B.Sc. (Honours) Part-II
Paper-III

Topic: Electrochemical Cells

UG
Subject-Chemistry

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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.

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:

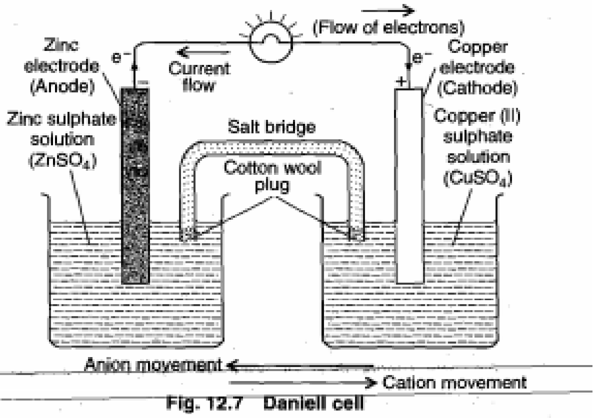


Fig. 12.7 Daniell cell

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

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,

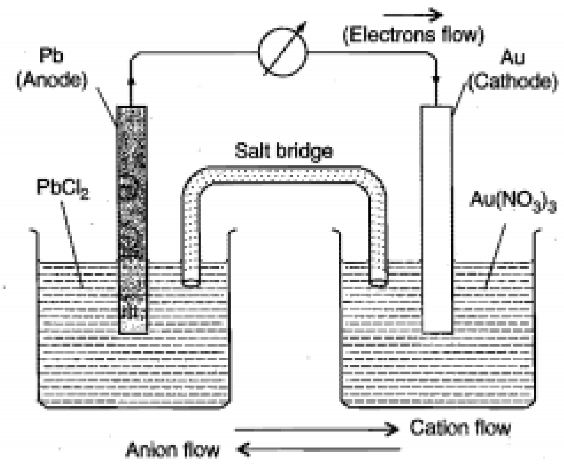


Fig. 12.8

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

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

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

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).

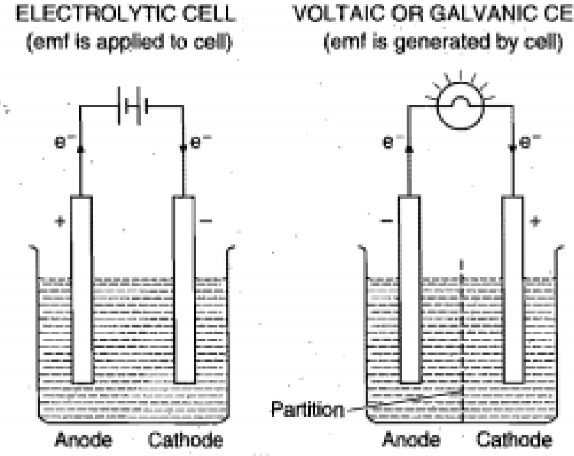


Fig. 12.9

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

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.

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:

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

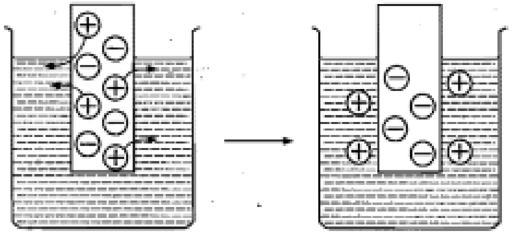


Fig. 12.10 (a)

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

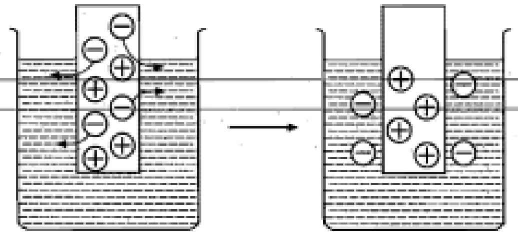


Fig. 12.10 (b)

(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.

$$\begin{aligned}\text{Emf of the cell} &= E_{\text{Anode}} + E_{\text{Cathode}}\\ &= \text{Oxidation potential of anode}\\ &\quad + \text{Reduction potential of cathode}\end{aligned}$$

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 ± 0.000... volt.

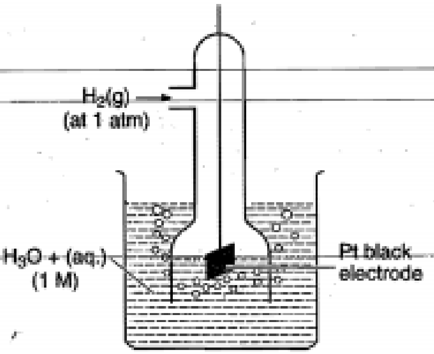


Fig. 12.11 Hydrogen electrode

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.

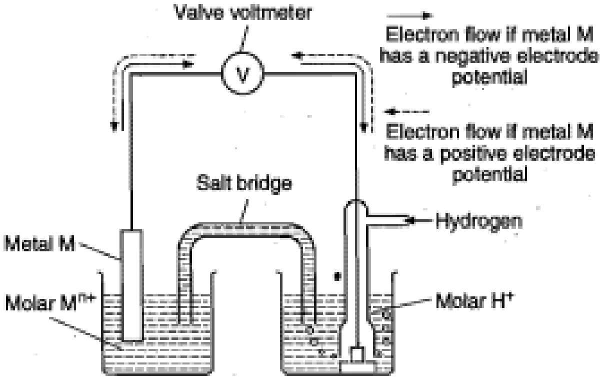


Fig. 12.12

(i) Determination of standard electrode potential of Zn / Zn²⁺ 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

$$\underset{\text{Anode }(-)}{\underline{\text{Zn} \mid \text{Zn}^{2+}(aq.)}} \,\|\, \underset{\text{Cathode }(+)}{\underline{2\text{H}^+(aq.) \mid \text{H}_2(g)}}$$

$$\underset{\text{(Oxidation)}}{\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-}\ ;\ \underset{\text{(Reduction)}}{2\text{H}^+ + 2e^- \longrightarrow \text{H}_2\uparrow}$$

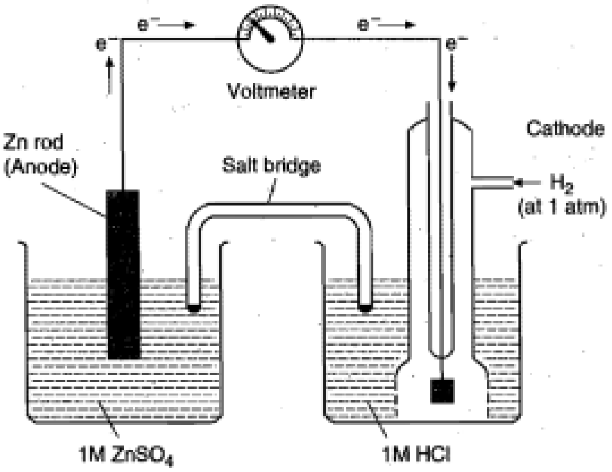


Fig. 12.13 Zn–H_2 electrochemical cell

The emf of the cell is 0.76 volt

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

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

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

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

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

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

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

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

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

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.

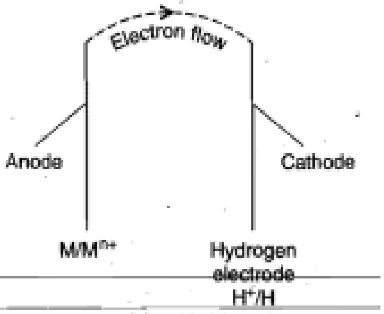


Fig. 12.14

(ii) Determination of standard electrode potential of Cu²⁺ / 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

$$\underset{\text{Anode }(-)}{\text{H}_2(g) \mid 2\text{H}^+(aq.)} \,\|\, \underset{\text{Cathode }(+)}{\text{Cu}^{2+}(aq.) \mid \text{Cu}}$$

$$\underset{\text{Oxidation}}{\text{H}_2 \longrightarrow 2\text{H}^+ + 2e^-}\ ;\ \underset{\text{Reduction}}{\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}}$$

The emf of the cell is 0.34 volt.

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

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

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

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

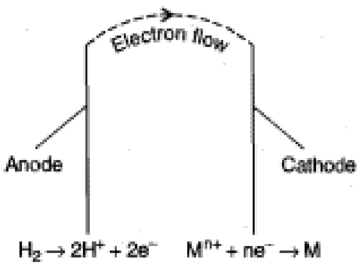


Fig. 12.15

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.

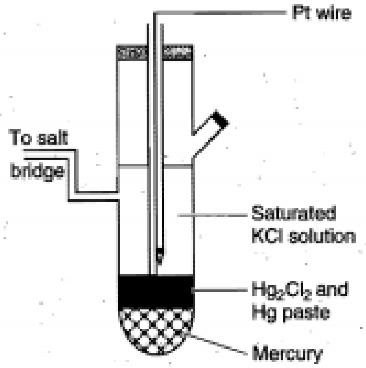


Fig. 12.16 Calomel electrode

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

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

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*.

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

$$\mathrm{Zn}(s) \,|\, \mathrm{Zn}^{2+}(aq) \,||\, \mathrm{Cu}^{2+}(aq.) \,|\, \mathrm{Cu}$$

Potential at zinc electrode (Anode)

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

Potential at copper electrode (Cathode)

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

Emf of the cell

$$\begin{aligned} E_{cell} &= E_{ox} + E_{red} \\ &= (E^\circ_{ox} + E^\circ_{red}) - \frac{0.0591}{n} \log_{10} \left[\frac{\mathrm{Zn}^{2+}}{\mathrm{Cu}^{2+}}\right] \\ &= E^\circ_{cell} - \frac{0.0591}{n} \log_{10} \left[\frac{\mathrm{Zn}^{2+}}{\mathrm{Cu}^{2+}}\right] \end{aligned}$$

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

$$\mathrm{Cu} \,|\, \mathrm{Cu}^{2+} \,||\, \mathrm{Ag}^+ \,|\, \mathrm{Ag}$$

The cell reaction is:

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

The two half-cell reactions are:

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

$$\mathrm{Ag}^+ + e^- \longrightarrow \mathrm{Ag}$$

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

$$2\mathrm{Ag}^+ + 2e^- \longrightarrow 2\mathrm{Ag}$$

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

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

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

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

$$\mathrm{Zn} \,|\, \mathrm{ZnSO_4} \,||\, \mathrm{CuSO_4} \,|\, \mathrm{Cu}$$

or

$$\underset{\text{Anode }(-)}{\mathrm{Zn} \,|\, \mathrm{Zn}^{2+}} \,||\, \underset{\text{Cathode }(+)}{\mathrm{Cu}^{2+} \,|\, \mathrm{Cu}}$$

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

$$\mathrm{Cu} \,|\, \mathrm{Cu(NO_3)_2} \,||\, \mathrm{AgNO_3} \,|\, \mathrm{Ag}$$

or

$$\underset{\text{Anode }(-)}{\mathrm{Cu} \,|\, \mathrm{Cu}^{2+}} \,||\, \underset{\text{Cathode }(+)}{\mathrm{Ag}^+ \,|\, \mathrm{Ag}}$$

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

$$\mathrm{Zn} \,|\, \mathrm{ZnSO_4} \,||\, \mathrm{H_2SO_4} \,|\, \mathrm{H_2(Pt)}$$

or

$$\underset{\text{Anode }(-)}{\mathrm{Zn} \,|\, \mathrm{Zn}^{2+}} \,||\, \underset{\text{Cathode }(+)}{2\mathrm{H}^+ \,|\, \mathrm{H_2(Pt)}}$$

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

$$\mathrm{Fe} \,|\, \mathrm{FeCl_2} \,||\, \mathrm{SnCl_2} \,|\, \mathrm{Sn}$$

or

$$\underset{\text{Anode }(-)}{\mathrm{Fe} \,|\, \mathrm{Fe}^{2+}} \,||\, \underset{\text{Cathode }(+)}{\mathrm{Sn}^{2+} \,|\, \mathrm{Sn}}$$

Note : Oxidation potential is $E^o_{M/M^{n+}}$ while reduction potential is represented as $E^o_{M^{n+}/M}$. The value of $E^o_{\mathrm{Zn/Zn^{2+}}}$ (oxidation potential of Zn) is + 0.76 volt and the value of $E^o_{\mathrm{Cu^{2+}/Cu}}$ (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.

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

$Ag(s) | AgNO_3\ (0.01\ M) || AgNO_3\ (0.05\ M) | Ag(s)$

(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:** $E^\circ_{Cell} = E^\circ_{Cathode} - E^\circ_{Anode}$

$$= E^\circ_{\text{Reduced species}} - E^\circ_{\text{Oxidised species}}$$
$$= 0.34 - (-2.37) = +2.71 \text{ V}]$$

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

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

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

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

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

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	↓ Increasing tendency to accept electrons Increasing strength as oxidising agent	$Li^+ + e^- = Li$	↑ Increasing strength as reducing agent Increasing tendency to lose electrons	– 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

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 joined with SHE, it acts as anode (–ve electrode), *i.e.*, oxidation occurs on this electrode. Similarly, the +ve sign of standard reduction potential indicates that the electrode when joined with SHE acts as cathode and reduction occurs on this electrode.

(ii) The substances which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials. All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.

(iii) The substances which are stronger oxidising agents than H^+ ion are placed below hydrogen in the series.

(iv) The metals on the top (having high negative values of standard reduction potentials) have the tendency to lose electrons readily. These are active metals. The activity of metals decreases from top to bottom. The non-metals on the bottom (having high positive values of standard reduction potentials) have the tendency to accept electrons readily. These are active non-metals. The activity of non-metals increases from top to bottom.

Applications of Electrochemical Series

(i) Reactivity of metals: The activity of the metal depends on its tendency to lose electron or electrons, *i.e.*, tendency to form cation (M^{n+}). This tendency depends on the magnitude of standard reduction potential. The metal which has high negative value (or smaller positive value) of standard reduction potential readily loses the electron or electrons and is converted into cation. Such a metal is said to be chemically active.

The chemical reactivity of metals decreases from top to bottom in the series. The metal higher in the series is more active than the metal lower in the series. For example,

(a) Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active. These react with cold water and evolve hydrogen. These readily dissolve in acids forming corresponding salts and combine with those substances which accept electrons.

(b) Metals like Fe, Pb, Sn, Ni, Co, etc., which lie a little down in the series do not react with cold water but react with steam to evolve hydrogen.

(c) Metals like Cu, Ag and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.

(ii) Electropositive character of metals: The electropositive character also depends on the tendency to lose electron or electrons. Like reactivity, the electropositive character of metals decreases from top to bottom in the electrochemical series. On the basis of standard reduction potential values, metals are divided into three groups:

(a) Strongly electropositive metals: Metals having standard reduction potential near about –2.0 volt or more negative like alkali metals, alkaline earth metals are strongly electropositive in nature.

(b) Moderately electropositive metals: Metals having values of reduction potentials between 0.0 and about –2.0 volt are moderately electropositive. Al, Zn, Fe, Ni, Co, etc., belong to this group.

(c) Weakly electropositive metals: The metals which are below hydrogen and possess positive values of reduction potentials are weakly electropositive metals. Cu, Hg, Ag, etc., belong to this group.

(iii) Displacement reactions:

(a) To predict whether a given metal will displace another, from its salt solution: A metal higher in the series will displace the metal from its solution which is lower in the series, *i.e.*, **the metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential.** A metal higher in the series has greater tendency to provide electrons to the cations of the metal to be precipitated.

(b) Displacement of one non-metal from its salt solution by another non-metal: A non-metal higher in the series (towards bottom side), *i.e.*, having high value of reduction potential will displace another non-metal with lower reduction potential, *i.e.*, occupying position above in the series. The non-metals which possess high positive reduction potentials have the tendency to accept electrons readily. These electrons are provided by the ions of the non-metal having low value of reduction potential. Thus, Cl_2 can displace bromine and iodine from bromides and iodides.

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

$$2I^- \longrightarrow I_2 + 2e^- \qquad \text{(Oxidation)}$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^- \qquad \text{(Reduction)}$$

[The activity or electronegative character or oxidising nature of the non-metal increases as the value of reduction potential increases.]

(c) Displacement of hydrogen from dilute acids by metals: The metal which can provide electrons to H^+ ions present in dilute acids for reduction, evolve hydrogen from dilute acids.

$$Mn \longrightarrow Mn^{n+} + ne^- \qquad \text{(Oxidation)}$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad \text{(Reduction)}$$

The metal having negative values of reduction potential possess the property of losing electron or electrons.

Thus, the metals occupying top positions in the electrochemical series readily liberate hydrogen from dilute acids and on descending in the series tendency to liberate hydrogen gas from dilute acids decreases.

The metals which are below hydrogen in electrochemical series like Cu, Hg, Au, Pt, etc., do not evolve hydrogen from dilute acids.

(d) Displacement of hydrogen from water: Iron and the metals above iron are capable of liberating hydrogen from water. The tendency decreases from top to bottom in electrochemical series.

Alkali and alkaline earth metals liberate hydrogen from cold water but Mg, Zn and Fe liberate hydrogen from hot water or steam.

(iv) Reducing power of metals: Reducing nature depends on the tendency of losing electron or electrons. More the negative reduction potential, more is the tendency to lose electron or electrons. **Thus, reducing nature decreases from top to bottom in the electrochemical series.** The power of the reducing agent increases as the standard reduction potential becomes more and more negative.

Sodium is a stronger reducing agent than zinc and zinc is a stronger reducing agent than iron.

Element	Na	Zn	Fe
Reduction potential	−2.71	− 0.76	− 0.44

$\xrightarrow[\text{Reducing nature decreases}]{}$

Alkali and alkaline earth metals are strong reducing agents.

(v) Oxidising nature of non-metals: Oxidising nature depends on the tendency to accept electron or electrons. More the value of reduction potential, higher is the tendency to accept electron or electrons. **Thus, oxidising nature increases from top to bottom in the electrochemical series.** The strength of an oxidising agent increases as the value of reduction potential becomes more and more positive.

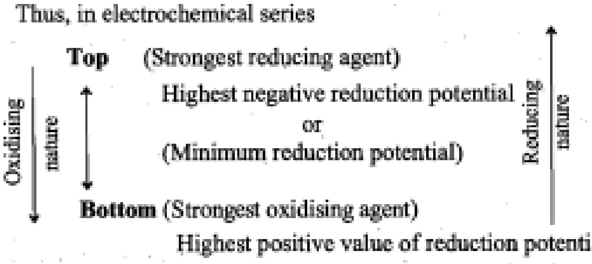
F_2 (Fluorine) is a stronger oxidant than Cl_2, Br_2 and I_2.

Cl_2 (Chlorine) is a stronger oxidant than Br_2 and I_2.

Element	I_2	Br_2	Cl_2	F_2
Reduction potential	+ 0.53	+ 1.06	+ 1.36	+ 2.85

$\xrightarrow[\text{Oxidising nature increases}]{}$

Thus, in electrochemical series



(vi) Thermal stability of metallic oxides: The thermal stability of the metal oxide depends on its electropositive nature. As the electropositivity decreases from top to bottom, the thermal stability of the oxide also decreases from top to bottom. The oxides of metals having high positive reduction potentials are not stable towards heat. The metals which come below copper form unstable oxides, *i.e.*, these are decomposed on heating.

$$Ag_2O \xrightarrow{\text{Heat}} 2Ag + \frac{1}{2}O_2$$

$$2HgO \xrightarrow{\text{Heat}} 2Hg + O_2$$

$$\left.\begin{matrix} BaO \\ Na_2O \\ Al_2O_3 \end{matrix}\right] \xrightarrow{\text{Heat}} \text{No decomposition}$$

(vii) Products of electrolysis: In case, two or more types of positive and negative ions are present in solution, during electrolysis certain ions are discharged or liberated at the electrodes in preference to others. **In general, in such competition the ion which is stronger oxidising agent (high value of standard reduction potential) is discharged first at the cathode.** The increasing order of deposition of few cations is:

$$K^+, Ca^{2+}, Na^+, Mg^{2+}, Al^{3+}, Zn^{2+}, Fe^{2+}, H^+, Cu^{2+}, Ag^+, Au^{3+}$$

$\xrightarrow[\text{Increasing order of deposition}]{}$

Similarly, the anion which is stronger reducing agent (low value of standard reduction potential) is liberated first at the anode.

The increasing order of discharge of few anions is:

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

$\xrightarrow[\text{Increasing order of discharge}]{}$

Thus, when an aqueous solution of NaCl containing Na^+, Cl^-, H^+ and OH^- ions is electrolysed, H^+ ions are discharged at cathode and Cl^- ions at the anode, *i.e.*, H_2 is liberated at cathode and chlorine at anode.

When an aqueous solution of $CuSO_4$ containing Cu^{2+}, SO_4^{2-}, H^+ and OH^- ions is electrolysed, Cu^{2+} ions are discharged at cathode and OH^- ions at the anode.

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad \text{(Cathodic reaction)}$$

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^- \qquad \text{(Anodic reaction)}$$

Cu is deposited on cathode while O_2 is liberated at anode.

(viii) Latimer diagram: Redox chemistry of an element can be understand by comparing the standard electrode potentials of the various oxidation states of the element. Latimer diagram showing relative stabilities of different oxidation states are given below :

Acid Medium

$$Fe \xrightarrow{E^\circ_{Fe/Fe^{2+}} = +0.44\text{ V}} Fe^{2+} \xrightarrow{E^\circ_{Fe^{2+}/Fe^{3+}} = -0.77\text{ V}} Fe^{3+}$$

Alkaline Medium

$$Fe \xrightarrow{E^\circ_{Fe/Fe^{2+}} = +0.88\text{ V}} Fe^{2+} \xrightarrow{E^\circ_{Fe^{2+}/Fe^{3+}} = +0.56\text{ V}} Fe^{3+}$$

In acid medium, the positive value of $E^\circ_{Fe/Fe^{2+}}$ indicates that iron will dissolve in acid medium to form Fe^{2+} ion; since $E^\circ_{Fe^{2+}/Fe^{3+}}$ is negative, hence +2 state of iron will be more state than +3 state in acid medium.

When the potential on right of a species is more positive (less negative) than that on the left, then the species will tend to undergo disproportionation.

Example :

Alkaline Medium

$$Cl^- \xrightarrow{E^\circ_{Cl^-/Cl_2} = -1.35\text{ V}} \frac{1}{2}Cl_2 \xrightarrow{E^\circ_{Cl_2/ClO^-} = -0.4\text{ V}} ClO^-$$

Thus, Cl_2 will undergo disproportionation into Cl^- and ClO^- ions in basic medium.

$$Cl_2 + 2OH^- \longrightarrow Cl^- + ClO^- + H_2O$$

(ix) Corrosion of metals: Corrosion is defined as the deterioration of a substance because of its reaction with its environment. This is also defined as the process by which metals have the tendency to go back to their combined state, *i.e.*, reverse of extraction of metals.

Thus, the process of weathering away of the metal due to attack of the atmospheric gases on the surface of the metal *resulting into the formation of compounds such as oxides, sulphates, sulphides, carbonates, etc., is called corrosion.*

The process of corrosion of iron is called rusting. Rust is chemically the hydrated oxide of iron having the formula $Fe_2O_3 \cdot xH_2O$. Other examples of corrosion of metals are tarnishing of silver and those of copper and bronze etc. Corrosion of copper and bronze forms a green coating on the surface. The corrosion of metals, particularly iron, causes damage to buildings, dams, bridges, etc., and we lose a lot of money every year.

Mechanism of Corrosion : Corrosion is a redox process by which metals are oxidised by oxygen in presence of moisture. The mechanism can be understood by taking the example of rusting of iron. The theory of rusting is called **electrochemical theory.** In this theory the process of rusting can be explained on the basis of formation of electrochemical cell on the surface of an iron object.

Rusting of iron involves the following steps :

Step 1 : The water vapours present in contact with iron surface have dissolved CO_2 and O_2 from air.

$$H_2O(l) + CO_2(g) \longrightarrow H_2CO_3(l)$$

Thus, the surface of iron is covered with an aqueous solution of carbonic acid, which undergoes dissociation to a small extent.

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-} \quad \text{(Ionisation of carbonic acid)}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{(Ionisation of water)}$$

Step 2 : Second step involves oxidation of iron. Oxidation of metal takes place at the point of strain. For example, a steel nail first corrodes at the tip and head. The tip of the nail acts as anode where iron is oxidised to ferrous ion.

$$Fe(s) \longrightarrow Fe^{2+} + 2e^- \quad \text{(Anodic process, oxidation)} \quad \ldots\text{(i)}$$

$$(E^\circ_{Fe^{2+}/Fe} = -0.44 \text{ volt})$$

Step 3 : The electrons flow along the nail to the areas containing impurities which act as cathode where oxygen (dissolved in water) is reduced to hydroxyl ions.

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

$$\text{(Cathodic process, reduction)}$$

$$(E^\circ_{red} = 1.23 \text{ volt})$$

The process of reduction involves the following two steps :

First of all H^+ ions are reduced to hydrogen atoms.

$$H^+ + e^- \longrightarrow [H] \quad \ldots\text{(ii)}$$

These hydrogen atoms combine with oxygen dissolved in water or from air.

$$4[H] + O_2 \longrightarrow 2H_2O \quad \ldots\text{(iii)}$$

Combining (ii) and (iii), we get

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O(l) \quad \ldots\text{(iv)}$$

$$(E^\circ_{red} = 1.23 \text{ volt})$$

Adding equations (i) and (iv), we get, the overall reactions of microcells established on the surface of iron.

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

$$(E^\circ_{cell} = 1.67 \text{ volt})$$

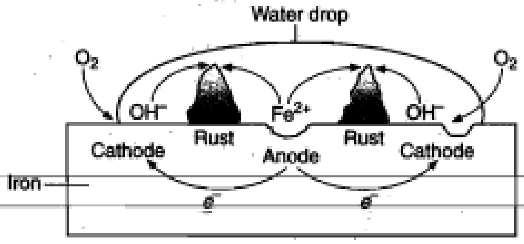
Step 4 : The ferrous ions (Fe^{2+}) formed in the previous step reacts with dissolved oxygen or oxygen from air to form ferric oxide (Fe_2O_3).

$$4Fe^{2+} + O_2 + 4H_2O \longrightarrow 2Fe_2O_3 + 8H^+(aq)$$

Hydration of ferric oxide gives rust.

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3 \cdot xH_2O$$

The process of rusting may be diagrammatically represented as in Fig. 12.17.



Oxidation : $Fe(s) \longrightarrow Fe^{2+}(aq.) + 2e^-$

Reduction : $O_2 + 4H^+(aq.) + 4e^- \longrightarrow 2H_2O(l)$

Atmospheric Oxidation $4Fe^{2+} + O_2 + 4H_2O(l) \longrightarrow 2Fe_2O_3(s) + 8H^+(aq.)$

$Fe_2O_3 + xH_2O \longrightarrow \underset{\text{Rust}}{Fe_2O_3 . xH_2O}$

Fig. 12.17 Rusting of iron

Factors Affecting Corrosion

1. Standard reduction potential : Lesser is the standard reduction potential, greater is the tendency of corrosion. In other words, more is the reactivity of metal, greater is the tendency of corrosion.

2. Strains and corrosion : Corrosion of metals occurs more readily at points of strain, bend, nick and scratches.

3. Impurity of metal and corrosion : Presence of impurity in metals increases the probability of their corrosion. Pure metals, *e.g.*, pure iron does not undergo rusting.

4. Salinity of water and corrosion : If water is saline, it helps in the flow of current in microelectrochemical cells on the surface of iron and hence, increases the process of corrosion.

5. Pollution and corrosion : The acidic oxides like CO_2, SO_2, NO_2 etc., present in air act as catalysts for corrosion. It should be noted that if iron is placed in vacuum, it does not undergo rusting.

Prevention of Rusting : Prevention of rusting is not only important from the point of view of economy but also from the point of view of safety. Prevention of corrosion not only saves money but also prevents accidents due to collapse of bridges and buildings.

Some important methods for preventing corrosion are described below:

1. Using antirust solution : Alkaline phosphate and alkaline chromate solutions are the commonly used antirust solutions. Alkaline phosphates tend to form an insoluble film of iron phosphate on the surface of iron, thereby protecting it from corrosion. In addition, the alkaline nature of an antirust solution decreases the availability of H^+ ions which facilitate the oxidation of Fe to Fe^{2+}. These solutions are used to prevent rusting of radiators of cars and water coolers.

2. Barrier protection : It is one of the simplest methods of preventing corrosion. In this method a barrier or coating is applied to prevent the surface of the metallic object from come in contact with the atmosphere. This can be achieved by the following methods :

(i) Oil paints on the surface of metal prevents its contact with moist air.

(ii) By applying grease or oil on the surface of iron tools and other objects, rusting can be prevented.

(iii) Nichrome (Ni + Cr) plating on the surface of iron also acts as a barrier between metal and atmosphere.

(iv) Bisphenol is an important chemical which can be applied on the surface of the metal to avoid its corrosion.

3. Sacrificial protection : In this method, the surface of iron is coated with a more active metal than iron. This active metal loses electrons, *i.e.*, undergo oxidation in preference to iron and hence, prevents the rusting of iron. So, long as the surface of iron is covered with such metals the corrosion of iron is prevented. If the surface is scratched or the coating is broken, even then the rusting of iron does not start.

Zinc metal is the most stable metal to cover iron surfaces. **The process of coating the iron surface by zinc is called galvanization.** Zinc metal present on the surface of iron forms a thin protective layer of basic zinc carbonate, *i.e.*, $ZnCO_3 \cdot Zn(OH)_2$ due to the reaction between zinc, oxygen, CO_2 and moisture in air.

$$Zn^{2+} + 2e^- \longrightarrow Zn(s); \qquad E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ volt}$$

$$Fe^{2+} + 2e^- \longrightarrow Fe(s); \qquad E^\circ_{Fe^{2+}/Fe} = -0.44 \text{ volt}$$

(Zinc will undergo oxidation in preference to iron.)

Since, standard reduction potential of zinc is less than iron, hence, iron will not undergo corrosion (oxidation) even when the zinc coating is broken due to scratches or some other mechanical stress.

Sometimes an iron surface is coated with tin metal and this process is known as **tinning** or tin plating. This method is not as effective as **galvanization.**

$$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s); \quad E^\circ_{Sn^{2+}/Sn} = -0.14 \text{ volt}$$

$$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s); \quad E^\circ_{Fe^{2+}/Fe} = -0.44 \text{ volt}$$

(Iron will undergo oxidation in preference to tin.)

Tinning is effective in checking the rusting of iron so long as the surface of iron is fully covered by tin. Once the tin coating is broken or scratched then rusting will start because standard reduction potential of iron is less than that of tin.

4. Electrical or Cathodic protection : If a buried steel pipe is connected to an active metal, *i.e.*, highly electropositive metal, say magnesium, a voltaic cell is formed; the active metal is the anode and iron becomes the cathode. Wet soil or moisture forms the electrolyte and the electrode reactions are :

$$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-; \quad E^\circ_{Mg^{2+}/Mg} = -2.37\,V$$

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq); \quad E^\circ_{red} = 1.23\,V$$

$$\textbf{Overall: } 2Mg(s) + O_2(g) + 2H_2O(l) \longrightarrow 2Mg^{2+} + 4OH^-; \quad E^\circ_{cell} = 3.60\,V$$

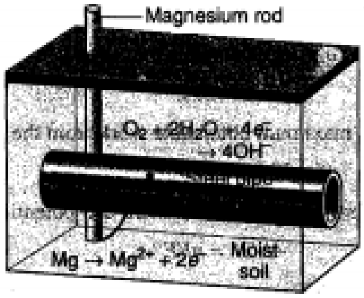


Fig. 12.18 Cathodic protection of a buried steel pipe

As the cathode, the iron containing steel pipe is protected fi oxidation. Of course, the magnesium rod is eventually consu and must be replaced, but this is cheaper than digging up the p line. This method is used to prevent the rusting of submarines. base line of oil refineries.

(x) Extraction of metals: A more electropositive metal displace a less electropositive metal from its salt's solution. T principle is applied for the extraction of Ag and Au by cyai process. Silver from the solution containing sodium arg cyanide, $NaAg(CN)_2$, can be obtained by the addition of zin it is more electropositive than Ag.

$$2NaAg(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2Ag$$

Concept of Equilibrium in Electrochemical Cell

In an electrochemical cell a reversible redox process t place, *e.g.*, in Daniell cell:

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

(1) At equilibrium mass action ratio becomes equa equilibrium constant,

i.e., $Q = K_e$

(2) Oxidation potential of anode = − Reduction potential cath

i.e., emf = Oxidation potential of anode + Reduction potential of cathode = 0

Cell is fully discharged.

According to Nernst equation:

$$E = E^\circ - \frac{0.0591}{n} \log_{10} Q \text{ at } 25^\circ C$$

At equilibrium, $E = 0,\ Q = K$

$$0 = E^\circ - \frac{0.0591}{n} \log_{10} K$$

$$K = \text{antilog}\left[\frac{nE^\circ}{0.0591}\right]$$

Work done by the Cell

Let n faraday charge be taken out of a cell of emf E; then v done by the cell will be calculated as:

$$\text{Work} = \text{Charge} \times \text{Potential}$$
$$= nFE$$

Work done by the cell is equal to decrease in free energy.

$$-\Delta G = nFE$$

Similarly, maximum obtainable work from the cell will be

$$W_{\text{max}} = nFE°$$

where, $E°$ = standard emf or standard cell potential.

$$-\Delta G° = nFE°$$

The Relationship among K, $\Delta G°$ and $E°$ Cell

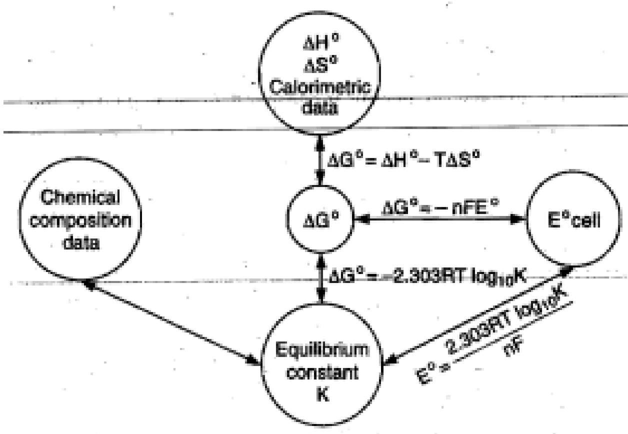


Fig. 12.19

Heat of Reaction in an Electrochemical Cell

Let n faraday charge flows out of a cell of emf E,

Then $$-\Delta G = nFE \quad \text{... (i)}$$

Gibbs-Helmholtz equation from thermodynamics may be given as:

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \quad \text{... (ii)}$$

From equations (i) and (ii), we get

$$-nFE = \Delta H + T\left[\frac{\partial(-nFE)}{\partial T}\right]_P = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$\Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P$$

Here, $\left(\frac{\partial E}{\partial T}\right)_P$ = Temperature coefficient of cell

Case I: When $\left(\frac{\partial E}{\partial T}\right)_P = 0$, then $\Delta H = -nFE$

Case II: When $\left(\frac{\partial E}{\partial T}\right) > 0$, then $nFE > \Delta H$, *i.e.*, process inside the cell is endothermic.

Case III: When $\left(\frac{\partial E}{\partial T}\right) < 0$, then $nFE < \Delta H$, *i.e.*, process inside the cell is exothermic.

12.24 PRIMARY VOLTAIC CELL (The Dry Cell)

In this cell, once the chemicals have been consumed, further reaction is not possible. It cannot be regenerated by reversing the current flow through the cell using an external direct current source of electrical energy. The most common example of this type is dry cell.

The container of the dry cell is made of zinc which also serves as one of the electrodes. The other electrode is a carbon rod in the centre of the cell. The zinc container is lined with a porous paper. A moist mixture of ammonium chloride, manganese dioxide, zinc chloride and a porous inert filler occupy the space between the paper lined zinc container and the carbon rod. The cell is sealed with a material like wax.

As the cell operates, the zinc is oxidised to Zn^{2+}

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad \text{(Anode reaction)}$$

The electrons are utilized at carbon rod (cathode) as the ammonium ions are reduced.

$$2NH_4^+ + 2e^- \longrightarrow 2NH_3 + H_2 \quad \text{(Cathode reaction)}$$

The cell reaction is

$$Zn + 2NH_4^+ \longrightarrow Zn^{2+} + 2NH_3 + H_2$$

Hydrogen is oxidised by MnO_2 in the cell.

$$2MnO_2 + H_2 \longrightarrow 2MnO(OH)$$

Ammonia produced at cathode combines with zinc ions to form complex ion.

$$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$$

E_{cell} is 1.6 volt.

Alkaline dry cell is similar to ordinary dry cell. It contains potassium hydroxide. The reactions in alkaline dry cell are:

$$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2e^- \quad \text{(Anode reaction)}$$

$$2MnO_2 + 2H_2O + 2e^- \longrightarrow 2MnO(OH) + 2OH^- \quad \text{(Cathode reaction)}$$

$$Zn + 2MnO_2 + 2H_2O \longrightarrow Zn(OH)_2 + 2MnO(OH) \quad \text{(Overall)}$$

E_{cell} is 1.5 volt.

Button cell : The button cells are usually pallet type flat in construction and look like a button in shape. Owing to their small sizes, they are used in small electronic devices like hearing aids, electronic watches etc. These cells are basically primary cells. Mercuric oxide button cell is the most commonly used button cell. In this cell, zinc anode and mercuric oxide plus carbon paste cathode is used. The electrolyte is a paste of ZnO and KOH.

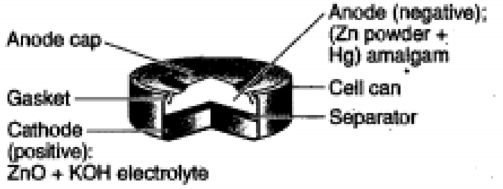


Fig. 12.20

The cell process is given below :

Anode : $$\underset{\text{(Amalgam)}}{Zn} + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$$

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

Overall : $$\underset{\text{Amalgam}}{Zn} + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

The potential of this cell is approximately 1.35 volt and it remains constant during its life because overall reaction does not involve any ion whose concentration can change during the process.

12.25 SECONDARY VOLTAIC CELL (Lead Storage Battery)

The cell in which original reactants are regenerated by passing direct current from external source, *i.e.*, it is recharged, is called secondary cell. Lead storage battery is the example of this type.

It consists of a group of lead plates bearing compressed spongy lead, alternating with a group of lead plates bearing lead dioxide, PbO_2. These plates are immersed in a solution of about 30% H_2SO_4. When the cell discharges, it operates as a voltaic cell. The spongy lead is oxidised to Pb^{2+} ions and lead plates acquire a negative charge.

$$Pb \longrightarrow Pb^{2+} + 2e^- \qquad \text{(Anode reaction)}$$

Pb^{2+} ions combine with sulphate ions to form insoluble lead sulphate, $PbSO_4$, which begins to coat lead electrode.

$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \qquad \text{(Precipitation)}$$

The electrons are utilised at PbO_2 electrode.

$$PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O \qquad \text{(Cathode reaction)}$$

$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \qquad \text{(Precipitation)}$$

Overall cell reaction is:

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O$$

E_{cell} is 2.041 volt.

When a potential slightly greater than the potential of battery is applied, the battery can be recharged.

$$2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 2H_2SO_4$$

After many repeated charge-discharge cycles, some of the lead sulphate falls to the bottom of the container, the sulphuric acid concentration remains low and the battery cannot be recharged fully.

Nickel-Cadmium storage cell : It is also a common storage battery. It is more expensive than the lead storage battery but it is light, therefore, used in calculators, portable power tools, etc.

It is a voltaic cell consisting of an anode of cadmium and a cathode of hydrated nickel oxide on nickel. The electrolyte in the cell is aqueous solution of potassium hydroxide. Electrode processes are given below :

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

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

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

In the recharging of the cell the process is reversed.

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

12.26 FUEL CELL

Fuel cells are another means by which chemical energy may be converted into electrical energy. The main disadvantage of a primary cell is that it can deliver current for a short period only. This is due to the fact that the quantity of oxidising agent and reducing agent is limited. But the energy can be obtained indefinitely from a fuel cell as long as the outside supply of fuel is maintained. One of the examples is the hydrogen-oxygen fuel cell. The cell consists of three compartments separated by a porous electrode. Hydrogen gas is introduced into one compartment and oxygen gas is fed into another compartment. These gases then diffuse slowly through the electrodes and react with an electrolyte that is in the central compartment. The electrodes are made of porous carbon and the electrolyte is a resin containing concentrated aqueous sodium hydroxide solution. Hydrogen is oxidised at anode and oxygen is reduced at cathode. The overall cell reaction produces water. The reactions which occur are:

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

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

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

This type of cells are used in space-crafts. Fuel cells are efficient and pollution free.

Thermodynamic efficiency of fuel cells is the ratio of the electrical free energy to the enthalpy of the reaction.

$$\eta = \frac{\Delta G}{\Delta H}$$

12.27 CONCENTRATION CELLS

If two plates of the same metal are dipped separately into two solutions of the same electrolyte and are connected with a salt bridge, the whole arrangement is found to act as a galvanic cell. In general, there are two types of concentration cells:

(i) Electrode concentration cells: In these cells, the potential difference is developed between two like electrodes at different concentrations dipped in the same solution of the electrolyte. For example, two hydrogen electrodes at different gas pressures in the same solution of hydrogen ions constitute a cell of this type.

$$\underset{\text{Anode}}{\underline{\text{Pt, H}_2\text{ (Pressure }p_1)}}\,|\text{H}^+|\,\underset{\text{Cathode}}{\underline{\text{H}_2\text{ (Pressure }p_2)\text{ Pt}}}$$

If $p_1 > p_2$, oxidation occurs at LHS electrode and reduction occurs at RHS electrode.

$$E_{\text{cell}} = \frac{0.0591}{2}\log\frac{(p_1)}{(p_2)} \text{ at } 25^\circ\text{ C}$$

In the amalgam cells, two amalgams of the same metal at two different concentrations are immersed in the same electrolytic solution.

$$M\,(\text{Hg }C_1)\,|M^{n+}|\,\text{Zn(Hg }C_2)$$

The emf of the cell is given by the expression

$$E_{\text{cell}} = \frac{0.0591}{n}\log\frac{C_1}{C_2} \text{ at } 25^\circ\text{ C}$$

(ii) Electrolyte concentration cells: In these cells, electrodes are identical but these are immersed in solutions of the same electrolyte of different concentrations. The source of electrical energy in the cell is the tendency of the electrolyte to diffuse from a solution of higher concentration to that of lower concentration. With the expiry of time, the two concentrations tend to become equal. Thus, at the start the emf of the cell is maximum and it gradually falls to zero. Such a cell is represented in the following manner:

(C_2 is greater than C_1).

$$M\,|\,M^{n+}(C_1)\,||\,M^{n+}(C_2)\,|\,M$$

or

$$\underset{\text{Anode}}{\underline{\text{Zn}\,|\,\text{Zn}^{2+}(C_1)}}\,||\,\underset{\text{Cathode}}{\underline{\text{Zn}^{2+}(C_2)\,|\,\text{Zn}}}$$

The emf of the cell is given by the following expression:

$$E_{\text{cell}} = \frac{0.0591}{n}\log\frac{C_{2\,(\text{RHS})}}{C_{1\,(\text{LHS})}} \text{ at } 25^\circ\text{ C}$$

The concentration cells are used to determine the solubility of sparingly soluble salts, valency of the cation of the electrolyte and transition point of the two allotropic forms of a metal used as electrodes, etc.

SOME SOLVED EXAMPLES

Example 43. *A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of* 10^{-6} *M hydrogen ions. The emf of the cell is* 0.118 *volt at* 25° *C. Calculate the concentration of hydrogen ions at the positive electrode.*

Solution: The cell may be represented as

$$\text{Pt}\,|\,\text{H}_2\text{ (1 atm)}\,|\,\underset{10^{-6}\,M}{\text{H}^+}\,||\,\underset{C\,M}{\text{H}^+}\,|\,\text{H}_2\text{ (1 atm)}\,|\,\text{Pt}$$

Anode (–ve): $\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$

Cathode (+ ve): $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$

$$E_{\text{cell}} = \frac{0.0591}{2}\log\frac{[\text{H}^+]^2_{\text{Cathode}}}{[10^{-6}]^2}$$

$$0.118 = (0.0591)\log\frac{[\text{H}^+]}{10^{-6}}$$

$$\log\frac{[\text{H}^+]_{\text{Cathode}}}{10^{-6}} = \frac{0.118}{0.0591} = 2$$

$$\frac{[\text{H}^+]_{\text{Cathode}}}{10^{-6}} = 10^2$$

$$[\text{H}^+]_{\text{Cathode}} = 10^{-6}\times 10^2 = 10^{-4}\ M$$

Example 44. *The emf of the cell*

$$Ag\,|\,AgI \text{ in } 0.05\,M\ KI\,|\,Sol.\ NH_4NO_3\,|\,0.05\,M\ AgNO_3\,|\,Ag$$

is 0.788 *volt at* 25° *C. The activity coefficient of KI and silver nitrate in the above solution is* 0.90 *each. Calculate (i) the solubility product of AgI and (ii) the solubility of AgI in pure water at* 25° *C.*

Solution: Ag^+ ion concentration on AgNO_3 side

$$= 0.9\times 0.05 = 0.045\,M$$

Similarly I^- ion concentration in 0.05 *M* KI solution

$$= 0.05\times 0.9 = 0.045\,M$$

$$E_{\text{cell}} = \frac{0.0591}{1}\log\frac{[\text{Ag}^+]_{\text{RHS}}}{[\text{Ag}^+]_{\text{LHS}}} = 0.0591\log\frac{0.045}{[\text{Ag}^+]_{\text{LHS}}}$$

or

$$\log\frac{0.045}{[\text{Ag}^+]_{\text{LHS}}} = \frac{0.788}{0.0591} = 13.33$$

$$[\text{Ag}^+]_{\text{LHS}} = \frac{0.045}{2.138\times 10^{13}}$$

$$= 2.105\times 10^{-15}\ M$$

$$\text{Solubility product of AgI} = [\text{Ag}^+][\text{I}^-]$$

$$= 2.105\times 10^{-15}\times 0.045$$

$$= 9.472\times 10^{-17}$$

$$\text{Solubility of AgI} = \sqrt{\text{Solubility product of AgI}}$$

$$= \sqrt{9.472\times 10^{-17}}$$

$$= 9.732\times 10^{-9}\text{ g mol L}^{-1}$$

$$= 9.732\times 10^{-9}\times 143.5\text{ g L}^{-1}$$

$$= 1.396\times 10^{-6}\text{ g L}^{-1}$$

Example 45. *The observed emf of the cell,*

$$Pt\,|\,H_2\ (1\,atm)\,|\,H^+\,(3\times 10^{-4}\ M)\,||\,H^+\,(M_1)\,|\,H_2\ (1\,atm)\,|\,Pt$$

is 0.154 *V. Calculate the value of* M_1 *and pH of cathodic solution.*

Solution:

$$E_{\text{cell}} = 0.0591\log\frac{M_1}{3\times 10^{-4}}$$

or

$$\log\frac{M_1}{3\times 10^{-4}} = \frac{0.154}{0.0591} = 2.6058$$

The pH of the solution is given by

$$pH = \frac{E_G^\circ - 0{\cdot}2422 - E}{0{\cdot}0591} \quad \text{at } 25°C \qquad ...(81)$$

The glass electrode has a number of advantages over other electrodes. It can be used even in strong oxidising solutions which interfere even with quinhydrone electrode. It can also be used in the presence of metallic ions, poisons, etc. It is simple to operate and is, therefore, extensively used in chemical, industrial, agricultural and biological laboratories.

Potentiometric Tirations. As discussed earlier, the potential of an electrode depends upon the concentration of the ion to which it is reversible in accordance with Nernst equation. In a titration, there is change in ionic concentration which can be followed by measuring the potential of a suitable electrode. The potentiometric titrations are, thus, those titrations which involve the measurement of electrode potentials with the addition of the titrant.

The potentiometric titrations generally fall into the following three categories :

1. Acid–Base Titrations
2. Oxidation–Reduction (Redox) Titrations
3. Precipitation Titrations

There are a number of advantages of potentiometric titrations over the ordinary titrations involving the use of indicators. Potentiometric titrations can be carried out in coloured solutions while indicators cannot be used in such cases. Also, in ordinary titrations, one must have a prior information about the relative strengths of acids and bases before a proper indicator is selected. However, no such information is required in the case of potentiometric titrations.

Acid–Base Titrations. Suppose we want to titrate a solution of HCl against NaOH. Any electrode whose potential depends upon H^+ ion concentration (*e.g.*, hydrogen electrode, quinhydrone electrode, glass electrode) is placed in the HCl solution. It is connected to a reference electrode (*e.g.*, calomel electrode, Ag,AgCl electrode) to form a galvanic cell. If hydrogen electrode is used as the H^+ indicating electrode and a saturated calomel electrode is used as the reference electrode, then the galvanic cell may by represented as

$$\text{Pt, } H_2(1 \text{ atm}),\ H^+(c{=}\text{unknown}) \ ||\ \text{KCl sat. soln ; } Hg_2Cl_2(s),\ Hg$$

The EMF of the cell is measured potentiometrically. It is given by

$$\begin{aligned} E \equiv E &= E_R - E_L = E_{\text{calomel}} - E_{\text{hydrogen}} \\ &= 0{\cdot}2422 - 0{\cdot}0591 \log H^+ = 0{\cdot}2422 + 0{\cdot}0591\, pH \qquad ...(82) \end{aligned}$$

Suppose 100 ml of 0·1 M HCl is to be titrated against 1 M NaOH (the titrant). The concentration of the titrant is usually 5 to 10 times higher than that of the solution to be titrated so that the volume change is as small as possible.

As the titration proceeds, the H^+ ion concentration goes on decreasing, *i.e.*, pH of the solution goes on increasing, hence, according to Eq. 82, the EMF of the cell goes on increasing. It is evident that the EMF of the cell would increase by 0·0591 volt for every ten–fold decrease in the concentration of H^+ ions or one unit increase in the pH of the solution.

Assuming, for the sake of simplicity of calculations, that there is no change in volume during the titration, it is evident that the addition of first 9 ml of NaOH solution will give a change of 0·0591 volt. However, the addition of next 0·90 ml will produce the same change and the addition of next 0·09 ml will also produce the same change and so on. Thus, the EMF of the cell changes slowly at first but more and more rapidly as the end point approaches.

After the end point, further addition of NaOH produces very little change in the H^+ ion concentration and hence there is very little change in the EMF of the cell.

A plot of E against the volume of NaOH added is shown in Fig. 7*(a)*. As can be seen, the EMF of the cell initially rises gradually and thereafter more rapidly near the equivalence point. Beyond the equilvalence point, the EMF of the cell again increases slightly on adding more of NaOH.

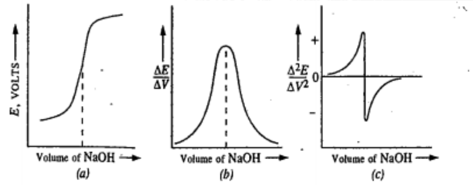


Fig. 7*(a)*. Potentiometric curve obtained in acid–base titration. Fig. 7 *(b)* and *(c)* determination of end point in acid–base titration.

Once the titration curve is obtained, the analyst has to determine, by inspection, where the curve is steepest. He may draw a vertical line through the steep portion of the curve and find the intersection of this line with the volume axis. There occurs some uncertainty in this procedure and this will be reflected in the ultimate volume reading. For a reaction that goes to completion, the titration curve is so steep near the equilvalence point that the uncertainty is small. However, for a reaction with small equilibrium constant, the precision with which the equilvalence point may be determined becomes poorer.

Fig. 7*(b)* shows a plot of the slope of the titration curve, that is, the change in the EMF with change in volume ($\Delta E/\Delta V$) against the volume of the titrant. The resulting curve rises to a maximum at the equivalence point. The volume at the equilvalence point is determined by drawing a vertical line from the peak to the volume axis. Of course, there is some uncertainty in locating exactly the peak. The more complete the reaction, the sharper the peak and hence the more accurate is the location of the equilvalence point.

Fig. 7*(c)* shows a plot of the change in the slope of a titration curve ($\Delta^2E/\Delta V^2$) against the volume of the titrant. At the point where the slope $\Delta E/\Delta V$ is a maximum, the derivative of the slope is zero. The equivalence point is located by drawing a vertical line from the point at which $\Delta^2E/\Delta V^2$ is zero on the volume axis. The steeper the portion of the curve joining the maximum and minimum value of $\Delta^2E/\Delta V^2$, the more complete is the titration reaction.

Example 31. 25 ml of a solution of HCl (0·1 M) is being titrated potentiometrically against a standard (0·1 M) solution of NaOH using a hydrogen electrode as the indicator electrode and saturated calomel electrode (SCE) as the reference electrode. What would be the EMF of the cell initially and after the addition of 20, 24·9, 24·95, 25·00 25·05, 25·10 and 30·00 ml of NaOH solution ? Comment on the data obtained.

Solution : The galvanic cell formed in this case may be represented as follows :

$$\text{Pt, } H_2(1 \text{ atm}),\ H^+\ (c{=}\text{unknown})\ ||\ \text{KCl sat. soln., } Hg_2Cl_2\ (s),\ Hg$$

The EMF of the cell would be given

$$\begin{aligned} E &= E_{\text{SCE}} - E_{\text{hydrogen}} = 0{\cdot}2422 - 0{\cdot}0591 \log H^+ \\ &= 0{\cdot}2422 + 0{\cdot}0591\, pH \text{ at } 25°C \qquad \text{(Eq. 82)} \end{aligned}$$

Initial pH of the titration solution, *viz.*, 0·1 M HCl = $-\log [H^+] = -\log (0{\cdot}1) = 1$ so that $E = 0{\cdot}3013$ V.

Since the product of volume of the solution in ml and the concentration in mol dm^{-3} of a solute gives the amount of the solute in millimoles, hence

Amount of HCl initially present in the titration solution = $25 \times 0{\cdot}1 = 2{\cdot}5$ millimoles

The amount of NaOH in 20 ml of 0·1 M solution added during titration = $20 \times 0{\cdot}1 = 2{\cdot}0$ millimoles

Cathode reaction :

$$4e^- + 2CO_2 + O_2 \longrightarrow 2CO_3^{2-}$$

Overall fuel cell reaction :

$$CO + H_2 + O_2 \longrightarrow CO_2 + H_2O$$

The efficiency of the coal-fired fuel cells is greater than 55%.

In coal-fired fuel cells, **solid electrolytes** have also been used in place of molten alkali carbonate. In one of the cells of this type, ZrO_2 stabilised by Y_2O_3 is used as the solid electrolyte which exhibits adequate ionic conductivity at the temperatures of operation (*viz.*, 1000°C and above). In the case of fuel cells using solid electrolytes, the cathode material is porous strontium-doped $LaMnO_3$ and the anode is Ni or ZrO_2. The efficiency of this type of cells is at least 33% which is greater than that obtained in thermal power plants.

Hydrogen–Oxygen Fuel Cells in Manned Space Flights. The hydrogen–oxygen fuel cells are playing important role in some of the manned space flights. The electrolyte used in these cells is an ion–exchange material and not a solution of KOH or NaOH. The ion–exchange material which is used in the form of a membrane *allows easy passage of protons.*

The graphite electrode on one side of the membrane is impregnated with Pt metal catalyst. This electrode acts as the cathode. This is in contact with H_2.

H_2 fuel ionises on the metal–catalyst and the protons produced by the electricity–producing reaction, *viz.*, $H_2(g) \longrightarrow 2H^+ + 2e^-$, pass through the thin (0·1 mm thick) membrane since it allows free proton mobility, as mentioned above and reach the other graphite electrode which is also impregnated with platinum catalyst . This acts as the anode. This electrode is in contact with O_2. Here the following reaction occurs :

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

The protons required for this reaction are those which come through the membrane from the ionisation of H_2 on the other side of the membrane as stated above.

It may be mentioned that this type of fuel cell is slated for development as part of the electrochemical engine to be used in automobiles in place of the too heay lead-acid batteries that are being used at present in vehicular transportation. The electrochemical engine will have a far greater efficiency than the internal combustion engine. The main advantage would be the elimination of hazardous air polltants such as CO, NO_x, SO_2, etc., which are inherently associated with the internal combustion engine.

Recently, a **zinc–air fuel cell (ZAFC)**, in which zinc metal is used in place of hydrogen gas, has been developed in the U.S.A. as a source of power in automobiles. In this cell, the OH^- ions produced by the reduction of oxygen of the air ($O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-$), brought about in the presence of a catalyst, travel through the liquid electrolyte (NaOH or KOH) and reach the zinc anode (comprising of a perforated pack of zinc pellets) where they react to form zinc oxide ($Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$). These oxidation–reduction reactions generate electricity, the overall fuel cell reaction being $2Zn + O_2 \longrightarrow 2ZnO$.

The zinc oxide produced dissolves in the electrolyte. The spent electrolyte is pumped out and subjected to a special treatment for the regeneration of zinc in the form of zinc pellets. The regenerated electrolyte and the zinc pellets are used again.

Fuel cells are associated with a number of advantages. Their efficiency is very high. About 75 per cent of chemical energy can be converted into electrical energy. The individual cells can be stacked and connected in series to generate higher voltages. They are also very light.

However, there are a number of engineering porblems which shall have to be solved before fuel cells become practical sources of electrical energy. Once it is done, fuel cell technology would bring revolution in the area of energy production.

Applications of EMF Measurements

The EMF measurements find a number of useful applications. Some of these are given below.

1. Determination of Activity Coefficients of Electrolytes. Suppose we want to determine the activity coefficient of hydrochloric acid. Consider a cell without liquid junction containing HCl. The two electrodes are so chosen that one is reversible with respect to the cation of the electrolyte (in this case, the H^+ ion) and the other is reversible with respect to the anion (*i.e.*, the Cl^- ion). Evidently, the first electrode is the hydrogen electrode and the other can be the silver–silver chloride electrode. Accordingly, the cell arrangement is as follows :

$$Pt\ ;\ H_2(g)\ (1\ atm)\ |\ HCl\ (m)\ |\ AgCl(s),\ Ag(s)$$

where *m* is the molality of HCl solution.

The cell reaction is

$$1/2\ H_2(g) + AgCl(s) \rightleftharpoons Ag(s) + H^+(m) + Cl^-(m)$$

According to Eq. 20, the EMF of the cell at 25°C is given by

$$E = E^\circ - 0{\cdot}0591 \log \frac{a_{H^+} a_{Cl^-}}{\left(a_{H_2}\right)^{1/2}} \qquad \text{...(61)}$$

$$= E^\circ - 0{\cdot}0591 \log a_{H^+} a_{Cl^-} \qquad \text{...(62)}$$

because activity of each of Ag(*s*), AgCl(*s*) and $H_2(g)$ at 1 atm pressure is taken as unity.

As already discussed,

$$a_{H^+} a_{Cl^-} = (a_\pm)^2 = (\gamma_\pm m)^2 = \gamma_\pm^2 m^2 \qquad \text{(Eqs. 43 and 44)}$$

where $\gamma_\pm$ and *m* are the mean ionic activity coefficient and the molality of HCl, respectively. Substituting in Eq. 62, we get

$$E = E^\circ - 0{\cdot}0591 \log \gamma_\pm^2 m^2 \qquad \text{...(63)}$$

$$= E^\circ - 0{\cdot}1182 \log \gamma_\pm - 0{\cdot}1182 \log m \qquad \text{...(64)}$$

Rearranging,

$$E + 0{\cdot}1182 \log m = E^\circ - 0{\cdot}1182 \log \gamma_\pm \qquad \text{...(65)}$$

The two unknowns E° and $\gamma_\pm$ in Eq. 65 can be determined by measuring the EMFs of the cell over various concentrations of HCl, including dilute concentrations. At infinite dlution, $m=0$ and $\gamma_\pm=1$ so that $\log \gamma_\pm=0$. Thus, a plot of $E+0{\cdot}1182 \log m$ versus *m*, extrapolated to $m=0$ gives E° as the *y*–intercept. Knowing the value of E°, the mean ionic activity coefficient $\gamma_\pm$ of HCl at any other concentration can be determined from the EMF data of the cell at that concentration.

Alternatively, we can use the Debye–Hückel limiting law (DHLL) equation, *viz.*,

$$\log \gamma_\pm = -0{\cdot}509\ |z_+ z_-|\ I^{1/2} \qquad \text{...(66)}$$

to substitute for the $\log \gamma_\pm$ term in Eq. 65, giving

$$E + 0{\cdot}1182 \log m = E^\circ + 0{\cdot}0602\ I^{1/2} \qquad \text{...(67)}$$

Thus, a plot of $E + 0{\cdot}1182 \log m$ versus $I^{1/2}$ will give a straight line at low concentrations where the limiting law is valid. The extrapolation of this plot to $I^{1/2}=0$ gives E° as the *y*–intercept of the line.

In practice, however, an extension of the DHLL is needed to make a satisfactory linear extrapolation. For a uni–univalent electrolyte in dilute aqueous solution at 25°C, an empirical extension of Eq. 66 is

$$\log \gamma_\pm = -0{\cdot}509\ m^{1/2} + bm \qquad \text{...(68)}$$

where *b* is an empirical constant.

Substituting this equation in Eq. 65 and rearranging the terms, we obtain

$$E + 0{\cdot}1182 \log m - 0{\cdot}0602\, m^{1/2} = E' = E^\circ - (0{\cdot}1182\, b)m \qquad \ldots(69)$$

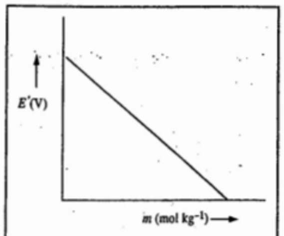


Fig. 4. Determination of E°.

This equation shows that the left hand side (which we have designated as E'), when plotted against m, will give a straight line whose intercept at $m=0$, is E° (Fig. 4).

Example 25. Consider the following cell :

Ag(s), Ag$^+$(a=0·001 m) || Ag$^+$(c=0·1 m, a unknown), Ag(s) Its EMF at 25°C is + 1·11V. *(a)* Write the cell reaction and *(b)* Calculate the activity coefficient of the Ag$^+$ ion in 0·1 m solution.

Solution : *(a)* The cell reaction is

$$Ag^+\ (c=0{\cdot}1\ m,\ a=\text{say},\ x) \rightleftharpoons Ag^+(a=0{\cdot}001\ m)$$

It is a concentration cell with *no net reaction*. Hence,

$$E = -\,0{\cdot}0591 \log (0{\cdot}001/x)$$

$$\log \frac{0{\cdot}001}{x} = -\frac{1{\cdot}11\,V}{0{\cdot}0591V} = -\,1{\cdot}878$$

$$\log x = \log 0{\cdot}001 + 1{\cdot}878 = -\,1{\cdot}122 = \bar{2}{\cdot}878$$

Taking antilogs, x=0·076.Thus, a = 0·076. Hence, the activity coefficient

$$\gamma = a/c = 0{\cdot}076/0{\cdot}1 = \mathbf{0{\cdot}76}$$

Example 26. EMF of the cell Cd(s), CdCl$_2$(m=0·02) | AgCl(s), Ag(s) is found to be 0·780 V at 25°C. Using the standard potentials, *viz.*, $E^\circ_{Cd^{2+},Cd} = -\,0{\cdot}403$ V and $E^\circ_{AgCl,Cl^-} = +\,0{\cdot}222$ V, calculate the mean ionic activity coefficient of CdCl$_2$ at this temperature.

Solution : The half-cell reactions are :

(i) R.H.E. : $2AgCl\ (s) + 2e^- \rightleftharpoons 2Ag(s) + 2Cl^-$; $E^\circ_l = +\,0{\cdot}222$ V

(ii) L.H.E. : $2Cd(s) \rightleftharpoons Cd^{2+}(aq) + 2e^-$; $E^\circ_l = -\,0{\cdot}403$ V

Hence, adding Eqs. *(i)* and *(ii)*, we get

$$Cd(s) + 2AgCl(s) \rightleftharpoons Cd^{2+}(aq) + 2Ag(s) + 2Cl^-(aq),$$

$$E^\circ = E^\circ_R - E^\circ_L = 0{\cdot}222 - (-\,0{\cdot}403) = 0{\cdot}625\ V$$

CdCl$_2$ ionises in solution as $CdCl_2(aq) \rightleftharpoons Cd^{2+}(aq) + 2Cl^-(aq)$

Thus, the number of ions produced on ionization of CdCl$_2$ = 3 with x=1 and y=2. Hence,

$$a_{CdCl_2} = (a_\pm)^{x+y} = (a_+)^x\,(a_-)^y\ ;\ a_+ = \gamma_+ m_+ = \gamma_+ mx = \gamma_+ m \qquad (\because\ x = 1)$$

$$a_- = \gamma_- m_- = \gamma_- my = 2\gamma_- m \qquad (\because\ y = 2)$$

$$\therefore\ a_{CdCl_2} = (a_\pm)^3 = (\gamma_+ m)\,(2\gamma_- m)^2 = 4(\gamma_+ \gamma_-^2)\, m^3 = 4(\gamma_\pm)^3 m^3$$

The EMF of the cell is given by $E = E^\circ - \frac{0{\cdot}0591}{2} \log a_+ a_-^2 = E^\circ - \frac{0{\cdot}0591}{2} \log\,(a_\pm)^3$ at 25°C

or
$$0{\cdot}780 = 0{\cdot}625 - 0{\cdot}0295 \log\,[4(\gamma_\pm)^3 m^3]$$

$$\log 4(\gamma_\pm)^3 m^3 = -\frac{0{\cdot}780 - 0{\cdot}625}{0{\cdot}0295} = -\,5{\cdot}2546 = \bar{6}{\cdot}754$$

Taking antilogs, $4(\gamma_\pm)^3 m^3 = 5{\cdot}57\times10^{-6}$

$$\therefore\ \gamma_\pm = \left(\frac{5{\cdot}57\times10^{-6}}{4m^3}\right)^{1/3} = \left(\frac{5{\cdot}57\times10^{-6}}{4(0{\cdot}02)^3}\right)^{1/3} = \mathbf{0{\cdot}558}$$

Example 27. Calculate the EMF of the following cell at 25°C :

Cd(s), CdCl$_2$(m=0·005, $\gamma_\pm$=0·817) | AgCl(s), Ag(s)

using the data given in the last example.

Solution : As shown in the last example, E° = 0·625 V

Also, $a_{CdCl_2} = (a_\pm)^3 = 4(\gamma_\pm)^3 m^3$

The EMF of the cell is given by

$$E = E^\circ - \frac{0{\cdot}0591}{2}\log(a_+ a_-^2) = E^\circ - \frac{0{\cdot}0591}{2}\log(a_\pm)^3$$

$$= E^\circ - 0{\cdot}0295 \log\,[4\gamma_\pm)^3 m^3]$$

$$= 0{\cdot}625 - 0{\cdot}0295 \log\,[4(0{\cdot}817)^3(0{\cdot}005)^3] = \mathbf{0{\cdot}819\ V}$$

2. Determination of Transport Numbers. As has been shown earlier, the EMF of a concentration cell *with transference*, represented by $E_{w.t.}$, in which the end electrodes are reversible with respect to cation, is given by Eq. 57, *viz.*,

$$E_{w.t.} = t_-(RT/F) \ln (a_2/a_1) \qquad \ldots(i)$$

The EMF of the same cell with the same solutions but *without transference*, denoted by $E_{w.o.t.}$, is given by Eq. 54, *viz.*,

$$E_{w.o.t.} = (RT/F) \ln (a_2/a_1) \qquad \ldots(ii)$$

Dividing *(i)* by *(ii)*, we have

$$t_- = E_{w.t.}/E_{w.o.t.} \qquad \ldots(61)$$

Thus, the ratio of the EMFs of the two concentration cells, one with transference and the other without transference, gives the *transference number of the anion*, if the end electrodes are reversible with respect to the *cation*.

If the end electrodes are reversible with respect to the *anion*, then the ratio of the two EMFs will give the transference number of the *cation* of the electrolyte.

3. Determination of Valency of Ions in Doubtful Cases. The valency of mercurous ion was in doubt for a considerable time. It was finally established by determining the EMF of a concentration cell of the type given below :

Mercury, Mercurous nitrate solution (c_1) || Mercurous nitrate solution (c_2), Mercury

The salt bridge represented by the two vertical lines connecting the two solutions contains saturated solution of ammonium nitrate.

The EMF of the cell, E, assuming the activity coefficients to be equal to unity, is given by the expression

$$E = (RT/nF) \ln (c_2/c_1)$$