Unit -12

Electrochemistry

After reading this unit, the students will be able to:

- Give the characteristics of a Redox reaction. (Understanding)
- Determine the oxidation number of an atom of any element in a pure substance. (Applying)
- Define oxidation and reduction in terms of a change in oxidation number. (Applying)
- Use the oxidation-number change method to identify atoms being oxidized or reduced in redox reactions. (Applying)
- Use the oxidation-number change method to balance redox equations. (Applying)
- Balance redox reactions that take place in acid solutions. Break a redox reaction into oxidation and reduction half reactions. (Applying)
- Use the half reaction method to balance an unbalanced a redox equation. (Applying)
- Define cathode, anode, electrode potential and S.H.E. (Standard Hydrogen Electrode). (Remembering)
- Identify the substance oxidized and the substance reduced in a dry cell. (Applying)

Teaching

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Assessment

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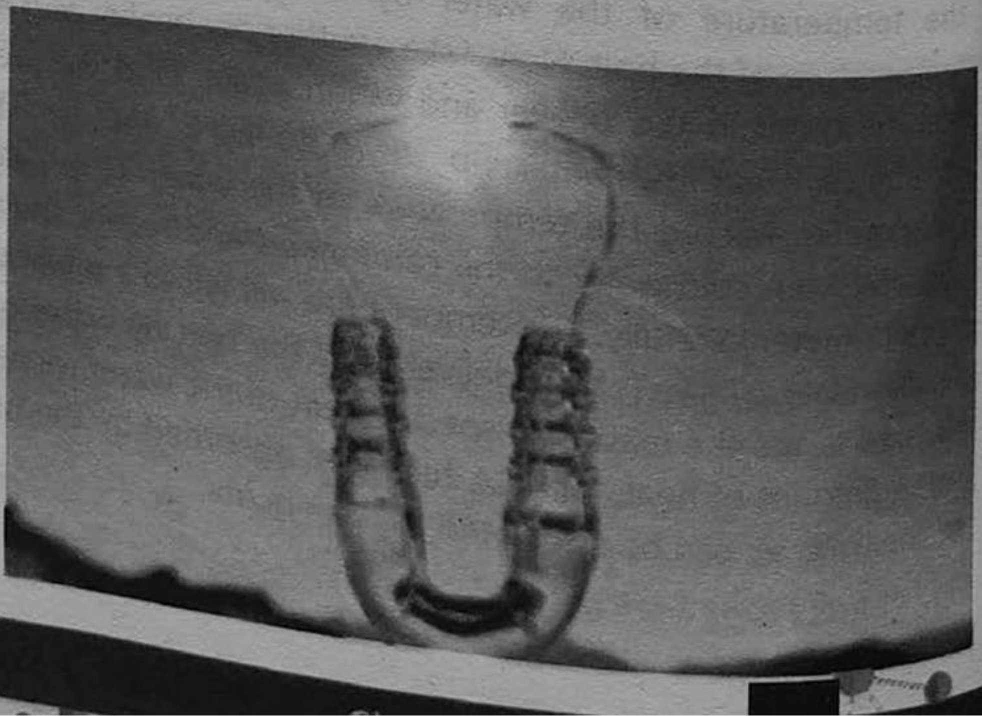
Weightage %

08



- Use the activity series of metals to predict the products of single replacement reactions. (Applying)
- Define cell potential and describe how it is determined. (Understanding)
- Describe the reaction that occurs when a lead storage battery is recharged. (Applying)
- Explain how a fuel cell produces electrical energy. (Applying)
- Define the standard electrode potential of an electrode. (Remembering)
- Distinguish between electrical terms such as coulomb, ampere and volt. (Understanding)
- State and explain Faraday's laws. (Understanding)
- Describe how dry cell supplies electricity. (Understanding)
- Explain how a lead storage battery produces electricity. (Understanding)
- Define corrosion and describe simple methods like electroplating and galvanizing for its prevention. (Applying)

Introduction

Electrochemistry is the branch of chemistry which deals with the chemical changes that take place in the matter by passage of electric current and conversion of chemical energy into electrical energy and vice versa. The passage of electricity through the solutions of acids, bases and salts is accompanied by a chemical change. Such substances which allow electric current to pass through them in solution form or in molten form are called electrolytes.

In this unit, you will refresh your knowledge about certain basic terminologies used in the field of electrochemistry.

Conductors

Substances which allow the flow of electric current through them are known as conductors. The flow of current in metallic conductors, e.g. Cu, Ag etc. is due to the movement of electrons in the metal without any chemical change, while passage of electricity through the solutions of acids, bases and salts is accompanied by a chemical change.

Electrolytes

The substance which in solution or in molten state conducts electricity is called an electrolyte. Electrolytes may be strong or weak depending upon the extent of ionization.

Strong Electrolytes

The substance which is completely converted into its ions in the solution or in the molten state is called a strong electrolyte e.g. NaCl, NaOH and H_2SO_4.

Weak Electrolytes

The substance which is partially dissociated into its ions is called a weak electrolyte e. g. NH_4OH and H_2CO_3.

Electrolytic Conduction or Electrolysis

Electrolysis is a phenomenon in which chemical change takes place at the surface of electrodes due to the passage of the electric current. On passing the current through an electrolytic solution, ions migrate to the opposite electrodes where the gain and loss of electrons take place which bring about the chemical change.

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Application of Redox Reactions and Electrolysis

Some important applications of electrolysis on industrial scale are as follows:

1) Batteries use oxidation and reduction reactions to produce direct current (DC).
2) Inside the rocket propellant, a redox reaction takes place.
3) Many metals are separated from their ores with the help of redox reactions.
4) Production of hydrogen gas by electrolysis of water.
5) Manufacture of heavy water, D_2O.
6) The metals, like Na, K, Mg, Al etc. are obtained by electrolysis of fused electrolytes containing these metals.
7) Compounds, like NaOH, KOH, Na_2CO_3, $KClO_3$, $KMnO_4$ etc. are synthesized by electrolysis.
8) Electroplating is the process of coating an object made of inferior metal with a superior metal by electrolysis is known as electroplating.
9) Purification of metal by electrolysis. In this method pure metal is deposited at cathode from a solution containing metal ions, e.g. Ag, Cu etc., where anode is a piece of impure metal.

12.1 Oxidation-Reduction Concepts

12.1.1 Oxidation and Reduction

Oxidation and reduction can be defined in different ways.

A. The Classical Concept

According to this concept, oxidation and reduction are defined as

i. The addition of oxygen is oxidation while the removal of oxygen is reduction. e.g. SO_2 is oxidized to SO_3 by gaining O while CO_2 is reduced to C by removal of O.

$$2SO_2 + O_2 \longrightarrow 2SO_3 \quad \text{(oxidation)}$$
$$CO_2 \longrightarrow C + O_2 \quad \text{(reduction)}$$

ii. The removal of H_2 is oxidation while its addition leads to reduction reaction. e.g. NH_3 is oxidized to N_2 while Cl_2 is reduced to HCl.

$$2NH_3 \longrightarrow N_2 + 3H_2 \quad \text{(oxidation)}$$
$$H_2 + Cl_2 \longrightarrow 2HCl \quad \text{(reduction)}$$

B. Electron Transfer Concept

This concept is about the transfer of electrons from one element to another. The concept is explained below.

The atom which loses electrons is said to be oxidized and this process is called oxidation. The atom which gains electrons is reduced and the phenomenon is called the reduction. In terms of oxidation number an increase in oxidation number is oxidation and decrease in oxidation number is reduction. For example

$$Al_{(s)} \longrightarrow Al^{3+}_{(aq)} + 3\bar{e} \quad \text{(Electron loss and increase in oxidation number; oxidation)}$$

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \quad \text{(Addition of electron and decrease in oxidation number; reduction)}$$

$$2Al_{(s)} + 3Cu^{2+}_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3Cu_{(s)} \quad \text{(Net reaction)}$$

12.1.2 Oxidation State or Oxidation Number

The oxidation state is the apparent charge, positive or negative, which an atom would have in a molecule or ion. It is different from the valency because valency is only a number while oxidation state indicates the positive or negative charge of the atom. The oxidation state of an atom is described by its oxidation number which is assigned according to the following rules.

Rules for assigning the Oxidation number

i. The oxidation number of a free element is zero, e.g. oxidation number of H_2, O_2 and Mn is zero.

ii. The oxidation number of hydrogen in its compounds is +1 but in metal hydrides it is −1, e.g. NaH and MgH_2.

iii. The oxidation number of oxygen in the compounds is -2 but in peroxides it is −1 and in OF_2 is +2.

iv. The oxidation numbers of the elements of groups I, II and III in the compounds are +1, +2 and +3 respectively.

v. The oxidation number of the halogens of group VII in the binary compounds is −1.

vi. The algebraic sum of the oxidation numbers of all the atoms in a molecule is zero.

vii. The algebraic sum of the oxidation numbers of all the atoms in an ion is equal to the charge on the ion.

Example 12.1:

Calculate the oxidation number of Cr in $K_2Cr_2O_7$.

Oxidation Number of K = +1
Oxidation Number of O =-2
Oxidation Number of Cr = X

Putting these values in the formula $K_2Cr_2O_7$

$2(+1) + 2X + 7(-2) = 0$

$2 + 2X - 14 = 0$ $2X = 12$ $X = 6$

Practice Problem: 12.1

Calculate the oxidation number of S in H_2SO_4.

12.1.3 Recognizing oxidation and reduction reactions

Oxidation reduction reactions are reactions in which electrons are lost by an atom or ion in one reactant and gained by an atom or ion in another reactant. In order to tell whether a redox reaction has occurred or not, we need a way to keep track of electrons and assign oxidation numbers to the atoms or ions involved in a chemical reaction.

In any redox reaction, you can recognize the species oxidized or reduced by noting the change in their oxidation number. A species with an increase in oxidation number is said to be oxidized and the one with decrease in oxidation number is said to be reduced as clear from the following example. In organic reactions, the concept of addition or removal of oxygen or hydrogen can also be helpful in such case.

Example 12.2:

Determine which element is oxidized and which one is reduced in the following reactions.

a) $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

b) $2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$

Solution:

a. Zn is oxidized (oxidation number: $0 \rightarrow +2$); H^+ is reduced (Oxidation number $+1 \rightarrow 0$).

b. Al is oxidized (oxidation number: $0 \rightarrow +3$); Cu^{2+} is reduced ($+2 \rightarrow 0$).

Thus when oxidation occurs, an element loses electrons and its oxidation number increases (become more positive). When reduction occurs, an element gains electrons and it oxidation number decreases or is reduced (becomes more negative).

(i) Oxidizing Agent

The substance which oxidizes other substances and itself gets reduced during this process is called oxidizing agent. The oxidation number of the oxidizing agent is decreased in the reaction e.g. the oxidation number of Cl_2 in above reaction is decreased from 0 to -1, therefore, Cl_2 is an oxidizing agent.

(ii) Reducing Agent

The substance which reduces other substances and itself gets oxidized during this process is called reducing agent. The oxidation number of the reducing agent is increased e.g. the oxidation number of Na in above reaction is increased from 0 to +1 so it is a reducing agent.

Balancing Oxidation Reduction Equations

A large variety of chemical reactions involve oxidation and reduction processes which are expressed in the form of chemical equations. There are two systematic ways for balancing these equations.

12.1.4 Balancing Redox Equations by Oxidation Number Method

Oxidation and reduction are simultaneous processes; collectively called redox process. If one substance in a reaction is oxidized, it loses electrons and acts as reducing agent, then the other substance, simultaneously, is reduced, gains electrons and acts as oxidizing agent. The number of electron gained and lost must be equal. This principle builds the basis of balancing the redox equation. The following steps are involved in balancing equations by oxidation number method.

i. Write down the skeleton of the unbalanced redox equation.
ii. Write the oxidation numbers over the symbol of the elements whose oxidation numbers change during the reaction.

iii. Identify the oxidizing and reducing agents, which undergo change in their oxidation number.

iv. Indicate the change in oxidation number by means of arrows which show the number of electrons gained or lost.

v. Multiply the formula of the oxidizing and the reducing agents by a number such that the number of electrons lost during oxidation becomes equal to the gain of electrons during reduction.

vi. Balance the rest of the equation by simple inspection.

Example 12.3

Let us balance the following equation by oxidation number method, by using the above mentioned steps.

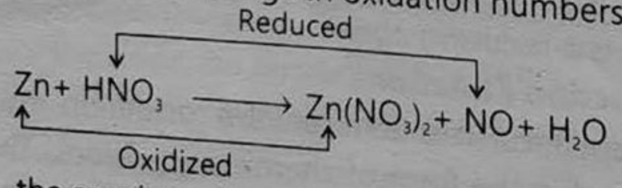
(i) $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$

(ii) Oxidation number of Zn is 0, oxidation number of Zn in $Zn(NO_3)_2$ is +2. Oxidation numbers of Zn increases from 0 to +2, so it is oxidized and is a reducing agent. Oxidation number of N decreases from +5 in HNO_3 to +2 in NO so it is reduced and acts as an oxidizing agent.

(iii) Write the oxidation numbers over the symbols of the elements oxidized and reduced.

$$\overset{0}{Zn} + HN^{+5}O_3 \longrightarrow Zn^{+2}(NO_3)_2 + N^{+2}O + H_2O$$

(iv) Indicate the change in oxidation numbers by means of arrows.



Hence, the species reduced and oxidized can be written as follows:

a) $Zn^0 \longrightarrow Zn^{2+} + 2e^-$ (Zn oxidized)

b) $HN^{+5}O_3 + 3e^- \longrightarrow N^{2+}O$ (N reduced)

(v) Multiply equation (a) by 3 and (b) by 2, so that the number of electrons gained becomes equal to the number of electrons lost. By this way we get coefficients of different species appeared in equation given in part (i) above which takes the following form

$$3Zn + 2HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + O_2$$

(vi) Add six more NO_3 in the form of HNO_3 to the reactant's side, to balance $6NO_3$ of $Zn(NO_3)_2$ in the products side. Also balance H and O atom by inspection.

$$3Zn + 2HNO_3 + 6HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$

Now the final balanced equation is:

$3Zn + 8HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$

12.1.5. Balancing the Redox Equations by the Half Reaction Method

This method of balancing is also called the *ion electron method.* No oxidation numbers are assigned in this method. It applies to redox reactions taking place in aqueous medium. The following steps are used for balancing redox equation by this method.

i. Split the equation into two half reactions, one for oxidation and the other for reduction showing only the oxidizing and reducing agents.
ii. Balance number of atoms on both sides of the two half reactions independently. In neutral medium H_2O and H^+ can be added on either side.
iii. In acidic medium the H^+ ion may be used for greater number of oxygen and H_2O can be added to the other side.
iv. Balance the charge by adding electrons (e) to the side deficient in negative charge.
v. Multiply each half reaction by a number chosen so that the total number of electrons lost by the reducing agent equals the number of the electrons gained by the oxidizing agent.
vi. Add the two half reactions resulting from the multiplications. Cancel anything appearing to both sides in the net equation.
vii. Check the final equation by counting the number of atoms and the net charge on either side.

Example 12.4

Balance the following equation of the reaction taking place in acidic medium by ion electron method.

$I^- + NO_2 \longrightarrow I_2 + NO$

i) Split the reaction into two half reactions, one for oxidation and the other for reduction.

a) $I^- \longrightarrow I_2$ (increase in oxidation number shows oxidation)

b) $NO_2 \longrightarrow NO$ (decrease in oxidation number of N shows reduction)

ii) Balance the number of O-atoms on each half reaction by adding H^+ (oxygen excess side) and H_2O to other side. Also multiply I^- by 2 in Equation (a)

a) $2I^- \longrightarrow I_2$

b) $NO_2 + 2H^+ \longrightarrow NO + H_2O$

iii) Balance the charges on both sides of each half reaction by adding electrons to either side.

a) $2I^- \longrightarrow I_2 + 2e^-$

b) $NO_2 + 2H^+ + 2e^- \longrightarrow NO + H_2O$

iv) The total number of electrons lost and gained in the two half reactions are the same. So adding the two half reactions after canceling the electrons gained with the lost, we get a balanced net equation.

a) $2I^- \longrightarrow I_2 + 2e^-$

b) $NO_2 + 2H^+ + 2e^- \longrightarrow NO + H_2O$

Balanced equation $2H^+ + NO_2 + 2I^- \longrightarrow NO + I_2 + H_2O$

12.1.6 Chemistry of Some Important Oxidizing and Reducing Agents

a) Reaction of Oxidizing Agents

Potassium dichromate ($K_2Cr_2O_7$) and $KMnO_4$ (potassium permanganate) are strong oxidizing agents.

1. **Potassium dichromate** ($K_2Cr_2O_7$) is a strong oxidizing agent. In presence of dilute sulphuric acid it acts as a strong oxidizing agent and oxidizes a number of compounds. In all these reactions chromium ion is reduced from +6 to +3 oxidation state.

i) It oxidizes iodide to iodine

$$K_2\overset{+6}{Cr}_2O_7 + 6K\overset{-1}{I} + 7H_2SO_4 \longrightarrow \overset{+3}{Cr}_2(SO_4)_3 + 4K_2SO_4 + 3\overset{0}{I}_2 + 7H_2O$$

ii) It oxidizes ferrous salts to ferric salts.

$$K_2\overset{+6}{Cr}_2O_7 + 6\overset{+2}{Fe}SO_4 + 7H_2SO_4 \longrightarrow \overset{+3}{Cr}_2(SO_4)_3 + 3\overset{+3}{Fe}_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

2. **Potassium permanganate ($KMnO_4$)** is a strong oxidizing agent. In presence of dilute sulphuric acid it acts as a strong oxidizing agent and oxidizes a number of compounds.

i) $KMnO_4$ oxidizes KI in the presence of (dil) H_2SO_4 to I_2.

$$2K\overset{+7}{Mn}O_4 + 10K\overset{-1}{I} + 8H_2SO_4 \longrightarrow 2\overset{+2}{Mn}SO_4 + 6K_2SO_4 + 5\overset{0}{I}_2 + 8H_2O$$

ii) $KMnO_4$ oxidizes oxalic acid in the presence of sulphuric acid to CO_2

$$2K\overset{+7}{Mn}O_4 + 5(COO)_2H_2 + 3H_2SO_4 \longrightarrow 2\overset{+2}{Mn}SO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

b) Reactions of Reducing Agents

H_2S and SO_2 are reducing agents.

1. **Hydrogen sulphide (H_2S)** is reducing agent in acidic medium.

i) It reduces halogens to halogen acids.

$$H_2\overset{-2}{S} + Cl_2 \longrightarrow 2HCl + \overset{0}{S}$$

$$H_2\overset{-2}{S} + Br_2 \longrightarrow 2HBr + \overset{0}{S}$$

ii. It reduces ferric salt to ferrous salt

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

2. **Sulphur dioxide (SO_2)** is reducing agent in the acidic medium

i. SO_2 reacts with KIO_3 and reduces it to I_2.

$$2\overset{+1}{K}\overset{+5}{I}O_3 + 5\overset{+4}{S}O_2 + 4H_2O \longrightarrow 2\overset{+1}{K}H\overset{+6}{S}O_4 + 3H_2\overset{+6}{S}O_4 + \overset{0}{I_2}$$

ii. SO_2 reduces $KMnO_4$ in acidic medium.

$$2K\overset{+7}{Mn}O_4 + 5\overset{+4}{S}O_2 + 2H_2O \longrightarrow K_2\overset{+6}{S}O_4 + 2\overset{+2}{Mn}\overset{+6}{S}O_4 + 2H_2\overset{+6}{S}O_4$$

12.2 Electrodes, Electrode Potential and Electrochemical Series

An electrolytic cell is composed of two electrodes suspended in an electrolytic solution. They are connected to a battery. The electrode, by which electrons enter the solution, are connected to the negative terminal of the battery and serves as a cathode, while anode is connected to the positive terminal of the battery where the electrons leave the cell. The electrodes are metallic plates, wires, or rods through which the current enters or leaves the electrolyte in a cell. The positive electrode is called anode and the negative electrode is called cathode in electrolytic cell. The electrolytic solution contains ions produced by the spontaneous dissociation of the dissolved electrolyte. The positive ions, called cations move towards the negative electrode (cathode), whereas, the negative ions which are called anions move towards the positive electrode (anode).

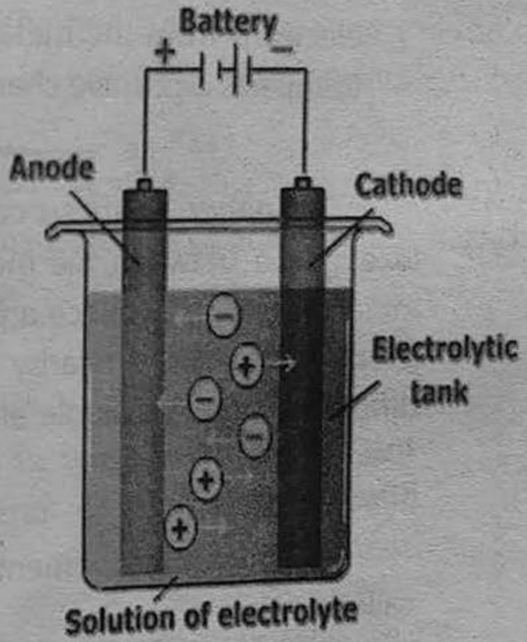


Figure 12.1 Electrolytic Cell

When the current passes through the solution, the anions move towards the anode. They get discharged by giving their electrons to the electrode. The loss of electrons at anode is called oxidation. On the other hand, the cations tend to move towards the cathode. They gain the electrons from the electrode and neutralize their charge. Hence, reduction occurs at cathode. The two half-cell reactions taking place at the two electrodes are as follows:

At anode $2X^{-1} \longrightarrow X_2 + 2e^-$ (oxidation)

At cathode $M^{+2} + 2e^- \longrightarrow M$ (reduction)

Net Reaction $2X^{-1} + M^{+2} \longrightarrow X_2 + M$

In the above reaction two electrons are gained by the metal ion and it is deposited on cathode whereas the same number of electrons are lost in oxidation. The net result is that the number of electrons gained in reduction is equal to the number of electrons lost in oxidation.

Electrode Potential

When a metal strip is placed in a solution of its own ions, there are tw possible tendencies.

(1) The metal atoms may dissolve as positive ions.

$$M \longrightarrow M^{+} + e^{-} \qquad (12.1)$$

In this way, the electrons are deposited on the metal strip and it acquire negative charge, let us call it as an electrode.

(2) Another possibility is that the metal ions present in solution may take u electrons from the metal and get discharged as atoms on the metal surface It imparts a positive charge to the metal plate.

$$M^{+} + e^{-} \longrightarrow M \qquad (12.2)$$

In either of these cases a separation of negative and positive charges takes place between the metal plate and the solution immediately close to the metal surface, and hence a potential difference is set up between the metal plate (electrode) and the nearby solution surrounding the metal plate. This potentia difference is called single electrode potential or simply electrode potential. Thus *the electrode potential of an element is the potential difference between an aqueous solution of its ions and the element when it is in equilibrium with that solution.* Such arrangement of an electrode dipping into a solution of ions is called a *half-cell*.

It is impossible to measure the potential difference between an electrode and the solution making up a half cell. If a high resistant volt meter is used for this purpose, one probe of the volt meter is connected to the metal electrode and the other probe must be dipped into the solution. The dipped metal probe will act as another half-cell creating its own electrode potential. Thus the voltmeter will read the difference in potential between the two electrodes rather than the potential of the electrode under investigation. In such case, when it is difficult to measure the absolute value of electrode potential, one electrode must be arbitrarily assigned a zero value of potential and the value of other electrod is measured with reference to this electrode, considered as a standard electrod For this purpose, hydrogen electrode is used as a standard electrode and potential has arbitrarily been assigned a zero value. This is called as stand *hydrogen electrode (SHE)*. The potential of all other electrodes is measured w reference to SHE.

The potential created when an electrode is in contact with one mola solution of its own ions at 298 K at one atmosphere pressure is known a standard electrode potential of the element with reference to the standar hydrogen electrode. It is represented as E°. Now, whenever the electrod potential of an element is to be measured its half-cell is connected with SHE an a voltmeter, connected between them, reads directly the potential of the electrode under investigation since the potential of the SHE is chosen to be zero.

A rod of zinc, for example, will bear an accumulation of negative charges. This is due to the ionization of some of its atoms. The negative charge on the Zn-rod will attract an atmosphere of positively charged zinc ions around the rod to form an electrical double layer as shown in Fig. 12.2. The equilibrium can, therefore, be represented as:

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

The potential of Zn electrode can be measured by connecting this half-cell with the SHE.

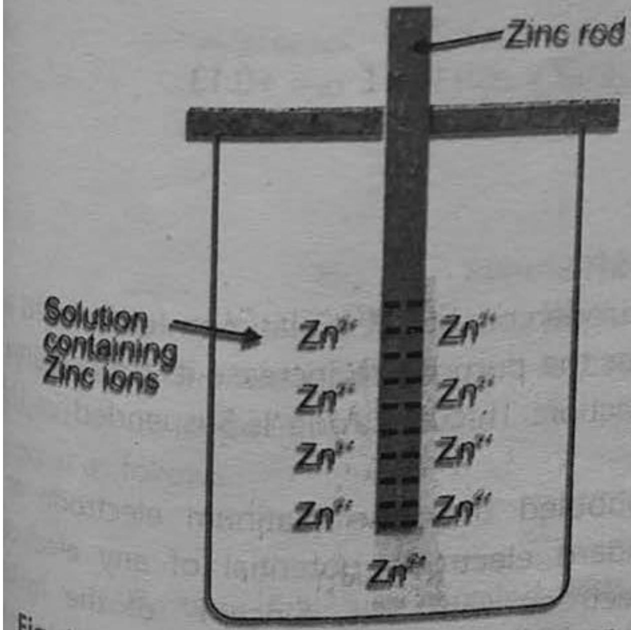


Fig. 12.2: Equilibrium between zinc and its ions in solution

Reading Check

- Differentiate between oxidising agent and reducing agent with examples.
- Define electrodes, electrode potential and oxidation number.
- Name the two types of electrodes and the ions discharged on them.

Cell Reaction and Cell Voltage

Table 12.1 can be used to predict the reaction and voltage of any cell consisting of any two standard electrodes. The net reaction undergoing in a cell is the algebraic sum of the two half reactions taking place at the two electrodes. For instance, the H_2/Cu^{2+} cell reaction can be summed up as follows

$$H_2 + Cu^{2+} \longrightarrow 2H^+ + Cu$$

The cell voltage recorded by a voltmeter is the sum of the two half-cel potentials, one for oxidation and the other for reduction. Hence, the cell potentia can be written as;

$E^o_{cell} = E^o_{Red} + E^o_{Ox}$

or $E^o_{Cell} = E^o_{cathode} - E^o_{anode}$

Example 12.5

Calculate $E°_{Cell}$ from the following half-cell reactions.

$Zn \rightarrow Zn^{2+} + 2e^-$ $E°_{Red} = -0.76V$ or $E°_{Ox} = +0.76V$

$Cu^{2+} + 2e^- \rightarrow Cu$ $E°_{Red} = +0.34V$

$E^o_{cell} = E^o_{Red} + E^o_{OX}$

$E^o_{Cell} = 0.34 + 0.76 = 1.10\ V$

Example 12.6

Calculate cell potential of a galvanic cell composed of the following two half cells. Write their half-cell reactions.

Pb^{2+}/Pb $E^o_{Red} = -0.13V$

Cl_2/Cl^- $E^o_{Red} = +1.36V$

$Pb \rightarrow Pb^{2+} + 2e^-$ $E^o_{Red} = -0.13$ or $E^o_{Ox} = +0.13$

$Cl_2 + 2e^- \rightarrow 2Cl^-$ $E^o_{Red} = +1.36V$

$E^o_{cell} = E^o_{red} + E^o_{OX}$

$E^o_{Cell} = 1.36V + 0.13V = 1.49V$

Standard Hydrogen Electrode, SHE

A standard hydrogen electrode consists of a platinum foil, coated with a layer of finely divided platinum for the purpose to increase its surface area and hence, to increase the rate of reaction. This electrode is suspended in 1M HC solution at 25°C.

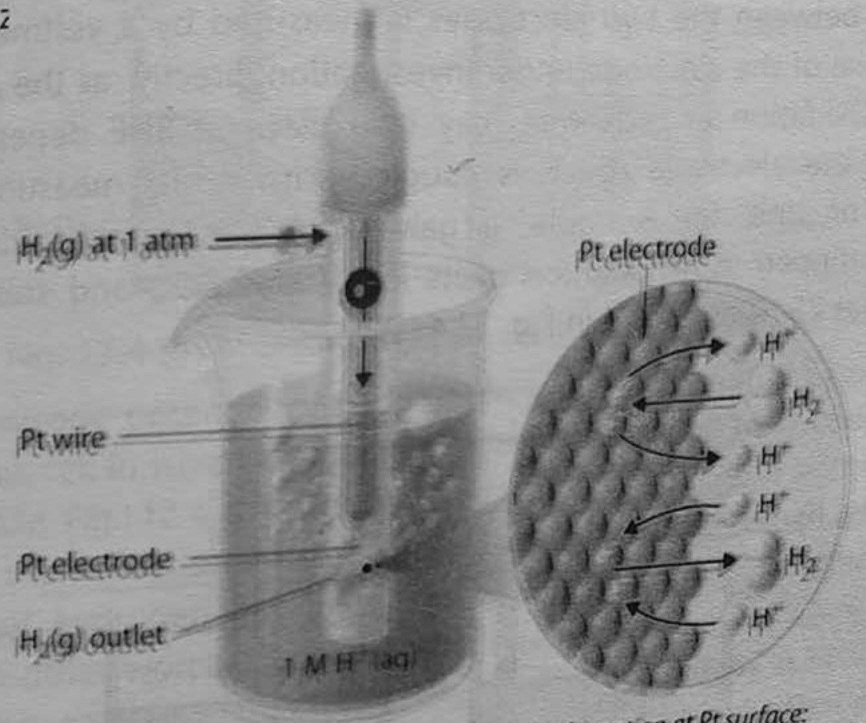
Pure hydrogen gas is bubbled over the platinum electrode at one atmospheric pressure. The standard electrode potential of any electrode is obtained by combining the electrode with SHE. Since E° of the hydrogen electrode is zero in either case i.e. reduction as well as oxidation (as shown below), so the measured potential is the standard electrode potential of the other electrode. When SHE acts as anode, oxidation of hydrogen gas takes place at the surface of the electrode as follows.

$$H_{2(g)} \rightleftharpoons 2H^+_{(aq)} + 2e^- \qquad E^o_{Ox} = 0\ volt$$

Here, E^o stands for standard oxidation potential, symbolically written $E°_{(H_2/2H^+)}$ and when SHE acts as cathode, reduction of hydrogen ions takes pl at the surface of the SHE as follows,

$$2H^{+}_{(aq)(1M)} + 2e^{-} \rightleftharpoons H_{2(g)\ (1\ atm)} \qquad E^{o}_{Red} = 0\ volt$$

In this case E^{o}_{Red} shows the standard reduction potential represented as $E^{o}(2H^{+}/H_2)$.In both of these cases the electrode potential of SHE is arbitrarily given the value as z



half-reaction at Pt surface:
$2H^{+}(aq) + 2e^{-} \rightleftharpoons H_2(g)$

Fig. 12.3 Standard hydrogen electrode

Hydrogen electrode when coupled with the electrode which has positive E^{o}_{Red} value, the electrode will act as cathode and SHE as the anode. e.g. E^{o}_{Red} value of Cu is positive (+ 0.34V), the reaction of H_2/Cu cell will spontaneously occur as follows.

$$H_2 \longrightarrow 2H^{+} + 2e^{-} \quad \text{(oxidation)}$$
$$Cu^{2+} + 2e^{-} \longrightarrow Cu \quad \text{(reduction)}$$

Whereas, if SHE is coupled with Zn electrode then reduction will take place at SHE, because the value of E^{o}_{Red} for Zn is negative as compared to SHE. The two half reactions are as under.

$$Zn \longrightarrow Zn^{2+} + 2e^{-} \quad \text{(oxidation)}$$
$$2H^{+} + 2e^{-} \longrightarrow H_2 \quad \text{(reduction)}$$

Measurement of Electrode Potential

We can use the SHE to measure the potentials of other electrodes. For the measurement of electrode potential the concerned electrode is joined electrically with the standard hydrogen electrode (SHE) and a galvanic cell is established. The two solutions are separated by a porous partition or a salt bridge containing a concentrated solution of potassium chloride. The salt bridge is used to provide a highly conducting path between the two electrolytic solutions. The potential difference between the two electrodes is measured by a voltmeter which gives the potential of the electrode under investigation directly as the potential of SHE is zero. Oxidation or reduction may take place at SHE depending upon the nature of the electrode which is coupled with it. To measure the electrode potential of zinc, for example, a galvanic cell is established between zinc electrode dipped in 1M solution of its ions (as $ZnSO_4$) and standard hydrogen electrode at 25 °C as shown in Fig. 12.4 (a).

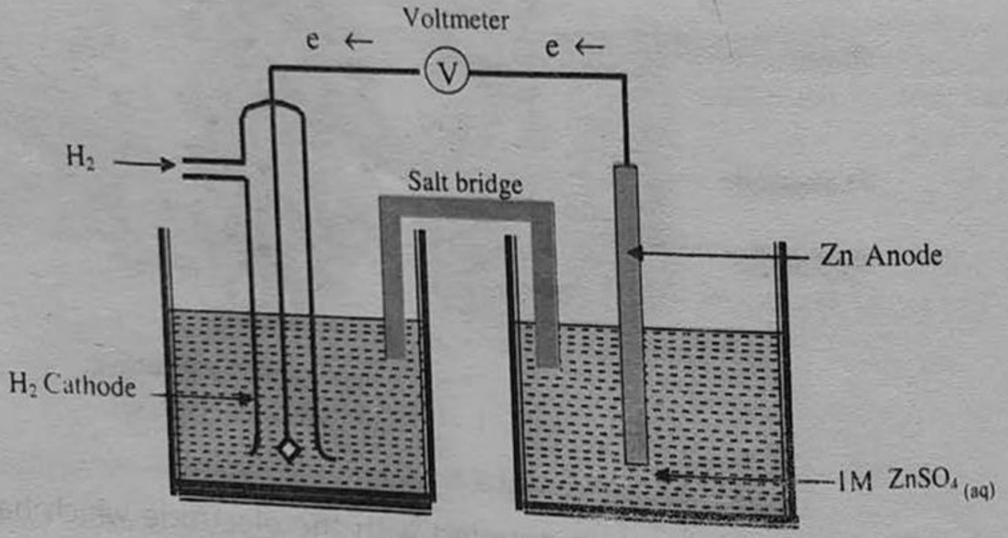


Fig.12.4(a) Measurement of electrode potential of Zn

Under the standard conditions, the voltmeter reads 0.76 volts and the deflection of the voltmeter needle is in such a direction as to indicate that zinc has a greater tendency to give off electrons than hydrogen. In other words, the half reaction

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ has greater tendency to occur than $H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$ by 0.76 volts. The standard electrode potential of zinc is, therefore, 0.76 volts. It is called oxidation potential of Zn and is given positive sign. The reduction potential of Zn-electrode is -0.76 volt. The electrode reactions are shown as follows.

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

At cathode $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ (reduction)

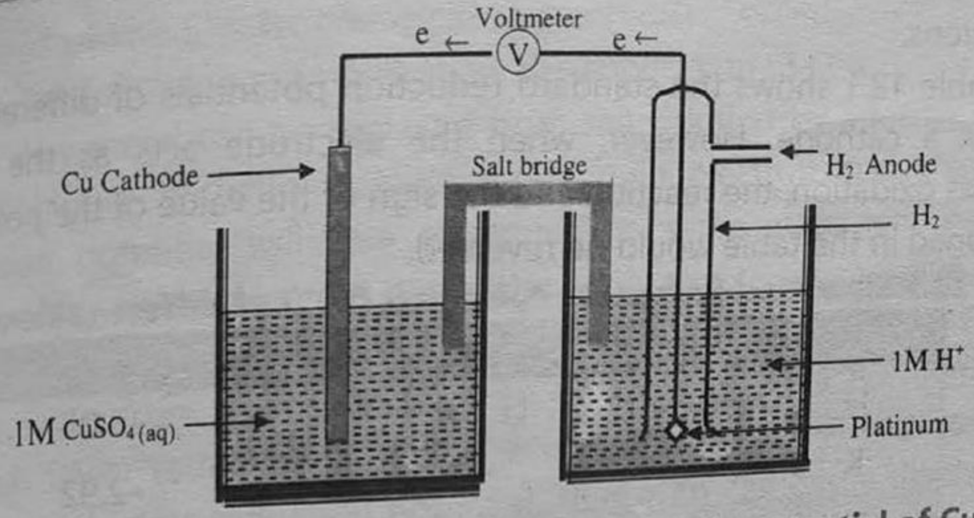


Fig. 12.4 (b) Measurement of electrode potential of Cu

The electrode potential of copper can also be measured using the same type of galvanic cell in which copper is an electrode dipped in 1M solution of its ions (say $CuSO_4$) Fig. 12.4 (b). Under standard conditions, the voltmeter reads 0.34 volts and the deflection f the needle of the voltmeter is in such a direction as to indicate that hydrogen has a greater tendency to give off electrons than copper has. In other words, the half reaction $H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$ has a greater tendency to occur than $Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$ by 0.34 volt. So the standard electrode potential of Cu is 0.34 volts. It is called reduction potential of Cu. When the sign is reversed, then the -0.34 V is called oxidation potential of Cu electrode. The reactions taking place at the two electrodes are shown as follows.

At anode $H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$ (oxidation)

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

Electrochemical Series

Every element has its own tendency to give or take electrons. This tendency has been represented in terms of their oxidation or reduction potentials, respectively. The standard electrode potentials of a large number of elements have been measured using standard hydrogen electrode (SHE) as the reference electrode. These elements can be arranged in increasing order of the reduction potential. The arrangement of elements in order of increasing reduction potential values is called electrochemical series (E.C.S) or activity series. According to the recommendations of IUPAC these potentials are listed as *standard reduction potentials* (E^o_{Red})in Table 12.1.The standard oxidation potential, on the other hand, can be determined just by reversing the sign of the standard reduction potential without changing the numerical value. The voltage created by a cell is actually the difference between the reduction potentials of the two half reactions.

Table 12.1 shows the standard reduction potentials of different elements, acting as a cathode. However, when the electrode acts as the anode and undergoes oxidation, the reaction and the sign of the value of the potential which is mentioned in the table would be reversed.

Table 12.1:Standarad Reduction Potentials (E°_{Red}) of different Elements

Element	Half Cell Reduction Reaction	E° (Volts)
Li	$Li^+ + e^- \rightleftharpoons Li$	-3.05
K	$K^+ + e^- \rightleftharpoons$	-2.92
Ba	$Ba^{2+} + 2e^- \rightleftharpoons Ba$	-2.90
Ca	$Ca^{2+} + 2e^- \rightleftharpoons Ca$	-2.76
Na	$Na^+ + e^- \rightleftharpoons Na$	-2.71
Mg	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.38
Al	$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.67
Mn	$Mn^{+2} + 2e^- \rightleftharpoons Mn$	-1.03
Zn	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
Cr	$Cr^{3+} + 3e^- \rightleftharpoons Cr$	-0.74
Fe	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
Ni	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	-0.25
Pb	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13
H_2	$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
Cu	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
I_2	$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
Fe	$Fe^{3+} + 3e^- \rightleftharpoons Fe$	+0.77
Ag	$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
Hg	$Hg^{2+} + 2e^- \rightleftharpoons Hg$	+0.09
Br_2	$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.08
$C1_2$	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
Au	$Au^{3+} + 3e^- \rightleftharpoons Au$	+1.50
F_2	$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87

Features of the Electrochemical series (ECS)

The following examples show the application of ECS.

Any metal can be replaced from salt solution by another metal. Element having higher reduction potential will gain electron and that having lowe reduction potential will lose electron. The same statement can be given in another way as the element placed higher in the series can give electron to the element below it in the ECS and replace it from its salt solution. For example, Zn displaces Cu from $CuSO_4$ because Zn (E°=-0.76V) is placed higher in the series and has lower reduction potential, while Cu (E°=+0.34V) is placed lower in the series with higher reduction potential. Hence, Zn can easily displace Cu from its solution.

$$Zn_{(s)} + CuSO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

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

Similarly, Cu metal is oxidized by silver as Cu is higher in ECS (lower reduction potential) and silver (E°=+0.80V) is lower in the series (higher reduction potential)

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

Moreover, if two metals are made the electrodes a Galvanic cell, the metal with lower reduction potential will act as anode and the one with the higher reduction potential as cathode

12.3 Types of Electrochemical Cells

A device in which interconversion of electrical and chemical energies takes place, is called an electrochemical cell. Electrochemical cells are of two types.

1. Electrolytic Cell

In electrolytic cells, the electrical energy from an external source is used to bring about a chemical change within the cell. Electrolytic purification of metals, electroplating and charging of batteries are application of electrolytic cells.

2. Voltaic or Galvanic Cell

It is a device in which chemical energy is converted into electrical energy. For example, dry cells and lead storage batteries are galvanic cells.

12.3.1 Electrolytic Cell

It is a device in which a non-spontaneous chemical reaction is carried out by passing electric current from outside. The electrolytic cell consists of a vessel containing electrolyte in which two metallic plates acting as electrodes, are suspended. The electric current enters and leaves the cell through these electrodes. The electrode connected to the negative terminal of the battery is called cathode while the other one connected to the positive terminal is anode.

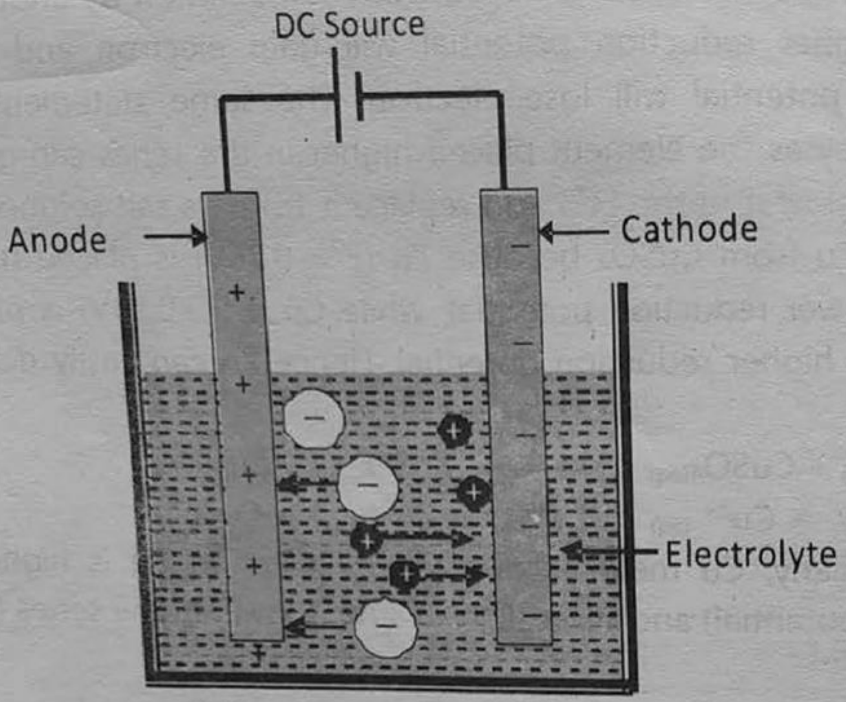


Figure 12.5: Electrolytic cell

When electric current is passed through the electrolytic solution, its ions move towards the respective electrodes. The anions liberate electrons at the anode and are oxidized. These electrons pass through the outer circuit to the cathode. The cations which surround the cathode, consume those electrons, get reduced and deposited or liberated at the cathode. Remember that the number of electrons lost at the anode is always equal to the number of electrons gained at the cathode.

Self-Assessment

1. Differentiate between oxidation and reduction potential with an example.
2. How reduction potential value effect the position of elements in the electrochemical series.

12.3.2 Electrolysis of Aqueous NaCl

Caustic soda, NaOH is very important industrial chemical, manufactured on a large scale by the electrolysis of aqueous solution of NaCl. The electrolysis is carried out in a cell called Nelson's cell (Fig. 12.6). It is an oblong steel tank containing a concentrated aqueous solution of NaCl. The graphite anode is suspended in the solution. Cathode is made of a sheet of perforated steel. When connected to the battery, the half reactions taking place at the electrodes are as follows.

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

At anode $2Cl^- \longrightarrow Cl_2 + 2e^-$ (oxidation)

At cathode $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ (reduction)

Overall reaction $2NaCl_{(s)} + 2H_2O \longrightarrow 2Na^+ + H_2 + Cl_2 + 2OH^-$

$$2Na^+ + 2OH^- \longrightarrow 2NaOH$$

Cl_2 is released at anode and H_2 at cathode. NaOH is collected at the bottom of the cell.

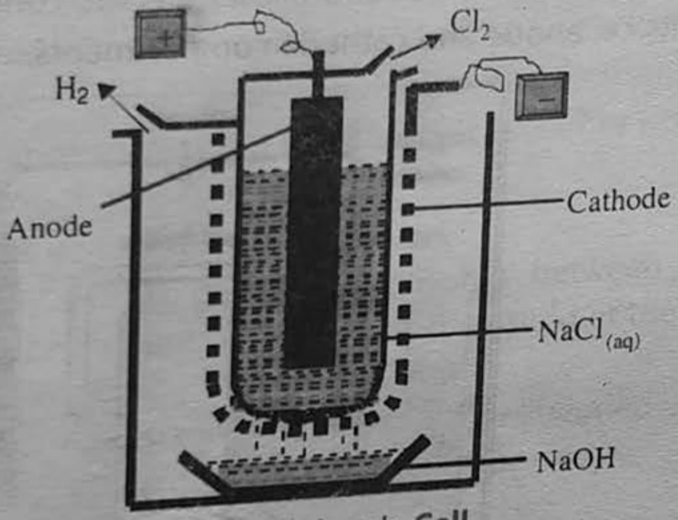


Figure 12.6 Nelson's Cell

Advantages of the Electrolytic Cell

1. Charging of the lead storage batteries is done electrolytically by passing the current through the discharged battery so that the reactions are reversed and the battery is recharged.
2. Various types of electrolytic cells are employed on industrial scale for the manufacture/extraction of industrially important metals and gases e.g. manufacture of NaOH, Na, Mg, Al, Cl_2 etc.
3. Electrolytic cells can be used for the purification of some important metal like Cu etc.
4. Copper, silver, chrome, nickel and tin plating is done by various types of electrolytic cells, for the purpose of protection, beauty and repair of the metal.

12.3.3 Voltaic Cell

In the voltaic cell a spontaneous oxidation-reduction reaction occurs and electrical current is produced. It consists of two half cells externally connected with a metallic wire acting as a conductor. At each half-cell one half of the total cell reaction takes place. At one electrode electrons enter resulting in reduction reaction while at the other they leave the solution and oxidation takes place. A typical example of the voltaic cell ~~is that of a~~ Daniell cell.

Daniell Cell:

As you have studied in your ninth grade, this cell has a Zn electrode dipped into 1M $ZnSO_4$ solution and a Cu electrode immersed in a 1M solution of Cu^{2+} ions. These two half cells are externally connected through a metallic wire while internally they are connected by a salt bridge. The salt bridge contains an aqueous KCl solution in a gel and allows electric connectivity between the two compartments i.e. anode and cathode compartments.

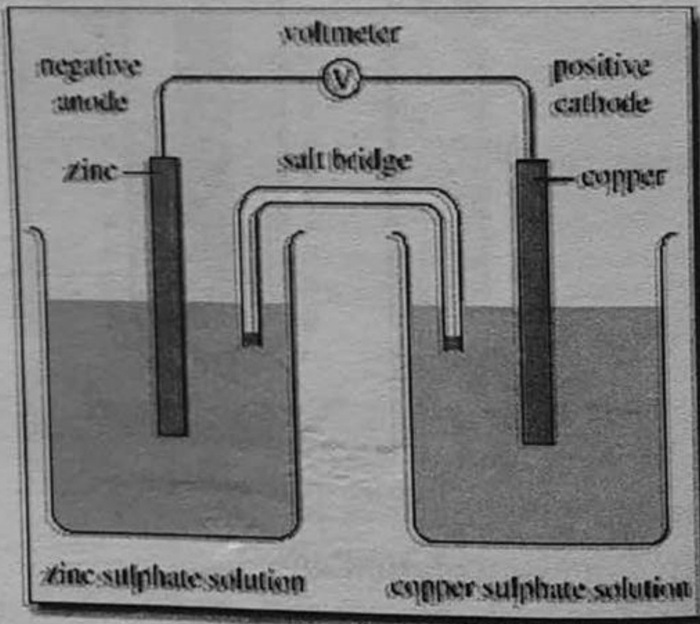


Fig: 12.7 Daniell Cell

Zn tends to lose electrons more readily than Cu giving its electrons to the electrode at the anode and get oxidized. Electrons flow from the Zn electrode to the Cu electrode through external circuit. The Cu^{2+} ions, surrounding the cathode, pick up the electrons and get deposited as neutral metal at the copper cathode where reduction of Cu^{+2} takes place. The following half reactions occur at the electrodes.

At anode $Zn \longrightarrow Zn^{2+} + 2e^-$ $E^\circ_{Ox} = +0.76V$

At cathode $Cu^{2+} + 2e^- \longrightarrow Cu$ $E^\circ_{Red} = +0.34V$

Net reaction $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ $E^\circ_{Cell} = 1.10V$

The cell is represented as follows,

$Zn_{(s)}/Zn^{2+}_{(aq)}(1M)//\ Cu^{2+}_{(aq)}(1M)/Cu_{(s)}$

Tidbit

Some Electrical Terms

A *Coulomb* is the SI unit for quantity of electricity, it is defined as the quantity of electric charge carried by a current of on ampere flowing through a wire for one second. 1 Coulomb =1 ampere x1 sec or 1C=1Ax1s.

Ampere: It is basic SI unit used for measuring the rate of electron flow or electric current in an electric conductor. One ampere of current represents one coulomb of electric charge (carried by 6.24×10^{18} electrons) moving through a specific point in one second. 1 Ampere= 1Coulomb/second.

Volt: It is the measure of how strongly an electric current is sent around an electric circuit. It is unit of electric potential or electromotive force. A potential of one volt appears across a resistance of one ohm when a current of one ampere flows through that resistance. $V = IR$

★ Faraday's Laws of Electrolysis

Michael Faraday (1813) gave a relationship between the quantity of electricity passed and the amount of substances deposited at the electrode.

Faraday's First Law:

The amount of any substance (W) deposited or liberated at an electrode is directly proportional to the quantity of electricity (Q) passed.

$$W \propto Q$$

Or $$W = ZQ \qquad (12.3)$$

Where, W is the mass in gram, Q is amount of charge in Coulombs and Z is the proportionality constant. Z is called the *electrochemical equivalent*. When Q=1C then Eq.(12.3) becomes

$$W = Z \qquad (12.4)$$

Here with the help of Eq. (12.4) we can now define the electrochemical equivalent as the mass of substance liberated when one Coulomb electricity is passed through the electrolyte solution.

Moreover, amount of charge, Q = I t where, I is current in amperes and t is time in seconds. Thus, we can also write Eq.(12.3) as

$$W = Z\,I\,t \qquad (12.5)$$

Faraday's Second Law

It states that, 'if the same amount of electricity is passed through the solutions of different electrolytes, the amounts of different substances deposited are in the ratio of their chemical equivalents. Or the masses of different substances liberated for the same quantity of electric charge during the electrolysis are proportional to their equivalent masses. Suppose a certa amount of current passing through the dil. $CuSO_4$ and dil. $AgNO_3$ solutions f the same interval of time, then, we will find that the ratio of the masses liberated silver and copper is 107.88/31.54 because equivalent mass of silver 107.88 and that of copper is 31.548.

Thus $W \propto$ Equivalent mass (e)

Also from the Faradays first law

$W \propto Q$ or $W \propto It$

Combining above two equations we get $W \propto Ite$

Introducing the proportionality constant l/F, we get.

$$W = \frac{1}{F} Ite \qquad (12.6)$$

Where "F" is called Faraday's constant which is equal to 965 Coulomb/mol.

Faraday's second law can also be derived mathematically from equati (12.6). It can be concluded from this equation that for a fixed amount of electric passed for a fixed time the term It/F assumes a fixed value and under t condition $W \propto e$ which, as the law states that the amount of substance, liberated, is directly proportional to the equivalent mass 'e'.

Example 12.7

A certain amount of current is passed through $AgNO_3$ solution for th hours. The net amount of Ag deposited was found to be 60.8 g. Calculate current when gram equivalents (e) of Ag is 107.8.

Solution

Time (t)=3 hours = 3 x 60 x 60 s

W (amount of Ag)= 60.8g

Gram equivalent mass of Ag (e)=107.8g, $F=96500\ C\ mol^{-1}$

$$W = \frac{1}{F} Ite$$

$$I = \frac{WF}{te}$$

$$I = \frac{60.8g \times 96500 c/mol}{3 \times 60 \times 60s \times 107.8g/mol} = 5.04A$$

12.3.4 Batteries

There are four major types of batteries.

1 **Primary batteries:**

These batteries are not reversible and once discharged cannot be recharged, e.g. dry cell.

2 **Secondary batteries:**

They are reversible and can be recharged, e.g. Lead storage battery.

3 **Solar batteries:**

They are photoelectrical cells and generate energy.

4 **Fuel batteries:**

They are the super batteries and have high charge density.

(i) Primary Batteries

Dry Cell

As you have studied in your previous class, the container of the cell is made of Zn, which acts as an anode. The container is lined with a porous paper, which separates anode from inside material. A graphite rod in the centre of the cell acts as cathode. Electrolyte is a moist mixture of NH_4Cl, MnO_2, $ZnCl_2$ and powdered carbon. The dry cell is sealed to prevent the evaporation of moisture. When the dry cell delivers current, Zn oxidizes to Zn^{2+} ions and leaves electrons on the Zn container. The electrons move through outer circuit to the graphite cathode, where NH_4^+ ions pick up the electrons and release NH_3 at the cathode. NH_3 produced at the cathode reacts with Zn^{2+} ions to form a complex ion. The redox reactions taking place at the two electrodes are as follows.

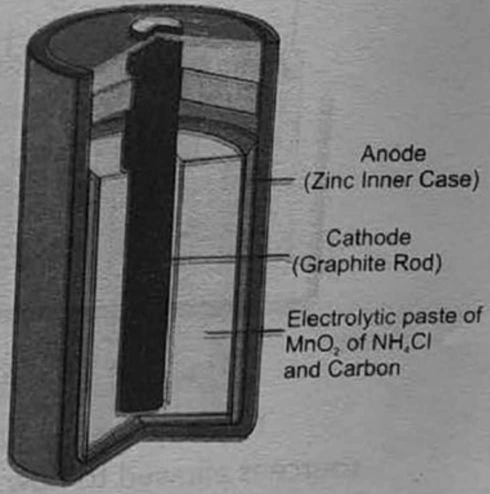


Fig. 12.8: The Dry Cell

At anode (Oxidation) $Zn \longrightarrow Zn^{2+} + 2e^-$

At cathode (Reduction) $2MnO_2 + 2NH_4^+ + 2e^- \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$

Net reaction $Zn + 2MnO_2 + 2NH_4^+ \longrightarrow Zn^{2+} + Mn_2O_3 + 2NH_3 + H_2O$

This is irreversible because Zn and NH_4^+ are consumed during the process of working and cannot be reversed back to their initial states by the application of the external electrical potential.

(ii) Secondary Batteries

The Lead Storage Battery

The lead storage battery commonly used in automobiles and generators. It is a combination of six voltaic cells of the same kind, arranged in series with the anode of one cell connected to the cathode of the other. The anodes are Pb plates while the cathodes are made of lead dioxide (PbO_2). Both the anode and cathode are immersed in an aqueous solution of sulfuric acid, which acts as the electrolyte (Fig.12.9). When the anodes and cathodes are connected, the current flows and the following reactions take place.

At Anode $Pb(s) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + 2H^+ + 2e^-$

At Cathode $PbO_2(s) + H_2SO_4(aq) + 2H^+ + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$

Net Reaction $Pb(s) + PbO_2(s) + 2H_2SO_4 \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

When the cell works insoluble $PbSO_4$ goes on depositing on both the electrodes, H_2SO_4 is consumed and water is formed.

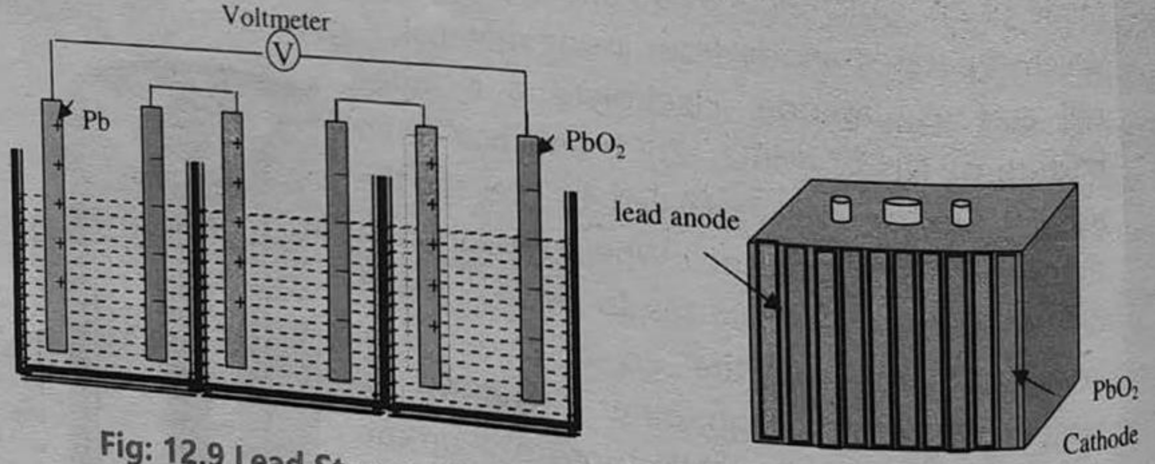


Fig: 12.9 Lead Storage Battery (internal and external)

It is a reversible battery. If, during recharging, the current from an external source is allowed to flow in the opposite direction all the above chemical changes are reversed and converts lead sulphate back to lead and lead dioxide on the respective electrodes. During recharging the negative electrode is connected to the negative terminal of the direct current (DC) source and positive electrode to the positive terminal of DC source. The reactions are;

At negative electrode: $PbSO_{4(s)} + 2e^- \rightarrow Pb_{(s)} + SO_4^{2-}$ (Reduction)

At positive electrode: $PbSO_{4(s)} + 2H_2O \rightarrow PbO_{2(s)} + 4H^+ + SO_4^{2-} + 2e^-$ (Oxidation)

Net reaction: $2PbSO_{4(s)} + 2H_2O \rightarrow Pb_{(s)} + PbO_{2(s)} + 2SO_4^{2-} + 4H^+$

Thus, Pb, PbO_2 and H_2SO_4 are reformed and the battery is again ready for generating useful electricity.

(iii) Fuel Cells

A fuel cell is a primary cell of special type which converts chemical energy of fuel directly to electrical energy. The chemicals that produce electricity are constantly replaced as soon as they are consumed. Fuel cells differ from common batteries such that in these, electricity is produced from chemical fuels fed to them as needed, so that their operating life is unlimited. One of the most important fuel cell is the hydrogen/oxygen fuel cell. In this cell the negative terminal (anode) is porous graphite coated with nickel and the positive terminal (cathode) is porous graphite coated with nickel and nickel oxide. The nickel and nickel oxide act as catalyst on the surface of the terminal. Nickel can be replaced by platinum.

Hydrogen is passed into the negative compartment of the cell and oxygen into the positive compartment. Under pressure the gases diffuse through the porous graphite terminals into the warm potassium hydroxide solution located between the terminals. At the anode, hydrogen reacts with hydroxide ions from the warm $KOH_{(aq)}$ and electrons are released. Thus, the reaction

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

Or $2H_2 \longrightarrow 4H^+ + 4e^-$

At cathode oxygen and water take electron to form hydroxide ions.

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

Adding above two equations we get the overall reaction as follows:

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

Fuel cells based on hydrogen and oxygen has a significant future as a power source for electric automobiles and in space vehicles. The cell is shown in Fig. 12.10. Electrodes are hollow tubes made of porous compressed carbon impregnated with platinum or nickel (increased surface area acts as a catalyst). The electrolyte is KOH. Hydrogen is oxidized at the anode giving electrons to the outer circuit while the electrons are accepted at the cathode where reduction occurs and in this way current flows. The cell products can be regenerated externally into fuel for returning to the cell.

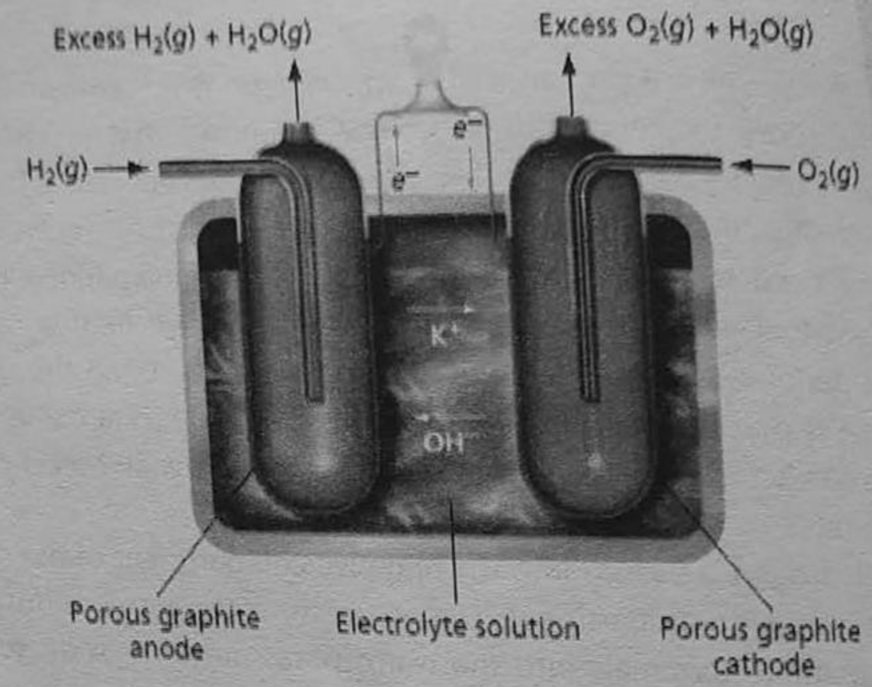


Figure 12.10: Hydrogen-Oxygen Fuel Cell

Fuel cells are very efficient and convert about 75% of the fuel into electricity. The major drawback of the fuels cells is that they are very costly. The gases must be of very high purity, otherwise even a trace of impurity may poison the platinum which severely degrades its efficiency.

12.3.5 Corrosion and its Prevention

The slow and continuous eating away of any metal by the action of environment is called corrosion e.g. pure iron is silvery white but when exposed to moist air its surface is corroded and converted to a reddish brown mass known as rust. The corrosion is not limited to iron only. Similarly, aluminium is most commonly used metal in house-hold things and to make airplanes. It has the tendency to react with atmospheric oxygen and form a layer of aluminium oxide (Al_2O_3). This layer protects it from further corrosion. Copper also corrode slowly and forms copper carbonate ($CuCO_3$) as a green layer on the copper surface which protects the metal from further corrosion. Similarly, silver utensils whe come into contact with the foodstuffs develop a layer of silver sulphide (Ag_2S The rust that forms on the surface of iron is too porous to protect the underlyi metal.

Chemically, rust of iron is hydrated iron (III) oxide. For rust formation the must be a thin film of water on the surface of the metal and air surrounding

The impurities or the strained portions are responsible for the formation of sma electrolytic cells, with anode of pure iron and cathode of impure or straine portions as shown in the diagram. Iron is oxidized at the anode producing Fe (I ions and electrons. It moves along the surface of the metal to cathode where i reacts with water and oxygen to form hydroxyl ions.

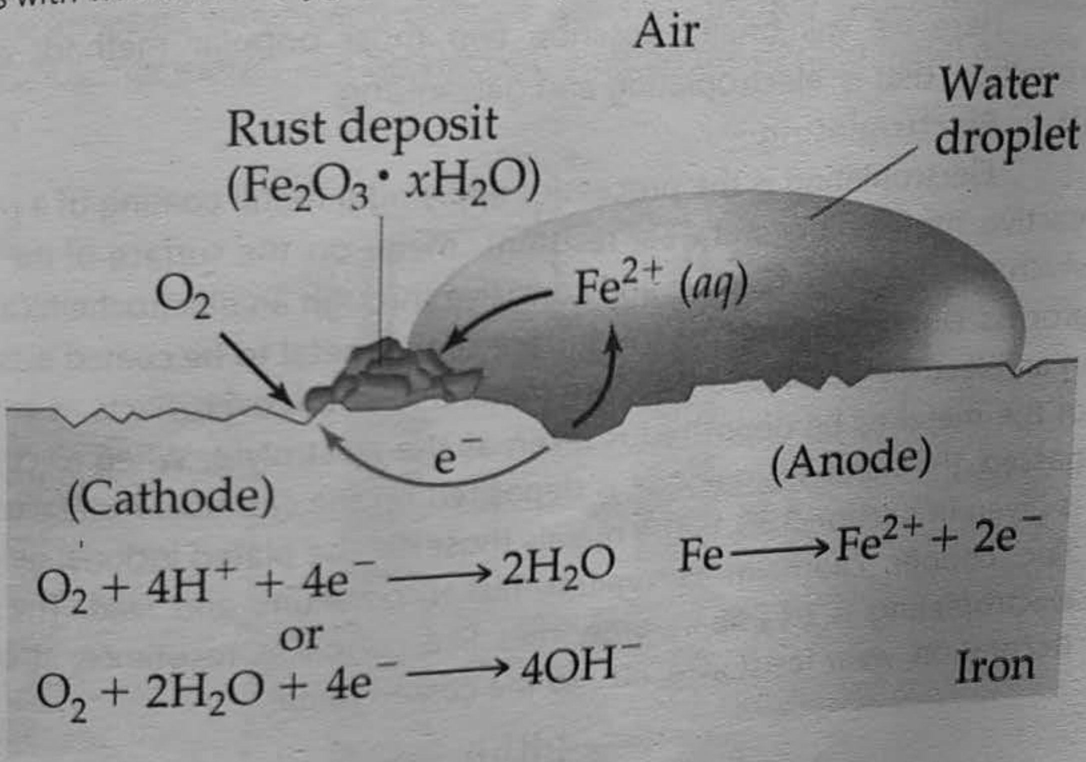


Fig. 12.11 Corrosion of iron piece

Anode $2Fe$ ¾¾® $2Fe^{+2}+4e^-$

Cathode $2H_2O+O_2+4e^-$ ¾¾® $4OH^-$

Fe (II) hydroxide, is further oxidized by atmospheric oxygen to form hydrated Fe(III) oxide, (rust).

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

$$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3$$

The rust of iron is soft and porous in nature and therefore, rusting cannot be prevented from further deeper atmospheric action. The result is that once corrosion starts it continues until the whole iron piece is rusted.

Few methods for preventing rust formation are as under.

1. Coating the metal surface with paint, grease etc.
2. Coating the metal with sacrificial metal such as zinc (galvanizing) or tin (tinning)

3. Dipping the iron into a phosphate bath (orthophosophoric acid with zinc & manganese phosphates)
4. Alloying the metal – steel formation
5. Electroplating with nickel or chromium
6. Cathodic protection

Here we will briefly describe two most popular methods of corrosion protection, that is, electroplating and galvanizing.

(i) Electroplating

Electroplating is the process of applying a metal coating of a precious, less reactive, more stable and wear resistant metal on the surface of the other metal which may be more reactive and corrosive through an electrochemical deposition process. During this process, the surface of the metal to be coated acts as cathode in an electrolytic cell and the pure metal that is to cover it acts as an anode. Salt of the metal to be deposited is taken as the electrolyte. When electric current is passed, the metal from anode is deposited on the cathode. A detailed discussion is given in section 12.9.1. The metals those can be plated include, gold, silver, tin, zinc, copper, cadmium, chromium, nickel, platinum, and lead. The purpose of electroplating is to impart properties like corrosion resistance, strength, shine, decoration, wear resistance, etc., to the coated metal.

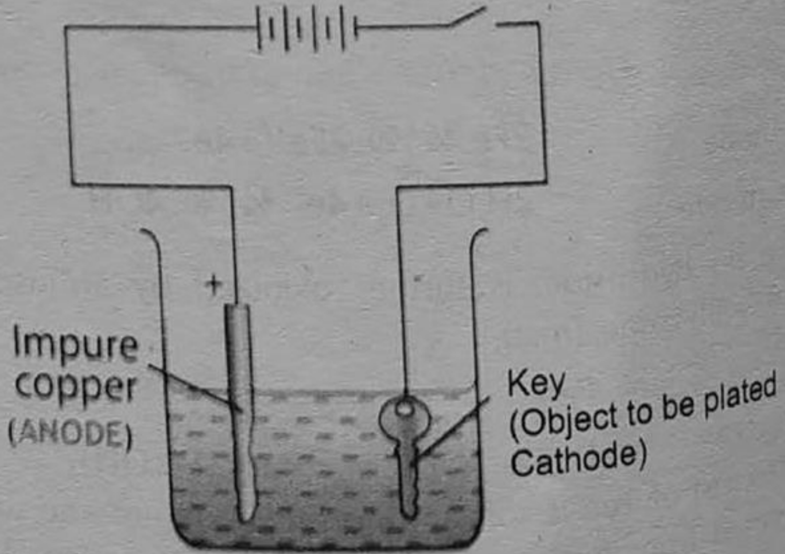


Fig: 12.12 Electroplating

(ii) Galvanizing

A typical electroplating cell in which an iron object is being electroplate with zinc. This process is also called as galvanizing. The anode is zinc metal piec and cathode is the object that is to be coated by zinc layer. The electrolyte is th zinc salt, like zinc sulphate. When the battery is turned on, zinc metal from the anode surface oxidizes and is dissolved as Zn^{2+} ions and at the same time zinc ions from the electrolyte solution are reduced at the cathode surface as zinc metal. Thus, the concentration of zinc in the solution remains the same and zinc electrode losses its weight and cathode gains weight due to deposition of zinc on it. Similarly, other metals can be electroplated on the desired metal objects.

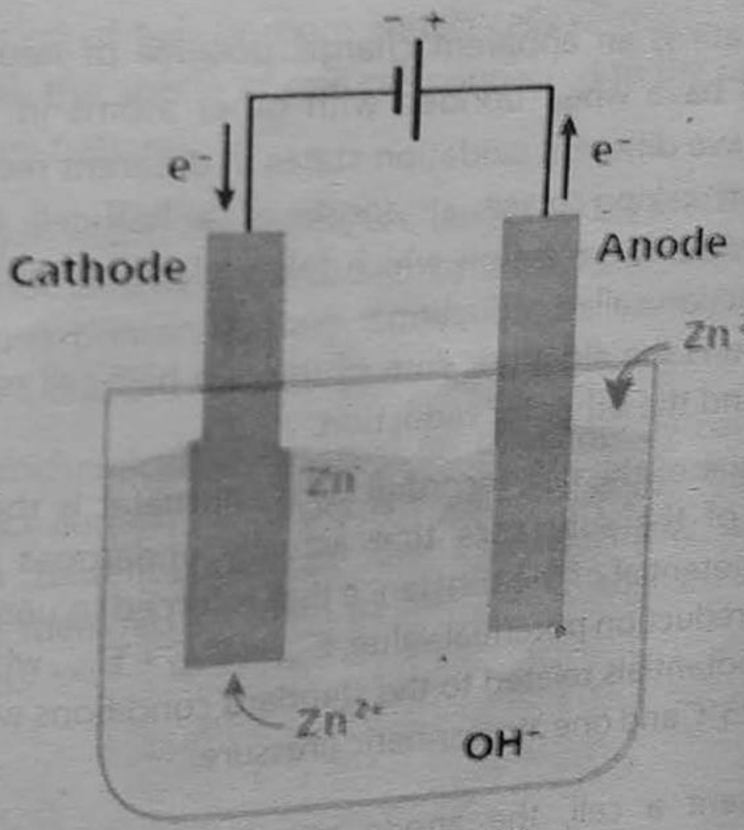


Fig. 12.13 Galvanizing

Self-Assessment

1. Define electroplating.
2. Explain three ways for prevention of corrosion.
3. Name the major types of batteries.
4. Give few advantages of the electrolytic cell.

KEY POINTS

- Loss of electrons is oxidation. There is an increase in oxidation number of the element oxidized.
- Gain of electrons is reduction. There is a decrease in oxidation number of the element reduced.
- Oxidation state is an apparent charge, positive or negative, which an atom would have when bonded with other atoms in a molecule. An atom may have different oxidation states in different molecules.
- The reaction taking place at anode is a half-cell reaction called, oxidation, while the reaction which takes place at cathode is another half-cell reaction called reduction.
- Cell reaction is the algebraic sum of the two half-cell reactions one for oxidation and the other for reduction.
- The potential of the cell recorded by a voltmeter is the sum of reduction potentials of the substance that actually undergoes reduction and the oxidation potential of the substance that is forced to undergo oxidation due to smaller reduction potential value. $E^\circ_{cell} = E^\circ_{Red} + E^\circ_{OX}$, where, E° denotes the standard potentials related to the standard conditions which is 1 M solution of ions at 25°C and one atmospheric pressure.
- To represent a cell, the anode at which oxidation takes place is represented at the left hand. Cathode is represented on the right hand. The ions of the two half cells are written in between separated by a double line which represents a salt-bridge. For example, the Daniel cell is represented as follows

$$Zn/Zn^{2+}\ (1M)\ //\ Cu^{2+}\ (IM)/Cu$$

- Electroplating is a process by which one metal is deposited over the other by electrolysis. The metallic article to be electroplated is made cathode and a sheet of pure metal to be deposited is made anode in a tank. Salt of the metal to be deposited acts as the electrolyte. When electric current is passed, the metal from anode is deposited on the cathode.

- The electrode potential of an electrode in contact with a solution of its ions of unit activity at 25°C and one atmospheric pressure, when measured relative to the standard hydrogen electrode is termed as standard electrode potential.
- An electrochemical device that generates electric current by carrying out spontaneous chemical reactions is called a battery. It is a combination of two or more voltaic cells of the same kind, arranged in series with the anode of one cell connected to the cathode of the other (secondary battery).
- A battery in which, the chemical changes taking place during working of a cell cannot exactly be reversed by passing a current in the opposite direction is primary battery. Such cells are irreversible and cannot be recharged, and once discharged are discarded e. g. dry cells.
- An electrochemical device used for continuously converting chemicals into direct current electricity is called fuel cells. Fuel cells differ from common batteries that in fuel cells electricity is produced from chemical fuels fed to them as needed, so that their operating life is unlimited.

EXERCISE

Choose the correct option.

1. Weak electrolyte in solution is

a) completely ionized
b) slightly ionized
c) never ionized
d) destroyed

2. Which one of the following is a strong electrolyte in solution?

a) Ammonium hydroxide
b) Carbonic acid
c) Potassium iodide
d) Acetic acid

3. In electrolytic cell the cathode has a charge

a) Positive
b) Negative
c) Neutral
d) Zero

4. The oxidation number of Cl in $HClO_3$ is

a) -I
b) + 1
c) + 3
d) + 5

5. The oxidation number of magnesium in $MgCO_3$ is

a) +3
b) +2
c) +1
d) -I

6. Which one of the following is a reduction reaction

a) $Br_2 \rightarrow 2Br^-$
b) $Fe^{2+} \rightarrow Fe^{3+}$
c) $Zn \rightarrow Zn^{2+}$
d) $Sn^{2+} \rightarrow Sn^{4+}$

7. A cell in which a non-spontaneous redox reaction is carried out by passing an electric current is a/an

a) Galvanic cell
b) Voltaic cell
c) Daniell cell
d) Electrolytic cell

8. Zinc rod acts as anode in the Daniell cell but acts as cathode when coupled with aluminum electrode, this is because the standard reduction potential of

a) Zn>Al
b) Zn < Al
c) Zn=Al
d) Zn=0

9. Electrolysis is a process in which the cations and anions liberated from electrolyte are

a) hydrated
b) hydrolyzed
c) charged
d) discharged

10. A cell which produces electric current by a redox reaction is called a/an

a) Voltaic cell
b) Electrolytic cell
c) Half-cell
d) Standard cell

11. The lead storage battery is a/an
    - a) Daniell cell
    - b) Voltaic cell
    - c) Dry cell
    - d) Electrolytic cell
12. The electrode potential of the standard hydrogen electrode is chosen as
    - a) 0 V
    - b) 1V
    - c) -1 V
    - d) 2V
13. A cathode has the reduction potential
    - a) Less than the anode
    - b) More than the anode
    - c) same as that of anode.
    - d) zero

Short Questions

1. What is the oxidation number of N in N_2O, NO_2, N_2O_3, HNO_3, and NH_4^+.
2. Na^+ is an oxidizing but Na is a reducing agent, why?
3. The lead storage battery is rechargeable. Why?
4. Why a solution of sugar is non-conductor but that of table salt is a good conductor of electricity?
5. NaCl is non-conductor in the solid state but is a good conductor in molten form. Why?
6. During electrolysis of fused NaCl, sodium metal is collected at cathode and not at anode, why?
7. SHE acts as anode with Cu electrode but acts as cathode when connected to Zn electrode.
8. In electroplating, the article to be plated is made cathode, why?

Numerical

1. Balance the following equation by Oxidation Number method

i. $KMnO_4 + H_2S + H_2SO_4 \longrightarrow KHSO_4 + MnSO_4 + S + H_2O$

ii. $Fe + V_2O_3 \longrightarrow Fe_2O_3 + VO$

iii. $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$

iv. $Mg + HCl \longrightarrow MgCl_2 + H_2$

v. $Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

vi. $KMnO_4 + KNO_2 + H_2SO_4 \longrightarrow MnSO_4 + KNO_3 + K_2SO_4 + H_2O$

2. Balance the following redox equations by the half reaction method

i. $Sn^{2+} + Fe^{3+} \longrightarrow Sn^{4+} + Fe^{2+}$ (Acidic medium)

ii. $Zn + Cr_2O_7^{2-} + H^+ \longrightarrow Zn^{2+} + Cr^{3+} + H_2O$ (Acidic medium)

iii. $H_2O_2 + MnO_4^- + H^+ \longrightarrow Mn^{2+} + O_2 + H_2O$ (Acidic medium)

iv. $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + I^-$ (Neutral)

3. Given the following cells at 25°C.

(a) Write the cell reactions

(b) Calculate the cell voltage

i. 1) Mg^{2+}/Mg $E^\circ_{Red} = -2.38\ V$
2) Cu^{2+}/Cu $E^\circ_{Red} = +0.34\ V$

ii. 1) $2H^+/H_2$ $E^\circ_{Red} = 0.00\ V$
2) Ag^+/Ag $E^\circ_{Red} = +0.80\ V$

Descriptive Questions

1. (a) Define the term electrolysis. State and explain Faraday's laws of electrolysis.
(b) A certain amount of current is passed through $CuSO_4$ solution for fifty minutes. The net amount of Cu deposited was found to be 25g. Calculate the current when Z = 1 and At. Mass of Cu is 63.5g.

2. What is an electrode potential? How it can be measured?

3. What is the difference between the following? Give examples.
i) Reversible and irreversible cells ii) Electrolytic and voltaic cell

4. i) Explain the term oxidation and reduction with example.
ii) What is oxidation state? Give the oxidation number of Mn in $KMnO_4$, MnO_2 and Mn_2O_7.

5. What is an electrolytic cell? Explain Daniell cell in detail.
a) Calculate the electrical energy obtained from a Daniell cell.
b) What are the half-cell reaction? Give the half-cell reactions of the Nelson's cell for the production of NaOH.

6. What are electrochemical cells? Explain it in detail.
7. Write down the types of batteries. Explain fuel cells?

Project

Take two lead pencils and sharp them from both the ends in order to expose the inner carbon cores. Take a beaker filled with 100 mL water acidified with sulphuric acid. Fix the two pencils in the beaker in vertical position about 2cm from each other. Connect the pencil cores with electrical wires with the terminals of a 9 volt battery, one pencil with the positive pole and other with the negative pole of the battery. When the battery is switched on you will see bubbles coming from the lower ends of the pencil cores. What do you think about the nature of the bubbles? Which reactions are carried out at the pencil ends? Identify the anode and the cathode?