

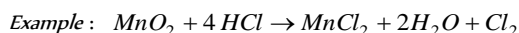
Chapter 13

Redox Reactions

Chemical reactions involve transfer of electrons from one chemical substance to another. These electron – transfer reactions are termed as oxidation-reduction or redox-reactions.

Molecular and Ionic equations

(1) **Molecular equations** : When the reactants and products involved in a chemical change are written in molecular forms in the chemical equation, it is termed as molecular equation.



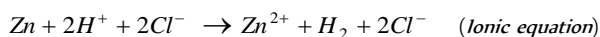
In above example the reactants and products have been written in molecular forms, thus the equation is termed as **molecular equation**.

(2) **Ionic equations** : When the reactants and products involved in a chemical change are ionic compounds, these will be present in the form of ions in the solution. The chemical change is written in ionic forms in chemical equation, it is termed as ionic equation. *Example,*



In above example the reactants and products have been written in ionic forms, thus the equation is termed as **ionic equation**.

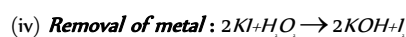
(3) **Spectator ions** : In ionic equations, the ions which do not undergo any change and equal in number in both reactants and products are termed as spectator ions and are not included in the final balanced equations. *Example,*



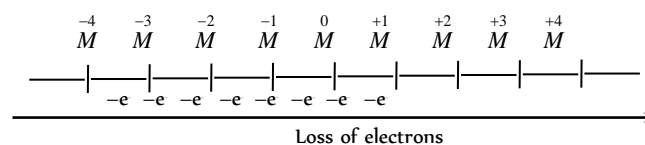
In above example, the Cl^- ions are the **spectator ions** and hence are not included in the final ionic balanced equation.

Oxidation-reduction and Redox reactions

(1) **Oxidation** : Oxidation is a process which involves; addition of oxygen, removal of hydrogen, addition of non-metal, removal of metal, Increase in +ve valency, loss of electrons and increase in oxidation number.



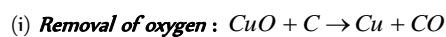
(vi) **Loss of electrons** (also known as de-electronation)



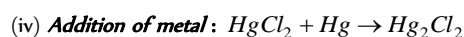
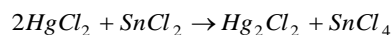
(vii) **Increase in oxidation number**



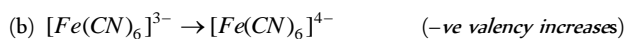
(2) **Reduction** : Reduction is just reverse of oxidation. Reduction is a process which involves; removal of oxygen, addition of hydrogen, removal of non-metal, addition of metal, decrease in +ve valency, gain of electrons and decrease in oxidation number.



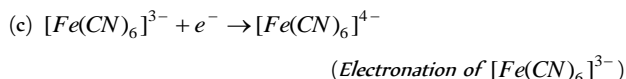
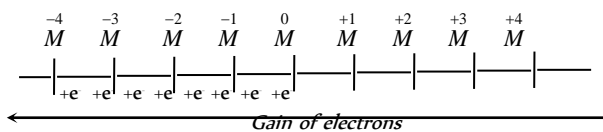
(iii) **Removal of non-metal**



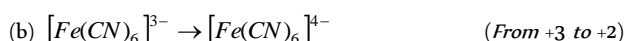
(v) **Decrease in +ve valency**



(vi) **Gain of electrons** (also known as electronation)



(vii) **Decrease in oxidation number**



(3) **Redox-reactions**

(i) An overall reaction in which oxidation and reduction takes place simultaneously is called **redox** or **oxidation-reduction reaction**. These reactions involve transfer of electrons from one atom to another. Thus every redox reaction is made up of two **half reactions**; One half reaction represents the oxidation and the other half reaction represents the reduction.

(ii) **Types of redox reaction**

(a) **Direct redox reaction** : The reactions in which oxidation and reduction takes place in the same vessel are called direct redox reactions.

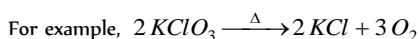
(b) **Indirect redox reaction** : The reactions in which oxidation and reduction takes place in different vessels are called indirect redox reactions. Indirect redox reactions are the basis of electro-chemical cells.

(c) **Intermolecular redox reactions** : In which one substance is oxidised while the other is reduced.



Here, Al is oxidised to Al_2O_3 while Fe_2O_3 is reduced to Fe .

(d) **Intramolecular redox reactions** : In which one element of a compound is oxidised while the other is reduced.



Here, Cl^{+5} in $KClO_3$ is reduced to Cl^{-1} in KCl while O^{2-} in $KClO_3$ is oxidised to O_2^0 .

Oxidising and Reducing agents

(i) **Definition** : The substance (atom, ion or molecule) that gains electrons and is thereby reduced to a low valency state is called an **oxidising agent**, while the substance that loses electrons and is thereby oxidised to a higher valency state is called a **reducing agent**.

Or

An **oxidising agent** is a substance, the oxidation number of whose atom or atoms decreases while a **reducing agent** is a substance the oxidation number of whose atom increases.

(2) **Important oxidising agents**

(i) Molecules made up of electronegative elements.

Example : O_2 , O_3 and X_2 (halogens).

(ii) Compounds containing an element which is in the highest oxidation state.

Example : $KMnO_4$, $K_2Cr_2O_7$, $Na_2Cr_2O_7$, CrO_3 , H_2SO_4 ,

HNO_3 , $NaNO_3$, $FeCl_3$, $HgCl_2$, $KClO_4$, SO_3 , CO_2 , H_2O_2 etc.

(iii) Oxides of elements, MgO , CuO , CrO_3 , CO_2 , P_4O_{10} , etc.

(iv) Fluorine is the strongest oxidising agent.

(3) **Important reducing agents**

(i) All metals e.g. Na , Zn , Fe , Al , etc.

(ii) A few non-metals e.g. C , H , S etc.

(iii) Hydrides : HCl , HBr , HI , H_2S etc.

(iv) A few compounds containing an element in the lower oxidation state (ous).

Example : $FeCl_2$, $FeSO_4$, $SnCl_2$, Hg_2Cl_2 , Cu_2O etc.

(v) Metallic hydrides e.g. NaH , LiH etc.

(vi) Organic compounds like $HCOOH$ and $(COOH)_2$ and their salts, aldehydes, alkanes etc.

(vii) Lithium is the strongest reducing agent in solution.

(viii) Cesium is the strongest reducing agent in absence of water.

Other reducing agents are $Na_2S_2O_3$ and KI .

(ix) Hypo prefix indicates that central atom of compound has the minimum oxidation state so it will act as a reducing agent.

Example : H_3PO_2 (hypophosphorous acid).

(4) **Substances which act as oxidising as well as reducing agents**

Examples : H_2O , SO_2 , H_2SO_3 , HNO , $NaNO$, $NaSO_3$, O_2 etc.

(5) **Tips for the identification of oxidising and reducing agents**

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

Example : $KMnO_4$, $K_2Cr_2O_7$, HNO_3 , H_2SO_4 , $HClO_4$ etc.

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

Example : H_2S , $H_2C_2O_4$, $FeSO_4$, $Na_2S_2O_3$, $SnCl_2$ etc.

(iii) If an element is in its intermediate oxidation state in a compound, the compound can function both as an oxidising agent as well as reducing agent.

Example : H_2O_2 , H_2SO_3 , HNO_2 , SO_2 etc.

(iv) If a highly electronegative element is in its highest oxidation state in a compound, that compound can function as a powerful oxidising agent.

Example : $KClO_4$, $KClO_3$, $KBrO_3$, KIO_3 etc.

(v) If an electronegative element is in its lowest possible oxidation state in a compound or in free state, it can function as a powerful reducing agent.

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

(6) **Equivalent weight of oxidising and reducing agents**

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

$$\text{Eq. wt. of O. A.} = \frac{\text{Molecular weight}}{\text{No. of electrons gained by one molecule}}$$

$$= \frac{\text{Molecular weight}}{\text{Change in O. N. per mole}}$$

$$\text{Eq. wt. of R. A.} = \frac{\text{Molecular weight}}{\text{No. of electrons lost by one molecule}} = \frac{\text{Molecular weight}}{\text{Change in O. N. per mole}}$$

Table : 13.1 Equivalent weight of few oxidising/reducing agents

Agents	O. N.	Product	O. N.	Change in O. N. per atom	Total Change in O. N. per mole	Eq. wt.
$\text{Cr}_2\text{O}_7^{2-}$	+ 6	Cr^{3+}	+ 3	3	$3 \times 2 = 6$	Mol. wt./6
$\text{C}_2\text{O}_4^{2-}$	+ 3	CO_2	+ 4	1	$1 \times 2 = 2$	Mol. wt./2
$\text{S}_2\text{O}_3^{2-}$	+ 2	$\text{S}_4\text{O}_6^{2-}$	+ 2.5	0.5	$0.5 \times 2 = 1$	Mol. wt./1
H_2O_2	– 1	H_2O	– 2	1	$1 \times 2 = 2$	Mol. wt./2
H_2O_2	– 1	O_2	0	1	$1 \times 2 = 2$	Mol. wt./2
MnO_4^- (Acidic medium)	+ 7	Mn^{2+}	+ 2	5	$5 \times 1 = 5$	Mol. wt./5
MnO_4^- (Neutral medium)	+ 7	MnO_2	+ 4	3	$3 \times 1 = 3$	Mol. wt./3
MnO_4^- (Alkaline medium)	+ 7	MnO_4^{2-}	+ 6	1	$1 \times 1 = 1$	Mol. wt./1

Oxidation number or Oxidation state

(1) **Definition** : Charge on an atom produced by donating or accepting electrons is called **oxidation number** or **oxidation state**. It is the number of effective charges on an atom.

(2) **Valency and oxidation number** : Valency and oxidation number concepts are different. 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. Points of difference between the two have been tabulated below

Oxidation number	Valency
O.N. 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.	It is the combining capacity of the element. No plus or minus sign is attached to it.
O.N. of an element may have different values. It depends on the nature of compound in which it is present.	Valency of an element is usually fixed.
O.N. of the element may be a whole number or fractional.	Valency is always a whole number.
O.N. of the element may be zero.	Valency of the element is never zero except of noble gases.

(3) Oxidation number and Nomenclature

(i) When an element forms two monoatomic cations (representing different oxidation states), the two ions are distinguished by using the ending-*ous* and *ic*. The suffix – *ous* is used for the cation with lower oxidation state and the suffix – *ic* is used for the cation with higher oxidation state.

For example : Cu (oxidation number +1) cuprous

Cu (oxidation number +2) cupric

(ii) **Albert Stock** proposed a new system known as **Stock system**. In this system, Roman numeral written in parentheses immediately after the name of the element indicates the oxidation states. For example,

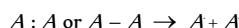
Cu_2O	Copper (I) oxide	SnO	Tin (II) oxide
FeCl_2	Iron (II) chloride	Mn_2O_7	Manganese (VII) oxide
$\text{K}_2\text{Cr}_2\text{O}_7$	Potassium dichromate (VI)	Na_2CrO_4	Sodium chromate (VI)

V_2O_5	Vanadium (V) oxide	CuO	Copper (II) oxide
SnO_2	Tin (IV) oxide	FeCl_3	Iron (III) chloride

(4) Rules for the determination of oxidation number of an atom :

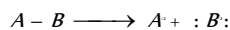
The following rules are followed in ascertaining the oxidation number of an atom,

(i) If there is a covalent bond between two same atoms then oxidation numbers of these two atoms will be zero. Bonded electrons are symmetrically distributed between two atoms. Bonded atoms do not acquire any charge. So oxidation numbers of these two atoms are zero.



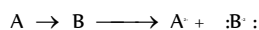
For example, Oxidation number of Cl in Cl_2 , O in O_2 and N in N_2 is zero.

(ii) If covalent bond is between two different atoms then electrons are counted towards more electronegative atom. Thus oxidation number of more electronegative atom is negative and oxidation number of less electronegative atom is positive. Total number of charges on any element depends on number of bonds.



The oxidation number of less electronegative element (A) is + 1 and + 2 respectively.

(iii) If there is a coordinate bond between two atoms then oxidation number of donor atom will be + 2 and of acceptor atom will be – 2.



(iv) The oxidation number of all the atoms of different elements in their respective elementary states is taken to be zero. For example, in N_2 , Cl_2 , H_2 , P_4 , S_8 , O_2 , Br_2 , Na , Fe , Ag etc. the oxidation number of each atom is zero.

(v) The oxidation number of a monoatomic ion is the same as the charge on it. For example, oxidation numbers of Na^+ , Mg^{2+} and Al^{3+} ions are + 1, + 2 and + 3 respectively while those of Cl^- , S^{2-} and N^{3-} ions are –1, –2 and –3 respectively.

(vi) The oxidation number of hydrogen is +1 when combined with non-metals and is -1 when combined with active metals called metal hydrides such as LiH , KH , MgH , CaH etc.

(vii) The oxidation number of oxygen is -2 in most of its compounds, except in peroxides like H_2O_2 , BaO_2 etc. where it is -1. Another interesting exception is found in the compound OF_2 (oxygen difluoride) where the oxidation number of oxygen is +2. This is due to the fact that fluorine being the most electronegative element known has always an oxidation number of -1.

(viii) In compounds formed by union of metals with non-metals, the metal atoms will have positive oxidation numbers and the non-metals will have negative oxidation numbers.

For example,

(a) The oxidation number of alkali metals (Li , Na , K etc.) is always +1 and those of alkaline earth metals (Be , Mg , Ca etc) is +2.

(b) The oxidation number of halogens (F , Cl , Br , I) is always -1 in metal halides such as KF , $AlCl_3$, $MgBr_2$, CdI_2 etc.

(ix) In compounds formed by the union of different elements, the more electronegative atom will have negative oxidation number whereas the less electronegative atom will have positive oxidation number.

For example,

(a) N is given an oxidation number of -3 when it is bonded to less electronegative atom as in NH_3 and Ni , but is given an oxidation number of +3 when it is bonded to more electronegative atoms as in NCl_3 .

(b) Since fluorine is the most electronegative element known so its oxidation number is always -1 in its compounds i.e. oxides, interhalogen compounds etc.

(c) In interhalogen compounds of Cl , Br , and I ; the more electronegative of the two halogens gets the oxidation number of -1. For example, in $BrCl_3$, the oxidation number of Cl is -1 while that of Br is +3.

(x) For neutral molecule, the sum of the oxidation numbers of all the atoms is equal to zero. For example, in NH_3 the sum of the oxidation numbers of nitrogen atom and 3 hydrogen atoms is equal to zero. For a complex ion, the sum of the oxidation numbers of all the atoms is equal to charge on the ion. For example, in SO_4^{2-} ion, the sum of the oxidation numbers of sulphur atom and 4 oxygen atoms must be equal to -2.

(xi) It may be noted that oxidation number is also frequently called as oxidation state. For example, in H_2O , the oxidation state of hydrogen is +1 and the oxidation state of oxygen is -2. This means that oxidation number gives the oxidation state of an element in a compound.

(xii) In the case of representative elements, the highest oxidation number of an element is the same as its group number while highest negative oxidation number is equal to (8 - Group number) with negative sign with a few exceptions. The most common oxidation states of the representative elements are shown in the following table,

Group	Outer shell configuration	Common oxidation numbers (states) except zero in free state
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Table : 13.2 Oxidation number of some elements in compounds, ions or chemical species

Element	Oxidation Number	Compounds, ions or chemical species
Sulphur (S)	-2	H_2S , ZnS , $NaHS$, $(SrS)_x$, BaS , CS_2
	0	S , S_2 , S_8 , SCN
	+1	S_2F_2 , S_2Cl_2
	+4	SO_2 , H_2SO_3 , $(SO_3)^-$, $SOCl_2$, $NaHSO_3$, $Ca[HSO_3]$, $[HSO_3] SF_6$

I A	ns^1	+1
II A	ns^2	+2
III A	$ns^2 np^1$	+3, +1
IV A	$ns^2 np^2$	+4, +3, +2, +1, -1, -2, -3, -4
V A	$ns^2 np^3$	+5, +3, +1, -1, -3
VI A	$ns^2 np^4$	+6, +4, +2, -2
VII A	$ns^2 np^5$	+7, +5, +3, +1, -1

(xiii) Transition metals exhibit a large number of oxidation states due to involvement of $(n-1)$ d electron besides ns electron.

(xiv) Oxidation number of a metal in carbonyl complex is always zero.

Example: Ni has zero oxidation state in $[Ni(CO)_4]$.

(xv) Those compounds which have only C , H and O the oxidation number of carbon can be calculated by following formula,

$$\text{Oxidation number of 'C'} = \frac{(n_O \times 2 - n_H)}{n_C}$$

Where, n_O is the number of oxygen atom, n_H is the number of hydrogen atom, n_C is the number of carbon atom.

For example, (a) CH_3OH ; $n_H = 4$, $n_C = 1$, $n_O = 1$

$$\text{Oxidation number of 'C'} = \frac{(1 \times 2 - 4)}{1} = -2$$

(b) $HCOOH$; $n_H = 2$, $n_O = 2$, $n_C = 1$

$$\text{Oxidation number of carbon} = \frac{(2 \times 2 - 2)}{1} = +2$$

(5) **Procedure for calculation of oxidation number** : By applying the above rules, we can calculate the oxidation numbers of elements in the molecules/ions by the following steps.

(i) Write down the formula of the given molecule/ion leaving some space between the atoms.

(ii) Write oxidation number on the top of each atom. In case of the atom whose oxidation number has to be calculated write x .

(iii) Beneath the formula, write down the total oxidation numbers of each element. For this purpose, multiply the oxidation numbers of each atom with the number of atoms of that kind in the molecule/ion. Write the product in a bracket.

(iv) Equate the sum of the oxidation numbers to zero for neutral molecule and equal to charge on the ion.

(v) Solve for the value of x .

	+ 6	H_2SO_4 , $(SO_4)^{2-}$, $[HSO_4]^-$, $BaSO_4$, $KHSO_4$, SO_2 , SF_6 , $H_2S_2O_8$, $(S_2O_8)^{2-}$
Nitrogen (N)	− 3	NH_3 , (NH_3) , AlN , Mg_3N_2 , $(N)^{3-}$, Ca_3N_2 , CN^-
	− 2	NH_2 , $(NH_2)^-$
	− 1	NH_2OH
	−1/3	NaN_3 , N_3H
	0	N_2
	+ 1	N_2O
	+ 2	NO
	+ 3	HNO_3 , $(NO_3)^-$, $NaNO_3$, N_2O_5 , NF_3
	+ 4	NO_2
	+ 5	HNO_2 , $(NO_2)^-$, KNO_2 , N_2O_4
Chlorine (Cl)	− 1	HCl , $NaCl$, $CaCl_2$, $AlCl_3$, ICl , ICl_3 , $SOCl_2$, CrO_2Cl_2 , KCl , K_2PtCl_6 , $HAuCl_4$, CCl_4
	0	Cl_2 , Cl_2
	+ 1	$HOCl$, $NaOCl$, $(OCl)^-$, Cl_2O
	+ 3	$KClO_3$, $(ClO_3)^-$, $HClO_3$
	+ 4	ClO_2
	+ 5	$(ClO_2)^-$, $KClO_4$, $NaClO_4$, $HClO_4$
	+ 7	$HClO_4$, Cl_2O_7 , $KClO_4$, $(ClO_4)^-$
Hydrogen (H)	− 1	NaH , CaH_2 , $LiAlH_4$, LiH
	+ 1	NH_3 , PH_3 , HF
Phosphorus (P)	− 3	PH_3 , (PH_3) , Ca_3P_2
	0	P_4
	+ 1	H_3PO_4 , KH_2PO_4 , $BaH_2P_2O_7$
	+ 3	PI_3 , PBr_3 , PCl_3 , P_2O_3 , H_3PO_3
	+ 5	$(PO_4)^{3-}$, $H_2PO_4^-$, $Ca_3(PO_4)_2$, $H_2P_2O_7$, P_2O_5 , PCl_5 , $(PO_3)^-$, $Mg_3P_2O_8$, ATP
Oxygen (O)	− 2	H_2O , PbO_2 , $(CO_3)^{2-}$, $(PO_4)^{3-}$, SO_2 , $(CO_3)^{2-}$, $HOCl$, $(OH)^-$, $(O)^{2-}$
	− 1	NaO_2 , BaO_2 , H_2O_2 , $(O_2)^{2-}$, Peroxides
	− 1/2	KO_2
	0	O_2 , O_2 , O_3
	+ 1	OF_2
	+ 2	OF_2
Carbon (C)	− 4	CH_4
	− 3	C_2H_2
	− 2	CH_2Cl_2 , C_2H_4
	− 1	CaC_2 , C_2H_2
	0	Diamond, Graphite, $C_2H_2O_2$, $C_2H_2O_2$, $HCHO$, CH_2Cl_2
	+ 2	CO , $CHCl_3$, HCN
	+ 3	H_2CO_3 , $(CO_3)^{2-}$
	+ 4	CO_2 , H_2CO_3 , $(HCO_3)^-$, CCl_4 , Na_2CO_3 , $CaCO_3$, CS_2 , CF_4 , $(CO)^+$

Chromium (Cr)	+ 3	$Cr_2(SO_4)_3, CrCl_3, Cr_2O_3, [Cr(H_2O)_6Cl_3]$
	+ 6	$K_2CrO_4, (CrO_4)^{2-}, K_2Cr_2O_7, (Cr_2O_7)^{2-}, KCrO_4Cl, CrO_4Cl, Na_2Cr_2O_7, CrO_3$
Manganese (Mn)	+ 2	$MnO, MnSO_4, MnCl_2, Mn(OH)_2$
	+ 8/3	Mn_2O_3
	+ 3	$Mn(OH)_3$
	+ 4	$MnO_2, KMnO_4$
	+ 6	$KMnO_4, (MnO_4)^{-}$
	+ 7	$KMnO_4, (MnO_4)^{-}, HMnO_4$
Silicon (Si)	- 4	$SiH_4, MgSi$
	+ 4	$SiO_2, K_2SiO_3, SiCl_4$
Iron (Fe)	$+\frac{8}{3}$	Fe_3O_4
	+ 2	$FeSO_4, (NH_4)_2SO_4$ (Ferrous ammonium sulphate), $K_2Fe(CN)_6, FeCl_2$
	+ 3	$K_3[Fe(CN)_6], FeCl_3$
Iodine (I)	+ 7	$H_4IO_6^-, KIO_4$
Osmium (Os)	+ 8	OsO_4
Xenon (Xe)	+ 6	XeO_4, XeF_6

(6) **Exceptional cases of evaluation of oxidation numbers** : The rules described earlier are usually helpful in determination of the oxidation number of a specific atom in simple molecules but these rules fail in following cases. In these cases, the oxidation numbers are evaluated using the concepts of chemical bonding involved.

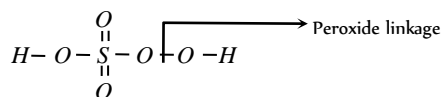
Type 1. In molecules containing peroxide linkage in addition to element-oxygen bonds. For example,

- (i) **Oxidation number of S in H_2SO_5**
(Permonosulphuric acid or Caro's acid)

By usual method; H_2SO_5

$$2 \times 1 + x + 5 \times (-2) = 0 \quad \text{or} \quad x = +8$$

But this cannot be true as maximum oxidation number for S cannot exceed + 6. Since S has only 6 electrons in its valence shell. This exceptional value is due to the fact that two oxygen atoms in H_2SO_5 shows peroxide linkage as shown below,



Therefore the evaluation of o.n. of sulphur here should be made as follows,

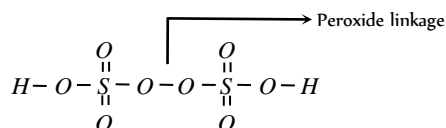
$$\begin{array}{ccccccc}
 2 \times (+1) & + & x & + & 3 \times (-2) & + & 2 \times (-1) \\
 \text{(for H)} & & \text{(for S)} & & \text{(for O)} & & \text{(for O-O)} \\
 \text{or} & 2 & + & x & - 6 & - 2 = 0 & \text{or} \quad x = + 6.
 \end{array}$$

- (ii) **Oxidation number of S in $H_2S_2O_8$**
(Peroxydisulphuric acid or Marshall's acid)

By usual method ; $H_2S_2O_8$

$$\begin{array}{l}
 1 \times 2 + 2x + 8 (-2) = 0 \\
 2x = +16 - 2 = 14 \quad \text{or} \quad x = + 7
 \end{array}$$

Similarly Caro's acid, Marshall's acid also has a peroxide linkage so that in which S shows +6 oxidation state.



Therefore the evaluation of oxidation state of sulphur should be made as follow,

$$\begin{array}{ccccccc}
 2 \times (+1) & + & 2 \times (x) & + & 6 \times (-2) & + & 2 \times (-1) = 0 \\
 \text{(for H)} & & \text{(for S)} & & \text{(for O)} & & \text{(for O-O)} \\
 \text{or} & 2 & + & 2x & - 12 & - 2 = 0 & \text{or} \quad x = + 6.
 \end{array}$$

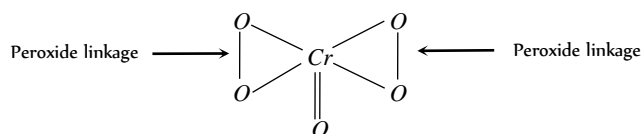
- (iii) **Oxidation number of Cr in CrO_5**

(Blue perchromate)

By usual method CrO_5 ; $x - 10 = 0$ or $x = + 10$

This cannot be true as maximum O. N. of Cr cannot be more than + 6. Since Cr has only five electrons in 3d orbitals and one electron in 4s orbital. This exceptional value is due to the fact that four oxygen atoms in CrO_5 are in peroxide linkage.

The chemical structure of CrO_5 is



Therefore, the evaluation of o.n. of Cr should be made as follows

$$\begin{array}{ccccccc}
 x & + & 1 \times (-2) & + & 4 (-1) = 0 \\
 \text{(for Cr)} & & \text{(for O)} & & \text{(for O-O)}
 \end{array}$$

$$\text{or } x - 2 - 4 = 0 \text{ or } x = +6.$$

Type II. In molecules containing covalent and coordinate bonds, following rules are used for evaluating the oxidation numbers of atoms.

(i) For each covalent bond between dissimilar atoms the less electronegative element is assigned the oxidation number of +1 while the atom of the more electronegative element is assigned the oxidation number of -1.

(ii) In case of a coordinate-covalent bond between similar or dissimilar atoms but the donor atom is less electronegative than the acceptor atom, an oxidation number of +2 is assigned to the donor atom and an oxidation number of -2 is assigned to the acceptor atom.

Conversely, if the donor atom is more electronegative than the acceptor atom, the contribution of the coordinate bond is neglected. *Examples,*

(a) *Oxidation number of C in $HC \equiv N$ and $HN \equiv C$*

The evaluation of oxidation number of C cannot be made directly by usual rules since no standard rule exists for oxidation numbers of N and C.

In such cases, evaluation of oxidation number should be made using indirect concept or by the original concepts of chemical bonding.

(b) *Oxidation number of carbon in $H-N \equiv C$*

The contribution of coordinate bond is neglected since the bond is directed from a more electronegative N atom (donor) to a less electronegative carbon atom (acceptor).

Therefore the oxidation number of N in $HN \equiv C$ remains -3 as it has three covalent bonds.

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

(for H) (for N) (for C)

$$\text{or } 1 + x - 3 = 0 \quad \text{or} \quad x = +2.$$

(c) *Oxidation number of carbon in $HC \equiv N$*

In $HC \equiv N$, N is more electronegative than carbon, each bond gives an oxidation number of -1 to N. There are three covalent bonds, the oxidation number of N in $HC \equiv N$ is taken as -3

$$\text{Now } HC \equiv N \therefore +1 + x - 3 = 0 \Rightarrow x = +2$$

Type III. In a molecule containing two or more atoms of same or different elements in different oxidation states.

(i) *Oxidation number of S in $Na_2S_2O_3$*

By usual method $Na_2S_2O_3$

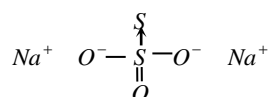
$$\therefore 2 \times (+1) + 2 \times x + 3(-2) = 0 \quad \text{or} \quad 2 + 2x - 6 = 0$$

$$\text{or } x = 2.$$

But this is unacceptable as the two sulphur atoms in $Na_2S_2O_3$ cannot have the same oxidation number because on treatment with dil. H_2SO_4 , one sulphur atom is precipitated while the other is oxidised to SO_2 .



In this case, the oxidation number of sulphur is evaluated from concepts of chemical bonding. The chemical structure of $Na_2S_2O_3$ is



Due to the presence of a co-ordinate bond between two sulphur atoms, the acceptor sulphur atom has oxidation number of -2 whereas the other S atom gets oxidation number of +2.

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

(for Na) (for O) (for S) (for coordinated S)

$$\text{or } +2 - 6 + x - 2 = 0 \quad \text{or} \quad x = +6$$

Thus two sulphur atoms in $Na_2S_2O_3$ have oxidation number of -2 and +6.

(ii) *Oxidation number of chlorine in $CaOCl$*
(bleaching powder)

In bleaching powder, $Ca(OCl)Cl$, the two Cl atoms are in different oxidation states i.e., one Cl having oxidation number of -1 and the other as OCl having oxidation number of +1.

(iii) *Oxidation number of N in NH_4NO_3*

$$\text{By usual method } NH_4NO_3; 2x + 4 \times (+1) + 3 \times (-1) = 0$$

$$2x + 4 - 3 = 0 \quad \text{or} \quad 2x = -1 \quad (\text{wrong})$$

No doubt NH_4NO_3 has two nitrogen atoms but one N has negative oxidation number (attached to H) and the other has positive oxidation number (attached to O). Hence the evaluation should be made separately for NH_4^+ and NO_3^-

$$NH_4^+ \quad x + 4 \times (+1) = +1 \text{ or } x = -3$$

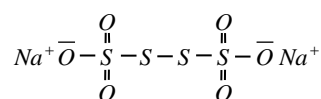
$$NO_3^- \quad x + 3(-2) = -1 \text{ or } x = +5.$$

(iv) *Oxidation number of Fe in Fe_3O_4*

In Fe_3O_4 , Fe atoms are in two different oxidation states. Fe_3O_4 can be considered as an equimolar mixture of FeO [iron (II) oxide] and Fe_2O_3 [iron (III) oxide]. Thus in one molecule of Fe_3O_4 , two Fe atoms are in +3 oxidation state and one Fe atom is in +2 oxidation state.

(v) *Oxidation number of S in sodium tetrathionate ($Na_2S_4O_6$)*

Its structure can be represented as follows,



The two S-atoms which are linked to each other have oxidation number zero. The oxidation number of other S-atoms can be calculated as follows

Let oxidation number of S = x.

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

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

$$x = +5.$$

Balancing of oxidation-reduction reactions

Though there are a number of methods for balancing oxidation - reduction reactions, two methods are very important. These are,

- (1) Oxidation number method
- (2) Ion - electron method

(1) **Oxidation number method** : The method for balancing redox reactions by oxidation number change method was developed by **Johnson**. In a balanced redox reaction, total increase in oxidation number must be equal to the total decrease in oxidation number. This equivalence provides the basis for balancing redox reactions. This method is applicable to both

molecular and ionic equations. The general procedure involves the following steps,

(i) Write the skeleton equation (if not given, frame it) representing the chemical change.

(ii) Assign oxidation numbers to the atoms in the equation and find out which atoms are undergoing oxidation and reduction. Write separate equations for the atoms undergoing oxidation and reduction.

(iii) Find the change in oxidation number in each equation. Make the change equal in both the equations by multiplying with suitable integers. Add both the equations.

(iv) Complete the balancing by inspection. First balance those substances which have undergone change in oxidation number and then other atoms except hydrogen and oxygen. Finally balance hydrogen and oxygen by putting H_2O molecules wherever needed.

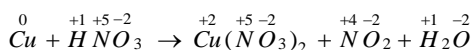
The final balanced equation should be checked to ensure that there are as many atoms of each element on the right as there are on the left.

(v) In ionic equations the net charges on both sides of the equation must be exactly the same. Use H^+ ion/ions in acidic reactions and OH^- ion/ions in basic reactions to balance the charge and number of hydrogen and oxygen atoms.

The following example illustrate the above rules,

Step: I $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$
(Skeleton equation)

Step: II Writing the oxidation number of all the atoms.



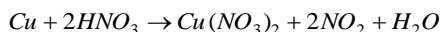
Step: III Change in oxidation number has occurred in copper and nitrogen.



Cu Increase in oxidation number of copper = 2 units per molecule

HNO_3 Decrease in oxidation number of nitrogen = 1 unit per molecule

Step: IV To make increase and decrease equal, equation (ii) is multiplied by 2.



Step: V Balancing nitrate ions, hydrogen and oxygen, the following equation is obtained.



This is the balanced equation.

(2) **Ion-electron method** (half reaction method)

Jette and **LaMev** developed the method for balancing redox-reactions by ion electron method in 1927. It involves the following steps

(i) Write down the redox reaction in ionic form.

(ii) Split the redox reaction into two half reactions, one for oxidation and other for reduction.

(iii) Balance each half reaction for the number of atoms of each element. For this purpose,

(a) Balance the atoms other than H and O for each half reaction using simple multiples.

(b) Add water molecules to the side deficient in oxygen and H to the side deficient in hydrogen. This is done in acidic or neutral solutions.

(c) In alkaline solution, for each excess of oxygen, add one water molecule to the same side and $2OH^-$ ions to the other side. If hydrogen is still unbalanced, add one OH^- ion for each excess hydrogen on the same side and one water molecule to the other side.

(iv) Add electrons to the side deficient in electrons as to equalise the charge on both sides.

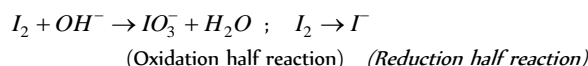
(v) Multiply one or both the half reactions by a suitable number so that number of electrons become equal in both the equations.

(vi) Add the two balanced half reactions and cancel any term common to both sides.

The following example illustrate the above rules

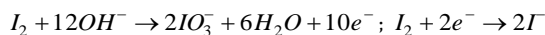
Step: I $I_2 + OH^- \rightarrow IO_3^- + I^- + H_2O$ (Ionic equation)

Step: II Splitting into two half reactions,

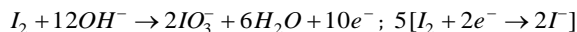


Step: III Adding OH^- ions, $I_2 + 12OH^- \rightarrow 2IO_3^- + 6H_2O$

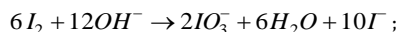
Step: IV Adding electrons to the sides deficient in electrons, (S)



Step: V Balancing electrons in both the half reactions.

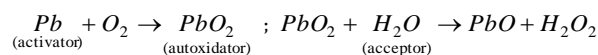


Step: VI Adding both the half reactions.

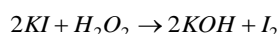
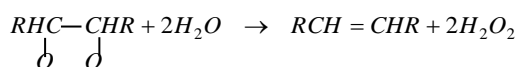
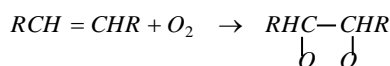


Autoxidation

(1) Turpentine and numerous other olefinic compounds, phosphorus and certain metals like Zn and Pb can absorb oxygen from the air in presence of water. The water is oxidised to hydrogen peroxide. This phenomenon of formation of H_2O_2 by the oxidation of H_2O is known as **autoxidation**. The substance such as turpentine or phosphorus or lead which can activate the oxygen is called **activator**. The activator is supposed to first combine with oxygen to form an addition compound, which acts as an **autoxidator** and reacts with water or some other acceptor so as to oxidise the latter. For example;



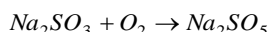
(2) The turpentine or other unsaturated compounds which act as activators are supposed to take up oxygen molecule at the double bond position to form unstable peroxide called **moloxide**, which then gives up the oxygen to water molecule or any other acceptor.



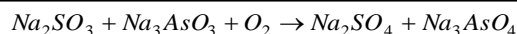
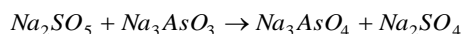
The evolution of iodine from KI solution in presence of turpentine can be confirmed with starch solution which turns blue.

(3) The concept of autoxidation help to explain the phenomenon of induced oxidation. Na_2SO_3 solution is oxidised by air but Na_3AsO_3

solution is not oxidised by air. If a mixture of both is taken, it is observed both are oxidised. This is induced oxidation.



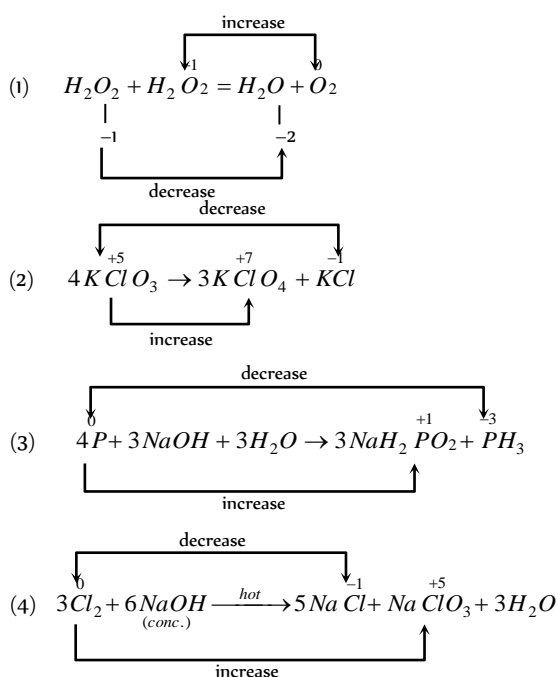
Moloxide



Disproportionation

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

Following are the some examples of *disproportionation*,



can act as both oxidising & reducing agent. For example, H_2O_2 , H_2SO_3 , HNO_3 , SO_2 etc.

Tips & Tricks

- ✍ If an element is in its highest possible oxidation state in a compound, it can act as an oxidising agent. for example, $KMnO_4$, $K_2Cr_2O_7$, HNO_3 , H_2SO_4 , $HClO_4$ etc.
- ✍ If an element is in its lowest oxidation state in a compound, it can act as a reducing agent. For example, H_2S , $H_2C_2O_4$, $FeSO_4$, Na_2SO_3 , SO_2 , $SnCl_2$, many metals etc.
- ✍ The strength of oxyacids of chlorine decrease in the order. $HClO_4 > HClO_3 > HClO_2 > HClO$
- ✍ If highly electronegative element is in its highest oxidation state in a compound that compound can act as powerful oxidant. For example, $KClO_4$, $KClO_3$, $KBrO_3$, KIO_3 etc.
- ✍ If an element is in intermediate oxidation state in a compound, it