

Electrochemistry

"Fine natures are like fine poems ; a glance at the first two lines suffices for a guess into the beauty that waits you if you read on."

1 INTRODUCTION

The free energy of physical and chemical process can be converted into electrical energy in a *galvanic cell*. In contrast we can also utilize electrical energy of *electrolytic cells*. In this chapter we will discuss the electrode potential, electrochemical cells, electrochemical series, Nernst equation, cells and batteries.

2 HALF-REACTIONS

Half-reactions are conceptual reactions. These reactions do not occur by one species releasing an electron and then another species accepting it. Electron transfer reactions normally proceed by a much more complex mechanism in which electron is never free. The electrons in these conceptual reactions are not ascribed a state, they are regarded as being 'in transit'.

Expressing a reaction in terms of Half-reactions :

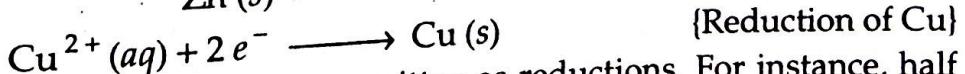
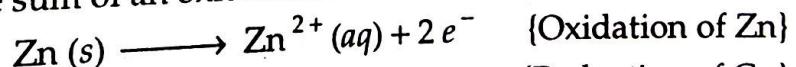
(i) *When the overall reaction is a redox reaction :*

Express the redox reaction as the sum of two half reactions, one involving oxidation (electron loss by a species) and the other reduction (electron gain).

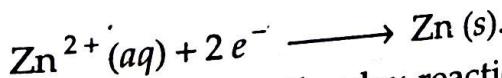
For example, for the reduction of Cu^{2+} ions by zinc metal, the redox reaction is



The above reaction is the sum of an oxidation and a reduction half reaction :



Generally, all the half-reactions are written as reductions. For instance, half reaction for the oxidation of zinc is expressed as reduction by reversing it as follows :



With this convention, the overall redox reaction is the difference of the two reduction half reactions.

In a half reaction, the oxidized and reduced substances form a **redox couple**, denoted as Ox/Red, for a half reaction : $\text{Ox} + ne^- \longrightarrow \text{Red}$.

(ii) *When the overall reaction is not a redox reaction :*

Such reactions can be expressed in terms of half reaction by first identifying one reactant species that undergoes reduction, and its corresponding reduction product. Then half-reaction for this process is written.

(E.1)

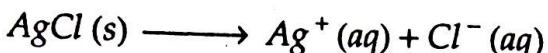
The second half reaction can be found by subtracting the overall reaction from this half-reaction. Sometimes an odd-looking equation is obtained by such subtraction but this can be rearranged so that all the stoichiometric numbers are positive.

Example 1. Express the following reactions in terms of half reactions :

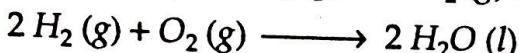
(i) The expansion of a hydrogen gas from initial pressure (p_0) to final pressure (p_1)



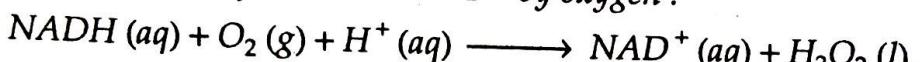
(ii) The dissolution of $AgCl(s)$



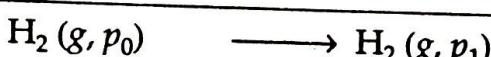
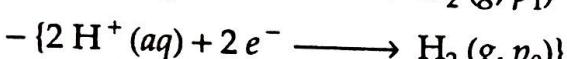
(iii) The formation of $H_2O(l)$ from $H_2(g)$ and $O_2(g)$ in acidic solution :



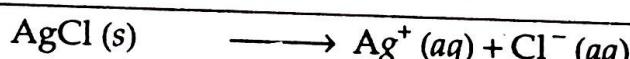
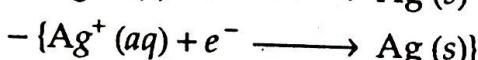
(iv) The oxidation of $NADH$ to NAD^+ by oxygen :



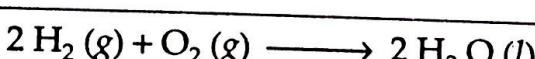
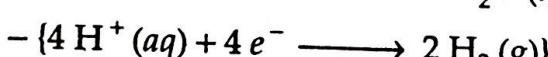
Solution. (i) $2 H^+(aq) + 2 e^- \longrightarrow H_2(g, p_1)$... (a)



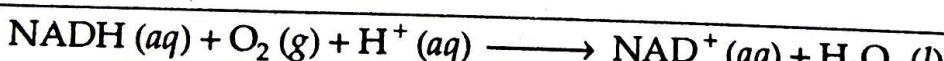
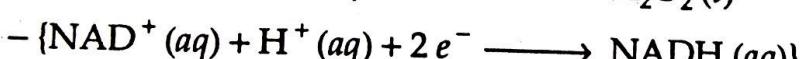
(ii) $AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$... (a)



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



(iv) $O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(l)$... (a)



3 ELECTRODE POTENTIAL

When a metal is in contact with a 1 M solution of its own ions at $25^\circ C$, it may either undergo oxidation reaction ($M \rightarrow M^{n+} + ne^-$) or reduction reaction ($M^{n+} + n e^- \rightarrow M$). Because of this, negative or positive charge is developed on the metal which attracts positively or negatively charged free ions in the solution.

This leads to the formation of a layer of negative ions [Figure 1 (i)] or positive ions [Fig. 1 (ii)] around metal electrode. Because of the formation of this layer (known as Helmholtz electrical double layer). A potential difference is set up between the metal and the solution. This prevents any further exchange of ions

between metal and solution. This potential difference becomes constant at equilibrium and is known as *standard electrode potential of metal*. It is the measure of the tendency of a metallic electrode to lose (*oxidation potential*) or gain (*reduction potential*) electrons, when it is in contact with its own salt solution of 1 M concentration at 25° C.

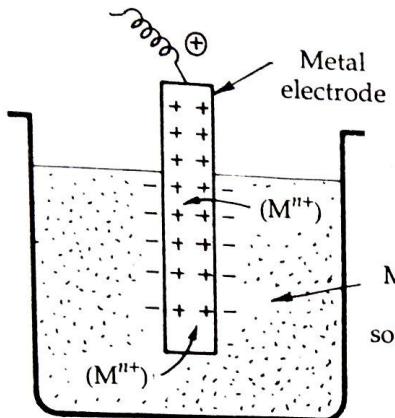


Fig. 1. (i). M^{n+} ions from solution enter in the metal, leaving behind their counter anions in solution. Thus positive charge develops on the surface of metal.

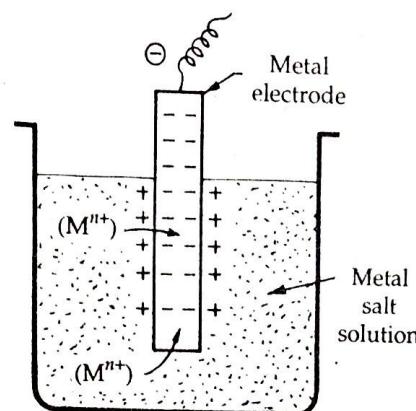
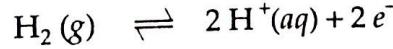


Fig. 1. (ii). M^{n+} ions moving from metal to solution leaving behind free electrons on metal and negative charge develops on the surface of metal.

3.1 Measurement of Electrode Potential

It is impossible to measure absolute value of single electrode potential because neither oxidation nor reduction takes place independently. It is possible to measure the potential difference between two electrodes with the help of the potentiometer. In other words, we can measure electrode potential with reference to a reference electrode. For this purpose, *standard hydrogen electrode* (S.H.E.) is selected. It consists of platinum foil or wire coated with platinum black dipped into a molar (1 M) solution of H^+ ions and hydrogen gas at 1 atmosphere pressure is continuously passed through it at 298 K. This electrode may serve as anode or cathode depending upon the nature of another electrode to which it is connected. Thus S.H.E. is a reversible electrode,



It is usually represented as Pt, $H_2(g)$, (1 atm)/ $H^+(1\text{ M})$.

The standard electrode potential (E°) of a standard hydrogen electrode has been arbitrarily fixed at zero. The standard electrode (half cell) potential of the other

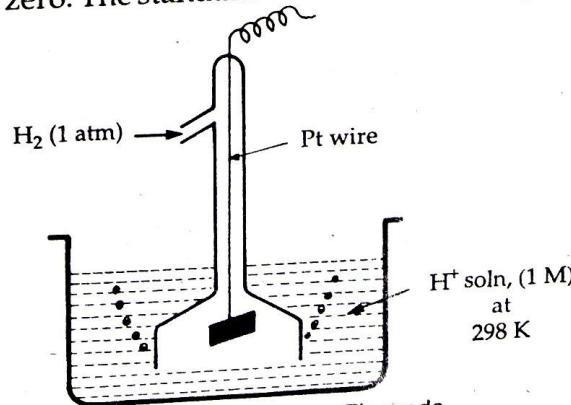


Fig. 2. Standard Hydrogen Electrode.

electrode can be determined by connecting it with S.H.E. and finding E°_{cell} experimentally. As the electrode potential of S.H.E. is equal to zero, the half cell potential of the other electrode would be equal to E° . If the above measurements are carried out under standard conditions (1 M concentration of ions, 1 atmosphere pressure and 298 K temperature) the potential of the electrode is known as *Standard Electrode Potential*. It is common practice to express all the electrode potentials as reduction potentials. The *standard reduction potential* of an electrode may be defined as the reduction potential of an electrode as determined with respect to a standard hydrogen electrode.

4 NERNST EQUATION

It tells us the effect of electrolyte concentration on electrode potential.

Consider a general electrode reaction :



$$\therefore \Delta G = \Delta G^\circ + RT \ln \frac{a_{\text{product}}}{a_{\text{reactant}}} \quad \dots(2)$$

Since $\Delta G = -nFE$ and $\Delta G^\circ = -nFE^\circ$. Hence

$$E = E^\circ - \frac{2.303 RT}{n F} \log \left(\frac{a_{\text{product}}}{a_{\text{reactant}}} \right). \quad \dots(3)$$

This is *Nernst Equation* where E is electrode potential, E° is standard electrode potential, F is Faraday of electricity, T is temperature, R is gas constant and a is activity.

At $T = 298$ K, putting the value of $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ and $F = 96500 \text{ C}$, we get $E = E^\circ - \frac{0.0591}{n} \log \left(\frac{a_{\text{product}}}{a_{\text{reactant}}} \right)$

In dilute solution, activities may be replaced by molar concentration terms,

$$\therefore E = E^\circ - \frac{0.0591}{n} \log \left(\frac{[M(s)]}{[M^{n+}(aq)]} \right)$$

For pure solid, $[M(s)] = 1$

$$\Rightarrow E = E^\circ - \frac{0.0591}{n} \log \left(\frac{1}{[M^{n+}(aq)]} \right) \quad \dots(4a)$$

The above equation is *Nernst Equation* for the electrode at 298 K.

And at any other temperature (T),

$$E = E^\circ - \frac{2.303 RT}{nF} \log \left[\frac{1}{[M^{n+}(aq)]} \right] \quad \dots(4b)$$

From the above equations, it can be concluded that

- (a) E increases as $[M^{n+}]$ is increased.
- (b) The electrode potential (E) decreases as temperature is increased.

Nernst equation can also be applied to any cell reaction such as



$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303 RT}{nF} \log \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right) \quad \dots(4c)$$

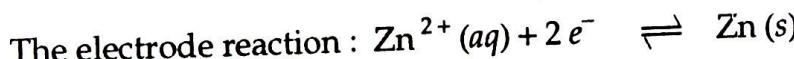
Applications of the Nernst Equation

(i) Nernst equation can be used to study the effect of electrolyte concentration on electrode potential.

Example 1. A Zinc rod is placed in a 0.1 M solution of zinc sulphate at 25° C. Calculate the potential of the electrode at this temperature, assuming 96% dissociation of ZnSO_4 and $E^{\circ}(\text{Zn}^{2+}/\text{Zn}) = 0.76 \text{ V}$.

Solution. Concentration of Zn^{2+} (with 96% dissociation)

$$= 0.1 \times \frac{96}{100} = 96 \times 10^{-3} \text{ M}$$



According to the Nernst equation, the potential of the electrode is

$$\begin{aligned} E &= E^{\circ} - \frac{RT}{nF} \ln \left(\frac{1}{\text{Zn}^{2+}} \right) \\ &= (-0.76) - \frac{8.314 \times 298}{2 \times 96500} \ln \left[\frac{1}{(96 \times 10^{-3})} \right] \end{aligned}$$

$$E = -0.79 \text{ volt}$$

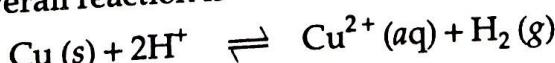
(ii) Nernst equation can also be used for the calculation of the potential of a cell under non-standard conditions.

Example 2. Calculate the potential of the following electrochemical cell at 25° C :



Given : $E^{\circ}_{\text{cathode}} = 0.00 \text{ V}$ and $E^{\circ}_{\text{anode}} = 0.34 \text{ V}$

Solution. The overall reaction is



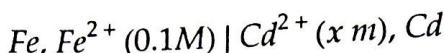
The potential of the cell is given by

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}] P_{\text{H}_2}}{[\text{H}^+]^2} \\ &= (0.00 - 0.34) - \frac{0.0591}{2} \log \left[\frac{(0.50)(0.95)}{(0.01)^2} \right] \end{aligned}$$

$$E_{\text{cell}} = -0.449 \text{ V}$$

(iii) Determination of unknown concentration of one of the ionic species in a cell is possible with the help of Nernst equation provided E°_{cell} and conc. of other ionic species is known.

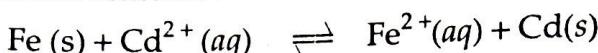
Example 3. Determine the concentration of Cd^{2+} ions in the following electrochemical cell,



assuming that activities equal concentrations.

Given the EMF of the cell $E = -0.02 \text{ V}$ and $E^\circ = 0.04 \text{ V}$ at 25°C .

Solution. Overall cell reaction :



$$\therefore E = E^\circ - \frac{0.0591}{2} \log \frac{[Fe^{2+}]}{[Cd^{2+}]}$$

$$\Rightarrow -0.02 = 0.04 - \frac{0.0591}{2} \log \left(\frac{0.1}{x} \right)$$

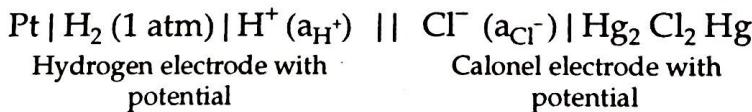
$$\Rightarrow x = 0.00093$$

$$\text{or } x = .001 \text{ M}$$

(iv) The pH of a solution can be calculated from the measurement of emf and Nernst equation.

Example 4. The emf of a cell measured by means of a hydrogen electrode against a saturated calomel electrode at 298 K is 0.4188 V . If the pressure of the $H_2(g)$ was maintained at 1 atm , calculate the pH of the unknown solution, given potential of reference calomel electrode is 0.2415 V .

Solution. The cell in this case is



$$\begin{aligned} E &= \frac{RT}{F} \ln a_{H^+} & E_{ref} &= 0.2415 \text{ V} & (\text{Given}) \\ &= \left(-\frac{2.303 RT}{F} \right) (-\log a_{H^+}) \\ &= -0.0591 \text{ pH} = E_L \end{aligned}$$

The emf of the cell is given by

$$\begin{aligned} E &= E_R - E_L \\ \Rightarrow E &= E_{ref} - (-0.0591 \text{ pH}) \\ \Rightarrow E &= E_{ref} + 0.0591 \text{ pH} \\ \Rightarrow \text{pH} &= \frac{E - E_{ref}}{0.0591} \\ \Rightarrow \text{pH} &= \frac{0.4188 - 0.2415}{0.0591} = 3.0. \end{aligned}$$

(v) Nernst equation can also be used for finding the valency of an ion or the number of electrons involved in the electrode reaction.

In general, oxidised state + $ne^- \rightleftharpoons$ Reduced state
 The potential of the electrode is given by

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Reduced state}]}{[\text{Oxidised state}]}$$

Thus by knowing E , E° , [oxidised state], [Reduced state], and temperature, we can easily calculate n , the number of electrons involved in the cell reaction and hence the valency of an ion.

5 IMPORTANCE OF REDUCTION ELECTRODE POTENTIAL, "ELECTROCHEMICAL SERIES"

A series in which the reduction electrode potentials of various electrodes have been arranged in the increasing order (downwards) is called '*electrochemical series*'.

The standard reduction potential of hydrogen electrode is zero. The electrodes above hydrogen have negative reduction potential while those placed below it have positive reduction potential.

Table 1 : Electrochemical Series

Electrode Reaction	Electrode	Standard Reduction Potential (in Volts)
$\text{Li}^+ (\text{aq}) + e^- \rightarrow \text{Li} (\text{s})$	$\text{Li} : \text{Li}^+ (\text{aq})$	-3.045
$\text{K}^+ (\text{aq}) + e^- \rightarrow \text{K} (\text{s})$	$\text{K} : \text{K}^+ (\text{aq})$	-2.930
$\text{Mg}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Mg} (\text{s})$	$\text{Mg} : \text{Mg}^{2+} (\text{aq})$	-2.370
$\text{Zn}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Zn} (\text{s})$	$\text{Zn} : \text{Zn}^{2+} (\text{aq})$	-0.763
$2 \text{H}^+ (\text{aq}) + 2e^- \rightarrow \text{H}_2 (\text{g})$	$\text{H}_2 : 2\text{H}^+ (\text{aq})$	+0.000
$\text{Cu}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Cu} (\text{s})$	$\text{Cu} : \text{Cu}^{2+} (\text{aq})$	+0.34
$\text{Ag}^+ (\text{aq}) + e^- \rightarrow \text{Ag} (\text{s})$	$\text{Ag} : \text{Ag}^+ (\text{aq})$	+0.79
$\text{F}_2 (\text{g}) + 2e^- \rightarrow 2\text{F}^- (\text{s})$	$\text{F}_2 : 2\text{F}^- (\text{aq})$	+2.87

5.1 Applications of Electrochemical Series

(i) To predict the relative oxidising and reducing powers :

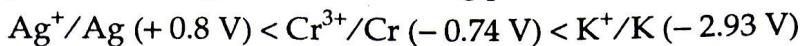
In an electrochemical series, the species which are placed above hydrogen are more difficult to be reduced and their standard reduction potential values are negative. The $\text{Li} : \text{Li}^+ (\text{aq})$ electrode has the least E° value and, therefore, it is reduced with most difficulty. Therefore, Li is the strongest reducing agent.

The species which are easily reduced than hydrogen are placed below it in electrochemical series and their E° values are positive. The $\text{F}_2 : 2\text{F}^- (\text{aq})$ electrode has the highest E° value and, therefore, F_2 has the greatest tendency to get reduced, it is consequently the strongest oxidising agent.

In general, oxidising agents have $+ E^\circ$ values.

Higher the positive value, stronger will be the oxidising agent and Reducing agents have $- E^\circ$ values, higher the negative value, stronger will be the reducing agent.

For example : Increasing order of reducing power of metals is :



(ii) *To predict whether a metal will react with acid to give H₂ gas :*

Metals above hydrogen in the electrochemical series have great tendency for oxidation so they displace hydrogen from acids.

(iii) *To predict the spontaneity of any redox reaction :*

For any spontaneous reaction $\Delta G = - \text{ve}$

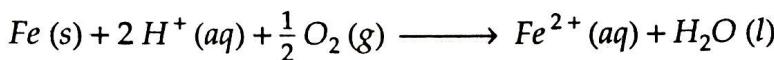
$$\text{Since } \Delta G = - n F E_{\text{cell}}$$

Hence E_{cell} should be positive for spontaneous reaction. E_{cell} is the e.m.f. of the cell and is calculated from the standard redox potentials by using the relation

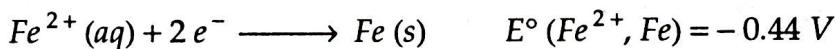
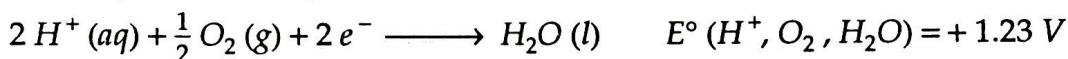
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

If E_{cell} is positive, the cell reaction is spontaneous, otherwise not.

Example 1. *For the corrosion of iron in acidic environment, one of the important reactions is*



the corresponding reduction half reactions and their standard potentials are given below :



Predict whether the reaction is spontaneous or not ?

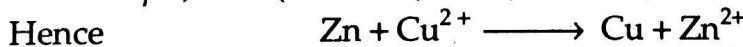
Solution. E° for the reaction $= (+ 1.23 \text{ V}) - (- 0.44 \text{ V}) = + 1.67 \text{ V}$.

As $E^\circ > 0$, it follows that reaction is spontaneous.

(iv) *To predict the replacement tendency (Relative).*

If a metal has Lower value of reduction potential, it shows a great tendency to assume the oxidised form and it will displace another metal (with higher value of reduction potential) from the solution of latter.

For Example, $E^\circ (\text{Cu}^{2+}/\text{Cu}) > E^\circ (\text{Zn}^{2+}/\text{Zn})$



Zinc will displace copper from its solution spontaneously.

(v) *To predict correct metallurgical methods :*

E° values of Cu, H₂O and Al are + 0.34, - 0.83 and - 1.66 V. It means Cu gets more easily reduced than water and water gets more easily reduced than aluminium. Hence, copper can be produced by the electrolysis of aqueous copper sulphate but not aluminium. This is due to the fact that when Al³⁺ (aq) is electrolyzed, the H₂O will be electrolysed but not Al³⁺ (aq).

(vi) *For calculation of equilibrium constants*

As $\Delta G^\circ = - RT \ln K_{\text{eq}}$ and $\Delta G^\circ = - n F E^\circ$

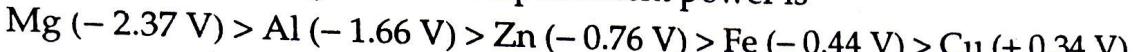
$$\therefore E^\circ = \frac{RT}{nF} \ln K_{\text{eq}}.$$

$$\Rightarrow \ln K_{\text{eq}} = \frac{nF E^\circ}{RT}.$$

Therefore, measurement of E° enables the determination of the equilibrium constant for the electrode reaction.

Example 2 (a). Arrange the following metals in the order in which they displace each other : Al, Cu, Fe, Mg, Zn. The standard reduction potentials of these metals are -1.66 V , $+0.34\text{ V}$, -0.44 V , -2.37 V and -0.76 V respectively.

Solution. Decreasing order of displacement power is



Because lower the reduction potential, more the tendency to lose electrons and thus more will be the displacement power.

Example 2 (b). Find K_{eq} for $\text{Cu}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$ at 25° C .

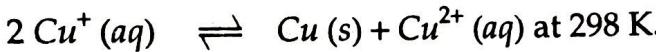
Given $E^\circ \text{Cu}^{2+}/\text{Cu} = 0.34\text{ V}$ and $E^\circ \text{Ag}^+/\text{Ag} = 0.80\text{ V}$

$$\text{Solution. } E^\circ_{cell} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.80 - 0.34 = 0.56\text{ V}$$

$$\therefore \ln K_{eq} = \frac{nFE^\circ}{RT} = \frac{2 \times 96500 \text{ C mol}^{-1} \times 0.56 \text{ V}}{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 43.62$$

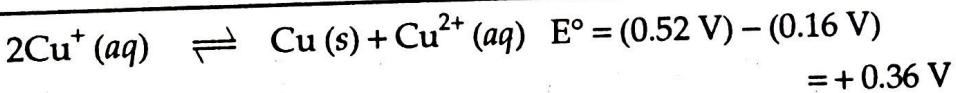
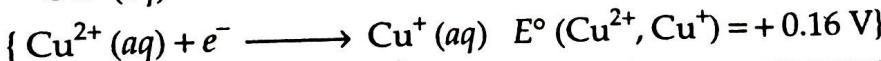
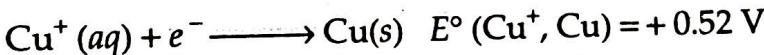
$$\Rightarrow K_{eq} = 8.8 \times 10^{18}$$

Example 3. Calculate the equilibrium constant for the disproportionation reaction



Given $E^\circ (\text{Cu}^+, \text{Cu}) = +0.52\text{ V}$ and $E^\circ (\text{Cu}^{2+}, \text{Cu}^+) = +0.16\text{ V}$.

Solution.

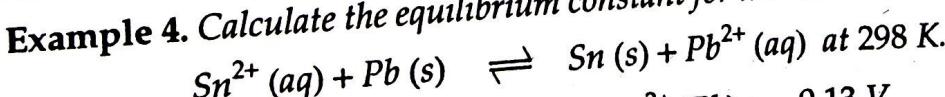


$$\text{Now } \ln k_{eq} = \frac{nFE^\circ}{RT} \\ = \frac{1 \times 96500 \times +0.36}{8.314 \times 298} = 14.022$$

$$\Rightarrow K_{eq} = 1.2 \times 10^6.$$

Because of the large value of K_{eq} , the equilibrium lies strongly towards the right and so Cu^+ disproportionates almost totally in solution.

Example 4. Calculate the equilibrium constant for the reaction



Given $E^\circ (\text{Sn}^{2+}/\text{Sn}) = -0.14\text{ V}$ and $E^\circ (\text{Pb}^{2+}/\text{Pb}) = -0.13\text{ V}$.

Solution. For the given reaction

$$E^\circ = E^\circ (\text{Sn}^{2+}/\text{Sn}) - E^\circ (\text{Pb}^{2+}/\text{Pb}) \\ = -0.14 - (-0.13) = -0.01\text{ V}$$

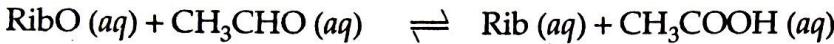
$$\therefore \ln K_{eq} = \frac{nFE^\circ}{RT} = \frac{2 \times 96500 \times (-0.01)}{8.314 \times 298} = -0.779$$

$$\text{so } K_{eq} = 0.46.$$

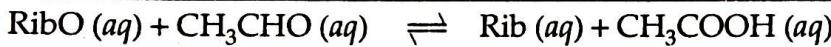
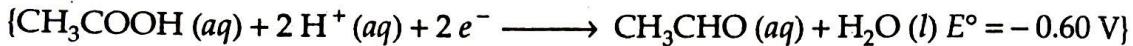
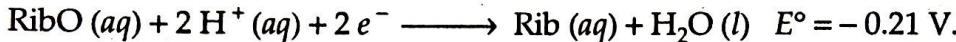
Example 5. The reduced and oxidized forms of riboflavin forms a couple with $E^\circ = -0.21\text{ V}$ in a solution in which $\text{pH} = 7$. Under the same conditions, the acetate/acetaldehyde couple has $E^\circ = -0.60\text{ V}$. What is the equilibrium constant for the reduction of riboflavin (Rib) by acetaldehyde in neutral solution at 25° C ?

Solution. Let Ribo is the oxidized form of riboflavin and Rib is its reduced form.

∴ The reaction can be written as



As H^+ does not appear in the overall reaction, the effect of pH on the individual 'standard' potential cancels and the E° may be treated as true standard potentials.



$$E^\circ = (-0.21\text{ V}) - (-0.60\text{ V}) = +0.39\text{ V}$$

$$\text{Now } \ln K = \frac{nFE^\circ}{RT} = \frac{2 \times 96500 \times 0.39}{8.314 \times 298} = 30.38$$

$$\Rightarrow K = 1.56 \times 10^{13}.$$

Note. From the above value, it might be easily concluded that riboflavin can be reduced by acetaldehyde in neutral solution. However, the reduction is too slow (\because energy is required to break the covalent bonds) to be practically feasible.

Example 6. What is the equilibrium constant for the reduction of riboflavin with rubredoxin in the reaction



Given that at $\text{pH} = 7$, the standard potential for riboflavin and rubredoxin are -0.21 V and -0.06 V respectively.

For the given reduction reaction

$$E^\circ = (-0.21) - (-0.06) = -0.15\text{ V}$$

$$\therefore \ln K_{eq} = \frac{nFE^\circ}{RT} = \frac{2 \times 96500 \times (-0.15)}{8.314 \times 298} = -11.68$$

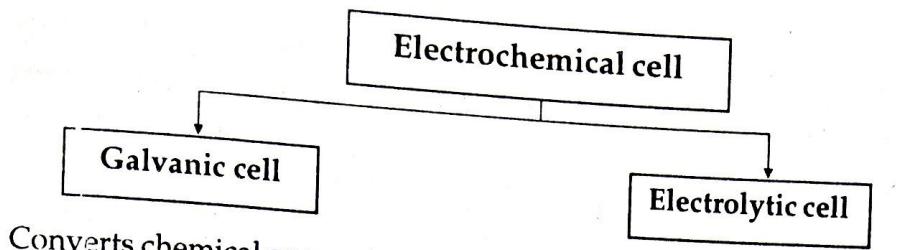
$$\Rightarrow K_{eq} = 8.42 \times 10^{-6}.$$

This extremely small value of K_{eq} indicates that reduction reaction is non-spontaneous in the forward direction.

6 ELECTROCHEMICAL CELLS

An electrochemical cell is a device for the conversion of electrical energy into chemical energy or vice-versa.

It can be divided into two classes viz. Galvanic cell and Electrolytic Cell.



Converts chemical energy into electric energy.

Examples : Dry cell or Lead storage battery

The electrical energy from an external source is used to bring about a chemical change.

Examples : Charging of lead storage battery. Electrolytic purification of metals.

In a Galvanic cell, the cathode has a higher potential than the anode.

This is because the species undergoing reduction reaction at cathode withdraws electrons from it. This leads to a development of positive charge on it, corresponding to a high potential.

Oxidation at the anode results in the transfer of electrons to it, so giving it a relative negative charge (corresponding to a low potential).

In an electrolytic cell, although oxidation takes place at anode but it does not occur spontaneously. Thus electrons must be withdrawn from the species in anodic compartment and there must be a supply of electrons to the cathode to drive the reduction. Therefore, in an electrolytic cell, the anode is made positive relative to the cathode so that electrons are effectively sucked out of the anode and pushed on to the cathode.

6.1 Galvanic Cell

The practical application of galvanic cell is Daniel Cell. It consists of zinc electrode, dipping in $ZnSO_4$ solution (say 1 M) and a copper electrode, dipping in $CuSO_4$ solution (say 1 M) taken in two different beakers.

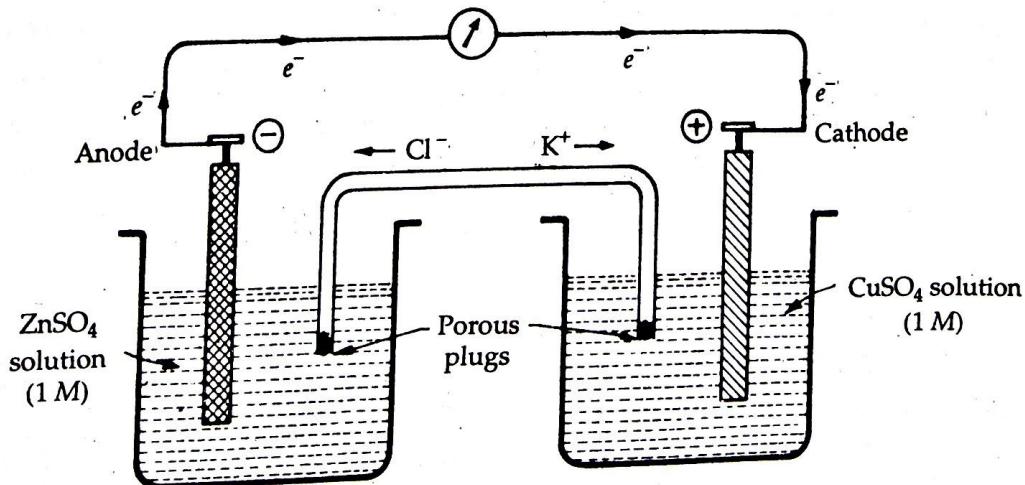


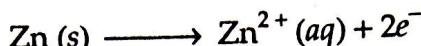
Fig. 3. Daniel cell.

The two solutions are connected by means of a *salt bridge*. Salt bridge is an inverted U-tube containing an aqueous solution of electrolyte such as

KCl, KNO₃, or K₂SO₄ (which does not react chemically during the process). Some gelatin or agar-agar is added to this aqueous solution of electrolyte to convert it into semisolid paste.

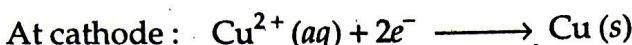
The moment the two electrodes are connected by a wire, the following reactions occur at different electrodes :

At anode :

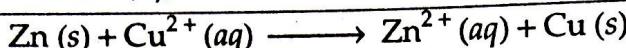


(Oxidation half reaction)

At cathode :



(Reduction half reaction)



(The complete cell reaction)

Oxidation, takes place at the anode and reduction takes place at the cathode. The electrons flow from anode to cathode. The transference of electrons from Zn anode to Cu cathode leads to the accumulation of positive charge around the anode due to the formation of Zn²⁺ ions and the accumulation of negative charge around cathode due to deposition of Cu²⁺ ions as copper on the cathode. The positive charge so accumulated around the anode will prevent the flow of electrons from it. Similarly, accumulation of negative charge around the cathode will prevent the acceptance of electrons from the anode. As the transference of electrons stops, the current in the electrical circuit also stops. At this stage, the salt bridge comes to the aid and restores the electrical neutrality of the solution in the two half cells. When the concentration of Zn²⁺ ions around the anode increases, sufficient number of Cl⁻ ions migrate from the salt bridge to the anode half cell. Similarly, sufficient number of K⁺ ions migrate from the salt bridge to cathode half cell for neutralizing excess negative charge due to the additional SO₄²⁻ ions in the cathode half cell. Thus the *salt bridge* provides cations and anions to replace the ions lost or produced in the two half cells. It maintains electrical neutrality of the two solutions in the two half cells. It allows the flow of current by completing the electrical circuit. It prevents intermixing of solution as well as ions in the two half cells, which may lead to a precipitation reaction.

6.2 Representation of a Galvanic Cell



or



- (a) On the left hand side anode is written and on the right hand side cathode is written.
- (b) Anode is written by writing the metal first and then the electrolyte. The two are separated by vertical line or semicolon.
- (c) Cathode is written by first writing the electrolyte and the metal thereafter. The two are separated by vertical line or semicolon.
- (d) The electrolyte may be represented either as complete formula of the whole compound or by ionic species.
- (e) The two half cells, anode and cathode, are separated by double vertical lines which indicates 'Salt bridge'.

6.3 EMF of an Electrochemical Cell

e.m.f. of cell = Reduction potential of cathode (written on right-hand side)
 – Reduction potential of anode (written on left-hand side)

$$\Rightarrow \boxed{E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}}$$

$$\boxed{E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}}$$

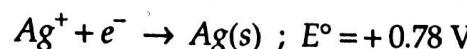
The cell reaction is feasible only when E_{cell} has positive value.

For example, for galvanic cell : $\text{Zn}(\text{s}) | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}(\text{s})$

$$E_{\text{cell}} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Zn}^{2+}/\text{Zn}}$$

And the cell reaction is $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$

Example 1. Given $\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}(\text{s}) ; E^\circ = -0.40 \text{ V}$



The overall cell reaction is : $\text{Cd}(\text{s}) + 2 \text{Ag}^+(\text{aq}) \rightarrow \text{Cd}^{2+}(\text{aq}) + 2 \text{Ag}(\text{s})$

Give the cell diagram and find the emf of the cell.

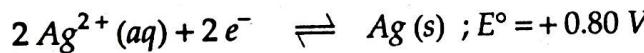
Solution. (a) The cell diagram is



and

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.78 - (-0.40) = 1.18 \text{ V}$$

Example 2. Knowing that $\text{Cu}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Cu}(\text{s}) ; E^\circ = +0.34 \text{ V}$



reason out whether 1 M AgNO_3 solution can be stored in a copper vessel or 1 M CuSO_4 solution can be stored in a silver vessel.

Solution. The standard reduction potential of silver is more than that of copper electrode. This means that silver can easily accept electrons and get reduced. As a result, copper can easily displace silver from its solution as



This means that if AgNO_3 is stored in copper vessel, copper will gradually go into solution as Cu^{2+} ions whereas silver will precipitate as

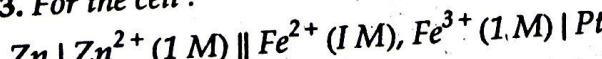


Thus, AgNO_3 cannot be stored in a copper vessel.

On the other hand, CuSO_4 cannot react with Ag because standard reduction potential of copper is less than silver.

Thus 1 M CuSO_4 solution can be stored in a silver vessel.

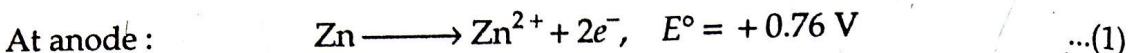
Example 3. For the cell :



Given $E^\circ(\text{Fe}^{3+} | \text{Fe}^{2+}) = +0.77 \text{ V}$ and $E^\circ(\text{Zn} | \text{Zn}^{2+}) = +0.76 \text{ V}$,

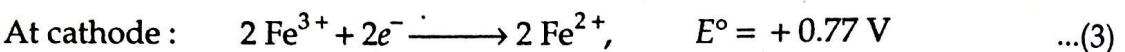
write the cell reaction and calculate the value of E°_{cell} for the above cell.

Solution. The equations for the half-reactions are :

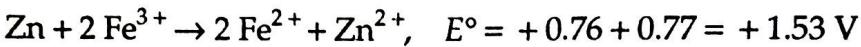


To obtain the equation for the cell reaction, the equation for the $\text{Fe}^{2+} | \text{Fe}^{3+}$ half-reaction must be multiplied by 2 (to obtain 2 mol electron) and combined with the $\text{Zn} | \text{Zn}^{2+}$ half reaction. It is to be noted that potential does not depend on the quantity of substance undergoing reaction so the value of the half-cell potential is not multiplied by 2.

Thus, reaction at cathode is re-written as :



And Now adding equations (1) and (3), we get desired cell reaction



A positive sign of E°_{cell} means that the reaction is spontaneous as written.

Example 4. Find the potential of a Daniel cell, initially containing 100 L each of 1.00 M Cu^{2+} ion and 1.00 M Zn^{2+} ion, after passage of 0.100×10^6 coulombs of charge.

Solution. Passage of electricity causes consumption of Cu^{2+} ions and the production of Zn^{2+} ions.

The quantities are :

$$(0.100 \times 10^6 \text{ C}) \left(\frac{1 \text{ mol } e^-}{96500 \text{ C}} \right) \left(\frac{1 \text{ mol } \text{M}^{2+}}{2 \text{ mol } e^-} \right) = 0.518 \text{ mol } \text{M}^{2+} \\ \equiv 0.52 \text{ mol } \text{M}^{2+}$$

$$\text{Thus } [\text{Zn}^{2+}] = 1.52 \text{ M} \quad \text{and} \quad [\text{Cu}^{2+}] = 0.48 \text{ M}$$

$$\text{And } E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log \left(\frac{\text{Zn}^{2+}}{\text{Cu}^{2+}} \right) \\ = 1.10 - \left(\frac{0.0592}{2} \right) \log \left(\frac{1.52}{0.48} \right) \\ = 1.09 \text{ V.}$$

Example 5. Determine the number of coulombs delivered by a Daniel cell, initially containing 1.00 L each of 1.00 M Cu^{2+} ion and 1.00 M Zn^{2+} ion, which is operated until its potential drops from 1.10 V to 1.00 V.

$$\text{Solution. } E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0592}{2} \right) \log \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$$

$$\Rightarrow 1.00 = 1.10 - (0.0296) \log \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$$

$$\Rightarrow \log \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right) = 3.38 \quad \Rightarrow \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 2399 \quad \Rightarrow \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} + 1 = 2400$$

$$\Rightarrow \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 2400$$

$$\text{As } [\text{Zn}^{2+}] + [\text{Cu}^{2+}] = 1 + 1 = 2 \text{ M (Always)}$$

$$\therefore \frac{2}{[\text{Cu}^{2+}]} = 2400 \Rightarrow [\text{Cu}^{2+}] = \frac{2}{2400} = 0.00083.$$

Essentially all the copper has been consumed; thus 2.00 mol of electrons or 193000 C has been delivered.

7 DETERMINATION OF FREE ENERGY FROM CELL POTENTIAL MEASUREMENTS

When an infinitesimal amount of current is drawn from or allowed to pass through a reversible electrochemical cell, the reversible electrical work at constant temperature and pressure is maximum and is equal to the product of voltage and the quantity of electricity.

Let us consider an electrochemical cell in which n equivalents of reactants are converted into the products, then the quantity of electricity that flows through the cell is nF .

where F = Faraday constant = 96485 Columbs per equivalent.

When this amount of electricity is transported through the cell of emf E volts, then the amount of electrical work done by the cell = nEF .

The work done by the cell is at the expense of the free energy decrease resulting from the cell reaction.

The electrical work is maximum only when the cell operates reversibly and the decrease in Gibbs' free energy is equal to the electrical work done by the cell.

i.e., Gibbs' free energy decrease = Electrical work obtainable from the cell

$$\Rightarrow (-\Delta G)_{T, P} = n EF$$

Criteria for spontaneity in terms of cell emf

- (i) If $\Delta G < 0$, or $E > 0$, reaction will be spontaneous;
- (ii) If $\Delta G = 0$, or $E = 0$, reaction will be equilibrium;
- (iii) If $\Delta G > 0$, or $E < 0$, reaction will be non-spontaneous.

8 TEMPERATURE DEPENDENCE OF EMF

From Gibbs-Helmholtz equation

$$\Delta G = \Delta H + T \left[\frac{\partial (\Delta G)}{\partial T} \right]_P \quad \dots(1)$$

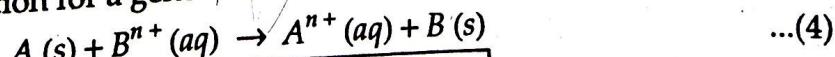
Since

$$\Delta G = -n E F \quad \dots(2)$$

$$\therefore \left[\frac{\partial (\Delta G)}{\partial T} \right]_P = \left[\frac{\partial (-n E F)}{\partial T} \right]_P = -n F \left(\frac{\partial E}{\partial T} \right)_P \quad \dots(3)$$

Here $\left(\frac{\partial E}{\partial T} \right)_P$ is the temperature coefficient of the cell.

Now Nernst equation for a general redox reaction



can be written as

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 RT}{nF} \log \frac{[A^{n+}]}{[B^{n+}]} \quad \dots(5)$$

where

$$E_{\text{cell}}^{\circ} = E_R^{\circ} - E_L^{\circ} = E_{B^{n+}/B}^{\circ} - E_{A^{n+}/A}^{\circ}$$

From equation (5), it is clear that if the temperature is increased, emf of the cell (E_{cell}) decreases.

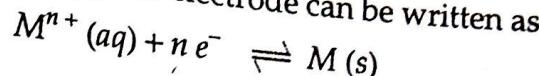
11 TYPES OF ELECTRODES

E.17

Important types of electrodes of an electrochemical cell can be grouped into the following types :

11.1 Metal-Metal Ion Electrode

It consists of a pure metal (M) in contact with a solution of its cation (M^{n+}). It is represented as $M^{n+}(aq)/M(s)$. Electrode reaction for this type of electrode can be written as



And Electrode potential $E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{a_M}{a_{M^{n+}}}$

Since $a_M = 1 \quad \therefore \quad E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} + \frac{RT}{nF} \ln a_{M^{n+}}$

Example : Zinc electrode dipping in $ZnSO_4$ solution or copper electrode dipping in $CuSO_4$ solution as in Daniel cell.

11.2 Metal-Metal Insoluble Salt Electrode

It consists of a metal (M) covered by layer of sparingly soluble salt ($M X$) immersed in a solution containing a common anion (X^-).

It is represented as $X^-(aq) || MX | M(s)$

Electrode reaction for the type of electrode can be written as



And the electrode potential

$$E_{X^-|MX|M} = E^{\circ}_{X^-|MX|M} - \frac{RT}{F} \ln a_{X^-}$$

Example : Calomel electrode, which consists of mercury, solid mercurous chloride and a solution of potassium chloride.

11.3 Metal-Amalgam Electrode

It is set up by placing the metal-amalgam in contact with a solution of metal ion.

It is more convenient to use the highly reactive metals in the form of amalgams since the activity of the metal is lowered by dilution with mercury.

It is represented as $M^{n+}(aq)/M(Hg)$

Electrode reaction : $M^{n+}(aq) + n e^- \rightleftharpoons M(Hg)$

$$\text{And Electrode potential : } E_{M^{n+}/M(Hg)} = E^{\circ}_{M^{n+}/M} - \frac{RT}{nF} \ln \left(\frac{a_{M(Hg)}}{a_{M^{n+}}} \right)$$

11.4 Gas-Ion Electrode

It consists of an inert metal (e.g., Pt) dipped in a solution containing ions to which the gas is reversible. The latter is continuously bubbled through the solution.

It is represented as $X^- (aq) | X_2 (P = X \text{ atm}) | Pt$

Electrode reaction : $X_2 (P) + 2 e^- \rightleftharpoons 2 X^- (aq)$

And Electrode potential : $E = E^{\circ}_{X^- | X_2 | Pt} - \frac{RT}{2F} \ln \left(\frac{a_{X^-}^2}{P_{X_2}} \right)$

Example : Standard hydrogen electrode.

11.5 Redox Electrode

It consists of an inert metal (e.g., Pt) dipped in a solution containing ions in two oxidation states of the substance (e.g., Fe^{2+} and Fe^{3+}).

It is represented as $\text{Pt}/M^{n_1+} (a_1), M^{n_2+} (a_2)$

Electrode reaction : $M^{n_1+} (a_1) + n e^- \rightleftharpoons M^{n_2+} (a_2)$

And Electrode potential : $E = E^{\circ}_{M^{n_1+}, M^{n_2+} / Pt} - \frac{RT}{nF} \ln \frac{a_2}{a_1}$

12 REFERENCE ELECTRODES

Reference electrode is an electrode of standard potential, with which we can compare the potentials of another electrodes.

Reference electrodes are broadly divided into two types :

12.1 Primary Reference Electrode

Standard hydrogen electrode is primary reference electrode which is used for cell potential measurements. Its potential is taken as zero at all temperatures. But it is quite cumbersome to set up a hydrogen electrode. It cannot be used in solutions containing redox systems. It is also readily affected by compounds of Hg, As, S and oxidising agents like Fe^{3+} , MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, etc., and consequently, this electrode cannot be used in solutions containing these ions.

Hence in view of the difficulties encountered, the secondary reference electrodes are used.

12.2 Secondary Reference Electrodes

They include calomel electrode, $\text{Ag}-\text{AgCl}$ electrode, glass electrode, Quinhydrone electrode etc.

12.2.1 Calomel electrode

Calomel electrode is commonly used as a secondary reference electrode for potential measurements.

Construction

Calomel electrode consists of a tube at the bottom of which a small amount of mercury is placed. It is covered with a

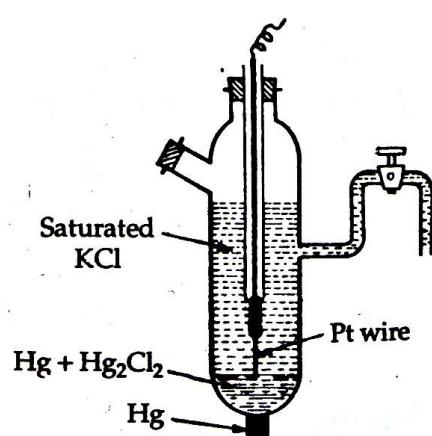
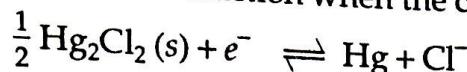


Fig. 4. Saturated calomel electrode.

paste of solid mercurous chloride, Hg_2Cl_2 (Calomel). A solution of potassium chloride is then placed over the paste. A platinum wire, dipping into the mercury layer, is used for making electrical contact. The side-tube is used for making electrical contact with a salt bridge.

Working. The electrode reaction when the cell acts as cathode is



and its potential is given by

$$E = E^\circ_{Cl^- | Hg_2Cl_2 | Pt} - \frac{RT}{F} \ln a_{Cl^-}$$

Thus, the potential of calomel electrode depends on the activity of the chloride ions (a_{Cl^-}) and increases as the activity of the chloride ions decreases. It has been found that the potential of the calomel electrode vary with the concentration of the potassium chloride solution used. The reduction potentials of the calomel electrode (on the hydrogen scale) at 298 K for various KCl concentrations are :

[KCl]	Saturated	1.0 N	0.1 N
Electrode Potential (in volt)	0.2422	0.2810	0.3335

When the KCl solution is saturated, 1.0 N and 0.1 N, it is respectively called as Saturated Calomel Electrode (SCE), Normal Calomel Electrode (NCE) and Decinormal Calomel Electrode (DNCE).

To obtain the potential of any other electrode it is combined with the calomel electrode and the emf of the resulting cell is measured. Knowing the cell emf and the electrode potential of the calomel electrode, the potential of the other electrode can be evaluated.

Advantages of Calomel electrode :

- (i) It is simple to construct,
- (ii) Results of cell potential measurements are reproducible and stable over a long period and does not vary with temperature.

12.2.2 Silver-silver chloride electrode

Ag – AgCl electrode is another widely used reference electrode.

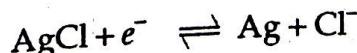
Construction and working

It is prepared by depositing a thin layer of AgCl electrolytically on a silver or platinum wire and it is then immersed in a solution containing chloride ions.

This electrode is represented as



and the electrode reaction is



The Ag – AgCl electrode is reversible with respect to the chloride ions. Its potential at 298 K with saturated KCl is 0.290 V and that with 0.1 N KCl is 0.199 V w.r.t. SHE.

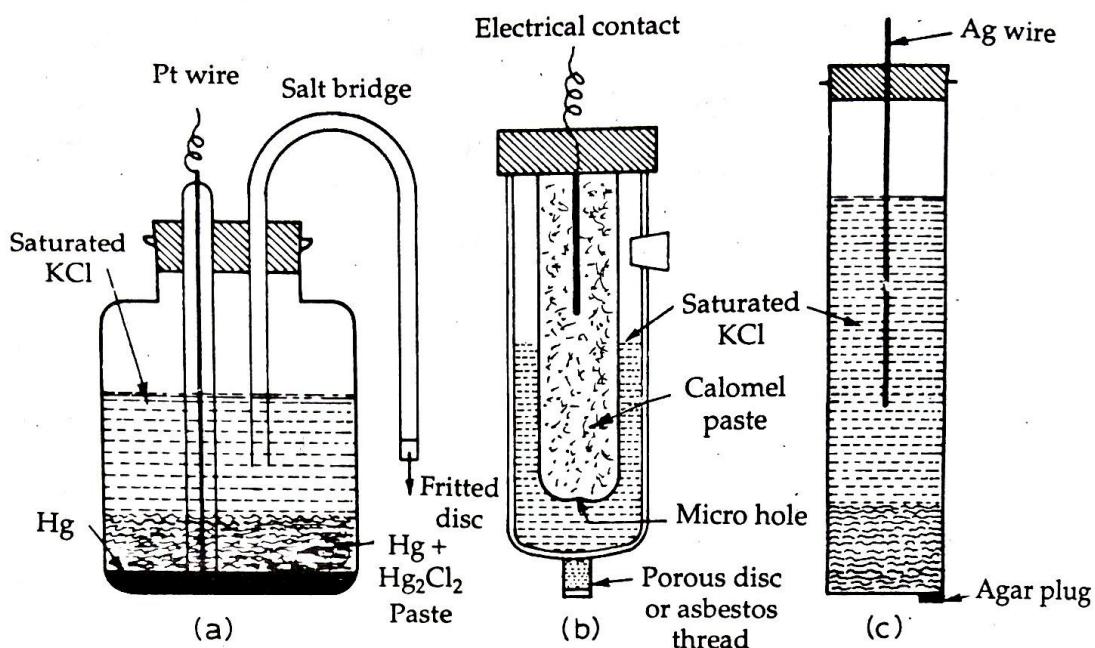


Fig. 5. Calomel electrode (a) with salt bridge (b) compact form (c) Ag-AgCl electrode.

Uses. (i) It is used in reference electrode probes which are employed to determine whether the potential distribution is uniform in ship's hulls and oil pipe lines protected by sacrificial anodes or by impressed current.

(ii) A portable reference electrode probe having a Ag – AgCl electrode as the reference is used for measuring the potential to a precision of ± 1 mV for such small objects like submerged oil pipelines, oil rigs and platforms. These probes are generally powered by a Ni – Cd battery and they can operate up to a depth of 300 metres.

Example 1. A hydrogen electrode with hydrogen gas at 1 atm and hydrogen ion at unit activity is suitably connected to a half-cell consisting of copper metal immersed in 1.00 M copper (II) sulphate solution. For the cell $\text{Pt} \mid \text{H}_2 \text{ (1 atm)} \mid \text{H}^+ \text{ (1 M)} \parallel \text{Cu}^{2+} \text{ (1 M)} \mid \text{Cu}$, the measured potential is 0.34 V. Find the standard electrode potential for the $\text{Cu} \mid \text{Cu}^{2+}$ half-cell ?

Solution. As all the species are in their standard states, and because the potential of the standard hydrogen electrode (SHE) is zero. The total potential of the cell may be attributed to the copper half-cell. Thus, the standard electrode potential of the $\text{Cu} \mid \text{Cu}^{2+}$ half cell is + 0.34 V.

Example 2. The potential of a silver/silver chloride electrode measured with respect to a saturated calomel electrode is - 0.022 V. Find the value of the standard reduction potential for the silver/silver chloride electrode.

$$\text{Solution. } E^\circ_{\text{cell}} = E^\circ_{(\text{Ag}/\text{AgCl})} - E^\circ_{(\text{SCE})}$$

$$\Rightarrow E^\circ_{(\text{Ag}/\text{AgCl})} = E^\circ_{\text{cell}} + E^\circ_{(\text{SCE})}$$

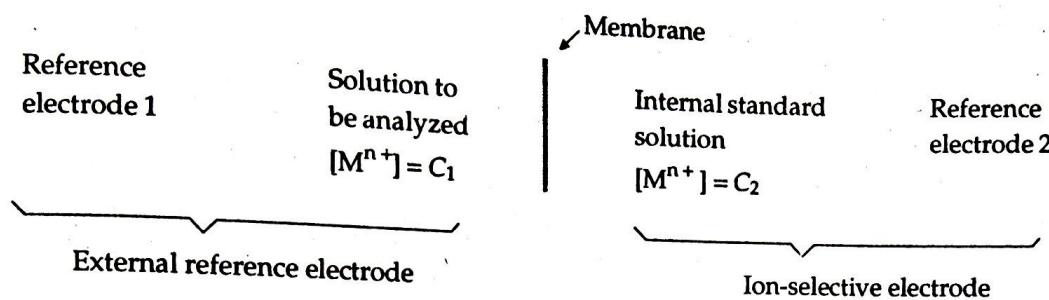
$$= (-0.022 \text{ V}) + (0.244 \text{ V}) = 0.222 \text{ V.}$$

ION-SELECTIVE ELECTRODES

Ion-selective electrodes have the ability to respond to certain specific ions (present in a mixture while ignoring others) and develop a potential. The potential developed is a measure of the concentration of the species of interest. These electrodes use a membrane which is sensitive to a particular chemical species.

Measurement of concentration of M^{n+} in a solution using ion-selective membrane electrode :

The cell schematic for this purpose can be given as



The membrane potential is given by the equation

$$E_{M^{n+}} = \frac{RT}{nF} \ln C_2/C_1 \quad \dots(1)$$

Suppose in a cell the reference electrode is anode and the membrane electrode is cathode,

∴ The cell potential $(E_{cell}) = E_{M^{n+}} - \Delta E_{ref}$

Here $\Delta E_{ref} = 0$ when identical reference electrodes are used.

As the concentration of M^{n+} in the internal reference electrode is constant, i.e., C_2 is a constant. Eqn. (1) thus reduces to

$$E_{cell} = \text{constant} - \frac{RT}{nF} \ln C_1 \quad \dots(2)$$

where C_1 is the concentration of M^{n+} in the solution to be analyzed.

Thus the cell potential depends on the selectivity of the membrane for the ion M^{n+} , which is to be analyzed.

If other ions are also present, then

$$E_{cell} = \text{constant} - \frac{RT}{nF} \ln \left\{ C + \sum_i K_i C_i \right\}$$

where C_i is the concentration of other ions present in the system.

For the membrane to selectively work K_i should be as small as possible.

The use of membranes is must in these ion-selective electrodes. Generally, following four types of membranes are used :

- (a) Glass membranes,
- (b) Solid state membranes,
- (c) Heterogeneous membranes and
- (d) Liquid membranes.

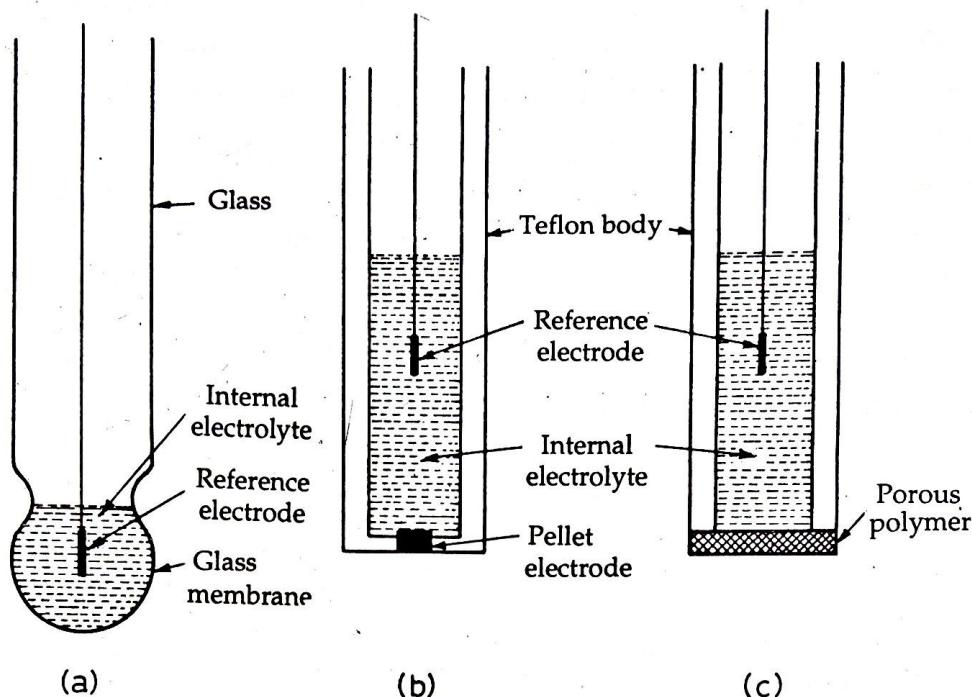


Fig. 6. Ion-selective electrodes with different types of membranes (a) glass (b) solid state (pellet) (c) liquid membrane on a porous polymer.

Materials used for solid state membranes include lanthanum trifluoride crystal doped with europium difluoride for fluoride ions and a pressed pellet of $\text{Ag}_2\text{S} + \text{AgCl}$ for chloride ions. The crystal is held in positive with epoxy resin and the electrode has a Teflon body.

Material used in liquid membrane electrode is usually a large organic molecule capable of specifically interacting with an anion or cation. The active organic molecule is adsorbed on to an inert porous support.

For alkali and alkaline earth metal cations, some of the liquid membrane electrode materials used are the phosphate diesters and neutral monocyclic crown ethers

tris-1, 10-phenanthroline Fe^{2+} (ClO_4^-)₂ is used for anions.

Several electrochemical systems are used as interface between chemical systems and electronic devices that display, record and manipulate data. The success of using this interface entirely depends on ion selective electrodes. An instrumental problem with the ion selective electrodes is the requirement of a high impedance voltmeter to monitor the potential difference between the measuring electrode and the external reference electrode. An error of 0.1 mV in the measurement of potential may result in 1% error in the ion analysis.

ELECTROCHEMISTRY

Applications of Ion-selective electrodes

(i) These electrodes are used in determining the concentration of gas using gas sensing electrodes. For example, an electrode which measures the level of CO_2 in blood samples makes use of a glass electrode used for measuring pH. The glass electrode is in contact with a very thin CO_2 permeable silicon rubber membrane soaked in a dil. Solution of NaHCO_3 . When the electrode is dipped in the blood sample, it allows the CO_2 to permeate into the membrane. CO_2 then reacts with NaHCO_3 and alters the pH. This change in pH is then sensed by the glass electrode. Hence, the potential of the glass electrode gives a measure of the CO_2 in the blood sample.

(ii) These electrodes are used in determining the concentrations of a number of cations such as H^+ , Li^+ , Na^+ , K^+ , Ag^+ , NH_4^+ , Pb^{2+} , Cd^{2+} , Cu^{2+} , Ca^{2+} , Mg^{2+} etc.

For instance, calcium ion electrode has important applications in physiological investigations because Ca^{2+} ion is known to influence bone formation, muscle contraction, cardiac expansion & contraction and nerve conduction.

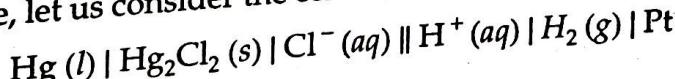
(iii) These ion-selective electrodes can also be used for finding out the concentration of anions such as F^- , NO_3^- , CN^- , S^{2-} and other halide ions.

(iv) H^+ -ion selective electrode is used for determining the pH of the solution.

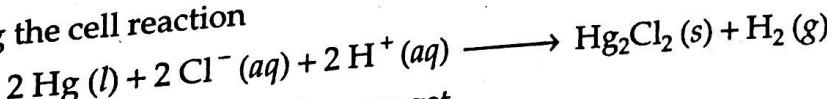
13.1 The Hydrogen Electrode and pH

The potential of a hydrogen electrode is directly proportional to the pH of the solution.

For example, let us consider the cell



having the cell reaction



Applying the Nernst equation, we get

$$E = E^\circ - \frac{RT}{2F} \ln \frac{P(\text{H}_2)}{[\text{H}^+]^2 [\text{Cl}^-]^2}$$

Let pressure of hydrogen gas $P(\text{H}_2) = 1 \text{ atm.}$

$$\therefore E = \left\{ E^\circ + \frac{RT}{F} \ln [\text{Cl}^-] \right\} + \frac{RT}{F} \ln [\text{H}^+]$$

$$E = E' - \frac{RT \ln 10}{F} \times \text{pH}$$

Thus, the pH of a solution can be measured by determining the potential of a cell in which a hydrogen electrode is one component.

Example 1. What range should a voltmeter have (in volts) to display changes of pH from 1 to 14 at 25°C if it is arranged to give a reading of 0 when $\text{pH} = 7$?

Solution. As $E = E' - \frac{RT \ln 10}{F} \times \text{pH}$... (1)

Given $E = 0$, when $\text{pH} = 7$.

Substituting these values in equation (1) above, we get

$$0 = E' - \frac{RT \ln 10}{F} \times 7 \Rightarrow E' = \frac{RT \ln 10}{F} \times 7 \quad \dots(2)$$

Thus equation (1) {with this value of E' } becomes :

$$E = \frac{RT \ln 10}{F} [7 - \text{pH}] \quad \dots(3)$$

when $\text{pH} = 1 \Rightarrow E = \frac{8.314 \times 298 \times \ln 10}{96500} (7 - 1) = + 0.36 \text{ V}$... (4)

when $\text{pH} = 7 \Rightarrow E = \frac{8.314 \times 298 \times \ln 10}{96500} (7 - 14) = - 0.41 \text{ V}$... (5)

Now, the range = E (from eqn. 4) – E (from eqn. 5)

$$= + 0.36 \text{ V} - (- 0.41 \text{ V})$$

$$= 0.77 \text{ V.}$$

14 GLASS ELECTRODE

Glass electrode is the universally employed electrode for pH measurement.

Construction. The glass electrode is made of a special glass of relatively low melting point and high electrical conductivity. It is a corning glass containing Na_2O (22%), CaO (6%) and SiO_2 (72%). The assembly of glass electrode [Fig. 7(a)]

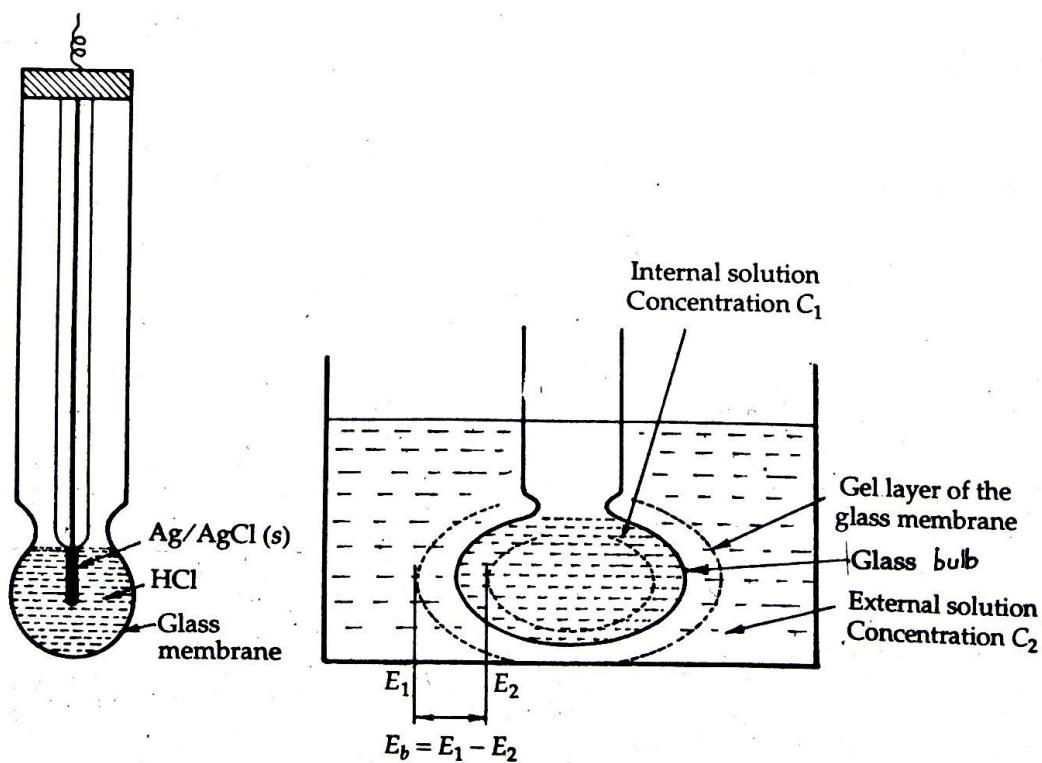
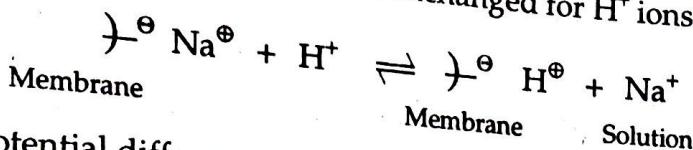


Fig. 7. Glass electrode.

and (b)] consists of a thin glass bulb filled with 0.1 N HCl and a silver wire coated with silver chloride is immersed in it. Here Ag/AgCl acts as an internal reference electrode. The glass electrode is represented as Ag | AgCl(s) | 0.1 M HCl | glass.

Principle. When the glass electrode is immersed in another solution, whose pH value is to be determined, there develops a potential between the two surfaces of the membrane. The potential difference developed is proportional to the difference in pH value.

Theory. The glass membrane of the glass electrode undergoes an ion exchange reaction, the Na⁺ ions on the glass are exchanged for H⁺ ions.



The potential difference or the boundary potential (E_B) at the interface is the result of the difference in potential ($E_1 - E_2$) developed across the gel layer of the glass membrane between the two liquids. This boundary potential is related to the concentration of acid solution inside the glass bulb (C_1) and concentration of the acid solution into which the glass bulb is dipped (C_2) by

$$E_B = E_1 - E_2 = \frac{RT}{nF} \ln (C_2/C_1)$$

As $C_1 = 0.1 \text{ M}$ (constant)

$$\therefore \text{Boundary potential } (E_B) = \frac{RT}{nF} \ln C_2 - L$$

where L is a constant and it depends on the pH of the solution taken in the bulb of glass electrode.

$$\text{When } C_1 = C_2 \Rightarrow E_B = 0$$

But during practice, it was observed that even when $C_1 = C_2$, a small potential is developed. This is called asymmetric potential (E_{ass}).

The potential of the glass (E_G) is given by

$$\begin{aligned} E_G &= E_B + E_{\text{Ag/AgCl}} + E_{ass} \\ &= \frac{RT}{nF} \ln C_2 + (-L + E_{\text{Ag/AgCl}} + E_{ass}) \end{aligned}$$

$$= -\frac{2.303 \times 8.314 \times 298}{1 \times 96500} \times (-\log \text{H}^+) + E_G^\circ$$

\Rightarrow

$$E_G = E_G^\circ - 0.0591 \text{ pH}$$

where E_G° is a constant equal to $(-L + E_{\text{Ag/AgCl}} + E_{ass})$

Limitations of glass electrode :

The glass electrode can be used up to a pH of 13 but becomes sensitive to Na^+ ions above pH = 9 resulting in an alkaline error. It leads to the alteration in the linear relationship between pH and glass electrode potential beyond pH = 9.

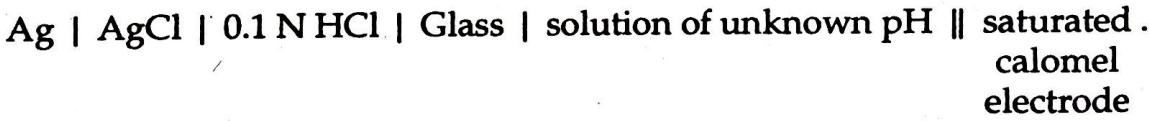
For the measurement of emf of the glass electrode, we cannot use ordinary potentiometers because of high resistance of glass. It is therefore, necessary to use special electronic potentiometers.

Advantages of glass electrode :

- Glass electrode is the most convenient and simple to use ;
- It is not easily poisoned ;
- Equilibrium is rapidly achieved ;
- The results are accurate ;
- It has no salt or protein error ;
- It can be used in turbid, coloured and colloidal solutions ;
- pH measurement is possible even with few mili litres of solution and
- It can be used both in alkaline and oxidising solutions ;

Measurement of pH of a solution using glass electrode

For the measurement of pH, the glass electrode is immersed in the solution whose pH is to be determined. It is then combined with a reference saturated calomel electrode. The cell assembly is represented as :



The emf of the cell at 298 K is given as

$$\begin{aligned} E_{\text{cell}} &= E_{\text{right}} - E_{\text{left}} = E_{\text{ref}} - E_G \\ \Rightarrow E_{\text{cell}} &= E_{\text{ref}} - E^\circ_G - 0.0591 \text{ pH} \\ \Rightarrow \text{pH} &= \frac{(E_{\text{ref}} - E^\circ_G) - E_{\text{cell}}}{0.0591} \end{aligned}$$

Thus, the cell emf is a linear function of the pH of the solution in which the glass electrode is dipped.

For pH measurements, E°_G is first measured by dipping the glass electrode in buffer solutions of known pH values. Once E°_G for a particular arrangement is determined the electrode is then placed in the solution of unknown pH, the emf of the cell is measured and using above equation, its pH can be calculated.

pH meter

pH meter is an instrument which is used for the direct measurement of pH of unknown solution. It is a solid state device employing a high resistance field effect transistor or an operational amplifier. The amplifier current drives a meter, which is calibrated in terms of both potential (in mV) and pH.

pH measurements by electrode calibration method

The electrode assembly is first immersed in a standard buffer solution of known pH value. The pH meter is calibrated to the pH of the buffer. The pH of the buffer (pH_b) is related to the cell potential $E_{\text{cell}}(b)$ as

$$\text{pH}_b = \frac{(E_{\text{ref}} - E^{\circ}_G) - E_{\text{cell}}(b)}{0.0591} \quad \dots(1)$$

Then, the electrode assembly is dipped in the solution of unknown pH. The pH of this solution (pH_s) is given by

$$\text{pH}_s = \frac{(E_{\text{ref}} - E^{\circ}_G) - E_{\text{cell}}(s)}{0.0591} \quad \dots(2)$$

Subtracting Eqn. (1) from equation (2), we get

$$\boxed{\text{pH}_s = \text{pH}_b + \frac{E_{\text{cell}}(b) - E_{\text{cell}}(s)}{0.0591}}$$

Thus in direct reading pH meters, it is not required to evaluate $E_{\text{ref}} - E^{\circ}_G$.

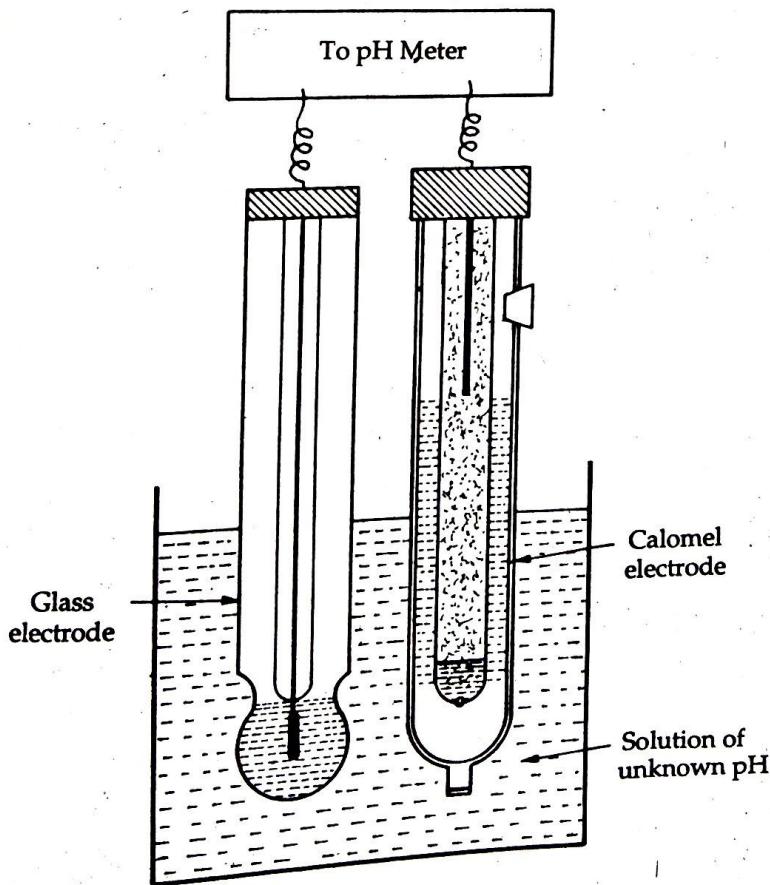
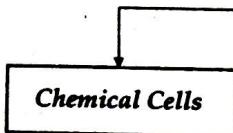


Fig. 8. Glass electrode-calomel electrode cell assembly for pH determination using a PH meter.

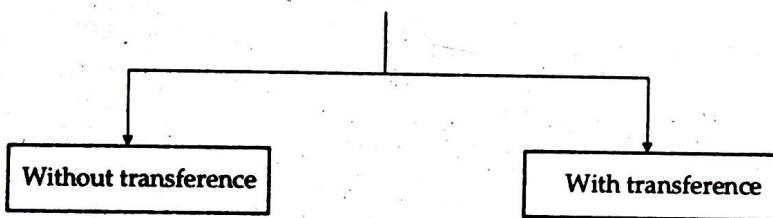
15 VARIETIES OF CELL

E.28

Electrochemical Cells



Here emf arises due to chemical reaction occurring in the cell

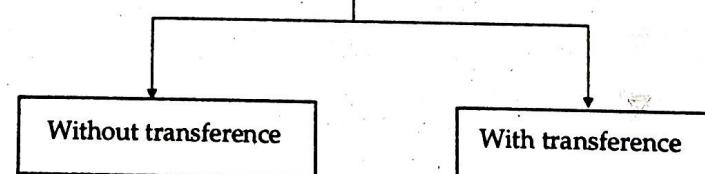
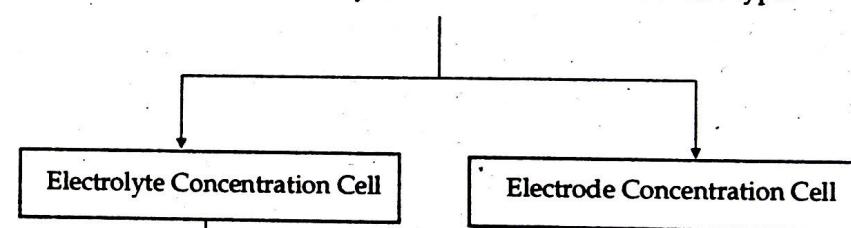


No Liquid junction because electrodes of the half cell are immersed in the same electrolyte.

Liquid junction potential also there.

Concentration Cells

Here emf arises due to the changes in the concentration of either the electrolytes or the electrodes. It is of two types



No Liquid junction potential

Liquid junction potential is also there. When the electrolytes of half cells are different or same at different concentrations, then on bringing them in contact, ions migrate across the liquid junction. This leads to development of liquid junction potential in addition to the potential difference due to the electrodes.

15.1 Concentration Cells

In Concentration cells, the emf arises due to the changes in the concentration of either the electrolytes or the electrodes. This is in contrast to galvanic cell, where emf arises from the decrease in free energy ($\Delta G = -nFE$) of the chemical reaction taking place in the cell.

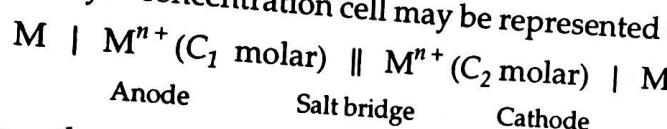
Concentration cells are of two types

- Electrode concentration cells and
- Electrolyte concentration cells.

In an electrode concentration cell, the electrodes themselves have different concentrations. They may be gas electrodes operating at different pressures or amalgams with different concentrations.

Let us briefly discuss electrolyte concentration cells. These cells consist of two identical electrodes immersed in two solutions of the same electrolyte at different concentrations. The electrodes of such cells are reversible to one of the ions of the electrolyte.

A general electrolyte concentration cell may be represented as



where C_1 and C_2 are the concentrations of active metal ions (M^{n+}) in contact with two electrodes respectively and $C_2 > C_1$.

$$\therefore \text{E.M.F. of cell} = E_{\text{Cathode}} - E_{\text{Anode}}$$

$$= \left\{ E^\circ + \frac{2.303 RT}{nF} \log C_2 \right\} - \left\{ E^\circ + \frac{2.303 RT}{nF} \log C_1 \right\}$$

$$\Rightarrow E_{\text{cell}} = \frac{2.303 RT}{nF} \log \left(\frac{C_2}{C_1} \right)$$

$$\text{At } 298^\circ \text{ K, } E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{C_2}{C_1} \right)$$

Thus, e.m.f. so developed is due to the mere transference of metal ions from the solution of higher concentration (C_2) to the solution of lower concentration (C_1).

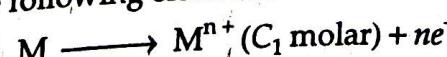
(i) If $C_1 = C_2$ then $E_{\text{cell}} = 0$

If the two concentrations are same, the system is at equilibrium and no net change can occur.

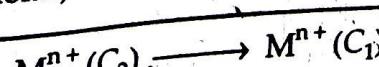
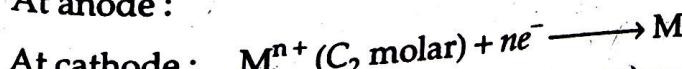
(ii) If $C_2 > C_1$ then $E_{\text{cell}} = + \text{ve}$

The larger the ratio (C_2/C_1), the larger will be the cell e.m.f. and the direction of spontaneous reaction is from more concentrated solution to less concentrated solution.

In such a concentration cell, the following electrode reactions take place :



At anode :



Cell reaction

An electrolyte concentration cell is a model of a neuron, which consists of a cell membrane with different concentrations of Na^+ and K^+ ions on either side.

A biological cell wall is one important example of a membrane system that resembles a concentration cell. The biological cell wall is more permeable to K^+ ions than to either Na^+ or Cl^- ions. Inside the cell, the concentration of K^+ ions is about 20 to 30 times that on the outside. This conc. is maintained by a specific operation fuelled by ATP and governed by enzymes.

When the system is approximately at equilibrium, potential difference between the two sides can be predicted to be

$$E \approx (25.7 \text{ mV}) \times \ln\left(\frac{20}{1}\right) = 77 \text{ mV.}$$

which is broadly correct :

Across a cell membrane, this potential difference is responsible for the transmission of nerve impulses. There is a high $[\text{K}^+]$ inside the cell and a high $[\text{Na}^+]$ outside, when a neuron is inactive. Under such circumstances, the potential difference across the cell wall is about - 70 mV.

When the cell wall is subjected to a pulse of about 20 mV, the structure of the membrane adjusts and it becomes permeable to Na^+ ions. As a consequence, there is a decrease in membrane potential as the Na^+ ions rush into the interior of the cell.

The change in potential difference triggers the adjacent part of the cell membrane, and the pulse of the collapsing potential passes along the nerve.

Behind the pulse the sodium and potassium pumps restore the conc. difference ready for the next pulse.

Liquid Junction Potentials

Whenever two dissimilar electrolyte solutions are placed in contact, a voltage difference (called the junction potential) develops at their interface.

Let us first discuss why the liquid junction potential develops ?

Consider a solution containing NaCl in contact with distilled water.

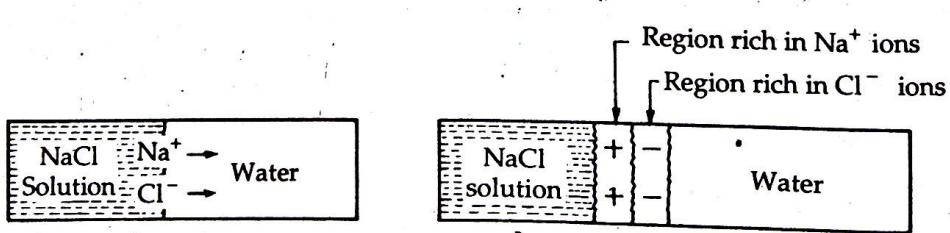


Fig. 9. Due to unequal mobilities of Na^+ and Cl^- , potential develops at the junction.

The Na^+ and Cl^- ions will begin to diffuse from the NaCl solution into the water phase. However, Cl^- ion has a greater mobility than Na^+ . That is, Cl^- diffuses faster than Na^+ . As a consequence, a region rich in Cl^- , with excess negative charge, develops at the front. Behind it is a positively charged region depleted of Cl^- . The result is an electric potential difference at the junction of the NaCl and H_2O phases.

The junction potential opposes the movement of Cl^- and accelerates the movement of Na^+ . The steady-state junction potential represents a balance between the unequal mobilities that create a charge imbalance and the tendency of the resulting charge imbalance to retard the movement of Cl^- .

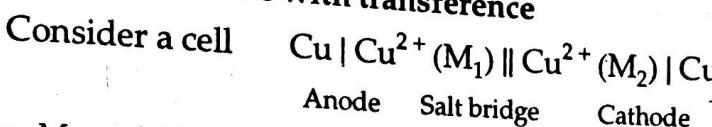
Because K^+ and Cl^- have similar mobilities ($7.62 \times 10^{-8} \text{ m}^2/\text{s} \cdot \text{V}$ and $7.91 \times 10^{-8} \text{ m}^2/\text{s} \cdot \text{V}$ respectively), junction potentials at the two interfaces of a KCl salt bridge are slight. This is why saturated KCl is used in salt bridges.

Notes. (a) The mobility of an ion is the terminal velocity that the particle achieves in an electric field of 1 V/m.

$$\therefore \text{Unit of mobility} = \frac{\text{Units of velocity}}{\text{Units of field}} = \frac{\text{m/s}}{\text{V/m}} = \text{m}^2/\text{s} \cdot \text{V}$$

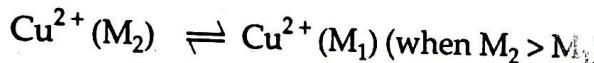
(b) Electrolyte concentration cells always have a liquid junction; electrode concentration cells do not.

(i) Concentration cells with transference



where M_1 and M_2 are the molar concentration of the Cu^{2+} ions in the two half-cells.

The net cell reaction is :



And at 25°C , the cell e.m.f. is given by

$$E_{\text{cell}} = \frac{0.0591}{2} \log \left(\frac{\text{M}_2}{\text{M}_1} \right)$$

Such a cell, where liquid junctions (solutions of different concentrations are connected through salt bridge) are involved are called as **concentration cells with transference**.

(ii) Concentration cells without transference

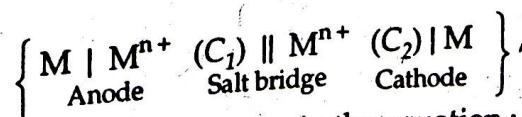
Let us now consider another cell in which the two half-cells are connected through the same solution (hence no liquid junction present) but different quantities of metal electrodes are dissolved in Hg.

For example, $\text{Cd}(\text{Hg}), [\text{Cd}] = \text{M}_1 | \text{CdSO}_4(\text{aq}) | \text{Cd}(\text{Hg}), [\text{Cd}] = \text{M}_2$

Because of the absence of liquid junction, no transfer of material takes place. Thus such cells are known as **concentration cells without transference** (or sometimes as **amalgam cells**). In such cells. The emf flows because of the difference in the electrode concentrations.

Applications of concentration cells

(i) The valency of the ion can be calculated, by substituting the measured value of emf of cell



and the values of C_1 , C_2 and temperature in the equation :

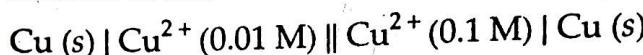
$$E_{\text{cell}} = \frac{2.303 \text{ RT}}{nF} \log \left(\frac{\text{C}_2}{\text{C}_1} \right).$$

Thus, the value of n , the number of electrons involved in the cell reaction or the valency of the ions can be calculated.

(ii) Solubility of sparingly soluble salt can also be determined.

Example 1. Two copper rods are placed in copper sulphate solution of concentration 0.1 M and 0.01 M separately in the form of a cell. Write the scheme of the cell and calculate its emf at 25° C .

Solution. The scheme of cell is :



$$\text{And emf of cell, } E_{\text{cell}} = \frac{0.0591}{2} \log \left(\frac{0.1}{0.01} \right) = 0.0296 \text{ V.}$$

Example 2. Find the valency of mercurous ions with the help of following cell :

Hg Anode	0.001 N mercurous nitrate in 0.1 N HNO_3	0.01 N mercurous nitrate in 0.1 N HNO_3	Cathode
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when the emf measured at 18° C is 0.029 volt ($F = 96,500$).

Solution. The given cell is concentration cell and its emf is given by :

$$E_{\text{cell}} = \frac{2.303 RT}{nF} \log \left(\frac{C_2}{C_1} \right)$$

Here, $E_{\text{cell}} = 0.029 \text{ V}$, $T = 291^\circ \text{ K}$, $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, $F = 96,500$, $C_1 = 0.001 \text{ N}$ and $C_2 = 0.01 \text{ N}$

Substituting these values in the above expression, we get

$$0.029 = \frac{2.303 \times 8.314 \times 291}{n \times 96500} \log \left(\frac{0.01}{0.001} \right)$$

$$\Rightarrow n = 2$$

Hence, the valency of mercurous ion is 2 and its formula is Hg_2^{2+} .

Example 3. Write equations for each half-reaction and calculate E_{cell} for the following concentration cell $\text{Zn} | \text{Zn}^{2+} (1.0 \text{ M}) || \text{Zn}^{2+} (0.15 \text{ M}) | \text{Zn}$. As the cell discharges, does the concentrations of the two solutions becomes smaller or larger ?

Solution. Equations for each half-reaction are :

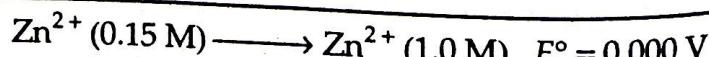
At anode (oxidation) :



At cathode (reduction) : $\text{Zn}^{2+} (0.15 \text{ M}) + 2e^- \longrightarrow \text{Zn}$

$$E^\circ = -0.763 \text{ V}$$

∴ Cell reaction :



The emf (E) of the cell is :

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{2.303 RT}{nF} \log \left(\frac{1}{0.15} \right) \\ &= 0.000 - \left(\frac{0.0591}{2} \right) \log \left(\frac{1}{0.15} \right) = -0.0244 \text{ V.} \end{aligned}$$

As E_{cell} is - ve, thus the spontaneous direction in which the cell discharges is to the left. Thus, during the cell discharge, the 1.0 M Zn^{2+} ion is used up and the $0.15\text{ M }Zn^{2+}$ is produced. It means, the two solutions approach each other in concentrations (just as they would if the solutions were mixed directly).