# 4
TOPIC

Electrochemistry

C11CH4

Learning Objectives

Upon completion of this topic, learners will:

- Explain the concept of balancing redox reaction
- Discuss the electrochemical cell
- Make use of the cell diagram
- Apply the principle of electrolysis to distinguish electrochemical cell
- Discuss the factors that influence the discharge of species
- Simplify cell reactions for the electrolysis of various species
- State Faraday's first and second laws, solving sample problems
- Discuss the various batteries, together with their applications and
- Explain how electroplating materials can prevent rusting and corrosion.

It is a well known fact that energy manifests itself in different forms which are interconvertible into one another. Among different forms of energy, the electrical energy plays a very significant role in our daily life. Many chemical transformations and industrial processes are based on electrical energy and its relationship with chemical energy. There are large number of spontaneous redox reactions which form the basis of *production of electrical energy*. The device in which such chemical processes are carried out is called ***electrochemical cell*** or ***galvanic cell.*** For example, Daniell cell is based on the following redox reaction

$$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+} + \text{Electrical Energy}$$
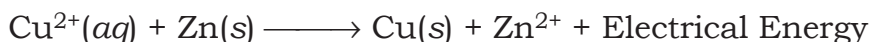
At the same time many of the non-spontaneous redox reactions can be made to occur *by the use of electrical energy.* Some examples are:

$$2H_2O(l) \xrightarrow{\text{Electricity}} 2H_2(g) + O_2(g)$$
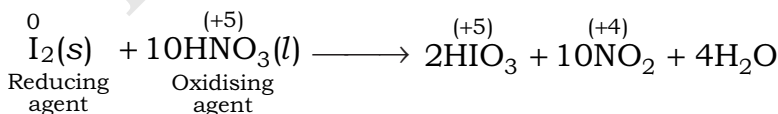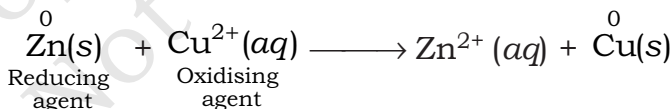
$$2Al_2O_3(l) \xrightarrow{\text{Electricity}} 4Al + 3O_2$$

The process associated with such transformation is called ***Electrolysis*** and the device used for electrolysis is called ***electrolytic cell.***

*The branch of chemistry which deals with the study of relationship between electrical energy and chemical energy and interconversion of one form of energy into another is called **electrochemistry.*** Electrochemistry is very vast and interdisciplinary branch of chemistry which finds tremendous applications. Its study is very important as it helps in development of new technologies which are economical and environment-friendly. In this unit we shall focus on the study of some aspects of electrochemical cells, batteries, fuel cells, electrolytic cells, conductance and its measurement.

▌▌ 4.1. REDOX REACTIONS

Chemical reactions involving oxidation and reduction processes are called *redox reactions.* **Oxidation** may be defined as the *process in which a species* (*atom, molecule or ion*) *increases oxidation number by losing one or more of electrons.* The substance undergoing oxidation is called **reducing agent. Reduction,** on the other hand, is *a process in which a species* (*atom, molecule or ion*) *decreases oxidation number by gaining one or more electrons.* The species undergoing reduction is called **oxidising agent.** Neither oxidation nor reduction can take place alone. These are complementary processes and occur side by side. **Redox reaction** can, thus, be termed *as the chemical reaction involving transferrence of electrons from reducing agent to oxidising agent.*

Some examples of redox reactions are as follows:

$$\underset{\substack{\text{Reducing} \\ \text{agent}}}{\overset{0}{Zn(s)}} + \underset{\substack{\text{Oxidising} \\ \text{agent}}}{Cu^{2+}(aq)} \longrightarrow Zn^{2+}(aq) + \overset{0}{Cu(s)}$$

$$\underset{\substack{\text{Reducing} \\ \text{agent}}}{\overset{0}{I_2(s)}} + \underset{\substack{\text{Oxidising} \\ \text{agent}}}{\overset{(+5)}{10HNO_3(l)}} \longrightarrow \overset{(+5)}{2HIO_3} + \overset{(+4)}{10NO_2} + 4H_2O$$

Redox reactions form the basis electrochemical cells and electrolytic cells which are discussed later in this chapter.

▌Classical Idea of Redox Reactions—Oxidation and Reduction Reactions

Oxygen present in our atmosphere combines with many elements to form their respective oxides. Thus, the term ***oxidation*** was originally

used to describe the **addition of oxygen** to an element or a compound. For example,

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

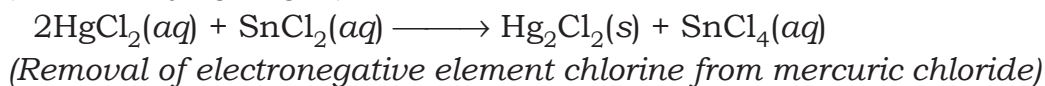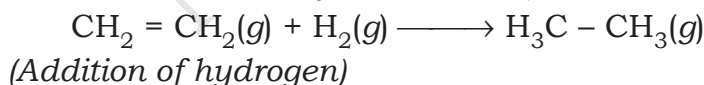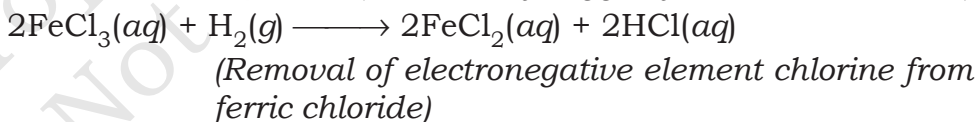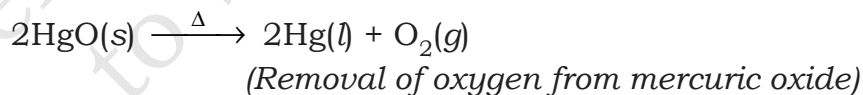$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$
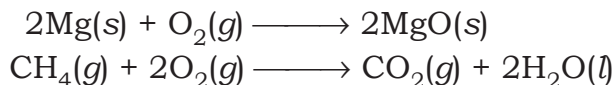
In the second reaction, methane is oxidised because of addition of oxygen to it. At the same time the hydrogen of methane molecule has been replaced by oxygen. In view of the above interpretation, the scope of term oxidation was broadened as process of **addition of oxygen** or **removal of hydrogen** from the substance. With the progress in chemistry the term oxidation was further extended to reactions which do not involve oxygen or hydrogen, and the process of **addition of electronegative** element or **removal of electropositive** element was also considered as **oxidation.** For example, addition of electronegative elements such as fluorine, chlorine, sulphur, etc. cause oxidation of magnesium.

$$Mg(s) + F_2(g) \longrightarrow MgF_2(s)$$

$$Mg(s) + S(s) \longrightarrow MgS(s)$$
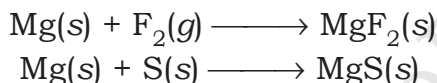
Similarly, removal of electropositive element, potassium causes oxidation of $K_4Fe(CN)_6$.

$$2K_4[Fe(CN)_6](aq) + H_2O_2(aq) \longrightarrow 2K_3[Fe(CN)_6](aq) + 2KOH(aq)$$

On similar grounds the *term reduction was considered as removal of oxygen or addition of hydrogen.* The terminology was further broadened as the knowledge of chemists grew. The *addition of electropositive element* or *removal* of *electronegative element* was also considered as *reduction process.* Some examples are:
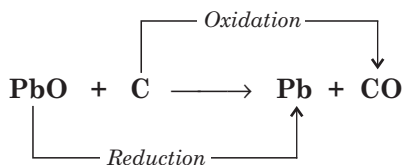
$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

(Removal of oxygen from mercuric oxide)

$$2FeCl_3(aq) + H_2(g) \longrightarrow 2FeCl_2(aq) + 2HCl(aq)$$

(Removal of electronegative element chlorine from ferric chloride)

$$CH_2 = CH_2(g) + H_2(g) \longrightarrow H_3C - CH_3(g)$$

(Addition of hydrogen)

$$2HgCl_2(aq) + SnCl_2(aq) \longrightarrow Hg_2Cl_2(s) + SnCl_4(aq)$$

(Removal of electronegative element chlorine from mercuric chloride)

Let us now sum up the definitions of oxidation and reduction process.

Oxidation. It is a process of *addition of oxygen or any electronegative radical or removal of hydrogen or any electropositive radical from a substance.*

Reduction. It is a process of *addition of hydrogen or any electropositive radical or removal of oxygen or any electronegative radical to a substance.*
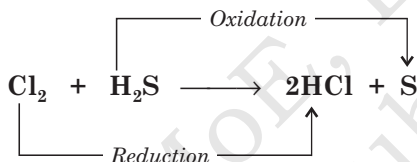
Some **examples** of oxidation and reduction reactions are:
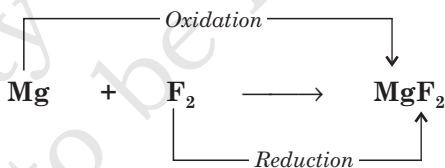
(*i*) *Reaction of PbO and carbon*

$$\overset{\overset{\displaystyle\text{Oxidation}}{\longrightarrow}}{\underset{\underset{\displaystyle\text{Reduction}}{\longleftarrow}}{PbO\ +\ C\ \longrightarrow\ Pb\ +\ CO}}$$

Here, oxygen is being removed from lead oxide (PbO) and is being added to carbon (C). Thus, PbO is *reduced* while C is *oxidised.*

(*ii*) *Reaction of H_2S and Cl_2*

$$\overset{\overset{\displaystyle\text{Oxidation}}{\longrightarrow}}{\underset{\underset{\displaystyle\text{Reduction}}{\longleftarrow}}{Cl_2\ +\ H_2S\ \longrightarrow\ 2HCl\ +\ S}}$$

Here, hydrogen is being removed from hydrogen sulphide (H_2S) and is being added to chlorine (Cl_2). Thus, H_2S is *oxidised* and Cl_2 is *reduced.*

(*iii*) *Reaction between Mg and F_2*

$$\overset{\overset{\displaystyle\text{Oxidation}}{\longrightarrow}}{\underset{\underset{\displaystyle\text{Reduction}}{\longleftarrow}}{Mg\ +\ F_2\ \longrightarrow\ MgF_2}}$$

Here, electronegative radicals fluoride ion is added to magnesium while electropositive radical Mg^{2+} is added to fluorine. Hence, Mg is *oxidised* and F_2 is *reduced.*

Looking at all the reactions given above we observe that oxidation and reduction always occurs simultaneously, hence the word **"redox"** was coined for this class of chemical reactions.

Oxidation Half and Reduction Half Reactions

Every redox reaction can be split up into two **half reactions,** one representing loss of electrons *i.e.,* **oxidation half reaction** while the other representing gain of electrons, *i.e.,* **reduction half reaction.** Some examples are given below:

(*i*) The reaction: **Zn + Cu^{2+} ⟶ Zn^{2+} + Cu,** can be split up into two half reactions as

$$Zn \longrightarrow Zn^{2+} + 2\bar{e} \qquad (Oxidation\ half\ reaction)$$
$$Cu^{2+} + 2\bar{e} \longrightarrow Cu \qquad (Reduction\ half\ reaction)$$

(*ii*) The reaction:

Sn^{2+} + 2Hg^{2+} ⟶ Sn^{4+} + Hg$_2$$^{2+}$, can be split up into half reaction as

$$Sn^{2+} \longrightarrow Sn^{4+} + 2\bar{e} \qquad (Oxidation\ half\ reaction)$$
$$2Hg^{2+} + 2\bar{e} \longrightarrow Hg_2^{2+} \qquad (Reduction\ half\ reaction)$$

Example. *Split the following redox reactions in the oxidation and reduction half reactions:*

(*a*) $2K\ (s)\ + Cl_2\ (g) \longrightarrow 2KCl(s)$

(*b*) $2Al(s) + 3Cu^{+2}\ (aq) \longrightarrow 2Al^{+3}(aq) + 3Cu(s)$

Solution. The oxidation half reaction is the one which represents oxidation and the reduction half reaction shows reduction

(*a*) $\overset{0}{K} \longrightarrow \overset{+1}{K} Cl + e^- $ (*Oxidation half reaction*)

         $\overset{0}{Cl_2}\ (g) + e^- \longrightarrow K\overset{-1}{Cl} $ (*Reduction half reaction*)

(*b*) $2Al \longrightarrow 2Al^{3+} + 6e^- $ (*Oxidation half reaction*)

     $3Cu^{+2}\ (aq) + 6e^- \longrightarrow Cu\ (s) $ (*Reduction half reaction*)
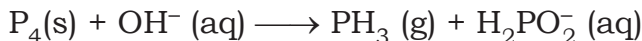
Balancing of Redox Reactions

For balancing of redox reactions we can either use oxidation number method or the half reaction method.

(*i*) **Oxidation number method:** To balance redox reactions by oxidation number method following steps are to be followed
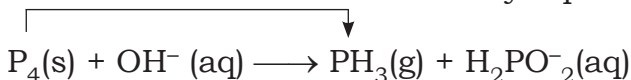
- Correct formula for each reactant should be written.
- Assign the change in oxidation number.
- Calculate the oxidation number per atom with respect to reactants. If more than one atom is present then multiply by number of atom.
- Balance the equation with respect to all atoms, Balance hydrogen and oxygen also.
- For acidic medium use H$^+$ ions while for basic medium use OH$^-$ ions.

- To balance hydrogen atom in the expression can be balanced by adding (H_2O) molecules to the reactants and products.
- Now same number of oxygen atoms on both sides of equation represent the balanced redox reaction.

Example: Balance the following equation by oxidation number method.

$$P_4(s) + OH^- (aq) \longrightarrow PH_3 (g) + H_2PO_2^- (aq)$$

Oxidation number decreased by 3 per atom

$$P_4(s) + OH^- (aq) \longrightarrow PH_3(g) + H_2PO^-_2(aq)$$

Oxidation number increased by 1 per atom

P_4 is acting both as an oxidizing agent as well as reducing agent.

Total number of increase in O.N. of P_4 in $H_2PO_2^- = 1 \times 4 = 4$

Total number of decrease in O.N. of P_4 in $PH_3 = 3 \times 4 = 12$

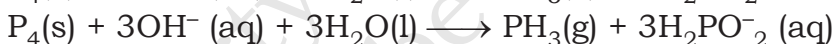Hence, multiply PH_3 by one and $H_2PO_2^-$ by 3 to balance the increase and decrease in oxidation number.

$$P_4(s) + OH^- (aq) \longrightarrow PH_3(g) + 3H_2PO^-_2(aq)$$

To balance O atoms, multiply OH^- by 6

$$P_4(s) + 6OH^- (aq) \longrightarrow PH_3(g) + 3H_2PO^-_2(aq)$$

To balance H atoms add $3H_2O$ to LHS and $3OH^-$ to the RHS we have

$$P_4(s) + 6OH^- (aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^- + 3OH^- (aq)$$

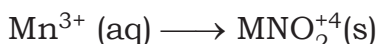$$P_4(s) + 3OH^- (aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO^-_2 (aq)$$

Hence balanced.

(*ii*) **Half reaction method:** In half reaction method, Oxidation half equation and reduction half equation is balanced separately then added together to give balanced equation.
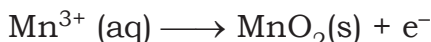
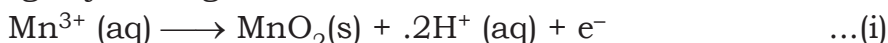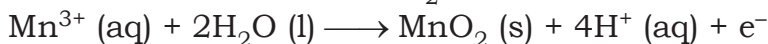**Example:** Balance following redox reaction by using half reaction method.

$$Mn^{2+} (aq) \longrightarrow Mn^{2+} (aq) + MnO_2(s) + H^+ (aq)$$

Oxidation half reaction:

$$Mn^{3+} (aq) \longrightarrow MNO_2^{+4}(s)$$

Balance oxidation number on both sides by adding one electron to product side.

$$Mn^{3+} (aq) \longrightarrow MnO_2(s) + e^-$$

Balance charge by adding 4H ions

$$Mn^{3+} (aq) \longrightarrow MnO_2(s) + .2H^+ (aq) + e^- \qquad \qquad ...(i)$$

Balance O atom by adding H_2O

Mn^{3+} (aq) + $2H_2O$ (l) $\longrightarrow$ MnO_2 (s) + $4H^+$ (aq) + e^-

This is balanced oxidation half reaction.

Reduction half equation

Mn^{+3} 3+ (aq) $\longrightarrow$ Mn^{+2} 2+ (aq)

Balance oxidation number by adding electron.

Mn^{3+} (aq) + e^- $\longrightarrow$ Mn^{2+} (aq)   ...(ii)

Adding equation (*i*) and (*ii*), we get balance redox equation

$2Mn^{3+}$(aq) + $2H_2O$ (l) $\longrightarrow$ MnO_2 (s) + Mn^{2+} (aq) + .$4H^+$(aq)

4.2. ELECTROCHEMICAL CELL

Daniel Cell

Daniel cell is a type of electrochemical cell invented in 1836 by John Frederic Daniel in 1836 a british chemist and meterologist. To make a Daniel Cell take two beakers, one containing copper sulphate solution and another containing, zinc sulphate solution, zinc rod is taken as anode and dipped in zinc sulphate solution while copper rod is taken as cathode and dipped in copper sulphate solutions. These two electrolytes are connected by a salt bridge (a U tube containing KCl or NH_4NO_3 solidified by boiling with agar-agar). Salt bridge is a link between two electrolytes without these actual mixing. Zinc and copper electrodes are connected in a circuit with connecting wire, a switch and an ammeter. When we put the switch on, a flow of current is observed in the circuit. There is a movement of electrons from anode to cathode through metallic wire. Movement of ions takes place through the salt bridge. At anode oxidation takes place and solid zinc converts into zinc ions while at cathode copper ions get reduced to copper metal and get deposited. The flow of free electrons produces electricity in the direction opposite to the direction of flow of electrons.

Representation of Daniel cell.

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

EMF of Daniel cell is 1.4 V.

Uses of Daniel Cell

Daniel cells are used to generate electricity and to store electricity. Daniel cells are used in development of battery and electrical telegraphy.

Unique thing about Daniel Cell

Unique design of Daniel cell separates the copper and zinc ions from each other which prevents the polarisation of from interrupting the electricity flow, while at the same time allow ions in the electrolytes to pass between two electrodes in order to complete the electric circuit.

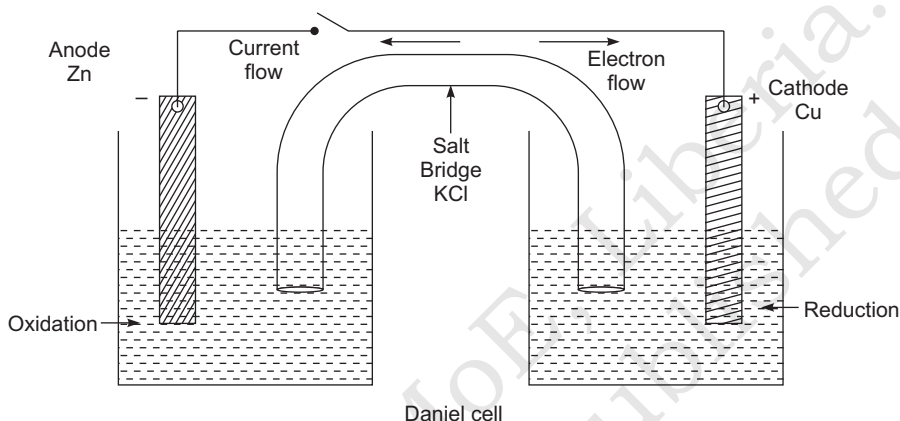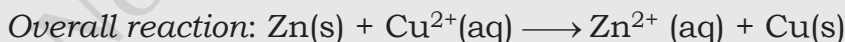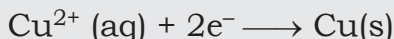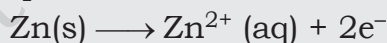*Daniel cell is a Galvanic cell but all Galvanic cells are not Daniel cells*

Fig. 4.1. Daniel cell

EXPERIMENT 1

Aim: To set up simple Daniell cell and determine its EMF.

Theory: When a copper electrode dipped in copper sulphate solution is connected to a zinc electrode dipped in the zinc sulphate solution, then electrons flow from zinc electrode to copper electrode and the chemical reactions take place as:

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

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

Apparatus and Chemicals: One beaker, a porous pot, connecting wires, milli voltmeter, sand paper, zinc strip, copper strip, 1 M $ZnSO_4$ solution and 1 M $CuSO_4$ solution.

Procedure:

1. Take copper sulphate solution in a clean beaker.
2. Clean the copper strip with the help of sand paper and dip it into copper sulphate solution.
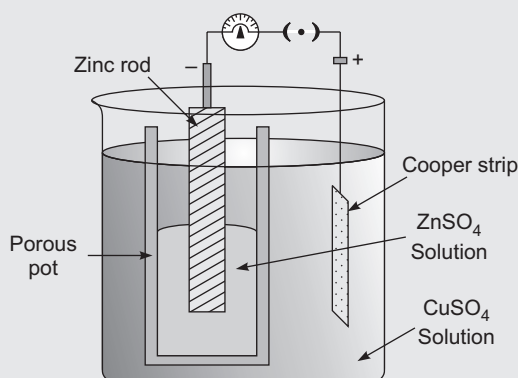3. Take zinc sulphate solution in a porous pot.

Fig. 4.2. A Daniell cell

4. Clean the zinc strip with the help of sand paper and dip it into zinc sulphate solution.

5. Keep the porous pot in the beaker.

6. Connect the copper strip with the positive terminal and zinc strip with the negative terminal a voltmeter as shown in Fig.

7. Note the position of the pointer in the voltmeter and record the reading in your note-book.

Observation:

The EMF of the Daniell cell is ...... volts.

Precautions:

1. The concentration of copper sulphate and zinc sulphate should neither be too low nor too high.

2. The porous pot should not be completely dipped into the copper sulphate solution, *i.e.*, the copy sulphate solution should not be allowed to enter the porous pot.

3. Clean zinc and copper strips with sand paper before use.

4. Carry out dilution of the solution carefully.

5. Note the reading only when the pointer becomes stable.

6. Connect copper strip with the positive terminal of voltmeter and zinc strip with negative terminal.

Galvanic Cells

The device in which chemical energy is converted into electrical energy is called **galvanic cell** (after the name of Luigi Galvani) or **electrochemical cell** or **voltaic cell** (after the name of Alessandro Volta)**.** In a galvanic cell, a redox reaction is carried out in an *indirect manner* and the decrease in

free energy during the chemical process is made to appear as electrical energy. An indirect redox reaction involves the occurrence of reduction and oxidation processes in separate vessels. In order to understand this phenomenon, let us consider the Zn—$CuSO_4$ reaction as the basis of the cell reaction.

In its simple form, a *zinc strip* is dipped in the $ZnSO_4$ solution and a *copper strip* is dipped in the $CuSO_4$ solution taken in separate beakers. The two metallic strips which act as electrodes are connected by the conducting wires through a voltmeter. The two solutions are joined by an inverted U-tube known as **salt bridge.** The U-tube is filled with the solution of some electrolyte such as KCl, KNO_3 or NH_4Cl to which *gelatin* or *agar-agar* has been added to convert it into semi-solid paste. A schematic diagram of this cell has been shown in Fig. 4.3.

The deflection in voltmeter indicates that there is a potential difference between the two electrodes. It has been found that the conventional current flows through the outer circuit from copper to zinc strip. It implies that the electrons flow occurs from zinc to copper strip.

Let us now understand the working of the cell.

(*i*) Zinc undergoes oxidation to form zinc ions

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

(*ii*) The electrons liberated during oxidation are pushed through the connecting wires to copper strip.

(*iii*) Copper ions move towards copper strip, pick up the electrons, and get reduced to copper atoms which are deposited at the copper strip.
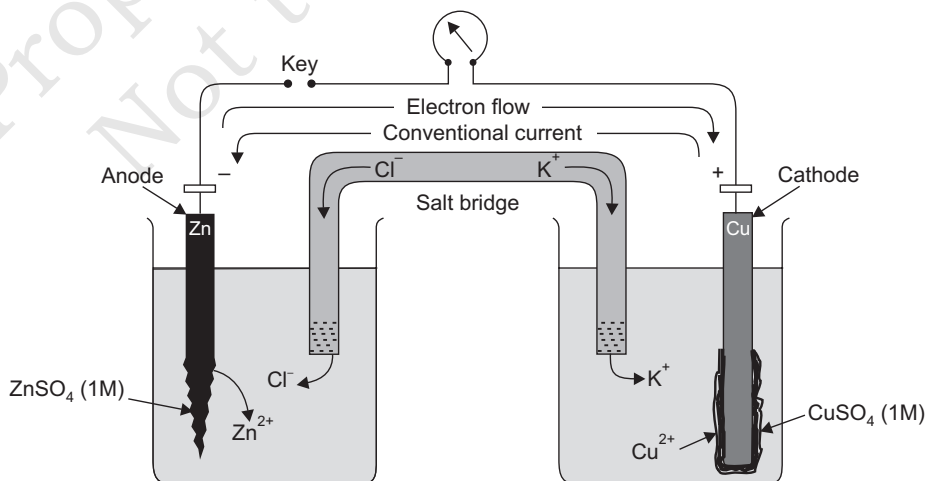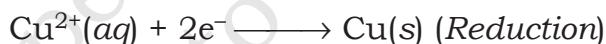
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \ (Reduction)$$

Fig. 4.3. Electrochemical cell.

The electrode at which *oxidation occurs* is **anode** and that at which *reduction occurs* is **cathode.** In the above cell, zinc strip is anode and the copper strip is cathode. Due to the oxidation process occurring at the anode it becomes a source of electrons and acquires a negative charge in the cell. Similarly, due to reduction process occurring at the cathode it acquires positive charge and becomes a receiver of the electrons. Thus, in the electrochemical cell, **anode electrode** acts as **negative terminal** and **cathode electrode** acts as **positive terminal.**

Salt Bridge and its Functions. Salt Bridge is a U-shaped tube containing a semi-solid paste of some inert electrolyte like KCl, KNO_3, NH_4Cl, etc., in *agar-agar* and *gelatine.* An inert electrolyte is one which:

(*a*) does not react chemically with the solution in either of the compartment.

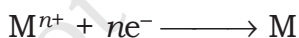(*b*) does not interfere with the net cell reaction.

Function of Salt Bridge. In the electrochemical cell a salt bridge serves two very important functions:

(*i*) *It allows the flow of current by completing the circuit.*

(*ii*) *It maintains electrical neutrality.*

Electrode Potential

When a strip of metal (M) is brought in contact with the solution containing its own ions (M^{n+}), then either of the following three possible processes can take place:

(*i*) The metal ion M^{n+} may collide with the metallic strip and bounce back without any change.

(*ii*) The metal ion M^{n+} may collide with the strip, gain *n* electrons and get converted into metal atom, *i.e.*, the ion is *reduced.*

$$M^{n+} + ne^- \longrightarrow M$$

(*iii*) The metal atom on the strip may lose *n* electrons and enter the solution as M^{n+} ion, *i.e.*, metal is *oxidised.*

$$M \longrightarrow M^{n+} + ne^-$$

The above changes have been shown in Fig. 4.4.

Now, if the metal has a relatively *high tendency to get oxidised*, its atoms would start losing electrons, change into positive ions and pass into the solution. The electrons lost, accumulate in the metal strip and cause it to develop *negative charge*. The negative charge developed on the strip does not allow metal atoms to continue losing electrons but it would reattract the metal ions from the solution in an attempt to neutralise

its charge. Ultimately, a state of equilibrium will be established between the metal and its ions at the interface.
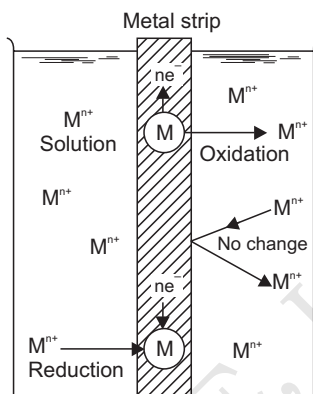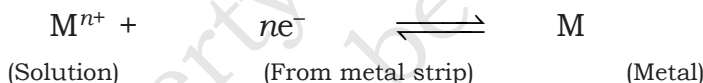
$$\underset{\text{(Metal strip)}}{M} \rightleftharpoons \underset{\text{(Solution)}}{M^{n+}} + \underset{\text{(In metal strip)}}{ne^-}$$

Fig. 4.4. Electrode equilibrium.

Similarly, if the metal ions have relatively *greater tendency to get reduced,* they will accept electrons at the strip from the metal atoms and consequently, a *net positive* charge is developed on the metal strip. Ultimately, a similar equilibrium is established between the metal ions and the metal atoms at the interface.

$$\underset{\text{(Solution)}}{M^{n+}} + \underset{\text{(From metal strip)}}{ne^-} \rightleftharpoons \underset{\text{(Metal)}}{M}$$

The development of negative and positive charges on the metal strip has been shown in Fig. 4.5 (*a*) and (*b*) respectively.

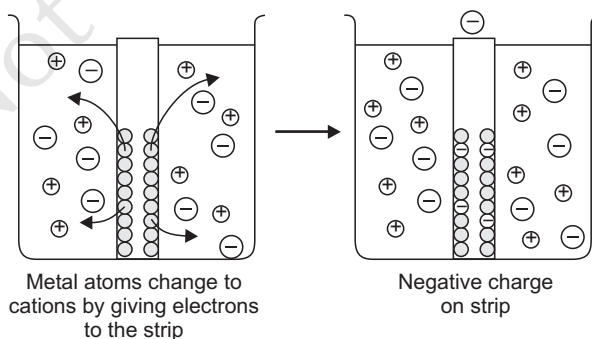Metal atoms change to
cations by giving electrons
to the strip

Negative charge
on strip

Fig. 4.5. (*a*) Development of –ve charge on metal strip.

Metal ions gain electrons
from the strip and get
deposited as metal atoms
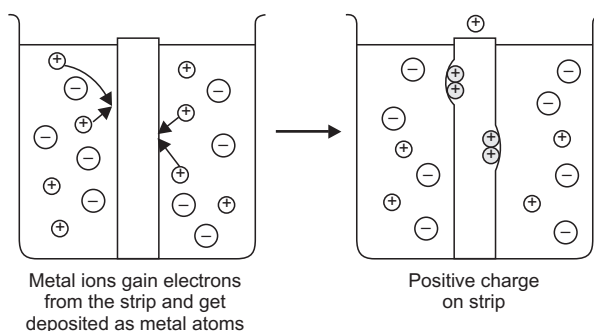
Positive charge
on strip

Fig. 4.5. (*b*) Development of +ve charge on the metal strip.

In either case, the separation of charges at the equilibrium state results in the electrical potential difference between the metal and the solution of its ions and is known as **electrode potential.**

The exact potential difference at the equilibrium depends on the **nature of metal, its ions, the concentration of ions** and the **temperature.**

Cell Potential or EMF of the Cell

The electrochemical cell consists of two half cells. The electrodes in these half cells have different electrode potentials. When the circuit is completed the loss of electrons occurs at the electrode having lower reduction potential whereas the gain of electrons occurs at the electrode with higher reduction potential. The difference in the electrode potentials of the two electrodes of the cell is termed as **electromotive force** (abbreviated as **EMF** or **emf**) or **cell voltage (E_{cell}).** Mathematically, it can be expressed as

$$\textbf{EMF} = \textbf{E}_{\textbf{red}} \ (Cathode) - \textbf{E}_{\textbf{red}} \ (Anode) \text{ or simply}$$

as $$\textbf{E}_{\textbf{cell}} = \textbf{E}_{\textbf{cathode}} - \textbf{E}_{\textbf{anode}}$$

Since in the representation of a cell, the cathode is written on right hand side and the anode on left hand side, therefore, EMF of a cell is also sometimes written as:

$$\textbf{EMF} = \textbf{E}_{\textbf{Right}} - \textbf{E}_{\textbf{Left}} = \textbf{E}_{\textbf{R}} - \textbf{E}_{\textbf{L}}$$

EMF of the cell may be defined as the *potential difference between the two terminals of the cell when either no current is drawn from it.* It is measured with the help of *potentiometer* or *vacuum tube voltmeter.*

The EMF of the cell depends on *nature of the reactants, concentration of the solutions in the two half cells,* and the *temperature.* The EMF of the cell at the standard state conditions is called standard EMF and can be calculated from the standard electrode potentials of the two half cells.

$$\text{E}^{\ominus}_{\text{cell}} = \text{E}^{\ominus}_{\text{cathode}} - \text{E}^{\ominus}_{\text{anode}}$$

Standard Hydrogen Electrode (SHE)

Standard hydrogen electrode (Fig. 4.6) consists of a platinum wire sealed into a glass tube and carrying a platinum foil at one end. The platinum foil is coated with finely divided platinum. The electrode is placed in beaker containing an aqueous solution of some acid having **one molar concentration of H⁺ ions.** Hydrogen gas at 1 bar pressure is continuously bubbled through the solution at a temperature of 298 K. The oxidation or reduction in the SHE takes place at platinum foil. Hence, it can act as **anode** as well as **cathode** and may be represented as:
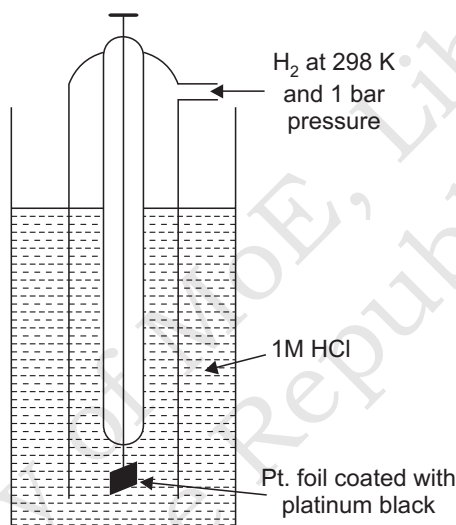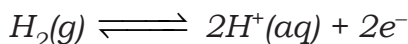

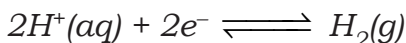**Fig. 4.6. Standard hydrogen electrode (SHE).**

Pt, $\frac{1}{2}$ H$_2$ (1 bar)/H⁺(1 M) or

H⁺(1 M)/$\frac{1}{2}$ H$_2$ (1 bar), Pt respectively.

*If SHE acts as **anode** then oxidation will take place at it as*

$$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$$

*If SHE acts as **cathode** then reduction will take place at it as*

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

Electrochemical Series

We have seen that different *metal/metal ion* combinations have different values of electrode potentials. The various elements can be arranged in order of increasing or decreasing values of their reduction potentials. *The arrangement of various elements in the order of increasing values*

of standard reduction potentials is called **electrochemical series.** The electrochemical series, also called activity series consisting of some electrodes along with their respective reduction reactions.

Applications of Electrochemical Series

Some of the important applications of electrochemical series are discussed as follows:

1. Comparing the Relative Oxidising and Reducing Powers of Various Substances. Substance with higher reduction potential have greater tendency to undergo reduction. For example, F_2 has highest reduction potential which means it is most easily reduced to F^- ions. In other words, F_2 the is best oxidising agent. Li^+ ion, on the other hand, had lowest reduction potential. Hence Li^+ is the weakest reducing agent or conversely Li metal is the best reducing agent. Thus, it can be concluded that *substances with* **higher reduction potentials** *are* **strong oxidising agents** *while substances with* **lower** *reduction potentials are* **strong reducing agents**.

2. Calculation of Standard EMF of the Cell ($E^\ominus_{cell}$). Standard EMF of the cell can be calculated by applying the formula

$$E^\ominus_{cell} = E^\ominus \text{ (cathode)} - E^\ominus \text{ (anode)}$$

The electrode with higher electrode potential ($E^\ominus$) act as cathode while that with lower electrode potential will act as anode.

3. Predicting the Feasibility of Redox Reaction. Electrochemical series help to predict the feasibility of the redox reaction in a given direction. In the given redox reaction, the species undergoing reduction should have relatively higher $E^\ominus$ value than the species which undergo oxidation. If this condition is fulfilled the redox reaction is feasible otherwise it is non-feasible.
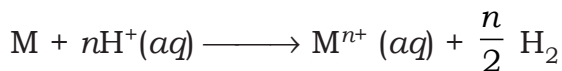
For example, let us predict whether the reaction

$$\textbf{Zn}^{2+} + \textbf{Cu} \longrightarrow \textbf{Zn} + \textbf{Cu}^{2+} \text{ is feasible or not.}$$

In the given reaction Zn^{2+} ions are getting reduced while Cu atoms are oxidised. This process will be feasible if $E^\ominus_{Zn^{2+}/Zn}$ is greater than $E^\ominus_{Cu^{2+}/Cu}$ but in fact, $E^\ominus_{Zn^{2+}/Zn}$ (– 0.76 V) is less than $E^\ominus_{Cu^{2+}/Cu}$ (0.34 V). Hence Zn^{2+} ions cannot oxidise Cu atoms. Thus, the given reaction is not feasible.

4. Predicting the Capability of Metal to Displace H$_2$ Gas from Acid. The chemical reaction between metal M and acid to liberate H$_2$ gas is represented by the reaction

$$M + nH^+(aq) \longrightarrow M^{n+} (aq) + \frac{n}{2} H_2$$

For the above reaction to occur, the $E^{\ominus}_{M^{n+}/M}$ should be smaller than $E^{\ominus}_{H^+/H_2}$. Thus, all metals lying above hydrogen in electrochemical series can liberate H$_2$ gas by reaction with acids. On the other hand, the metal lying below hydrogen in the electrochemical series cannot undergo such a reaction.

4.3. ELECTROLYTIC CELLS AND ELECTROLYSIS

So far we have been discussing the process of conversion of chemical energy into electrical energy by means of electrochemical cell. In the reverse process, the passage of electricity through the electrolytes in their molten or dissolved state can cause chemical changes under suitable conditions. **For example,** the passage of electricity through the acidified water results in the formation of hydrogen and oxygen gases. *The process of chemical decomposition of the electrolyte by the passage of electricity through its molten or dissolved state is called **electrolysis**.*

Electrolytic cell. The device in which the process of electrolysis is carried out is called electrolytic cell. It consists of:
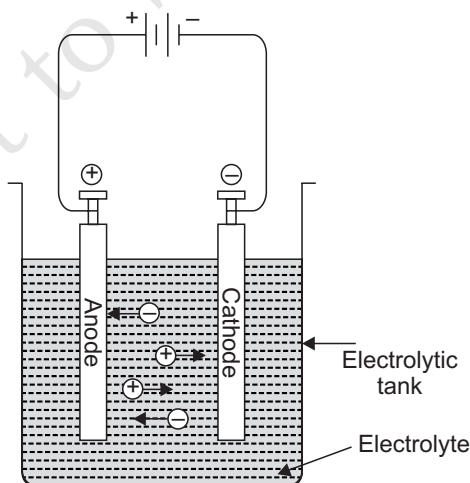

Fig. 4.7. Electrolytic cell.

(*i*) *Electrolytic tank,* which is made of some non-conducting material like glass, wood or bakelite.

(*ii*) *Electrolyte* in its dissolved state or molten state.

(*iii*) *Source of electricity;* an electrochemical cell or battery.

(*iv*) Two *metallic rods*, suspended in the electrolyte and connected to the battery through conducting wires. These rods are called *electrodes*. The electrode connected to the negative terminal of battery is called *cathode* while the other one which is connected to the positive terminal is called *anode*. The apparatus used to constitute electrolytic cell has been shown in Fig. 4.7.

Mechanism of Electrolysis

The process of electrolysis can be explained on the basis of the *theory of ionisation.* When an electrolyte is dissolved in water, it splits up into charged particles called *ions*. The positively charged ions are called cations while the negatively charged ions are called anions. The ions are free to move about in aqueous solution. When electric current is passed through the solution, the ions respond to the applied potential difference and their movement is directed towards the oppositely charged electrodes. The cations move towards the *negatively charged electrode* while *anions* move towards the *positively charged electrode*. The formation of products at the respective electrodes is due to **oxidation** (*loss of electrons*) at the anode and **reduction** (*gain of electrons*) at the **cathode**.

EXPERIMENT 2

Aim: To perform experiment on indicator of electrolysis.

Theory: During electrolysis when an indicator like phenolphthalein, is added to the electrolyte salt, it shows the change of pH of electrolyte solution during process of electrolysis. The colour of phenolphthalein changes to purple if the solution is basic in nature *i.e.,* if the pH of solution is more than 7. The phenolphthalein remains colourless if the solution is acidic or if it is neutral like water. During electrolysis if the concentration of positive ions (metal ions) increases in the solution the electrolytes will show purple colour.

Apparatus and chemicals: Beaker, drycell, connecting wires. Two graphite electrocles, electrolyte solution, phenolphthalein etc.

Procedure:

1. Take a beaker. Fill it more than half with electrolyte solution.

2. Add few drops of phenolphthalein solution to the electrolyte.

---

3. Arrange two electrodes and connect them with dry cell, a key as shown in the diagram.
4. Put the circuit on so that current passes through the electrolyte. As electrolyte dissociates into cations and anions.
5. Cations move towards cathode and anions move towards anode.
6. Phenolphthalein added in the electrolyte acts as an indicator. If the solution is acidic it remains colourless while if the solution is alkaline phenolphthalein gives purple colour to the electrolyte.
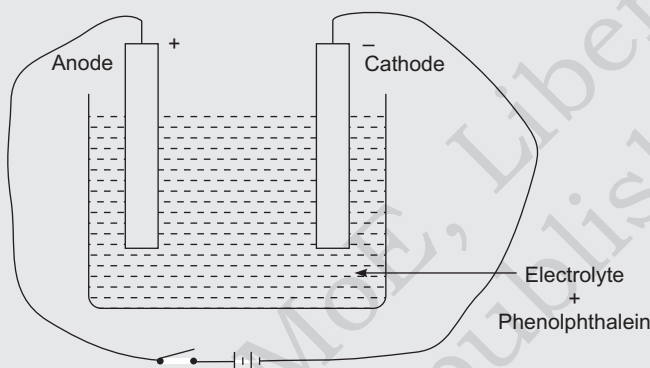

Fig. 4.8

Precautions:
1. Concentration of electrolyte should not be too high or too low.
2. Electrodes should be cleaned by sand paper before use.
3. Chemicals should be handled carefully.
4. Electrolyte should not be too heated.

Conclusion: The positive ions accumulate non-cathode (negative electrode). More purple colour is seen near a cathode. While less purple colour is seen towards the anode. If we stir the electrolyte, the uniform colour is seen throughout the electrolyte.

4.4. FACTORS INFLUENCING DISCHARGE OF SPECIES (IONS)

Ions are formed as a result of dissociation of electrolyte. When electric current is passed through the electrolyte, these ions move freely. The positively charged (particles) cations move towards negatively charged electrode (cathode) while negatively charge particles (anions) move towards positively charged electrode (anode). Discharge of species (ions) depends upon following factors:

1. **Position of metallic ions in electrochemical series:** During electrolysis those metallic ions which are placed lower in the electro chemical series are usually discharged in preference to those at the top of series. In case of non-metals, those which are placed higher up in the series are discharged in preference to those which are placed lower in the series.

2. **Concentration of Ions:** More is the concentration of an ion more are the chances of being discharged in preference to others. The distance of competing ions has to be close in the electro chemical series. If the distance of those two ions is not close in the electrochemical series this rule will not work.

Example: The Na^+ ion can not be discharged in preference to H^+ aqueous NaCl solution irrespective of the concentration of NaCl (aq) solution.

3. **Nature of Electrode:** Innert electrodes, made of less reactive material such as graphite, platinum etc have practically no role in deciding the preferential discharge of an ion on it. Active electrons which are made up of active material such as Cu, Ag, Ni, etc., actively take part in electrode reaction and have an active role in deciding the preferential discharge of ions. In such case anions migrate to the anode but do not get discharged, instead the active anode itself looses electron and forms ions.
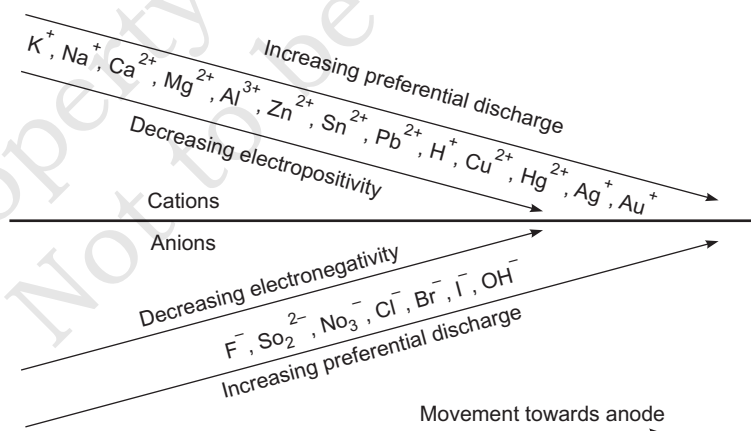

Fig. 4.9

Product of Electrolysis

The products of electrolysis, in general, depend on the following factors:

1. **Nature of the materials being electrolysed.** It is because of the fact that reactions occurring at the electrodes are controlled by their respective electrode potentials.

2. **Types of electrodes being used.** *Inert electrodes* such as Pt or Au do not participate in the electrode reactions. They simply act as source and sink for the electrons. *Active electrodes*, on the other hand, participate in the electrode reactions. Therefore, the electrolysis products of same electrolyte may differ in case of inert and active electrodes.

3. **Kinetic barrier and over voltage.** Sometimes thermodynamically feasible electrochemical reactions do not seem to occur because at lower voltage they are kinetically slow. Their slowness creates electrical resistance at the electrodes and they require extra voltage (or potential) than the theoretical value of their standard electrode potential. This extra voltage required is referred to as **over voltage.** Let us now discuss some examples of electrode reactions.
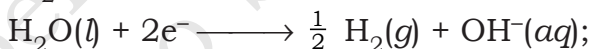
(*a*) **Cathodic reactions.** *Cathode electrode involves reduction process at its surface.* Therefore, for the different competing reduction processes, the one with *higher reduction potential, will preferably take place.* For example, during the electrolysis of aqueous solution of sodium chloride there is possibility of following reactions at the cathode:
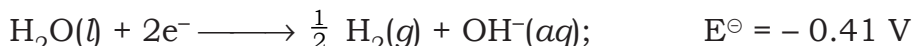
Reduction of Na$^+$ ions

$$Na^+(aq) + e^- \longrightarrow Na(s); \quad E^\ominus_{red} = -2.71 \text{ V}$$

Or

Reduction of H$_2$O molecules

$$H_2O(l) + 2e^- \longrightarrow \tfrac{1}{2} H_2(g) + OH^-(aq);$$

$$E^\ominus_{red} = -0.41 \text{ V}$$

The reduction of water will preferably take place at the cathode because $E^\ominus_{red}$ of water is higher. Hence, the product of electrolysis of aqueous solution of NaCl at the cathode will be H$_2$ gas instead of Na(s).
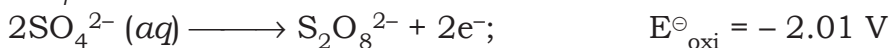
Similarly, during electrolysis of aqueous solution of copper sulphate reduction of Cu^{2+} ions will take place at the cathode in preference to the reduction of H$_2$O molecules because $E^\ominus_{Cu^{2+}/Cu}$ is greater than $E^\ominus_{H_2O/H_2}$.

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s); \qquad\qquad E^\ominus = 0.34 \text{ V}$$

$$H_2O(l) + 2e^- \longrightarrow \tfrac{1}{2} H_2(g) + OH^-(aq); \qquad E^\ominus = -0.41 \text{ V}$$

(*b*) **Anodic reactions.** *Anode electrode involves oxidation process at its surface.* Therefore, for different competing oxidation processes, the one with *higher oxidation potential* (or *lower reduction potential) will*
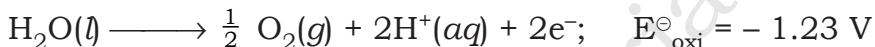
preferably occur. For example, if we carry out electrolysis of aqueous solution of copper sulphate using Pt electrodes, the competing oxidation processes at the anode are as follows:
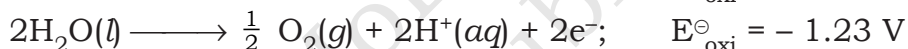
Oxidation of SO_4^{2-} ions

$$2SO_4^{2-} (aq) \longrightarrow S_2O_8^{2-} + 2e^-; \qquad E^\ominus_{oxi} = -2.01 \text{ V}$$

Or

Oxidation of water molecules

$$H_2O(l) \longrightarrow \tfrac{1}{2} \ O_2(g) + 2H^+(aq) + 2e^-; \qquad E^\ominus_{oxi} = -1.23 \text{ V}$$

As oxidation potential of water is higher, the product formed at the anode will be O_2 gas instead of $S_2O_8^{2-}$ ion.

Similarly, if the electrolysis of copper sulphate solution is carried out using *copper electrodes*, then the process occurring at the anode will be *oxidation of copper atoms to copper* ions instead of oxidation of water because oxidation potential of Cu is higher.
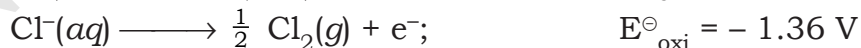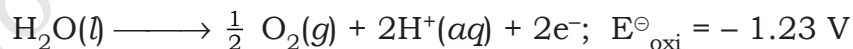
$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-; \qquad E^\ominus_{oxi} = -0.34 \text{ V}$$

$$2H_2O(l) \longrightarrow \tfrac{1}{2} \ O_2(g) + 2H^+(aq) + 2e^-; \qquad E^\ominus_{oxi} = -1.23 \text{ V}$$

Thus, in such a case copper from anode will go on dissolving into solution as Cu^{2+} ions while Cu^{2+} ions from solution will go on depositing at the cathode as copper atoms.

The above discussion leads us to a general conclusion that for different competing reactions at the electrodes:

Cathodic reaction will be the one with higher $E^\ominus_{red}$ value.

Anodic reaction will be the one with higher $E^\ominus_{oxi}$ value or lower $E^\ominus_{red}$ value.
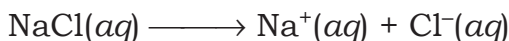
(*c*) Unexpected products due to overvoltage. In some cases the **unexpected results** are obtained due to *overvoltage*. For example, let us compare the oxidation potentials of Cl^- ion and water
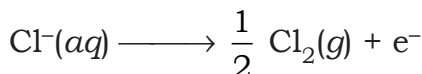
$$H_2O(l) \longrightarrow \tfrac{1}{2} \ O_2(g) + 2H^+(aq) + 2e^-; \quad E^\ominus_{oxi} = -1.23 \text{ V}$$

$$Cl^-(aq) \longrightarrow \tfrac{1}{2} \ Cl_2(g) + e^-; \qquad E^\ominus_{oxi} = -1.36 \text{ V}$$

Although oxidation potential of H_2O is more than that of Cl^- ions, yet during the electrolysis of *concentrated solution of sodium chloride*, the chloride ions oxidise in preference to H_2O molecules at the anode giving Cl_2 gas as the product.

In the light of the above discussion let us discuss the product formed during the electrolysis of some of the electrolytes.
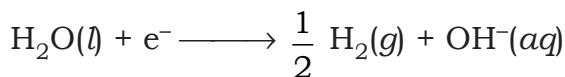
1. Electrolysis of Aqueous Solution of NaCl. NaCl in aqueous solutions ionises as

$$NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$$

Reaction at anode :

$$Cl^-(aq) \longrightarrow \frac{1}{2} Cl_2(g) + e^-$$

Reaction at cathode :

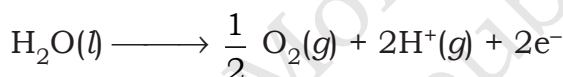$$H_2O(l) + e^- \longrightarrow \frac{1}{2} H_2(g) + OH^-(aq)$$

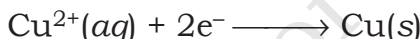Thus, Cl_2 gas is liberated at the anode whereas H_2 gas is liberated at the cathode.

2. Electrolysis of Copper Sulphate Solution Using Platinum inert Electrodes. Copper sulphate ionises in aqueous solution

$$CuSO_4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

Reaction at anode :

$$H_2O(l) \longrightarrow \frac{1}{2} O_2(g) + 2H^+(g) + 2e^-$$

Reaction at cathode :

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

Thus, copper is deposited at the cathode, and O_2 gas is liberated at the anode.

3. Electrolysis of Copper Sulphate Solution Using Copper Electrodes. Copper sulphate ionises as:

$$CuSO_4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

Reaction at anode :

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

Reaction at cathode :

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

Thus, copper dissolves at the anode and is deposited at the cathode.

EXPERIMENT 3

Aim: Determine electrolysis food (lemon juice).

Theory: Food items like lemon juice, salt, sugar etc have either acid or alkali in the those may be strong or weak acid or base. Hence while undergoing electrolysis those conduct electricity as those dissociated into ions.

Lemon juice contains citric acid which dissociates into Hydrogen ion (cation) and citrate ion (anion). Fee movement of those ions facilitate electrolysis.

Chemicals and apparatus: Electrodes (carbon rod as zinc plate as electrodes, connecting wire, galvanometer light bulb, lemon juice, galvanometer, light bulb. etc. Big bottle or beaker.

Procedure:

1. Take a beaker or bottle.
2. Take lemon juice in the beaker.
3. Make electric connections taking carbon rod and zinc road as electrodes, light bulb, galvanometer, a key and a dry cell.
4. When electrolysis is done on passage of current through the lemon juice, we see that galvanometer shows deflection and the bulb lights. It show that lemon juice is dissociated into ions and electric current flows through lemon juice.

Precautions:

1. Concentration of electrolyte should not be too high or too low.
2. Electrodes should be cleaned by sand paper before use.
3. Chemicals should be handled carefully.
4. Electrolyte should not be too heated.

Result/Conclusion: Lemon juice is a conductor of electricity.

Faraday's Laws of Electrolysis

The relationship between the quantity of electricity passed and the quantity of a substance liberated at the electrode is given in the form of Faraday's laws of electrolysis.

1. Faraday's First Law of Electrolysis. This law states that *the mass of a substance liberated at the electrode is directly proportional to the quantity of electricity passed through the electrolyte.*

$$m \propto Q \qquad \text{Here,} \qquad Q = \text{quantity of electricity}$$
$$\propto I \times t \qquad\qquad I = \text{current in amperes}$$
$$= Z \times I \times t \qquad\qquad t = \text{time in seconds}$$
$$Z = \text{constant of proportionality called}$$
$$\textit{electrochemical equivalent (ECE)}$$

If $I = 1$ ampere and $t = 1$ second, then $m = Z$

Thus, **electrochemical equivalent** *of a substance is the amount of substance liberated at the electrode when current of one ampere is passed through the electrolyte for one second.*

2. Faraday's Second Law of Electrolysis. This law states that *the amounts of different substances liberated by the same quantity of electricity passing through their electrolytic solution are directly proportional to their chemical equivalent masses (chemical equivalent mass of metal can be obtained by dividing its atomic mass with number of electrons required to reduce its cation). The law can also be stated as follows; when same quantity of electricity is passed through different electrolytes connected in series then the masses of the substances liberated at the electrodes are in the ratio of their chemical equivalent masses (atomic mass ÷ Number of electrons required to form the product) or the ratio of their electrochemical equivalents.*

For example, if the two electrolytic cells A (Containing $AgNO_3$ solution) and B (Containing $CuSO_4$ solution) are connected in series and same quantity of electricity is passed through the cells. Then the ratio of the mass of copper deposited at cathode in electrolytic cell B (x g) to that of silver deposited in cell A (y g) is equal to the ratio of their chemical equivalent masses.

$$\frac{\text{Mass of Cu}(x)}{\text{Mass of Ag}(y)} = \frac{\text{Chemical Equivalent Mass of Cu}}{\text{Chemical Equivalent Mass of Ag}} = \frac{Z_{Cu}}{Z_{Ag}}$$

Now, each copper (Cu^{2+}) ion requires 2 electrons to form Cu and each Ag^+ needs 1 electron to form Ag. Thus, chemical equivalent mass of Cu is 63.5/2 and that of Ag is 108/1.

Thus, the ratio $\dfrac{x}{y} = \dfrac{63.5}{2 \times 108}$.

‖ 4.5. DIFFERENCE BETWEEN ELECTROCHEMICAL CELL AND ELECTROLYTIC CELL

We have learnt that there are two types of cells namely: *electrochemical cells* and *electrolytic cells*. The former is a device which converts chemical energy into electrical energy. On the other hand, electrolytic cell is a device which converts electrical energy into chemical energy. The two cells also differ significantly with respect to the charges on the electrodes. For example, in electrochemical cell anode is negative whereas in electrolytic cell, the anode is positive. Similarly, cathode is positive in electrochemical cell whereas it is negative in the electrolytic cell. The main points of difference have been summed up as follows in Table 4.1.

Table 4.1. Differences between Galvanic Cell and Electrolytic Cell

Galvanic Cell	*Electrolytic Cell*
1. In galvanic cell, electrical energy is produced.	1. In electrolytic cell, electrical energy is consumed.
2. In galvanic cell, reaction taking place is spontaneous.	2. In electrolytic cell, reaction taking place is non-spontaneous.
3. The two half cells are set up in different containers and are connected through salt bridge or porous partition.	3. Both the electrodes are placed in the solution or molten electrolyte in the same container.
4. In galvanic cell, anode is negative and cathode is positive.	4. In electrolytic cell, the anode is positive and cathode is negative.
5. The electrons move from anode to cathode in external circuit.	5. The electrons are supplied by the external source. They enter through cathode and come out through anode.

4.6. BATTERIES

Any cell or battery that we employ as a source of electrical energy is basically an electrochemical cell. The term **battery** is used to represent the *arrangement of two or more galvanic cells connected in series.* Theoretically, indirect redox reaction is, primarily, the basis of all electrochemical cells. However, in practice the redox reaction used should give the arrangement which fulfills the following requirements:

(*i*) It should be *light* and *compact*;

(*ii*) Its voltage should not vary appreciably during its use;

(*iii*) It should provide power for a longer period; and

(*iv*) It should be rechargeable.

The galvanic cells can be broadly classified into two categories, namely; *primary cells* and *secondary cells*.

Primary Batteries

This type of batteries become dead over a period of time and the chemical reaction stops. They cannot be recharged or used again. Some common examples are *dry cell, mercury cell,* etc.

(*a*) **Dry Cell.** It is a compact form of *Leclanche cell* known after its discoverer. In this cell, *anode* consists of *zinc container* while *cathode* is

a *graphite rod* surrounded by powdered MnO_2 and carbon. The space between the electrodes is filled with the paste of NH_4Cl and $ZnCl_2$. The arrangement is shown in Fig. 4.10.
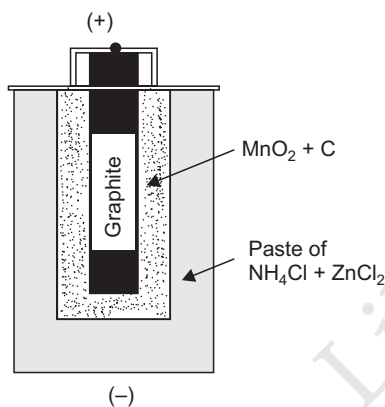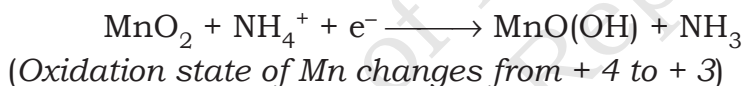

Fig. 4.10. A dry cell.

The reactions taking place at the electrodes are given in their simplified form as follows:
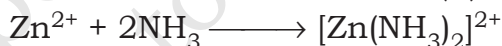
Cathode:

$$MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$$

(*Oxidation state of Mn changes from + 4 to + 3*)

Anode:

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

The zinc ions (Zn^{2+}) so produced combine with ammonia liberated in cathodic reaction to form diammine zinc (II) cation.

$$Zn^{2+} + 2NH_3 \longrightarrow [Zn(NH_3)_2]^{2+}$$

Dry cells do not have long life as NH_4Cl which is acidic, corrodes the zinc container even if the cell is not in use. The cell potential of dry cells lies in the range *1.25 V* to *1.5 V*.

(*b*) **Mercury Cell.** It is miniature cell which finds a frequent use these days to supply energy for watches, video cameras, hearing aids and other compact devices. In mercury cell the *anode* is *zinc-mercury amalgam* and the *cathode* is a paste of *mercury(II) oxide* and *carbon.* Electrolyte is a moist paste of KOH-ZnO. The arrangement in its simple form is shown in Fig. 4.11.
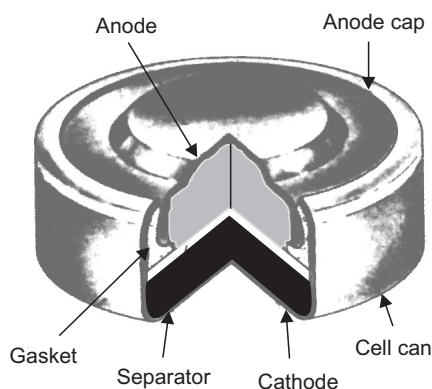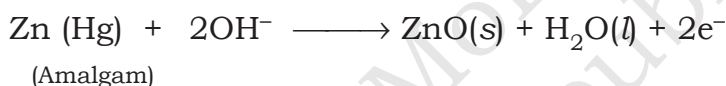
**Fig. 4.11. Commonly used mercury cell. The reducing agent
is zinc and the oxidising agent is mercury (II) oxide.**

The operating voltage for mercury cell is $\simeq$ 1.35 V and the cell reactions are as follows:

Anode:

$$Zn\ (Hg)\ +\ 2OH^-\ \longrightarrow\ ZnO(s) + H_2O(l) + 2e^-$$

(Amalgam)

Cathode:

$$HgO(s)\ +\ H_2O(l) + 2e^- \longrightarrow\ Hg(l) + 2OH^-$$

Net reaction:

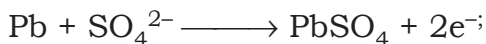$$Zn(Hg)\ +\ HgO(s)\ \longrightarrow\ ZnO(s) + Hg(l)$$

(Amalgam)

Such a cell shows constancy in its potential throughout its life.
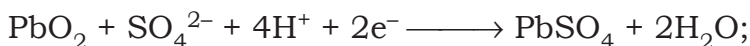
Secondary Batteries

This type of cells can be recharged by passing *direct current* through them and can be used again and again. Some examples are lead-storage battery, nickel-cadmium storage cell, etc. Let us study the working of *lead storage cell.*
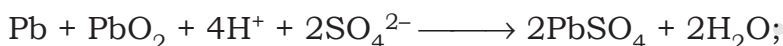
(*a*) **Lead-storage Battery.** It is the most frequently used battery in automobiles. It consists of six voltaic cells connected in series. In each cell *anode* is made of *spongy lead* and *cathode* is a grid of lead *packed with lead dioxide* (PbO_2). The electrolyte is the aqueous solution of H_2SO_4 which is 38% by mass. The reactions taking place in this type of cell can be represented as:

Anode:

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-; \qquad E^\ominus_{oxi} = 0.36 \text{ V}$$

Cathode:

$$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O; \\ E^\ominus_{red} = 1.69 \text{ V}$$

Net reaction:

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O; \\ E^\ominus_{cell} = 2.05 \text{ V}$$

During the working of the cell, the concentration of H_2SO_4 decreases as sulphate ions are consumed to form $PbSO_4$. The $PbSO_4$ precipitates and partially gets coated on both the electrodes. The water formed dilutes the sulphuric acid. With the decrease in the concentration of H_2SO_4 the density of the solution also decreases. The condition of the battery can be easily checked by measuring the density of the solution.

To enhance the output of the cell, the anode and cathode plates are arranged in alternating manner and they are separated by sheets of insulating material. The anode and cathode plates are separately connected to each other so as to increase the electrode area in contact with electrolyte solution. This increases current delivering capacity of the cell. The *groups of electrodes* constitute *one cell* are shown in Fig. 4.12. The cells are further connected in series so as to increase the voltage of the battery. In 6 volts battery there are 3 cells and in 12 volts battery there are 6 cells.
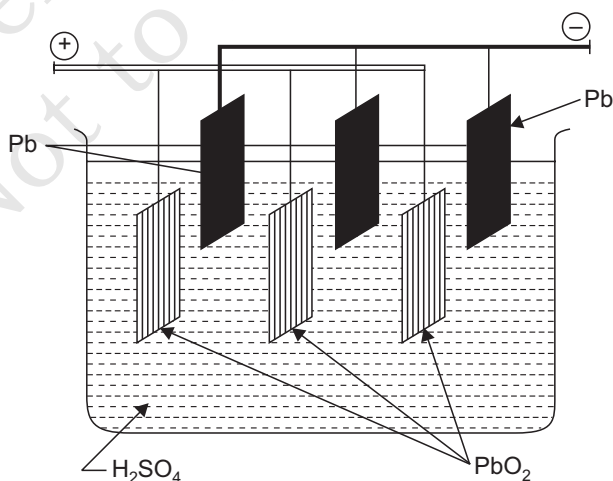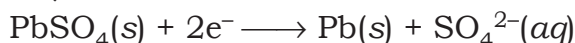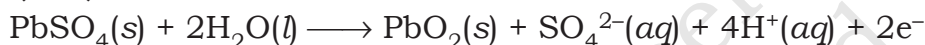

Fig. 4.12. Lead storage cell.

Recharging the battery. The battery can be recharged by connecting it to an external source of *direct current* with voltage greater than 12 V. It forces the electrons to flow in opposite directions resulting in the deposition of Pb on the anode and PbO_2 on the cathode.

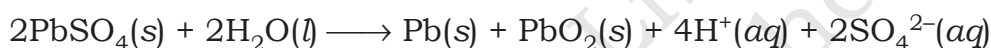During *recharging* operation, the cell behaves as *electrolytic cell*. The recharging reactions are:

Cathode (–ve):
$$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$$

Anode (+ve):
$$PbSO_4(s) + 2H_2O(l) \longrightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$$

Net:
$$2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)$$

Such an operation becomes possible because $PbSO_4$ formed during discharge operation is solid and sticks to the electrodes. Therefore, it is in a position to lose or gain electrons during electrolysis.

The discharging and recharging of lead storage battery has been shown in Figs. 4.13 (*a*) and 4.13 (*b*) respectively.

In an automobile, the battery is discharged when the engine is started. While running, the engine powers the alternator which produces electrical energy sufficient enough to recharge the battery. Thus, battery is constantly recharged as long as the automobile is being driven.
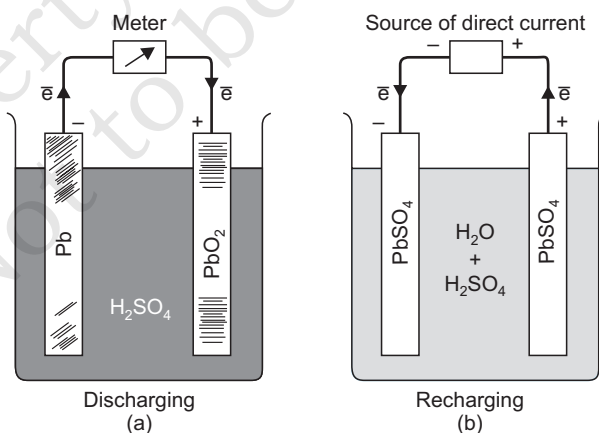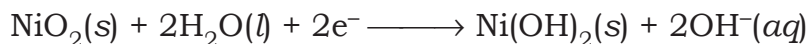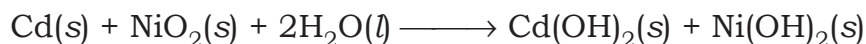

Fig. 4.13. Charging and recharging of lead storage cell.

(*b*) **Nickel-cadmium Storage Cell.** It is another rechargeable cell. It consists of *cadmium anode* and the cathode made of a metal grid containing *nickel (IV) oxide*. These are immersed in KOH solution. The reactions occurring are:

Anode:

$$Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$$

Cathode:

$$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$$

Net reaction:

$$Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

The cell is also called ***nicad cell*** and has *voltage* ≈ **1.4 V.**

As is evident, there are no gaseous products, the products formed adhere to the electrodes and can be reconverted by *recharging process.* This cell is becoming more popular these days and finds use in electronic watches and calculators.

Fuel Cells

In recent years, the scientists have designed the cells which convert **chemical energy of a fuel directly into electrical energy.** Such cells are called **fuel cells.** These are the voltaic cells in which, the fuels such as H_2, CO, CH_4, C_3H_8, etc., are used to generate electrical energy without the intervention of thermal devices like boiler, turbines, etc.

The conventional method of conversion of chemical energy of a fuel into electrical energy involves combustion of a fuel to liberate heat. The heat energy so produced is used to generate steam for spinning the turbines which are coupled to electrical generators. This process is approximately 40% efficient.

Fuel cells are designed in such a way that the materials to be oxidised and reduced at the electrodes are stored outside the cell and are constantly supplied to the electrodes. In fact, fuel cell is a *flow battery* that continues to operate as long as the reactants from out side are fed into it. One of the most successful fuel cells uses the reaction of *hydrogen* and *oxygen* to form water and is known as H_2—O_2 fuel cell. The H_2—O_2 fuel cell is also called **Bacon cell** after the name of its inventor and it had been used to power the *Apollo space Missions.* The water vapours produced during the reaction were condensed and added to drinking water supply for the astronauts. The experimental arrangement is shown in Fig. 4.14.
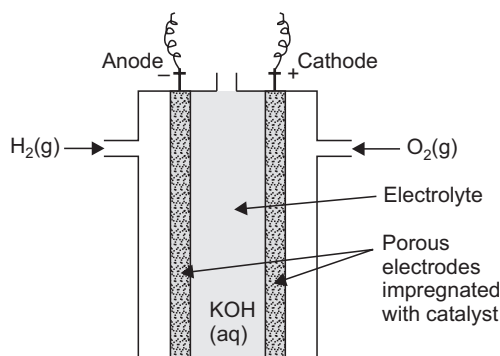
Fig. 4.14. A single bacon cell.

The cell consists of porous carbon electrodes which are impregnated with catalyst (Pt, Ag or CoO). Hydrogen and oxygen are bubbled through the electrodes into electrolyte which is an aqueous solution of NaOH or KOH.
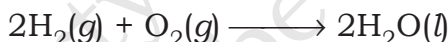
The electrode reactions are:

Anode:

$$[H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-] \times 2$$

Cathode:

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$

Net reaction:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

The cell runs continuously as long as the gases hydrogen and oxygen are supplied at the temperature 525 K and 50 atm. pressure.

Advantages of Fuel Cells

Some prominent advantages of fuel cells are being described as follows:

1. **Pollution Free Working.** There is no harmful or objectionable product formed in fuel cells. Hence they do not cause pollution problems.

2. **High Efficiency.** The efficiency of fuel cells is approximately 70—75%, which is much higher than the conventional cells.

4.7. CORROSION

It is commonly observed that surface of certain metallic objects slowly gets coated with oxide or some other salt of the metal on long exposure to the atmosphere. **For example**:

• silver gets tarnished,

- copper develops green coating on its surface,
- iron rusts, and
- lead loses its lustre.

In fact, such metals react with the gases or moisture present in the environment to develop the coating of undesirable compounds and the metal is slowly eaten up. This process in general is referred to as *corrosion.* **Corrosion** may, thus, be defined as *the process of slow conversion of metals into their undesirable compounds (usually oxides) by reaction with moisture and other gases present in the atmosphere.*

Factors Which Affect Corrosion

The factors which affect the rate of corrosion are:

(*i*) **Reactivity of the metal.** The more active metals are more prone to corrosion.

(*ii*) **Presence of impurities.** Presence of impurities helps in setting up a corrosion cell and makes the corrosion to occur rapidly. For example, pure iron does not rust.

(*iii*) **Air and moisture.** Air and moisture are quite helpful in corrosion. The presence of gases like CO_2 and SO_2 in air makes it still rapid. For example, no rusting is caused if iron is kept in vacuum.

(*iv*) **Strains in metal.** Strains in metal also help in corrosion. For example, in iron articles, rusting is more pronounced on the areas having bends, dents, scratches, nicks and cuts.

(*v*) **Presence of electrolytes.** The presence of electrolytes also makes the corrosion process faster. For example, iron rusts more rapidly in saline water in comparison to pure water.

Let us understand the **mechanism of corrosion** by studying the most familiar example of **rusting of iron.** Chemically rust is hydrated iron (III) oxide, $Fe_2O_3 \cdot xH_2O$. It is generally caused by moisture, CO_2, O_2 of air. Rust is a non-sticking brown-coloured material which can be easily removed by scratching. There are a number of theories about the mechanism of rusting. The most widely accepted theory is *electrochemical theory* which is being discussed here.

Electrochemical Theory of Rusting

According to this theory, the *impure iron* surface behaves like a small electrochemical cell in presence of water containing dissolved oxygen or carbon dioxide. Such a cell is also called *corrosion cell* or *corrosion couple.* In these miniature corrosion cells, pure iron acts as anode and
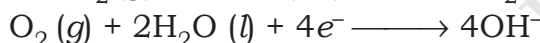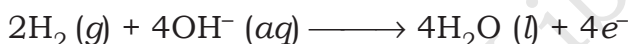
impurity site acts as cathode. Moisture having dissolved oxygen and carbon dioxide in it constitutes electrolytic solution.

Developments in Fuel Cells

One of the problem with H_2—O_2 fuel cells is that their power per unit mass is too low. This makes their practical use difficult in automobiles. Intensive developments are being done to use different catalysts and different electrolytes in these cells. Some examples of H_2—O_2 fuel cells which use different electrolytes are as follows:

(*i*) *Alkaline fuel cells (AFCs).* Here, the electrolyte is aqueous KOH
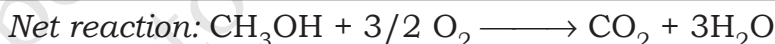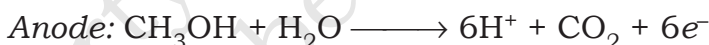
The reaction involved are

$$2H_2 (g) + 4OH^- (aq) \longrightarrow 4H_2O (l) + 4e^-$$
$$O_2 (g) + 2H_2O (l) + 4e^- \longrightarrow 4OH^-$$

(*ii*) *Phosphoric acid fuel cells (PFCs).* Here, the electrolyte is aqueous H_3PO_4
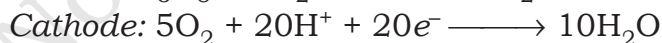
(*iii*) *Molten carbonate fuel cells.* The electrolyte is $K_2CO_3 (l)/Si_2CO_3 (l)$

In addition to this, the fuel cells based on the combustion of **hydrocarbons** like CH_4, C_2H_6, C_3H_8, etc, and **alcohols** such as CH_3OH, C_2H_5OH, etc., in the presence of catalysts, have been designed. Some examples are

(*i*) *Direct methanol fuel cell (DMFC).* Here, the electrolyte is polymer membrane and the electrode reactions are

Anode: $CH_3OH + H_2O \longrightarrow 6H^+ + CO_2 + 6e^-$
Cathode: $3/2\ O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$
_____
Net reaction: $CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 3H_2O$

(*ii*) *Propane oxygen fuel cell.* The electrode reactions are

Anode: $C_3H_8 + 6H_2O \longrightarrow 3CO_2 + 20H^+ + 20e^-$
Cathode: $5O_2 + 20H^+ + 20e^- \longrightarrow 10H_2O$
_____
Net reaction: $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 10H_2O$

In recent years **zinc-air fuel cell (ZAFC)** has been developed in U.S. as a source of power in automobiles. Here, electrolyte is aqueous alkali (KOH) and the electrode reactions are

Anode: $Zn + 2OH^- \longrightarrow Zn (OH) + 2e^-$
Cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^{-2}$
_____
Net reaction: $2Zn + 2O_2 + 2H_2O \longrightarrow 2\ Zn (OH)_2$

Anodic reaction involves oxidation of Fe atoms to Fe^{2+} ions

$$Fe(s) \longrightarrow Fe^{2+} (aq) + 2e^- ; E^{\ominus}_{oki} = -0.44 \text{ V} \qquad \dots (i)$$

The Fe^{2+} ions so produced go into solution and the electrons lost are pushed through in the metal to cathodic site.

The *cathodic reaction* involves the reduction of dissolved O_2 to H_2O in the presence of H^+ ions present in the electrolyte solution. The H^+ ions are believed to be formed by dissolution of CO_2 and other acidic gaseous oxides from the atmosphere in water
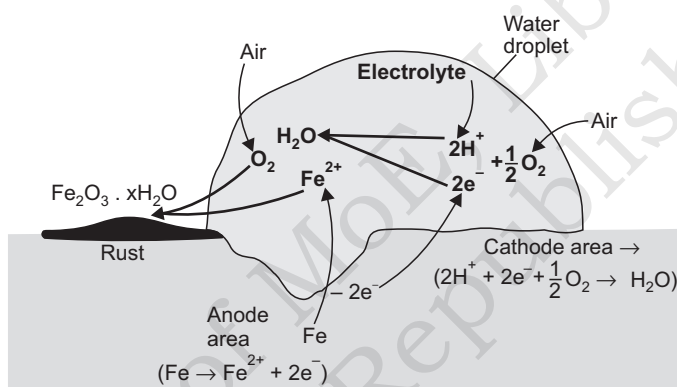
$$(CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-).$$

$$2H^+ + \tfrac{1}{2} O_2 + 2e^- \longrightarrow H_2O ; E^{\ominus}_{red} = 1.23 \text{ V} \qquad \dots(ii)$$

Fig. 4.15. Rusting of iron.

The net reaction of the corrosion cell can be obtained by adding equations (*i*) and (*ii*).

$$Fe + 2H^+ + \tfrac{1}{2} O_2 \longrightarrow Fe^{2+} + H_2O ; E^{\ominus}_{cell} = 1.67 \text{ V}$$

The ferrous ions so formed move through electrolyte and come at the surface of iron object where these are further oxidised to *ferric state* by atmospheric oxygen and constitute rust which is hydrated iron (III) oxide.

$$2Fe^{2+} + \tfrac{1}{2} O_2 + 2H_2O \longrightarrow Fe_2O_3 + 4H^+$$

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3.xH_2O$$

$$\text{(Rust)}$$

It is worth mentioning here, that H^+ ions play significant role in redox reaction leading to rusting. Decrease in the concentration of H^+ ions (*i.e.,* increasing the pH) makes rusting less favourable. It has been observed that at a pH > 9–10 rusting does not occur.

Prevention of Corrosion

Corrosion causes severe damage to briges, buildings, ships and all other structures made of metals espacially iron. Lot of money has to be spent every year to repair or replace the rusted structures. However, these are several methods for protecting metals from corrosion (iron from rusting). Some of these methods are being discussed as follows:

1. Barrier Protection. In this method, a barrier film is introduced between iron and atmospheric oxygen and moisture. Barrier protection can be achieved by any of the following methods:

   (*i*) *by painting the surface.*

  (*ii*) *by coating the surface with a thin film of oil or grease.*

 (*iii*) *by electroplating iron with some non-corrosive metal such as nickel, chromium, copper, etc.*

In this type of protection, if scratches or cracks appear in the protective layer then surface of iron may get exposed. In this region, moisture and oxygen may come in contact with iron and rusting starts. This rusting extends beneath the protective layer and eventually peels off the protective layer.

2. Sacrificial Protection. In this method, surface of iron is covered with a layer of *more active metal* like zinc. This active metal loses electrons in preference to iron and hence, prevents the rusting of iron. However, the covering metal gets consumed in due course of time, but so long as it is present, even the nearly uncovered surfaces of iron do not get rusted. In this way, scratches in the protective layer of this type are not harmful. This type of protection is called **sacrificial protection.**

Zinc metal is generally used for protecting iron and the process is called **galvanization.** Galvanized iron sheets maintain their shine due to the formation of a thin protective layer of basic zinc carbonate, $ZnCO_3$. $Zn(OH)_2$ due to the reaction between zinc, oxygen, CO_2 and moisture in air.

Zinc, magnesium and aluminium powders dissolved in paints can also be applied as protective layers. The well known aluminium paint contains aluminium powder suspended in varnish.

3. Electrical Protection. This is also a case of sacrificial protection. In this method, the exposed surface of iron is protected by connecting it to some more active metal such as magnesium. The other metals which can be used for this purpose are aluminium, zinc, etc. The more active metal acts as anode and loses electrons in preference to iron. The iron surface, acts as cathode. This method, therefore, is also called **cathodic**

protection of iron. Underground water pipes or tanks made of iron are protected by connecting them to more easily oxidisable metal as shown in Fig. 4.16.
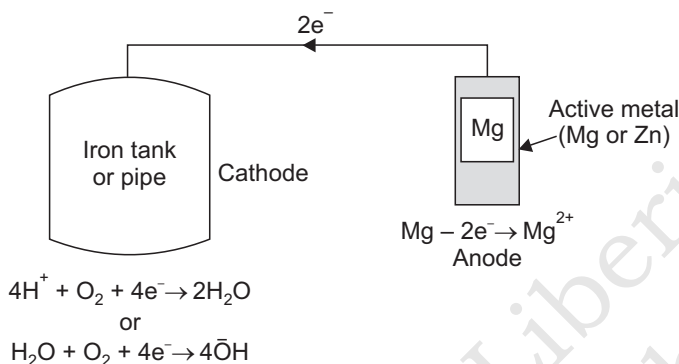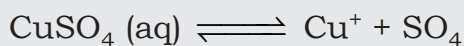

Fig. 4.16. Protection of underground pipe or tank.

4. Use of Anti-rust Solutions. The alkaline solutions of some phosphate and chromate salts act as anti-rust solutions. For example, when iron articles are dipped into the boiling and strongly alkaline solution of sodium phosphate, a protective insoluble film of iron phosphate is formed on them. This film protects the articles from rusting. The alkaline nature of solutions decreases the availability of H^+ ions which facilitate the oxidation of iron to Fe^{2+}.

EXPERIMENT 4

Aim: Electroplating of copper.

Theory: Electroplating is done to prevent objects from corrosion and for decoration purpose when any object is to be electroplated by copper that object is made cathode. Anode taken is of pure copper and aqueous solution of copper sulphate is used as electrolyte. When current is passed through the circuit copper ions are released from anode and a thin, fine, file of copper is deposited on cathode. An equivalent amount of copper is lost, by the pure copper anode and is dissolved in copper sulphate solution.

$$CuSO_4 \text{ (aq)} \rightleftharpoons Cu^+ + SO_4$$

Apparatus and chemicals: One beaker or a tub, pure copper rod for anode, the object to be plated, aqueous copper sulphate solution, connecting wires, a battery galvanometer, etc.

Procedure:

1. Take beaker or the tub.

2. Fill it more than half with aqueous copper sulphate solution.

3. Immerse copper rod and the object to be plated in aqueous solution and connect with the battery with the help of connecting wires, as shown in the picture.

4. Allow the current to flow in the circuit.

Observation: When current is passed through $CuSO_4$(aq) solution, we observe that a thin, fine film of copper is deposited on the surface of the object.

Pure copper anode

Object to be plated on cathode

$CnSO_4$(aq)

Copper electroplating

Fig. 4.17

Precautions:

1. Follow all electric safety precautions.

2. Ventilation should be good so that copper sulphate fumes do not accumulate in the lab or room as copper sulphate is poisonous.

3. Do not overheat the electrolyte ($CaSO_4$(aq))

4. Do not use rings and other jewelleries while doing electroplating.

EXPERIMENT 5

Aim: To extract and purify metal (copper) by using the process of electroplating.

Theory: For extraction and purification of copper electroplating can be used. Electrolyte of copper can be used. When electrolysis is done the copper ions get depleted from anode (Impure copper rod) and dissolve in copper sulphate (electrolyte). Copper sulphate dissociates into Cu^{++} ions and SO_4 ions. Copper ions depleted from anode get deposited on cathode after passing through the copper sulphate solution leaving

impurities in the base of vessel in which electrolyte is filled. Copper deposit on cathode is pure.

Procedure:

1. Take a beaker, bottle or any other vessel as per requirement and pour $CuSO_4$ (aq) solution in it.
2. Take impure copper rod as anode and pure rod as cathode.
3. Now pass too current through the electrolyte.

Observation: We see that thickness of anode decreases due to depletion of copper ions while thickness of cathode increases due to deposition of pure copper on it.

Precautions:

1. Concentration of electrolyte should not be too high or too low.
2. Electrodes should be cleaned by sand paper before use.
3. Chemicals should be handled carefully.
4. Electrolyte should not be too heated.

Hydrogen Economy

One of measure of progress and development of any country is the per capita consumption of energy. The energy requirement increases as more and more people aspire to improve their living standard. At present the main source of energy that drives our economy is carbonaceous fossil fuels such as coal, oil, gas, etc. The major drawbacks with fossil fuels are as under:

(*i*) Their reservoirs are getting exhaused very fast.

(*ii*) CO_2, the major product of their combustion is responsible for *Greenhouse Effect* which leads to serious globle problems.

Thus, the use of carbonaceous fuels has to be made limited so as to avoid these problems. Hydrogen economy is the future vision of energy. In fact, **hydrogen economy** *is a proposal of energy distribution system based on hydrogen gas as energy carrier.* The hydrogen could be used either for burning to generate heat or in fuel cells to generate electricity. Thus, hydrogen provides an alternative source of energy which is renewable as well as non-polluting. The vision of hydrogen economy lies in its production by electrolysis of water using solar energy and its use as fuel and making fuel cells. All these technologies are based on electrochemical principles.

4.8. PRACTICAL APPLICATIONS OF ELECTROLYSIS

Electrolysis is the process of chemical dissociation, when current is passed through an electrolyte. The electrolyte contains positive and negative ion which are the cause of passage of electric current through it. Electrolysis is used in industries for several purposes. Practical applications of electrolysis are:

1. **Electroplating:** Electroplating uses the process of electrolysis for coating an object with thin film of metal during electrolysis by an electrolytic solution. During electroplating the article to be plated is used as cathode in the electroplating process and the metal plated on the object is used as anode. The electrolytic solution on bath contains an electrolytic solution of the metal to be plated. When a low voltage electric current is passed through the electrolyte, the metal ions from the electrolyte gain electrons from the cathode (object) as metal coating. Some way metal atoms on the anode loose electrons on the anode and go as ions into the electrolyte. Metal ions from the anode keep on depleting from anode and keep on depositing on cathode via electrolyte keeping the concentration of metal ion in the electrolyte.

Quality of electroplating depends upon following factors:

(*a*) Concentration of metal ions to be deposited on the object has to be carefully controlled in the plating solution so that a fine uniform layer of the plating material is deposited on the object to be electroplated.

(*b*) The type of electrolyte and its concentration should be carefully selected.

(*c*) Such compound which control the acidity and increase the conductivity must be included in the solution.
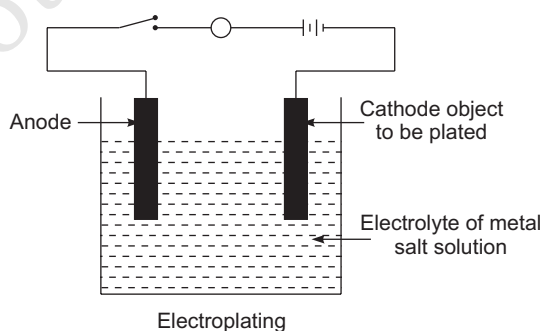

Electroplating

Fig. 4.18

(*d*) Metal to be deposited on the object has to be selected wisely as per requirement so as to make it brighter or smoother.

(*e*) It is better if anode is shaped like cathode where object is place, so as to achieve even metal coating.

(*f*) To get even deposit all over the object either cathode should be surrounded by several anodes or the cathodes must be rotated at uniform speed.

It is to be noted that for gold and silver plating, the electrolyte used should be alkaline white for nickel or copper plating the electrolyte should be acidic.

2. **Extraction and refining of metals:** In the process of extraction and refining of metal by using electrolysis, the impure metal rode is used as anode and the aquous solution of salt of metal to be refined is taken as electrolyte. When process of electrolysis is done, the metal from anode gets dissolved in the electrolyte and pure metal gets deposited on the cathode, maintaining the metal ion concentration in the electrolyte.

3. **Production of Chemicals:** Electrolysis is used in many industries for bulk production of chemicals like causic soda, potassium permanganate, ammonium per sulphate hydrogen, oxygen etc.

4. **Production of non-metal:** Electrolysis is used to obtain non-metals such as hydrogen, fluorine, chlorine. Hydrogen is obtained in the presence of electrolytes such as H_2SO_4, and KNO_2, through the electrolysis of water.

5. **Electrotyping:** Electroplating is an electrolytic process for making metal parts that exactly reproduce the given design. It is a special application of electroforming and mainly used to reproduce printing.

6. **Anodizing:** The process of deposition of a thin film of protective oxide on a surface of metal by using electrolytic process is known as anodizing. It is mainly used to protect the metal from corrosion.

6. **Electropolishing:** Electropolishing is an electrolytic process used to remove flaws from the surface of any metal part. In electrolytic polishing a layer of material, is removed from metallic surface to give it a polished surface.

7. **Electrocleaning:** It is the process of soil, scale, greese or corrosion from the surface of a metal. Here article to be cleaned is made cathode. When heavy current is passed through electrolyte caustic soda and hydrogen are produced which remove the greese from article surface. This type of cathodic cleaning zinc and aluminium articles are cleaned. In anodic cleaning article to be cleaned are made anode.

SUMMARY

- **Electrochemical Cell:** A device that converts chemical energy into electrical energy.
- **Anode:** In electrochemical cells, the anode is the electrode at which oxidation takes place. It is the negative terminal.
- **Cathode:** In electrochemical cells, the cathode is the electrode at which reduction takes place. It is the positive terminal.
- **Electrochemical Series:** Arrangement of various elements and electrode reactions in the increasing order of their reduction potentials.
- **Fuel Cell:** A device which converts chemical energy of a fuel directly into electrical energy.
- **Electrolyte:** A substance that dissociates in solution to produce ions and hence conducts electricity in dissolved state or molten state.
- **Degree of Dissociation (α):** Fraction of total number of molecules that dissociates in solution.

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^c}$$

- **Electrolysis:** The process of decomposition of electrolyte as a re sult of passage of electricity through its aqueous solution or through its molten state.

EVALUATION

1. Which of the following is the strongest oxidising agent?
   - (a) Cl^-
   - (b) Mn^{2+}
   - (c) MnO_4^-
   - (d) Cr^{3+}
2. Which among the following is the most stable oxidised species?
   - (a) Cr^{3+}
   - (b) MnO_4^-
   - (c) $Cr_2O_7^{2-}$
   - (d) Mn^{2+}
3. Which of the following is the strongest reducing agent?
   - (a) Cr^{3+}
   - (b) Cl^-
   - (c) Cr
   - (d) Mn
4. What is true about the cell constant of a conductivity cell?
   - (a) It changes with change of electrolyte.

    (*b*) It changes with change of concentration of electrolyte.

    (*c*) It changes with temperature of electrolyte.

    (*d*) It remains constant for given cell.

5. Which of the following statement is correct?

    (*a*) E_{cell} and $\Delta_r G$ of cell reaction both are extensive properties.

    (*b*) E_{cell} and $\Delta_r G$ of cell reaction both are intensive properties.

    (*c*) E_{cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive properties.

    (*d*) E_{cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property.

6. An electrochemical cell can behave like an electrolytic cell when

    (*a*) $E_{cell} = 0$ (*b*) $E_{cell} > E_{ext}$

    (*c*) $E_{ext} > E_{cell}$ (*d*) $E_{cell} = E_{ext}$

7. During charging of lead storage battery,

    (*a*) $PbSO_4$ cathode is reduced to Pb.

    (*b*) $PbSO_4$ anode is reduced to Pb.

    (*c*) $PbSO_4$ cathode is oxidised to Pb.

    (*d*) $PbSO_4$ anode is oxidised to PbO_2.

8. An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to

    (*a*) increase in number of ions

    (*b*) increase in ionic mobility

    (*c*) 100% ionisation of electrolyte at normal dilution

    (*d*) increase in both, *i.e.*, number of ions and ionic mobility of ions.

9. Identify the correct statement

    (*a*) Corrosion of iron can be minimized by forming an impermeable barrier at its surface

    (*b*) Iron corrodes in oxygen free water

    (*c*) Iron corrodes more rapidly in salt water because its electrochemical potential is higher.

    (*d*) Corrosion of iron can be minimized by forming a contact with another metal with higher reduction potential.

10. Consider the statement S_1 and S_2

S_1: Conductivity always increases with decrease in concentration of electrolyte.

S_2: Molar conductivity always increases with decrease in concentration of electrolyte.

Mark the correct answer:

    (*a*) Both S_1 and S_2 are wrong

    (*b*) S_1 is wrong S_2 is correct

   (c) S_1 is correct S_2 is wrong

   (d) Both S_1 and S_2 are correct

II. Descriptive Questions

  1. State and explain Faraday's first law of electrolysis.

  2. What is battery ?

  3. What are the fuel cells ? Explain the working of $H_2 - O_2$ fuel cell.

  4. Differentiate between electrochemical cell and electrolytic cell.

  5. What is uses of Daniel cell?

  6. What is meant by electrochemical cell?

  7. What are differences between galvanic cell and electrolytic cell?

  8. Define the fuel cells.

  9. Write the some advantages of fuel cell.

10. Explain the factors which affect the rate of corrosion.

III. Numerical Questions

  1. Identify oxidants and reductants in the following reactions.

    (a) $CH_4(g) + 4Cl_2 (g) \longrightarrow CCl_2(g) + 4HCl(g)$

    (b) $H_2S(aq) + Cl_2 (aq) \longrightarrow S(s) + Cl^-(aq)$

    (c) $MnO_4^- + C_2H_5OH(aq) \longrightarrow Mn^{+2} (aq) + CH_2COOH(aq)$

    (d) $AS_2S_2(s) + NO_3^-(aq) \longrightarrow AsO_4^{-2} (aq) + NO_2 (g) + S(s)$

  2. How many coulombs of electricity are required for

    (i) Oxidation of 90 g of water

   (ii) Reduction of 0.2 moles of CrO_7^{2-} and Cr^{3+}.

  (iii) Complete reduction of MnO_4^- ions in 500 ml of 0.5 m solution to Mn^{2+}
      ions.   (**Ans.** (i) 9.65×10^5 C (ii) 115800 C (iii) 120625 C)

  3. In the reactions given below, identify the species undergoing oxidation
    and reduction

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

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

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

  4. How many grams of chlorine can be produced by the electrolysis of molten
    NaCl by a current of 1.00 amp for 15 minutes?   (**Ans.** 0.33 g)

  5. The electrolysis of an acetate of an acetate solution produces ethane
    according to the reaction.

    $2CH_3COO^- \longrightarrow C_2H_6 + 2CO_2 + 2e-$ (**Ans.** 1.35 L, 2.70 L)

  6. Potassium chlorate is prepared by electrolysis of KCl in basic solution as

              $6OH^- + Cl^- \longrightarrow ClO_3^- + 3H_2O + 6e^-$

    What is the time required to produce 10 g of $KClO_3$ using current of 3
    amp?   (**Ans.** 4.37 ms)