Redox Reactions

Kumud Bala

Chemistry deals with the study of composition, structure and properties of varieties of matter and the change of one kind of matter into anther occurs through a number of different types of reactions. One important type of such reactions is reduction- oxidation or simply redox reaction (red from reduction and ox from oxidation). All these reaction are always accompanied by energy changes in form of heat, light or electricity. A number of phenomena both physical as well as biological fall in this category of reactions. These reactions are widely used in biological, pharmaceutical, industrial, metallurgical and agricultural areas. The importance of these reaction is evident from the fact that burning of different types of fuels such as wood, coal, kerosene, LPG, petrol, diesel, CNG etc. for obtaining energy for domestic, transport and other commercial purposes, electrochemical processes like manufacture of chlorine and caustic soda, corrosion of metals and operation of dry and wet batteries are diverse examples of redox reactions. Recently, environmental issues like hydrogen economy (use of liquid hydrogen as fuel) and development of ozone hole are also been regarded as redox phenomena. Whenever any substance is oxidized another substance is always reduced at the same time and vice versa. In other words, the oxidation reduction reactions always occur simultaneously i.e., they always go hand in hand or side by side called redox reactions.

Oxidation - according to classical concept- oxidation may be defined as a process which involves the addition of oxygen or any other electronegative element, or as a process which involve the remove of hydrogen or any other electropositive element. For example-

(i) $2\underline{Mg}\ (s) + O_2\ (g) \rightarrow 2MgO\ (s)$ (addition of oxygen)

(ii) $\underline{Mg}\ (s) + Cl_2\ (g) \rightarrow MgCl_2$ (addition of electronegative element chlorine)

(iii) $2\underline{H_2S} + O_2 \rightarrow 2S\ (s) + 2H_2O(l)$ (removal of hydrogen)

(iv) $2\underline{KI}\ (aq) + H_2O(l) + O_3\ (g) \rightarrow 2KOH\ (aq) + I_2(s) + O_2(g)$ (removal of electropositive element).

In all these reactions the compound underlined has undergone oxidation.

Oxidizing Agent or Oxidant- According to the classical concept, an oxidizing agent or oxidant is a substance which supplies oxygen or any other electronegative element, or removes hydrogen or any other electropositive element. An oxidizing agent after carrying out oxidation is itself reduced in a chemical reaction. For examples-

(i) $4HCl\ (aq) + \underline{MnO_2}(s) \rightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$

(ii) $H_2O_2(aq) + 2KI(aq) \rightarrow 2KOH\ (aq) + I_2(s)$. Manganese dioxide and hydrogen peroxide are oxidizing agents.

Reduction- according to classical concept- reduction may be defined as a process which involves the addition of hydrogen or any other electropositive element or removal of oxygen or any other electronegative element. For examples-

(i) $\underline{Br_2}(g) + H_2S(g) \rightarrow 2HBr\ (g) + S\ (s)$ (Addition of hydrogen)

(ii) $\underline{2HgCl_2}(aq) + SnCl_2(aq) \rightarrow Hg_2Cl_2\ (s) + SnCl_4(aq)$ (addition of electropositive element, mercury)

(iii) $\underline{CuO\ (s)} + H_2O(g) \rightarrow Cu(s) + H_2O(l)$ (removal of oxygen)

(iv) $\underline{2FeCl_3} + SO_2(g) + 2H_2O(l) \rightarrow 2FeCl_2(aq) + H_2SO_4(aq) + 2HCl(aq)$ (removal of electronegative element, chlorine).

In all these reactions the compounds underlined have undergone reduction.

Reducing Agent or Reductant- according to the classical concept." A reducing agent or reductant may be defined as a substance which supplies hydrogen or any other electropositive element, or removes oxygen or any other electronegative element. A reducing agent after carrying out reduction is itself oxidized in a chemical reaction." For examples-

(i) $CuO\ (s) + C(s) \rightarrow Cu\ (s) + CO\ (g)$

(ii) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

(iii) $Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(s) + Al_2O_3(s)$ carbon, carbon monoxide and aluminium are reducing agents.

(iv)

Oxidation- Reductions are Complementary: Whenever any substance is oxidized, another substance is always reduced at the same time and vice versa. In other words, oxidation and reduction are complementary i.e., they always go hand to hand or side by side. For example-

(i) $H_2S(g) + Cl_2(g) \rightarrow 2HCl(g) + S(s)$ here, H_2S is oxidized to S while Cl_2 is reduced to HCl

(ii) $SnCl_2(aq) + 2HgCl_2(aq) \rightarrow SnCl_4(aq) + Hg_2Cl_2(s)$ here, $SnCl_2$ is oxidized to $SnCl_4$ while $HgCl_2$

(iii) $MnO_2(s) + 4HCl(aq) \rightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$ here HCl is oxidized to Cl_2 while MnO_2 is reduced to $MnCl_2$

Oxidation –Reduction – Electron Transfer Concept- Any substance that loses electron is said to be oxidized and the one which gains electrons is said to be reduced. According to electronic concept- **Oxidation** may be defined as a process in which an atom or an ion loses one or more electrons. That is why oxidation is also called de-electronation. For example-

(i) loss of electron from the atom results in increase in positive charge

$Na \rightarrow Na^+ + e$

$Mg \rightarrow Mg^{+2} + 2e^-$

$Fe^{+2} \rightarrow Fe^{+3} + e^-$

$Sn^{+2} \rightarrow Sn^{+4} + 2e^-$

(ii) loss of electrons from the ions results in decrease in negative charge:

$MnO_4^{-2} \rightarrow MnO_4^- + e^-$

$2Cl^- \rightarrow Cl_2 + 2e^-$

$S^{-2} \rightarrow S + 2e^-$

Reduction- reduction may be defined as a process in which an atom or an ion gains one or more electrons. That is why reduction is also called electronation. For example-

(i) gain of electrons by an atom or an ion results in decrease in positive charge:

$Fe^{+3} + e^- \rightarrow Fe^{+2}$

$2Hg^{+2} + 2e- \rightarrow Hg_2^{+2}$

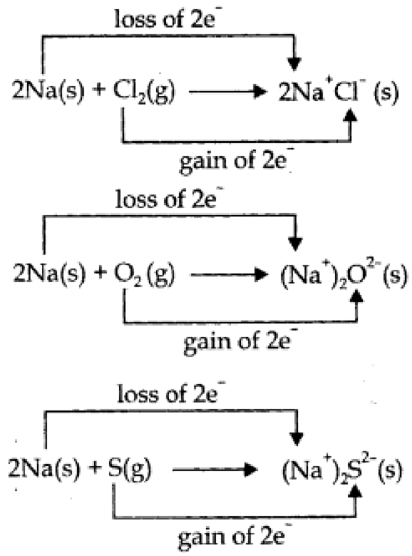
$Sn^{+4} + 2e^- \rightarrow Sn^{+2}$

(ii) gain of electrons by results in increase in negative charge

$Cl_2 + 2e^- \rightarrow 2Cl^-$

$MnO_4^- + e^- \rightarrow MnO_4^{-2}$ $S + 2e^- \rightarrow S^{-2}$

Oxidation – Reduction as an Electron- transfer process: since there cannot be a net gain or loss of electron in a chemical reaction, therefore, all chemical reactions involving loss or gain of electrons must occur simultaneously. In other words, in a chemical reaction, a substance can lose electrons only if there is present another substance which can gain electrons. For example-



$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$

$2Na(s) + S(s) \rightarrow Na_2S(s)$.

All these reactions are redox reactions because in each of these reactions, sodium is oxidized due to the addition of either oxygen or more electronegative element such as chlorine or sulphur. Simultaneously, oxygen, chlorine and sulphur are reduced because to each of these, the electropositive element sodium has been added. Na_2O, NaCl and Na_2S are all ionic compounds. These redox reactions may be rewritten as shown in the figure.:

Each of above redox reaction can be considered as a sum of two half reactions. One involving oxidation called oxidation half reaction and the other involving reduction called reduction half reaction.

Let us consider the oxidation of sodium by chlorine to form sodium chloride.-

$Na \rightarrow Na^{+} + e^{-}$ (oxidation half reaction)

$Cl_2 + 2e^{-} \rightarrow 2Cl^{-}$ (reduction half reaction)

In order to get the overall equation for redox reaction, the two half reactions are simply added if the number of elections lost during oxidation half reaction is equal to the number of electrons gained during the reduction half reaction. But if the number of electron lost during oxidation half reaction are different from the number of electrons gained during reduction half reaction, the two half reactions are multiplied by suitable integers so that when the two half equations are added, the electrons cancel out of the final redox equation. For example- during oxidation of sodium by chlorine, the number of electrons lost by each sodium atom is one while those gained by chlorine molecule are two, therefore, the oxidation half equation is multiplied by 2 and then added to the reduction half equation to get the equation for the overall redox reaction as:

$Na(s) \rightarrow Na^{+} + e^{-}$]X 2 (oxidation half reaction)

$\underline{Cl_2(g) + 2e^{-} \rightarrow 2Cl^{-}}$ (reduction half reaction)

$2Na(s) + Cl_2(g) \rightarrow 2Na^{+}Cl^{-}(s)$

Similarly- $Na(s) \rightarrow Na^{+} + e^{-}$]X 2 (oxidation half reaction)

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

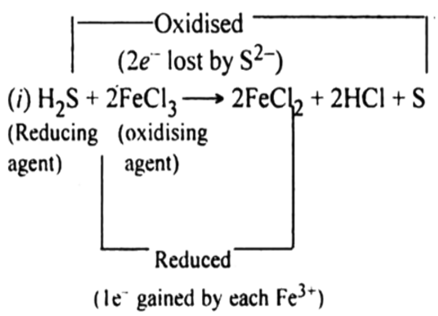
$2Na(s) + S(s) \rightarrow Na_2{}^{+}S(s)$ (overall redox reaction)

Similarly- $Na(s) \rightarrow Na^{+} + e^{-}$]X 4 (oxidation half reaction)

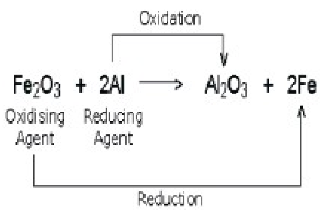
$\underline{O_2(g) + 4e^{-} \rightarrow 2O^{-2}}$ (reduction half reaction)

$2Na(s) + S(s) \rightarrow Na_2{}^{+}S(s)$ (overall redox reaction)

Thus, oxidation- reduction or redox reactions may be regarded as electron-transfer reactions in which the electrons are transferred from one reactant to the other. A substance (atom, ion or molecule) which can readily lose electrons to other substance is called a reducing agent or a reductant while a substance (atom, ion or molecule) which can readily accept electrons from other substance is called an oxidizing agent or an oxidant. Reducing agents donate electrons to other substances while oxidizing agents accept electrons from other substances, therefore, reducing agents are electron donors while oxidizing agents are electron acceptors. For example is shown in figure.-



Here, H_2S reduces $FeCl_3$ to $FeCl_2$ while it gets oxidized to S. Conversely, $FeCl_3$ oxidizes H_2S to S while itself gets reduced to $FeCl_2$. Therefore, H_2S acts as a reducing agent while $FeCl_3$ acts as an oxidizing agent.



Here, Al reduces Fe_2O_3 to Fe while itself gets oxidized to Al_2O_3. Fe_2O_3 oxidizes Al to Al_2O_3 while gets reduced to Fe. Therefore, Al acts as a reducing agent while Fe_2O_3 acts as an oxidizing agent. Reducing agents after reducing other substances themselves get oxidized while oxidizing agents after oxidizing other substances themselves get reduced in the process.

We conclude that-

(i) Oxidation is a process in which one or more electrons are lost
(ii) Reduction is a process in which one or more electrons gained.
(iii) Oxidant is a substance which can accept one or more electrons.
(iv) Reductant is a substance which can donate one or more electrons.
(v) In a redox reaction, oxidant is reduced by accepting electrons and reductant is oxidized by losing electrons.

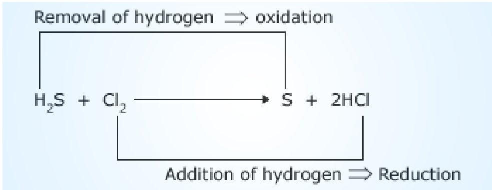
Eaxmple1- Identify the species undergoing oxidation and reduction in the following reaction:

(i) $H_2S(g) + Cl_2 (g) \rightarrow 2HCl (g) + S(s)$

(ii) $3Fe_3O_4(s) + 8Al(s) \rightarrow 9Fe\ 9S0 + 4Al_2O_3(s)$

(iii) $2Na (s) + H_2(g) \rightarrow 2NaH(s)$

Solution-



(i) H_2S is oxidized because a more electronegative element, chlorine is added to hydrogen (or a more electropositive element hydrogen has been removed from H_2S) chlorine has been reduced because hydrogen is added to it. In terms of electronic concept,
(ii) Aluminium is oxidized because oxygen is added to it. Ferrous ferric oxide (Fe_3O_4) is reduced because oxygen has been removed from it.
(iii) Sodium has been oxidized and hydrogen has been reduced.

$Na\ (s) \rightarrow Na^+ + e^-$]X 2 (oxidation half reaction)

$\underline{H_2(g) + 4e^- \rightarrow 2H^-}$ (reduction half reaction)

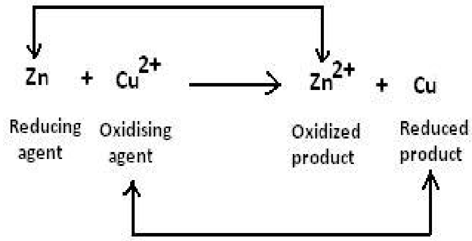
$2Na(s) + H_2(g) \rightarrow 2Na^+H^-(s)$

Example2- Identify the oxidant and reductant in following reactions:

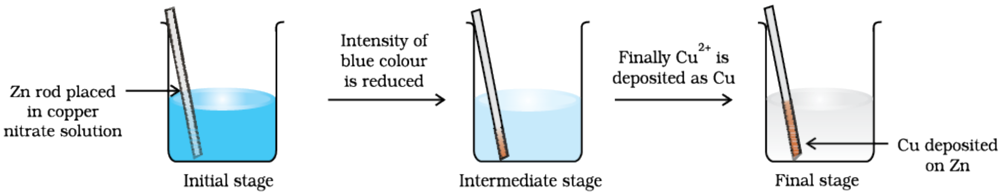
(i) $Zn(s) + ½\ O_2(g) \rightarrow ZnO(s)$
(ii) $CH_4(g) + 4Cl_2(g) \rightarrow CCl_4 (g) + 4HCl (g)$
(iii) $I_2(aq) + 2S_2O_3^{-2} (aq) \rightarrow 2I^- (aq) + S_4O_6^{-2}(aq)$
(iv) $Zn(s) + 2H^- (aq) \rightarrow Zn^{-2}(aq) + H_2(g)$

Solution: (i) Zinc donates electrons to O to give zinc ions and oxide ions. Thus, Zn acts as reducing agent while oxygen acts as an oxidant.
Solution (ii) CH_4 is oxidized and acts as reductant while Cl_2 is reduced and acts as oxidant
Solution. (iii) I_2 gains electrons and is reduced. Therefore it acts as oxidant. $S_2O_3^{-2}$ acts as reductant.
Solution (iv) zinc loses electrons and gets oxidized. Therefore, it acts as reductant. Hydrogen gets reduced and acts an oxidant.

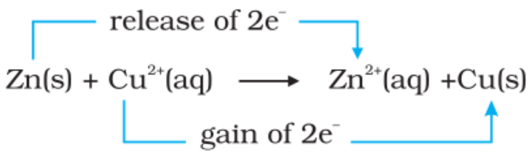
Redox Reactions in Aqueous Solution: redox reactions are very common in our daily life. Whenever we use a battery, a redox reaction occurs. A simple example of an oxidation- reduction reaction is the reaction between zinc metal and copper (II) salt in aqueous solution:

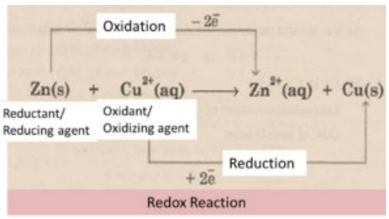


Let us study this reaction: Take a strip of zinc metal and clean it with a sand paper. Now, place it in a solution of copper nitrate solution in a beaker for about one hour. We observe that a spontaneous reaction take place and the following changes are observed: (i) Zinc strip gradually starts dissolving and it loses its weight.



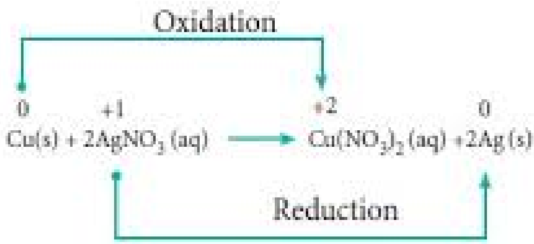
(ii) Reddish brown copper metal starts depositing on the zinc strip. (iii) the blue colour of copper nitrate starts fading and ultimately becomes colourless. The formation of Zn^{+2} ions, among the products can be easily detected when the blue colour of the solution due to Cu^{+2} has disappeared. If we pass hydrogen sulphide gas through the solution, formation of white precipitate of zinc sulphide (ZnS), on making the solution alkaline with ammonium hydroxide, indicates the presence of Zn^{+2} ions in the solution. (iv) the reaction is exothermic and the solution becomes hot. (v) the solution remains electrically neutral. In this reaction, zinc loses electrons to form Zn^{+2}ions. Therefore, zinc gets oxidized whereas Cu^{+2} ions accept electrons and get reduced. Zn^{+2} ions go into the solution so the weight of zinc strip gradually decreases. Cu^{+2} ions present in the solution are accepting the electron given by zinc and are getting reduced to copper. As a result, copper metal either gets deposited on the zinc strip or gets precipitated at the bottom of the beaker. $Zn(s) + Cu^{+2} + NO_3^-\ (aq) \rightarrow Zn^{+2}(aq) + Cu\ (s) + NO_3^-(aq)$. In this reaction NO_3^- participate and we may write the reaction as:





Zinc displaces Cu^{+2} ions from the $Cu(NO_3)_2$ solution. In this reaction zinc acts as a reducing agent while Cu^{+2} ions act as oxidizing agent. Let us now investigate the state of equilibrium of this reaction. For this purpose, place a rod of copper in zinc sulphate solution. We will notice that no visible reaction occurs. If we pass H_2S gas through the solution, there will be no black precipitate of copper sulphide indicating that no reaction has occurred. The state of equilibrium for the above reaction between zinc and $CuSO_4$ solution greatly favour the products over the reactants. Similarly, when we dip a strip in a silver nitrate solution, copper gets oxidized and goes into the solution whereas Ag^+ ions accept electrons and get reduced.

Thus, copper is oxidized to Cu^{+2} and Ag^+ is reduced to Ag (s). Therefore, copper acts as an oxidizing agent while silver ions act as a reducing agent. The equilibrium greatly favours the products Cu^{+2} and Ag (s). For the purpose of comparison, let us now place a rod of cobalt metal in nickel sulphate solution. $Co + Ni^{+2} \rightarrow Co^{+2}\ (aq) + Ni\ (s)$. At equilibrium, chemical tests reveal that both Ni^{+2} and Co^{+2} (aq) are present in moderate concentration. In other words, neither the reactants (Co(s) and Ni^{+2} ions) nor products (Co^{+2} and Ni(s)) are greatly favored. The results of experiments discussed above reveal that zinc releases electrons to copper and copper releases electrons to silver. Therefore, the electron- releasing tendency of these three metals is in the order: Zn> Cu > Ag. By conducting more experiments between various other metals and their combinations with suitable metal ions, we have developed a metal activity series or electrochemical series.



Assignment

1. Reduction involves ------
   (A) gain of electron (B) addition of oxygen
   (C) increase in oxidation number (D) loss of electrons

2. In the reaction: $Cl_2 + 2OH^- \rightarrow OCl^- + Cl^- + H_2O$
   (A) OH^- is oxidizing and Cl^- is reducing agent
   (B) Cl_2 is oxidizing and OH^- is reducing agent
   (C) OH^- is both oxidizing and reducing agent
   (D) Cl_2 is both oxidizing and reducing agent

3. The increasing electron releasing tendencies of Cu, Ag, Fe, Zn are in the order:
   (A) Ag, Cu, Fe, Zn (B) Cu, Ag, Fe, Zn (C) Zn, Cu, Fe, Ag (D) Fe, Zn, Cu, Ag

4. The following four colourless salt solutions are placed in separate test tubes and a strip of a copper is placed in each. Which of the following solution will finally turn blue?
   (A) NaCl (B) $AgNO_3$ (C) $ZnSO_4$ (D) $Cd(NO_3)_2$

5. When Zn is added to $CuSO_4$ solution, copper is precipitated because of:
   (A) reduction of Zn (B) hydrolysis of $CuSO_4$ (C) oxidation of Zn (D) reduction of SO_4^{-2} ions

6. Which of the following is not an example of redox reaction?
   (A) $CuO + H_2 \rightarrow Cu + H_2O$ (B) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
   (C) $2K + F_2 \rightarrow 2KF$ (D) $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$

7. Which of the following is a redox reaction?
   (A) $NaCl + KNO_3 \rightarrow NaNO_3 + KCl$ (B) $CaC_2O_4 + 2HCl \rightarrow CaCl_2 + H_2C_2O_4$
   (C) $Mg(OH)_2 + 2NH_4Cl \rightarrow MgCl_2 + 2NH_4OH$ (D) $Zn + AgCN \rightarrow 2Ag + Zn(CN)_2$

8. In the reaction: $H_2S + H_2O_2 \rightarrow S + 2H_2O$
   (A) H_2S is an acid and H_2O_2 is a base
   (B) H_2S is a base and H_2O_2 is an acid
   (C) H_2S is an oxidizing agent and H_2O_2 is a reducing agent
   (D) H_2S is a reducing agent and H_2O_2 is an oxidizing agent

9. In the reaction: $2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$ the oxidizing agent is -----
   (A) $FeSO_4$ (B) H_2SO_4 (C) H_2O_2 (D) both H_2SO_4 and H_2O_2

10. Identify the correct statement (s) in reflection to the following reaction:
    $Zn + HCl \rightarrow ZnCl_2 + H_2$
    (A) zinc is acting as an oxidant (B) chlorine is acting as a reductant
    (C) hydrogen ion is acting as an oxidant (D) zinc is acting as a reductant

Answers

1. (A) 2. (D) 3. (A) 4. (B) 5. (C) 6. (D) 7. (D) 8. (D) 9. (C) 10. (C), (D)

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