ₄) ₃ : | 2x - 6 = 0, | x = + 3 | |
| 5. | Cr in CrO ₂ Cl ₂ : | 2x - 6 = 0, | x = + 3 | |
| 6. | Cr in K ₂ Cr ₂ O ₇ : | 2 + 2x - 14 = 0, | x = + 6 | |
| 7. | Cr in K ₂ CrO ₄ : | 2 + x - 8 = 0, | x = + 6 | |
| 8. | Cr in Cr ₂ O ₇ ⁻² : | 2x - 14 = -2, | 2x = 12 | x = + 6 |
| 9. | Cr in CrO ₄ ⁻² : | x - 8 = -2, | x = + 6 | |
| 10. | Cr in Cr (NH ₃) ₄ SO ₄ : | x - 2 = 0, | x = + 2 | |
| | (Here, Oxidation Number of NH ₃ is zero) | | | |
| 11. | Oxidation Number of Cr in [Cr(NH ₃) ₄] ⁺² : | | x = + 2 | |
| 12. | Oxidation Number of Cr in Na ₂ CrO ₄ : | +2 + x - 8 = 0, | x = + 6 | |
| 13. | Oxidation Number of Cr in Cr(CO) ₆ : | | x = 0 | |
| | (Oxidation Number of Cr = 0) | | | |

7.1.5 OXIDATION NUMBER OF Mn IN ITS COMPOUNDS

- | | | | |
|----|---|-----------------|---------|
| 1. | Mn in MnO : | x - 2 = 0, | x = + 2 |
| 2. | Mn in Mn ₂ O ₃ : | 2x - 6 = 0, | x = + 3 |
| 3. | Mn in MnSO ₄ : | x - 2 = 0, | x = + 2 |
| 4. | Mn in Mn ₂ (SO ₄) ₃ : | 2x - 6 = 0, | x = + 3 |
| 5. | Mn in K ₂ MnO ₄ : | +2 + x - 8 = 0, | x = + 6 |
| 6. | Mn in KMnO ₄ : | +1 + x - 8 = 0, | x = + 7 |
| 7. | Mn in Mn(CO) ₁₀ : | x + 10(0) = 0 | x = 0 |
| 8. | Mn in MnO ₄ ⁻ | x - 8 = - 1 | x = + 7 |
| 9. | Mn in Mn (C ₂ O ₄) ₂ .2H ₂ O : | x - 4 = 0, | x = + 4 |

7.1.6 OXIDATION STATE

Oxidation state of an atom is defined as oxidation number per atom.

e.g. In K_2MnO_4 , Oxidation number of Mn = +6

Oxidation state of Mn = Mn^{6+}

However, for all practical purposes oxidation state is often expressed as oxidation number.

7.2 VALENCY AND OXIDATION NUMBER

Valency of an element represents the power or capacity of the element to combine with the other element. The valency of an element is numerically equal to the number of hydrogen atoms or chlorine atoms or twice the number of oxygen atoms that combine with one atom of that element. It is also equal to the number of electrons lost or accepted or shared by the atoms of an element.

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

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

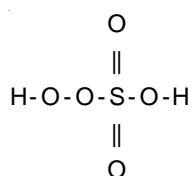
For example, in the following compounds of carbon, the oxidation number varies from -4 to +4 but valency of carbon is 4 in all the compounds.

Compound	CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
Oxidation number of carbon	-4	-2	0	+2	+4

EVALUATION OF OXIDATION NUMBER

Determine Oxidation number of the element underlined in each of the following :

(a) H_2SO_5 :



$$\therefore 2 \times 1 + x + 5 \times (-2) = 0$$

$$\therefore x = +8 \text{ (wrong)}$$

But this can not be true as maximum oxidation number for S can not exceed +6. The exceptional value is due to the fact that O atom in H_2SO_5 show peroxide linkage. Therefore evaluation of oxidation number should be made as :

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

$$\begin{array}{cccc}
 \text{(for H)} & \text{(for S)} & \text{(for O)} & \text{(for O-O)} \\
 \end{array}$$

$$\therefore x = +6$$

(b) $\underline{\text{NH}_4\text{NO}_3}$: $2 \times x + 4 \times 1 + 3(-2) = 0 \quad \therefore x = +1$ (wrong)

No doubt NH_4NO_3 has two N atoms but one N atom has negative Oxidation Number (attached to H) and the other has +ve Oxidation Number (attached to O). Therefore, evaluation should be made separately for NH_4^+ & NO_3^- .

NH_4^+ $x + 4 \times (+1) = +1$; $\therefore x = -3$ (Oxidation Number of N in NH_4^+)

NO_3^- $x + 3 \times (-2) = -1$; $\therefore x = +5$ (Oxidation Number of N in NO_3^-)

(c) $\underline{\text{HCN}}$: The evaluation can not be made directly by using rules since we have no standard rule for oxidation number of N and C i.e. two values are unknown. In all such cases evaluation of oxidation number should be made by indirect concept or by the original concepts of bonding.

(i) Each covalent bond contributes for one unit value for oxidation number.

(ii) Covalently bonded atom with less electronegativity acquires +ve Oxidation Number whereas other with more electronegativity acquires -ve Oxidation number.

(iii) In case of coordinate bond assign +2 value for Oxidation Number to atom from which coordinate bond is directed to other a more electronegative atom and -2 value to more electronegative atom.

(iv) If coordinate bond is directed from more electronegative atom to less electronegative atom, then neglect contribution for coordinate bond. Thus for $\text{H} - \text{C} \equiv \text{N}$.

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

Note : \therefore N has three covalent bonds and more electronegative than carbon.

$$\therefore \text{Oxidation Number of N} = -3$$

(d) $\underline{\text{H} - \text{N} \equiv \text{C}}$: $1 + (-3) + x = 0$; $\therefore x = +2$

[The contribution of coordinate bond is neglected because the bond is directed from more electronegative to less electronegative carbon atom.]

(e) $\underline{\text{Fe}_3\text{O}_4}$: $3 \times x + 4 \times (-2) = 0$; $\therefore x = + (8/3)$

or $\therefore \text{Fe}_3\text{O}_4$ is a mixed oxide of FeO . Fe_2O_3

\therefore Fe has two Oxidation Numbers +2 and +3.

However factually speaking Oxidation Numbers of Fe in Fe_3O_4 is an average value of these two (i.e. +2 & +3)

$$\text{Average Oxidation Number} = \frac{1^2(+2) + 2^2(+3)}{3} = +\frac{8}{3}$$

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

Put sum of Oxidation Numbers of $\text{SO}_4 = -2$

Sum of Oxidation Numbers in $(\text{NH}_4)_2\text{SO}_4 = 0$ [$(\text{NH}_4)_2\text{SO}_4$ is a complete molecule]

Sum of Oxidation Numbers in $\text{H}_2\text{O} = 0$ [H_2O is complete molecule]

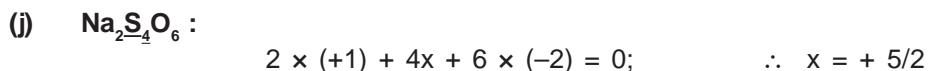
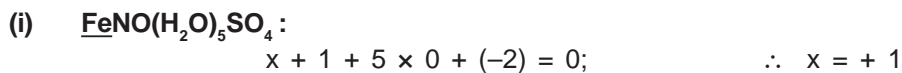
$$x + (-2) + 0 + 0 = 0; \quad \therefore x = +2$$

(g) $\underline{\text{Fe}_{0.94}\text{O}}$: $x \times 0.94 + (-2) = 0$; $x = 200/94$

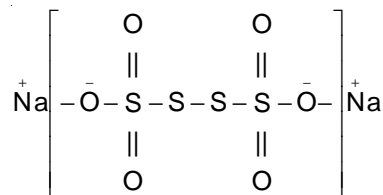
(h) $\underline{\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]}$: NO in iron complexes has NO^+ nature.

$$\text{Thus } 2 \times 1 + x + 5 \times (-1) + 1 = 0$$

$$\text{(for Na) (for Fe) (for CN) (for NO);} \quad \therefore x = +2$$



Here also this value is the average oxidation Number of S. The structure of $\text{Na}_2\text{S}_4\text{O}_6$ may be written as :

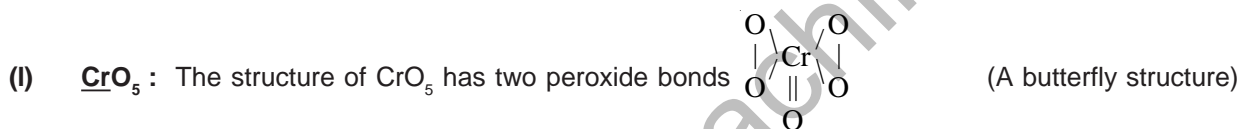


Oxidation Number of each S atom in S – S atom involved in pure covalent bond is zero.

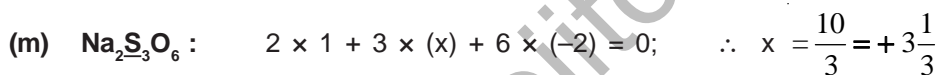
$$\text{Average Oxidation Number} = \frac{+5+5+0+0}{4} = +\frac{5}{2}$$



Oxidation Number of $\text{CH}_3 = 1$; Oxidation Number of O = -2
 $\therefore 2 \times (+1) + x + (-2) = 0$; $x = 0$



$$\therefore x + 4 \times (-1) + 1 \times (-2) = 0$$
; $x = +6$



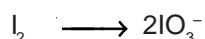
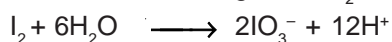
8. BALANCING OF EQUATIONS :

Two methods are generally used to balance a redox equation.

8.1 BY OXIDATION STATE METHOD :

Step I & II of ion electron methods should be changed accordingly as shown below in each case (i.e. neutral, acidic or alkaline) medium. The other steps to be followed as usual.



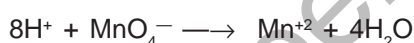
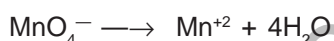
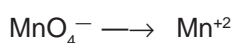
BALANCING OF HALF REACTIONS**Example 1 :** $I_2 \longrightarrow IO_3^-$ (acidic medium)**Step I** Balance atoms other than O & H if needed**Step II** Balance O atoms using H^+ & H_2O as reported in step 4 of acidic medium earlier**Step III** Balance charge by electrons**Example 2 :** $S_2O_3^{2-} \longrightarrow SO_2$ (basic medium)**Step I** $S_2O_3^{2-} \longrightarrow 2SO_2$ **Step II** $S_2O_3^{2-} + 2OH^- \longrightarrow 2SO_2 + H_2O$ (By H_2O & OH^-)**Step III** $S_2O_3^{2-} + 2OH^- \longrightarrow 2SO_2 + H_2O + 4e^-$ **8.2 ION ELECTRON METHOD :**

This method involves three sets of rules depending upon the nature of equation to be balanced in neutral, acidic or alkaline medium.

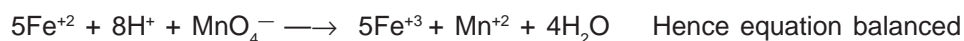
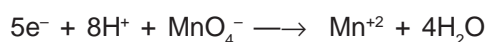
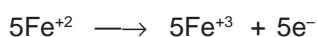
- Divide the overall reaction into oxidation half and reduction half reactions.
- Balance the half reactions w.r.t. charges and electrons.
- Equalize the electrons lost and gained by multiplying the half reactions with suitable integers. Simultaneously oxygen and Hydrogen will also be balanced.
- Add the two half reactions.



Balancing in acidic medium

First half reaction

Multiplying equation 2 with 5 and adding with equation 1

**9. EQUIVALENT WEIGHT OF OXIDANTS AND REDUCTANTS**

By using oxidation number, equivalent weight of oxidising and reducing substance can be determined as follows

$$\text{Equivalent weight of a oxidant} = \frac{\text{Molecular weight of molecule or ion}}{\text{Electrons accepted by one molecule or ion}}$$

$$= \frac{\text{Molecular weight of molecule or ion}}{\text{Total change in oxidation number}}$$

$$\text{Equivalent weight of a reductant} = \frac{\text{Molecular weight of molecule or ion}}{\text{Electrons released by one molecule or ion}}$$

$$= \frac{\text{Molecular weight of molecule or ion}}{\text{Total change in oxidation number}}$$