Chapter 7

Electrochemistry

Major Concepts

7.1 Oxidation and reduction
7.2 Oxidation states and rules for assigning oxidation states
7.3 Oxidizing and reducing agents.
7.4 Oxidation - reduction reactions
7.5 Electrochemical cells
7.6 Electrochemical industries
7.7 Corrosion and its prevention

Time allocation

Teaching periods	18
Assessment periods	03
Weightage	18%

Students Learning Outcomes

Students will be able to:

- Define oxidation and reduction in terms of loss or gain of oxygen or hydrogen.
- Define oxidation and reduction in terms of loss or gain of electrons.
- Identify the oxidizing and reducing agents in a redox reaction.
- Define oxidizing and reducing agents in a redox reaction.
- Define oxidation state.
- State the common rules used for assigning oxidation numbers to free elements, ions (simple and complex), molecules, atoms .
- Determine the oxidation number of an atom of any element in a compound.
- Describe the nature of electrochemical processes.
- Sketch an electrolytic cell, label the cathode and the anode.
- Identify the direction of movement of cations and anions towrds respective electrodes.
- List the possible uses of an electrolytic cell.
- Sketch a Daniel cell, labelling the cathode, the anode, and the direction of flow of the electrons.
- Describe how a battery produces electrical energy.
- Identify the half-cell in which oxidation occurs and the half-cell in which reduction occurs given a voltaic cell.
- Distinguish between electrolytic and voltaic cells.
- Describe the methods of preparation of alkali metals.
- Describe the manufacture of sodium metal from fused NaCl.
- Identify the formation of by products in the manufacture of sodium metal from fused NaCl.

- Describe the method of recovering metal from its ore.
- Explain electrolytic refining of copper.
- Define corrosion.
- Describe rusting of iron as an example of corrosion.
- Summarize the methods used to prevent corrosion.
- Explain electroplating of metals on steel (using examples of zinc, tin and chromium plating).

Introduction

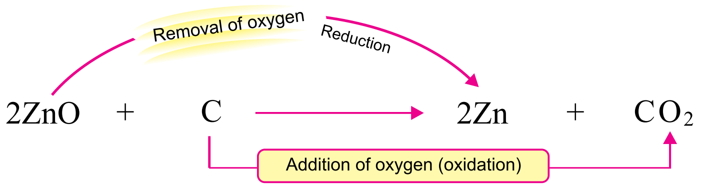
Electrochemistry is the branch of Chemistry that deals with the relationship between electricity and chemical reactions. It involves oxidation and reduction reactions, which are also known as redox reactions. Redox reactions either take place spontaneously and produce electricity or electricity is used to drive non-spontaneous reactions. Spontaneous reactions are those which take place on their own without any external agent. Non-spontaneous reactions are those which take place in the presence of an external agent. These reactions take place in galvanic or electrolytic cells. Electrolysis of fused sodium chloride produces sodium metal and that of brine solution produces sodium hydroxide. The corrosion process of iron along with its preventions, are discussed in detail.

7.1 OXIDATION AND REDUCTION REACTIONS

One concept of oxidation and reduction is based upon either addition or removal of oxygen or addition or removal of hydrogen in a chemical reaction. So according to this concept:

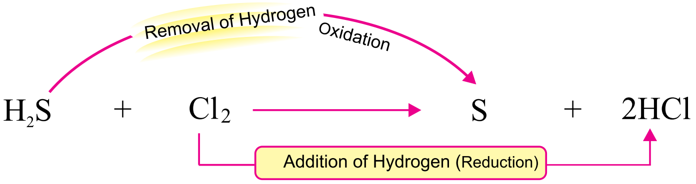
***Oxidation** is defined as addition of oxygen or removal of hydrogen during a chemical reaction. **Reduction** is defined as addition of hydrogen or removal of oxygen during a chemical reaction.* Both of these processes take place simultaneously in a reaction, we can say **where there is oxidation there is reduction.**

Let us first discuss an example to understand the concept based on **addition and removal of oxygen.** A reaction between zinc oxide and carbon takes place by the removal of oxygen (reduction) from zinc oxide and addition of oxygen (oxidation) to carbon. It is represented as



$$2ZnO + C \longrightarrow 2Zn + CO_2$$

Let us have another example based upon **removal or addition of hydrogen**. A reaction between hydrogen sulphide and chlorine takes place by oxidation of hydrogen sulphide and reduction of chlorine. Hydrogen is being removed from H2S and added to chlorine. It is represented as



So, *a chemical reaction in which oxidation and reduction processes are involved is called* ***oxidation- reduction reaction or redox reaction***.

7.1.1 Oxidation and Reduction in Terms of Loss or Gain of Electron

In chemistry, there are many chemical reactions which do not involve oxygen or hydrogen, but they are considered redox reactions. To deal with these reactions, new concept 'loss or gain of electrons' is used. Therefore, reactions which involve *'loss or gain of electrons' are also called oxidation and reduction reactions.* According to this concept:

Oxidation *is loss of electrons by an atom or an ion. e.g.*

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^-$$
$$Fe^{+2}_{(aq)} \longrightarrow Fe^{+3}_{(aq)} + e^-$$

Reduction *is gain of electrons by an atom or ion. e.g.*

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$
$$Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$$

The overall redox reaction is sum of both processes, written as

$$Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + H_{2(g)}$$

Let us have another simple example to understand this concept. A reaction between sodium metal and chlorine takes place in three steps.

First sodium atom losses an electron, to form sodium ion, such as:

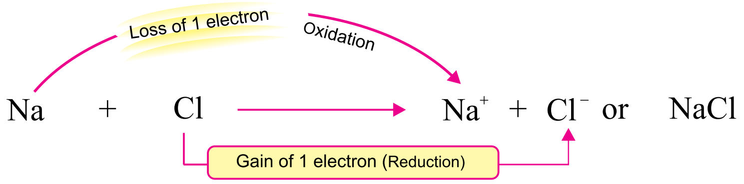
$$Na_{(s)} \xrightarrow{\text{oxidation}} Na^+_{(g)} + 1e^-$$

Simultaneously, this electron is accepted by chlorine atom (reduction process), as chlorine atom needs one electron to complete its octet. As a result, chlorine atom changes to chloride ion. Such as;

$$Cl_{(g)} + 1e^- \xrightarrow{\text{reduction}} Cl^-_{(g)}$$

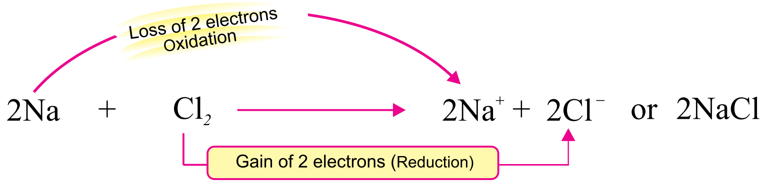
Ultimately, both these ions attract each other to form sodium chloride.

Complete redox reaction is sum of the oxidation and reduction reactions between sodium and chlorine atoms and it is represented as:



$$Na + Cl \longrightarrow Na^+ + Cl^- \text{ or } NaCl$$

Keep in mind chlorine element exists as a molecule (Cl_2) not as atoms (Cl). Therefore, the actual balanced chemical reaction is represented as:



$$2Na + Cl_2 \longrightarrow 2Na^+ + 2Cl^- \text{ or } 2NaCl$$

We can summarize all these concepts as:

Oxidation	**Reduction**
Addition of oxygen	Removal of oxygen
Removal of hydrogen	Addition of hydrogen
Loss of electrons	Gain of electrons

***Test yourself* 7.1**

i. *How can you justify that a reaction between magnesium and oxygen is a redox reaction, while the reaction shows only addition of oxygen (oxidation)*

$$2\,Mg + O_2 \longrightarrow 2\,MgO$$

ii. *A reaction between carbon and oxygen involved only addition of oxygen (oxidation), but, it is called a redox reaction. Comment on this.*

iii. *Oxidation and reduction proceed simultaneously. Explain, with an example.*

iv. *Identify which of the following is oxidation or reduction reaction*

a. $K \longrightarrow K^+ + 1e^-$

b. $Br + 1e^- \longrightarrow Br^-$

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

d. $I^- \longrightarrow I + 1e^-$

e. $Fe^{+2} \longrightarrow Fe^{+3} + 1e^-$

v. *An element M reacts with another element X to form MX_2. In terms of loss or gain of electrons, identify the element which is oxidized and which is reduced.*

vi. *How can you justify that the following reaction is not only an oxidation reaction but also a complete redox reaction.*

$$FeO + CO \longrightarrow Fe + CO_2$$

vii. *Explain the term oxidation on the basis of electronic concept with an example*

7.2 OXIDATION STATE AND RULES FOR ASSIGNING OXIDATION STATE

Oxidation state or oxidation number ***(O.N.)*** *is the apparent charge assigned to an atom of an element in a molecule or in an ion.* For example: in HC1, oxidation number of H is + 1 and that of CI is –1.

Rules for assigning oxidation numbers (O.N.)

I. The oxidation number of all elements in the free state is zero.
ii. The oxidation number of an ion consisting of a single element is the same as the charge on the ion.
iii. The oxidation number of different elements in the periodic table is: in Group 1 it is +1, in Group 2 it is +2 and in Group 13 it is +3.
iv. The oxidation number of hydrogen in all its compounds is +1. But in metal hydrides it is -1.
v. The oxidation number of oxygen in all its compounds is -2. But it is -1 in peroxides and +2 in OF_2.
vi. In any substance, the more electronegative atom has the negative oxidation number.
vii. In neutral molecules, the algebraic sum of the oxidation numbers of all the elements is zero.
viii. In ions, the algebraic sum of oxidation number equals the charge on the ion.

Remember!

It is important to note that while ***assigning oxidation numbers*** *the sign precedes the number. It is written as +2. Whereas, the apparent charge on an atom, ion or molecule which is called* ***valency****, is written as the sign followed by the number i.e. 2+.*

Example 7.1

Find oxidation number of nitrogen in HNO_3 when the oxidation numbers of H =+1 and O = –2.

Solution

By applying formula in compound, sum of all oxidation numbers is zero. In case of this compound HNO_3 it becomes:

$$[O.N.\text{ of H}] + [O.N.\text{ of N}] + 3[O.N.\text{ of O}] = 0$$

Putting the values in above formula

$$\begin{aligned} [+1] + [O.N.\text{ of N}] + 3[-2] &= 0 \\ +1 + O.N.\text{ of N} + [-6] &= 0 \\ \text{or} \quad O.N.\text{ of Nitrogen} &= 6 - 1 \\ &= +5 \end{aligned}$$

Example 7.2

Calculate the oxidation number of sulphur in H2SO4, when O. N. of H = +1 and O.N. of O = –2.

Solution

Applying the formula for H_2SO_4,

$$2[O.N.\text{ of H}] + [O.N.\text{ of S}] + 4[O.N.\text{ of O}] = 0$$

Putting the values in above formula

$$\begin{aligned} 2[+1] + [O.N.\text{of S}] + 4[-2] &= 0 \\ 2 + [O.N.\text{ of S}] - 8 &= 0 \\ O.N.\text{ of S} &= 8 - 2 = +6 \end{aligned}$$

Example 7.3

Find out the oxidation number of chlorine in $KClO_3$,

As O.N. of K = +1 and O.N. of O = –2

Solution

Putting the values in formula, we get

$$\begin{aligned} [+1] + [O.N.\text{of Cl}] + 3[-2] &= 0 \\ [+1] + [O.N.\text{ Cl}] + [-6] &= 0 \\ O.N.\text{ of Cl} &= 6-1 \\ &= +5 \end{aligned}$$

Test yourself 7.2

i. *Find out the oxidation numbers of the following elements marked in bold in the formulae:*
$Ba_3(\mathbf{P}O_4)_2$, $Ca\mathbf{S}O_4$, $Cu(\mathbf{N}O_3)_2$, $Al_2(\mathbf{S}O_4)_3$

ii. *In a compound MX_3, find out the oxidation number of M and X.*

iii. *Why the oxidation number of oxygen in OF_2 is +2*

iv. *In H_2S, SO_2 and H_2SO_4 the sulphur atom has different oxidation number. Find out the oxidation number of sulphur in each compound.*

v. *An element X has oxidation state 0. What will be its oxidation state when it gains three electrons?*

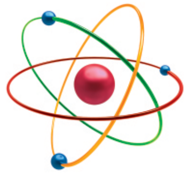
vi. *An element in oxidation state +7 gains electrons to be reduced to oxidation state +2. How many electrons did it accept?*

vii. *If the oxidation state of an element changes from +5 to –3. Has it been reduced or oxidized? How many electrons are involved in this process?*

7.3 OXIDIZING AND REDUCING AGENTS

An **oxidizing agent** *is the specie that oxidise a substance by taking electrons from it.* The substance (atom or ion) which is reduced itself by gaining electrons is also called oxidizing agent. Non-metals are oxidizing agents because they accept electrons being more electronegative elements.

Reducing agent *is the specie that reduces a substance by donating electron to it.* The substance (atom or ion) which is *oxidized* by losing electrons is also called reducing agent. Almost all metals are good reducing agents because they have the tendency to lose electrons. An outline of oxidation and reduction processes is given below.



Oxidation *is 'losing electrons in a chemical reaction'*

Reduction *is 'gaining electrons in a chemical reaction'*

Reducing agent *– is a substance that oxidizes itself and reduces other.*

Oxidizing agent *– is a substance that reduces itself and oxidizes other.*

7.4 OXIDATION - REDUCTION REACTIONS

Chemical reactions in which the oxidation state of one or more substances changes are called **oxidation-reduction** or **redox** reactions. Following are the examples of redox reactions. Each reaction system consists of oxidizing and reducing agents.

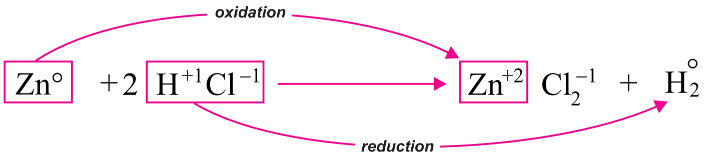
Let us discuss a reaction of zinc metal with hydrochloric acid:

$$Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$$

The oxidation states or oxidation numbers of all the atoms or ions in this reaction are indicated below:

$$Zn^{\circ} + 2H^{+1}Cl^{-1} \longrightarrow Zn^{+2}Cl_2^{-1} + H_2^{\circ}$$

Let us find out the atoms that are oxidized or reduced or whether there is a change in their oxidation state, it is indicated as follows:



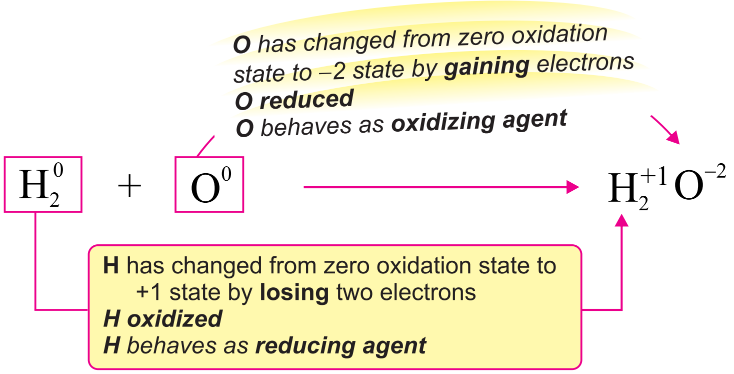
Similarly, in the case of formation of water from hydrogen and oxygen gases, redox reaction takes place as follows:

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$$

The oxidation states or oxidation numbers of all the atoms or ions in this reaction are:

$$2H_2^{\circ} + O_2^{\circ} \longrightarrow 2H_2^{+1}O^{-2}$$

Let us find out the atoms that are oxidized or reduced in this reaction; with the help of figure below:



$$\boxed{H_2^0} + \boxed{O^0} \longrightarrow H_2^{+1}O^{-2}$$

O *has changed from zero oxidation state to –2 state by* ***gaining*** *electrons*
O reduced
O *behaves as* ***oxidizing agent***

H has changed from zero oxidation state to +1 state by **losing** two electrons
H oxidized
H *behaves as* ***reducing agent***

Test yourself 7.3

i. *In the following reaction, how can you justify that H_2S is oxidized and SO_2 is reduced.*
$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$

ii. *The reaction between MnO_2 and HCl is a redox reaction written as balance chemical equation.*
$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$
Find out:
   a. *The substance oxidized.*
   b. *The substance reduced.*
   c. *The substance which acts as an oxidizing agent.*
   d. *The substance which acts as a reducing agent.*

iii. *The following reactions are redox reactions.*
Find out the element which has been reduced and the element which has been oxidized.
   a. $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$
   b. $Cu + 2AgNO_3 \longrightarrow Cu(NO_3)_2 + 2Ag$
   c. $H_2S + Cl_2 \longrightarrow 2HCl + S$

iv. *Why the following reaction is not a redox reaction. Explain with reasons?*
$NaOH + HCl \longrightarrow NaCl + H_2O$

7.5 ELECTROCHEMICAL CELLS

Electrochemical cell *is a system in which two electrodes are dipped in the solution of an electrolyte which are connected to the battery.* Electrochemical cell is an energy storage device in which either a chemical reaction takes place by using electric current (electrolysis) or chemical reaction produces electric current(electric conductance).

Electrochemical cells are of two types.

i. Electrolytic cells ii. Galvanic cells

7.5.1 Concept of Electrolytes

The substances, which can conduct electricity in their aqueous solutions or molten states, are called **electrolytes.** For example, solutions of salts, acids or bases are good electrolytes. The electricity cannot pass through solid NaCl but in aqueous solution and in molten state, it does conduct. Electrolytes are classified into two groups depending upon their extent of ionization in solution.

7.5.1.1 Strong Electrolytes

The electrolytes which ionize almost completely in their aqueous solutions and produce more ions, are called **strong electrolytes**. Example of strong electrolytes are aqueous solutions of NaCl, NaOH and H_2SO_4, etc.

$$NaOH_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + OH^-_{(aq)}$$

7.5.1.2 Weak Electrolytes

The electrolytes which ionize to a small extent when dissolved in water and could not produce more ions are called **weak electrolytes.** Acetic acid (CH_3COOH) and $Ca(OH)_2$ when dissolved in water, ionize to a small extent and are good examples of weak electrolytes. Weak electrolytes do not ionize completely. For example, ionization of acetic acid in water produces less ions:

$$CH_3COOH_{(l)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

As a result the weak electrolyte is a poor conductor of electricity.

7.5.1.3 Non-Electrolytes

The substances, which do not ionize in their aqueous solutions and do not allow the current to pass through their solutions, are called **non-electrolytes**. For example, sugar solution and benzene are non-electrolytes.

7.5.2 Electrolytic cells

The type of electrochemical cell in which a non-spontaneous chemical reaction takes place when electric current is passed through the solution, is called an **electrolytic cell.** The process that takes place in an electrolytic cell is called electrolysis. It is *defined as the chemical decomposition of a compound into its components by passing current through the solution of the compound or in the molten state of the compound.* Examples of these cells are Downs cell, Nelson's cell.

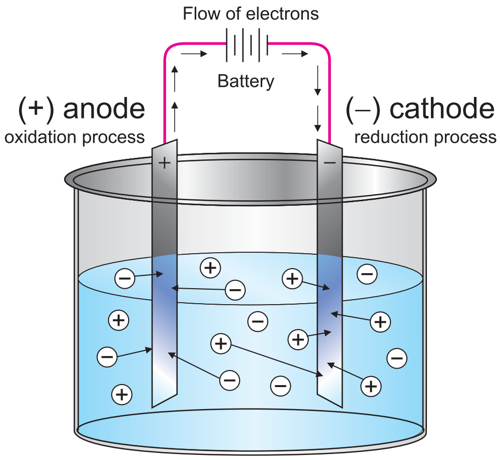


Fig. 7.1 Electrolytic cell

7.5.2.1 Construction of an Electrolytic Cell

An electrolytic cell consists of a solution of an electrolyte, two electrodes (anode and cathode) that are dipped in the electrolytic solution and connected to the battery. The electrode connected to positive terminal is called anode and electrode connected to the negative terminal is called cathode as shown in figure 7.1.

7.5.2.2 Working of an Electrolytic Cell

When electric current is applied from battery, the ions in the electrolyte migrate to their respective electrodes. The anions, which are negatively charged, move towards the anode and discharge there by losing their electrons. Thus *oxidation takes place at anode.* While cations, which are positively charged ions, move towards cathode. *Cations gain electrons from the electrode and as a result reduction takes place at cathode.* For example, when fused salt of sodium chloride is electrolysed the following reactions take place during this process:

$$NaCl_{(s)} \longrightarrow Na^{+}_{(l)} + Cl^{-}_{(l)}$$

Oxidation reaction at anode:

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

Reduction reaction at cathode:

$$2Na^{+}_{(l)} + 2e^{-} \longrightarrow 2Na_{(l)}$$

Overall reaction:

$$2Na^{+}_{(l)} + 2Cl^{-}_{(l)} \longrightarrow 2Na_{(l)} + Cl_{2(g)}$$

7.5.2.3 Electrolysis of Water

Pure water is a very weak electrolyte. It ionizes to a very small extent. The concentrations of hydrogen ions (H^{+}) and hydroxyl ions (OH^{-}) are both at 10^{-7} mol dm^{-3} respectively. When a few drops of an acid are added in water, its conductivity improves.

$$4H_2O_{(l)} \xrightarrow{\text{acid}} 4H^{+}_{(aq)} + 4OH^{-}_{(aq)}$$

When an electric current is passed through this acidified water, OH^{-} **anions** *move towards positive electrode (anode)* and H^{+} **cations** *move towards negative electrode (cathode)* and discharge takes place at these electrodes. They produce oxygen and hydrogen gases respectively at anode and cathode as shown in figure 7.2.

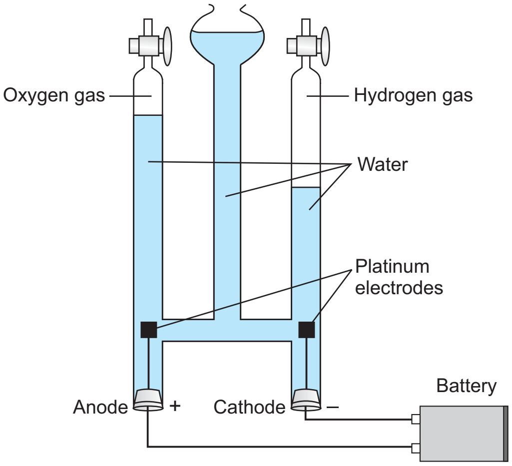


Fig. 7.2 Electrolytic cell showing electrolysis of water

The redox reaction taking place in the electrolytic bath can be shown as following:

Oxidation reaction at anode:

$$4OH^-_{(aq)} \longrightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^-$$

Reduction reaction at cathode:

$$4H^+_{(aq)} + 4e^- \longrightarrow 4H_{(g)}$$

$$4H_{(g)} \longrightarrow 2H_{2(g)}$$

Overall reaction:

$$2H_2O_{(l)} \longrightarrow 2H_{2(g)} + O_{2(g)}$$

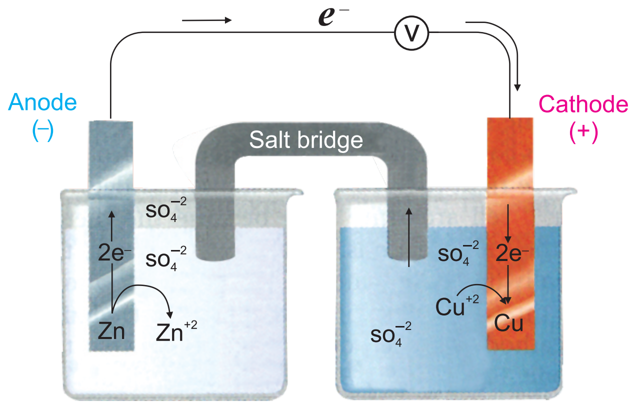
7.5.3. Galvanic Cell

The electrochemical cell in which a spontaneous chemical reaction takes place and generates electric current is called **galvanic or voltaic cell**. Example of this type of cell is a Daniel cell.

7.5.3.1 Construction of a Daniel Cell

A galvanic cell consists of two cells, each called as **half-cell**, connected electrically by a salt bridge. In each of the half-cell, an electrode is dipped in 1 *M* solution of its own salt and connected through a wire to an external circuit. Figure.7.3 shows a typical galvanic cell.

A. Volta (1745-1827) was an Italian physicist known especially for the development of the first electric cell in 1800.



Zinc sulphate solution Copper sulphate solution

The left half-cell consists of an electrode of zinc metal dipped in 1 *M* solution of zinc sulphate. The right half cell is a copper electrode dipped in I *M* solution of copper sulphate. Salt bridge is a U shaped glass tube. It consists of saturated solution of strong electrolyte supported in a jelly type material. The ends of the U tube are sealed with a porous material like glass wool. The function of the salt bridge is to keep the solutions of two half cells neutral by providing a pathway for migration of ions.

7.5.3.2 Working of the Cell

The Zn metal has tendency to lose electrons more readily than copper. As a result oxidation takes place at Zn-electrode. The electrons flow from Zn-electrode through the external wire in a circuit to copper electrode. These electrons are gained by the copper ions of the solution and copper atoms deposit at the electrode. The respective oxidation and reduction processes going on at two electrodes are as follows:

Half-cell reaction at anode (oxidation)

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^{-}$$

Half-cell reaction at cathode (reduction)

$$Cu^{+2}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)}$$

Overall galvanic reaction is the sum of these two half-cell reactions

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

As a result of redox reaction, electric current is produced. The batteries which are used for starting automobiles, running calculators and toys and to lit the bulbs work on the same principle.

A Comparison of Electrolytic and Galvanic Cells

Electrolytic cell	Galvanic cell
i. It consists of one complete cell, connected to a battery.	It consist of two half cells connected through a salt bridge.
ii. Anode has positive charge while cathode has negative charge	Anode has negative charge while cathode has positive charge.
iii. Electrical energy is converted into chemical energy	Chemical energy is converted into electrical energy
iv. Current is used for a non-spontaneous chemical reaction to take place.	Redox reaction takes place spontaneously and produces electric current

***Test yourself* 7.4**

i. Why are the strong electrolytes termed as good conductors?
ii. Does non-electrolytes forms ions in solution?
iii. What is difference between a strong electrolyte and a weak electrolyte?
iv. Identify a strong or weak electrolyte among the following compounds: $CuSO_4$, $H2CO_3$, $Ca(OH)_2$, *HCl*, $AgNO_3$
v. Which force drives the non-spontaneous reaction to take place?
vi. Which type of chemical reaction takes place in electrolytic cell?
vii. What type of reaction takes place at anode in electrolytic cell?
viii. Why the positively charged electrode is called anode in electrolytic cell?
ix. In the electrolysis of water, towards which terminal H^+ *ions move?*
x. In the electrolysis of water, where is the oxygen produced?
xi. Towards which electrode of the electrolytic cell moves the cations and what does they do there ?
xii. How the half-cells of a galvanic cell are connected? What is function of salt bridge?

7.6 ELECTROCHEMICAL INDUSTRIES

7.6.1 Manufacture of Sodium Metal from Fused NaCl

On the industrial scale, molten sodium metal is obtained by the electrolysis of fused NaCl in the **Downs cell**. This electrolytic cell is a circular furnace. In the center there is a large block of graphite, which acts as an anode while cathode around it is made of iron as shown in figure 7.4.

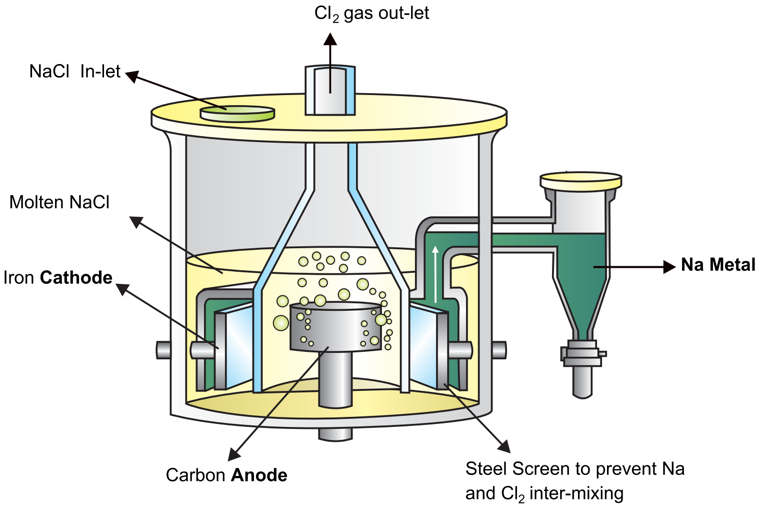


Fig. 7.4 Downs Cell for production of Sodium Metal

7.6.1.1 Working of Downs Cell

The fused NaCl produces Na^+ and Cl^- ions, which migrate to their respective electrodes on the passage of electric current. The electrodes are separated by steel gauze to prevent the contact between the products. The Cl^- ions are oxidized to give Cl_2 gas at the anode. It is collected over the anode within an inverted cone-shaped structure. While Na^+ are reduced at cathode and molten Na metal floats on the denser molten salt mixture from where it is collected in a side tube. Following reactions take place during the electrolysis of the molten sodium chloride:

Molten NaCl ionizes as:

$$2NaCl_{(s)} \rightleftharpoons 2Na^+_{(l)} + 2Cl^-_{(l)}$$

Half-cell reaction at anode (oxidation)

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

Half-cell reaction at cathode (reduction)

$$2Na^+_{(l)} + 2e^- \longrightarrow 2Na_{(l)}$$

Overall galvanic reaction is the sum of these two half-cell reactions

$$2NaCl_{(fused)} \longrightarrow Cl_{2(g)} + 2Na_{(l)}$$

7.6.2 Manufacture of NaOH from Brine

On industrial scale caustic soda (sodium hydroxide) NaOH, is produced in Nelson's cell by the electrolysis of aqueous solution of NaCl called brine. The schematic diagram of the cell is shown in figure 7.5. It consists of a steel tank in which graphite anode is suspended in the center of a U shaped perforated iron cathode. This iron cathode is internally lined with asbestos diaphragm. Electrolyte brine is present inside the iron cathode.

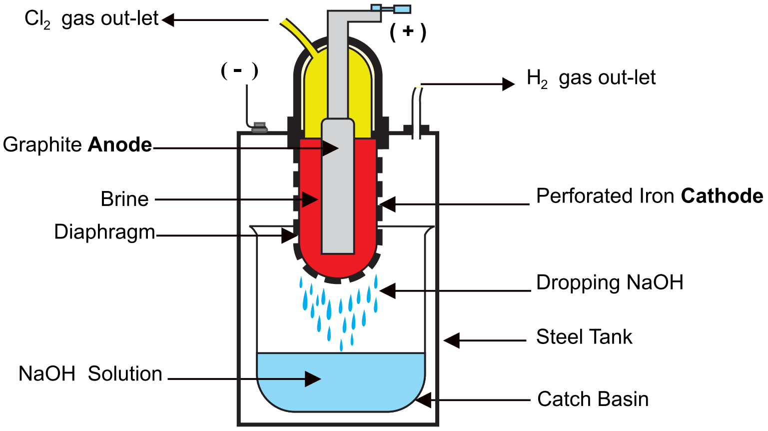


Fig. 7.5 Nelson's Cell for production of NaOH

Working of Nelson's Cell

Aqueous solution of sodium chloride consists of Na^+, Cl^-, H^+ and OH^- ions. These ions move towards their respective electrodes and redox reactions take place at these electrodes. When electrolysis takes place Cl^- ions are discharged at anode and Cl_2 gas rises into the dome at the top of the cell. The H^+ ions are discharged at cathode and H_2 gas escapes through a pipe. The sodium hydroxide solution slowly percolates into a catch basin.

Brine ionizes to produce ions:

$$2NaCl_{(aq)} \longrightarrow 2Na^+_{(aq)} + 2Cl^-_{(aq)}$$

Reaction at anode (oxidation):

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

Reaction at cathode (reduction):

$$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$$

$$2Na^+_{(aq)} + 2OH^-_{(aq)} \longrightarrow 2NaOH_{(aq)}$$

Overall cell reaction of this process:

$$2NaCl_{(aq)} + 2H_2O_{(l)} \longrightarrow H_{2(g)} + Cl_{2(g)} + 2NaOH_{(aq)}$$

Test yourself 7.5

i. Anode of Downs cell is made of a non-metal, what is its name? What is the function of this anode?
ii. Where does the sodium metal is collected in Downs cell?
iii. What is the name of the by-product produced in the Downs cell?
iv. Are anodes of Downs cell and Nelson cell made of same element? If yes, what is its name ?
v. What is the shape of cathode in Nelson's cell? Why is it perforated?
vi. Which ions are discharged at cathode in Nelson's cell and what is produced at cathode?

7.7 CORROSION AND ITS PREVENTION

Corrosion *is slow and continuous eating away of a metal by the surrounding medium.* It is a redox chemical reaction that takes place by the action of air and moisture with the metals. The most common example of corrosion is rusting of iron.

7.7.1 Rusting of Iron

Corrosion is a general term but *corrosion of iron is called* ***rusting***. The important condition for rusting is moist air (air having water vapours in it). There will be no rusting in water vapours free of air or air free of water.

Now we study the chemistry of the rusting process. Stains and dents on the surface of the iron provide the sites for this process to occur. This region is called anodic region and following oxidation reaction takes place here:

$$2Fe_{(s)} \longrightarrow 2Fe^{+2}_{(aq)} + 4e^{-}$$

This loss of electrons damage the object. The free electrons move through iron sheet ,until they reach to a region of relatively high O_2 concentration near the surface surrounded by water layer as shown in figure 7.6. This region acts as cathode and electrons reduce the oxygen molecule in the presence of H^+ ions:

$$O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-} \longrightarrow 2H_2O_{(l)}$$

The H^+ ions are provided by the carbonic acid, which is formed because of presence of CO_2 in water. That is why acidic medium accelerates the process of rusting.

The overall redox process is completed without the formation of rust.

$$2Fe_{(s)} + O_{2(g)} + 4H^{+}_{(aq)} \longrightarrow 2Fe^{+2}_{(aq)} + 2H_2O_{(l)}$$

The Fe^{+2} formed spreads through out the surrounding water and react with O_2 to form the salt $Fe_2O_3.nH_2O$ which is called **rust**. It is also a redox reaction.

$$2Fe^{+2}_{(aq)} + \tfrac{1}{2}O_{2(g)} + (2+n)H_2O_{(l)} \longrightarrow Fe_2O_3 . nH_2O_{(s)} + 4H^{+}_{(aq)}$$

The rust layer of iron is porous and does not prevent further corrosion. Thus rusting continues until the whole piece of iron is eaten away

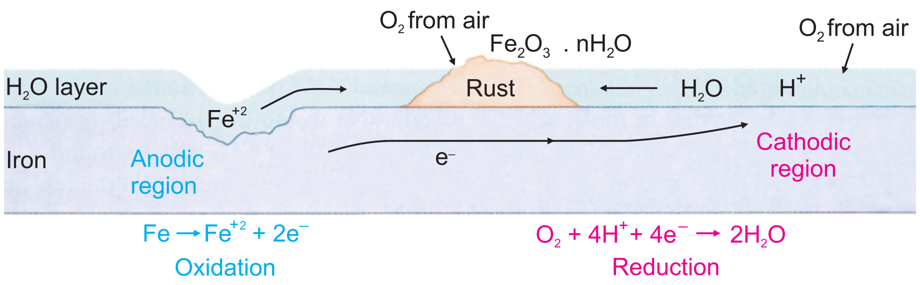


Fig. 7.6 Rusting of iron.

Does Aluminium Rust?

Aluminium corrodes but it does not rust. Rust refers only to iron and steel corrosion. A very hard material aluminium oxide protects the aluminium from further corrosion. In comparison to that when iron corrodes, its color changes and produces large red flakes known as rust. Unlike aluminium oxide, the expanding and flaking of rust exposes new metal surface to further rusting.

7.7.2 Prevention of Corrosion

7.7.2.1 Removal of stains

The regions of stains in an iron rod act as the site for corrosion. If the surface of iron is properly cleaned and stains are removed, it would prevent rusting.

7.7.2.2 Paints and greasing

Greasing or painting of the surface can prevent the rusting of iron. With development of technologies, modern paints contain a combination of chemicals called stabilizers that provide protection against the corrosion in addition to prevention against the weathering and other atmospheric effects.

7.7.2.3 Alloying

Alloy *is a homogeneous mixture of one metal with one or more other metals or non-metals.* Alloying of iron with other metals has proved to be very successful technique against rusting. The best example of alloying is the 'stainless steel', which is a good combination of iron, chromium and nickel.

7.7.2.4 Metallic coating

The best method for protection against the corrosion of metals exposed to acidic conditions is coating the metal with other metal. Corrosion resistant metals like Zn, Sn and Cr are coated on the surface of iron to protect it from corrosion. It is the most widely applied technique in the food industry where food is 'tin-packed'. The containers of iron are coated with tin to give it a longer life. Metallic coating can take place by physical as well as electrolytic methods.

1- Physical Methods (galvanizing and tin coating)

a. Zinc coating or Galvanizing

The process of coating a thin layer of zinc on iron is called galvanizing. This process is carried out by dipping a clean iron sheet in a zinc chloride bath and then heating it. After this iron sheet is removed, rolled into molten zinc metal bath and finally air-cooled. Advantage of galvanizing is that zinc protects the iron against corrosion even after the coating surface is broken.

b. Tin Coating

It involves the dipping of the clean sheet of iron in a bath of molten tin and then passing it through hot rollers. Such sheets are used in the beverage and food cans. The tin protects the iron only as long as its protective layer remains intact. Once it is broken and the iron is exposed to the air and water, a galvanic cell is established and iron rusts rapidly.

Test yourself 7.6

i. What is the difference between corrosion and rusting?
ii. What happens to iron in the rusting process?
iii. Rusting completes in how many redox reactions?
iv. Explain the role of O_2 in rusting?
v. State the best method for protection of metal from corrosion.
vi. What do you mean by galvanizing ?
vii. What is the advantage of galvanizing?
viii. Why tin plated iron is rusted rapidly when tin layer is broken?
ix. Name the metal which is used for galvanizing iron?

2- Electrolytic method (Electroplating)

Electroplating *is depositing of one metal over the other by means of electrolysis.* This process is used to protect metals against corrosion and to improve their appearance. Principle of electroplating is to establish an electrolytic cell in which anode is made of the metal to be deposited and cathode of the object on which metal is to deposit. The electrolyte is in aqueous solution of a salt of the respective metal.

Procedure for Electroplating

In this process the object to be electroplated is cleaned with sand, washed with caustic soda solution and finally it is thoroughly washed with water. The anode is made of the metal, which is to be deposited like Cr, Ni. The cathode is made up of the object that is to be electroplated like some sheet made up of iron. The electrolyte in this system is a salt of the metal being deposited. The electrolytic tank is made of cement, glass or wood in which anode and cathode are suspended. These electrodes are connected with a battery. When the current is passed, the metal from anode dissolves in the solution and metallic ions migrate to the cathode and discharge or deposit on the cathode (object). As a result of this discharge, a thin layer of metal deposits on the object, which is then pulled out and cleaned. Some examples of electroplating are discussed here.

a. Electroplating of Silver

The electroplating of silver is carried out by establishing an electrolytic cell. The pure piece of silver strip acts as anode that is dipped in silver nitrate solution. The cathode is the metallic object to be coated such as spoon. When the current is passed through the cell, the anode dissolves to produce Ag+ ions, that migrate towards the cathode. At cathode they are discharged and deposited on the object e.g. spoon. The chemical reaction can be represented as:

At anode: $Ag_{(s)} \longrightarrow Ag^{+}_{(aq)} + e^{-}$

At cathode: $Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$

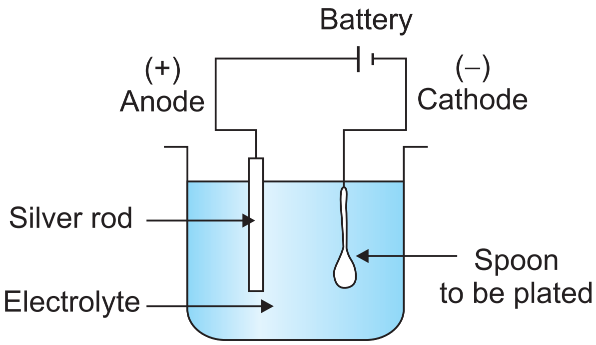


Fig. 7.7 Electroplating of an object.

Common examples of silver plating are tablewares, cutlery, jewelry and steel objects.

b. Electroplating of Chromium

The electroplating of chromium is carried out in the same way as that of silver. The object to be electroplated is dipped in aqueous solution of chromium sulphate containing a little sulphuric acid, that acts as an electrolyte. The object to be electroplated acts as cathode while anode is made of antimonial lead. The electrolyte ionizes and provides Cr^{3+} ions, which reduce and deposit at cathode.

Electrolyte produces the following ions:

$$Cr_2(SO_4)_{3(s)} \xrightarrow{\text{water}} 2Cr^{+3}_{(aq)} + 3SO_4^{-2}{}_{(aq)}$$

Reactions at the electrodes are as follows:

At anode $4OH^{-}_{(aq)} \longrightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^{-}$

At cathode $Cr^{+3}_{(aq)} + 3e^{-} \longrightarrow Cr_{(s)}$

For practical convenience, the steel is usually plated first with nickel or copper and then by chromium because it does not adhere well on the steel surface. Moreover, it allows moisture to pass through it and metal is stripped off. The nickel or copper provides adhesion and then chromium deposited over the adhesive layer of copper lasts longer. This type of electroplating resists corrosion and gives a bright silvery appearance to the object.

c. Electroplating of zinc

The target metal is cleaned in alkaline detergent solutions and it is treated with acid, in order to remove any rust or surface scales. Then, the zinc is deposited on the metal by immersing it in a chemical bath containing electrolyte zinc sulphate. A current is applied, which results in depositing of zinc on the target metal i.e. cathode.

d. Electroplating of tin

Tin is usually electroplated on steel by placing the steel into a container containing a solution of tin salt. The steel is connected to an electrical circuit, acting as cathode. While the other electrode made of tin metal acts as anode. When an electrical current passes through the circuit, tin metal ions present in the solution deposit on steel.

e. Electrolytic refining of copper

Impure copper is refined by the electrolytic method in the electrolytic cell. Impure copper acts as anode and a pure copper plate acts as cathode as shown in figure 7.8. Copper sulphate solution in water is used as an electrolyte.

Oxidation reaction takes place at the anode. Copper atoms from the impure copper lose electrons to the anode and dissolve in solution as copper ions:

$$Cu_{(s)} \longrightarrow Cu^{+2}_{(aq)} + 2e^-$$

Reduction reaction takes place at the cathode. The copper ions present in the solution are attracted to the cathode. Where they gain electrons from the cathode and become neutral and deposit on the cathode.

$$Cu_{(aq)}^{+2} + 2e^- \longrightarrow Cu_{(s)}$$

In the process, impure copper is eaten away and purified copper atoms deposit on the cathode.

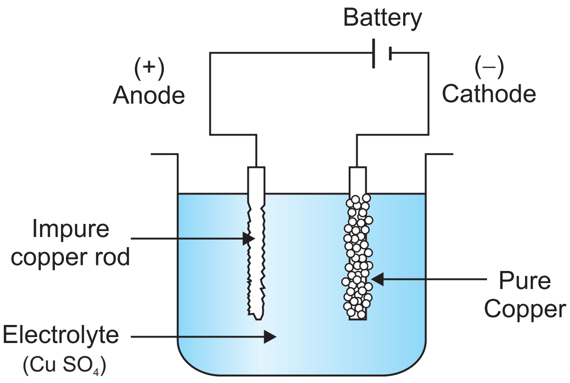


Fig. 7.8 Refining of copper in an electrolytic cell.

Test yourself 7.7

i. *Define electroplating?*
ii. *How electroplating of zinc is carried out?*
iii. *Which material is used to make cathode in electroplating ?*
iv. *Why is the anode made up of a metal to be deposited during electrolysis?*

A COMPARISON OF EFFECT OF Al_2O_3 AND Fe_2O_3 FORMATION ON THEIR PARENT METALS

Aluminium has a great tendency to corrosion. However, aluminium corrosion is aluminium oxide (AI_2O_3), a very hard material that actually protects the aluminium from further corrosion. Aluminium oxide corrosion also looks a lot more like aluminium, so it isn't as easy to notice as rusted iron.

When iron corrodes the color changes and it actually expands. This expanding and color change can produce large red flakes that we all know as rust. Unlike aluminium oxide, the expanding and flaking of rust in iron exposes new metal to further rusting. That is why it is so important to provide a barrier to stop rust.

INTERACTION OF CHEMISTRY WITH PHOTOGRAPHY

In early nineteenth century photographers produced crude images using papers covered with silver nitrate or silver chloride. The exposure of light on photographic plate initiated chemical reaction. The light exposed portion became dark, depending the amount or time of exposure. That exposed plate was later on developed to show the image. Those early days "photographs" darkened with time because of ongoing chemical reaction on them. Later on procedures were developed to make the image permanent by use of mercury vapors, followed by washing with sodium hyposulfite ($Na_2S_2O_3$). It dissolved away the silver iodide from the unexposed portion of the plate and stopped the reaction further. Although, technologically more advanced, the basic procedures developed originally are still used in all silver-based photography today.

EXPLAIN HOW DECORATIVE AND PRACTICAL OBJECTS CONTAINING SILVER CAN DIFFER SIGNIFICANTLY IN THEIR PROPERTIES AND DURABILITY DEPENDING ON WHETHER THEY ARE SOLID, THICKLY PLATED WITH SILVER OR THINLY PLATED WITH SILVER.

Pure silver, also called fine silver, is relatively soft, very malleable, and easily damaged so it is commonly combined with other metals to produce a more durable product. The most popular of these alloys is sterling silver, which consists of 92.5 percent silver and 7.5 percent copper. Although, any metal can make up the 7.5 percent non-silver portion of sterling, centuries of experimentation have shown copper to be its best companion, improving the metal's hardness and durability without affecting its beautiful color. The small amount of copper added to sterling has very little effect on the metal's value. Instead, the price of the silver item is affected by the labour involved in making the item, the skill of the craftsperson, and the beauty of the design. Care should also be taken to prevent silver tarnish in air, (a dulling that naturally occurs when silver reacts with sulfur or hydrogen sulfide in the ambient air.) Likewise, the art of covering a metal with other metal is also used as silver plating. Depending upon the nature of the object, the *layer of silver upon a metal is kept thick. It may be for decorative purpose of some industrial applications. Plating by silver metal has vast applications.*

Key Points

- Oxidation is addition of oxygen or removal of hydrogen or loss of electrons by an element and as a result oxidation number increases.
- Reduction is addition of hydrogen or removal of oxygen or gain of electrons by an element and as a result oxidation number decreases.
- Oxidation number is the apparent charge on an atom. It may be positive or negative.
- Oxidizing agents are the species that oxidize the other element and reduce themselves. Non-metals are oxidizing agents.
- Reducing agents are species that reduce the other elements and oxidize themselves. Metals are reducing agents.
- Chemical reactions in which the oxidation state of species change are termed as redox reaction. A redox reaction involves oxidation and reduction processes taking place simultaneously.
- Redox reactions either take place spontaneously and produce energy or electricity is used to drive the reaction.
- The process in which electricity is used for the decomposition of a chemical compound is called electrolysis. It takes place in electrolytic cells such as Downs cell and Nelson's cell.
- Galvanic cells are those in which spontaneous reactions take place and generate electric current. They are also called voltaic cells.
- Sodium metal is manufactured from fused sodium chloride in the Downs cell.
- NaOH is manufactured from brine in Nelson's cell.
- Corrosion is slow and continuous eating away of a metal by the surrounding medium. The most common example of corrosion is rusting of iron.
- The rusting principle is electrochemical redox reaction, in which iron behaves as anode. Iron is oxidized to form rust $Fe_2O_3 . nH_2O$.
- Corrosion can be prevented by many methods. The most important is electroplating .
- Electroplating is depositing of one metal over the other by means of electrolysis .
- Iron can be electroplated by tin, zinc, silver or chromium.

EXERCISE

Multiple Choice Questions

Put a (✓) on the correct answer

1. Spontaneous chemical reactions take place in:

(a) Electrolytic cell (b) Galvanic cell
(c) Nelson's cell (d) Downs cell

2. Formation of water from hydrogen and oxygen is:

(a) Redox reaction (b) Acid-base reaction
(c) Neutralization (d) Decomposition

3. Which one of the following is not an electrolytic cell?

(a) Downs cell (b) Galvanic cell
(c) Nelson's cell (d) Both a and c

4. The oxidation number of chromium in $K_2Cr_2O_7$ is:

(a) +2 (b) +6
(c) +7 (d) +14

5. Which one of the following is not an electrolyte?

(a) Sugar solution (b) Sulphuric acid solution
(c) Lime solution (d) Sodium chloride solution

6. The most common example of corrosion is:

(a) Chemical decay (b) Rusting of iron
(c) Rusting of aluminium (d) Rusting of tin

7. Nelson's cell is used to prepare caustic soda along with gases. Which of the following gas is produced at cathode:

(a) Cl_2 (b) H_2
(c) O_3 (d) O_2

8. During the formation of water from hydrogen and oxygen, which of the following does not occur:

(a) Hydrogen has oxidized (b) Oxygen has reduced
(c) Oxygen gains electrons (d) Hydrogen behaves as oxidizing agent

9. The formula of rust is:

(a) $Fe_2O_3.nH_2O$ (b) Fe_2O_3
(c) $Fe(OH)_3.nH_2O$ (d) $Fe(OH)_3$

10. In the redox reaction between Zn and HC1, the oxidizing agent is:

(a) Zn (b) H^+
(c) Cl^- (d) H_2

Short answer questions.

1. Define oxidation in terms of electrons. Give an example.
2. Define reduction in terms of loss or gain of oxygen or hydrogen. Give an example.
3. What is difference between valency and oxidation state?
4. Differentiate between oxidizing and reducing agents
5. Differentiate between strong and weak electrolytes.
6. How electroplating of tin on steel is carried out?
7. Why steel is plated with nickel before the electroplating of chromium.
8. How can you explain, that following reaction is oxidation in terms of increase of oxidation number?

$$Al^{\circ} \longrightarrow Al^{+3} + 3e^{-}$$

9. How can you prove with an example that conversion of an ion to an atom is an oxidation process?
10. Why does the anode carries negative charge in galvanic cell but positive charge in electrolytic cell? Justify with comments.
11. Where do the electrons flow from Zn electrode in Daniel's cell?
12. Why do electrodes get their names 'anode' and cathode in galvanic cell?
13. What happens at the cathode in a galvanic cell?
14. Which solution is used as an electrolyte in Nelson's cell?
15. Name the by-products produced in Nelson's cell?
16. Why is galvanizing done?
17. Why an iron grill is painted frequently?
18. Why is O_2 necessary for rusting?
19. In electroplating of chromium, which salt is used as an electrolyte?
20. Write the redox reaction taking place during the electroplating of chromium?
21. In electroplating of silver, from where Ag^+ ions come and where they deposit?
22. What is the nature of electrode used in electrolyting of chromium?

Long Answer Questions

1. Describe the rules for assigning the oxidation state

2. Find out the oxidation numbers of the underlined elements in the following compounds.

   (a) $Na_2\underline{S}O_4$ (b) $Ag\underline{N}O_3$ (c) $K\underline{Mn}O_4$

   (d) $K_2\underline{Cr}_2O_7$ (e) $H\underline{N}O_2$

3. How can a non-spontaneous reaction be carried out in an electrolytic cell? Discuss in detail.

4. Discuss the electrolysis of water.

5. Discuss the construction and working of a cell in which electricity is produced.

6. How can we prepare NaOH on commercial scale? Discuss its chemistry along with the diagram.

7. Discuss the redox reaction taking place in the rusting of iron in detail.

8. Discuss, why galvanizing is considered better than that of tin plating.

9. What is electroplating? Write down procedure of electroplating.

10. What is the principle of electroplating? How electroplating of chromium is carried out?