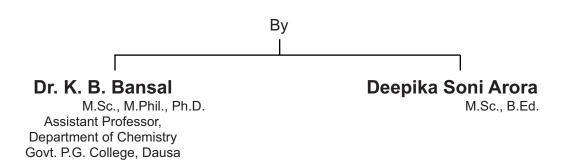
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We are extremely pleased to present this book according to latest syllabus of NCERT. The book has been written in easy and simple language so that students may assimilate the subject easily. We hope that students will get benefitted from it and teachers will appreciate our efforts. In comparison to other books available in market, this book has many such features which make it a unique book:

- 1. Theoretical subject-material is given in adequate and accurate description along with pictures.
- 2. The latest syllabus of NCERT is followed thoroughly.
- 3. Complete solutions of all the questions given at the end of the chapter in the textbook are given in easy language.
- 4. Topic wise summary is also given in each chapter for the revision of the chapter.
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- 6. At the end of every chapter, multiple choice questions asked in various competitive exams are also given with solutions.

Valuable suggestions received from subject experts, teachers and students have also been given appropriate place in the book.

We wholeheartedly bow to the Almighty God, whose continuous inspiration and blessings have made the writing of this book possible.

We express our heartfelt gratitude to the publisher – Mr. Pradeep Mittal and Manoj Mittal of Sanjiv Prakashan, all their staff, laser type center and printer for publishing this book in an attractive format on time and making it reach the hands of the students.

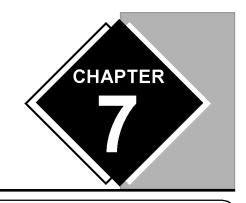
Although utmost care has been taken in publishing the book, human errors are still possible, hence, valuable suggestions are always welcome to make the book more useful.

In anticipation of cooperation!

Authors **Dr. K. B. Bansal Deepika Soni Arora**

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REDOX REACTIONS

III Chapter Overview

- 7.1 Classical Idea of Redox Reactions-Oxidation and Reduction Reaction
- 7.2 Redox Reactions in Terms of Electron Transfer Reactions
- 7.3 Oxidation Number
- 7.4 Redox Reactions and Electrode Processes.

In chemistry, redox reactions are very important. Many physical and biological phenomena are related to redox reactions. They are used in biology, pharmaceutical, metal manufacturing, industrial sector and agricultural science. Electrochemical processes for obtaining energy from combustion of various types of fuels in domestic transport and commercial sectors, extraction of active metals and non-metals, metal corrosion, manufacturing of chemical compounds like chlorine and caustic soda and in operation of dry and wet batteries, only redox and metabolic reactions are used. Nowadays, processes like use of liquid hydrogen as fuel and ozone hole also appear to be related to redox reactions.

7.1 Classical Idea of Redox Reactions—Oxidation and Reduction Reaction

Initially the term oxidation was used for the combination of elements and compounds with oxygen such as magnesium and sulphur on reacting with oxygen, form their corresponding oxides.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$
$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

Oxidation: (i) Addition of oxygen or any other electronegative elements or radicals like F, Cl, Br, I or S is called oxidation.

Example:
$$2Zn(s) + O_2(g) \longrightarrow 2ZnO(s)$$

 $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$
 $Mg(s) + F_2(g) \longrightarrow MgF_2(s)$
 $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$
 $Mg(s) + S(s) \longrightarrow MgS(s)$
 $2FeCl_2(s) + Cl_2(g) \longrightarrow 2FeCl_3(s)$
 $SnCl_2(aq) + Cl_2(g) \longrightarrow SnCl_4(aq)$

(ii) The removal of hydrogen or any electropositive element from a substance is also called oxidation.

Example:
$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

Here in CH₄, oxygen has replaced hydrogen, that is, hydrogen is being removed.

$$CH_3-CH_2-OH \longrightarrow CH_3CHO + H_2$$

In this reaction, H_2 is being released from C_2H_5OH and CH_3CHO is being formed, hence here C_2H_5OH is being oxidized.

$$H_2S + I_2 \longrightarrow S + 2HI$$

 $4HI + O_2 \longrightarrow 2I_2 + 2H_2O$
 $2H_2S + O_2 \longrightarrow 2S + 2H_2O$

Hydrogen is being released from H_2S and HI, hence their oxidation is taking place.

$$2KI + H_2O_2 \longrightarrow 2KOH + I_2$$

$$2K_4[Fe(CN)_6](aq) + H_2O_2(aq) \longrightarrow 2K_3Fe(CN)_6](aq) + 2KOH(aq)$$

In both of these reactions, electropositive element K is being released, hence, oxidation is taking place.

(iii) Increase in valency of any element is also termed as oxidation.

Example :
$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

In this reaction the valency of P is changing from 3 to 5. Hence, here PCl₃ is being oxidized to PCl₅.

* Reduction:

(i) The removal of oxygen or other electronegative element from a substance is called reduction.

Example:
$$2HgO \xrightarrow{\Delta} 2Hg + O_2$$

 $ZnO + H_2 \longrightarrow Zn + H_2O$

Here, oxygen is getting removed from HgO and ZnO. Hence, the reduction of HgO and ZnO is taking place.

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$$

 $2FeCl_3 + H_2 \longrightarrow 2FeCl_2 + 2HCl$

In both of the reactions, chlorine is removed from ferric chloride (FeCl₃) to form $FeCl_2$ (ferrous chloride). Hence, reduction is taking place.

$$2Hg_2Cl_2 \longrightarrow 2HgCl_2 + Cl_2$$

Here, Hg_2Cl_2 is getting reduced to $HgCl_2$ because Cl_2 is being removed.

(ii) The joining of hydrogen or any electropositive element with any substance is called reduction.

Example :
$$CH_2 = CH_2 + H_2 \longrightarrow CH_3 - CH_3$$

 $H_2 + Cl_2 \longrightarrow 2HCl$

Here, hydrogen is being added to ethene and chlorine. Hence, their reduction is taking place.

$$Cl_2 + Mg \longrightarrow MgCl_2$$

In this reaction, electropositive element (Mg) is

being added to Cl₂; hence, Cl₂ is being reduced in MgCl₂.

(iii) The decrease in valency of an element is also called reduction.

Example: $2\text{FeCl}_3(s) \longrightarrow 2\text{FeCl}_2(s) + \text{Cl}_2(g)$

Here, the valency of Fe is changing from 3 to 2. Hence, FeCl₃ is being reduced to FeCl₂.

Oxidation and reduction processes occur simultaneously. Hence, they are complements to each other. If one substance is oxidized in a reaction, then another substance will be reduced, that is why they are combinedly called redox reaction (Reduction + Oxidation).

The substance which is reduced is called oxidizing agent because it oxidizes another substance and substance which is oxidized is called reducing agent because it reduces another substance.

Example:

$$2\text{HgCl}_2(aq) + \text{SnCl}_2(aq) \longrightarrow \text{Hg}_2\text{Cl}_2(s) + \text{SnCl}_4(aq)$$

In this reaction mercuric chloride $(HgCl_2)$ is getting reduced to mercurrous chloride (Hg_2Cl_2) while stanus chloride $(SnCl_2)$ is being oxidized to stannic chloride $(SnCl_4)$.

Similarly in the reaction:

$$Fe(s) + CuSO_4(aq) \longrightarrow FeSO_4(aq) + Cu(s)$$

The Fe is being oxidized to $FeSO_4$, while $CuSO_4$ is getting reduced to Cu.

Examples of NCERT Textbook

Example 7.1: In the reactions given below, identify the species undergoing oxidation and reduction:

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

(ii)
$$3Fe_3O_4(s) + 8Al(s) \longrightarrow 9Fe(s) +$$

 $4Al_2O_3(s)$

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

Sol.: (i) H₂S is oxidised because a more electronegative element chlorine is added to hydrogen (or a more electropositive element hydrogen has

been removed from S). Chlorine is reduced due to addition of hydrogen to it.

- (ii) Aluminium is oxidised because oxygen is added to it. Ferrous ferric oxide (Fe₃O₄) is reduced because oxygen has been removed from it.
- (iii) With the careful application of the concept of electronegativity only we may infer that sodium is oxidised and hydrogen is reduced.

Reaction (iii) chosen here prompts us to think in terms of another way to define redox reactions.

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

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

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

$$2Cl^{-} \longrightarrow Cl_{2} + 2e^{-}$$

$$[Fe(CN)_{6}]^{4-} \longrightarrow [Fe(CN)_{6}]^{3-} + e^{-}$$

$$H_{2}S \longrightarrow 2H^{+} + S + 2e^{-}$$

When any atom loses electron, it get converted to positive charged ions but when positively charged ion

* Electronic Concept of Oxidation and Reduction

Oxidation: When in any atom, molecule or ion, the oxidation number increases due to the removal of an electron then this reaction is called oxidation.

In oxidation there is increase in positive charge or decrease in negative charge. Hence oxidation is a **Deelectronation** process.

Example:
$$Mg \longrightarrow Mg^{2+} + 2e^{-}$$

loses electrons, it get more positive charged and when an anion gives up an electron, it gets converted into a less negatively charged molecule or a neutral molecule. But when a molecule gives up an electron, it form cation and other species.

Reduction: The process is which an atom, molecule or ion accepts an electron is called reduction. Therefore, reduction causes a decrease in the oxidation number and this leads to decrease in positive charge or increase in negative charge. Therefore, reduction is an electronation process.

Example :
$$Cl + e^{-} \longrightarrow Cl^{-}$$

 $S + 2e^{-} \longrightarrow S^{2-}$
 $Na^{+} + e^{-} \longrightarrow Na$

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

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

$$MnO_{4}^{-} + e^{-} \longrightarrow MnO_{4}^{2^{-}}$$

$$O_{2} + 4e^{-} \longrightarrow 2O^{2^{-}}$$

$$MnO_{2} + 4H^{+} + 2e^{-} \longrightarrow Mn^{2^{+}} + 2H_{2}O$$

When an electron is accepted by a neutral atom then it gets converted to negatively charged ions (anion). But the cation becomes less positively charged or neutral by accepting the electron and when anion accept electron it get more negatively charged. But when an electron is accepted by molecule, then different species are formed.

7.2 Redox Reactions in Terms of Electron Transfer Reactions

Based on previous studies we know that, in the following reactions oxygen, sulphur and chlorine (electronegative elements) are combining with sodium. Hence, sodium is being oxidized. But at the same time oxygen, sulphur and chlorine are also being reduced because positive element sodium is combining with them.

$$4\text{Na(s)} + \text{O}_2(g) \longrightarrow 2\text{Na}_2\text{O(s)}$$
(Sodium oxide)
$$2\text{Na(s)} + \text{S(s)} \longrightarrow \text{Na}_2\text{S(s)}$$
(Sodium sulphide)
$$2\text{Na(s)} + \text{Cl}_2(g) \longrightarrow 2\text{NaCl(s)}$$
(Sodium chloride)

Since, the products obtained from the above reactions are ionic compounds, they can be written as follows:

$$[Na^+]_2O^{2-}(s)$$
, $[Na^+]_2S^{2-}(s)$ and $Na^+Cl^-(s)$

Therefore, the above reactions are shown as follows:

(i)
$$2\text{Na(s)} + \frac{1}{2} O_2(g) \longrightarrow (\text{Na}^+)_2 O^{2-}(s)$$

$$2e \text{ gaining}$$

$$2e \text{ looses}$$
(ii) $2\text{Na(s)} + S(s) \longrightarrow (\text{Na}^+)_2 S^{2-}(s)$

$$2e \text{ gaining}$$

$$2e \text{ looses}$$
(iii) $2\text{Na(s)} + \text{Cl}_2(g) \longrightarrow 2\text{Na}^+ + \text{Cl}^-(s)$

$$2e \text{ gaining}$$

These reactions can be written in two terms as follows, in one term electrons are removed while in other term electrons are gained.

Example: Formation of NaCl by reaction of sodium and chlorine:

$$2Na(s) \longrightarrow 2Na^{+}(g) + 2e^{-}$$

$$Cl_{2}(g) + 2e^{-} \longrightarrow 2Cl^{-}(g)$$

Both of these terms are called half reactions. Out of these, the first step in which electrons are being removed is called oxidation half reaction and the second step in which electrons are being accepted is called reduction half reaction.

By adding both half reactions, a complete reaction is obtained which is as follows:

$$2Na(s) + Cl_2(g) \longrightarrow 2Na^+Cl^-(s)$$
 or $2NaCl(s)$

Similarly, in the above reactions, sodium is being oxidized and oxygen and sulphur are being reduced. Therefore, it can be said that removal of electrons by species (atomic molecule or ion) is called oxidation and acceptance of electrons by a species is called reduction.

* Oxidising agent and reducing agent :

Oxidant: The substance which oxidizes another substance and is itself reduced is called oxidizing agent. Hence, the oxidizing agent is an electrophilic reagent. Therefore, the oxidizing capacity of a substance is proportional to its tendency to accept electrons. When the element present in any compound is in its highest oxidation state, then that compound will be a strong oxidizing agent.

Following are examples of main oxidizing agent : $K_2Cr_2O_7$, $KMnO_4$, $CuSO_4$, $HClO_4$, HNO_3 , F_2 , Cl_2 , Br_2 , I_2 , $C_6H_5HO_2$ etc.

Reductant: The substance which reduces another substance and itself gets oxidized is called a reducing agent. Therefore, reducing agent is an electron donating reagent. Hence, the reducing ability of a substance is proportional to its tendency to donate electrons. When the element present in any compound is at its lowest oxidation state then that compound will be a strong reducing agent.

Following are the examples of strong reducing agents:

FeSO₄, FeSO₄.(NH₄)₂SO₄.6H₂O, Metals, H₂S, HI, HBr, HCl, Ferrous oxalate (FeC₂O₄), Oxalic acid (H₂C₂O₄), Sodium thiosulphate (Na₂S₂O₃), Lithium Aluminium Hydride (LiAlH₄), Sodium Borohydride (NaBH₄).

There are some compounds in which the elements present are in intermediate oxidation states, then they act as both oxidizing agents and reducing agents.

Example : H_2O_2 , SO_2 , MnO_2 and O_3 .

Redox Reaction: In the reactions of oxidation and reduction, the substance that gives electrons is oxidized and the substance that accepts electrons is reduced and the entire reaction is called redox reaction.

Examples of NCERT Textbook

Example 7.2 : Justify that the reaction :
$$2Na(s) + H_2(g) \longrightarrow 2NaH(s)$$
 is a redox change.

Sol.: Since in the above reaction the compound formed is an ionic compound, which may also be represented as Na⁺H⁻(s), this suggests that one half reaction in this process is:

$2Na(s) \longrightarrow 2Na^{+}(g) + 2e^{-}$ and the other half reaction is : $H_2(g) + 2e^{-} \longrightarrow 2H^{-}(g)$

This splitting of the reaction under examination into two half reactions automatically reveals that here sodium is oxidised and hydrogen is reduced. Therefore, the complete reaction is a redox change.

7.2.1 Competitive Electron transfer reactions:

When a strip of zinc metal is treated with copper nitrate for about an hour, then a red layer of copper get deposited on the strip of zinc metals and the blue colour of aqueous solution disappers. These tests can be interpreted as follows: Here Zn^{+2} ion is formed from Zn and Cu is formed from Cu^{+2} ion due to which the blue colour of the solution disappears and in this way the formed copper get deposited on the strip of zinc in form of red layer. If H_2S gas is passed in Zn^{+2} solution then white precipitate of zinc sulphide (ZnS) is obtained which can be seen by making the solution alkaline with

NH₃. The reaction which takes place between zinc and copper nitrate solution is as follows:

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

In this reaction, electrons are being removed from Zn and Zn^{+2} is being formed, hence it is oxidized and the electrons obtained from zinc metal are accepted by Cu^{+2} due to which it is being reduced to copper.

Donating
$$2e^{-}$$

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

$$Accept $2e$$$

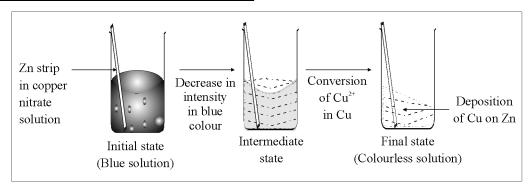
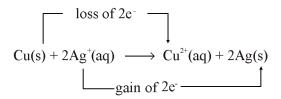


Fig. 7.1: Redox reaction between zinc and copper nitrate.

Redox Reactions 5

To study this reaction in equilibrium, when we put the strip of copper in $ZnSO_4$ (zinc sulphate) solution, no reaction takes place. It can be confirmed by passing H_2S gas is the solution. When H_2S gas is passed in the solution, the precipitate of CuS is not formed. From this it can be concluded that above reaction do not take place in backward direction. Hence, the backward reaction is not possible.

Now we study for one more reaction by taking a solution of silver nitrate. We put a rod of copper metal in aqueous solution of silver nitrate. We observe that after few minutes, the colour of solution gets blue. The colour of solution gets changes because of the formation of Cu^{+2} ions in solution. The reaction can be represented as :



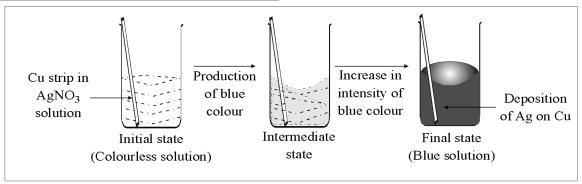


Fig. 7.2: Redox reaction between silver nitrate and copper metal.

In this reaction copper looses electron and Cu^{+2} ion is getting formed. Hence, Cu is oxidizing into Cu^{+2} . These electrons are accepted by Ag^+ , so it is getting reduced to Ag *i.e.* the state of equilibrium is favourable towards the formation of Cu^{+2} and Ag.

For comparative study, we study another reaction. When nickel sulphate $(NiSO_4)$ and cobalt metal react, the reaction occurs as follows:

From the experimental study of this reaction it is observed that at equilibrium the concentration of both $\mathrm{Ni^{+2}(aq)}$ and $\mathrm{Co^{+2}(aq)}$ is moderate. This proves that this condition is neither in favour of the reactants nor in favour of the products.

From the examples studied above, we know that zinc gives electron to copper ion, copper gives electron to silver ion. Therefore, the order of their electron donating ability is as follows: Zn > Cu > Ag. Similarly, metal activity series or electrochemical series can be made on the basis of reactivity of other metals. In this way, with the help of competition of electrons between metals, a cell can be made from which electrical energy can be obtained.

This type of cell is called galvanic cell which will be studied later in detail.

7.3 Oxidation Number

The oxidation number fixed in a compound reflects its oxidation state, which is determined on the basis that the electron pair of a covalent bond is associated only with the more electronegative element or the charge on any atom present in the molecule of a compound or element. It is called the oxidation number of that atom. This charge occurs due to the transfer of electron.

In co-ordination bond when donor atom is less electronegative and the atom which is accepting electron

is more electronegative, then the oxidation number of donor atom will be +2 while that of gainer atom will be -2.

Same rule applies in co-ordinate bond between similar atom. But when in covalent bond the donor atom is more electronegative and acceptor atom is less electronegative, then it is not included in oxidation number.

Example : In Na⁺Cl⁻ the oxidation number of Na is = +1 while that of Cl is = -1.