Redox Reactions

Redox Reactions: Oxidation and Reduction Reactions

Classical Idea of Redox Reactions Oxidation

- Addition of oxygen or any other electronegative element or removal of hydrogen or any other electropositive element
- Examples:

Addition of oxygen

$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(s)} + 2H_2O_{(l)}$

Addition of electronegative element

$Mg_{(s)} + Cl_{2(s)} \rightarrow MgCl_{2(s)}$

$Zn_{(s)} + S_{(s)} \rightarrow ZnS_{(s)}$

Removal of hydrogen

$2H_2S_{(g)} + O_{2(g)} \rightarrow 2S_{(s)} + 2H_2O_{(l)}$

Removal of electropositive element

$2K_4[Fe(CN)_6]_{(aq)} + H_2O_{2(aq)} \rightarrow 2K_3[Fe(CN)_6]_{(aq)} + 2KOH_{(aq)}$

- Oxidising agents:
- Substances that oxidises other substance by accepting electrons or by providing oxygen or an electronegative ion, or by removing hydrogen or electropositive ion.
- In this process they reduce themselves.

State	Oxidising agents
Solid	Manganese dioxide (MnO_2), red lead, lead dioxide (PbO), potassium permanganate ($KMnO_4$), potassium dichromate ($K_2Cr_2O_7$), bleaching powder etc.
Liquid	Hydrogen peroxide (H_2O_2), concentrated nitric acid (HNO_3), concentrated sulphuric acid (H_2SO_4), bromine (Br_2) etc.

Gas	Oxygen, ozone (O_3), chlorine, etc.

- Tests for oxidising agents
- Strongly heating them releases oxygen which is good supporter of combustion and increases the flame of a burning splinter
- Bubbling hydrogen sulphide gas through the solution of oxidising agents leads to formation of a yellow precipitate of sulphur
- Warming them with concentrated hydrochloric acid releases chlorine gas which bleaches moist litmus paper
- Reacting them with acidified potassium iodide solution releases iodine gas; it turns freshly prepared starch solution blue

Reduction

- Addition of hydrogen or any other electropositive element or removal of oxygen or any other electronegative element
- Examples:

Addition of hydrogen

$CH_2{=}CH_{2(g)} + H_{2(g)} \rightarrow H_3C{-}CH_{3(g)}$

Addition of electropositive element

(Hg to $HgCl_2$)

$2HgCl_{2(aq)} + SnCl_{2(aq)} \rightarrow Hg_2Cl_{2(s)} + SnCl_{4(aq)}$

Removal of oxygen

$2HgO_{(s)} \xrightarrow{\Delta} 2Hg_{(l)} + O_{2(g)}$

Removal of electronegative element (Cl from $FeCl_3$) −−−

$2FeCl_{3(aq)} + H_{2(g)} \rightarrow 2FeCl_{2(aq)} + 2HCl_{(aq)}$

- Reducing agents:

- Substances that reduce other substances by providing electrons, or by providing hydrogen or an electropositive ion, or by removing oxygen or an electronegatiove ion.

- In this process they oxidise themselves.

State	**Reducing agents**

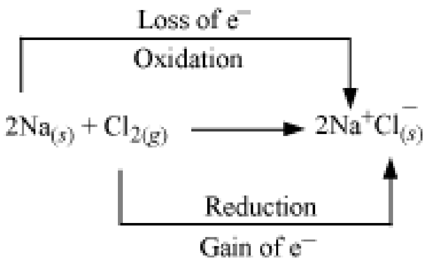
Solid	Carbon, metals such as zinc, aluminium, copper, sodium, stannous chloride ($SnCl_2$), glucose ($C_6H_{12}O_6$), etc.
Liquid	Hydrogen peroxide (H_2O_2), hydrogen iodide (HI), hydrogen bromide (HBr), etc.
Gas	Hydrogen sulphide (H_2S), carbon monoxide (CO), etc.

- Tests for reducing agents
- Heating them with black copper (II) oxide changes the oxide to red copper metal
- When warmed with nitric acid, they give out brown fumes of nitrogen dioxide.
- Adding dilute potassium permanganate solution to them decolourises the potassium permanganate solution
- Adding acidified potassium dichromate solution to them changes the colour of potassium dichromate solution from orange to green
- Adding iron (III) salts to them changes the colour of the salts from yellow to green (iron (II) salts are formed)

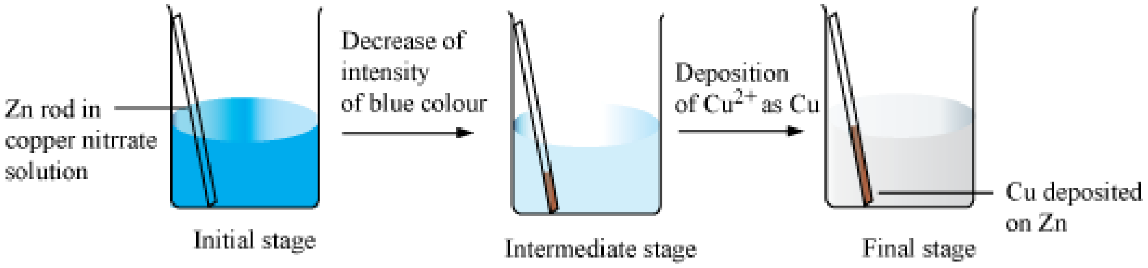
When oxidation and reduction occur simultaneously, such types of reactions are called **redox reactions**.

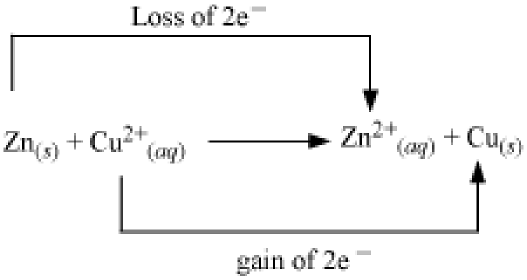
Redox Reactions in Terms of Electron Transfer Reactions

- Oxidation −−− Loss of electrons by any species
- Reduction −−− Gain of electrons by any species
- Oxidizing agent −Acceptor of electrons
- Reducing agent − Donor of Electrons
- Examples:



- Competitive electron transfer reactions
- Reaction between metallic zinc and the aqueous solution of copper nitrate:





- Reaction between metallic copper and the aqueous solution of zinc sulphate:

  $Cu_{(s)} + Zn^{2+}_{(aq)} \rightarrow$ No reaction

  That is, Zn has greater tendency to lose electrons than Cu.

- Metal activity series or electrochemical series:

$$\xrightarrow[\text{Decreasing order of tendency to lose electrons}]{\text{K} > \text{Na} > \text{Li} > \text{Mg} > \text{Al} > \text{Zn} > \text{Fe} > \text{Co} > \text{Cu} > \text{Ag} > \text{Au}}$$

Differences between oxidation and reduction

Oxidation	Reduction
It is addition of oxygen	It is removal of oxygen

It is removal of hydrogen	It is addition of hydrogen
It is addition of an electronegative atom/ion	It is removal of an electronegative atom/ion
It is removal of electropositive atom/ion	It is addition of electropositive atom/ion
There is an increase in positive valency	There is a decrease in positive valency
There is a decrease in negative valency	There is an increase in negative valency
Loss of electrons occur	Gain of electrons occur

Oxidation Number

Oxidation number represents the charge of an atom that it would have, if all other atoms are removed from it as ions.

Rules to Determine Oxidation Number

- The oxidation number of a free element is always zero. For example, each atom in H_2, N_2, O_2 have oxidation number zero.
- The oxidation number of a monoatomic ion is equal to the charge of the ion. For example, Mg^{2+} has oxidation number +2; Cl^- has oxidation number −1.
- The oxidation number of oxygen in compounds is usually −2.

  Exception −
- In case of peroxides (H_2O_2, Na_2O_2), it is −1 and in case of superoxides (KO_2, RbO_2), it is $-\frac{1}{2}$.
- When bonded to fluorine:

  In OF_2, it is +2 and in O_2F_2, it is +1.
- The oxidation number of hydrogen is usually +1.

  Exception: In hydrides, it is −1.

- The oxidation number of fluorine in all compounds is −1. Other halogens (Cl, Br, and I) also have oxidation number −1. (exception − when bonded to oxygen, they have positive oxidation numbers)

- In a neutral compound, the sum of the oxidation numbers of all the atoms is zero; while in a polyatomic ion, it is equal to the charge of the ion. For example, the sum of the oxidation numbers for CO_3^{2-} is −2.

Example

Calculate the oxidation number of sulphur in H_2SO_3.

Solution:

Let the oxidation number of S be x.

$$\overset{+1}{H_2}\overset{x}{S}\overset{-2}{O_3}$$

Now, $2 \times (+1) + x + 3(-2) = 0$ (Since it is a neutral compound)

$\Rightarrow 2 + x - 6 = 0$

$\Rightarrow x = +4$

Hence, the oxidation number of S in H_2SO_3 is +4.

Stock Notation

- Representation of oxidation number by putting a Roman numeral in parenthesis after the symbol of the metal in molecular formula

- Example − Au(I)Cl, Au(III)Cl_3, Sn(II)Cl_2, Mn(IV)O_2, Fe_2(III)O_3, Hg_2 (I)Cl_2

Oxidation

- Increase in the oxidation number of the element in the given substance

Reduction

- Decrease in the oxidation number of the element in the given substance

Redox reaction

- Reaction involving change in oxidation number of the reacting species

Oxidizing Agent (Oxidant)

- Reagent that increases the oxidation number of an element in a given substance

Reducing agent (Reductant)

- Reagent that decreases the oxidation number of an element in a given substance

Types of Redox Reactions

- **Combination Reactions**
- Denoted by A + B → C
- Examples:

$$\overset{0}{C}(s)+\overset{0}{O}_2(g)\xrightarrow{\Delta}\overset{+4}{C}\overset{-2}{O}_2(g)$$
$$3\overset{0}{Mg}(s)+\overset{0}{N}_2(g)\longrightarrow\overset{+2}{Mg}_3\overset{-3}{N}_2(s)$$

- **Decomposition Reactions**
- Opposite of combination reactions
- A compound breaks down into two or more components, at least one of which must be in the elemental form
- Some examples of decomposition reactions which are redox reactions:

$$2\overset{+1}{H}_2\overset{-2}{O}(l)\longrightarrow 2\overset{0}{H}_2(g)+\overset{0}{O}_2(g)$$
$$2\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O}_3(s)\longrightarrow 2\overset{+1}{K}\overset{-1}{Cl}(s)+3\overset{0}{O}_2(g)$$

- All decomposition reactions are not redox reactions. For example:

$$\overset{+2}{Ca}\overset{+4}{C}\overset{-2}{O}_3(s)\xrightarrow{\Delta}\overset{+2}{Ca}\overset{-2}{O}(s)+\overset{+4}{C}\overset{-2}{O}_2(g)$$

- **Displacement Reactions**

- Denoted by X + YZ → XZ + Y
- An ion (or an atom) in a compound is replaced by an ion (or an atom) of another element
- **Metal displacement**: Metal in a compound can be displaced by another metal in the un-combined state.

$$\overset{+2}{\mathrm{Cu}}\overset{+6}{\mathrm{S}}\overset{-2}{\mathrm{O}}_4(aq)+\overset{0}{\mathrm{Zn}}(s)\longrightarrow\overset{0}{\mathrm{Cu}}(s)+\overset{+2}{\mathrm{Zn}}\overset{+6}{\mathrm{S}}\overset{-2}{\mathrm{O}}_4(aq)$$

$$\overset{+3}{\mathrm{Cr}_2}\overset{-2}{\mathrm{O}_3}(s)+2\overset{0}{\mathrm{Al}}(s)\longrightarrow\overset{+3}{\mathrm{Al}_2}\overset{-2}{\mathrm{O}_3}(s)+2\overset{0}{\mathrm{Cr}}(s)$$

- **Non-metal displacement**: These reactions include hydrogen displacement and oxygen displacement (which occurs rarely)

  Examples:

$$2\overset{0}{\mathrm{Na}}(s)+2\overset{+1}{\mathrm{H}_2}\overset{-2}{\mathrm{O}}(l)\longrightarrow2\overset{+1}{\mathrm{Na}}\overset{-2}{\mathrm{O}}\overset{+1}{\mathrm{H}}(aq)+\overset{0}{\mathrm{H}_2}(g)$$

$$\overset{0}{\mathrm{Mg}}(s)+2\overset{+1}{\mathrm{H}_2}\overset{-2}{\mathrm{O}}(l)\longrightarrow\overset{+2}{\mathrm{Mg}}(\overset{-2}{\mathrm{O}}\overset{+1}{\mathrm{H}})_2(s)+\overset{0}{\mathrm{H}_2}(g)$$

$$\overset{0}{\mathrm{Mg}}(s)+\overset{+1}{\mathrm{H}}\overset{-1}{\mathrm{Cl}}(aq)\longrightarrow\overset{+2}{\mathrm{Mg}}\overset{-1}{\mathrm{Cl}_2}(aq)+\overset{0}{\mathrm{H}_2}(g)$$

(Displacement of hydrogen)

$$2\overset{+1}{\mathrm{H}_2}\overset{-2}{\mathrm{O}}(l)+2\overset{0}{\mathrm{F}_2}(g)\longrightarrow4\overset{+1}{\mathrm{H}}\overset{-1}{\mathrm{F}}(aq)+\overset{0}{\mathrm{O}_2}(g)$$

(Displacement of oxygen)

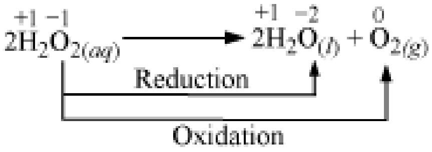
$$\overset{0}{\mathrm{Cl}_2}(g)+2\overset{+1}{\mathrm{K}}\overset{-1}{\mathrm{Br}}(aq)\longrightarrow2\overset{+1}{\mathrm{K}}\overset{-1}{\mathrm{Cl}}(aq)+\overset{0}{\mathrm{Br}_2}(l)$$

(Displacement of bromine)

$$\overset{0}{\mathrm{Cl}_2}(g)+2\overset{+1}{\mathrm{K}}\overset{-1}{\mathrm{I}}(aq)\longrightarrow2\overset{+1}{\mathrm{K}}\overset{-1}{\mathrm{Cl}}(aq)+\overset{0}{\mathrm{I}_2}(s)$$

(Displacemnt of iodine)

- **Disproportionation Reactions**
- A special type of redox reaction in which an element in one oxidation state is simultaneously oxidised or reduced
- For example:



$$2\overset{+1}{H}_2\overset{-1}{O}_{2(aq)} \longrightarrow 2\overset{+1}{H}_2\overset{-2}{O}_{(l)} + \overset{0}{O}_{2(g)}$$

- Phosphorus, sulphur, and chlorine undergo disproportionation in an alkaline medium.

$$\overset{0}{P}_4(s) + 3OH^-(aq) + 3H_2O(l) \longrightarrow \overset{-3}{P}H_3(g) + 3H_2\overset{+1}{P}O_2^-(aq)$$

$$\overset{0}{S}_8(s) + 12OH^-(aq) \longrightarrow 4\overset{-2}{S}^{2-}(aq) + 2\overset{+2}{S}_2O_3^{2-}(aq) + 6H_2O(l)$$

$$\overset{0}{Cl}_2(g) + 2OH^-(aq) \longrightarrow \overset{+1}{Cl}O^-(aq) + \overset{-1}{Cl}^-(aq) + H_2O(l)$$

Balancing of Redox Reactions

Oxidation number method

- This method is illustrated by taking the following example.
- Potassium dichromate (VI) [i.e., $K_2Cr_2O_7$] reacts with sodium sulphite [i.e., Na_2SO_3] in an acid solution to produce chromium (III) ion and sulphate ion.
- **Steps involved in this method:**
- First write the skeletal ionic equation for the given reaction.

$$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \longrightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$$

- Identify the oxidation number of all the elements.

$$\overset{+6}{Cr}_2\overset{-2}{O}_7^{2-}(aq) + \overset{+4}{S}\overset{-2}{O}_3^{2-}(aq) \longrightarrow \overset{+3}{Cr}^{+3}(aq) + \overset{+6}{S}\overset{-2}{O}_4^{2-}(aq)$$

- Calculate the increase and decrease of oxidation number and make them equal.

$$\overset{+6}{Cr}_2\overset{-2}{O}_7^{2-}(aq) + 3\overset{+4}{S}\overset{-2}{O}_3^{2-}(aq) \longrightarrow 2\overset{+3}{Cr}^{3+}(aq) + 3\overset{+6}{S}\overset{-2}{O}_4^{2-}(aq)$$

- Add H^+ or OH^- ions to the expression on the appropriate side so that the total ionic charges of reactants and products are equal. In acidic medium, use H^+ ions and in basic medium, use OH^- ion.

  The given reaction occurs in the acidic medium and therefore, $8H^+$ are added on the left to make ionic charges equal.

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+ \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$$

- Count the hydrogen atoms on the two sides and then add appropriate number of water molecules (i.e., $4H_2O$) on the right to achieve balanced redox reaction.

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(l)$$

Half-reaction method

- Here two half-equations are balanced separately and then added together to give a balanced equation.

  This method can be best explained by using the following example.

- In basic solution, permanganate (VII) ion [i.e., MnO_4^-] oxidises iodide ion [i.e., I^-] to produce molecular iodine [i.e., I_2] and manganese (IV) oxide [i.e., MnO_2].

- **Steps involved in this method:**

- First write the skeletal ionic equation for the given reaction.

$$MnO_4^-(aq) + I^-(aq) \longrightarrow MnO_2(s) + I_2(s)$$

- Separate the equation into two half-reactions.

  Oxidation half-reaction: $\overset{-1}{I^-}(aq) \longrightarrow \overset{0}{I_2}(s)$

  Reduction half-reaction: $\overset{+7}{Mn}O_4^-(aq) \longrightarrow \overset{+4}{Mn}O_2(s)$

- Balance the atoms other than O and H in each of the oxidation half-reactions. Here, Mn is already balanced.

$$2I^-(aq) \longrightarrow I_2(s)$$

- Balance the number of oxygen atoms in the reduction half-reaction by adding water molecule. Here, two water molecules are added on the right side.

$$MnO_4^-(aq) \longrightarrow MnO_2(s) + 2H_2O(l)$$

- Balance the number of hydrogen atoms by adding H^+ ions on the left.

$$MnO_4^-(aq) + 4H^+(aq) \longrightarrow MnO_2(s) + 2H_2O(l)$$

- Since the reaction takes place in a basic solution, for four H^+ ions, add four OH^- ions to both sides of the equation.

  $MnO_4^-(aq) + 4H^+(aq) + 4OH^-(aq) \longrightarrow MnO_2(s) + 2H_2O(l) + 4OH^-(aq)$ Replacing H^+ and OH^- ions with water, we obtain $MnO_4^-(aq) + 2H_2O(l) \longrightarrow MnO_2(s) + 4OH^-(aq)$

- Add electrons to balance the charges of the two half-reactions.

$$2I^-(aq) \longrightarrow I_2(s) + 2e^-$$
$$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$$

To equalize the number of electrons, multiply the oxidation half-reaction by 3 and reduction half-reaction by 2.

$$6I^-(aq) \longrightarrow 3I_2(s) + 6e^-$$
$$2MnO_4^-(aq) + 4H_2O(l) + 6e^- \longrightarrow 2MnO_2(s) + 8OH^-(aq)$$

- Add the two half-reactions to achieve the overall reaction and cancel the electrons on each side.

$$6I^-(aq) + 2MnO_4^-(aq) + 4H_2O(l) \longrightarrow 3I_2(s) + 2MnO_2(s) + 8OH^-(aq)$$

- Lastly, verify the equation whether it contains same type and number of atoms and the same charges on both sides.

Titrations Involving Redox Reactions; Redox Reactions and Electrode Processes

Redox Reactions as the Basis for Titrations

- In acid-base systems, titration method is used to determine the strength of solution.
- Similarly, in redox system, titration method is used to determine the strength of reductant/oxidant using a redox sensitive indicator.
- Usage of indicator in redox titration:
- If the reagent itself is intensely coloured, then it acts as the self indicator. For example, permanganate ion, MnO_4^-

The visible end point in this case is achieved after the last of the reductant (Fe^{2+} or $C_2O_4^{2-}$) is oxidized and the first lasting tinge of pink colour appears at MnO_4^- concentration as low as 10^{-6} mol dm^{-3} (10^{-6} mol L^{-1}).

- $Cr_2O_7^{2-}$ is not a self-indicator, but it oxidizes the diphenylamine indicator just after the equivalence point to produce intense blue colour (signalling the end point).
- There is another method in which reagents such as Cu(II) are able to oxidise I^- ions.

$$2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow Cu_2I_2(s) + I_2(aq)$$

I_2 itself gives an intense blue colour with starch and has a very specific reaction with $S_2O_3^{2-}$ (thiosulphate) ion.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

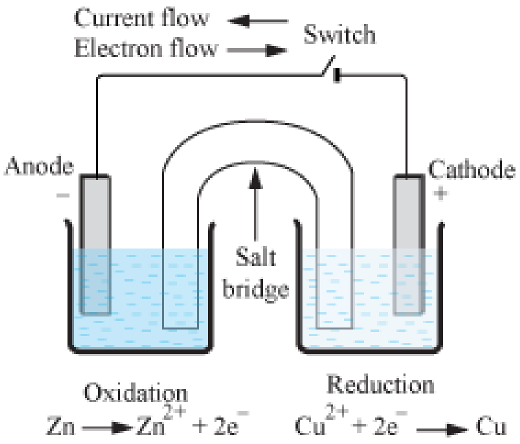
Thus, addition of starch after the liberation of I_2 from the reaction of Cu^{2+} and I^- ions gives intense blue colour and this colour disappears as soon as the iodine is consumed by $S_2O_3^{2-}$ ions.

Redox Reactions and Electrode Processes

- **Redox couple**
- Defined as having together the oxidised and reduced forms of a substance taking part in oxidation or reduction half-reaction.
- Represented by separating the oxidised and reduced forms by a vertical line or a slash representing an interface
- For example, when zinc rod is dipped in $CuSO_4$ solution, zinc is oxidised to Zn^{2+} ions and Cu^{2+} ions get reduced to metallic copper.

Here, redox couples are Zn^{2+}/Zn and Cu^{2+}/Cu.

- **Daniel Cell**
- Experimental set-up:



- Salt bridge contains the solution of KCl or NH_4NO_3 usually solidified by boiling with agar agar and later cooled to a jelly-like substance.

- When the switch is off, no reaction takes place in either of the beakers. Hence, no current flows through the metallic wire.

- As soon as the switch is on, the following observations are made.

  (i) The transfer of electrons takes place through the metallic wire connecting the two rods (shown in figure).

  (ii) The electricity from solution in one beaker to the other flows by the migration of ions through the salt bridge.

- The potential associated with each electrode is called electrode potential.

  When

  Concentration of each species = 1

  Temperature = 298 K

  Pressure = 1 atmosphere,

  then the potential of each electrode is called **Standard electrode potential** $(E^{\ominus})$

- Standard electrode potential for hydrogen electrode (or H^+/H_2 redox couple) is taken as zero.

- The negative value of $E^{\ominus}$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.

The positive value of $E^{\ominus}$ indicates that the redox couple is a weaker reducing agent than the H^+/H_2 couple.