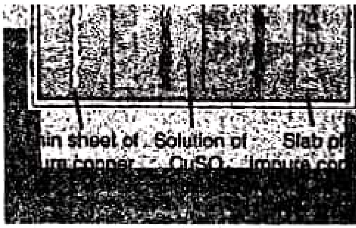

ELECTROCHEMISTRY

SECTION I : ELECTROLYTES AND ELECTROLYSIS

12.1 INTRODUCTION

Electrochemistry deals with the interactions of electrical energy with chemical species. It is broadly divided into two categories, namely (i) production of chemical change by electrical energy (phenomenon of electrolysis) and (ii) conversion of chemical energy into electrical energy, *i.e.*, generation of electricity by spontaneous redox reactions. In this chapter both of these aspects will be described. All electrochemical reactions involve transfer of electrons and are, therefore, oxidation-reduction (redox) reactions.

Substances which allow the passage of electric current through them are called **electrical conductors** or simply conductors. Those which do not allow the flow of electric current through them are termed **insulators.** Electrical conductors are of two types:

(i) Metallic or electronic conductors: Conductors which transfer electric current by transfer of electrons, without transfer of any matter, are known as **metallic or electronic conductors.** Metals such as copper, silver, aluminium, etc., non-metals like carbon (graphite—an allotropic form of carbon) and various alloys belong to this class. These materials contain electrons which are relatively free to move. The passage of current through these materials has no observable effect other than a rise in their temperature.

(ii) Electrolytic conductors: Conductors like aqueous solutions of acids, bases and salts in which the flow of electric current is accompanied by chemical decomposition are known as **electrolytic conductors.** The substances whose aqueous solutions allow the passage of electric current and are chemically decomposed, are termed **electrolytes.**

The substances whose aqueous solutions do not conduct electric current are called **non-electrolytes.** Solutions of cane sugar, glycerine, alcohol, etc., are examples of non-electrolytes.

In order to pass the current through an electrolytic conductor (aqueous solution or fused electrolyte), two rods or plates (metallic conductors) are always needed which are connected with the terminals of a battery. These rods or plates are known as **electrodes.** The electrode through which the current enters the electrolytic solution is called the **anode** (positive electrode) while the electrode through which the current leaves the electrolytic solution is known as **cathode** (negative electrode). The electrolytic solution conducts electricity not by virtue of flow of electrons as in metallic conductors but as a result of movement of charged particles called **ions** towards the respective oppositely charged electrodes. The ions which carry positive charge and move towards cathode are termed **cations** while ions carrying negative charge which move towards anode are called **anions.** When these ions reach the boundary between a metallic and an electrolytic conductor, electrons are being either attached to or removed from the ions. Removal of electrons is termed **oxidation** (de-electronation) which occurs at anode while addition of electrons is called **reduction** (electronation) that takes place at cathode. Hence, flow of electrons through the outer circuit from anode to cathode across the boundary is accompanied by oxidation and reduction.

Distinction between metallic and electrolytic conduction

Metallic conduction	Electrolytic conduction
1. Electric current flows by movement of electrons.	Electric current flows by movement of ions.
2. No chemical change occurs.	Ions are oxidised or reduced at the electrodes.
3. It does not involve the transfer of any matter.	It involves transfer of matter in the form of ions.
4. Ohm's law is followed.	Ohm's law is followed.
5. Resistance increases with increase of temperature.	Resistance decreases with increase of temperature.
6. Faraday's law is not followed.	Faraday's law is followed.

SECTION III : ELECTROCHEMICAL CELL

12.10 ELECTROCHEMICAL CELL

Electrochemical cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge. Electrochemical cells are of two types:

(a) Electrolytic cell
(b) Galvanic or voltaic cell

(a) Electrolytic Cell

It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

(b) Galvanic or Voltaic Cell

It is a device in which a redox reaction is used to convert chemical energy into electrical energy, *i.e.*, electricity can be obtained with the help of oxidation and reduction reaction. The chemical reaction responsible for production of electricity takes place in two separate compartments. Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode. The compartments containing the electrode and the solution of the electrolyte are called **half-cells.** When the two compartments are connected by a salt bridge and electrodes are joined by a wire through galvanometer the electricity begins to flow. This is the simple form of voltaic cell.

12.11 DANIELL CELL

It is designed to make use of the spontaneous redox reaction between zinc and cupric ions to produce an electric current (Fig. 12.7). It consists of two half-cells. The half-cell on the left contains a zinc metal electrode dipped in $ZnSO_4$ solution. The half-cell on the right consists of copper metal electrode in a solution of $CuSO_4$. The half-cells are joined by a salt bridge that prevents the mechanical mixing of the solution.

When the zinc and copper electrodes are joined by a wire, the following observations are made:

(i) There is a flow of electric current through the external circuit.
(ii) The zinc rod loses its mass while the copper rod gains in mass.
(iii) The concentration of $ZnSO_4$ solution increases while the concentration of copper sulphate solution decreases.
(iv) The solutions in both the compartments remain electrically neutral.

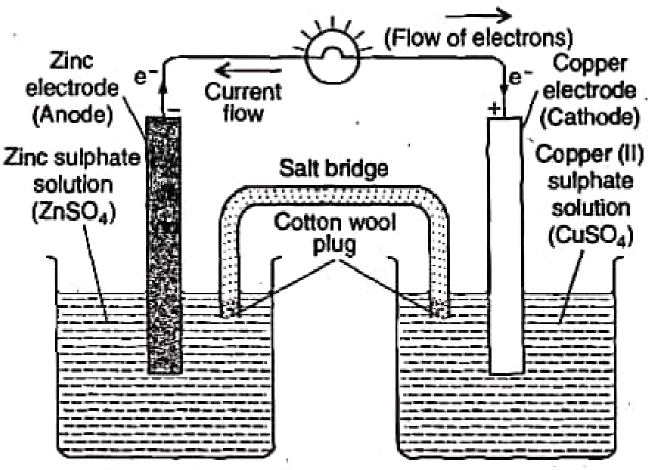

Fig. 12.7 Daniell cell

During the passage of electric current through external circuit, electrons flow from the zinc electrode to the copper electrode. At the zinc electrode, the zinc metal is oxidised to zinc ions which go into the solution. The electrons released at the electrode travel through the external circuit to the copper electrode where they are used in the reduction of Cu^{2+} ions to metallic copper which is deposited on the electrode. Thus, the overall redox reaction is:

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

Thus, indirect redox reaction leads to the production of electrical energy. At the zinc rod, oxidation occurs. It is the anode of the cell and is negatively charged while at copper electrode, reduction takes place; it is the cathode of the cell and is positively charged.

Thus, the above points can be summed up as:

(i) Voltaic or Galvanic cell consists of two **half-cells.** The reactions occurring in half-cells are called **half-cell reactions.** The half-cell in which oxidation occurs is called **oxidation half-cell** and the reaction taking place in it is called **oxidation half-cell reaction.** Similarly, the half-cell in which reduction occurs is called **reduction half-cell** and the reaction taking place in it is called **reduction half-cell reaction.**
(ii) The electrode where oxidation occurs is called anode and the electrode where reduction occurs is termed cathode.
(iii) Electrons flow from anode to cathode in the external circuit.
(iv) Overall ion movement during the operation of the galvanic cell shows that negative ions (anions) move away from cathode where they are present in excess, towards anode, where they are needed to balance the charge of the positive ions (cations) formed. Similarly, cations move away from the anode where they are in excess, towards the cathode, where they balance the anions left in excess.

Example : An $Au(NO_3)_3$ solution containing a gold electrode is connected by means of salt bridge to a $PbCl_2$ solution containing lead electrode. The cell can be correctly represented as,

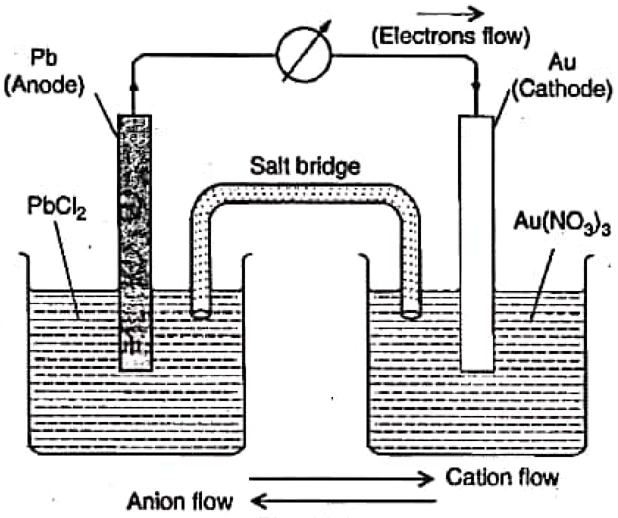

Fig. 12.8

Difference in electrolytic cell and galvanic cell

	Electrolytic cell	Galvanic cell
1.	Electrical energy is converted into chemical energy.	Chemical energy is converted into electrical energy.
2.	Anode is positive electrode. Cathode is negative electrode.	Anode is negative electrode. Cathode is positive electrode.
3.	Ions are discharged on both the electrodes.	Ions are discharged only on the cathode.
4.	If the electrodes are inert, concentration of the electrolyte decreases when the electric current is circulated.	Concentration of the anodic half-cell increases while that of cathodic half-cell decreases when the two electrodes are joined by a wire.
5.	Both the electrodes can be fitted in the same compartment.	The electrodes are fitted in different compartments.

(v) Chemical energy is converted into electrical energy.

(vi) The net reaction is the sum of two half-cell reactions. The reactions in Daniell cell can be represented as:

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

Reduction half reaction, $Cu^{2+}(aq.) + 2e^- \longrightarrow Cu(s)$

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

Electrode Signs

The signs of the anode and cathode in the voltaic or galvanic cells are opposite to those in the electrolytic cells (Fig. 12.9).

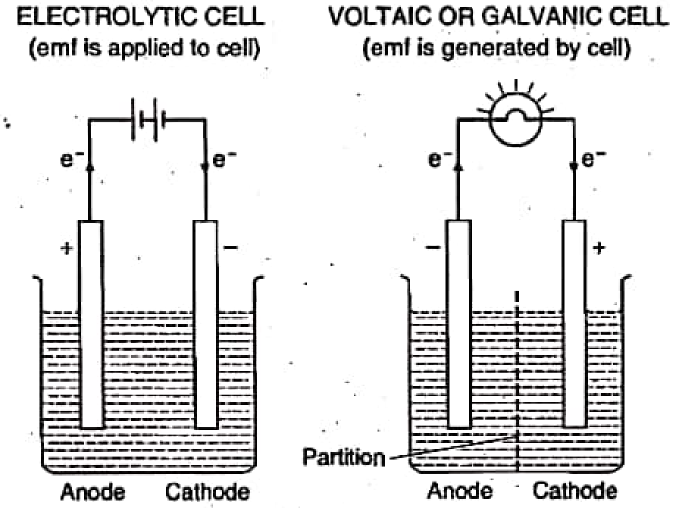

Fig. 12.9

	Electrolytic cell		Voltaic or Galvanic cell	
	Anode	Cathode	Anode	Cathode
Sign	+	−	−	+
Electron flow	out	in	out	in
Half reaction	oxidation	reduction	oxidation	reduction

12.12 SALT BRIDGE AND ITS SIGNIFICANCE

Salt bridge is usually an inverted U-tube filled with concentrated solution of inert electrolytes. An inert electrolyte is one whose ions are neither involved in any electrochemical change nor do they react chemically with the electrolytes in the two half-cells. Generally salts like KCl, KNO_3, NH_4NO_3, etc., are used. For the preparation of salt bridge, gelatin or agar-agar is dissolved in a hot concentrated aqueous solution of an inert electrolyte and the solution thus formed is filled in the U-tube. On cooling the solution sets in the form of a gel in the U-tube. The ends of the U-tube are plugged with cotton wool as to minimise diffusion effects. This is used as a salt bridge.

Significance of salt bridge: The following are the functions of the salt bridge:

(i) It connects the solutions of two half-cells and completes the cell circuit.

(ii) It prevents transference or diffusion of the solutions from one half-cell to the other.

(iii) It keeps the solutions in two half-cells electrically neutral. In anodic half-cell, positive ions pass into the solution and there shall be accumulation of extra positive charge in the solution around the anode which will prevent the flow of electrons from anode. This does not happen because negative ions are provided by salt bridge. Similarly, in cathodic half-cell, negative ions will accumulate around cathode due to deposition of positive ions by reduction. To neutralise these negative ions, sufficient number of positive ions are provided by salt bridge. Thus, salt bridge maintains electrical neutrality.

(iv) It prevents liquid-liquid junction-potential, *i.e.*, the potential difference which arises between two solutions when in contact with each other.

A broken vertical line or two parallel vertical lines in a cell reaction indicates the salt bridge.

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$

Salt bridge can be replaced by a porous partition which allows the migration of ions without allowing the solutions to intermix.

12.13 REPRESENTATION OF AN ELECTROCHEMICAL CELL (Galvanic Cell)

The following universally accepted conventions are followed in representing an electrochemical cell:

(i) The anode (negative electrode) is written on the left hand side and cathode (positive electrode) on the right hand side.

(ii) A vertical line or semicolon (;) indicates a contact between two phases. The anode of the cell is represented by writing metal first and then the metal ion present in the electrolytic solution. Both are separated by a vertical line or a semicolon. For example,

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+} \text{ or } \mathrm{Zn};\mathrm{Zn}^{2+}$$

The molar concentration or activity of the solution is written in brackets after the formula of the ion. For example,

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+}(1\,M) \text{ or } \mathrm{Zn} \mid \mathrm{Zn}^{2+}(0.1\,M)$$

(iii) The cathode of the cell is represented by writing the cation of the electrolyte first and then metal. Both are separated by a vertical line or semicolon. For example,

$$\mathrm{Cu}^{2+} \mid \mathrm{Cu} \text{ or } \mathrm{Cu}^{2+};\mathrm{Cu} \text{ or } \mathrm{Cu}^{2+}(1\,M) \mid \mathrm{Cu}$$

(iv) The salt bridge which separates the two half-cells is indicated by two parallel vertical lines.

(v) Sometimes negative and positive signs are also put on the electrodes.

The Daniell cell can be represented as:

$$\overset{-}{\mathrm{Zn}} \mid \mathrm{ZnSO}_4(aq.) \parallel \mathrm{CuSO}_4(aq.) \mid \overset{+}{\mathrm{Cu}}$$

Anode Salt bridge Cathode

Oxidation half-cell Reduction half-cell

or $$\mathrm{Zn} \mid \mathrm{Zn}^{2+} \parallel \mathrm{Cu}^{2+} \mid \mathrm{Cu}$$

or $$\mathrm{Zn} \mid \mathrm{Zn}^{2+}(1\,M) \parallel \mathrm{Cu}^{2+}(1\,M) \mid \mathrm{Cu}$$

12.14 ELECTRODE POTENTIAL

When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called **electrode potential.** For example, when a plate of zinc is placed in a solution having Zn^{2+} ions, it becomes negatively charged with respect to solution and thus a potential difference is set-up between zinc plate and the solution. This potential difference is termed the electrode potential of zinc. Similarly, when copper is placed in a solution having Cu^{2+} ions, it becomes positively charged with respect to solution. A potential difference is set-up between the copper plate and the solution. The potential difference thus developed is termed as electrode potential of copper. The potential difference is established due to the formation of electrical double layer at the interface of metal and the solution. The development of negative charge (as on zinc plate) or positive charge (as on copper plate) can be explained in the following manner. When a metal rod is dipped in its salt solution, two changes occur:

$$M(s) \longrightarrow M^{n+}(aq.) + ne^-$$

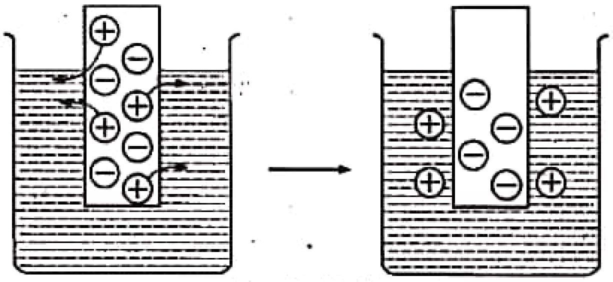

Fig. 12.10 (a)

$$M^{n+}(aq.) + ne^- \longrightarrow M(s)$$

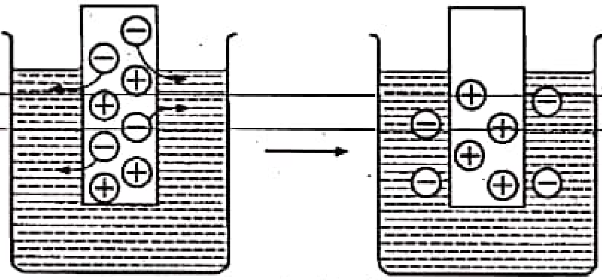

Fig. 12.10 (b)

(a) Oxidation : Metal ions pass from the electrode into solution leaving an excess of electrons and thus a negative charge on the electrode.

(b) Reduction : Metal ions in solution gain electrons from the electrode leaving a positive charge on the electrode.

(i) The conversion of metal atoms into metal ions by the attractive force of polar water molecules.

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

The metal ions go into the solution and the electrons remain on the metal making it negatively charged. The tendency of the metal to change into ions is known as **electrolytic solution pressure.**

(ii) Metal ions start depositing on the metal surface leading to a positive charge on the metal.

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

This tendency of the ions is termed **osmotic pressure.**

In the beginning, both these changes occur with different speeds but soon an equilibrium is established.

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

In practice, one effect is greater than the other, if first effect is greater than the second, the metal acquires a negative charge with respect to solution and if the second is greater than the first, it acquires positive charge with respect to solution, thus in both the cases a potential difference is set-up.

The magnitude of the electrode potential of a metal is a measure of its relative tendency to lose or gain electrons, *i.e.*, it is a measure of the relative tendency to undergo oxidation (loss of electrons) or reduction (gain of electrons). The magnitude of potential depends on the following factors:

(i) Nature of the electrode,
(ii) Concentration of the ions in solution,
(iii) Temperature.

Depending on the nature of the metal electrode to lose or gain electrons, the electrode potential may be of two types:

(i) Oxidation potential: When electrode is negatively charged with respect to solution, *i.e.*, it acts as anode. Oxidation occurs.

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

(ii) Reduction potential: When electrode is positively charged with respect to solution, *i.e.*, it acts as cathode. Reduction occurs.

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

It is not possible to measure the absolute value of the single electrode potential directly. Only the difference in potential between two electrodes can be measured experimentally. It is, therefore, necessary to couple the electrode with another electrode whose potential is known. This electrode is termed as **reference electrode.** The emf of the resulting cell is measured experimentally. The emf of the cell is equal to the sum of potentials on the two electrodes.

Emf of the cell = $E_{\text{Anode}} + E_{\text{Cathode}}$
= Oxidation potential of anode
+ Reduction potential of cathode

Knowing the value of reference electrode, the value of other electrode can be determined.

12.15 STANDARD ELECTRODE POTENTIAL

In order to compare the electrode potentials of various electrodes, it is necessary to specify the concentration of the ions present in solution in which the electrode is dipped and the temperature of the half-cell. The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 *M*) at 25° C (298 K) is called **standard electrode potential.**

According to the IUPAC convention, the reduction potential alone can be called as the electrode potential ($E°$), *i.e.*, the given value of electrode potential can be regarded as reduction potential unless it is specifically mentioned that it is oxidation potential. Standard reduction potential of an electrode means that reduction reaction is taking place at the electrode. If the reaction is reversed and written as oxidation reaction, the numerical value of electrode potential will remain same but the sign of standard potential will have to be reversed. Thus,

Standard reduction potential = – Standard oxidation potential

or Standard oxidation potential = – Standard reduction potential

12.16 REFERENCE ELECTRODE (Standard Hydrogen Electrode, SHE or NHE)

Hydrogen electrode is the primary standard electrode. It consists of a small platinum strip coated with platinum black as to adsorb hydrogen gas. A platinum wire is welded to the platinum strip and sealed in a glass tube as to make contact with the outer circuit through mercury. The platinum strip and glass tube is surrounded by an outer glass tube which has an inlet for hydrogen gas at the top and a number of holes at the base for the escape of excess of hydrogen gas. The platinum strip is placed in an acid solution which has H^+ ion concentration 1 *M*. Pure hydrogen gas is circulated at one atmospheric pressure. A part of the gas is adsorbed and the rest escapes through holes. This gives an equilibrium between the adsorbed hydrogen and hydrogen ions in the solution.

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

The temperature of the cell is maintained at 25° C. By international agreement the standard hydrogen electrode is arbitrarily assigned a potential of exactly $\pm 0.000\ldots$ volt.

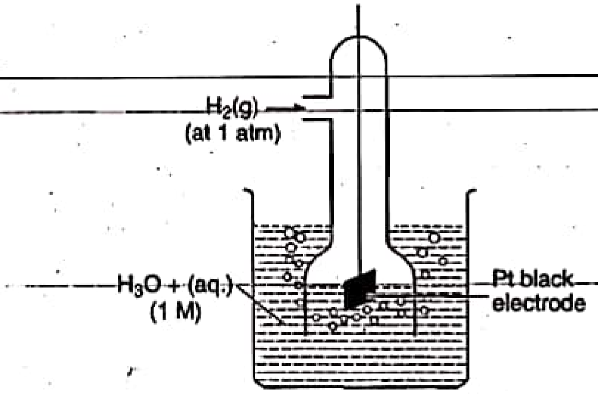

Fig. 12.11 Hydrogen electrode

The hydrogen electrode thus obtained forms one of two half-cells of a voltaic cell. When this half-cell is connected with any other half-cell, a voltaic cell is constituted. The hydrogen electrode can act as cathode or anode with respect to other electrode.

SHE half reaction	Electrode potential
$H_2 \longrightarrow 2H^+ + 2e^-$	0.0 V (Anode)
$2H^+ + 2e^- \longrightarrow H_2$	0.0 V (Cathode)

12.17 MEASUREMENT OF ELECTRODE POTENTIAL

The measurement of electrode potential of a given electrode is made by constituting a voltaic cell, *i.e.*, by connecting it with a standard hydrogen electrode (SHE) through a salt bridge. 1 *M* solution is used in hydrogen half-cell and the temperature is maintained at 25° C. The emf of the cell is measured either by a calibrated potentiometer or by a high resistance voltmeter, *i.e.*, a valve voltmeter. The reading of the voltmeter gives the electrode potential of the electrode in question with respect to the hydrogen electrode. The standard electrode potential of a metal may be determined as it is the potential difference in volt developed in a cell consisting of two electrodes: the pure metal is in contact with a molar solution of one of its ions and the standard hydrogen electrode.

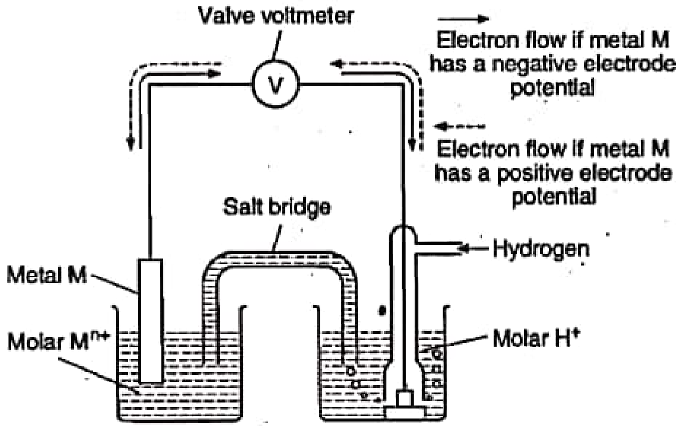

Fig. 12.12

(i) Determination of standard electrode potential of Zn/Zn^{2+} electrode: A zinc rod is dipped in 1 *M* zinc sulphate solution. This half-cell is combined with a standard hydrogen electrode through a salt bridge. Both the electrodes are connected with a voltmeter as shown in Fig. 12.13. The deflection of the voltmeter indicates that current is flowing from hydrogen electrode to metal electrode or the electrons are moving from zinc rod to hydrogen electrode. The zinc electrode acts as an anode and the hydrogen electrode as cathode and the cell can be represented as

$$\underset{\text{Anode}(-)}{Zn\,|\,Zn^{2+}(aq.)}\;||\;\underset{\text{Cathode}(+)}{2H^+(aq.)\,|\,H_2(g)}$$

$$\underset{\text{(Oxidation)}}{Zn \longrightarrow Zn^{2+} + 2e^-}\;;\;\underset{\text{(Reduction)}}{2H^+ + 2e^- \longrightarrow H_2\uparrow}$$

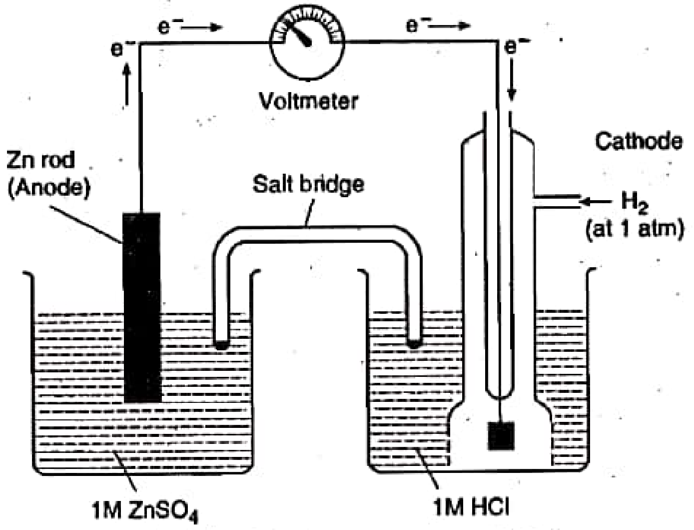

Fig. 12.13 Zn–H_2 electrochemical cell

The emf of the cell is 0.76 volt

$$E_{Cell} = E^\circ_{Anode} + E^\circ_{Cathode}$$

$$0.76 = E^\circ_{Anode} + 0 \text{ or } E^\circ_{Anode} = +0.76\text{ V}$$

As the reaction on the anode is oxidation, *i.e.*,

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

E°_{Anode} is the standard oxidation potential of zinc. This potential is given the positive sign.

$$E^\circ_{ox}(Zn/Zn^{2+}) = +0.76\text{ volt}$$

So, standard reduction potential of Zn, *i.e.*, $E^\circ(Zn^{2+}/Zn)$

$$= -E^\circ_{ox} = -(+0.76)$$

$$= -0.76\text{ volt}$$

The emf of such a cell gives the positive value of standard oxidation potential of metal *M*. The standard reduction potential (E°) is obtained by reversing the sign of standard oxidation potential.

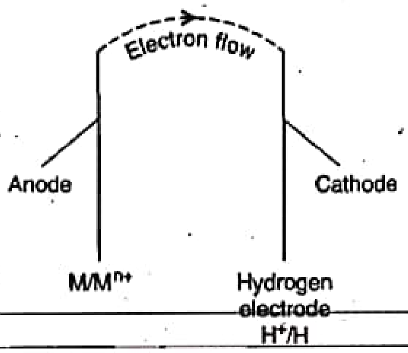

Fig. 12.14

(ii) Determination of standard electrode potential of Cu^{2+}/Cu, electrode: A copper rod is dipped in 1 *M* solution of $CuSO_4$. It is combined with hydrogen electrode through a salt bridge. Both the electrodes are joined through a voltmeter. The deflection of the voltmeter indicates that current is flowing from copper electrode towards hydrogen electrode, *i.e.*, the electrons are moving from hydrogen electrode to copper electrode. The hydrogen electrode acts as an anode and the copper electrode as a cathode. The cell can be represented as

$$\underset{\text{Anode}(-)}{H_2(g)\,|\,2H^+(aq.)}\;||\;\underset{\text{Cathode}(+)}{Cu^{2+}(aq.)\,|\,Cu}$$

$$\underset{\text{Oxidation}}{H_2 \longrightarrow 2H^+ + 2e^-}\;;\;\underset{\text{Reduction}}{Cu^{2+} + 2e^- \longrightarrow Cu}$$

The emf of the cell is 0.34 volt.

$$E^\circ_{Cell} = E^\circ_{Anode} + E^\circ_{Cathode}$$

$$0.34 = 0 + E^\circ_{Cathode}$$

Since, the reaction on the cathode is reduction, *i.e.*, $Cu^{2+} + 2e^- \longrightarrow Cu$, $E^\circ_{Cathode}$ is the standard reduction potential of copper. This is given the + ve sign.

E°, *i.e.*, standard reduction potential of $Cu^{2+}/Cu = 0.34$ volt

So, E°_{ox} (standard oxidation potential of copper) $= -0.34$ volt

The emf of such a cell gives positive value of reduction potential of metal electrode. The standard oxidation potential of this electrode is obtained by reversing the sign of standard reduction potential.

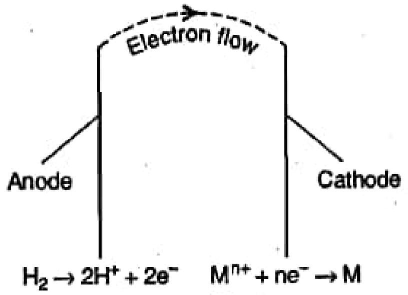

Fig. 12.15

It is thus concluded that at the metal electrode which acts as anode with respect to hydrogen electrode (cathode), the reduction potential is given the minus sign and at the metal electrode which acts as cathode with respect to hydrogen electrode (anode), the reduction potential is given the positive sign.

The standard electrode potentials (oxidation or reduction) of various elements can be measured by combining the electrode in question with a standard hydrogen electrode and measuring the emf of the cell constituted.

12.18 EMF OF A GALVANIC CELL

Every galvanic or voltaic cell is made up of two half-cells, the oxidation half-cell (anode) and the reduction half-cell (cathode). The potentials of these half-cells are always different. On account of this difference in electrode potentials, the electric current moves from the electrode at higher potential to the electrode at lower potential, *i.e.*, from cathode to anode. The direction of the flow of electrons is from anode to cathode.

$$\text{Anode} \underset{\text{Flow of current}}{\overset{\text{Flow of electrons}}{\rightleftarrows}} \text{Cathode}$$

The difference in potentials of the two half-cells is known as the electromotive force **(emf) of the cell or cell potential.**

The emf of the cell or cell potential can be calculated from the values of electrode potentials of the two half-cells constituting the cell. The following three methods are in use:

(i) When oxidation potential of anode and reduction potential of cathode are taken into account:

$$E^\circ_{\text{cell}} = \text{Oxidation potential of anode} + \text{Reduction potential of cathode}$$

$$= E^\circ_{\text{ox}} \text{ (anode)} + E^\circ_{\text{red}} \text{ (cathode)}$$

(ii) When reduction potentials of both electrodes are taken into account:

$$E^\circ_{\text{cell}} = \text{Standard Reduction potential of cathode} - \text{Standard Reduction potential of anode}$$

$$= E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}$$

$$= E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

(iii) When oxidation potentials of both electrodes are taken into account:

$$E^\circ_{\text{cell}} = \text{Oxidation potential of anode} - \text{Oxidation potential of cathode}$$

$$= E^\circ_{\text{ox}} \text{ (anode)} - E^\circ_{\text{ox}} \text{ (cathode)}$$

Difference between emf and potential difference: The potential difference is the difference between the electrode potentials of the two electrodes of the cell under any condition while emf is the potential generated by a cell when there is zero electron flow, *i.e.*, it draws no current. The points of difference are given ahead:

Emf	Potential difference
1. It is the potential difference between two electrodes when no current is flowing in the circuit.	It is the difference of the electrode potentials of the two electrodes when the cell is under operation.
2. It is the maximum voltage that the cell can deliver.	It is always less than the maximum value of voltage which the cell can deliver.
3. It is responsible for the steady flow of current in the cell.	It is not responsible for the steady flow of current in the cell.

12.19 REVERSIBLE AND IRREVERSIBLE CELLS

Daniell cell has the emf value 1.09 volt. If an opposing emf exactly equal to 1.09 volt is applied to the cell, the cell reaction,

$$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$$

stops but if it is increased infinitesimally beyond 1.09 volt, the cell reaction is reversed.

$$Cu + Zn^{2+} \longrightarrow Zn + Cu^{2+}$$

Such a cell is termed a **reversible cell.** Thus, the following are the two main conditions of reversibility:

(i) The chemical reaction of the cell stops when an exactly equal opposing emf is applied.

(ii) The chemical reaction of the cell is reversed and the current flows in opposite direction when the opposing emf is slightly greater than that of the cell.

Any other cell which does not obey the above two conditions is termed as **irreversible.** A cell consisting of zinc and copper electrodes dipped into the solution of sulphuric acid is irreversible. Similarly, the cell

$$Zn \mid H_2SO_4(aq.) \mid Ag$$

is also irreversible because when the external emf is greater than the emf of the cell, the cell reaction,

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

is not reversed but the cell reaction becomes

$$2Ag + 2H^+ \longrightarrow 2Ag^+ + H_2$$

12.20 SOME OTHER REFERENCE ELECTRODES

Since, a standard hydrogen electrode is difficult to prepare and maintain, it is usually replaced by other reference electrodes, which are known as secondary reference electrodes. These are convenient to handle and are prepared easily. Two important secondary reference electrodes are described here.

(i) Calomel electrode: It consists of mercury at the bottom over which a paste of mercury-mercurous chloride is placed. A solution of potassium chloride is then placed over the paste. A platinum wire sealed in a glass tube helps in making the electrical contact. The electrode is connected with the help of the side tube on the left through a salt bridge with the other electrode to make a complete cell.

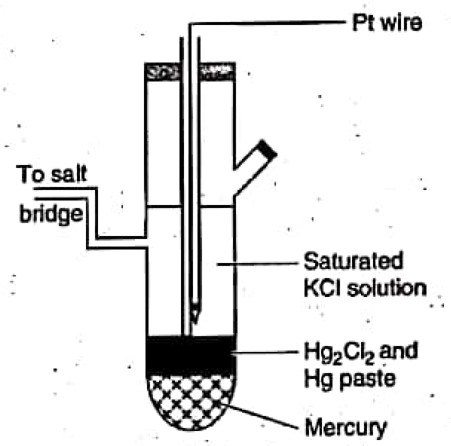

Fig. 12.16 Calomel electrode

The potential of the calomel electrode depends upon the concentration of the potassium chloride solution. If potassium chloride solution is saturated, the electrode is known as saturated calomel electrode (SCE) and if the potassium chloride solution is 1 *N*, the electrode is known as normal calomel electrode (NCE) while for 0.1 *N* potassium chloride solution, the electrode is referred to as decinormal calomel electrode (DNCE). The electrode reaction when the electrode acts as cathode is:

$$\frac{1}{2}Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$$

The reduction potentials of the calomel electrodes on hydrogen scale at 298 K are as follows:

Saturated KCl	0.2415 V
1.0 *N* KCl	0.2800 V
0.1 *N* KCl	0.3338 V

The electrode potential of any other electrode on hydrogen scale can be measured when it is combined with calomel electrode. The emf of such a cell is measured. From the value of electrode potential of calomel electrode, the electrode potential of the other electrode can be evaluated.

(ii) Silver-silver chloride electrode: This is another widely used reference electrode. It is reversible and stable and can be combined with cells containing chlorides without inserting liquid junctions.

Silver chloride is deposited electrolytically on a silver or platinum wire and it is then immersed in a solution containing chloride ions. Its standard electrode potential with respect to the standard hydrogen electrode is 0.2224 V at 298 K. The electrode is represented as:

$$Ag \,|\, AgCl \,|\, Cl^-$$

The electrode reaction is:

$$AgCl + e^- \longrightarrow Ag + Cl^-$$

12.21 PREDICTION FOR OCCURRENCE OF A REDOX REACTION

Any redox reaction would occur spontaneously if the free energy change (ΔG) is negative. The free energy is related to cell emf in the following manner:

$$\Delta G^\circ = -nFE^\circ$$

where, n is the number of electrons involved, F is the value of Faraday and E° is the cell emf. ΔG can be negative if E° is positive.

When E° is positive, the cell reaction is spontaneous and serves as a source of electrical energy.

To predict whether a particular redox reaction will occur or not, write down the redox reaction into two half reactions, one involving oxidation reaction and the other involving reduction reaction. Write the oxidation potential value for oxidation reaction and reduction potential value for reduction reaction. Add these two values, if the algebraic summation gives a positive value, the reaction will occur, otherwise not.

[**Note :** The true conditions for operating voltaic cells are :
$\Delta G < 0,\ E > 0$]

12.22 ELECTRODE AND CELL POTENTIALS—NERNST EQUATION

The electrode potential and the emf of the cell depend upon the nature of the electrode, temperature and the activities (concentrations) of the ions in solution. The variation of electrode and cell potentials with concentration of ions in solution can be obtained from thermodynamic considerations. For a general reaction such as

$$m_1A + m_2B + \ldots \rightleftharpoons n_1X + n_2Y + \ldots \qquad \ldots \text{(i)}$$

occurring in the cell, the Gibbs free energy change is given by the equation

$$\Delta G = \Delta G^\circ + 2.303RT\log_{10}\frac{a_X^{n_1} \times a_Y^{n_2} \ldots}{a_A^{m_1} \times a_B^{m_2} \ldots} \qquad \ldots \text{(ii)}$$

where, 'a' represents the activities of reactants and products under a given set of conditions and ΔG° refers to free energy change for the reaction when the various reactants and products are present at standard conditions. The free energy change of a cell reaction is related to the electrical work that can be obtained from the cell, *i.e.*, $\Delta G = -nFE_{cell}$ and $\Delta G^\circ = -nFE^\circ$. On substituting these values in eq. (ii), we get

$$-nFE_{cell} = -nFE^\circ_{cell} + 2.303RT\log_{10}\frac{a_X^{n_1} \times a_Y^{n_2} \ldots}{a_A^{m_1} \times a_B^{m_2} \ldots} \qquad \ldots \text{(iii)}$$

or

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log_{10}\frac{a_X^{n_1} \times a_Y^{n_2} \ldots}{a_A^{m_1} \times a_B^{m_2} \ldots} \qquad \ldots \text{(iv)}$$

This equation is known as Nernst equation.

Putting the values of $R = 8.314\ JK^{-1}\ mol^{-1}$, $T = 298$ K and $F = 96500$ C, eq. (iv) reduces to

$$E = E^\circ - \frac{0.0591}{n}\log_{10}\frac{a_X^{n_1} \times a_Y^{n_2} \ldots}{a_A^{m_1} \times a_B^{m_2} \ldots} \qquad \ldots \text{(v)}$$

$$= E^\circ - \frac{0.0591}{n}\log_{10}\frac{[\text{Products}]}{[\text{Reactants}]} \qquad \ldots \text{(vi)}$$

Potential of single electrode (Anode): Consider the general oxidation reaction,

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

Applying Nernst equation,

$$E_{ox} = E^\circ_{ox} - \frac{0.0591}{n} \log_{10} \frac{[M^{n+}]}{[M]}$$

where, E_{ox} is the oxidation potential of the electrode (anode), E°_{ox} is the standard oxidation potential of the electrode.

[Note: The concentration of pure solids and liquids are taken as unity.]

$$E_{ox} = E^\circ_{ox} - \frac{0.0591}{n} \log_{10} [M^{n+}]$$

Let us consider a Daniell cell to explain the above equations. The concentrations of the electrolytes are not 1 *M*.

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

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

Potential at zinc electrode (Anode)

$$E_{ox} = E^\circ_{ox} - \frac{0.0591}{n} \log_{10} [Zn^{2+}]$$

Potential at copper electrode (Cathode)

$$E_{red} = E^\circ_{red} + \frac{0.0591}{n} \log_{10} [Cu^{2+}]$$

Emf of the cell

$$E_{cell} = E_{ox} + E_{red}$$

$$= (E^\circ_{ox} + E^\circ_{red}) - \frac{0.0591}{n} \log_{10} \left[\frac{Zn^{2+}}{Cu^{2+}}\right]$$

$$= E^\circ_{cell} - \frac{0.0591}{n} \log_{10} \left[\frac{Zn^{2+}}{Cu^{2+}}\right]$$

The value of $n = 2$ for both zinc and copper.

Let us consider an example, in which the values of *n* for the two ions in the two half-cells are not same. For example, in the cell

$$Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$$

The cell reaction is:

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

The two half-cell reactions are:

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

$$Ag^+ + e^- \longrightarrow Ag$$

The second equation is multiplied by 2 to balance the number of electrons.

$$2Ag^+ + 2e^- \longrightarrow 2Ag$$

$$E_{ox} = E^\circ_{ox} - \frac{0.0591}{2} \log_{10} [Cu^{2+}]$$

$$E_{red} = E^\circ_{red} + \frac{0.0591}{2} \log_{10} [Ag^+]^2$$

$$E_{cell} = E_{ox} + E_{red} = E^\circ_{ox} + E^\circ_{red} - \frac{0.0591}{2} \log_{10} \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$= E^\circ_{cell} - \frac{0.0591}{2} \log_{10} \frac{[Cu^{2+}]}{[Ag^+]^2}$$

SOME SOLVED EXAMPLES

Example 31. *Construct the cells in which the following reactions are taking place. Which of the electrodes shall act as anode (negative electrode) and which one as cathode (positive electrode)?*

(a) $Zn + CuSO_4 = ZnSO_4 + Cu$

(b) $Cu + 2AgNO_3 = Cu(NO_3)_2 + 2Ag$

(c) $Zn + H_2SO_4 = ZnSO_4 + H_2$

(d) $Fe + SnCl_2 = FeCl_2 + Sn$

Solution: It should always be kept in mind that the metal which goes into solution in the form of its ions undergoes oxidation and thus acts as negative electrode (anode) and the element which comes into the free state undergoes reduction and acts as positive electrode (cathode):

(a) In this case Zn is oxidised to Zn^{2+} and thus acts as anode (negative electrode) while Cu^{2+} is reduced to copper and thus acts as cathode (positive electrode). The cell can be represented as

$$Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$$

or

$$\underset{\text{Anode }(-)}{Zn \mid Zn^{2+}} \parallel \underset{\text{Cathode }(+)}{Cu^{2+} \mid Cu}$$

(b) In this case Cu is oxidised to Cu^{2+} and Ag^+ is reduced to Ag. The cell can be represented as

$$Cu \mid Cu(NO_3)_2 \parallel AgNO_3 \mid Ag$$

or

$$\underset{\text{Anode }(-)}{Cu \mid Cu^{2+}} \parallel \underset{\text{Cathode }(+)}{Ag^+ \mid Ag}$$

(c) In this case, Zn is oxidised to Zn^{2+} and H^+ is reduced to H_2. The cell can be represented as:

$$Zn \mid ZnSO_4 \parallel H_2SO_4 \mid H_2(Pt)$$

or

$$\underset{\text{Anode }(-)}{Zn \mid Zn^{2+}} \parallel \underset{\text{Cathode }(+)}{2H^+ \mid H_2(Pt)}$$

(d) Here, Fe is oxidised to Fe^{2+} and Sn^{2+} is reduced to Sn. The cell can be represented as:

$$Fe \mid FeCl_2 \parallel SnCl_2 \mid Sn$$

or

$$\underset{\text{Anode }(-)}{Fe \mid Fe^{2+}} \parallel \underset{\text{Cathode }(+)}{Sn^{2+} \mid Sn}$$

Note : Oxidation potential is $E^\circ_{M/M^{n+}}$ while reduction potential is represented as $E^\circ_{M^{n+}/M}$. The value of $E^\circ_{Zn/Zn^{2+}}$ (oxidation potential of Zn) is + 0.76 volt and the value of $E^\circ_{Cu^{2+}/Cu}$ (reduction potential of copper) is + 0.34 volt. The electrode having lower value of reduction potential acts as an anode while that having higher value of reduction potential acts as cathode.

Example 32. *Consider the reaction,*

$$2Ag^+ + Cd \longrightarrow 2Ag + Cd^{2+}$$

The standard electrode potentials for $Ag^+ \longrightarrow Ag$ *and* $Cd^{2+} \longrightarrow Cd$ *couples are* 0.80 *volt and* − 0.40 *volt respectively.*

(*i*) *What is the standard potential E° for this reaction?*

(*ii*) *For the electrochemical cell, in which this reaction takes place which electrode is negative electrode?*

Solution: (i) The half reactions are:

$$2Ag^+ + \underset{\substack{\text{Reduction}\\ \text{(Cathode)}}}{2e^-} \longrightarrow 2Ag,$$

$E^\circ_{Ag^+/Ag} = 0.80$ volt (Reduction potential)

$$Cd \longrightarrow \underset{\substack{\text{Oxidation}\\ \text{(Anode)}}}{Cd^{2+}} + 2e^-,$$

$E^\circ_{Cd^{2+}/Cd} = -0.40$ volt (Reduction potential)

or $E^\circ_{Cd/Cd^{2+}} = +0.40$ volt

$E^\circ = E^\circ_{Cd/Cd^{2+}} + E^\circ_{Ag^+/Ag} = 0.40 + 0.80 = 1.20$ volt

(ii) The negative electrode is always the electrode whose reduction potential has smaller value or the electrode where oxidation occurs. Thus, Cd electrode is the negative electrode.

Example 33. *Consider the cell,*

$$Zn\,|\,Zn^{2+}(aq.)(1.0\,M)\,||\,Cu^{2+}(aq.)(1.0\,M)\,|\,Cu$$

The standard electrode potentials are:

$Cu^{2+} + 2e^- \longrightarrow Cu(aq.)$; $E^\circ = 0.350$ volt

$Zn^{2+} + 2e^- \longrightarrow Zn(aq.)$; $E^\circ = -0.763$ volt

(*i*) *Write down the cell reaction.*

(*ii*) *Calculate the emf of the cell.*

Solution: (i) Reduction potential of Zn is less than copper, hence Zn acts as anode and copper as cathode.

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

At cathode $Cu^{2+} + 2e^- \longrightarrow Cu$ (Reduction)

Cell reaction $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

(ii) $E^\circ_{cell} = E^\circ_{Zn/Zn^{2+}} + E^\circ_{Cu^{2+}/Cu}$

= Oxi. potential of zinc + Red. potential of copper

$E^\circ_{Zn^{2+}/Zn} = -0.763$ (Reduction potential)

$E^\circ_{Zn/Zn^{2+}} = +0.763$ (Oxidation potential)

and $E^\circ_{Cu^{2+}/Cu} = 0.350$ (Reduction potential)

So, $E^\circ_{cell} = 0.763 + 0.350 = 1.113$ volt

Example 34. *Write the electrode reactions and the net cell reactions for the following cells. Which electrode would be the positive terminal in each cell?*

(*a*) $Zn\,|\,Zn^{2+}\,||\,Br^-, Br_2\,|\,Pt$ (*b*) $Cr\,|\,Cr^{3+}\,||\,I^-, I_2\,|\,Pt$

(*c*) $Pt\,|\,H_2, H^+\,||\,Cu^{2+}\,|\,Cu$ (*d*) $Cd\,|\,Cd^{2+}\,||\,Cl^-, AgCl\,|\,Ag$

Solution:

(a) Oxidation half reaction, $Zn \longrightarrow Zn^{2+} + 2e^-$

Reduction half reaction, $Br_2 + 2e^- \longrightarrow 2Br^-$

Net cell reaction $Zn + Br_2 \longrightarrow Zn^{2+} + 2Br^-$

Positive terminal—Cathode Pt

(b) Oxidation half reaction, $[Cr \longrightarrow Cr^{3+} + 3e^-] \times 2$

Reduction half reaction, $[I_2 + 2e^- \longrightarrow 2I^-] \times 3$

Net cell reaction $2Cr + 3I_2 \longrightarrow 2Cr^{3+} + 6I^-$

Positive terminal—Cathode Pt

(c) Oxidation half reaction, $H_2 \longrightarrow 2H^+ + 2e^-$

Reduction half reaction, $Cu^{2+} + 2e^- \longrightarrow Cu$

Net cell reaction $H_2 + Cu^{2+} \longrightarrow Cu + 2H^+$

Positive terminal—Cathode Cu

(d) Oxidation half reaction, $Cd \longrightarrow Cd^{2+} + 2e^-$

Reduction half reaction,

$[AgCl + e^- \longrightarrow Ag + Cl^-] \times 2$

Net cell reaction $Cd + 2AgCl \longrightarrow Cd^{2+} + 2Ag + 2Cl^-$

Positive terminal—Cathode Ag

Example 35. *Will Fe be oxidised to* Fe^{2+} *by reaction with* 1.0 *M HCl? E° for* $Fe/Fe^{2+} = +0.44$ *volt.*

Solution: The reaction will occur if Fe is oxidised to Fe^{2+}.

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

Writing two half reactions,

$Fe \longrightarrow Fe^{2+} + 2e^-$ Oxidation; $E^\circ_{Fe/Fe^{2+}} = 0.44$ volt

$2H^+ + 2e^- \longrightarrow H_2$ Reduction; $E^\circ_{H^+/H} = 0.0$ volt

Adding; emf = 0.44 volt

Since, emf is positive, the reaction shall occur.

Example 36. *The values of E° of some of the reactions are given below:*

$I_2 + 2e^- \longrightarrow 2I^-$; $E^\circ = +0.54$ volt

$Cl_2 + 2e^- \longrightarrow 2Cl^-$; $E^\circ = +1.36$ volt

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$; $E^\circ = +0.76$ volt

$Ce^{4+} + e^- \longrightarrow Ce^{3+}$; $E^\circ = +1.60$ volt

$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$; $E^\circ = +0.15$ volt

On the basis of the above data, answer the following questions:

23. Calculate the emf of the following concentration cell at 25°C:

$Ag(s) \mid AgNO_3\ (0.01\ M) \parallel AgNO_3\ (0.05\ M) \mid Ag(s)$

(a) − 0.414 V (b) 0.828 V

(c) 0.414 V (d) 0.0414 V

[Ans. (d)]

[Hint: $E = E^\circ - \frac{0.0591}{n} \log_{10} Q$

($\because E^\circ = 0$ for all concentration cells)

$$= 0 - \frac{0.0591}{1} \log_{10}\left(\frac{0.01}{0.05}\right) = 0.0414\ \text{V}]$$

24. The equilibrium constant of the reaction:

$$Cu(s) + 2Ag^+(aq.) \rightleftharpoons Cu^{2+}(aq.) + 2Ag(s)$$

$E^\circ = 0.46$ V at 298 K is: [CBSE (Med.) 2007]

(a) 2.0×10^{10} (b) 4.0×10^{10}

(c) 4.0×10^{15} (d) 2.4×10^{10}

[Ans. (c)]

[Hint: $K = \text{antilog}\left[\frac{nE^\circ}{0.059}\right] = \text{antilog}\left[\frac{2 \times 0.46}{0.059}\right]$

$= \text{antilog } 15.593$

$= 3.9 \times 10^{15}$

$\approx 4 \times 10^{15}$]

25. The cell reaction of a cell is:

$$Mg(s) + Cu^{2+}(aq.) \rightleftharpoons Cu(s) + Mg^{2+}(aq.)$$

If the standard reduction potentials of Mg and Cu are − 2.37 and + 0.34 V respectively. The emf of the cell is: [JEE (WB) 2007]

(a) 2.03 V (b) − 2.03 V (c) + 2.71 V (d) − 2.71 V

[Ans. (c)]

[Hint: $E^\circ_{\text{Cell}} = E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}$

$= E^\circ_{\text{Reduced species}} - E^\circ_{\text{Oxidised species}}$

$= 0.34 - (-2.37) = +2.71$ V]

26. The equilibrium constant of the following redox reaction at 298 K is 1×10^8

$$2Fe^{3+}(aq.) + 2I^-(aq.) \rightleftharpoons 2Fe^{2+}(aq.) + I_2(s)$$

If the standard reduction potential of iodine becoming iodide is + 0.54 V. What is the standard reduction potential of Fe^{3+}/Fe^{2+}? [PMT (Kerala) 2008]

(a) + 1.006 V (b) − 1.006 V

(c) + 0.77 V (d) − 0.77 V

(e) − 0.652 V

[Ans. (c)]

[Hint: $E^\circ = \frac{0.059}{n} \log_{10} K$

$= \frac{0.059}{2} \log_{10} 10^8 = 0.236$

$E^\circ_{\text{Cell}} = E^\circ_{\text{Reduced species}} - E^\circ_{\text{Oxidised species}}$

$0.236 = E^\circ_{Fe^{3+}/Fe^{2+}} - 0.54$

$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77$V]

12.23 ELECTROCHEMICAL SERIES

By measuring the potentials of various electrodes *versus* standard hydrogen electrode (SHE), a series of standard electrode potentials has been established. When the electrodes (metals and non-metals) in contact with their ions are arranged on the basis of the values of their standard reduction potentials or standard oxidation potentials, the resulting series is called the **electrochemical** or **electromotive** or **activity series** of the elements.

By international convention, the standard potentials of electrodes are tabulated for reduction half reactions, indicating the tendencies of the electrodes to behave as cathodes towards SHE. Those with positive E° values for reduction half reactions do in fact act as cathodes *versus* SHE, while those with negative E° values of reduction half reactions behave instead as anodes *versus* SHE. The electrochemical series is shown in the given table:

Standard Aqueous Electrode Potentials at 25° C
'The Electrochemical Series'

Element	Electrode Reaction (Reduction)	Standard Electrode Reduction potential E°, volt
Li	$Li^+ + e^- = Li$	− 3.05
K	$K^+ + e^- = K$	− 2.925
Ca	$Ca^{2+} + 2e^- = Ca$	− 2.87
Na	$Na^+ + e^- = Na$	− 2.714
Mg	$Mg^{2+} + 2e^- = Mg$	− 2.37
Al	$Al^{3+} + 3e^- = Al$	− 1.66
Zn	$Zn^{2+} + 2e^- = Zn$	− 0.7628
Cr	$Cr^{3+} + 3e^- = Cr$	− 0.74
Fe	$Fe^{2+} + 2e^- = Fe$	− 0.44
Cd	$Cd^{2+} + 2e^- = Cd$	− 0.403
Ni	$Ni^{2+} + 2e^- = Ni$	− 0.25
Sn	$Sn^{2+} + 2e^- = Sn$	− 0.14
H_2	$2H^+ + 2e^- = H_2$	0.00
Cu	$Cu^{2+} + 2e^- = Cu$	+ 0.337
I_2	$I_2 + 2e^- = 2I^-$	+ 0.535
Ag	$Ag^+ + e^- = Ag$	+ 0.799
Hg	$Hg^{2+} + 2e^- = Hg$	+ 0.885
Br_2	$Br_2 + 2e^- = 2Br^-$	+ 1.08
Cl_2	$Cl_2 + 2e^- = 2Cl^-$	+ 1.36
Au	$Au^{3+} + 3e^- = Au$	+ 1.50
F_2	$F_2 + 2e^- = 2F^-$	+ 2.87

↓ Increasing tendency to accept electrons
Increasing strength as oxidising agent

↑ Increasing strength as reducing agent
Increasing tendency to lose electrons

Characteristics of Electrochemical Series

(i) The negative sign of standard reduction potential indicates that an electrode when joined with SHE acts as anode and oxidation occurs on this electrode. For example, standard reduction potential of zinc is − 0.76 volt. When zinc electrode is

The process of chemical decomposition of an electrolyte by passage of electric current through its solution is called electrolysis.

Or

Chemical change (oxidation and reduction) occurring at electrodes when electric current is passed through electrolytic solution is called electrolysis.

Molecules of an electrolyte when dissolved in water split up into ions, *i.e.*, into cations and anions. On passing current, these ions move towards oppositely charged electrodes. On reaching the electrodes the ions lose their charge either by accepting electrons or losing electrons and thereby deposited at the respective electrodes or undergo a secondary change. For example, when electric current is passed through a solution of hydrochloric acid, the H^+ ions move towards cathode and Cl^- ions move towards anode.

$$HCl \rightleftharpoons H^+ + Cl^-$$

Cathode	Anode
$H^+ + e^- \longrightarrow H$	$Cl^- \longrightarrow Cl + e^-$
$2H \longrightarrow H_2$	$2Cl \longrightarrow Cl_2$
(Reduction)	(Oxidation)

The decomposition of HCl into H_2 and Cl_2 as a result of passage of current is termed electrolysis of HCl. It is, thus, a process in which electric current brings the chemical change.

The device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical change is done is known as **electrolytic cell.** An electrolytic cell consists of a vessel for the electrolytic solution or fused electrolyte and two metallic electrodes immersed in the reaction material which are connected to a source of electric current. The metallic electrodes which do not react with ions or final products are called **inert electrodes.** Inert electrodes are usually used in an electrolytic cell.

12.2 PREFERENTIAL DISCHARGE THEORY

If an electrolytic solution consists of more than two ions and the electrolysis is done, it is observed that all the ions are not discharged at the electrodes simultaneously but certain ions are liberated at the electrodes in preference to others. This is explained by **preferential discharge theory.** It states that if more than one type of ions are attracted towards a particular electrode, then the one discharged is the ion which requires least energy. The potential at which the ion is discharged or deposited on the appropriate electrode is termed the discharge or deposition potential. The values of discharge potential are different for different ions. For example, the discharge potential of H^+ ions is lower than Na^+ ions when platinum or most of the other metals* are used as cathodes. Similarly, discharge potential of Cl^- ions is lower than that of OH^- ions. This can be explained by some examples given below:

(i) Electrolysis of sodium chloride solution

The solution of sodium chloride besides Na^+ and Cl^- ions possesses H^+ and OH^- ions due to ionisation of water. However, the number is small as water is a weak electrolyte. When potential difference is established across the two electrodes, Na^+ and H^+ ions move towards cathode and Cl^- and OH^- ions move towards anode. At cathode H^+ ions are discharged in preference to Na^+ ions as the discharge potential of H^+ ions is lower than Na^+ ions. Similarly at anode, Cl^- ions are discharged in preference to OH^- ions.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode	At anode
$H^+ + e^- \longrightarrow H$	$Cl^- \longrightarrow Cl + e^-$
$2H \longrightarrow H_2$	$2Cl \longrightarrow Cl_2$

Thus, Na^+ and OH^- ions remain in solution and the solution when evaporated yields crystals of sodium hydroxide.

(ii) Electrolysis of copper sulphate solution using platinum electrodes

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode	At anode
$Cu^{2+} + 2e^- \longrightarrow Cu$	$2OH^- \longrightarrow H_2O + O + 2e^-$
	$O + O \longrightarrow O_2$

Copper is discharged at cathode as Cu^{2+} ions have lower discharge potential than H^+ ions. OH^- ions are discharged at anode as these have lower discharge potential than SO_4^{2-} ions. Thus, copper is deposited at cathode and oxygen gas is evolved at anode.

(iii) Electrolysis of sodium sulphate solution using inert electrodes

$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode	At anode
$H^+ + e^- \longrightarrow H$	$2OH^- \longrightarrow H_2O + O + 2e^-$
$2H \longrightarrow H_2$	$O + O \longrightarrow O_2$

Hydrogen is discharged at cathode as H^+ ions have lower discharge potential than Na^+ ions. OH^- ions are discharged at anode as these have lower discharge potential than SO_4^{2-} ions. Thus, hydrogen is evolved at cathode and oxygen is evolved at anode, *i.e.*, the net reaction describes the electrolysis of water. The ions of Na_2SO_4 conduct the current through the solution and take no part in the overall chemical reaction.

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*When Hg is used as a cathode, Na^+ ions have lower discharge potential than H^+ ions.

The decreasing order of discharge potential or the increasing order of deposition of some of the ions is given below:

For cations: $K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, H^+, Cu^{2+}, Hg^{2+}, Ag^+$

For anions: $SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-$

(iv) Electrolysis of copper sulphate solution using copper electrodes

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

At cathode, copper is deposited.

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

At anode, the copper of the electrode is oxidised to Cu^{2+} ions or SO_4^{2-} ions dissolve equivalent amount of copper of the anode.

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

or $$Cu + SO_4^{2-} \longrightarrow CuSO_4 + 2e^-$$

Thus, during electrolysis, copper is transferred from anode to cathode.

(v) Electrolysis of silver nitrate solution using silver electrodes

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$

At cathode, silver is deposited.

$$Ag^+ + e^- \longrightarrow Ag$$

At anode, the silver of the electrode is oxidised to Ag^+ ions which go into the solution or NO_3^- ions dissolve equivalent amount of silver of the electrode.

$$Ag \longrightarrow Ag^+ + e^-$$

$$Ag + NO_3^- \longrightarrow AgNO_3 + e^-$$

Table 12.1 Some More Examples of Electrolysis

Electrolyte	Electrode	Cathodic reaction	Anodic reaction
Aqueous acidified $CuCl_2$ solution	Pt	$Cu^{2+} + 2e^- \longrightarrow Cu$	$2Cl^- \longrightarrow Cl_2 + 2e^-$
Molten $PbBr_2$	Pt	$Pb^{2+} + 2e^- \longrightarrow Pb$	$2Br^- \longrightarrow Br_2 + 2e^-$
Sodium chloride solution	Hg	$2Na^+ + 2e^- \longrightarrow 2Na$	$2Cl^- \longrightarrow Cl_2 + 2e^-$
Silver nitrate solution	Pt	$Ag^+ + e^- \longrightarrow Ag$	$2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$
Sodium nitrate solution	Pt	$2H^+ + 2e^- \longrightarrow H_2$	$2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

12.3 FARADAY'S LAWS OF ELECTROLYSIS

The relationship between the quantity of electric charge passed through an electrolyte and the amount of the substance deposited at the electrodes was presented by Faraday in 1834, in the form of laws of electrolysis.

(i) Faraday's first law

When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge passed through the electrolyte.

If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation:

$$W \propto Q$$

A coulomb is the quantity of charge when a current of one ampere is passed for one second. Thus, amount of charge in coulombs,

$$Q = \text{current in amperes} \times \text{time in seconds}$$
$$= I \times t$$

So, $$W \propto I \times t$$

or $$W = Z \times I \times t$$

where, Z is a constant, known as **electrochemical equivalent,** and is characteristic of the substance deposited.

When a current of one ampere is passed for one second, *i.e.*, one coulomb ($Q = 1$), then

$$W = Z$$

Thus, **electrochemical equivalent** can be defined as the **mass of the substance deposited by one coulomb of charge or by one ampere of current passed for one second.** For example, when a charge of one coulomb is passed through silver nitrate solution, the amount of silver deposited is 0.001118 g. This is the value of electrochemical equivalent of silver.

(ii) Faraday's second law

When the same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses.

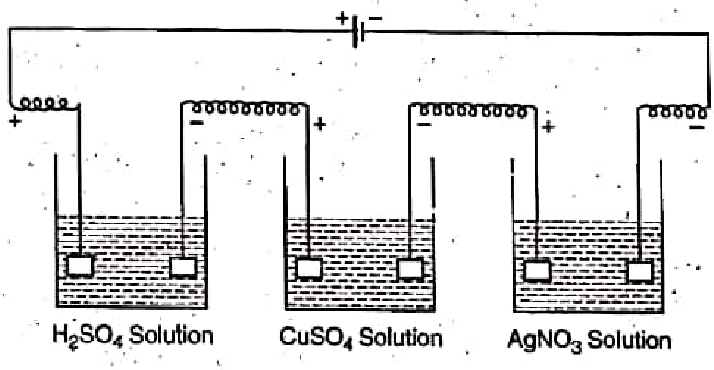

Fig. 12.1 Voltameters arranged in series

The law can be illustrated by passing same quantity of electric current through three voltameters containing solutions of H_2SO_4, $CuSO_4$ and $AgNO_3$ respectively as shown in Fig. 12.1. In the first voltameter, hydrogen and oxygen will be liberated; in the second, copper will be deposited and in the third, silver will be deposited.

$$\frac{\text{Mass of hydrogen}}{\text{Mass of copper}} = \frac{\text{Equivalent mass of hydrogen}}{\text{Equivalent mass of copper}}$$

or
$$\frac{\text{Mass of copper}}{\text{Mass of silver}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of silver}}$$

or
$$\frac{\text{Mass of silver}}{\text{Mass of hydrogen}} = \frac{\text{Equivalent mass of silver}}{\text{Equivalent mass of hydrogen}}$$

It is observed that by passing one coulomb of electric charge,

$$\text{Hydrogen evolved} = 0.00001036\text{ g},$$
$$\text{Copper deposited} = 0.0003292\text{ g},$$
and
$$\text{Silver deposited} = 0.001118\text{ g}$$

These masses are in the ratio of their equivalent masses. From these masses, the amount of electric charge required to deposit one equivalent of hydrogen or copper or silver can be calculated.

$$\text{For hydrogen} = \frac{1}{0.00001036} \approx 96500\text{ coulomb}$$

$$\text{For copper} = \frac{31.78}{0.0003292} \approx 96500\text{ coulomb}$$

$$\text{For silver} = \frac{107.88}{0.001118} \approx 96500\text{ coulomb}$$

This follows that 96500 coulomb of electric charge will deposit one g-equivalent of any substance. 96500 coulomb is termed as one **Faraday** and is denoted by F.

Again according to first law,

$$W = Z \times Q$$

When, $Q = 96500$ coulomb, W becomes gram equivalent mass (E).

Thus,
$$E = Z \times 96500$$

or
$$Z = \frac{E}{96500}$$

$$\frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

Fundamental unit of charge: As one g-equivalent of an ion is liberated by 96500 coulomb, it follows that charge carried by one g-equivalent of an ion is 96500 coulomb. If the valency of an ion is 'n', then one mole of these ions will carry a charge of nF coulomb. One g-mole of an ion contains 6.02×10^{23} ions. Then,

$$\text{The charge carried by an ion} = \frac{nF}{6.02 \times 10^{23}}\text{ coulomb}$$

For $n = 1$,

$$\text{The fundamental unit of charge} = \frac{F}{6.02 \times 10^{23}}$$

i.e.,
$$\frac{96500}{6.02 \times 10^{23}} = 1.6 \times 10^{-19}\text{ coulomb}$$

or
$$1\text{ coulomb}^{*} = 6.24 \times 10^{18}\text{ electrons}$$

The rate of flowing of electric charge through a conductor is called the electric current.

$$\text{Electric current} = \frac{\text{Electric charge}}{\text{Time}}$$

$$1\text{ ampere} = \frac{1\text{ coulomb}}{1\text{ second}}$$

Volt is a unit of electrical potential difference. It is defined as potential energy per unit charge.

$$1\text{ volt} = \frac{1\text{ joule}}{1\text{ coulomb}} = \frac{1\text{ newton} \times 1\text{ metre}}{1\text{ ampere} \times 1\text{ second}}$$

$$\begin{aligned}\text{Electrical energy} &= \text{Potential difference} \times \text{Quantity of charge}\\ &= V \times Q\\ &= V \times I \times t \qquad (I = \text{ampere};\ t = \text{second})\\ &= \text{watt-second}\end{aligned}$$

Faraday's Law for Gaseous Electrolytic Product

We know that,
$$\begin{aligned}W &= ZQ\\ &= ZIt\end{aligned}$$

$$W = \frac{ItE}{96500} \qquad \text{... (i)}$$

where,
$$Z = E/96500$$

Equation (i) is used to calculate the mass of solid substance dissolved or deposited at an electrode.

For the gases, we use

$$V = \frac{ItV_e}{96500} \qquad \text{...(ii)}$$

***Coulomb:** It is the unit of electric charge. It is the amount of charge that moves past any given point in a circuit when a current of 1 ampere is supplied for one second.

$$1\text{ coulomb} = 1\text{ ampere-second}$$

It is also defined as the amount of charge which is required to deposit by electrolysis 0.001118 g of silver from a solution of silver nitrate.

An electron has 1.6×10^{-19} coulomb of negative charge. Hence, one coulomb of charge is carried by 6.24×10^{18} electrons. 1 mole of electrons carry a charge of 96500 coulomb. This quantity of charge is called **Faraday.**

Charge carried by 1 mole of electrons

$$\begin{aligned}&= (6.023 \times 10^{23})(1.6 \times 10^{-19})\\ &= 96368\text{ coulomb}\\ &\approx 96500\text{ coulomb}\end{aligned}$$

where, V = Volume of gas evolved at STP at an electrode

V_e = Equivalent volume

= Volume of gas evolved at an electrode at STP by 1 faraday charge

Illustration

O_2: $M = 32,\ E = 8$

$32\ g\ O_2 \equiv 22.4\ L$ at STP

$8\ g\ O_2 \equiv 5.6\ L$ at STP

$\begin{bmatrix} M = \text{Molecular mass} \\ E = \text{Equivalent mass} \end{bmatrix}$

Thus, V_e of $O_2 = 5.6\ L$

H_2: $M = 2,\ E = 1$

$2\ g\ H_2 \equiv 22.4\ L$ at STP

$1\ g\ H_2 \equiv 11.2\ L$ at STP

Thus, V_e of $H_2 = 11.2\ L$

Cl_2: $M = 71,\ E = 35.5$

$71\ g\ Cl_2 \equiv 22.4\ L$ at STP

$35.5\ g\ Cl_2 \equiv 11.2\ L$ at STP

Thus, V_e of $Cl_2 = 11.2\ L$

12.4 APPLICATIONS OF ELECTROLYSIS

The phenomenon of electrolysis has wide applications. The important ones are:

(1) Determination of equivalent masses of elements: According to second law of electrolysis when the same quantity of electric current is passed through solutions of salts of two different metals taken in two different cells, the amounts of the metals deposited on the cathodes of the two cells are proportional to their equivalent masses of the respective metals. If the amounts of the metals deposited on the cathodes be W_A and W_B respectively, then

$$\frac{W_A}{W_B} = \frac{\text{Equivalent mass of } A}{\text{Equivalent mass of } B}$$

Knowing the equivalent mass of one metal, the equivalent mass of the other metal can be calculated from the above relationship. The equivalent masses of those non-metals which are evolved at anodes can also be determined by this method.

(2) Electrometallurgy: The metals like sodium, potassium, magnesium, calcium, aluminium, etc., are obtained by electrolysis of fused electrolytes.

Fused electrolyte	Metal isolated
$NaCl + CaCl_2 + KF$	Na
$CaCl_2 + CaF_2$	Ca
Al_2O_3 + cryolite	Al
$MgCl_2$ (35%) + NaCl (50%) + $CaCl_2$ (15%)	Mg
NaOH	Na
$KCl + CaCl_2$	K

(3) Manufacture of non-metals: Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.

(4) Electro-refining of metals: The metals like copper, silver, gold, aluminium, tin, etc., are refined by electrolysis.

(5) Manufacture of compounds: Compounds like NaOH, KOH, Na_2CO_3, $KClO_3$, white lead, $KMnO_4$, etc., are manufactured by electrolysis.

(6) Electroplating: The process of coating an inferior metal with a superior metal by electrolysis is known as **electroplating.**

The aims of electroplating are:

(i) To prevent the inferior metal from corrosion.

(ii) To make it more attractive in appearance.

The object to be electroplated is made the cathode and block of the metal to be deposited is made the anode in an electrolytic bath containing a solution of a salt of the anodic metal. On passing electric current in the cell, the metal of the anode dissolves out and is deposited on the cathode-article in the form of a thin film. The following are the requirements for fine coating:

(i) The surface of the article should be free from greasy matter and its oxide layer. The surface is cleaned with chromic acid or detergents.

(ii) The surface of the article should be rough so that the metal deposited sticks permanently.

(iii) The concentration of the electrolyte should be so adjusted as to get smooth coating.

(iv) Current density must be the same throughout.

For electroplating	Anode	Cathode	Electrolyte
With copper	Cu	Object	$CuSO_4$ + dilute H_2SO_4
With silver	Ag	Object	$KAg(CN)_2$
With nickel	Ni	Object	Nickel ammonium sulphate
With gold	Au	Object	$KAu(CN)_2$
With zinc	Zn	Iron objects	$ZnSO_4$
With tin	Sn	Iron objects	$SnSO_4$

Thickness of Coated Layer

Let the dimensions of metal sheet to be coated be (a cm × b cm).

Thickness of coated layer = c cm

Volume of coated layer = $(a \times b \times c)\ \text{cm}^3$

Mass of the deposited substance = volume × density

$= (a \times b \times c) \times d$ g

$$\therefore \quad (a \times b \times c) \times d = \frac{I \times t \times E}{96500}$$

Using above relation we may calculate the thickness of coated layer.

Note: Sometimes radius of atom of deposited metal is given instead of density, *e.g.*,

Radius of silver atom $= 10^{-8}$ cm

Atomic mass of Ag = 108

Mass of single silver atom $= \dfrac{108}{6.023 \times 10^{23}}$ g

Volume of single atom $= \dfrac{4}{3} \times \pi R^3$

$$= \frac{4}{3} \times 3.14 \times (10^{-8})^3 \text{ cm}^3$$

$$\text{Density of Ag} = \frac{\text{Mass of single atom}}{\text{Volume of single atom}}$$

$$= \frac{108 / 6.023 \times 10^{23}}{\frac{4}{3} \times 3.14 \times (10^{-8})^3} = 42.82 \text{ g/cm}^3$$

Current Efficiency

Sometimes the ammeter shows false current due to mechanical fault. In this case,

$$\% \text{ current efficiency} = \frac{\text{Actual current}}{\text{Ammeter current}} \times 100$$

[**Note :** The conditions for the operating electrolytic cell are:
$\Delta G > 0$ and $E < 0$]

SOME SOLVED EXAMPLES

Example 1. *Find the charge in coulomb on 1 g-ion of N^{3-}.*

Solution: Charge on one ion of N^{3-}

$$= 3 \times 1.6 \times 10^{-19} \text{ coulomb}$$

$$\text{one g-ion} = 6.02 \times 10^{23} \text{ ions}$$

Thus, charge on one g-ion of N^{3-}

$$= 3 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{23}$$

$$= 2.89 \times 10^5 \text{ coulomb}$$

Example 2. *How much charge is required to reduce (a) 1 mole of Al^{3+} to Al and (b) 1 mole of MnO_4^- to Mn^{2+}?*

Solution: (a) The reduction reaction is:

$$\underset{1\text{ mole}}{Al^{3+}} + \underset{3\text{ mole}}{3e^-} \longrightarrow Al$$

Thus, 3 mole of electrons are needed to reduce 1 mole of Al^{3+}.

$$Q = 3 \times F$$

$$= 3 \times 96500 = 289500 \text{ coulomb}$$

(b) The reduction reaction is:

$$\underset{1\text{ mole}}{MnO_4^-} + 8H^+ + \underset{5\text{ mole}}{5e^-} \longrightarrow Mn^{2+} + 4H_2O$$

$$Q = 5 \times F$$

$$= 5 \times 96500 = 482500 \text{ coulomb}$$

Example 3. *How much electric charge is required to oxidise (a) 1 mole of H_2O to O_2 and (b) 1 mole of FeO to Fe_2O_3?*

Solution: (a) The oxidation reaction is:

$$\underset{1\text{ mole}}{H_2O} \longrightarrow \frac{1}{2} O_2 + 2H^+ + \underset{2\text{ mole}}{2e^-}$$

$$Q = 2 \times F$$

$$= 2 \times 96500 = 193000 \text{ coulomb}$$

(b) The oxidation reaction is:

$$FeO + \frac{1}{2} H_2O \longrightarrow \frac{1}{2} Fe_2O_3 + H^+ + e^-$$

$$Q = F = 96500 \text{ coulomb}$$

Example 4. *Exactly 0.4 faraday electric charge is passed through three electrolytic cells in series, first containing $AgNO_3$, second $CuSO_4$ and third $FeCl_3$ solution. How many grams of each metal will be deposited assuming only cathodic reaction in each cell?*

Solution: The cathodic reactions in the cells are respectively,

$$\underset{\substack{1\text{ mole}\\108\text{ g}}}{Ag^+} + \underset{\substack{1\text{ mole}\\1\text{ F}}}{e^-} \longrightarrow Ag$$

$$\underset{\substack{1\text{ mole}\\63.5\text{ g}}}{Cu^{2+}} + \underset{\substack{2\text{ mole}\\2\text{ F}}}{2e^-} \longrightarrow Cu$$

and

$$\underset{\substack{1\text{ mole}\\56\text{ g}}}{Fe^{3+}} + \underset{\substack{3\text{ mole}\\3\text{ F}}}{3e^-} \longrightarrow Fe$$

Hence, $\text{Ag deposited} = 108 \times 0.4 = 43.2 \text{ g}$

$$\text{Cu deposited} = \frac{63.5}{2} \times 0.4 = 12.7 \text{ g}$$

and $\text{Fe deposited} = \frac{56}{3} \times 0.4 = 7.47 \text{ g}$

Example 5. *An electric current of 100 ampere is passed through a molten liquid of sodium chloride for 5 hours. Calculate the volume of chlorine gas liberated at the electrode at NTP.*

Solution: The reaction taking place at anode is:

$$\underset{71.0\text{ g}}{2Cl^-} \longrightarrow \underset{\substack{71.0\text{ g}\\1\text{ mole}}}{Cl_2} + \underset{2 \times 96500\text{ coulomb}}{2e^-}$$

$$Q = I \times t = 100 \times 5 \times 60 \times 60 \text{ coulomb}$$

The amount of chlorine liberated by passing $100 \times 5 \times 60 \times 60$ coulomb of electric charge

$$= \frac{1}{2 \times 96500} \times 100 \times 5 \times 60 \times 60 = 9.3264 \text{ mole}$$

$$\text{Volume of } Cl_2 \text{ liberated at NTP} = 9.3264 \times 22.4 = 208.91 \text{ L}$$

Example 6. *A 100 watt, 110 volt incandescent lamp is connected in series with an electrolytic cell containing cadmium sulphate solution. What mass of cadmium will be deposited by the current flowing for 10 hours?*

Solution: We know that,

$$\text{Watt} = \text{ampere} \times \text{volt}$$

$$100 = \text{ampere} \times 110$$

$$\text{Ampere} = \frac{100}{110}$$

$$\text{Quantity of charge} = \text{ampere} \times \text{second}$$

$$= \frac{100}{110} \times 10 \times 60 \times 60 \text{ coulomb}$$

The cathodic reaction is:

$$\underset{112.4\text{ g}}{Cd^{2+}} + \underset{2 \times 96500\text{ C}}{2e^-} \longrightarrow Cd$$

Mass of cadmium deposited by passing $\frac{100}{110}\times 10\times 60\times 60$ coulomb charge

$$=\frac{112.4}{2\times 96500}\times\frac{100}{110}\times 10\times 60\times 60=19.0598\text{ g}$$

Example 7. *In an electrolysis experiment, a current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold salt and the second cell contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode in the second cell. Also calculate the magnitude of the current in ampere.*

Solution: We know that,

$$\frac{\text{Mass of Au deposited}}{\text{Mass of Cu deposited}}=\frac{\text{Eq. mass of Au}}{\text{Eq. mass of Cu}}$$

$$\text{Eq. mass of Au}=\frac{197}{3}\ ;\ \text{Eq. mass of Cu}=\frac{63.5}{2}$$

Mass of copper deposited

$$=9.85\times\frac{63.5}{2}\times\frac{3}{197}\text{ g}=4.7625\text{ g}$$

Let Z be the electrochemical equivalent of Cu.

$$E=Z\times 96500$$

or $$Z=\frac{E}{96500}=\frac{63.5}{2\times 96500}$$

Applying $$W=Z\times I\times t$$

$$t=5\text{ hour}=5\times 3600\text{ second}$$

$$4.7625=\frac{63.5}{2\times 96500}\times I\times 5\times 3600$$

or $$I=\frac{4.7625\times 2\times 96500}{63.5\times 5\times 3600}=0.804\text{ ampere}$$

Example 8. *How long has a current of 3 ampere to be applied through a solution of silver nitrate to coat a metal surface of 80 cm^2 with 0.005 mm thick layer? Density of silver is 10.5 g/cm^3.*

Solution: Mass of silver to be deposited

$$=\text{volume}\times\text{density}$$

$$=\text{Area}\times\text{thickness}\times\text{density}$$

Given: Area $=80\text{ cm}^2$, thickness $=0.0005$ cm and density $=10.5\text{ g/cm}^3$

$$\text{Mass of silver to be deposited}=80\times 0.0005\times 10.5$$

$$=0.42\text{ g}$$

Applying to silver $$E=Z\times 96500$$

$$Z=\frac{108}{96500}\text{ g}$$

Let the current be passed for t seconds.

We know that, $$W=Z\times I\times t$$

So, $$0.42=\frac{108}{96500}\times 3\times t$$

or $$t=\frac{0.42\times 96500}{108\times 3}=125.09\text{ second}$$

Example 9. *What current strength in ampere will be required to liberate 10 g of chlorine from sodium chloride solution in one hour?*

Solution: Applying $E=Z\times 96500$ (E for chlorine $=35.5$),

$$35.5=Z\times 96500$$

or $$Z=\frac{35.5}{96500}\text{ g}$$

Now, applying the formula

$$W=Z\times I\times t$$

where, $W=10\text{ g}$, $Z=\frac{35.5}{96500}$, $t=60\times 60=3600$ second

$$I=\frac{10\times 96500}{35.5\times 3600}=7.55\text{ ampere}$$

Example 10. *0.2964 g of copper was deposited on passage of a current of 0.5 ampere for 30 minutes through a solution of copper sulphate. Calculate the atomic mass of copper. (1 faraday = 96500 coulomb)*

Solution: Quantity of charge passed

$$=0.5\times 30\times 60=900\text{ coulomb}$$

900 coulomb deposit copper = 0.2964 g

$$96500\text{ coulomb deposit copper}=\frac{0.2964}{900}\times 96500=31.78\text{ g}$$

Thus, 31.78 is the equivalent mass of copper.

$$\text{At. mass}=\text{Eq. mass}\times\text{Valency}$$

$$=31.78\times 2=63.56$$

Example 11. *19 g of molten $SnCl_2$ is electrolysed for some time using inert electrodes until 0.119 g of Sn is deposited at the cathode. No substance is lost during electrolysis. Find the ratio of the masses of $SnCl_2 : SnCl_4$ after electrolysis.*

Solution: The chemical reaction occurring during electrolysis is:

$$\underset{2\times 190\text{ g}}{2SnCl_2}\longrightarrow\underset{261\text{ g}}{SnCl_4}+\underset{119\text{ g}}{Sn}$$

119 g of Sn is deposited by the decomposition of 380 g of $SnCl_2$.

So, 0.119 g of Sn is deposited by the decomposition of

$$\frac{380}{119}\times 0.119=0.380\text{ g of }SnCl_2$$

Remaining amount of $SnCl_2=(19-0.380)=18.62$ g

380 g of $SnCl_2$ produce = 261 g of $SnCl_4$