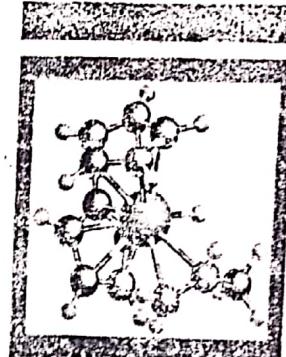


Chapter 2

ELECTROCHEMICAL ENERGY SYSTEMS



CHAPTER OUTLINE

Introduction, Electrochemical cell, Classification of electrochemical cells, differences of galvanic and electrolytic cells, Galvanic cell, Electrochemical conventions, Origin of electrode Potential, Electrode potentials, standard electrode potentials and electrochemical series, Measurement of electrode potentials and IUPAC sign, Nernst equation for single electrode potential, E.M.F. of a cell, Types of electrodes or half cells, Types of ion selective electrodes, Applications of ion selective electrodes, How an ion selective electrode works, Reference electrodes, Factors affecting the potential of a reference electrode, Limitations of primary reference electrode and advantages of secondary reference electrode, Ion-selective glass electrode, Determination of pH of a Solution using a glass electrode and a calomel electrode, Determination of pH of a solution using a glass and a common Ag/AgCl electrode, concentration Cells. Practice exercises, Review questions.

ELECTRODE POTENTIALS AND CELLS

Chemical reactions involving transfer of electrons are called *oxidation* and reduction *reactions* or *redox reactions*. A spontaneous electrode redox process is always accompanied by a decrease in free energy. Spontaneous redox reaction at the electrode occurs as a result of the different abilities of metals to give up their electrons and the ability of electrons to flow through the circuit. It is observed that when two dissimilar metals, one with higher electrode potential, is connected to the other of lower potential and are immersed in their own respective metal ion solutions, the metals spontaneously develop a tendency to lose or gain electrons at their respective electrodes. In other words, spontaneous redox reactions of a voltaic cell take place at the two electrodes with a decrease of free energy.

2.1 ELECTROCHEMICAL CELL

An electrochemical cell is a device consisting of two electrodes, each in contact with a solution of its own ions, transforms the free energy change of the redox reaction at the electrodes into electrical energy.

Energy is the driving force for chemical reactions in electrodes. In a redox reaction, the free energy released in a reaction due to movement of charged particles give rise to a 'potential difference'. The maximum

potential difference between the two electrodes is called the *electromotive force*, E , in volts for a galvanic cell. Therefore, the Gibb's free energy, ΔG , is the negative value of the maximum available electrical work. The electrical work W_{\max} is the product of the charge and the potential of the cell.

$$\text{emf (V)} = \frac{\text{Work (J)}}{\text{Charge (C)}}$$

$$E = \frac{-w}{q}$$

$$w = -qE \text{ & } q = nF \text{ & } w_{\max} = \Delta G$$

$$\Delta G = -nFE$$

*L.M.F. = Max. i.e.,
for different i.e.,
the tendency*

Standard condition:

$$\boxed{\Delta G^\circ = -nFE^\circ}$$

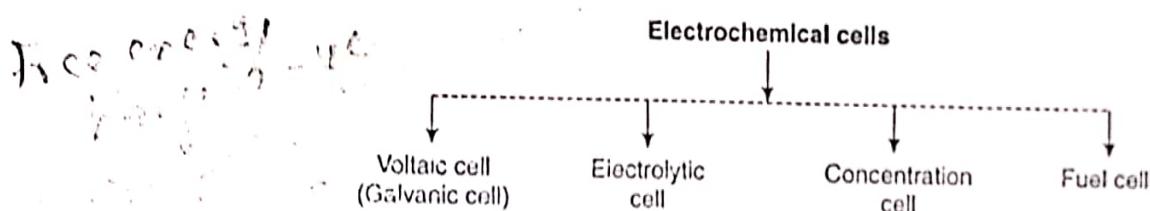
where, q is the charge in Coulombs and E is the potential in volts. Note also that $q = nF$, and $F = 96485 \text{ C}$ is the Faraday constant, whereas n is the number of moles of electrons in the reaction equation.

The working principle of a electrochemical cell is the transformation of the change of free energy of the redox reactions of the electrodes into electrical energy, i.e.,

$$\Delta G = -nFE; \quad (\text{if, the cell potential (E) is +ve})$$

In a redox reaction, the energy released in a reaction due to movement of charged particles give rise to a potential difference. The maximum potential difference is called the *electromotive force*, (emf), E in volts. From the above, it should be apparent that the potential difference between the electrodes of a cell is a measure of the tendency for the cell reaction to take place: the more positive the cell potential, the greater the tendency for the reaction to proceed to spontaneity.

Electrochemical cells are classified into the following types as shown below:



Voltaic Cell or Galvanic Cell (Fig. 2.1(a))

The free energy change in a galvanic cell, or in a spontaneous cell reaction, must be negative and the potential difference of the electrodes (cell voltage) must be positive.

- Energy is released from spontaneous redox reaction.
- System does work on load/surroundings.
- Anode (-ve): oxidation.
- Cathode (+ve): reduction.

In a galvanic cell, the free energy change of electrode redox reactions are converted into electric energy; i.e., $\Delta G = -nFE$.

The common examples of galvanic cells are primary irreversible cells (dry cells), secondary cells (lead storage battery, Ni-Cd battery, etc.).

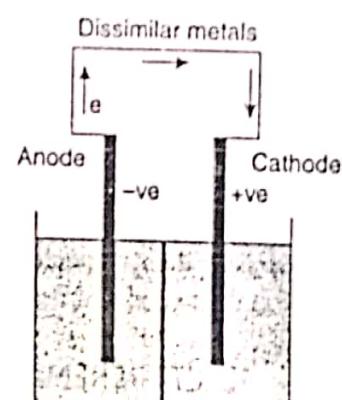


Fig. 2.1 (a) A galvanic cell

Electrolytic Cell (Fig. 2.1(b))

It is a device in which electrical energy from an external source can be used to bring about chemical reactions.

- Energy is absorbed to drive non-spontaneous redox reaction.
- Surroundings (power supply) do work on system (cell).
- Anode (+ve): oxidation.
- Cathode (-ve): reduction.

In electrolytic cells, the reaction is being driven in the non-spontaneous direction by external electrical force and the free energy change is positive, i.e., $-nFE = \Delta G$.

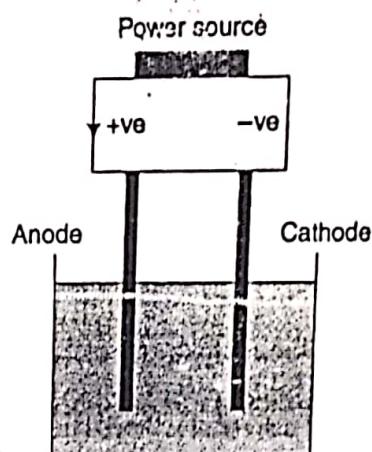


Fig. 2.1 (b) An electrolytic cell

Concentration Cell

A concentration cell is also an electrochemical device that generates electrical energy when two electrodes of the same metal are in contact with solutions of its ions at different concentrations.

In concentration cells, too, the free energy change of electrode reactions are converted into electric energy, i.e., $\Delta G = -nFE$.

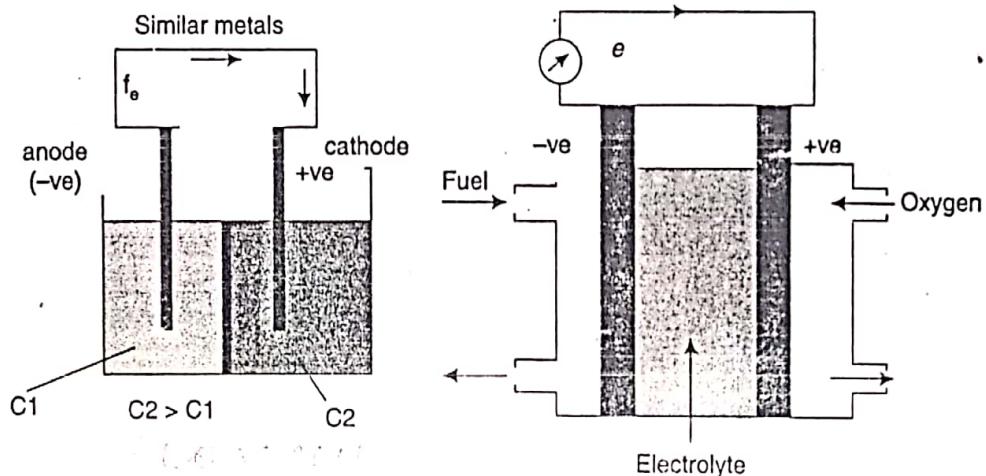


Fig. 2.1 (c) concentration cell (d) fuel cell

Fuel Cell (Fig. 2.1(d))

In contrast to the above, a fuel cell is also an electrochemical device which operates with continuous replenishment of the fuel at the electrode and no charging is required.

In a fuel cell, the free energy change of electrode redox reactions are converted into electric energy; that is, $\Delta G = -nFE$.

2.2 DIFFERENCES BETWEEN A GALVANIC CELL AND AN ELECTROLYTIC CELL

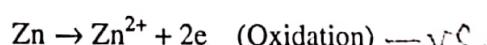
<i>Galvanic cell</i>	<i>Electrolytic cell</i>
<ol style="list-style-type: none"> It is a device to convert chemical energy into electrical energy. The redox reaction occurring at the electrodes are spontaneous. The electrodes are of dissimilar metals. Each metal is dipped in its own ions. Each electrode is inserted in its own ions and both have separate compartments. The two electrolyte solutions are connected by a salt bridge. -ve electrode of the cell is an anode. +ve electrode of the cell is a cathode. 	<ol style="list-style-type: none"> It is a device to convert electrical energy into chemical energy. The redox reaction occurring at the electrodes are non-spontaneous and takes place only when electrical energy is supplied. The electrodes used may be dissimilar or of the same metal. Only one electrolyte is taken. Both the electrodes are inserted in the same electrolyte solution. No salt bridge is needed. +ve electrode of the cell is an anode. -ve electrode of the cell is a cathode.

2.3 A DANIEL CELL

A Daniel cell is the best example of a galvanic cell. It consists of two electrodes of dissimilar metals, Zn and Cu; each electrode is in contact with a solution of its own ions; ZnSO_4 and CuSO_4 respectively.

In other words, each electrode of a galvanic cell may be regarded as a 'half cell'. The two solutions are connected by a salt bridge. The redox electrode reactions of the Daniel cell can be represented as two half cell reactions. They are

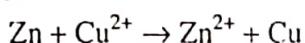
At the anode,



At the cathode,



The overall cell redox reaction is



If $E^\circ_{\text{Cu}^{2+}/\text{Cu}} > E^\circ_{\text{Zn}^{2+}/\text{Zn}}$, electrode reactions of the cell takes place spontaneously and the cell potential (E) is +ve.

The electrode potential is a quantitative measure of the driving force or tendency of the half-reaction to occur. In a Daniel cell (Fig. 2.2), when the Zn electrode is coupled with the Cu electrode, the tendency of Zn (lower reduction potential) to dissolve and form Zn^{2+} ions is greater than the tendency of Zn^{2+} ions to get deposited and therefore, Zn half-cell acquires negative charge. In other words, the tendency of copper (high reduction potential) to go into solution as Cu^{2+} is less than the tendency of Cu^{2+} ions to get deposited as Cu at the copper half-cell. The copper half-cell, thus becomes positively charged.

By IUPAC convention, the half cell at which the oxidation electrode reaction takes place is called the anode, whereas the electrode reaction is the reduction process, and the electrode is called the cathode.

Therefore, in the Daniel cell, Zn, is a negative electrode (anode) and copper is the +ve electrode (cathode). The electron flows from the zinc half cell to the copper half cell of the Daniel cell. The free energy change of the above electrode reactions is converted to generate electric energy.

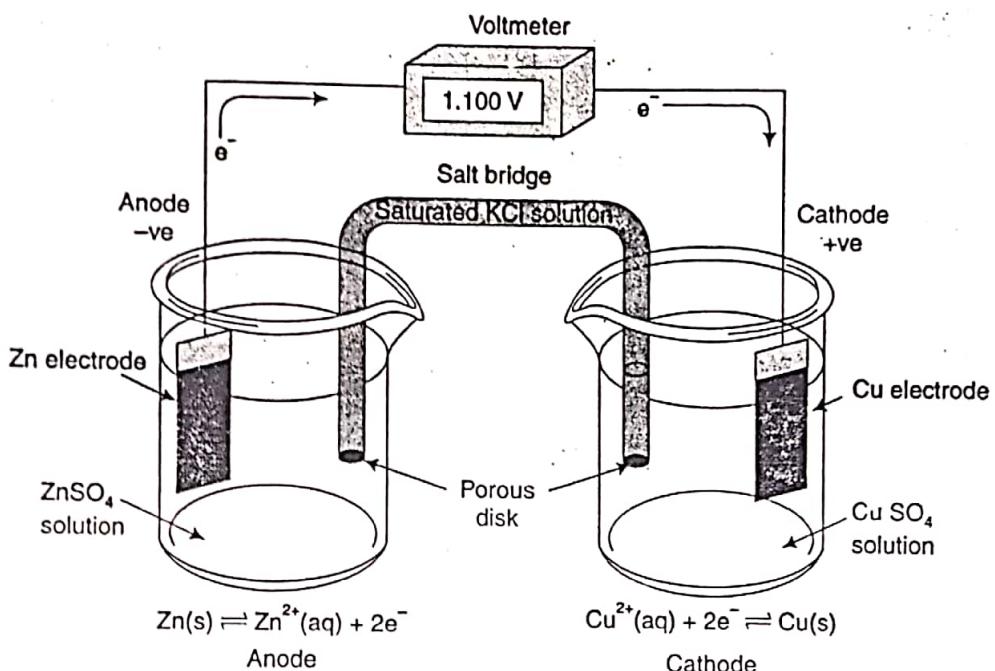


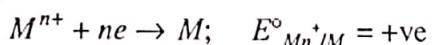
Fig. 2.2 A Daniel cell

2.4 ELECTROCHEMICAL CONVENTIONS*

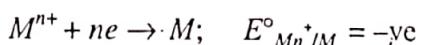
In the study of various types of electrochemical cells, the following conventions have to be strictly adopted. They are.

1. Sign of the Electrode Potential If reduction reaction takes place at the cathode of the cell, then the sign of the electrode potential is +ve. The sign of the electrode potential of anode in terms of reduction potential of the cell is -ve. That is,

At the cathode,



At the anode,

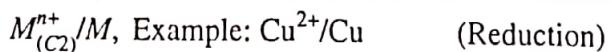


Not necessarily as stated above, it is observed that in actual practice an electrochemical cell can be constructed with both either +ve or -ve reduction potentials; however, in each case, one of the electrodes should have higher reduction potential than the other.

2. Representation of an Electrode If oxidation reaction takes place at the anode half-cell, then the electrode is conveniently represented as



If reduction reaction takes place at the cathode, then the electrode is represented as



The vertical line indicates the interface between the metal and their ions.

3. Representation of a Cell The following points have to be noted to represent an electrochemical cell.

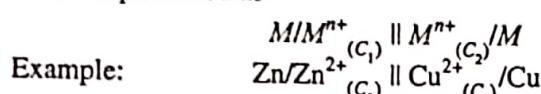
(a) 'Anode' is always written on the left hand side.



(b) 'Cathode' of the cell is written on the right hand side of the anode.



(c) Two vertical (||) lines denotes the interface between the two salt solutions. Therefore, a complete cell can be represented as



4. EMF of a cell An electrochemical cell is obtained by coupling two half cells, in which one of the electrodes has a higher reduction potential than the other, i.e.,

$$E^\circ_{\text{cathode}} > E^\circ_{\text{anode}}$$

EMF of a cell is defined "as the algebraic difference between the reduction potentials of the cathode and the anode".

The measured EMF of a cell is

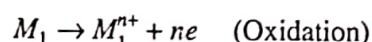
$$E_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

where E°_{cathode} is the standard reduction electrode potential of the cathode and E°_{anode} = standard reduction electrode potential of the anode.

5. Electrode and Cell Reactions The net cell reaction is the sum of the two half cell reactions that takes place in the cell.

For any electrochemical cell, the two electrode reactions are

(a) At the anode,



(b) At the cathode,



The electrical energy (nFE) is always produced at the expense of the decrease of free energy ($-\Delta G$) of the redox electrode processes of the cell.

$$\Delta G = -nFE$$

and hence, the emf of the cell is +ve; if $E^\circ_{\text{cathode}} > E^\circ_{\text{anode}}$, the cell reaction is spontaneous.

Example 2.1 The electrodes reduction potentials of Zn and Cu electrodes are -0.76 and $+0.34$ V respectively. Calculate the EMF of the Daniel cell.

Solution Since, $E^\circ_{Cu^{2+}/Cu} > E^\circ_{Zn^{2+}/Zn}$, the two half cell reactions are as follows:

At anode, $Zn \rightarrow Zn^{2+} + 2e$ (Oxidation); $E^\circ_{Zn/Zn^{2+}} = +0.76$ V

At the cathode, $Cu^{2+} + 2e \rightarrow Cu$ (Reduction); $E^\circ_{Cu^{2+}/Cu} = 0.34$ V

By convention, we have

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{Cu^{2+}/Cu} + E^\circ_{Zn^{2+}/Zn} \\ &= 0.34 - (-0.76) = 1.10 \text{ V.} \end{aligned}$$

Example 2.2 Represent a cadmium-copper cell. Give the electrode and net cell reactions. If the standard reduction potentials of Cd and Cu are -0.40 and 0.34 V respectively, calculate the standard emf of the cell.

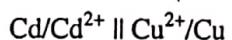
Solution

In this problem,

$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} > E^\circ_{\text{Cd}^{2+}/\text{Cd}}$$

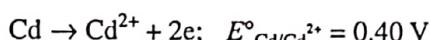
Cd acts as the anode and Cu behaves as the cathode.

(a) Cell representation



(b) Electrode reactions

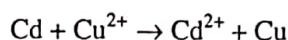
At anode,



At cathode,



(c) The net cell reaction



(d) Calculation of standard emf of the cell.

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Cd}^{2+}/\text{Cd}} \quad \text{Since, } E^\circ_{\text{Cd/Cd}^{2+}} = -E^\circ_{\text{Cd}^{2+}/\text{Cd}} \\ &= 0.34 - (-0.40) = 0.74 \text{ V} \end{aligned}$$

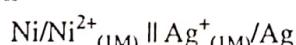
Example 2.3 The oxidation potential of a nickel half cell is 0.25 V and the reduction electrode potential of a silver half cell is 0.80 V. (a) Represent nickel-silver cell. (b) Give their electrode and net cell reactions.

(c) Calculate the standard emf of Ni - Ag cell.

$E^\circ_{\text{Ag}^+/\text{Ag}} > E^\circ_{\text{Ni}^{2+}/\text{Ni}}$

Solution:

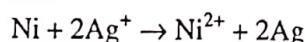
(a) Cell representation



At anode, $\text{Ni} \rightarrow \text{Ni}^{2+} + 2e; \quad E^\circ_{\text{Ni/Ni}^{2+}} = 0.25 \text{ volt}$

At cathode, $2\text{Ag}^+ + 2e \rightarrow 2\text{Ag}; \quad E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ volt}$

(b) The net cell reaction is



(c) The standard emf of Ni - Ag cell

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Ni}^{2+}/\text{Ni}} \\ &= 0.80 - (-0.25) \quad \text{Since, } E^\circ_{\text{Ni/Ni}^{2+}} = -E^\circ_{\text{Ni}^{2+}/\text{Ni}} \\ &= 1.05 \text{ V} \end{aligned}$$

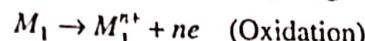
25 THE ORIGIN OF ELECTRODE POTENTIAL

If a metal piece is dipped in water or a solution of its own ions, the observed potential is zero because the rate of oxidation process of the metal in such a situation is equal to the rate of reduction at the metal surface,



Therefore, a state of equilibrium is attained between the two tendencies of their electrode processes in a cell and hence, the electrode potential is zero.

However, it can be observed that the situation is entirely different when two dissimilar metals are electrically connected to obtain an electrochemical cell. The driving force for the spontaneous electrode reactions arise as a result of the observed difference in the electrode potentials of the two electrodes. As a result of the driving force, the electrons released are pushed through the external circuit from the anode to the cathode. If $E^\circ_{M_2} > E^\circ_{M_1/M_2}$, then, the one with the higher reduction potential induces the metal of lower reduction potential to oxidize and the electrode reaction moves in the forward direction only. It is observed that when two dissimilar metals with a potential difference constitute an electrochemical cell, a metal of lower reduction electrode potential has a higher tendency to undergo oxidation giving its ions.



In such a case, a metal electrode of a cell is in contact with an ionic solution, a potential (oxidation) is developed [Fig. 2.3(a)] due to the interaction of the charged metal interface and the surrounding ions in the solution.

Simultaneously, the electrode process taking place at the other electrode of higher reduction potential is the reduction of ions to metal at the metal interface. A potential (reduction) is developed [Fig. 2.3(b)] due to the interaction of the charged metal interface and the surrounding ions in the solution.

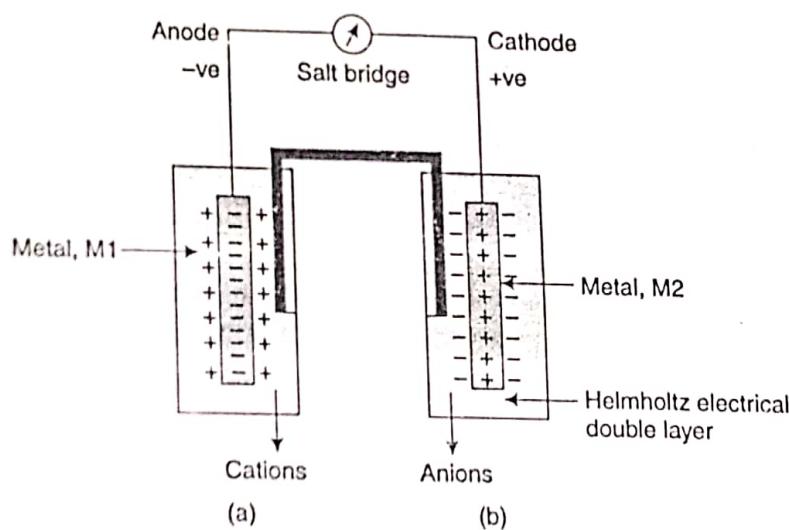
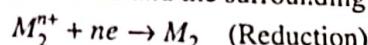


Fig. 2.3 Origin of electrode potential

In the above cell (Fig. 2.3), M_1 and M_2 are dissimilar metal electrodes (half-cells) dipped in their own ionic solutions respectively. The redox reactions takes place at the two half-cells and ultimately a dynamic equilibrium is established between the +ve/-ve charges at the electrode interface. Therefore, due to the interaction of opposite charges at the respective electrodes, +ve (a) or -ve (b) ions remain close to the metal. This charged layer around an electrode is called the Helmholtz electrical double layer (Fig. 2.4).

As a result, a potential exists between the interface of a metal electrode (M) and its ionic solution (M^{n+}) at a particular temperature. This is called its *electrode potential*.

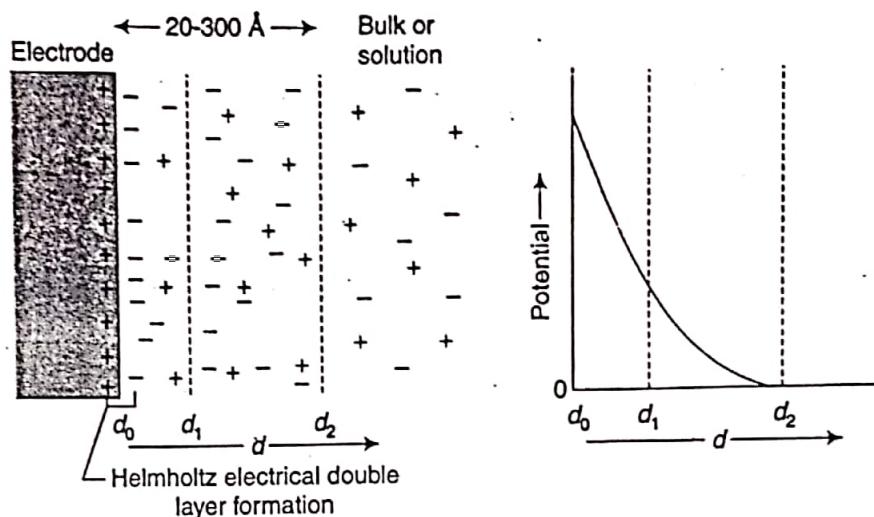


Fig. 2.4 Formation of the Helmholtz electrical double layer at the metal and ionic solution

2.6 ELECTRODE POTENTIALS

1. Single Electrode Potential An electrochemical cell can be obtained by coupling two electrodes of metals having a difference in their standard electrode potentials, i.e., $E^\circ_{\text{cathode}} > E^\circ_{\text{anode}}$. When two dissimilar metals are in contact with their own ions in a cell, the metals have a tendency to lose or gain electrons during their electrode processes. Therefore, the electrode potential or single electrodes potential of a metal electrode, of a cell is dependent on the measure of the metal to lose or gain electrons, when it is in contact with a solution of its own ions.

Single electrode potential can, thus, be defined as the potential established at the interface between the metal (M) and the ionic solution (M^{n+}) when it is in contact with a solution of its own ions. It is denoted as $E^\circ_{M^{n+}/M}$ (or $E^\circ_{M/M^{n+}}$).

When two electrodes are coupled to form a cell, the one with the lower reduction electrode potential value acts as the anode due to the oxidation electrode process. The electrode having the higher reduction electrode potential value acts as the cathode.

It is observed that the value of single electrode potential, E , in a cell depends on

- the nature of the metal electrode, M .
- the concentration of metal ions, M^{n+} , and
- the temperature.

2. Standard Electrode Potentials (Electrochemical Series) The standard electrode potentials of a large number of half-cells have been measured using SHE (Standard Hydrogen Electrode) as the reference electrode ($E^\circ = 0$).

The electrode potential of electrode/half-cells can be measured in their standard states.

The standard electrode potential is defined as the potential of an electrode measured at 298 K and unit (1M) metal in concentration.

The standard electrode potentials of two half-cells are denoted as, $E^\circ_{M^{n+}/M}$ or $E^\circ_{M/M^{n+}}$.

Table 2.1 Standard Electrode Potentials in Aqueous Solution at 298 K

Cathode (Reduction) Half-Reaction	Standard Potential E° (volts)
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li(s)}$	-3.04
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K(s)}$	-2.92
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ca(s)}$	-2.76
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na(s)}$	-2.71
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg(s)}$	-2.38
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al(s)}$	-1.66
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn(s)}$	-0.76
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr(s)}$	-0.74
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe(s)}$	-0.41
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd(s)}$	-0.40
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni(s)}$	-0.23
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn(s)}$	-0.14
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb(s)}$	-0.13
$\text{Fe}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Fe(s)}$	-0.04
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	0.15
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu}^+(\text{aq})$	0.16
$\text{AgCl}(\text{s}) + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^-(\text{aq})$	0.22
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34
$\text{ClO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{ClO}_2^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.35
$\text{Cu}^+(\text{aq}) + \text{e}^- \rightarrow \text{Cu(s)}$	0.52
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	0.54
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	0.77
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Hg(l)}$	0.80
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag(s)}$	0.80
$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg(l)}$	0.85
$\text{ClO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.90
$2\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}(\text{aq})$	0.90
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	1.07
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	1.33
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}(\text{aq})$	1.44
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	1.49
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Co}^{2+}(\text{aq})$	1.82
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	2.87

3. Applications of Electrochemical Series

- (i) Comparison of the relative oxidizing and reducing powers It can be remarked from Table 2.1 that greater the reduction potential, more easily is the element/ion reduced. F_2 has the highest

reduction potential (2.87) and Li^+ (-3.04) has the lowest reduction potential. Therefore, it is evident that F_2 can be reduced most easily whereas Li^+ ions are reduced with great difficulty. In other words, Li^+ ions will be oxidized most easily and hence is the best reducing agent and vice versa.

- (ii) **Relative activities of the metals** The relative activities of few metals are given as, $\text{Mg} > \text{Zn} > \text{Fe} > \text{Cu} > \text{Ag}$.

This depicts that greater the oxidation potential of a metal, more easily it can lose electrons and hence greater is its reactivity. As result, a metal with a greater oxidation potential can displace metals with lower oxidation potentials from their salt solution.

- (iii) **To calculate the standard EMF of any electrochemical cell** In an electrochemical cell, oxidation and reduction reactions occur at the electrodes.

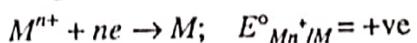
The EMF of the cell is the algebraic difference of their reduction potential.

- (iv) **To predict the spontaneity of redox reaction**. The free energy change in a galvanic cell, or in a spontaneous reaction, must be negative and the EMF of the cell must be positive. In other words, if the EMF of the cell is negative, the redox reaction is non-spontaneous.

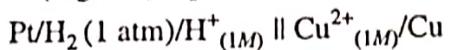
2.7 MEASUREMENT OF ELECTRODE POTENTIALS AND IUPAC* SIGN

The single electrode potential of a half-cell can be determined always by coupling this with a reference electrode, *standard hydrogen electrode* (SHE). In accordance with the IUPAC convention, the sign of the electrode potentials can be obtained thus:

- I. Determination of Standard Electrode Potential of the Cathode** If the electrode process of a half cell is reduction when the referred electrode is coupled with a standard hydrogen electrode (SHE) as shown in Fig. 2.5. The electrode potential is assigned a +ve value.

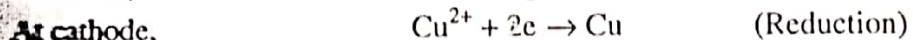


Example: Consider a cell (Fig. 2.5) represented as.



In a copper electrode is connected with a standard hydrogen electrode, reduction takes place at the electrode.

The electrode reactions are



$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} > E^\circ_{\text{SHE}}$$

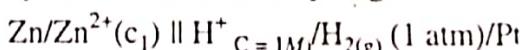
Hence, according to the electrochemical convention, "the potential of a copper electrode is taken as +ve".

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - (0) = E^\circ_{\text{Cu}^{2+}/\text{Cu}}$$

Thus, $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ is positive.

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{H}_2} \\ &= 0.34 - (0) = 0.34 \text{ V} \end{aligned}$$

- II. Determination of Standard Electrode Potential of the Anode** A cell is constructed by assuming zinc as the anode; and is coupled with a standard hydrogen electrode (SHE), as shown in Fig. 2.6.



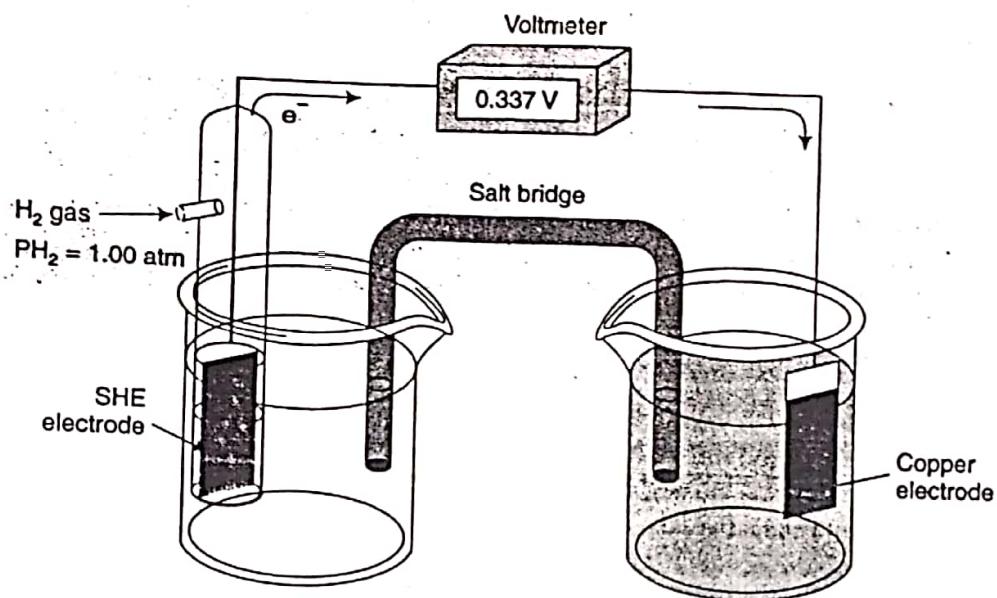


Fig. 2.5 A cell to determine potential of a cathode

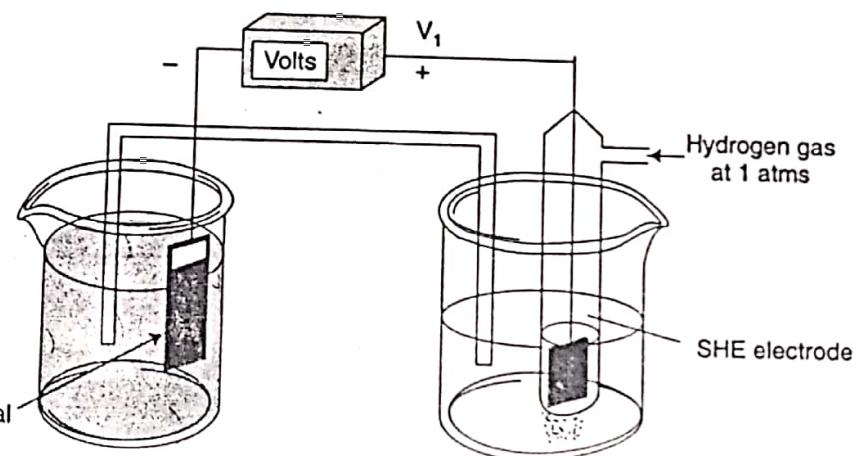
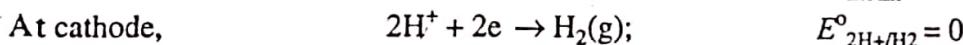
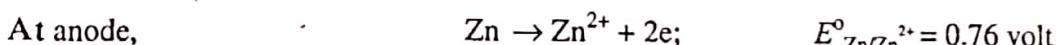


Fig. 2.6 A cell to determine potential of an anode

$$E^\circ_{\text{SHE}} > E^\circ_{\text{Zn}^{2+}/\text{Zn}}$$

The electrode reactions of the cell are



The EMF of the cell is

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{H}^+/\text{H}_2} - E^\circ_{\text{Zn}^{2+}/\text{Zn}}$$

$$E^\circ = 0 - E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -[E^\circ_{\text{Red}}] = -\text{ve}$$

Hence, the electrode potential of the anode is 'negative'.

Example:

$$\begin{aligned} E^{\circ}_{Zn/Zn^{2+}} &= -(-0.76) = 0.76 \text{ V (Oxidation potential)} \\ &= -0.76 \text{ V (Reduction potential)} \end{aligned}$$

In brief, it can be remarked that

$$E^{\circ}_{\text{oxidation}} = -E^{\circ}_{\text{reduction}}$$

2.8 DERIVATION OF NERNST EQUATION FOR THE SINGLE ELECTRODE POTENTIAL

In electrochemical cells, the potential of an electrode is found to depend on these factors:

1. Nature of the electrode.
2. Concentration of metal ions.
3. Temperature.

With a thermodynamic reasoning, Nernst showed that the free energy change of any one of the electrode processes is related to the potential developed (E) at the electrode with a concentration of M^{n+} ions at the interface at T° absolute.

In a electrochemical cell, if the reduction electrode process takes place at the cathode then,



The decrease of free energy change ($-\Delta G$) accompanying the reduction reaction at the cathode is given

$$\Delta G = \Delta G^{\circ} + RT \ln K \quad (2)$$

where ΔG° is the decrease of free energy accompanying the above electrode reaction when all the reactants and products are in their standard states (298 K and 1 M) and K denotes the ratio of the concentration of products and reactants at the equilibrium electrode reaction.

$$K = \left[\frac{M}{M^{n+}} \right]$$

The free energy change of the reduction electrode reaction [Eq. (1)] is

$$\Delta G = \Delta G^{\circ} + 2.303 RT \log_{10} \frac{[M]}{[M^{n+}]} \quad (3)$$

The electrical energy of a reversible cell is given by the decrease of free energy ($-\Delta G$) of the electrode reaction occurring in the cell. This free energy change is equal to the *electrical net work done* (W_{net}) by the cell, i.e.,

$$-W_{\text{net}} = \Delta G$$

Thus, the potential is developed at the electrode at the expense of the decrease in free energy of the electrode process.

$$\Delta G = -nFE$$

where E denotes the single electrode potential, in *volts* and nF denotes the quantity of electricity produced in *coulombs*, n = number of electrons liberated at one electrode.

and similarly, $\Delta G^{\circ} = -nFE^{\circ}$ at standard conditions.

Standard free energy change (ΔG°) is defined as the change in free energy which takes place when the reactants in the standard state (1 atm, 298 K) are converted into the products in their standard state.

Hence,

$$-nFE = -nFE^\circ + 2.303 RT \log_{10} \left[\frac{1}{M^{n+}} \right] \quad (4)$$

Dividing by $-nF$, we have

$$E = E^\circ - \frac{2.303 RT}{nF} \log_{10} \left[\frac{1}{M^{n+}} \right] \quad (5)$$

$$E = E^\circ + \frac{2.303 RT}{nF} \log_{10} [M^{n+}] \quad (6)$$

or

$$E = E^\circ + \frac{0.0591}{n} \log_{10} [M^{n+}] \quad (7)$$

where R, n, F have their usual significance. Equation (6) is known as the *Nernst equation* for single electrode potential.

In general, for any redox electrode processes of the cell



The potentials of the electrodes are given as,

At cathode,

$$E = E^\circ + \frac{0.0591}{n} \log_{10} [M^{n+}] \quad (\text{Reduction})$$

At anode,

$$E = E^\circ - \frac{0.0591}{n} \log_{10} [M^{n+}] \quad (\text{Oxidation})$$

2.9 EMF OF A CELL

Let us consider a cell.

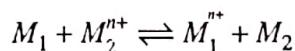
If,

$$E^\circ_{\text{cathode}} > E^\circ_{\text{anode}}$$

$$M_1|M^{n+}_{(C1)} \parallel M^{n+}_{(C2)}|M_2$$

which is obtained by connecting two half-cells or electrodes.

The net cell reaction is as given



The EMF of the cell is

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303 RT}{nF} \log_{10} \left[\frac{M^{n+}_1}{M^{n+}_2} \right]$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303 RT}{nF} \log_{10} \left[\frac{M^{n+}_1}{M^{n+}_2} \right]$$

$$E^\circ_{\text{cell}} = E^\circ_{M^{n+}_2/M_2} - E^\circ_{M^{n+}_1/M_1} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

where, M^{n+}_1 = Oxidized state of metal M_1 ,

M^{n+}_2 = Oxidized state of metal M_2 ,