Oxidation:

a. Oxygen is added. $2Mg+O_2 \rightarrow 2MgO$2Mg+O2→2MgO

b. Hydrogen is being removed. $H_2S+Cl_2 \rightarrow 2HCl+S$H2S+Cl2→2HCl+S

c. Positive charge increases. $Fe^{2+} \rightarrow Fe^{3+}+e^-$Fe2+→Fe3++e−

d. Removal of electron $Sn^{2+} \rightarrow Sn^{4+}+2e^-$Sn2+→Sn4++2e−

Reduction:

a. Oxygen is being removed. $CuO+C \rightarrow Cu+CO$ CuO+C→Cu+CO

b. Hydrogen is added. $S+H_2 \rightarrow H_2S$S+H2→H2S

c. Positive charge decreases. $Fe^{3+}+e^- \rightarrow Fe^{2+}$Fe3++e−→Fe2+

d. Addition of electron. $Fe^{3+}+e^- \rightarrow Fe^{2+}$Fe3++e−→Fe2+

Oxidation Number

- When an element transitions from its elemental free state to its combined form in molecules, it develops an imaginary or seeming charge over each atom.
- It is determined using an arbitrary set of rules.
- In a certain bonded condition, it is a relative charge.
- A more practical way of employing oxidation number to keep track of electron-shifts in chemical reactions involving the synthesis of compounds has been created.
- The complete transfer of electrons from a less electronegative atom to a more electronegative atom is always expected in this procedure.

Rules Governing Oxidation Number

The following rules can be used to calculate the oxidation number of elements in various compounds. It is important to remember that the electronegativity of the element is the foundation of these rules.

Atom of Fluorine:

Fluorine is the most electronegative of all the elements (known). In all of its compounds, it has an oxidation number of –1.

Atom of Oxygen:

Oxygen atoms have an oxidation number of –2 in general, as well as in their oxides.

I. peroxide (e.g. H_2O_2, Na_2O_2)H2O2,Na2O2) is -1−1
II. super oxide (e.g. KO_2KO2) is $-1/2$−1/2
III. ozonide (e.g. KO_3KO3) is $-1/3$−1/3
IV. in OF_2OF2 is $+2$ in O_2F_2+2 in O2F2 is $+1$+1

Hydrogen Atom:

The hydrogen atom has an oxidation number of +1 in general. However, it is –1 in metallic hydrides (e.g. NaH, KH).

Halogen Atom:

In general, all halogen atoms (Cl, Br, and I) have an oxidation number of –1.

If a halogen atom is connected to a more electronegative atom than the halogen atom, the oxidation numbers will be positive.

e.g. $KClO_3, HIO_3, HClO_4, KBrO_3$KClO3,HIO3,HClO4,KBrO3.

Metals:

a. The oxidation number of alkali metals (Li, Na, K, Rb, etc.) is always +1.

b. The oxidation number of alkaline earth metals (Be, Mg, Ca, etc.) is always +2.

c. The oxidation number of aluminium is always +3.

Note that a metal's oxidation number might be negative or zero.

d. In the free state or in allotropic forms, an element's oxidation number is always zero.

e.g. O_2^0, S_8^0, P_4^0O20,S80,P40

e. The sum of all the oxidation numbers of the atoms in a molecule is zero.

f. The charge on an ion is equal to the sum of the oxidation numbers of all the atoms in the ion.

g. If an element's group number is n in the contemporary periodic table, its oxidation number can range from (n – 10) to (n – 18). (but it is mainly applicable for p-block elements).

Calculation of Average Oxidation Number: Solved Examples

Example-1 : Calculate oxidation number of underlined element

a. $Na_2S^{-}_{-2}$Na2S_2

b. $Na_2S^{-}_{-4}$Na2S_4

a. Let oxidation number of S-atom is xx. Now work accordingly with the rules given before.

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

b. Let oxidation number of S-atom is x
$\therefore (+1)\times 2+(x)\times 4+(-2)\times 6=0$
$x=+2.5$
It is vital to note that $Na_2S_2O_3$ has two S-atoms, whereas $Na_2S_4O_6$ has four S-atoms. However, none of the sulphur atoms in either compound has an oxidation number of +2 or + 2.5; instead, the average of the oxidation numbers on each sulphur atom is used. As a result, we should strive to determine each sulphur atom's specific oxidation number in these compounds.

Individual Oxidation Number Calculation:

It's vital to remember that in order to calculate the individual oxidation number of an element in its compound, you'll need to know the structure of the compound and follow the steps below.

This is the formula:

Number of electrons in the valence shell minus number of electrons taken up after bonding = oxidation number

Recommendations: It is based on an element's electronegativity.

1. Bonded pair electrons are evenly shared by each element if there is a bond between similar types of atoms and each atom has the same sort of hybridisation.

Consider the Following Scenario:

Calculate each Cl-oxidation atom's number in the Cl_2 molecule.

I : Number of electrons in the valence shell $=7$
Number of electrons taken up after bonding $=7$
$\therefore$ oxidation number $=7-7=0$

II : similarly, oxidation number $=7-7=0$=7−7=0
If a bond exists between different types of atoms, such as A – B (if B is more electronegative than A), the bound pair of electrons are tallied with the B-atom after bonding.

Consider the following scenario:
Calculate each atom's oxidation number in the HCl molecule.

Electron of H-atom is now counted with Cl-atom, because Cl-atom is more electronegative than H-atom

H:H: Number of electrons in the valence shell $=1$=1
Number of electrons taken up after bonding $=0$=0
Oxidation number of $\mathrm{H}=1-0=+1$H=1−0=+1
Cl:Cl: Number of electrons in the valence shell $=7$=7
Number of electrons taken up after bonding $=8$=8
Oxidation number of $\mathrm{Cl}=7-8=-1$Cl=7−8=−1

Solved Examples Example – 2
Calculate individual oxidation number of each S-atom in $Na_2S_2O_3$Na2S2O3 (sodium thiosulphate) with the help of its structure.

I (the middle S-atom) is sp^3 hybridised (25 percent s-character), while II (the terminal S-atom) is sp^2 (33 percent s-character). As a result, the terminal sulphur atom has a higher electronegative charge than the central sulphur atom. With the terminal S-atom, the shared pair of electrons is now counted.

I, S-atom: Number of electrons in the valence shell $=6$=6
Number of electrons left after bonding $=0$=0
Oxidation number of central SS-atom $=6-0=+6$=6−0=+6
II, S-atom : Number of electrons in the valence shell $=6$=6
Number of electrons left after bonding $=8$=8
Oxidation number of terminal S-atom $=6-8=-2$=6−8=−2
Now, you can also calculate Average Oxidation number of $\mathrm{S}=6+(-2)2=+2$S=6+(−2)2=+2 (as we have calculated before)

Miscellaneous Examples:

In order to determine the exact or individual oxidation number we need to take help from the structures of the molecules. Some special cases are discussed as follows :

From the structure, it is evident that in CrO_5 there are two peroxide linkages and one double bond. The contribution of each peroxide linkage is -2. Let the oxidation number of Cr is x.

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

$\therefore$ Oxidation number of $Cr=+6$ Ans.

From the structure, it is evident that in H_2SO_5, there is one peroxide linkage, two sulphur-oxygen double bonds and one OH group.

Let the oxidation number of $S=x$.

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

or $x+2-8$ or $x-6=0$ or $x=6$

$\therefore$ Oxidation number of S in H_2SO_5 is $+6$ Ans.

Paradox of Fractional Oxidation Number:

The structural parameters demonstrate that the atoms of the element for whom fractional oxidation state is realised are truly present in distinct oxidation states, and the fractional oxidation number is the average of oxidation state of all atoms of the element under investigation. The following bonding scenarios are shown by the species' C_3O_2, Br_3O_8 structure:

In each species, the element highlighted with an asterisk (*) has a different oxidation number than the rest of the atoms of the same element. This demonstrates that two carbon atoms in C_3O_2 are each in the +2 oxidation state, while the third is in the zero oxidation state, giving a total of +4/3. The realistic picture, on the other hand, is +2 for two terabytes.

Likewise in Br_3O_8, each of the two terminal bromine atoms are present in $+6$ oxidation state and the middle bromine* is present in $+4$ oxidation state. Once again the average, that is different from reality, is $+16/3$.

Oxidising and Reducing Agent:

Oxidising Agent or Oxidant :

Oxidising agents are substances that can oxidise others while reducing themselves during a chemical process. Oxidants are chemicals that cause an element's oxidation number to decrease or gain electrons in a redox process. e.g. $KMnO_4, K_2Cr_2O_7, HNO_3$KMnO4,K2Cr2O7,HNO3, conc. H_2SO_4H2SO4 etc are powerful oxidising agents.

Reducing Agent or Reductant :

Reducing agents are substances that can both reduce and oxidise other molecules during a chemical reaction. Reductants are reagents that increase the oxidation number of an element or cause the element to lose electrons in a redox reaction. e.g. $KI, Na_2S_2O_3$KI,Na2S2O3 etc are the powerful reducing agents.

Redox Reaction:

A redox reaction is one in which both oxidation and reduction occur at the same time. The overall increase in oxidation number must match the total reduction in oxidation number in all redox processes e.g.

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$