8. REDOX REACTIONS

Redox reactions involve oxidation and reduction. The important concepts relating to redox reactions are:

I. **Classical Concept**: According to this concept *oxidation is the process of addition of oxygen/electronegative element to a substance or removal of hydrogen/electropositive element from a substance.*

Reduction is the process of removal of oxygen/electronegative element from a substance or addition of hydrogen/electropositive element to a substance.

Substance which is oxidised is called reducing agent and the substance which is reduced is called oxidising agent.

If oxidation and reduction take place simultaneously, the process is called *Redox reaction*.

i.e. reduction + oxidation → Redox reactions

E.g. $Zn + CuO \rightarrow ZnO + Cu$

Here Zn is converted to ZnO. i.e oxygen is added to Zn. So it is oxidised and hence the reducing agent. CuO is converted to Cu. i.e. oxygen is removed from Cu. So it is reduced and hence it is the oxidising agent.

Other examples are:

1. $FeCl_3 + H_2 \rightarrow FeCl_2 + 2HCl$

Here the electronegative Cl atom is removed from $FeCl_3$. So it is reduced. H_2 is oxidised since an electronegative Cl atom is added to it. $FeCl_3$ is the oxidising agent and H_2 is the reducing agent.

2. $2\ H_2S(g) + O_2\ (g) \rightarrow 2\ S\ (s) + 2\ H_2O\ (l)$

Here H_2S is oxidised and O_2 is reduced.

II. **Electronic Concept**: According to this concept *oxidation is the process of removal (losing) of electron and reduction is the process of addition (gaining) of electron*. A redox reaction is the process of exchange of electrons between two or more substances.

A substance that accepts electron is called oxidising agent and a substance that donates electron is called a reducing agent.

E.g. In the reaction $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, Zn loses two electrons and forms Zn^{2+}. So it is oxidised. Cu^{2+} gains two electrons and forms Cu. So it is reduced. Here Zn is the reducing agent and Cu^{2+} is the oxidising agent.

Other examples are:

1. Reaction between Cu and Ag^+

release of $2e^-$

$$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

gain of $2e^-$

Here Cu loses two electrons. So it is oxidised and is the reducing agent. Ag^+ accepts an electron. So it is reduced and is the oxidising agent.

In the first example, Cu is reduced while in the second reaction it is oxidised. So the oxidation or reduction of a metal depends on the nature of the metal to which it is combined.

The series in which the different metals are arranged in the decreasing order of their reactivity is called ***electrochemical series or reactivity series***. Generally, *a metal lying above in the reactivity series can displace another metal from its salt solution*. For example Zn can displace copper from an aqueous solution of copper sulphate, since Zn lies above Cu in the electrochemical series.

2. Reaction between cobalt and nickel ion.

release of $2e^-$

$$Co(s) + Ni^{2+}(aq) \longrightarrow Co^{2+}(aq) + Ni(s)$$

gain of $2e^-$

Here Co is oxidised to Co^{2+} and Ni^{2+} is reduced to Ni.

Oxidation number (Oxidation state)

Oxidation number of an element in a compound is the residual charge on the element when all the other atoms are removed from it as ions. For example oxidation number of Mn in $KMnO_4$ is the residual charge on Mn when one K atom and four O atoms removed from it as K^+ and O^{2-} ions respectively.

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Rules used for the calculation of oxidation number

1. The oxidation number of all elements in the free or the uncombined state is zero. For e.g. oxidation number of H_2, O_2, Cl_2, O_3, P_4, S_8, Na, Mg, Al etc. is zero.
2. For simple ions, the oxidation number is equal to the charge on the ion. Thus Na^+ ion has an oxidation number of +1, Mg^{2+} ion +2, Fe^{3+} ion +3, Cl^- ion $^-1$, O^{2-} ion $^-2$ and so on.
3. All alkali metals have oxidation number of $^+1$ and all alkaline earth metals have an oxidation number of $^+2$. Aluminium shows an oxidation number of $^+3$ in all of its compounds.
4. The common oxidation number of oxygen is $^-2$. But in peroxides (e.g., H_2O_2, Na_2O_2), oxidation number of oxygen is $^-1$ and in superoxides (e.g., KO_2, RbO_2), it is $^-½$. In oxygen difluoride (OF_2) and dioxygen difluoride (O_2F_2), the oxygen is assigned an oxidation number of $^+2$ and $^+1$ respectively.
5. The common oxidation number of hydrogen is $^+1$. But in hydrides, H shows an oxidation number of -1.
6. The common oxidation number of halogens is -1. Fluorine shows only -1 oxidation number in all of its compounds. But other halogens show positive oxidation numbers also in their oxides and oxoacids.
7. The algebraic sum of the oxidation number of all the atoms in a compound is zero.
8. In polyatomic ion, the sum of the oxidation numbers of all the atoms is equal to the charge on the ion.

Stock Notations

Alfred Stock proposed some notations to represent the oxidation number of a metal in a compound. According to this, the oxidation number is represented in Roman numeral in brackets after the symbol of the metal in the molecular formula. Thus aurous chloride and auric chloride are written as Au(I)Cl and Au(III)Cl_3. Similarly, stannous chloride and stannic chloride are written as Sn(II)Cl_2 and Sn(IV)Cl_4.

III. Oxidation number Concept: According to this concept, *oxidation is the process of increase in the oxidation number of an element and reduction is the process of decrease in the oxidation number of an element. A reagent that can increase the oxidation number of an element in a given substance is called oxidising agent or oxidant and a reagent which lowers the oxidation number of an element in a given substance is called reducing agent or reductant*. A redox reaction is a reaction which involves change in oxidation number of the interacting species.

For e.g. in the reaction $\overset{+2\,+4\,-2}{CuSO_4}(aq) + \overset{0}{Zn}(s) \rightarrow \overset{0}{Cu}(s) + \overset{+2\,+4\,-2}{ZnSO_4}(aq)$, the oxidation number of Zn increases from 0 to +2 and that of Cu in $CuSO_4$ decreases from +2 to 0. So Zn is oxidised and Cu in $CuSO_4$ is reduced.

In the reaction $\overset{+3\,-2}{Cr_2O_3}(s) + 2\overset{0}{Al}(s) \xrightarrow{\Delta} \overset{+3\,-2}{Al_2O_3}(s) + 2\overset{0}{Cr}(s)$, the oxidation number of Cr decreases from +3 to 0. So it is reduced and is the oxidising agent. The oxidation number of Al increases from 0 to +3. So it is oxidised and is the reducing agent.

Types of redox reactions

1. **Combination reactions**: A combination reaction may be denoted as A + B → C

Here either A or B or both A and B must be in the elemental form. All combustion reactions are combination redox reactions, since here one of the reactants is O_2. Examples are:

$$\overset{0}{C}(s) + \overset{0}{O_2}(g) \xrightarrow{\Delta} \overset{+4\,-2}{CO_2}(g)$$

$$3\overset{0}{Mg}(s) + \overset{0}{N_2}(g) \xrightarrow{\Delta} \overset{+2\,-3}{Mg_3N_2}(s)$$

$$\overset{-4+1}{CH_4}(g) + 2\overset{0}{O_2}(g) \xrightarrow{\Delta} \overset{+4\,-2}{CO_2}(g) + 2\overset{+1\,-2}{H_2O}(l)$$

2. **Decomposition reactions**

Decomposition reactions are the opposite of combination reactions. It involves the breakdown of a compound into two or more components, in which at least one must be in the elemental state. It may be denoted as: C → A + B. Examples are:

$$\overset{+1\ -2}{2H_2O}\,(l) \xrightarrow{\Delta} \overset{0}{2H_2}\,(g) + \overset{0}{O_2}(g)$$

$$\overset{+1\ -1}{2NaH}\,(s) \xrightarrow{\Delta} \overset{0}{2Na}\,(s) + \overset{0}{H_2}(g)$$

$$\overset{+1\ +5\ -2}{2KClO_3}\,(s) \xrightarrow{\Delta} \overset{+1\ -1}{2KCl}\,(s) + \overset{0}{3O_2}(g)$$

All decomposition reactions are not redox reactions. For example, decomposition of calcium carbonate is not a redox reaction, since it does not involve any change in the oxidation number.

$$\overset{+2\ +4\ -2}{CaCO_3}\,(s) \xrightarrow{\Delta} \overset{+2\ -2}{CaO}(s) + \overset{+4\ -2}{CO_2}(g)$$

3. **Displacement reactions**: Here an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be denoted as: X + YZ → XZ + Y

Displacement reactions are divided into two - metal displacement and non-metal displacement.

a) ***Metal displacement reactions***: Here a metal in a compound is displaced by another metal in the uncombined state. These reactions find many applications in metallurgical processes in which pure metals are obtained from their compounds in ores. Some examples are:

$$\overset{+2\ +4\ -2}{CuSO_4}(aq) + \overset{0}{Zn}\,(s) \rightarrow \overset{0}{Cu}(s) + \overset{+2\ +4\ -2}{ZnSO_4}\,(aq)$$

$$\overset{+5\ -2}{V_2O_5}\,(s) + \overset{0}{5Ca}\,(s) \xrightarrow{\Delta} \overset{0}{2V}\,(s) + \overset{+2\ -2}{5CaO}\,(s)$$

$$\overset{+4\ -1}{TiCl_4}\,(l) + \overset{0}{2Mg}\,(s) \xrightarrow{\Delta} \overset{0}{Ti}\,(s) + \overset{+2\ -1}{2\ MgCl_2}\,(s)$$

$$\overset{+3\ -2}{Cr_2O_3}\,(s) + \overset{0}{2\ Al}\,(s) \xrightarrow{\Delta} \overset{+3\ -2}{Al_2O_3}\,(s) + \overset{0}{2Cr}(s)$$

b) ***Non-metal displacement reactions***: The non-metal displacement redox reactions mainly include hydrogen displacement. All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) will displace hydrogen from cold water. Less active metals such as magnesium and iron react with steam and produce hydrogen gas.

$$\overset{0}{2Na}(s) + \overset{+1\ -2}{2H_2O}(l) \rightarrow \overset{+1\ -2\ +1}{2NaOH}(aq) + \overset{0}{H_2}(g)$$

$$\overset{0}{Ca}(s) + \overset{+1\ -2}{2H_2O}(l) \rightarrow \overset{+2\ -2\ +1}{Ca(OH)_2}\,(aq) + \overset{0}{H_2}(g)$$

$$\overset{0}{Mg}(s) + \overset{+1\ -2}{2H_2O}(l) \xrightarrow{\Delta} \overset{+2\ -2\ +1}{Mg(OH)_2}(s) + \overset{0}{H_2}(g)$$

$$\overset{0}{2Fe}(s) + \overset{+1\ -2}{3H_2O}(l) \xrightarrow{\Delta} \overset{+3\ -2}{Fe_2O_3}(s) + \overset{0}{3H_2}(g)$$

Most of the metals react with acids and liberate Hydrogen.

$$\overset{0}{Zn}(s) + \overset{+1\ -1}{2HCl}(aq) \rightarrow \overset{+2\ -1}{ZnCl_2}\,(aq) + \overset{0}{H_2}\,(g)$$

$$\overset{0}{Mg}\,(s) + \overset{+1\ -1}{2HCl}\,(aq) \rightarrow \overset{+2\ -1}{MgCl_2}\,(aq) + \overset{0}{H_2}\,(g)$$

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$$\overset{0}{Fe}(s) + 2\overset{+1\,-1}{HCl}(aq) \rightarrow \overset{+2\,-1}{FeCl_2}(aq) + \overset{0}{H_2}(g)$$

Other examples of non-metal displacement reactions are:
Fluorine can displace O_2 from water. Chlorine can displace bromine and iodide from their aqueous salt solutions.

$$2\overset{+1\,-2}{H_2O}(l) + 2\overset{0}{F_2}(g) \rightarrow 4\overset{+1\,-1}{HF}(aq) + \overset{0}{O_2}(g)$$

$$\overset{0}{Cl_2}(g) + 2\overset{+1\,-1}{KBr}(aq) \rightarrow 2\overset{+1\,-1}{KCl}(aq) + \overset{0}{Br_2}(l)$$

$$\overset{0}{Cl_2}(g) + 2\overset{+1-1}{KI}(aq) \rightarrow 2\overset{+1\,-1}{KCl}(aq) + \overset{0}{I_2}(s)$$

4. **Disproportionation reactions**: These are a special type of redox reaction. In a disproportionation reaction, an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances always contains an element that can exist in at least three oxidation states. The element in the reactant is in the intermediate oxidation state and both higher and lower oxidation states of that element are formed in the reaction.
E.g. The decomposition of hydrogen peroxide.

$$2\overset{+1\,-1}{H_2O_2}(aq) \rightarrow 2\overset{+1\,-2}{H_2O}(l) + \overset{0}{O_2}(g)$$

Here the oxygen of peroxide is in –1 state and it is converted to zero oxidation state in O_2 and –2 oxidation state in H_2O.

Another e.g. is:

$$\overset{0}{P_4}(s) + 3OH^-(aq) + 3H_2O(l) \rightarrow \overset{-3}{PH_3}(g) + 3\overset{+1}{H_2PO_2^-}$$

Balancing of Redox Reactions

There are two methods for balancing a redox reaction – Oxidation number method and half reaction method.

1. ***Oxidation Number Method***: This method involves the following steps:

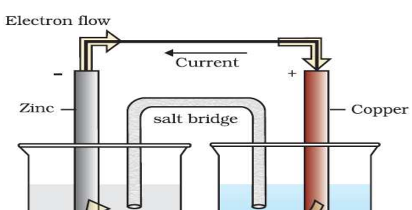
Step 1: Write the correct formula for each reactant and product.
Step 2: Assign the oxidation number of each elements and identify the atoms which undergo change in oxidation number.
Step 3: Calculate the change in oxidation number per atom and equate them by multiplying with suitable coefficients.
Step 4: Balance all the atoms except oxygen and hydrogen.
Step 5: Now equate the ionic charges on both sides of the equation by adding H^+ or OH^- ions on the appropriate side. If the reaction is carried out in acidic solution, use H^+ ions in the equation; if in basic solution, use OH^- ions.
Step 6: Make the numbers of hydrogen atoms in the expression on the two sides equal by adding water (H_2O) molecules to the reactants or products. Now, also check the number of oxygen atoms.

2. ***Half reaction method***: In this method, the equation is divided into 2 half reactions – oxidation half reaction and reduction half reaction. They are balanced separately and then added together to get the net balanced equation. The different steps involved in this method are:

Step 1: Produce unbalanced equation for the reaction in ionic form. Assign the oxidation number of each element and find out the substance oxidised and reduced.
Step 2: Separate the equation into half reactions - oxidation half reaction and reduction half reaction.
Step 3: Balance the atoms other than O and H in each half reaction individually.
Step 4: For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms. In basic medium also add equal number of OH^- ions on both sides of the equation.
Step 5: Now balance the ionic charges. For this add electrons to one side of the half reaction. Make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate coefficients.
Step 6: Now add the two half reactions to get the overall reaction and cancel the electrons on each side.
Step 7: Verify that the equation contains the same type and number of atoms and the same charges on both sides.

REDOX REACTIONS AND ELECTRODE PROCESSES

Redox reactions find applications in electrode processes in electrochemical cells. An **electrochemical cell (Galvanic cell)** is *a device that converts chemical energy of a redox reaction to electrical energy*. Any electrochemical cell contains two electrodes – anode and cathode. *The electrode at which oxidation takes place is the anode and the other electrode at which*



reduction occurs is the cathode. An example for electrochemical is ***Daniel cell***. It contains a Zn rode dipped in $ZnSO_4$ solution and Copper rode dipped in $CuSO_4$ solution. The two solutions are connected externally by a metallic wire through a voltmeter and a switch and internally by a salt bridge.

The reaction taking place in a Daniel cell is

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

This reaction is a combination of two half reactions:

(i) $Cu^{2+} + 2e^- \rightarrow Cu(s)$ (reduction half reaction)

(ii) $Zn(s) \rightarrow Zn^{2+} + 2e^-$ (oxidation half reaction)

The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called **half-cells** or **redox couples**. The copper electrode may be called the reduction half cell and the zinc electrode, the oxidation half-cell.

The flow of current is possible only if there is a potential difference between the copper and zinc rods. The potential associated with each electrode is known as electrode potential. It is the tendency of the electrode to lose or gain electron. The potential of each electrode is said to be the Standard Electrode Potential when the concentration of the electrolyte is unity and if the reaction is carried out at 298K.

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