- **Indirect redox reaction (Electrochemical reaction) :** A reaction in which the reacting species which is capable of losing electrons (reducing agent) and that capable of gaining electrons (oxidising agent) are kept separately and the transfer of electrons from one species to another does not take place directly is called an indirect redox reaction.

  In an indirect redox reaction, each of the reactants is kept in a separate container in contact with a rod/ sheet of a metallic conductor (electronic conductor) called an electrode. Electrical contact between the two reactants is established by placing a conducting salt bridge between the two.

OXIDATION NUMBER

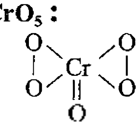
- Oxidation number of an element is defined as the charge which an atom of the element has in its ion or in combined state with other atoms. Oxidation number can also be defined as the number of electron which the atom of an element loses or gains in going from its natural free state to a particular compound or ion. Oxidation number is also called oxidation state. It can be positive, negative, zero or even in fraction.
- **Rules for assigning oxidation number**

Rules	Oxidation no.	Examples
Atoms of different elements in elementary state and in allotropic form.	zero (0)	N_2, Cl_2, O_2, P_4, S_8
Monoatomic ions	same as charge	$Na^+(1)$, $Mg^{2+}(2)$, $Cl^-(-1)$
Hydrogen: - with non-metals - with metals	 +1 –1	 H_2O, H_2S, HCl LiH, CaH_2, KH
Oxygen : - in peroxides - with fluorine	–2 (mostly) –1 +1, +2	H_2O, CaO, NaOH H_2O_2, BaO_2 O_2F_2, OF_2 (respectively)
Alkali metal (IA)	+1	Li, Na, K, etc.
Alkaline earth metals (IIA)	+2	Be, Mg, Ca, etc.
Fluorine (most electronegative)	–1 (always)	HF, OF_2, LiF

Illustration 1

Find the oxidation number of Cr in CrO_5.

Soln.: Structure of CrO_5 :



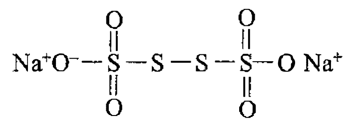
In CrO_5, one of the oxygen is doubly bonded to Cr (Cr= O) and has been assigned an oxidation number of –2, whereas four of the oxygen have peroxo linkage (O – O) and should be assigned –1 oxidation number. Now, we can calculate oxidation number of Cr.

$$x + 1(-2) + 4(-1) = 0 \Rightarrow x = +6$$

Illustration 2

~~Find the oxidation~~ number of S in $Na_2S_4O_6$.

Soln.: Structure of $Na_2S_4O_6$:

 or $(S_4O_6)^{2-}$

In $Na_2S_4O_6$, two of the S-atoms are bonded to sulphur only on both sides (S – S) and thus have oxidation number zero.

$$2(+1)+2(x)+6(-2)+2(0)=0 \Rightarrow x = \frac{10}{2} = +5$$

Illustration 3

~~Identify oxidant~~ and reductant in the following reactions.

(i) $2Cu_2O_{(s)} + Cu_2S_{(s)} \rightarrow 6Cu_{(s)} + SO_{2(g)}$

(ii) $3Mg_{(s)} + N_{2(g)} \rightarrow Mg_3N_{2(s)}$

(iii) $Zn + 2AgCN \rightarrow 2Ag + Zn(CN)_2$

Soln.: (i) $2\overset{+1\ -2}{Cu_2O} + \overset{+1\ -2}{Cu_2S} \rightarrow 6\overset{0}{Cu} + \overset{+4\,-2}{SO_2}$

- Oxidation state of sulphur changes from – 2 in Cu_2S to + 4 in SO_2 *i.e.*, it is getting oxidised and hence Cu_2S acts as reductant or reducing agent.
- Oxidation state of copper changes from +1 in Cu_2O to zero in elemental copper *i.e.*, it is getting reduced and hence Cu_2O acts as oxidant or oxidising agent.

(ii) $3\overset{0}{Mg} + \overset{0}{N_2} \rightarrow \overset{+2\ -3}{Mg_3N_2}$

- Oxidation state of magnesium changes from zero (Mg) to + 2 (Mg_3N_2), thus Mg acts as reductant.
- Oxidation state of nitrogen changes from zero (N_2) to –3 (Mg_3N_2), thus N_2 acts as oxidant.

(iii) $\overset{0}{Zn} + 2\overset{+1}{Ag}CN \rightarrow 2\overset{0}{Ag} + \overset{+2}{Zn}(CN)_2$

- Oxidation states of Zn changes from zero (Zn) to + 2 ($Zn(CN)_2$), thus Zn act as reductant.
- Oxidation state of Ag changes from + 1 (AgCN) to zero (Ag), thus AgCN acts as oxidising agent.

Balancing Redox Reactions

- Redox reactions can be balanced with the help of two methods.
  - **Oxidation number method :** This method involves the following steps:

    Step 1 : Write the skeleton redox reaction.

    Step 2 : Write the oxidation number of atoms above the symbol and identify elements undergoing oxidation or reduction.

Step 3 : Balance, increase in oxidation number and decrease in oxidation number by multiplying the half-reaction with suitable integer.

Step 4 : Balance the atoms other than hydrogen and oxygen.

Step 5 : Balance hydrogen and oxygen:

– **Acidic medium:** Add H_2O to balance 'O' and then add H^+ to balance H.

– **Basic medium:** Add OH^- to balance charge and then add H_2O to balance H and O.

Illustration 4

Balance the following reaction in basic medium:

$MnO_4^- + H_2O_2 \rightarrow MnO_2 + O_2$

Soln.: Oxidation Number Method :

Step (i): $MnO_4^- + H_2O_2 \rightarrow MnO_2 + O_2$

Step (ii):

Oxidation number increases by 1 per O atom

$$\overset{+7}{Mn}O_4^- + H_2\overset{-1}{O_2} \longrightarrow \overset{+4}{Mn}O_2 + \overset{0}{O_2}$$

Oxidation number decreases by 3 per Mn atom

Step (iii): Total increase in oxidation number = $1 \times 2 = 2$

Total decrease in oxidation number = 3

Step (iv): Multiply O terms by 3 and Mn terms by 2 to equalise increase and decrease in oxidation number.

$2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2$

Step (v): $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2$

Step (vi): $2MnO_4^- + 3H_2O_2 \rightarrow$

$2MnO_2 + 3O_2 + 2OH^- + 2H_2O$

➤ **Ion-electron method :** This method involves following steps:

Step 1: Write down the equation in ionic form.

Step 2: Split the reaction into two half reactions; one for oxidation and other for reduction.

Step 3: Balance each half reaction by using following rules:

– First balance the atoms which undergo oxidation or reduction.

– Balance the atoms other than hydrogen and oxygen using simple multiples.

– In acidic and neutral solution : Add water molecules to the side deficient in oxygen and H^+ to the side deficient in hydrogen.

– In basic medium : For each excess of oxygen add H_2O to the same side and two OH^- ions to the other side. If hydrogen is still unbalanced, add one OH^- ion for each excess of hydrogen on same side and one water molecule to the other side.

Step 4: Add electrons to the side deficient in electrons to balance charge.

Step 5: Multiply two half reactions by suitable integer to equalise number of electrons in both reactions.

Illustration 5

Balance the following equation by ion-electron method in basic medium.

$Cl_2 \rightarrow ClO_3^- + Cl^-$

Soln.: Step (i): $\overset{0}{Cl_2} \rightarrow \overset{+5}{Cl}O_3^- + \overset{-1}{Cl^-}$

Oxidation (oxidation number increases by 5)

Step (ii): $\overset{0}{Cl_2} \longrightarrow [\overset{+5}{Cl}O_3]^- + Cl^{-1}$

Reduction (oxidation number decreases by 1)

Step (iii): $Cl_2 \rightarrow ClO_3^-$ (Oxidation half reaction) $\quad Cl_2 \rightarrow Cl^-$ (Reduction half reaction)

Step (iv):

(a) $Cl_2 \rightarrow 2ClO_3^-$ $\qquad$ $Cl_2 \rightarrow Cl^-$

(b) $Cl_2 \rightarrow 2ClO_3^- + 10e^-$ $\qquad$ $Cl_2 + 2e^- \rightarrow 2Cl^-$

(c) $Cl_2 + 12OH^- \rightarrow 2ClO_3^- + 10e^-$

(d) $Cl_2 + 12OH^- \rightarrow 2ClO_3^- + 10e^- + 6H_2O$

Step (v):

$Cl_2 + 12OH^- \rightarrow 2ClO_3^- + 10e^- + 6H_2O$

$[Cl_2 + 2e^- \rightarrow 2Cl^-] \times 5$

$6Cl_2 + 12OH^- \rightarrow 2ClO_3^- + 6H_2O + 10Cl^-$

i.e., $3Cl_2 + 6OH^- \rightarrow ClO_3^- + 5Cl^- + 3H_2O$