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Redox Reactions

Chemical reactions which involves both oxidation as well as reduction process simultaneously, are known as redox reactions ('red' from reduction and 'ox' from oxidation). All these reactions are always accompanied by energy change in the form of heat, light or electricity.

Oxidation and Reduction

	Oxidation	Reduction
	It involves	It involves
(i)	Addition of oxygen to an element or compound, or the removal of hydrogen from a compound. e.g. $2Mg + O_2 \longrightarrow 2MgO$ $2H_2S + O_2 \longrightarrow 2H_2O + 2S$	Addition of hydrogen to an element or compound, or the removal of oxygen from a compound. e.g. $H_2S + Cl_2 \longrightarrow 2HCl + S$ $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$
(ii)	Addition of electronegative element or removal of any other electropositive element. $Zn + S \longrightarrow ZnS$ $2KI + Cl_2 \longrightarrow 2KCl + I_2$	Addition of electropositive element or removal of any other electronegative element. $2HgCl_2 + SnCl_4 \longrightarrow Hg_2Cl_2 + SnCl_4$ $SiCl_4 + 4Na \longrightarrow Si + 4NaCl$
(iii)	Oxidation is the loss of electrons by an atom, ion or molecule. It is also known as de-electronation. $Zn \longrightarrow Zn^{2+} + 2e^-$	Reduction is the gain of electrons by an atom, ion or molecule. This process is known as electronation. $Cu^{2+} + 2e^- \longrightarrow Cu$
(iv)	Oxidation involves increase in oxidation number.	Reduction involves decrease in oxidation number.
(v)	Oxidation is caused by an oxidising agent.	Reduction is caused by a reducing agent.

Reductants and Oxidants

Oxidant or oxidising agent is a chemical substance which can accept one or more electrons and causes oxidation of some other species. In other words, the oxidation number of oxidant decreases in a redox reaction.

Important Oxidants

Molecules of most electronegative elements such as O_2, O_3, halogens.

Compounds having element in its highest oxidation state,
e.g. $K_2Cr_2O_7$, $KMnO_4$, $HClO_4$, H_2SO_4, $KClO_3$, $Ce(SO_4)_2$.

Oxides of metals and non-metals such as MgO, CrO_3, CO_2, etc.

Reductant or reducing agent is a chemical substance which can give one or more electrons and causes reduction of some other species. In other words, the oxidation number of reductant increases in a redox reaction.

Important Reductants

All metals such as Na, Al, Zn, etc., and some non-metals, e.g. C, S, P, H_2, etc.

Metallic hydrides like NaH, LiH, KH, CaH_2, etc.

The compounds having an element in its lowest oxidation state such as $H_2C_2O_4$, $FeSO_4$, Hg_2Cl_2 $SnCl_2$, H_2S, SO_2, $Na_2S_2O_3$, etc.

SO_2, HNO_2 and H_2O_2 can act both as oxidant as well as reductant.

$$\text{Eq. wt. of oxidant/reductant} = \frac{\text{molar mass}}{\text{change in oxidation number}}$$

For disproportionation reaction,

Eq. wt. of oxidant/reductant = sum of eq. wt. of two half reactions

e.g.
$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

$$\text{Eq. wt. of } H_3PO_3 = \frac{M}{2} + \frac{M}{6} = \frac{2M}{3}$$

Oxidation Number

The oxidation number is defined as the charge which an atom appears to have when all other atoms are removed from it as ions. It may have + or – sign.

An element may have different values of oxidation number depending upon the nature of compound in which it is present.

Oxidation number of an element may be a whole number (Positive or negative) or fractional or zero.

Important Points for Determining Oxidation Number

(i) The algebraic sum of the oxidation numbers of all the atoms in an uncharged (neutral) compound is zero. In an ion, the algebraic sum is equal to the charge on the ion.

(ii) All elements in the elementary state have oxidation number zero, e.g. He, Cl_2, S_8, P_4, etc.

(iii) As fluorine is the most electronegative element, it always has an oxidation number of – 1 in all of its compounds.

(iv) In compounds containing oxygen, the oxidation number of oxygen is – 2 except in peroxides (–1) such as Na_2O_2, in OF_2 and in O_2F_2 (+2 and + 1 respectively).

(v) In all compounds, except ionic metallic hydrides, the oxidation number of hydrogen is +1. In metal hydrides like NaH, MgH_2, CaH_2, LiH, etc., the oxidation number of hydrogen is –1.

(vi) Oxidation number for alkali metals is +1 and for alkaline earth metals is + 2.

(vii) Oxidation number of metal in amalgams is zero.

(viii) In case of coordinate bond, it gives +2 value of oxidation number to less electronegative atom and –2 value to more electronegative atom when coordinate bond is directed from less electronegative atom to more electronegative atom.

(ix) If coordinate bond is directed from more electronegative to less electronegative atom then its contribution be zero for both the atoms.

(x) For *p*-block elements [Except F and O], the highest oxidation number is equal to their group number and lowest oxidation number is equal to the group number minus eight.

(xi) In transition elements the lowest oxidation number is equal to the number of *ns* electrons and highest oxidation number is equal to number of '*ns*' and $(n-1)d$ unpaired electrons.

Determination of Oxidation Number of Underlined Element

(i) $K_2\underline{\mathbf{Cr}}_2O_7$

Solution

$$\underset{(2\times 1)}{K_2}\quad \underset{(2\times x)}{Cr_2}\quad \underset{(-2\times 7)}{O_7}$$

$$2+2x-14=0\,;\quad x=+6$$

(ii) $[\underline{\mathbf{Fe}}(CN)_6]^{4-}$

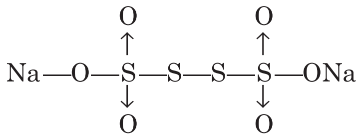
Solution

$$[\underset{\substack{\downarrow\\ x}}{Fe}\ \underset{\substack{\downarrow\\ -1}}{(CN)_6}]^{4-}$$

$$x-6=-4\ \Rightarrow\ x=2$$

(iii) $Na_2\underline{S}_4O_6$

Solution



Oxidation number of Na = + 1

Oxidation number of O = − 2

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

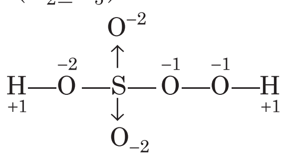
$x = 5/2$, this is average oxidation number, because the compound has two types of sulphur atom.

ON of sulphur bonded with coordinate bond = 5

ON of sulphur which have S—S bond = 0

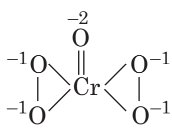
$$\therefore \text{Average oxidation number} = \frac{5+5+0+0}{4} = \frac{5}{2}$$

(iv) Caro's acid ($H_2\underline{S}O_5$)



$$2 + x - 6 - 2 = 0 \quad \Rightarrow \quad x = 6$$

(v) $\underline{Cr}O_5$



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

(vi) $\underline{C}_3O_2$ (carbon suboxide)

$$\overset{-2}{O}=\overset{2+}{C}=\overset{0}{C}=\overset{2+}{C}=\overset{-2}{O}$$

(vii) $\underline{N}H_4\underline{N}O_3$

There are two types of nitrogen atoms. Therefore, evaluation should be made separately as

Oxidation number of N in NH_4^+

$$x + 4(+1) = +1 \Rightarrow x = -3$$

Oxidation number of N in NO_3^-

$$y + 3 \times (-2) = -1 \Rightarrow y = 5$$

Stock Notations

The oxidation states of elements exhibiting variable oxidation states are specified by **Roman numerals** such as I, II, III, IV, etc., within parenthesis after the symbol or name of the element. This system was introduced for the first time by German chemist, Alfred **Stock** and is known as **Stock** notation. This may be illustrated as

Formula of the compound	Chemical name	Stock notation
Cu_2O	Cuprous oxide	Copper (I) oxide; $Cu_2(I)O$
Fe_2O_3	Ferric oxide	Iron (III) oxide; $Fe_2(III)O_3$
$HgCl_2$	Mercuric chloride	Mercury (II) chloride; Hg(II) Cl_2
$SnCl_2$	Stannous chloride	Stannous (II) chloride, Sn(II) Cl_2

Types of Redox Reactions

(i) **Combination reactions** The reactions in which two atoms or molecules combine together to form a third molecule are **combination reactions.**

e.g. $2\overset{0}{Mg}(s) + \overset{0}{O_2}(g) \longrightarrow 2\overset{+2}{Mg}\overset{-2}{O}(s)$

(ii) **Decomposition reactions** The reactions in which molecule breaks down to form two or more components are called **decomposition reactions.**

e.g. $2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$

(iii) **Displacement reactions** The reactions in which an atom (or ion) of a compound is replaced by another ion (or atom) of same nature are called displacement reactions.

These are of the following two types :

(a) **Metal displacement reactions** When a metal in the compound is displaced by some other metal in the elemental state.

e.g. $CuSO_4(aq.) + Zn(s) \longrightarrow Cu(s) + ZnSO_4(aq.)$

(b) **Non-metal displacement reactions** In these reactions, a metal or a non-metal displaces another non-metal from its compound.

e.g. $Mg(s) + 2H_2O(g) \longrightarrow Mg(OH)_2(aq.) + H_2(g)$

(iv) **Intermolecular redox reactions** In such reactions, oxidation and reduction take place separately in two compounds.

e.g. $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$

$Sn^{2+} \longrightarrow Sn^{4+}$ (oxidation)

$Fe^{3+} \longrightarrow Fe^{2+}$ (reduction)

(v) **Intramolecular redox reactions** In these reactions, oxidation and reduction take place in a single compound. e.g.

$$2K\overset{+5}{Cl}\overset{-2}{O_3} \longrightarrow 2K\overset{-1}{Cl} + 3\overset{0}{O_2}$$

(vi) **Disproportionation reactions** These reactions involve reduction and oxidation of same element of a compound. e.g.

$$\overset{0}{Cl_2} + 2OH^- \longrightarrow \overset{+1}{Cl}O^- + Cl^- + H_2O$$

This reaction is also known as **autoredox reaction**.

$$2\overset{+1}{H_2}\overset{-1}{O_2}(aq) \longrightarrow 2\overset{+1}{H_2}\overset{-2}{O}(l) + \overset{0}{O_2}(g)$$

Classification of Redox Reactions

Direct Redox Reactions

Chemical reaction in which oxidation as well as reduction is carried out simultaneously in the same container, is known as direct redox reaction. In such reactions, energy is generally liberated in the form of heat energy.

Indirect Redox Reactions

A reaction in which oxidation and reduction are carried out separately in two separate half-cells, is known as indirect redox reaction. In such reactions, energy is generally liberated in the form of electrical energy.

Balancing of Redox Chemical Equations

Every chemical equation must be balanced according to law of conservation of mass. In a balanced chemical equation, the atoms of various species involved in the reactants and products must be equal in number. Redox reaction can be balanced through

(i) Ion electron method (ii) Oxidation number method.

Ion Electron Method (Half Reaction Method)

This method of balancing was developed by Jette and Lamer in 1927. For example, balance the equation

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$$

It involves the following steps.

***Step* I** Write the redox reaction in ionic form.

$$Cu + H^+ + NO_3^- \longrightarrow Cu^{2+} + NO + H_2O$$

***Step* II** Split the redox reaction into its oxidation-half and reduction half-reaction.

$$Cu \xrightarrow{\text{oxidation}} Cu^{2+}$$

and $$NO_3^- \xrightarrow[\text{(Removal of O)}]{\text{Reduction}} NO$$

***Step* III** Balance atoms of each half-reaction (except H and O) by using simple multiples.

$$Cu \longrightarrow Cu^{2+} \quad \text{and} \quad NO_3^- \longrightarrow NO$$

(Except H and O, all atoms are balanced)

***Step* IV** Balance H and O as

(i) **For acidic and neutral solutions** Add H_2O molecule to the side deficient in oxygen and H^+ to the side deficient in hydrogen.

$$Cu \longrightarrow Cu^{2+} \quad \text{and} \quad \underset{\substack{\uparrow \\ \text{to balance H}}}{\boxed{4H^+}} + NO_3^- \longrightarrow NO + \underset{\substack{\uparrow \\ \text{to balance O}}}{\boxed{2H_2O}}$$

(ii) **For alkaline solutions** For each excess of oxygen, add one water molecule to the same side and OH^- ion to the other side to balance H.

***Step* V** Add electrons to the side deficient in electrons.

$$Cu \longrightarrow Cu^{2+} + 2e^-$$

$$3e^- + 4H^+ + NO_3^- \longrightarrow NO + 2H_2O$$

***Step* VI** Equalise the number of electrons in both the reactions by multiplying a suitable number.

$$[Cu \longrightarrow Cu^{2+} + 2e^-] \times 3$$

$$[NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O] \times 2$$

***Step* VII** Add the two balanced half reactions and cancel common terms of opposite sides.

$$3Cu \longrightarrow 3Cu^{2+} + 6e^-$$

$$2NO_3^- + 8H^+ + 6e^- \longrightarrow 2NO + 4H_2O$$

$$3Cu + 2NO_3^- + 8H^+ \longrightarrow 3Cu^{2+} + 2NO + 4H_2O$$

***Step* VIII** *Convert the ionic reaction into molecular form by adding spectator ions.*

$$3Cu + 2NO_3^- + 8H^+ + 6NO_3^- \longrightarrow 3Cu^{2+} + 2NO + \underset{\text{spectator ion}}{6NO_3^-} + 4H_2O$$

or $$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

(Ions which are present in solution but do not take part in the redox reaction, are omitted while writing the net ionic equation of a reaction and are known as spectator ions.)

Oxidation Number Method

For example, balance the equation

$$Mg + HNO_3 \longrightarrow Mg(NO_3)_2 + N_2O + H_2O$$

It involves the following steps.

***Step* I** Write the skeleton equation (if not given)

***Step* II** Assign oxidation number of each atom

Reduction

$$\overset{0}{Mg} + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \longrightarrow \overset{+2}{Mg}(\overset{+5}{N}\overset{-2}{O_3})_2 + \overset{+1}{N_2}\overset{-2}{O},$$

oxidation

***Step* III** Balance atoms other than H and O in two processes.

change in OS = 10 – 2 = 8

$$Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + N_2O$$

change in OS = 2 – (0) = 2

***Step* IV** Equalize the total increase or decrease in oxidation number.

$$4Mg + 2HNO_3 \longrightarrow 4Mg(NO_3)_2 + N_2O$$

***Step* V** Balance H and O

$$8H^+ + 4Mg + 2HNO_3 + 8NO_3^- \longrightarrow 4Mg(NO_3)_2 + N_2O + 5H_2O$$

$$4Mg + 10HNO_3 \longrightarrow 4Mg(NO_3)_2 + N_2O + 5H_2O$$

Redox Reactions in Daily Life

Oxidation processes

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It involves in
- Corrosion
- Bleaching
- Antiseptics
- Combustion of fuel

Reduction processes

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It involves in
- Photography
- Antioxidants
- Photosynthesis
- Metallurgy