Redox reactions

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Electronic concept of oxidation and reduction

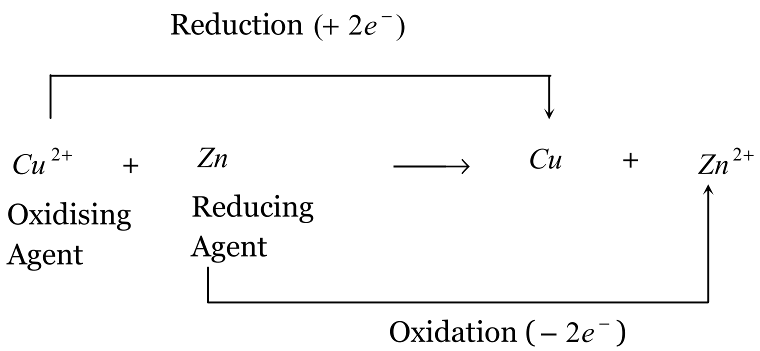
(1) *Oxidation* : Process of loss of electrons by an atomic system.

(2) *Reduction* : Process of gain of electrons by an atomic system.

(3) *Oxidising agent* : The chemical species which gains electrons and get reduced during the chemical reactions.

(4) *Reducing agent* : The chemical species which losses electrons and get oxidised during the chemical reactions.

- Chemical reactions involving oxidation and reduction are called **Redox Reactions**, redox reactions involve transferrence of electrons from reducing agent to oxidising agent.



Note : ❑ Neither oxidation nor reduction can take place alone. They are complementary process and always go side by side.

Oxidation number or oxidation state

Oxidation number (*O.N.*) of an element in a compound is the residual charge which its atom appears to have when all other atoms in a molecule are removed as ions by counting the shared electrons with more electronegative atom.

(1) **Rules for Calculating Oxidation Number**

(i) *O.N.* of element in free state is zero.

(ii) *O.N.* of element in monoatomic ion is equal to the charge on the ion.

(iii) *O.N.* of fluorine in its compounds is always-1.

(iv) Other halogens can exhibit different oxidation states. For example, *O.N.* of *Cl* in *I–Cl* is –1 but in ClF_3 it is +3.

(v) *O.N.* of alkaline metals in their compounds is +1.

(vi) *O.N.* of alkali earths in their compounds is +2.

(vii) *O.N.* of oxygen (O) in its compounds is –2 with the exception of peroxides and the compounds of oxygen and fluorine.

(viii) In peroxides $(H_2O_2, BaO_2, Na_2O_2$ etc.) *O.N.* of *O* is –1.

(ix) In compounds of oxygen and fluorine, *O* has positive *O.N.* for example, in $F_2O, (O.N. = +2)$ and $F_2O_2 (O.N. = +1)$.

(x) H atom in its compounds has *O.N.* =+1 with the exception of metal hydrides $(LiH, CaH_2,$ etc.) Where *O.* No. of *H is* –1.

(xi) In a molecule, the sum of *O.N.* of all the atoms is equal to zero while in polyatomic ion the sum of *O.N.*of all the atom is equal to charge on the ion.

Example – *O.N.* of S in $SO_3^{2-} \rightarrow x - 3(-2) = -2$ or $x = +4$.

O.N. of P in $H_3PO_2 \rightarrow x + 3(+1) + 2(-2) = 0$ or $x = +1$.

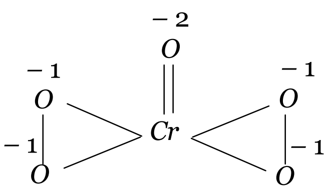
O.N. of Fe in $K_4[Fe(CN)_6] \rightarrow 4(+1) + x + 6(-1) = 0$ or $x = +2$.

O.N. of *S* in $SO_3 \rightarrow x - 6 = 0$ or $x = +6$.

O.N. of *S* in $SO_2 \rightarrow x - 4 = 0$ or $x = +4$.

O.N. of *Cr* in CrO_5

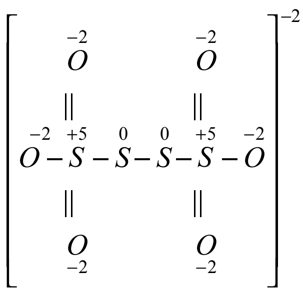
↓



O.N. of *Cr* = + 6

O.N. of S atoms in $S_4O_6^{2-}$

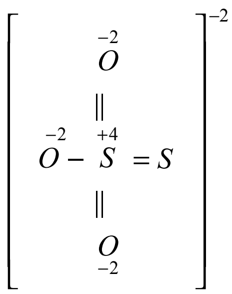
↓



Two *S* atoms have O.N. = + 5
While the other two have O.N. = 0
Average O.N. of *S* = + 25

O.N. of S atoms in $S_2O_3^{2-}$

↓



One S atom has *O.N.* =+4
The other S atom has *O.N.*=0
Average *O.N.* of $S = \frac{4}{2} = +2$.

(xii) Oxidation number of non-metalic element in different compounds can vary from (8–*G*) to +*G* where, *G* is number of valence electrons. Exception being *B, 'O', F.* For example S has 6 valence electrons. The *O. N.* of S can vary from –2 to +6.

(xiii) Oxidation number of transition metal, cannot be beyond (n–1) d+ns electrons.

(xiv) For element exhibiting variable oxidation states. It can act as oxidising agent when it is in highest oxidation state and reducing agent only, when it is in lowest oxidation state. For example, $H_2S(O.N.$ of $S = -2)$ can act as reducing agent only while $SO_3(O.N.$ of $S = +6)$ can act as oxidising only but $SO_2(O.N.$ of $S = +4)$ can act as oxidising as well as reducing agent.

(xv) *Fractional oxidation states:* Super oxides of alkali metals such as KO_2, CsO_2 etc. The oxidation state of alkali metal is $+1$ and oxidation state of oxygen is -0.5. Similarly *O.N.* of *B* in B_4O_{10} is -2.5 .

Oxidation and reduction in terms of oxidation number

(1) Oxidation: Chemical process involving increase in oxidation number.

(2) Reduction: Chemical process involving decrease in oxidation number.

(3) Oxidising agent: substance which undergoes decrease in oxidation number of one or more of its element.

(4) Reducing agent: Substance which undergoes increase in oxidation number of one or more of its elements.

(5) List of some common oxidising agents :

Reagent	***Chemical change***	***Element Changing O.N.***	***Change in O.N.***
F_2	$F_2 \rightarrow 2F^-$	*F*	$0 \rightarrow -1$
O_3	$O_3 \rightarrow H_2O$	*O*	$0 \rightarrow -2$
H_2O_2	$H_2O_2 \rightarrow H_2O$	*O*	$-1 \rightarrow -2$
$KMnO_4 / H_2SO_4$	$MnO_4^{-1} \rightarrow MnO_4^{-2}$	*Mn*	$+7 \rightarrow +2$
$KMnO_4 / KOH$	$MnO_4^- \rightarrow MnO_4^{-2}$	*Mn*	$+7 \rightarrow +6$
$KMnO_4 / H_2O$	$MnO_4^- \rightarrow MnO_2$	*Mn*	$+7 \rightarrow +4$
$Conc. HNO_3$	$HNO_3 \rightarrow NO_2$	*N*	$+5 \rightarrow +4$
$K_2Cr_2O_7 / H_2SO_4$	$Cr_2O_7^{2-} \rightarrow Cr^{3+}$	*Cr*	$+6 \rightarrow +3$
KIO_3 / HCl	IO_3^-	*I*	$+5 \rightarrow -1$

(6) Metal ions in their highest oxidation state like $Fe^{3+}, Cu^{2+}, Hg^{2+}$, etc., also act oxidising agents.

(7) List of some common reducing agents:

Reagent	***Chemical Change***	***Element changing O.N.***	***Change in O.N.***
Metal atoms	$M \rightarrow M^{n+}$	***M***	$0 \rightarrow +n$
Alkali metals	$M \rightarrow M^+$	***M***	$0 \rightarrow +1$
Carbon	$C \rightarrow CO_2$	***C***	$0 \rightarrow +4$
S_8	$S_8 \rightarrow SO_2$	***S***	$0 \rightarrow +4$
$S_2O_3^{2-}$	$S_2O_3^{2-} \rightarrow S_4CO_6^{2-}$	***S***	$+2 \rightarrow +2.5$
KI	$I^- \rightarrow I_2$	***I***	$-1 \rightarrow 0$
$C_2O_4^{2-}$	$C_2O_4^{2-} \rightarrow CO_2$	***C***	$+3 \rightarrow +4$
H_2S	$H_2S \rightarrow S$	***S***	$-2 \rightarrow 0$

(vii) Metal ions in their lowest oxidation states such as Fe^{2+}, Sn^{2+}, Cu^+, etc., also act as reducing agents.

Balancing of redox reactions

(1) *Principle* : Number of electrons lost during oxidation and those gained during reduction must be equal.

(2) *Ion-Electron method* : (*Jette and Lamev*)

(i) Find *O.N.* of each element and thus, determine the elements undergoing oxidation or reduction.

(ii) Write oxidation and reduction half reactions putting appropriate number of electron to reactants or products side.

(iii) Balance *O* atoms in each half reaction by adding number of H_2O molecules to the side falling short of *O* atoms.

(iv) Balance H atoms for ionic equation by adding H^+ ions to the side falling short of H atoms in case medium is acidic.

(v) In case of basic medium balance H atoms by adding H_2O molecules to the side falling short of H atoms and equal number of OH^- to the other side.

(vi) Equalise the number of electron lost or gained and add the two half reaction.

Example : Let us balance the equation. $MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$. Here *Mn* changes its *O.N.* form + 7 (in MnO_4^-) to +2 (Mn^{2+}) and *C* changes its *O.N.* from + 3 (C_2O_4) to +4(CO_2). Thus, writing oxidation and reduction half reactions

$\overset{+3}{C_2}O_4^{2-} \rightarrow 2\overset{+4}{C}O_2 + 2e^-$ Oxidation ; $\overset{+7}{Mn}O_4^- + 5e^- \rightarrow Mn^{2+}$ *Reduction*

Balancing O and H atoms

$[C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-] \times 5$; $[MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O] \times 2$

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2\overset{2+}{Mn} + 10CO_2 + 8H_2O$$

(3) **Oxidation number method (***Jonson*):

(i) Write skeleton equation with *O.N.* of each element.

(ii) Determine increases and decrease of *O.N.* per atom

(iii) Equalise increase and decrease in *O.N.* on reactant side.

(iv) Balance the equation w.r.t. atoms other than H and O atoms.

(v) Balance H and O atoms in the similar way as in ion-electron method.

Example: Let us balance the equation $MnO_2 + Cl^+ \rightarrow Mn^{2+} + Cl_2 + H_2O$ in acidic medium

O. N. decrease by 2 per atom

$$\overset{+4}{Mn}O_2 + Cl^- \longrightarrow Cl_2 + Mn^{2+} + H_2O$$

O.N. increase by 1 per atom

Now, multiply MnO_2 by 1 and Cl^- by 2 to equalise increase and decrease

$MnO_2 + 2Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O$

Atoms other then *H*, and *O* are balanced. Now balance H and *O* atoms

$$MnO_2 + 2Cl^- + 4H^+ \rightarrow Mn^{2+} + Cl_2 + 2H_2O\,.$$

Spectator ion

Species that are present in the solution but do not take part in the reaction and are also omitted while writing the net ionic reaction are called spectator ions or by stander ion e.g. $Zn + 2H^+ + 2Cl^- \rightarrow Zn^{++} + 2Cl^- + H_2$. In this reaction Cl^- ions are omitted and are called as spectator ions and appear on the reactants as well as product side.

Autoxidation

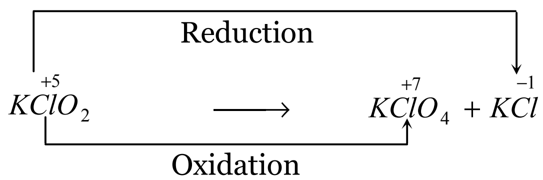
Turpentine, phosphorus and metals like Zn and Pb can absorb oxygen from air in the presence of water. In this process water automatically gets oxidised to hydrogen peroxide. The phenomenon of formation of H_2O_2 by the oxidation of H_2O is known as autoxidation.

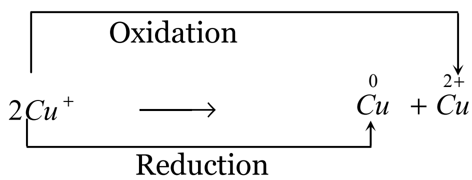
$$Pb + O_2 \rightarrow PbO_2\,;\;\; PbO_2 + H_2O \rightarrow PbO + H_2O_2$$

Disproportionation

It is a process in which the substance acts as oxidising as well reducing agent simultaneously.

Example –





Stock notations

The method of representing oxidation number of a metal by Roman numbers I, II, III, etc. with in parenthesis is known as stock notation *e.g.* $FeSO_4$ as iron (II) sulphate.

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