

1. Electrolytes

Solid and liquid substances, which are able to conduct the electric current, can be roughly divided into two categories i.e. metallic conductors and electrolytic conductors.

In metallic conductors or electronic conductors, the electric current is carried by the mobile electrons. When an electric potential is applied to metallic conductors, the electrons start moving in one direction while the positive ions remain stationary. Thus, the flow of electricity is not accompanied by any appreciable movement of the matter.

Electrolytic conductors or electrolytes are distinguished from metallic conductors by the fact that the current is carried by ions and not by electrons. The application of an electrical potential causes these charged particles of matter to move, the positive ions move towards the cathode and the negative ions move towards the anode. Thus, passage of an electric current through an electrolyte is always accompanied by transfer of matter. This transfer is manifested by changes in concentration, and also by visible separation of material at the points where the electric current enters and leaves the electrolyte. Electrolytes generally employed are salts in molten form or salts dissolved in water.

2. ELECTROLYSIS

Let us take two rods of suitable metal called electrodes, which are inserted in the electrolyte solution of MCl . The rods are now connected to a source of electromotive force (E.M.F.). The electrode at which the electrons enter the cell is called the negative electrode or cathode while that at which the electrons leave is known as the positive electrode or anode. The cations carry a positive charge, the anions carry negative charge. As soon as the electrodes are connected to battery, the cations (M^+) start moving towards cathode, take up electrons from the rod and get reduced to deposit as metal (M) while anions (Cl^-) move towards anode and get

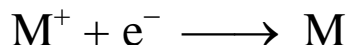
ELECTROCHEMISTRY

oxidised to release Cl_2 gas. Thus, at anode, electrons are released at the rod and go into the battery. Thus, anode becomes positive electrode. The electrons from the battery enter cathode, making it negatively charged. Thus, flow of electrons takes place from anode to cathode outside the cell and inside the cell, electrons indirectly flow from cathode to anode.

The electrode at which oxidation takes place is called anode and the electrode at which reduction takes place is called cathode. The electrodes are named anode or cathode depending upon the reaction occurring on them and not on the basis of sign of the electrodes.

The reactions at the two electrodes are:

At cathode:



At anode:

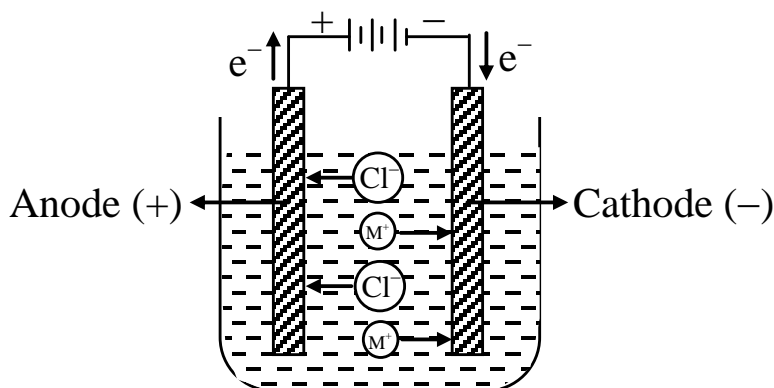
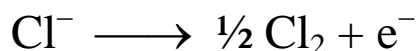


Figure 1. Electrolytic cell

Therefore, electrolysis is a process of chemical decomposition of the electrolyte by the passage of electric current. It is carried out in a cell called electrolytic cell. This cell converts electrical energy into chemical energy. The principles of electrolytic conduction are best illustrated by reference to an electrolytic cell such as shown in figure 1. The entire assembly except that of the external battery is known as the electrolytic cell.

There are two types of electrodes used in the electrolytic cell, namely attackable and non-attackable. The attackable electrodes participate in the electrode reaction. They are made up of reactive metals like Zn, Cu, Ag etc. In such electrodes, atom of the metal gets oxidised into the corresponding cation, which is passed into the solution. Thus, such anodes get dissolved and their mass decreases. On the other hand, non-attackable electrodes do not participate in the electrode reaction as they are made up

of unreactive elements like Pt, Au, graphite etc. Such electrodes do not dissolve and their mass remains same.

3. Faraday's Laws of Electrolysis

Faraday established the relationship between the quantity of electricity passed through an electrolyte and the amount of material liberated or deposited at the electrode. The quantity of electricity is equal to the product of the current strength and the time for which it is passed. The results of Faraday's finding can be put in the form of two laws of electrolysis.

3.1 First Law of Electrolysis

The amount of any substance deposited or dissolved at a particular electrode is proportional to the quantity of electricity utilized i.e. $w \propto Q$.

$$\text{or } w \propto (I \times t)$$

$$\text{or } w = ZIt$$

where w is the mass of substance deposited or liberated in gram, Q is the amount of charge utilized in coulombs, I is the current strength in amperes, t is the time for which current flows through the cell in seconds and Z is the electrochemical equivalent. Remember that Q is not the amount of charge passed but it is the amount of charge utilized.

Electrochemical equivalent is the mass of substance deposited in gram either by passing one coulomb of charge or by passing one ampere of current for one second.

One faraday is the quantity of charge carried by one mole of electrons.

$$\therefore 1F = 1.6 \times 10^{-19} \times 6.023 \times 10^{23} \approx 96500 \text{ coulombs}$$

or One Faraday is the quantity of charge which must be passed in order to deposit or dissolve one gram equivalent of any substance.

Let 'E' be the equivalent mass of a substance deposited at any electrode. Since, 96500 coulombs of charge is required to deposit E g of a substance,

therefore one coulomb of charge would deposit $\left(\frac{E}{96500}\right)$ g, which is the electrochemical equivalent (Z) of the substance.

$$\therefore w = \frac{EIt}{96500} \text{ [As } Z = \frac{E}{96500}]$$

As mass of substance deposited, $w = V \times d = A \times l \times d$

$$A \times l \times d = \frac{EIt}{96500}$$

where A is the area of the article to be electroplated, l is the thickness of layer deposited and d is the density of metal deposited.

The above formula finds application in electroplating of metals.

An important use of this equation lies in its application for the measurement of quantity of electricity or of current strength or the time taken for discharge of an ion or cathode area or thickness of deposited layer or density of metal deposited, whichever is unknown.

3.2 Second Law of Electrolysis

The amounts of different substances deposited or dissolved by the same quantity of electricity are proportional to their respective chemical equivalent weights.

$$w = \frac{EIt}{96500}$$

It can be rearranged as $\frac{w}{E} = \frac{It}{96500} = \frac{Q}{96500}$ = Number of equivalents

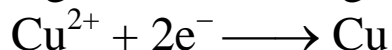
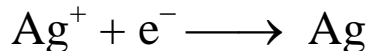
$$\therefore \frac{w}{E} = \text{Constant [as charge utilized is same]}$$

This means that if the quantity of charge passed through electrolytic cells connected in series is same, the equivalents of substances deposited at various electrodes would be same. Another way of stating this law is that the same quantity of electricity will produce chemically equivalent quantities of all substances resulting from chemical processes. A direct

ELECTROCHEMISTRY

consequence of Faraday's second law is that 96500 coulombs of electricity will yield one equivalent of any substance.

For example, consider the given reactions at two different cathodes in two different electrolytic cells connected in series.



Let us assume x mole of electrons is passed through both the cells.

Mole of Ag deposited = x

Equivalent of Ag deposited = $x \times 1 = x$

Mole of Cu deposited = $\frac{x}{2}$

Equivalent of Cu deposited = $\frac{x}{2} \times 2 = x$

Thus, it is evident that the equivalents of both metals (Ag & Cu) deposited are same (i.e. x), when same number of mole of electrons are passed, which implies passage of same quantity of electricity.

The Faraday's laws are universally accepted laws, applicable at all temperatures, for non-aqueous, aqueous solutions and fused electrolytes and whether the electrode reaction leads to metal deposition or not. The law is even valid during simultaneous discharge of two species in the solution.

4. Qualitative Aspects of Electrolysis

In the electrolysis process we have discussed above, we have taken molten salt as electrolyte, which contains only one cation and one anion. Now, if the electrolyte taken contains more than one cation and more than one anion (for example, aqueous solution of the ionic electrolyte), then the cation and anion that will get discharged depends on the ability of cation to get reduced and the ability of anion to get oxidised.

The ability of an ion to get oxidised or reduced depends upon the size, mass, positive charge, negative charge etc. Thus, it is not possible to

ELECTROCHEMISTRY

predict qualitatively that which ion would be discharged first, as one factor might enhance the ability to discharge while the other factor may hamper it. This can only be predicted on the basis of quantitative value assigned based on the cumulative effect of all the factors responsible for an ion's ability to discharge. The value is referred as standard potential, which is determined by keeping the concentration of ion as 1 M, pressure of gas at 1 atm, and the measurement done at 25°C. For a cation, the standard reduction potential (SRP) values are compared. The cation having higher standard reduction potential value is discharged in preference to cation with lower SRP value provided the ions are at 1 M concentration. For an anion, the standard oxidation potential (SOP) values are compared and anion having higher SOP is preferentially discharged, if the concentration is 1 M for each of the ion. The SRP values at 25°C for some of the reduction half reactions are given in the table below.

S. No.	Reduction half-cell reaction	E° in volts at 25°C
1.	$\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$	+ 2.65
2.	$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \longrightarrow 2\text{SO}_4^{2-}$	+ 2.01
3.	$\text{Co}^{3+} + \text{e}^- \longrightarrow \text{Co}^{2+}$	+ 1.82
4.	$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \longrightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	+ 1.65
5.	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+ 1.52
6.	$\text{Au}^{3+} + 3\text{e}^- \longrightarrow \text{Au}$	+ 1.50
7.	$\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$	+ 1.36
8.	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+ 1.33
9.	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+ 1.229
10.	$\text{Br}_2 + 2\text{e}^- \longrightarrow 2\text{Br}^-$	+ 1.07
11.	$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \longrightarrow \text{NO} + 2\text{H}_2\text{O}$	+ 0.96
12.	$2\text{Hg}^{2+} + 2\text{e}^- \longrightarrow \text{Hg}_2^{2+}$	+ 0.92
13.	$\text{Cu}^{2+} + \text{I}^- + \text{e}^- \longrightarrow \text{CuI}$	+ 0.86

ELECTROCHEMISTRY

14.	$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	+ 0.799
15.	$\text{Hg}_2^{2+} + 2\text{e}^- \longrightarrow 2 \text{Hg}$	+ 0.79
16.	$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$	+ 0.77
17.	$\text{I}_2 + 2\text{e}^- \longrightarrow 2\text{I}^-$	+ 0.535
18.	$\text{Cu}^+ + \text{e}^- \longrightarrow \text{Cu}$	+ 0.53
19.	$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$	+ 0.34
20.	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Hg} + 2\text{Cl}^-$	+ 0.27
21.	$\text{AgCl} + \text{e}^- \longrightarrow \text{Ag} + \text{Cl}^-$	+ 0.222
22.	$\text{Cu}^{2+} + \text{e}^- \longrightarrow \text{Cu}^+$	+ 0.15
23.	$\text{Sn}^{4+} + 2\text{e}^- \longrightarrow \text{Sn}^{2+}$	+ 0.13
24.	$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$	0.00
25.	$\text{Fe}^{3+} + 3\text{e}^- \longrightarrow \text{Fe}$	– 0.036
26.	$\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$	– 0.126
27.	$\text{Sn}^{2+} + 2\text{e}^- \longrightarrow \text{Sn}$	– 0.14
28.	$\text{AgI} + \text{e}^- \longrightarrow \text{Ag} + \text{I}^-$	– 0.151
29.	$\text{Ni}^{2+} + 2\text{e}^- \longrightarrow \text{Ni}$	– 0.25
30.	$\text{Co}^{2+} + 2\text{e}^- \longrightarrow \text{Co}$	– 0.28
31.	$\text{Cd}^{2+} + 2\text{e}^- \longrightarrow \text{Cd}$	– 0.403
32.	$\text{Cr}^{3+} + \text{e}^- \longrightarrow \text{Cr}^{2+}$	– 0.41
33.	$\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}$	– 0.44
34.	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$	– 0.74
35.	$\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$	– 0.762
36.	$2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{OH}^-$	– 0.828
37.	$\text{Mn}^{2+} + 2\text{e}^- \longrightarrow \text{Mn}$	– 1.18
38.	$\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$	– 1.66
39.	$\text{H}_2 + 2\text{e}^- \longrightarrow 2\text{H}^-$	– 2.25
40.	$\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$	– 2.37
41.	$\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$	– 2.71
42.	$\text{Ca}^{2+} + 2\text{e}^- \longrightarrow \text{Ca}$	– 2.87

ELECTROCHEMISTRY

43.	$\text{Ba}^{2+} + 2\text{e}^{-} \longrightarrow \text{Ba}$	- 2.90
44.	$\text{Cs}^{+} + \text{e}^{-} \longrightarrow \text{Cs}$	- 2.92
45.	$\text{K}^{+} + \text{e}^{-} \longrightarrow \text{K}$	- 2.93
46.	$\text{Li}^{+} + \text{e}^{-} \longrightarrow \text{Li}$	- 3.03

When solution of an electrolyte contains more than one type of cations and anions at concentrations different from 1 M, the discharge of an ion does not depend solely on standard potentials but also depends on the concentration of ion in the solution. This value is referred as potential, called as reduction potential for cation and oxidation potential for anion. The relation between reduction potential and standard reduction potential is given by Nernst equation, as

$$E_{\text{RP}} = E_{\text{RP}}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{concentration of product}]}{[\text{concentration of reactant}]}$$

where E_{RP} = Reduction potential of cation and E_{RP}° = Standard reduction potential of cation.

Thus, it is possible that a cation (A^{+}) with lower standard reduction potential getting discharged in preference to cation (B^{+}) having higher standard reduction potential because their concentrations might be such that the reduction potential of A^{+} is higher than that of B^{+} .

When two metal ions in the solution have identical values of their reduction potentials, the simultaneous deposition of both the metals will occur in the form of an alloy.

Illustration 1.

In the refining of silver by electrolytic method, what will be the weight of 100 g of silver anode if 5 ampere of current is passed for 2 hr. The purity of silver anode is 95% by weight.

Solution:

In the electro refining, pure Ag from the anode gets oxidized and deposit at cathode. Thus, the mass of anode decreases while that of cathode increases.

ELECTROCHEMISTRY

At anode: $\text{Ag} \longrightarrow \text{Ag}^+ + \text{e}^-$

$$\text{Mole of electrons passed} = \frac{5 \times 2 \times 60 \times 60}{96500}$$

$$\text{Mole of Ag oxidised} = \frac{5 \times 2 \times 3600}{96500} = 0.373$$

$$\text{Mass of Ag oxidised} = 0.373 \times 108 = 40.284 \text{ g}$$

$$\text{Mass of silver in the anode initially} = 95 \text{ g}$$

$$\text{Mass of silver left in the anode after refining} = 95 - 40.284 = 54.716 \text{ g}$$

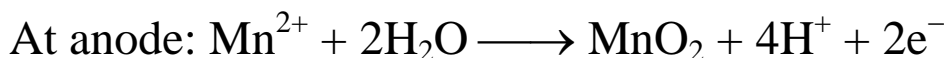
$$\therefore \text{Weight of silver anode after refining} = 54.716 + 5 = 59.716 \text{ g}$$

Illustration 2.

The electrosynthesis of MnO_2 is carried out from a solution of MnSO_4 in $\text{H}_2\text{SO}_4(\text{aq})$. If a current of 25.5 ampere is used with a current efficiency of 85%, how long would it take to produce 1 kg of MnO_2 ?

Solution:

During electrosynthesis of MnO_2 , the reactions occurring at the two electrodes are



Let the time required to produce 1 kg of MnO_2 be t seconds.

$$\text{Mole of electrons required} = \frac{25.5 \times t}{96500} \times \frac{85}{100}$$

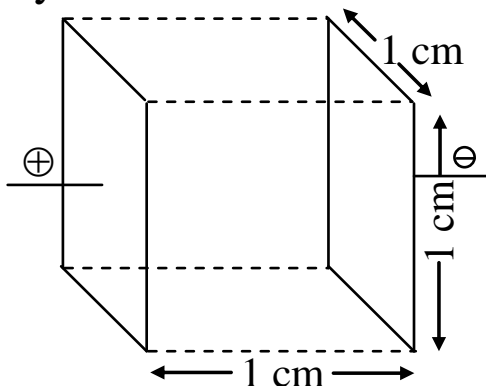
$$\text{Mole of } \text{MnO}_2 \text{ produced} = \frac{25.5 \times t}{96500} \times \frac{85}{100} \times \frac{1}{2}$$

$$\text{Mass of } \text{MnO}_2 \text{ produced} = \frac{25.5 \times t}{96500} \times \frac{85}{100} \times \frac{1}{2} \times 87 = 1000$$

$$\therefore t = 1.023 \times 10^5 \text{ sec or } 28.43 \text{ hr}$$

5. Electrolytic Conductance

Molten electrolytes and the aqueous solutions of electrolytes contain free ions and conduct electricity due to the movement of ions.



We know that Ohm's law is applicable to metallic conductors but it is also valid for electrolytic conductors. According to the Ohm's law, the resistance of a conductor is directly proportional to the length and is inversely proportional to the area of cross-section of the conductor.

$$\therefore R \propto \frac{l}{a} \quad \text{or} \quad R = \rho \times \frac{l}{a}$$

where 'l' is the length and 'a' is the area of cross-section of the solution column held between the electrodes and ρ is the resistivity of the solution.

Now, if $l = 1$ unit of length and $a = 1$ unit of area, the $R = \rho$ i.e., ρ is the resistance of the solution held between the electrodes of unit area of cross-section each and separated by a distance of one unit from each other. Unit of resistance is ohm and that of resistivity is ohm \times m in SI unit.

5.1 Conductivity of Solutions

For solutions, it is more convenient to think of conductance (G) rather than resistance. Conductance (G) is related to the resistance (R) by the relation,

$$\text{Conductance (G)} = \frac{1}{\text{Resistance (R)}} \quad \text{or} \quad G = \frac{1}{R}$$

ELECTROCHEMISTRY

The unit of conductance (G) is ohm^{-1} or mho. The unit ohm^{-1} is now a days called Siemens (S). Therefore, $1 \text{ ohm}^{-1} = 1 S$.

$$G = \frac{1}{\rho} \times \frac{a}{l} = k \frac{a}{l}$$

where k is called conductivity of the solution.

This gives,

$$k = G \times \frac{l}{a} = \frac{1}{R} \times \frac{l}{a}$$

$$\text{Conductivity (k)} = \frac{l/a}{R} = \frac{\text{Cell constant}}{\text{Resistance}}$$

The quantity $1/\rho$ is termed as specific conductance or conductivity (k).

Now, if $l = 1$ unit of length and $a = 1$ unit of area, then $k = G$

Thus, the conductivity may be defined as the conductance of any solution held between two electrodes of one unit area each and separated by a distance of one unit.

The units of conductivity depends upon the units in which the quantities G , l and a are measured. G is measured in the units of ohm^{-1} or Siemen.

In SI system of units, the length (l) is expressed in metre (m) unit and the area of cross-section (a) is expressed in square metre (m^2). The unit of conductivity (k) is then derived as

$$k = \frac{G \times l}{a} = \frac{S \times m}{m^2} = S \text{ m}^{-1}$$

Thus, the SI unit of conductivity (k) is $S \text{ m}^{-1}$ (Siemens / metre). It should be noted that $1 S \text{ m}^{-1} = 1 \text{ ohm}^{-1} \text{ m}^{-1}$.

In CGS system, length (l) is measured in cm, and the area of cross - section (a) in centimeter square (cm^2). So, the units of conductivity (k) in CGS system is

$$k = G \times \frac{l}{a} = \frac{S \times \text{cm}}{\text{cm}^2} = S \text{ cm}^{-1}$$

6. Equivalent Conductivity

In order to compare the conductivities of different electrolytes, it is convenient to use a quantity called equivalent conductivity. The equivalent conductivity (Λ_{eq}) of an electrolyte in solution may be defined as

“The conducting power of all the ions furnished by one equivalent of an electrolyte in any solution is termed as its equivalent conductivity.”

Thus, equivalent conductivity (Λ_{eq}) is expressed as:

$$\Lambda_{eq} = \frac{\text{Conductivity (k)}}{\text{Concentration in equivalents per unit volume (C}_{eq}\text{)}}$$

$$\therefore \Lambda_{eq} = \frac{k}{C_{eq}}$$

Actual mathematical form of this relationship and the units of Λ_{eq} depend upon the units in which the conductivity (k) and concentration (C_{eq}) are expressed.

If the conductivity is measured in $S\text{ cm}^{-1}$ and concentration is measured in equivalent/litre, then the expression of Λ_{eq} becomes

$$\begin{aligned}\Lambda_{eq} &= \frac{k\text{ S cm}^{-1}}{C_{eq}\text{ equiv dm}^{-3}} = \frac{k}{C_{eq}} \times \frac{1\text{ S cm}^{-1} \times 1\text{ dm}^3}{1\text{ equiv}} \\ &= \frac{k}{C_{eq}} \times \frac{1\text{ S cm}^{-1} \times (10\text{ cm})^3}{1\text{ equiv}} \\ &= \frac{1000\text{ k}}{C_{eq}}\text{ S cm}^2\text{ equiv}^{-1} \\ \Lambda_{eq} &= \frac{1000\text{ k}}{\text{Normality of the solution}}\text{ S cm}^2\text{equiv}^{-1}.\end{aligned}$$

The equivalent conductivity is expressed by $\Lambda_{eq} = \frac{k}{C_{eq}}$ where C_{eq} is the concentration of electrolyte in terms of equivalents per unit volume. By

definition, the volume of solution containing 1 equivalent of the electrolyte is given by

$$V_{\text{eq}} = \frac{1}{C_{\text{eq}}}$$

$$\Lambda_{\text{eq}} = k \times V_{\text{eq}}$$

When C_{eq} is expressed in terms of equivalent per litre, then V_{eq} has the units of litre per equivalent.

$$\begin{aligned}\text{So, } \Lambda_{\text{eq}} &= k(\text{S cm}^{-1}) \times V_{\text{eq}} (\text{dm}^3 \text{ per equivalent}) \\ &= k(\text{S cm}^{-1}) \times V_{\text{eq}} [(10 \text{ cm})^3 \text{ per equivalent}] \\ &= 1000 k(\text{S cm}^{-1}) \times V_{\text{eq}} (\text{cm}^3 \text{ per equivalent})\end{aligned}$$

$$\therefore \Lambda_{\text{eq}} = 1000 k V_{\text{eq}} \text{ S cm}^2 \text{ equivalent}^{-1}$$

7. Molar Conductivity (Λ_m)

The conducting power of a solution can also be described in terms of molar conductivity (Λ_m). The molar conductivity (Λ_m) may be defined as “The conducting power of all the ions furnished by one mole of an electrolyte in any solution is termed as its molar conductivity”.

Thus, molar conductivity is expressed as Molar conductivity

$$(\Lambda_m) = \frac{\text{Conductivity (k)}}{\text{Concentration in moles per unit volume (C}_m\text{)}} = \frac{k}{C_m}$$

Actual mathematical form and the units of Λ_m depend upon the units in which the conductivity (k) and concentration (C_m) are expressed.

When the conductivity is measured in S cm^{-1} and concentration is measured in mol/litre, then the expression of Λ_m becomes

$$\begin{aligned}\Lambda_m &= \frac{k \text{ S cm}^{-1}}{C_m \text{ mol dm}^{-3}} = \frac{k}{C_m} \times \frac{1 \text{ S cm}^{-1} \times 1 \text{ dm}^3}{1 \text{ mol}} \\ &= \frac{k}{C_m} \times \frac{1 \text{ S cm}^{-1} \times (10 \text{ cm})^3}{1 \text{ mol}}\end{aligned}$$

$$= \frac{1000 \text{ k}}{C_m} \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m = \frac{1000 \text{ k}}{\text{Molarity of the solution}} \text{ S cm}^2 \text{ mol}^{-1}.$$

Molar conductivity is expressed by $\Lambda_m = \frac{k}{C_m}$ where C_m is the concentration of the solution in moles per unit volume. By definition, the volume of solution containing one mole of electrolyte is given by $V_m = \frac{1}{C_m}$

$$\therefore \Lambda_m = k \times V_m$$

When C_m is expressed in terms of moles per litre, then V_m has the unit of 1 litre per mole. So,

$$\begin{aligned}\Lambda_m &= k(\text{S cm}^{-1}) \times V_m(\text{dm}^3 \text{ per mol}) \\ &= k(\text{S cm}^{-1}) \times V_m [(10 \text{ cm})^3 \text{ per mol}] \\ \Lambda_m &= 1000 \text{ k } V_m \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

8. Relationship Between Molar And Equivalent Conductivities

According to the definition, $\Lambda_m = \frac{k}{C_m} \dots(\text{i})$

and $\Lambda_{eq} = \frac{k}{C_{eq}} \dots(\text{ii})$

For a solution containing a certain mass of solute per unit volume of the solution (let us say 'w' gram per litre), we can write

$$C_m = \frac{w}{\text{Molar mass of the electrolyte}}$$

$$C_{eq} = \frac{w}{\text{Equivalent mass of the electrolyte}}$$

From these relations, we can write

$$\frac{C_m}{C_{eq}} = \frac{\text{Equivalent mass of the electrolyte}}{\text{Molar mass of the electrolyte}}$$

We know that molar mass of an electrolyte = $z \times$ Equivalent mass of the electrolyte where z is the number of equivalents of electrolytic charge per mole of the electrolyte. (For example, n -factor of electrolyte).

$$\therefore \frac{C_m}{C_{eq}} = \frac{1}{z} \quad \dots(\text{iii})$$

Using equation (i) and (ii), we get $\frac{C_m}{C_{eq}} = \frac{\Lambda_{eq}}{\Lambda_m} \quad \dots(\text{iv})$

Then, from equation (iii) and (iv), we get

$$\frac{\Lambda_{eq}}{\Lambda_m} = \frac{1}{z} \quad \text{or} \quad \Lambda_m = z \times \Lambda_{eq}$$

where z can have values equal to 1, 2, 3,

9. Kohlrausch's Law

At very low concentrations, the molar conductivity of a strong electrolyte tends to reach a limiting value. This value of molar conductivity is called the molar conductivity at infinite dilution (Λ_m^∞). At such high dilutions, the interionic attractions become negligible and each ion migrates independent of the other ions. These observations were used by Kohlrausch to postulate a famous law called Kohlrausch's law of independent ion migration. The Kohlrausch's law in terms of molar conductivity is stated as follows "At infinite dilution, the molar conductivity of an electrolyte can be expressed as the sum of the contributions from its individual ions".

$$\Lambda_m^\infty = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty \quad \dots(\text{v})$$

where v_+ and v_- are the number of cations and anions per formula unit of electrolyte respectively and λ_+^∞ and λ_-^∞ are the molar conductivities of the cation and anion at infinite dilution respectively.

The use of equation (v) in expressing the molar conductivity of an electrolyte at infinite dilution is illustrated below.

1. Molar Conductivity of HCl

The molar conductivity of HCl at infinite dilution can be expressed as,

$$\Lambda_{\text{HCl}}^\infty = (v_{\text{H}^+} \lambda_+^\infty) + (v_{\text{Cl}^-} \lambda_{\text{Cl}^-}^\infty)$$

For HCl, $v_{\text{H}^+} = 1$ and $v_{\text{Cl}^-} = 1$

So, $\Lambda_{\text{HCl}}^\infty = (1 \times \lambda_+^\infty) + (1 \times \lambda_{\text{Cl}^-}^\infty)$

$$\Lambda_{\text{HCl}}^\infty = \lambda_{\text{H}^+}^\infty + \lambda_{\text{Cl}^-}^\infty$$

2. Molar Conductivity of MgCl₂

For MgCl₂, the molar conductivity at infinite dilution can be expressed as,

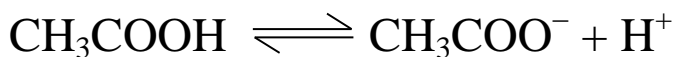
$$\Lambda_{\text{MgCl}_2}^\infty = (v_{\text{Mg}^{2+}} \lambda_{\text{Mg}^{2+}}^\infty) + (v_{\text{Cl}^-} \lambda_{\text{Cl}^-}^\infty)$$

For MgCl₂, $v_{\text{Mg}^{2+}} = 1$ and $v_{\text{Cl}^-} = 2$

So, $\Lambda_{\text{MgCl}_2}^\infty = (1 \times \lambda_{\text{Mg}^{2+}}^\infty) + (2 \times \lambda_{\text{Cl}^-}^\infty)$

$$\Lambda_{\text{MgCl}_2}^\infty = \lambda_{\text{Mg}^{2+}}^\infty + 2\lambda_{\text{Cl}^-}^\infty$$

3. Molar Conductivity of CH₃COOH



So, the molar conductivity of CH₃COOH (acetic acid) at infinite dilution can be expressed as,

$$\Lambda_{\text{CH}_3\text{COOH}}^\infty = (v_{\text{H}^+} \lambda_{\text{H}^+}^\infty) + (v_{\text{CH}_3\text{COO}^-} \lambda_{\text{CH}_3\text{COO}^-}^\infty)$$

For CH₃COOH, $v_{\text{H}^+} = 1$ and $v_{\text{CH}_3\text{COO}^-} = 1$

ELECTROCHEMISTRY

$$\therefore \Lambda_{\text{CH}_3\text{COOH}}^{\infty} = \lambda_{\text{H}^+}^{\infty} + \Lambda_{\text{CH}_3\text{COO}^-}^{\infty}$$

The molar conductivity of a weak electrolyte at infinite dilution (Λ_m^{∞}) cannot be determined by extrapolation method. But Λ_m^{∞} values for weak electrolytes can be determined by using the Kohlrausch's equation. According to the Kohlrausch's law, the molar conductivity of acetic acid (CH_3COOH) is given by,

$$\begin{aligned}\Lambda_{\text{CH}_3\text{COOH}}^{\infty} &= (v_{\text{H}^+} \lambda_{\text{H}^+}^{\infty}) + (v_{\text{CH}_3\text{COO}^-} \lambda_{\text{CH}_3\text{COO}^-}^{\infty}) \\ &= (1 \times \lambda_{\text{H}^+}^{\infty}) + (1 \times \lambda_{\text{CH}_3\text{COO}^-}^{\infty})\end{aligned}$$

Considering the values of $\lambda_{\text{H}^+}^{\infty}$ and $\lambda_{\text{CH}_3\text{COO}^-}^{\infty}$, we get

$$\Lambda_{\text{CH}_3\text{COOH}}^{\infty} = (349.8 + 40.9) \text{ S cm}^2 \text{ mol}^{-1} = 390.7 \text{ S cm}^2 \text{ mol}^{-1}$$

Sometimes, the molar conductivity values for the ions are not available. In such cases, following procedure is adopted.

(i) Select a series of strong electrolytes such that the sum/difference of molar conductivities of their ions gives the molar conductivities of the ions of weak electrolyte. Generally, three strong electrolytes are chosen.

(ii) Measure Λ_m^{∞} values of these salts (strong electrolytes) at various concentrations (C_m) and plot Λ_m against $\sqrt{C_m}$ for each salt separately. Determine Λ_m^{∞} for each salt (strong electrolyte) by extrapolation method.

(iii) Add and/or subtract the equations to get the Λ_m^{∞} of the weak electrolyte. Let us determine the molar conductivity of a weak electrolyte, MA at infinite dilution. For this purpose, we take three salts MCl, NaA and NaCl and determine their Λ_m^{∞} values by extrapolation method. Then, according to the Kohlrausch's law

$$\Lambda_{\text{MCl}}^{\infty} = \lambda_{\text{M}^+}^{\infty} + \lambda_{\text{Cl}^-}^{\infty}$$

$$\Lambda_{\text{NaA}}^{\infty} = \lambda_{\text{Na}^+}^{\infty} + \lambda_{\text{A}^-}^{\infty}$$

and
$$\Lambda_{\text{NaCl}}^{\infty} = \lambda_{\text{Na}^+}^{\infty} + \lambda_{\text{Cl}^-}^{\infty}$$

From these equations, one can write,

ELECTROCHEMISTRY

$$\Lambda_{\text{MCl}}^{\infty} + \Lambda_{\text{NaA}}^{\infty} - \Lambda_{\text{NaCl}}^{\infty} = (\lambda_{\text{M}^{+}}^{\infty} + \lambda_{\text{Cl}^{-}}^{\infty}) + (\lambda_{\text{Na}^{+}}^{\infty} + \lambda_{\text{A}^{-}}^{\infty}) - (\lambda_{\text{Na}^{+}}^{\infty} + \lambda_{\text{Cl}^{-}}^{\infty}) = \lambda_{\text{M}^{+}}^{\infty} + \lambda_{\text{A}^{-}}^{\infty} = \Lambda_{\text{MA}}^{\infty}$$

$$\text{So, } \Lambda_{\text{MA}}^{\infty} = \Lambda_{\text{MCl}}^{\infty} + \Lambda_{\text{NaA}}^{\infty} - \Lambda_{\text{NaCl}}^{\infty}$$

Thus, the molar conductivity of a weak electrolyte at infinite dilution can be obtained from the $\Lambda_{\text{m}}^{\infty}$ values of three suitable strong electrolytes.

Illustration 3.

The value of $\Lambda_{\text{m}}^{\infty}$ for HCl, NaCl and $\text{CH}_3\text{CO}_2\text{Na}$ are 426.1, 126.5 and $91 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. Calculate the value of $\Lambda_{\text{m}}^{\infty}$ for acetic acid.

Solution:

Using Kohlrausch's law,

$$\Lambda_{\text{HCl}}^{\infty} = \lambda_{\text{H}^{+}}^{\infty} + \lambda_{\text{Cl}^{-}}^{\infty} \quad \dots(\text{i})$$

$$\Lambda_{\text{CH}_3\text{CO}_2\text{Na}}^{\infty} = \lambda_{\text{CH}_3\text{CO}_2^{-}}^{\infty} + \lambda_{\text{Na}^{+}}^{\infty} \quad \dots(\text{ii})$$

$$\text{and } \Lambda_{\text{NaCl}}^{\infty} = \lambda_{\text{Na}^{+}}^{\infty} + \lambda_{\text{Cl}^{-}}^{\infty} \quad \dots(\text{iii})$$

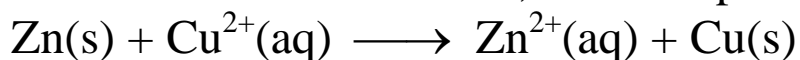
Adding equations (i) and (ii) and subtracting equation (iii), we get

$$\begin{aligned} \Lambda_{\text{HCl}}^{\infty} + \Lambda_{\text{CH}_3\text{CO}_2\text{Na}}^{\infty} - \Lambda_{\text{NaCl}}^{\infty} &= \lambda_{\text{H}^{+}}^{\infty} + \lambda_{\text{Cl}^{-}}^{\infty} + \lambda_{\text{CH}_3\text{CO}_2^{-}}^{\infty} + \lambda_{\text{Na}^{+}}^{\infty} - \lambda_{\text{Na}^{+}}^{\infty} - \lambda_{\text{Cl}^{-}}^{\infty} \\ &= \lambda_{\text{H}^{+}}^{\infty} + \lambda_{\text{CH}_3\text{CO}_2^{-}}^{\infty} = \Lambda_{\text{CH}_3\text{CO}_2\text{H}}^{\infty} \end{aligned}$$

$$\therefore \Lambda_{\text{CH}_3\text{CO}_2\text{H}}^{\infty} = (426.1 + 91 - 126.5) = \mathbf{390.6 \text{ S cm}^2 \text{ mol}^{-1}}$$

10. Electrochemical Cells

Let us take a zinc rod, which is dipped in a solution of CuSO_4 taken in a beaker as shown in figure 2. After some time, we see that the Zn rod starts dissolving and Cu starts depositing on its surface. This happens because Zn gets oxidised to Zn^{2+} ions, which passes into the solution and 2 electrons remain on the Zn rod. Then, Cu^{2+} ion from the solution takes up these 2 electrons to form Cu, which deposits on the Zn rod.



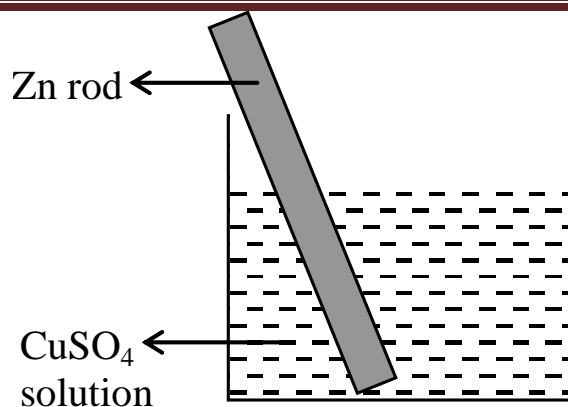


Figure 2.

In this reaction, Zn acts as reducing agent, which is able to reduce Cu^{2+} to Cu by transferring 2 electrons and Cu^{2+} ion acts as an oxidising agent, which oxidises Zn to Zn^{2+} ions and itself gets reduced to Cu. In this case, there is a direct transfer of electrons from Zn rod to Cu^{2+} ion and some heat is also evolved.

The above experiment is slightly modified in a manner that for the same redox reaction, transfer of electrons takes place indirectly and the heat of the reaction is converted into electrical energy. This necessitates the separation of Zn rod from CuSO_4 solution. Such cells in which the oxidised and reduced species are separated and connected through electrical wires are called electrochemical cells.

Electrochemical cells are the cells in which chemical energy is transformed into electrical energy. This means that chemical reactions produce electric current. An electrochemical cell consists of two half-cells or electrodes. The electrodes are metallic conductors dipped in an electrolyte, which is an ionic conductor dissolved in water. A metallic rod and its electrolyte comprise an electrode or half - cell compartment. The two electrodes may share the same or different electrolyte. The various kinds of electrode used are

- (i) Metal - metal ion electrode
- (ii) Gas - gas ion electrode
- (iii) Redox electrode and

(iv) **Metal–insoluble metal salt–anion electrode:** which are discussed in a separate section later. In a given electrochemical cell, combination of any of the two electrodes can be used. The cell may even contain same type of electrodes with different concentration of electrolytes. When an ‘inert metal’ is part of the electrode, it acts as a source of electrons, but does not take part in the reaction. If the electrolytes are different, two compartments may be joined by a salt bridge, which is a concentrated electrolyte solution in agar-agar jelly that completes the electrical circuit and enables the cell to function. Thus, salt bridge provides an electrical contact between the solutions without allowing them to mix with each other.

The simplest electrochemical cell to study is Daniel cell, which is shown in the figure 3. This is prepared by dipping Zn rod in a solution of ZnSO_4 in one beaker and by dipping Cu strip in a solution of CuSO_4 in another beaker. It consists of two redox couples, $\text{Zn}^{2+} | \text{Zn}$ at one end and $\text{Cu}^{2+} | \text{Cu}$ at the other end. Since Zn has a higher oxidation potential than Cu, so it has higher tendency to get oxidised than Cu and conversely Cu^{2+} has higher tendency to get reduced than Zn^{2+} . At this stage, no reaction takes place in either of the beakers. Now, the two half–cells are connected by connecting wire through an ammeter. As soon as the connection is made, Zn rod starts dissolving i.e. Zn atom changes to Zn^{2+} by losing 2 electrons. The Zn^{2+} ion passes into the solution, thereby increasing its concentration and 2 electrons remain on the Zn rod. Thus, ZnSO_4 solution now has +2 unit extra charge and Zn rod has –2 unit extra charge. Thus, there is a charge separation of 4 units between the Zn rod and ZnSO_4 solution. This charge separation develops a potential referred as oxidation potential since oxidation takes place on this electrode. The potential is called standard oxidation potential, if concentration of Zn^{2+} in the solution is 1 M. Similar potential is developed at $\text{Cu}^{2+} | \text{Cu}$ half-cell also, when Cu^{2+} discharges and deposits on Cu rod. This potential is referred as reduction potential as reduction takes place on this electrode. The potential is called standard reduction potential, if the concentration of Cu^{2+} in the solution is 1 M.

ELECTROCHEMISTRY

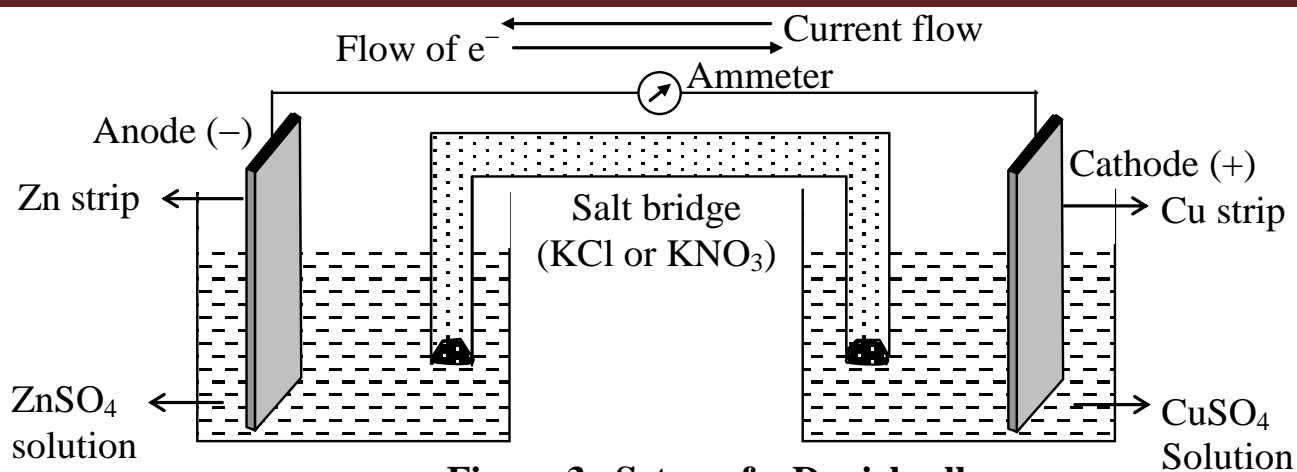


Figure 3. Setup of a Daniel cell

The zinc rod which has the electron left by the zinc (that got oxidized) becomes negatively charged while the Cu rod which lost electrons to Cu^{2+} becomes positively charged. Thus, electric current flows through the connected wire, which is indicated by a deflection in ammeter showing that a chemical reaction is occurring in the cell. During the course of reaction, zinc rod gets dissolved and copper gets deposited on the copper rod. Thus, the concentration of the anode solution increases while that of cathode solution decreases. The flow of electrons occur from the zinc rod to copper rod in the external circuit and indirectly from cathode to anode in the internal circuit. The current flow is in the direction opposite to electron flow. The reactions occurring at the two electrodes are

At anode: $\text{Zn(s)} \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$

At cathode: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu(s)}$

This current flow stops after some time. Think, why it happens? As zinc rod dissolves, let one mole of Zn atom dissolves to form Zn^{2+} , which passes into the solution and 2 mole of electrons remain on the rod. Thus, rod becomes negatively charged and the solution becomes positively charged. With the passage of time, the solution becomes so much positively charged that any Zn atom getting oxidised and trying to get into solution, would be repelled by the solution and thus the oxidation of Zn stops. Same phenomenon occurs at cathode and the reduction of Cu^{2+} at cathode ceases. As the flow of electrons stop, so does the flow of current. This problem can be removed with the use of salt bridge. The salt bridge

ELECTROCHEMISTRY

contains a highly soluble electrolyte (like KCl , NH_4NO_3 , NH_4Cl , KNO_3 etc) in which ionic mobilities of cation and anion are of comparable order. Now, let us examine the function of salt bridge. Since zinc ions are produced as electrons leave the zinc electrode, this tends to produce a net positive charge in the left compartment. The salt bridge then throws cations having equivalent charge into the solution to maintain electrical neutrality. Thus, the salt bridge keeps the solution neutral by passing appropriate amounts of cations or anions to the two half-cells (compartments). Thus, the purpose of the salt bridge is to prevent any net charge accumulation in either compartment. Salt bridge does not participate chemically in the cell reaction but it is essential for the cell to operate. With the use of salt bridge, the flow of electrons becomes continuous and cell continues to operate. But after some more time, cell ceases to operate. Can you guess why it stops operating now?

Cell Notation of An Electrochemical Cell

- (i) Anode is written on the left side and cathode is written on the right side.
- (ii) Phase boundaries are indicated by vertical bar or slash.
- (iii) Concentration of the electrolytes in the anode and cathode must be written in parenthesis.
- (iv) In case of a gas, the partial pressure is to be mentioned in atm or mm Hg.
- (v) A comma is used to separate two chemical species present in the same solution.
- (vi) A double vertical line i.e. $||$ denotes that a salt bridge is present.
- (vii) EMF of the cell is written on the extreme right of the representation.

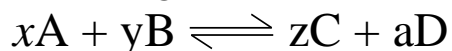
For example,

- (i) $\text{Zn(s)} | \text{ZnSO}_4(c_1 \text{ M}) || \text{CuSO}_4(c_2 \text{ M}) | \text{Cu(s)}$; E_{cell}
- (ii) $\text{Pt} | \text{H}_2(P_1 \text{ atm}) | \text{HCl}(c \text{ M}) | \text{AgCl(s)} | \text{Ag}$; E'_{cell}
- (iii) $\text{Pt} | \text{Fe}^{2+}(c_1 \text{ M}), \text{Fe}^{3+}(c_2 \text{ M}) || \text{Ag}^+(c \text{ M}) | \text{Ag}$; E''_{cell}

Note: In some cell representations (as in (ii) above), the salt bridge is not indicated which implies that the electrolyte is common to both anode and cathode compartments.

11. Cell Potential and Nernst Equation

Nernst equation is used to relate either half-cell potential or EMF of a cell with the concentration of the involved species. Let us first consider a redox change occurring in a electrochemical cell,



where A, B, C and D are the species whose concentrations vary i.e. they are either gases or solution phases. For species A, the free energy per mole

of A can be given thermodynamically as $G_A = G_A^\circ + RT \ln [A]$

For x moles A, $xG_A = xG_A^\circ + xRT \ln[A] = xG_A^\circ + RT \ln[A]^x$

Similarly, for all other species,

$$yG_B = yG_B^\circ + RT \ln [B]^y$$

$$zG_C = zG_C^\circ + RT \ln [C]^z$$

and $aG_D = aG_D^\circ + RT \ln [D]^a$

Now, the free energy change for the overall cell reaction can be deduced as $\Delta G = (zG_C + aG_D) - (xG_A + yG_B)$

$$= zG_C^\circ + RT \ln[C]^z + aG_D^\circ + RT \ln [D]^a - xG_A^\circ - RT \ln [A]^x - yG_B^\circ - RT \ln[B]^y$$

$$= (zG_C^\circ + aG_D^\circ) - (xG_A^\circ + yG_B^\circ) + RT \ln \frac{[C]^z [D]^a}{[A]^x [B]^y}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[C]^z [D]^a}{[A]^x [B]^y} \quad \dots(i)$$

where ΔG° is the free energy change when all the reactants and products are present at one molar concentration.

Any spontaneous reaction occurring in a cell, occurs with a decrease in free energy. This decrease in free energy brings in an equivalent amount of electrical work obtainable from a given system over and above any PdV

ELECTROCHEMISTRY

energy that can be delivered to the surrounding. This can be calculated by the total charge driven through cell and the potential difference. Thus

$$-\Delta G = \text{Total charge} \times \text{EMF of the cell}$$

$$-\Delta G = nF \times E_{\text{cell}}$$

[Negative sign indicates decrease of free energy and it implies that as E_{cell} becomes more and more positive, ΔG will become more and more negative, making the reaction spontaneous]

$$\text{Similarly, } -\Delta G^\circ = nFE_{\text{cell}}^\circ$$

Therefore, equation (i) can be written as

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + RT \ln \frac{[C]^z[D]^a}{[A]^x[B]^y}$$

Dividing both the sides by $-nF$ gives,

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln \frac{[C]^z[D]^a}{[A]^x[B]^y}$$

Putting $T = 298 \text{ K}$, $R = 8.314 \text{ J/mol K}$, $F = 96500 \text{ C}$, we get

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{n} \log \frac{[C]^z[D]^a}{[A]^x[B]^y} \dots(\text{ii})$$

The equation (ii) is called Nernst equation, which is applicable to half-cell reactions as well as to complete cell reactions.

Daniel cell represented as $\text{Zn(s)} \mid \text{Zn}^{2+} (c_1 \text{ M}) \parallel \text{Cu}^{2+} (c_2 \text{ M}) \mid \text{Cu(s)}$ assumes that Zn is the anode and Cu is the cathode. Such an assumption would be true only if the cell potential (E_{cell}) is positive.

The cell potential is given in the following three ways of which we would choose the third one in all our problems.

$$E_{\text{cell}} = E_{\text{RP(Cathode)}} + E_{\text{OP(Anode)}}$$

$$\text{or } E_{\text{cell}} = E_{\text{OP(Anode)}} - E_{\text{OP(Cathode)}}$$

$$\text{or } E_{\text{cell}} = E_{\text{RP(Cathode)}} - E_{\text{RP(Anode)}}$$

$E_{\text{RP(Cathode)}}$ is the reduction potential of the cathode while $E_{\text{RP(Anode)}}$ is reduction potential of the anode. $E_{\text{OP(Cathode)}}$ is the oxidation potential of the cathode while $E_{\text{OP(Anode)}}$ is the oxidation potential of the anode.

ELECTROCHEMISTRY

Now, let us find the EMF of Daniel cell using Nernst equation. Since we need to represent the reduction potential of cathode and anode, we first need to write the relevant reduction reactions.

For cathode: $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$

$$E_{\text{Cu}^{2+}|\text{Cu}} = E_{\text{Cu}^{2+}|\text{Cu}}^{\circ} - \frac{RT}{nF} \log Q_c (\text{or } Q_{pc})$$

$E_{\text{Cu}^{2+}|\text{Cu}}^{\circ}$ is the standard reduction potential of the given half reaction, R is the universal gas constant, T is the absolute temperature at which cell works, F is the Faraday constant and n is the number of mole of electrons as seen in the reaction. The expression in the log term should be that of K_c or K_{pc} . This means that if reaction involves no gases, then the expression in the log term should be that of K_c while if a gas is involved then the expression in the log term should be that of K_{pc} . In these expressions, the concentration should always be in moles per liter while the partial pressure should be in atmosphere units.

$$\therefore E_{\text{Cu}^{2+}|\text{Cu}} = E_{\text{Cu}^{2+}|\text{Cu}}^{\circ} - \frac{0.059}{n} \log \frac{1}{[\text{Cu}^{2+}]}$$

For anode: $\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$

$$E_{\text{Zn}^{2+}|\text{Zn}} = E_{\text{Zn}^{2+}|\text{Zn}}^{\circ} - \frac{0.059}{n} \log \frac{1}{[\text{Zn}^{2+}]}$$

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

$$\therefore E_{\text{cell}} = E_{\text{Cu}^{2+}|\text{Cu}}^{\circ} - \frac{0.059}{n} \log \frac{1}{[\text{Cu}^{2+}]} - E_{\text{Zn}^{2+}|\text{Zn}}^{\circ} + \frac{0.059}{n} \log \frac{1}{[\text{Zn}^{2+}]}$$

$$E_{\text{cell}} = E_{\text{Cu}^{2+}|\text{Cu}}^{\circ} - E_{\text{Zn}^{2+}|\text{Zn}}^{\circ} - \frac{0.059}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

ELECTROCHEMISTRY

Note: Since E_{cell} has been defined as $E_{\text{RP(cathode)}} - E_{\text{RP(Anode)}}$, the Nernst expression holds good even if the number of mole of electrons of the two half reactions are different.

For example, consider the cell,



For cathode: $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$

$$E_{\text{Cu}^{2+}|\text{Cu}} = E_{\text{Cu}^{2+}|\text{Cu}}^{\circ} - \frac{0.059}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

For cathode: $\text{H}^+ + \text{e}^- \longrightarrow \frac{1}{2} \text{H}_2$

$$E_{\text{H}^+|\text{H}_2} = E_{\text{H}^+|\text{H}_2}^{\circ} - \frac{0.059}{1} \log \frac{[\text{P}_{\text{H}_2}]^{1/2}}{[\text{H}^+]}$$

$$\therefore E_{\text{cell}} = E_{\text{Cu}^{2+}|\text{Cu}}^{\circ} - E_{\text{H}^+|\text{H}_2}^{\circ} - \frac{0.059}{2} \log \frac{1}{[\text{Cu}^{2+}]} + \frac{0.059}{1} \log \frac{[\text{P}_{\text{H}_2}]^{1/2}}{[\text{H}^+]}$$

It is also possible to balance the electrons in both the half-cell reactions and then subtract $E_{\text{RP(Anode)}}$ from $E_{\text{RP(Cathode)}}$ That is,

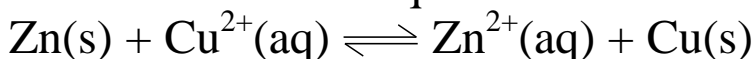
For anode: $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$

$$E_{\text{H}^+|\text{H}_2} = E_{\text{H}^+|\text{H}_2}^{\circ} - \frac{0.059}{2} \log \frac{\text{P}_{\text{H}_2}}{[\text{H}^+]^2}$$

$$E_{\text{cell}} = E_{\text{Cu}^{2+}|\text{Cu}}^{\circ} - E_{\text{H}^+|\text{H}_2}^{\circ} - \frac{0.059}{2} \log \frac{[\text{H}^+]^2}{[\text{Cu}^{2+}]\text{P}_{\text{H}_2}}$$

12. Relation Between Standard Free Energy And Equilibrium Constant

Let us assume that the redox change occurring in Daniel cell attains equilibrium. At equilibrium, the reduction potential values of the two electrodes become equal and EMF of the cell becomes zero.



ELECTROCHEMISTRY

The equilibrium constant for this reaction is given as $K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]}$

Applying Nernst equation to the complete cell reaction,

$$E_{cell} = E_{cell}^{\circ} - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\therefore E_{cell}^{\circ} = \frac{RT}{nF} \ln K_{eq} \quad [\text{as } E_{cell} = 0]$$

$$\therefore nFE_{cell}^{\circ} = RT \ln K_{eq}$$

$$-\Delta G^{\circ} = RT \ln K_{eq}$$

$$\Delta G^{\circ} = -2.303 RT \log K_{eq}$$

[**Note:** This relation is valid for many equilibrium constants like K_w , K_p , K_c , K_{sp} , K_f , K_d etc.]

Some other important relations involving enthalpy change and entropy change during the redox change are

$$(a) \Delta H = nF \left[T \left(\frac{dE}{dT} \right) - E \right] \text{ where } \frac{dE}{dT} \text{ is called as temperature coefficient}$$

representing the change of EMF with the change of temperature, n is the number of mole of electrons involved, F is one Faraday, E is EMF of the cell at temperature T and T is the absolute temperature. Depending upon

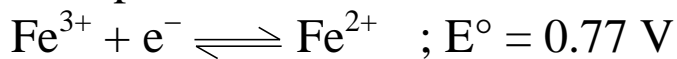
the value of $\left(\frac{dE}{dT} \right)$, ΔH can be negative or positive i.e. reaction can be exothermic or endothermic.

$$(b) \Delta S = nF \left(\frac{dE}{dT} \right). \text{ When } \left(\frac{dE}{dT} \right) \text{ is negative, the change in entropy would}$$

also be negative and when $\left(\frac{dE}{dT} \right)$ is positive, change in entropy would be favoured i.e. ΔS would be positive.

Illustration 4.

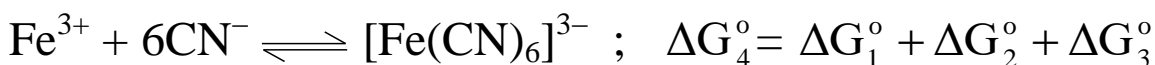
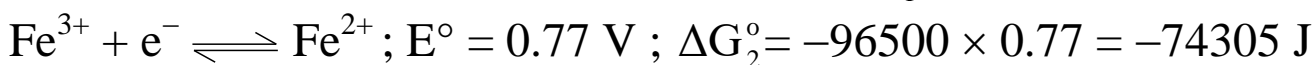
Given the overall formation constant of the $[\text{Fe}(\text{CN})_6]^{4-}$ ion as 10^{35} and the standard potentials for the half reactions,



Calculate the overall formation constant of the $[\text{Fe}(\text{CN})_6]^{3-}$ ion.

Solution:

Let K_f be the formation constant of $[\text{Fe}(\text{CN})_6]^{3-}$ ion.



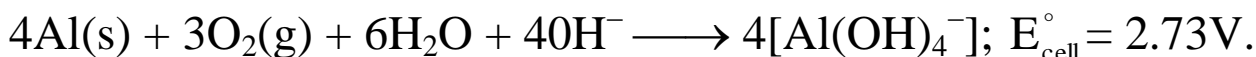
$$\Delta G_4^\circ = -239269.69 \text{ J}$$

$$\Delta G_4^\circ = -2.303 RT \log K_f'$$

$$\therefore K_f' = 8.59 \times 10^{41}$$

Illustration 5

For the reaction,



If $\Delta G_f^\circ(\text{OH}^-) = -157 \text{ kJ mol}^{-1}$ and $\Delta G_f^\circ(\text{H}_2\text{O}) = -237.2 \text{ kJ mol}^{-1}$,

Determine $\Delta G_f^\circ(\text{Al} | \text{OH})_4^-$.

Solution:

The ΔG° and E_{cell}° are related by

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -12 \times 96500 \times 2.73 = -3.16 \times 10^3 \text{ kJ}$$

$$\Delta G^\circ = 4\Delta G_f^\circ(\text{Al}(\text{OH})_4^-) - 6\Delta G_f^\circ(\text{H}_2\text{O}) - 4\Delta G_f^\circ(\text{OH}^-)$$

(since ΔG_f° of $\text{Al}(\text{s})$ and $\text{O}_2(\text{g})$ are zero)

$$\begin{aligned} \Delta G_f^\circ(\text{Al}(\text{OH})_4^-) &= \frac{-3.16 \times 10^3 + (6 \times -237.2) + (4 \times -157)}{4} \\ &= -1.30 \times 10^3 \text{ kJ mol}^{-1} \end{aligned}$$

13. Types of Half Cells/Electrodes

13.1 Metal - Metal Ion Half Cell

In this type of half-cell, the metal rod is dipped in a solution of the corresponding metal ion having concentration c M. The assembly is shown in figure 4.

The given half-cell when functions as anode can be represented as $M(s) | M^{n+}(c M)$

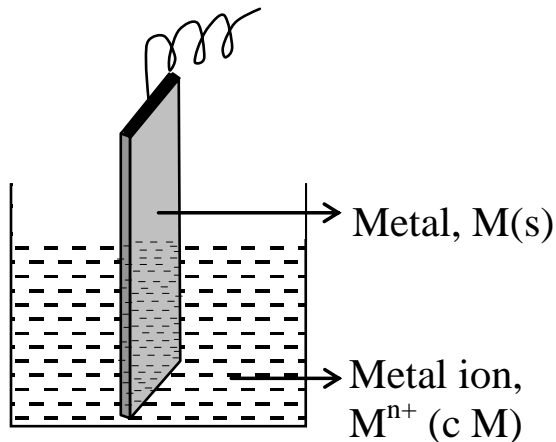


Figure 4. Metal-metal ion half-cell

The anodic half-cell reaction is $M(s) \longrightarrow M^{n+}(aq) + ne^{-}$

The representation of the half-cell when it functions as cathode is



The cathodic half-cell reaction is $M^{n+}(aq) + ne^{-} \longrightarrow M(s)$

Examples of this type of half-cell when used as cathode are $Cu^{2+} | Cu$, $Zn^{2+} | Zn$, $Ag^{+} | Ag$, $Sn^{2+} | Sn$ etc. The half cells or electrodes used in Daniel cell are of the metal-metal ion type.

For such type of half-cells, very active metals cannot be used, because they react with water. For such highly reactive metals, an amalgam of the metal in mercury is used instead of pure metal.

13.2 Gas - Gas Ion Half Cell

In a gas-gas ion half-cell, a gas is bubbled into a solution of the gas ion, with a platinum rod having a sheet coated with platinum black being dipped in the gas ion solution.

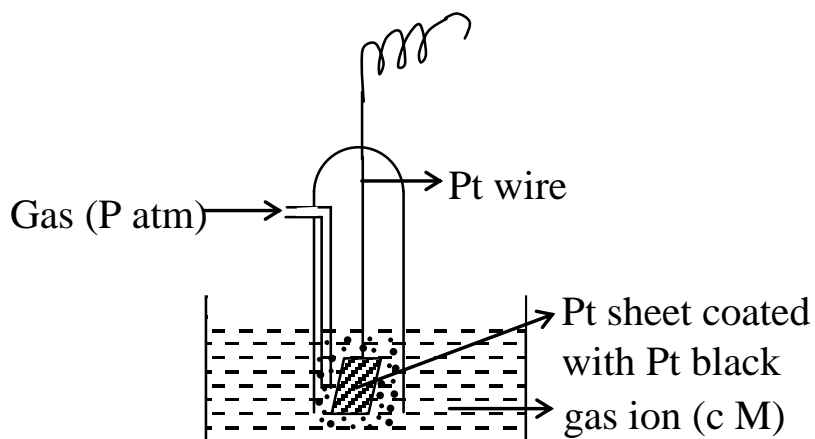


Figure 5. Gas-gas ion half-cell

Platinum is used for making electrical contact because the gases are non-conducting and the platinum do not react with gas ions as it is an unreactive metal. Platinum black is used over the platinum sheet, which gives it a large surface area for the adsorption of gases. The half-cell assembly is shown in figure 5.

The given half-cell when functions as anode can be represented as $\text{Pt} \mid \text{Gas (P atm)} \mid \text{Gas ion (c M)}$.

Let us consider a hydrogen gas half-cell, functioning as anode. It is represented as $\text{Pt} \mid \text{H}_2 (\text{P atm}) \mid \text{H}^+ (\text{c M})$ and the anodic half-cell reaction is $\text{H}_2(\text{Pt}) \longrightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^- (\text{Pt})$.

The chlorine gas half-cell when functions as anode can be represented as $\text{Pt} \mid \text{Cl}_2(\text{P atm}) \mid \text{Cl}^- (\text{c M})$ and the anodic half-cell reaction is $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$.

The oxygen gas half-cell when functions as anode can be represented as $\text{Pt} \mid \text{O}_2 (\text{P atm}) \mid \text{OH}^- (\text{c M})$ and the anodic half-cell reaction is $2\text{OH}^- \longrightarrow \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^-$.

The gas-gas ion half-cell when functions as cathode can be represented as $\text{Gas ion (c M)} \mid \text{Gas (P atm)} \mid \text{Pt}$.

Let us consider a hydrogen half-cell, functioning as cathode. It is represented as $\text{H}^+ (\text{c M}) \mid \text{H}_2 (\text{P atm}) \mid \text{P}$ and the cathodic half-cell reaction is $2\text{H}^+ (\text{aq}) + 2\text{e}^- (\text{Pt}) \longrightarrow \text{H}_2 (\text{Pt})$.

The hydrogen electrode is called standard hydrogen electrode when the concentration of H^+ ion is 1 M and the pressure of H_2 gas is 1 atm. The standard hydrogen electrode (SHE) functions as reference electrode and is used for the measurement of standard reduction potentials of other half-cells or couples. The standard reduction potential values obtained in this manner are arranged in the decreasing order to give electrochemical series.

13.3 Redox Half Cell

In redox half-cell, a platinum rod is dipped in a solution containing two different oxidation states of a metal ion (M^{n_1+} and M^{n_2+} , where n_2 is greater than n_1). The half-cell assembly is shown in figure 6.

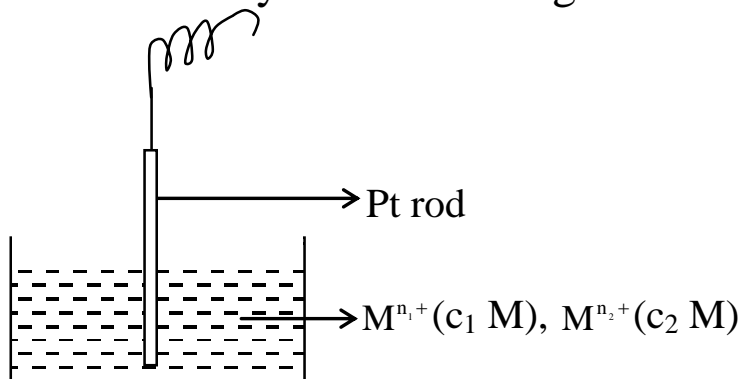
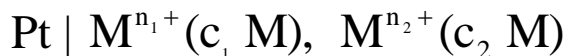


Figure 6. Redox half-cell

The given half-cell when functions as anode can be represented as



and the anodic half-cell reaction is $\text{M}^{n_1+} \longrightarrow \text{M}^{n_2+} + (n_2 - n_1)\text{e}^-$.

The redox half-cell when functions as cathode can be represented as

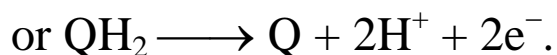
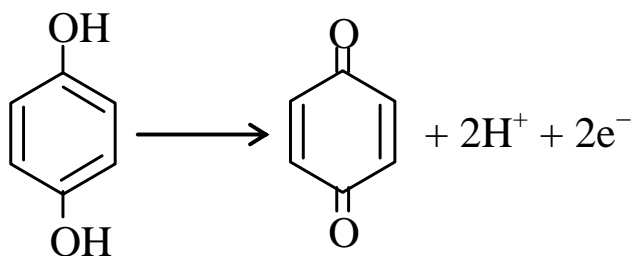


and the cathodic half-cell reaction is $\text{M}^{n_2+} + (n_2 - n_1)\text{e}^- \longrightarrow \text{M}^{n_1+}$.

ELECTROCHEMISTRY

Examples of this type of half-cell when used as anode are $\text{Pt} | \text{Cr}^{2+} (c_1 \text{ M}), \text{Cr}^{3+} (c_2 \text{ M})$; $\text{Pt} | \text{Fe}^{2+} (c_1 \text{ M}), \text{Fe}^{3+} (c_2 \text{ M})$; $\text{Pt} | \text{Sn}^{2+} (c_1 \text{ M}), \text{Sn}^{4+} (c_2 \text{ M})$ etc. In such half cells, the oxidising and reducing agents are both metal ions.

Redox half-cell can also be made with organic molecules that can exist in two different oxidation states. A couple of hydroquinone (QH_2) and quinone (Q) forms a redox half-cell. Its representation, when it functions as anode is $\text{Pt} | \text{QH}_2(1 \text{ M}), \text{Q}(1 \text{ M}), \text{H}^+ (c \text{ M})$ and the anodic half-cell reaction is



This redox electrode having organic molecules is called quinhydrone electrode because of the charged complex formed between quinone and hydroquinone.

13.4 Metal–Insoluble Metal Salt – Anion Half Cell

Let us take an example of such a half-cell, which functions as cathode, as $\text{Cl}^- (c \text{ M}) | \text{AgCl} | \text{Ag}$. The assembly of this half-cell is made by dipping a rod of silver coated with a paste of saturated AgCl at the bottom, in a solution of ionic electrolyte like KCl , NaCl or HCl . The cation part in the electrolyte must have standard reduction potential less than the standard reduction potential of the cation of the metal salt. The half-cell assembly is shown in figure 7.

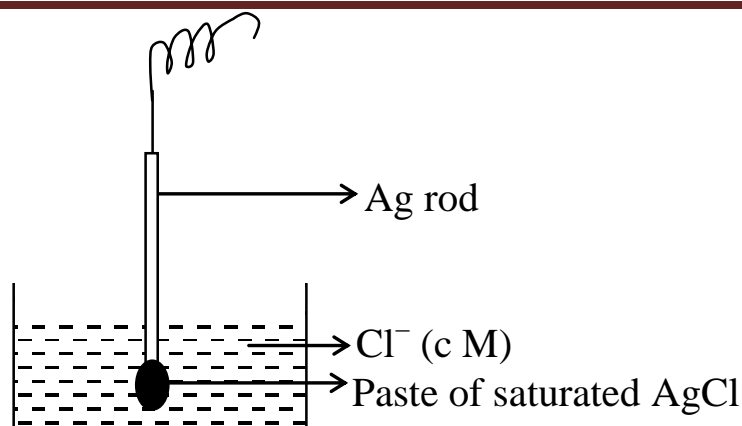
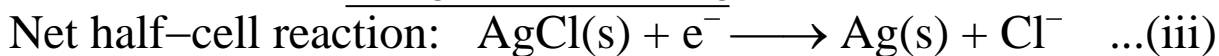
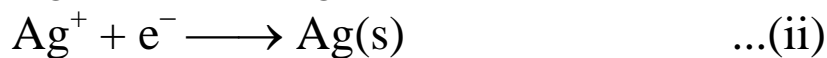
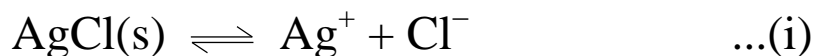


Figure 7. Metal-insoluble metal salt-anion half-cell

The cathodic half-cell reaction is



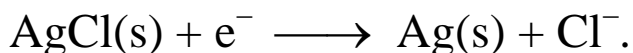
Applying Nernst equation to the net half-cell reaction, gives

$$E_{\text{Cl}^- | \text{AgCl} | \text{Ag}} = E_{\text{Cl}^- | \text{AgCl} | \text{Ag}}^\circ - \frac{RT}{F} \ln[\text{Cl}^-] \quad \dots(\text{iv})$$

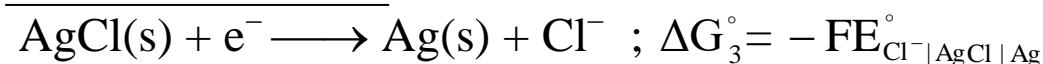
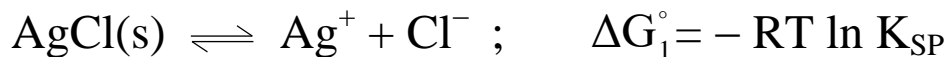
(AgCl and Ag do not appear in the expression as they are pure solids).

Now, if we are given $E_{\text{Ag}^+ | \text{Ag}}^\circ$, concentration of Cl^- and K_{SP} of AgCl, how

can we calculate the half-cell potential ($E_{\text{Cl}^- | \text{AgCl} | \text{Ag}}$) for the reaction,



In Nernst equation, can $E_{\text{Ag}^+ | \text{Ag}}^\circ$ be replaced for $E_{\text{Cl}^- | \text{AgCl} | \text{Ag}}^\circ$. Let us see.



ELECTROCHEMISTRY

It is evident that ΔG_2° is not equal to ΔG_3° as ΔG_1° is not zero. Thus, $E_{\text{Ag}^+|\text{Ag}}^\circ$, is not equal to $E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^\circ$ and we can not replace $E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^\circ$ by $E_{\text{Ag}^+|\text{Ag}}^\circ$. But using Hess's law, we can calculate $E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^\circ$ as

$$\Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ - RT \ln K_{\text{SP}} - FE_{\text{Ag}^+|\text{Ag}}^\circ = -FE_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^\circ.$$

Dividing this equation by $-F$, $\frac{RT}{F} \ln K_{\text{SP}} + E_{\text{Ag}^+|\text{Ag}}^\circ = E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^\circ$

Substituting the value of $E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^\circ$ in equation (i) gives

$$\therefore E_{\text{Cl}^-|\text{AgCl}|\text{Ag}} = E_{\text{Ag}^+|\text{Ag}}^\circ + \frac{RT}{F} \ln K_{\text{SP}} - \frac{RT}{F} \ln [\text{Cl}^-]$$

$$E_{\text{Cl}^-|\text{AgCl}|\text{Ag}} = E_{\text{Ag}^+|\text{Ag}}^\circ - \frac{RT}{F} \ln \frac{[\text{Cl}^-]}{K_{\text{SP}}}$$

Since, $E_{\text{Ag}^+|\text{Ag}}^\circ$, concentration of Cl^- and K_{SP} of AgCl are given, the reduction potential ($E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}$) for the reaction,

$\text{AgCl(s)} + e^- \longrightarrow \text{Ag(s)} + \text{Cl}^-$ can be calculated.

Another metal-insoluble metal salt-anion half-cell is calomel electrode, which is also used as a reference electrode. When calomel half-cell is used as cathode, it is represented as

$\text{Cl}^- (\text{c M}) | \text{Hg}_2\text{Cl}_2 | \text{Hg}$ and the cathodic half-cell reaction is

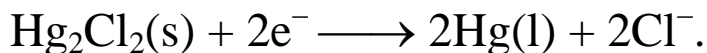


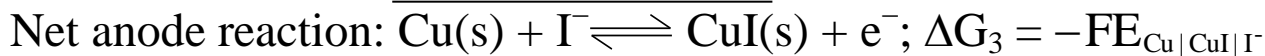
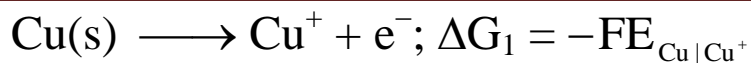
Illustration 6.

The K_{SP} of CuI is $1.1 \times 10^{-12} \text{ M}^2$. Determine EMF of the cell, represented as $\text{Cu} | \text{CuI} | \text{I}^- (1 \text{ M}) || \text{Cu}^+ (1 \text{ M}) | \text{Cu}$.

Solution:

The anode of the given cell is of metal-insoluble metal salt-anion type half-cell while cathode is of the type metal-metal ion. The half-cell reactions at anode are

ELECTROCHEMISTRY



According to Hess's law, we know

$$\Delta G_1 + \Delta G_2 = \Delta G_3$$

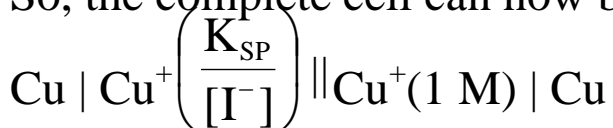
$$\therefore \Delta G_1 = \Delta G_3 \text{ (as } \Delta G_2 = 0)$$

$$\therefore -FE_{\text{Cu}|\text{Cu}^+} = -FE_{\text{Cu}|\text{CuI}|\text{I}^-}$$

$$\text{So, } E_{\text{Cu}|\text{Cu}^+} = E_{\text{Cu}|\text{CuI}|\text{I}^-}$$

Since, the E value of $\text{Cu} \longrightarrow \text{Cu}^+ + \text{e}^-$ and E value of $\text{Cu} + \text{I}^- \longrightarrow \text{CuI} + \text{e}^-$ are same, the representation of anode can be changed from metal-metal insoluble salt – anion half-cell to metal-metal ion half-cell, provided the concentration of Cu^+ in both the half-cells is same.

So, the complete cell can now be represented as



Reactions occurring at the two electrodes are



Applying Nernst equation gives

$$E_{\text{cell}} = E_{\text{Cu}_\text{C}^+|\text{Cu}}^\circ - E_{\text{Cu}_\text{A}^+|\text{Cu}}^\circ - \frac{RT}{F} \ln \frac{[\text{Cu}_\text{A}^+]}{[\text{Cu}_\text{C}^+]}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ + \frac{RT}{F} \ln \frac{[\text{Cu}_\text{C}^+]}{[\text{Cu}_\text{A}^+]}$$

$$E_{\text{cell}} = \frac{RT}{F} \ln \frac{[\text{Cu}_\text{C}^+]}{[\text{Cu}_\text{A}^+]} \text{ (as } E_{\text{cell}}^\circ = 0)$$

$$E_{\text{cell}} = \frac{RT}{F} \ln \frac{[\text{Cu}_c^+] \times [\text{I}^-]}{K_{\text{sp}}} = 0.059 \log \frac{1 \times 1}{1.1 \times 10^{-12}} = \mathbf{0.705 \text{ V}}$$

14. Concentration Cells

The cells whose E_{cell}° is zero are called concentration cells. This means that the two compartments (cathode and anode) of the electrochemical cell involve same chemical species but the concentrations of the chemical species in the two compartments are different. The concentration cells are of basically two types.

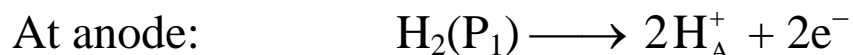
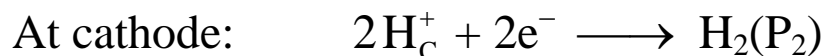
- (a) Electrode concentration cells and
- (b) Electrolyte concentration cells

14.1 Electrode Concentration Cells

In such cells, two similar electrodes at different concentrations/pressures are dipped in the same solution with similar concentration. Let us have an electrochemical cell represented as



For the given cell, the reactions occurring are



Since the H^+ concentration at the anode and cathode are same, so the net reaction is independent of the concentration of the electrolyte. Applying Nernst equation to the net cell reaction gives

$$E_{\text{cell}}(25^\circ\text{C}) = E_{\text{H}_c^+ \mid \text{H}_2(\text{P}_2)}^\circ - E_{\text{H}_A^+ \mid \text{H}_2(\text{P}_1)}^\circ - \frac{0.059}{2} \log \left(\frac{\text{P}_2}{\text{P}_1} \right)$$

$$E_{\text{cell}}(25^\circ\text{C}) = E_{\text{cell}}^\circ - \frac{0.059}{2} \log \left(\frac{\text{P}_2}{\text{P}_1} \right)$$

$$\text{or } E_{\text{cell}}(25^{\circ}\text{C}) = -\frac{0.059}{2} \log \left(\frac{P_2}{P_1} \right) \quad (\text{since, } E_{\text{cell}}^{\circ} = 0)$$

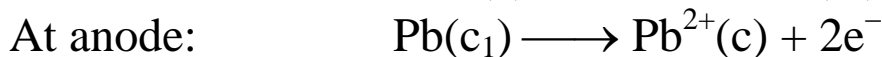
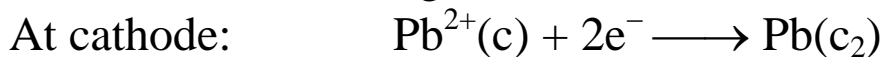
$$E_{\text{cell}}(25^{\circ}\text{C}) = \frac{0.059}{2} \log \left(\frac{P_1}{P_2} \right)$$

The EMF of the given cell would be positive when $P_1 > P_2$ and the cell reaction would be spontaneous.

Another example of the electrode concentration cell is that of an amalgam with two different concentrations of the same metal dipped in same electrolyte solution.

The cell is represented as $\text{Hg-Pb}(c_1 \text{ M}) \mid \text{PbSO}_4(c \text{ M}) \mid \text{Hg-Pb}(c_2 \text{ M})$.

The reactions for the given cell are



Since, the concentration of Pb^{2+} for the two half cells is same as the electrolyte solution for the two compartments is same, so the net reaction is independent of the electrolyte concentration. Applying Nernst equation to the net cell reaction gives

$$E_{\text{cell}}(25^{\circ}\text{C}) = E_{\text{Pb}^{2+}(c) \mid \text{Pb}(c_2)}^{\circ} - E_{\text{Pb}^{2+}(c) \mid \text{Pb}(c_1)}^{\circ} - \frac{0.059}{2} \log \frac{c_2}{c_1}$$

$$E_{\text{cell}}(25^{\circ}\text{C}) = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{c_2}{c_1}$$

$$E_{\text{cell}}(25^{\circ}\text{C}) = -\frac{0.059}{2} \log \frac{c_2}{c_1} \quad (\text{since } E_{\text{cell}}^{\circ} = 0)$$

$$E_{\text{cell}}^{\circ}(25^{\circ}\text{C}) = \frac{0.059}{2} \log \frac{c_1}{c_2}$$

The net cell reaction would be spontaneous, when the EMF of the cell is positive, which is possible only when $c_1 > c_2$.

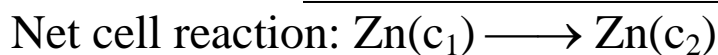
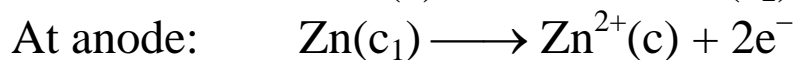
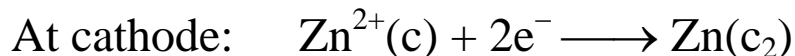
Illustration 7.

Calculate the EMF of the electrode concentration cell

Hg–Zn (c_1 M) | Zn^{2+} (c M) | Hg–Zn (c_2 M) at 25°C , if the concentration of the zinc amalgam are 2 g per 100 g of mercury and 1 g per 100 g of mercury in anode and cathode half cell respectively.

Solution:

The reactions at the two half cells are



Applying Nernst equation to the net cell reaction gives

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{2} \log \frac{c_2}{c_1} = \frac{0.059}{2} \log \frac{c_1}{c_2} \quad (\text{since } E_{\text{cell}}^\circ = 0)$$

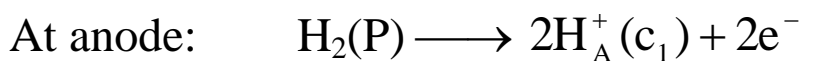
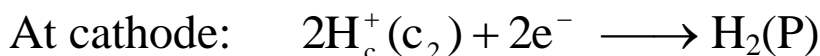
$$E_{\text{cell}} = \frac{0.059}{2} \log \left(\frac{2/65.4}{1/65.4} \right) = 8.8 \times 10^{-3} \text{ V}$$

14.2 Electrolyte Concentration Cells

In such cells, two electrodes of the same metal are dipped in solutions of metal ions of different concentrations. Let us have an electrochemical cell represented as $\text{Pt} | \text{H}_2(\text{P atm}) | \text{HA}(c_1 \text{ M}) || \text{HB}(c_2 \text{ M}) | \text{H}_2(\text{P atm}) | \text{Pt}$.

In such cells, HA and HB would represent strong acids, if their K_a 's are not given while they would be weak acids, if their K_a 's are mentioned.

For the given cell, the reactions occurring are



The net cell reaction is independent of the pressure terms as the pressure of H_2 in the two half cells is same.

Applying Nernst equation to the net cell reaction gives

ELECTROCHEMISTRY

$$E_{\text{cell}}(25^{\circ}\text{C}) = E_{\text{H}_c^+|\text{H}_2}^{\circ} - E_{\text{H}_A^+|\text{H}_2}^{\circ} - \frac{0.059}{1} \log \frac{[\text{H}_A^+]}{[\text{H}_C^+]}$$

$$= E_{\text{cell}}^{\circ} - 0.059 \log \frac{c_1}{c_2}$$

$$E_{\text{cell}}(25^{\circ}\text{C}) = 0.059 \log \frac{c_2}{c_1} \quad (\text{since } E_{\text{cell}}^{\circ} = 0)$$

The net cell reaction would be feasible spontaneously only when the EMF of the cell is positive, which is possible only when concentration of H^+ in cathode compartment (c_2) is greater than the concentration of H^+ in anode compartment (c_1).

Illustration 8.

Calculate the EMF of the following galvanic cell

$\text{Zn} \mid \text{Zn}^{2+}(0.01\text{M}) \parallel \text{Zn}^{2+}(0.1\text{M}) \mid \text{Zn}$ at 298 K.

Solution:

The reactions at the two half cells are

At cathode: $\text{Zn}_C^{2+} + 2e^- \longrightarrow \text{Zn}$

At anode: $\text{Zn} \longrightarrow \text{Zn}_A^{2+} + 2e^-$

Net cell reaction: $\text{Zn}_C^{2+} \longrightarrow \text{Zn}_A^{2+}$

Applying Nernst equation to the net cell reaction gives

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Zn}_A^{2+}]}{[\text{Zn}_C^{2+}]}$$

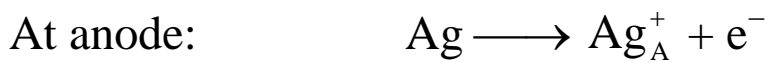
$$E_{\text{cell}} = \frac{0.059}{2} \log \frac{[\text{Zn}_C^{2+}]}{[\text{Zn}_A^{2+}]} \quad (\text{since } E_{\text{cell}}^{\circ} = 0)$$

$$E_{\text{cell}} = \frac{0.059}{2} \log \frac{0.1}{0.01} = \mathbf{0.0295 \text{ V}}$$

Let us consider another electrochemical cell as $\text{Ag} \mid \text{Ag}_2\text{CrO}_4$ (saturated soln.) \parallel AgCl (saturated soln.) $\mid \text{Ag}$ and the solubility products of Ag_2CrO_4 and AgCl are $(K_{\text{sp}})_1$ and $(K_{\text{sp}})_2$ respectively. The saturated solution of Ag_2CrO_4 and AgCl , each will give some $[\text{Ag}^+]$

ELECTROCHEMISTRY

and the $[Ag^+]$ in the two compartments will not be same. So, the given cell would be an electrolyte concentration cell. For the given cell, the reactions occurring are



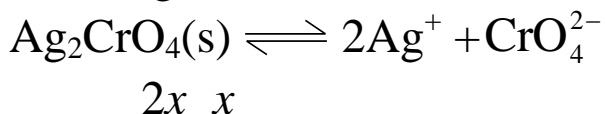
Applying Nernst equation gives

$$E_{\text{cell}}(25^\circ\text{C}) = E_{Ag_C^+|Ag}^\circ - E_{Ag_A^+|Ag}^\circ - 0.059 \log \frac{[Ag_A^+]}{[Ag_C^+]}$$

$$E_{\text{cell}}(25^\circ\text{C}) = E_{\text{cell}}^\circ - 0.059 \log \frac{[Ag_A^+]}{[Ag_C^+]}$$

$$E_{\text{cell}}(25^\circ\text{C}) = 0.059 \log \frac{[Ag_C^+]}{[Ag_A^+]} \quad (\text{since } E_{\text{cell}}^\circ = 0)$$

The $[Ag^+]$ in anode and cathode half-cells is written in terms of K_{sp} as



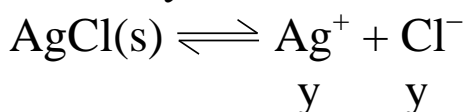
Let 'x' moles per litre be the solubility of Ag_2CrO_4 .

$$\therefore (K_{\text{sp}})_1 = [Ag^+]^2 [CrO_4^{2-}] = (2x)^2 x = 4x^3$$

$$\therefore x = \sqrt[3]{\frac{(K_{\text{sp}})_1}{4}}$$

$$[Ag_A^+] = 2x = 2 \times \sqrt[3]{\frac{(K_{\text{sp}})_1}{4}}$$

Similarly, let the solubility of $AgCl$ be 'y' moles/litre.



$$(K_{\text{sp}})_2 = [Ag^+] [Cl^-] = y^2$$

$$\therefore y = [Ag_C^+] = \sqrt{(K_{\text{sp}})_2}$$

Substituting the values of $[Ag_A^+]$ and $[Ag_C^+]$ in the expression of E_{cell} give

$$E_{\text{cell}} = 0.059 \log \frac{\sqrt{(K_{\text{sp}})_2}}{2 \times \sqrt[3]{\frac{(K_{\text{sp}})_1}{4}}}$$

For the net cell reaction to be spontaneous, $\sqrt{(K_{\text{sp}})_2}$ has to be greater than $2 \times \sqrt[3]{\frac{(K_{\text{sp}})_1}{4}}$, so that the EMF of the cell would be positive.

Illustration 9.

Calculate the potential of the cell,

Mn(s) | MnCl₂ (0.001 M) | HCl (0.01 M) | O₂ (0.25 atm) | Pt.

Given that $E^\circ = -1.185 \text{ V}$ for Mn²⁺ | Mn couple and 1.229 V for the O₂ | H₂O, H⁺ couple.

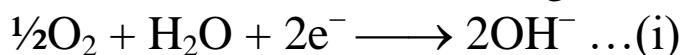
Solution:

Let us first analyze each electrode separately. The anode is a simple metal–metal ion electrode.

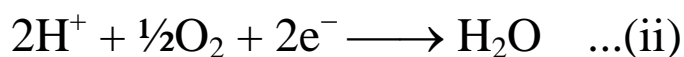


The cathode is written as HCl (0.01 M) | O₂ (0.25 atm) | Pt

At cathode, the reaction occurring is

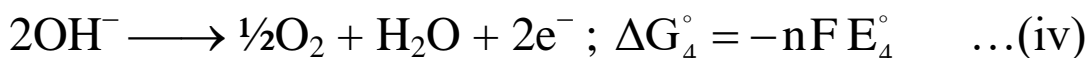


The E° (1.229 V) is given for the half cell O₂|H₂O, H⁺ in which the reaction is

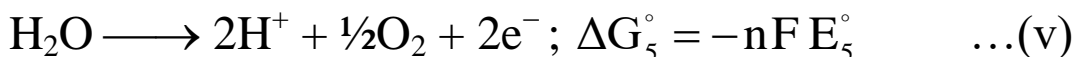


Method I:

Therefore we need to find out the E° of reaction (i). In order to find out this, we should relate reaction (i) and (ii). They are related as



[Reverse of reaction (i)]



[Reverse of reaction (ii)]

ELECTROCHEMISTRY

We know, $\Delta G_3^\circ + \Delta G_4^\circ = \Delta G_5^\circ - RT \ln (K_w)^2 - nFE_4^\circ = -nFE_5^\circ$

On solving, $E_4^\circ = -0.403V$

$$\therefore E_1^\circ = 0.403V$$

Net cell reaction is $\frac{1}{2}O_2 + H_2O + Mn \longrightarrow Mn^{2+} + 2OH^-$

$$E_{\text{cell}} = E_{O_2|OH^-}^\circ - E_{Mn^{2+}|Mn}^\circ - \frac{0.059}{2} \log \frac{[Mn^{2+}][OH^-]^2}{(P_{O_2})^{1/2}}$$

$$E_{\text{cell}} = 0.403 - (-1.185) - \frac{0.059}{2} \log \frac{10^{-3} \times (10^{-12})^2}{\sqrt{0.25}} = \mathbf{2.37\ V}$$

Method II:

We can replace the cathode of the given cell by the half cell, $O_2|H_2O, H^+$ because we have already learnt in metal-insoluble salt-anion electrode that the potential of the two half cells is same.

Thus, the cell representation becomes

$Mn(s) | MnCl_2 (0.001\ M) || H^+ (0.01\ M), H_2O | O_2 (0.25\ atm) | Pt$

At anode: $Mn \longrightarrow Mn^{2+} + 2e^-$

At cathode: $2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O$

Net cell reaction: $Mn + 2H^+ + \frac{1}{2}O_2 \longrightarrow Mn^{2+} + H_2O$

$$E_{\text{cell}} = E_{O_2|H_2O, H^+}^\circ - E_{Mn^{2+}|Mn}^\circ - \frac{0.059}{2} \log \frac{[Mn^{2+}]}{[H^+]^2 (P_{O_2})^{1/2}}$$

$$E_{\text{cell}} = 1.229 - (-1.185) - \frac{0.059}{2} \log \frac{10^{-3}}{(10^{-2})^2 \times \sqrt{0.25}} = \mathbf{2.37\ V}$$

15. Types of Batteries

A battery is an electrochemical cell, or a series of combined electrochemical cells, that can be used as a source of direct electric current at a constant voltage. The operation of a battery is similar in principle to that of the electrochemical cells except that they are completely self

ELECTROCHEMISTRY

contained and require no salt bridge. There are generally two types of batteries.

(a) Primary batteries and

(b) Secondary batteries

A primary battery acts as a source of electricity without being previously charged by an electric current from an external source. In such a battery, electrical energy is obtained at the expense of chemical reactivity as long as the active materials are present. A battery, which can be recharged, after it has been used once is called secondary battery. Certain chemical changes occur when the cell is charged with electricity and these changes are reversed during discharging process.

Various primary batteries in use are dry cell battery, nickel–cadmium battery, mercury battery, fuel cell etc. The secondary battery, which is widely used is lead storage battery.

15.1 Dry Cell Battery

The most common dry cell (a cell without fluid component) is the Leclanche cell used in flash lights and transistor radios. The anode of the cell consists of a zinc can or container that is in contact with manganese dioxide (MnO_2) and an electrolyte. The electrolyte consists of NH_4Cl and ZnCl_2 in water, to which starch (as inert filler) is added to thicken the solution to a paste like consistency so that it is less likely to leak. The anode is usually covered with a steel jacket to shield it from the atmosphere. The cathode is a graphite rod which serves as an inert electrode. The graphite rod is in the center of the cell and is surrounded by MnO_2 and electrolyte. The interior section of a dry cell battery is shown in figure 8. At anode, zinc is oxidised to Zn^{2+} while at the cathode, Mn^{+4} from MnO_2 is reduced to Mn^{+3} in the form of Mn_2O_3 .

At anode:
$$\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^{-}$$

At cathode:
$$2\text{MnO}_2(\text{s}) + 2\text{NH}_4^{+} + 2\text{e}^{-} \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + 2\text{NH}_3 + \text{H}_2\text{O}$$

Cell reaction:
$$\text{Zn(s)} + 2\text{MnO}_2(\text{s}) + 2\text{NH}_4^{+} \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + \text{Zn}^{2+} + 2\text{NH}_3 + \text{H}_2\text{O}$$

ELECTROCHEMISTRY

Actually, this equation is an over simplification of a complex process. The voltage produced by a dry cell is about 1.5 V.

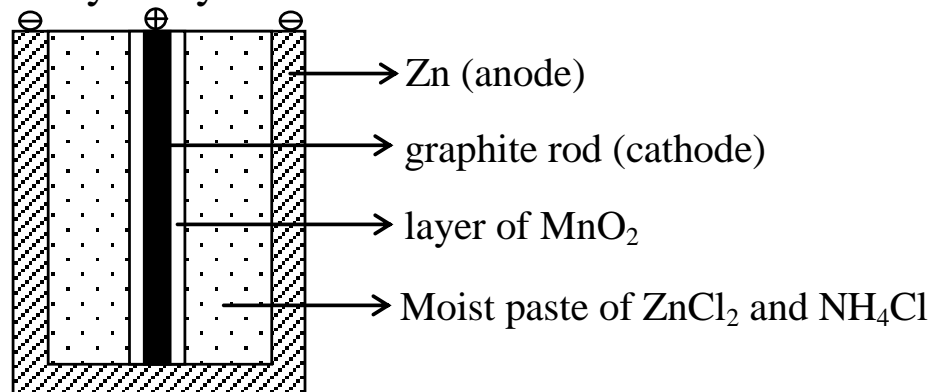
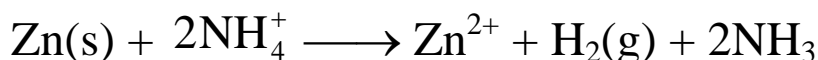


Figure 8. Interior section of a dry cell battery

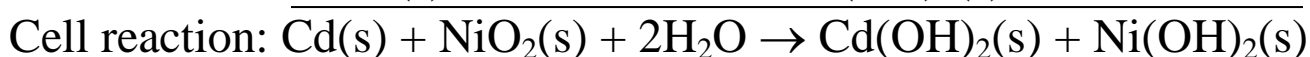
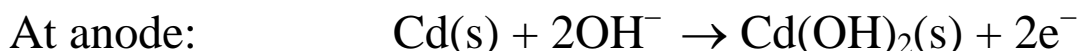
The dry cell is not rechargeable, as the Zn^{2+} ions produced at the anode migrate through the electrolyte paste and combine with NH_3 produced at the cathode to form the complex ion, $[\text{Zn}(\text{NH}_3)_4]^{2+}$. One major problem with the dry cell is that if dry cell battery lie unused for over a year, it splits and leaks due to the following reaction between Zn and NH_4^+ (from NH_4Cl), which slowly eats away the zinc can.



This problem can be removed, if NH_4Cl in the electrolyte paste is replaced by KOH . The cell is then referred as alkaline dry cell, which is more expensive than the acid form (containing acid salt, NH_4Cl) but it lasts longer because there is no corrosion of Zn by NH_4^+ ions.

15.2 Nickel-Cadmium Battery

Nickel–cadmium battery is a portable and rechargeable battery. It is recently developed and has advantages over the dry cell battery. Although it is more expensive than a dry cell, the added expense is worthwhile as it can be recharged. It is used in electronic calculators and other battery powered devices. The reactions at the two electrodes are



The cell reaction can be readily reversed because the reaction products $[\text{Ni}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$] adhere to the electrode surface. The nickel–cadmium battery delivers a constant voltage throughout its life time since the voltage (EMF) is concentration independent as all the substances involved in the net cell reaction are pure solid or pure liquid.

15.3 Mercury Battery

The mercury battery consists of a zinc anode (amalgamated with mercury) in contact with strongly alkaline electrolyte containing zinc oxide and mercury (II) oxide. The cathode is a graphite rod, which serves as an inert electrode. The entire battery is contained in a stainless steel cylinder. The interior section of a mercury battery is shown in figure 9.

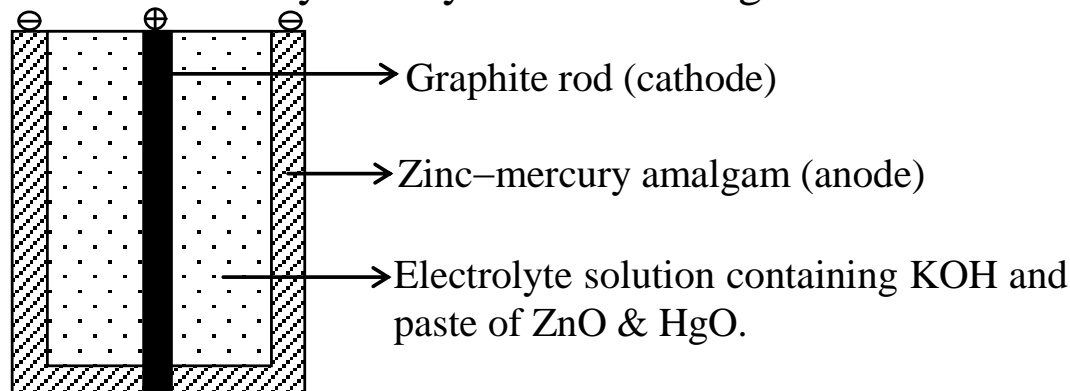
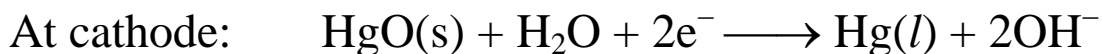


Figure 9. Interior section of a mercury battery

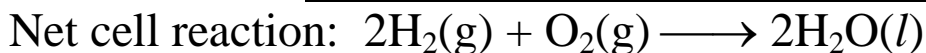
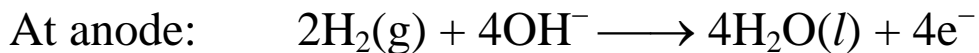
The cell reactions are



The mercury battery provides a constant voltage of 1.35 V through out its life. This is possible because the net cell reaction involves only pure components (pure solids and pure liquids) and EMF of the cell is concentration independent. The mercury battery has higher capacity and longer life, which makes it ideal for use in pacemakers, hearing aids, electric watches etc.

15.4 Fuel Cells

A hydrogen–oxygen fuel cell consists of an electrolyte solution, such as KOH solution and two inert carbon electrodes. Hydrogen and oxygen gases are bubbled through the anode and cathode compartments, where the following reactions takes place.



The standard emf of the cell is 1.23 V, which indicates that the cell reaction is spontaneous under standard conditions. The porous carbon electrodes serve as electrical conductors and also provide the necessary surfaces for the initial decomposition of the molecules into atomic species, prior to electron transfer. A hydrogen–oxygen fuel cell assembly is shown in figure 10.

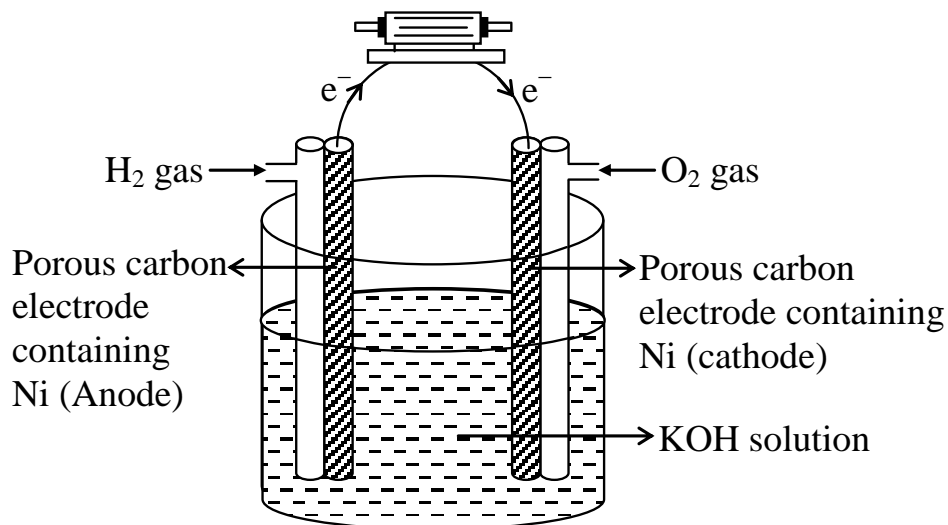


Figure 10.

Unlike batteries, fuel cells do not store chemical energy. Reactants must be constantly resupplied and products must be constantly removed from a fuel cell. The fuel cells are not widely used, the most successful application of fuel cells till date has been in space vehicles to produce pure water, needed for the consumption by astronauts. The operation of a lead storage battery during discharging is shown in figure 11.

15.5 Lead Storage Battery

The lead storage battery commonly used in automobiles consists of six identical cells joined together in series. It is a reversible cell, acting as electrochemical cell when discharged and it functions as electrolytic cell during charging process. The reactions occurring at anode and cathode get reversed during charging and discharging process. Each cell of a lead storage battery has a lead anode and a cathode made of lead dioxide powder packed in a metal plate (lead grid). The anode is also a lead grid with interstices filled with spongy lead. Both the cathode and the anode are immersed in an aqueous solution of sulfuric acid (35% by weight), which acts as an electrolyte.

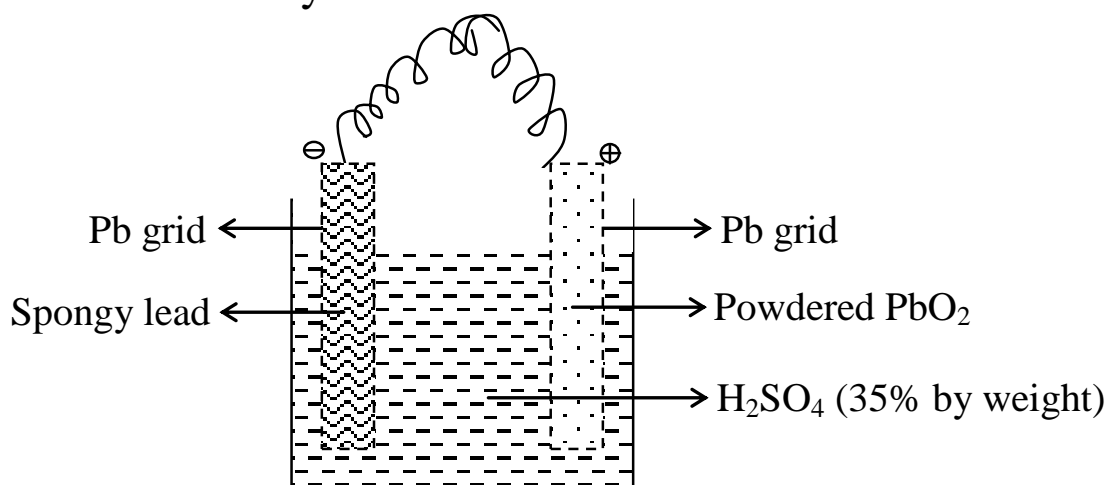
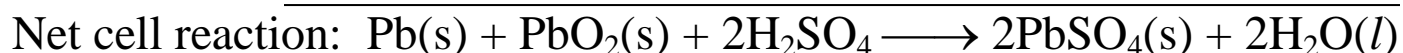


Figure 11. Lead storage battery during discharging process

During discharging of lead storage battery, at anode, Pb is oxidised to Pb^{2+} and an insoluble white precipitate of PbSO_4 is formed, which remains within the lead grid. At cathode, Pb^{4+} (from PbO_2) is reduced to Pb^{2+} and PbSO_4 again precipitates out. As the cell is discharged, the interstices of both lead grids get filled with PbSO_4 . The reaction during discharging process are



ELECTROCHEMISTRY

Under normal operating conditions, each cell produces a potential of 2V. Thus, a total of 12 V from six cells is used to power the ignition circuit of the automobile and its other electrical devices.

The lead storage battery is represented as



The anode and cathode both are of the metal–insoluble salt–anion type.

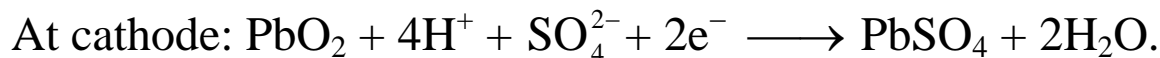
The cell reactions are easily reversed, if the PbSO_4 is freshly precipitated, but on long standing, PbSO_4 changes its crystalline structure and ages to a less reactive form, which cannot be reconverted back into Pb and PbO_2 .

Four aspects of the operation of a lead storage battery are worth noting. First, there is no salt bridge or porous barrier and both the electrodes are immersed in the same solution. This is because, the oxidizing agent (PbO_2) and reducing agent (Pb) as well as their oxidation and reduction products (PbSO_4) are pure solids and will not migrate to the other half cell. Second, the battery is rechargeable i.e. normal electrochemical reactions are reversed by applying an external voltage at the cathode and the anode. At this stage, battery functions as electrolytic cell. Third, as the battery is used, the electrolyte solution becomes more dilute as H_2O is produced and H_2SO_4 is used up. Thus, the density of electrolyte solution decreases and the degree to which the battery has been discharged can be checked by measuring the density of the electrolyte with a hydrometer. Fourth, the temperature coefficient for a lead storage battery is $1.5 \times 10^{-4} \text{ V/}^\circ\text{C}$ i.e. there is a decrease in voltage of $1.5 \times 10^{-4} \text{ V}$ for every degree drop in temperature. Thus, even for 40°C change in temperature, the decrease in voltage amounts to only $6 \times 10^{-3} \text{ V}$, which is about $\frac{6 \times 10^{-3}}{12} \times 100 = 0.05\%$

of the operating voltage. This change is almost insignificant. With the decrease of temperature, the viscosity of the electrolyte increases and the ions move much more slowly in viscous medium, leading to a decrease in the power output of the battery. Thus, people living in cold climates sometimes have trouble in starting their cars.

Illustration 10.

During the discharge of a lead storage battery, the density of H_2SO_4 falls from ρ_1 g/cc to ρ_2 g/c.c. H_2SO_4 of density of ρ_1 g/c.c is X% by weight and that of density of ρ_2 g/c.c. is Y% by weight. The battery holds V litre of acid before discharging. Calculate the total charge released at anode of the battery. The reactions occurring during discharging are

**Solution:**

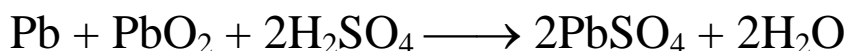
Mass of acid solution before discharge of lead storage battery (LSB)

$$= (V \times 10^3 \times \rho_1) \text{ g}$$

$$= (1000 \times V\rho_1) \text{ g}$$

$$\begin{aligned} \text{Mass of } \text{H}_2\text{SO}_4 \text{ before discharge of LSB} &= \left(1000 \times V\rho_1 \times \frac{X}{100} \right) \text{ g} \\ &= (10 \times V\rho_1 X) \text{ g} \end{aligned}$$

Net reaction during discharging:



From the reaction, it is evident that the moles of electron exchanged (lost at anode and gain at cathode) is equal to the moles of H_2SO_4 consumed or moles of H_2O produced. Let the moles of H_2SO_4 produced be x , then

$$\text{Mass of } \text{H}_2\text{O} \text{ produced during discharge of LSB} = (18x) \text{ g}$$

$$\text{Mass of } \text{H}_2\text{SO}_4 \text{ consumed during discharge of LSB} = (98x) \text{ g}$$

$$\therefore \text{Mass of } \text{H}_2\text{SO}_4 \text{ after discharge of LSB} = [(10 V\rho_1 X) - 98x] \text{ g}$$

$$\begin{aligned} \text{Mass of acid solution after discharge of LSB} &= [(1000 V\rho_1) - 98x + 18x] \\ &= [(1000 V\rho_1) - 80x] \text{ g} \end{aligned}$$

$$\therefore \% \text{ of } \text{H}_2\text{SO}_4 \text{ after discharge of LSB}$$

$$\begin{aligned} &= \frac{\text{Mass of } \text{H}_2\text{SO}_4 \text{ after discharge}}{\text{Mass of acid solution after discharge}} \times 100 \\ Y &= \frac{[(1000 \times V\rho_1 X) - 98x]}{[(1000 \times V\rho_1) - 80x]} \times 100 \end{aligned}$$

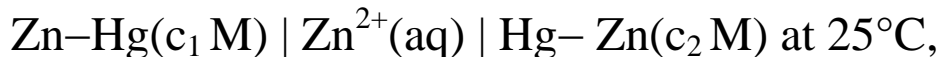
x can be calculated as all other quantities are known.

\therefore Total charge released at cathode, $Q = nF = xF$

Fundamental Solved Examples

Example 1.

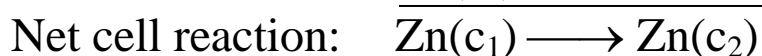
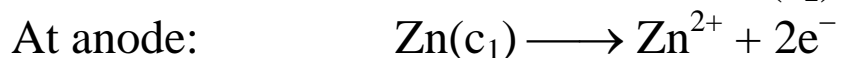
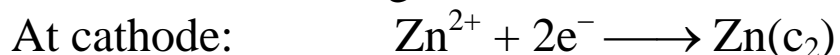
Calculate the EMF of the electrode concentration cell,



if the concentrations of the zinc amalgam are : $c_1 = 10$ g per 100 g of mercury and $c_2 = 1$ g per 100 g of mercury.

Solution:

The cell reactions in the given electrode concentration cell are



$$E_{\text{cell}} = \frac{0.059}{2} \log \frac{c_1}{c_2} \quad (\text{since } E_{\text{cell}}^\circ = 0)$$

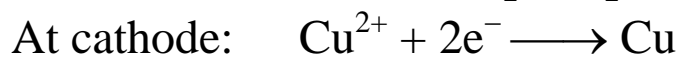
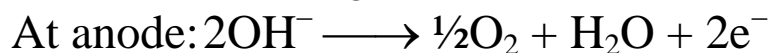
$$E_{\text{cell}} = 0.0295 \log \left(\frac{10}{1} \right) = 0.0295 \text{ V}$$

Example 2.

Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the original solution.

Solution:

The reactions occurring at the anode and cathode would be



$$\text{Total charge passed} = \frac{2 \times 10^{-3} \times 16 \times 60}{96500} = 1.9896 \times 10^{-5}$$

ELECTROCHEMISTRY

$$\text{Mole of Cu}^{2+} \text{ deposited} = \frac{1.9896 \times 10^{-5}}{2}$$

The absorbance of the solution is directly proportional to concentration of solution. Since absorbance was reduced to 50% of its original value, the initial moles of Cu^{2+} would be two times the moles of Cu^{2+} deposited (reduced).

$$\text{Initial moles of Cu}^{2+} = \frac{1.9896 \times 10^{-5}}{2} \times 2 = 1.9896 \times 10^{-5}$$

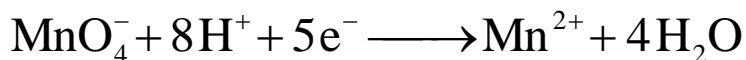
$$[\text{CuSO}_4] = \frac{1.9896 \times 10^{-5} \times 1000}{250} = 7.958 \times 10^{-5} \text{ M}$$

Example 3.

By how much is the oxidising power of the $\text{MnO}_4^- | \text{Mn}^{2+}$ couple decreases if the H^+ concentration is decreased from 1 M to 10^{-4} M at 25°C . Assume that the concentration of other species do not change.

Solution:

In acidic medium, MnO_4^- acts as oxidizing agent and reduces to Mn^{2+} as per the reaction



$$E_{\text{MnO}_4^- | \text{Mn}^{2+}} = E_{\text{MnO}_4^- | \text{Mn}^{2+}}^{\circ} - \frac{0.059}{5} \log \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-] [\text{H}^+]^8}$$

$$= E_{\text{MnO}_4^- | \text{Mn}^{2+}}^{\circ} - \frac{0.059}{5} \log \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-] (1)^8}$$

$$E'_{\text{MnO}_4^- | \text{Mn}^{2+}} = E_{\text{MnO}_4^- | \text{Mn}^{2+}}^{\circ} - \frac{0.059}{5} \log \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-] [10^{-4}]^8}$$

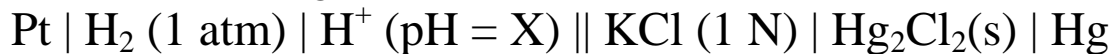
$$\begin{aligned} \therefore (E_{\text{MnO}_4^- | \text{Mn}^{2+}} - E'_{\text{MnO}_4^- | \text{Mn}^{2+}}) \\ = \frac{0.059}{5} \left[\log \frac{[\text{MnO}_4^-] (1)^8}{[\text{Mn}^{2+}]} \times \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-] (10^{-4})^8} \right] = 0.3776 \text{ V} \end{aligned}$$

ELECTROCHEMISTRY

Thus, the oxidizing power of $\text{MnO}_4^- | \text{Mn}^{2+}$ couple decreases by 0.3776 V from its standard value.

Example 4.

EMF of the following cell is 0.67 V at 298 K.

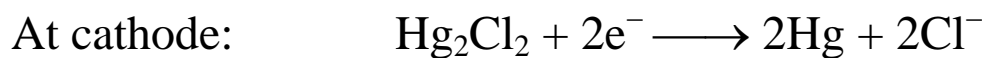
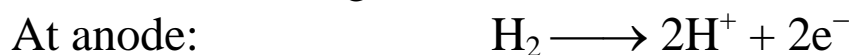


Calculate pH of the anode compartment.

Given: $E^\circ_{\text{Cl}^- | \text{Hg}_2\text{Cl}_2 | \text{Hg}} = 0.28 \text{ V}$.

Solution:

The reactions occurring in the electrochemical cell are



$$\therefore E_{\text{cell}} = E^\circ_{\text{Cl}^- | \text{Hg}_2\text{Cl}_2 | \text{Hg}} - E^\circ_{\text{H}^+ | \text{H}_2} - \frac{0.059}{2} \log \frac{[\text{Cl}^-]^2 [\text{H}^+]^2}{P_{\text{H}_2}}$$

(Hg and Hg_2Cl_2 do not appear as they are pure liquid and pure solid respectively)

$$0.67 = 0.28 - \frac{0.059}{2} \log \frac{[\text{H}^+]^2 \times (1)^2}{1} = 0.28 - 0.059 \log [\text{H}^+]$$

$$0.67 = 0.28 + 0.059 \text{ pH}$$

$$\therefore \text{pH} = 6.61$$

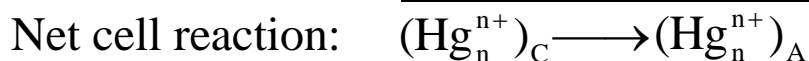
Example 5.

The EMF of the cell, $\text{Hg} | \text{Mercurous nitrate} (0.01 \text{ M}) || \text{Mercurous nitrate} (0.1 \text{ M}) | \text{Hg}$ was found to be 0.0295 V at 25°C. Calculate the molecular formula of mercurous nitrate.

Solution:

Let the formula of mercurous nitrate be $\text{Hg}_n(\text{NO}_3)_n$.

For the given cell, the reactions occurring at two electrodes are



ELECTROCHEMISTRY

So, this is an electrolyte concentration cell for which $E_{\text{cell}}^{\circ} = 0$. The E_{cell} will be given as

$$\therefore E_{\text{cell}} = -\frac{0.059}{n} \log \frac{[\text{Hg}_n^{n+}]_A}{[\text{Hg}_n^{n+}]_C}$$
$$0.0295 = \frac{0.059}{n} \log \frac{[\text{Hg}_n^{n+}]_C}{[\text{Hg}_n^{n+}]_A} = \frac{0.059}{n} \log \frac{0.1}{0.01}$$
$$n = 2$$

Thus, the formula of mercurous nitrate is $\text{Hg}_2(\text{NO}_3)_2$.

Example 6.

A current of 1.7 Ampere is passed through 300 ml of 0.16 M solution of ZnSO_4 for 230 sec with a current efficiency of 90%. Find the molarity of Zn^{2+} after the deposition of Zn. Assume that the volume of the solution remains constant during electrolysis.

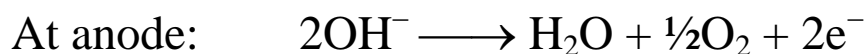
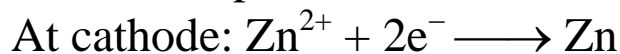
Solution:

In order to solve such problems, it has to be assumed that anode is made up of some inert material (like graphite, Pt etc), which is incapable of getting oxidized while cathode is made up of zinc strip.

Another assumption is that the solution of ZnSO_4 being aqueous contains cations H^+ and Zn^{2+} but the ion that get discharged at cathode is Zn^{2+} and not H^+ , since otherwise the molarity of solution will not change. This means that the reduction potential of Zn^{2+} is higher than that of H^+ .

The third assumption is that the volume of solution remains unchanged during electrolysis. This assumption is already mentioned in the problem.

When current is passed, the following reactions occur at cathode & anode.



$$\text{Mole of electrons passed} = \frac{1.7 \times 90 \times 230}{100 \times 96500}$$

ELECTROCHEMISTRY

$$\text{Mole of Zn}^{2+} \text{ reduced} = \frac{1.7 \times 90 \times 230}{100 \times 96500 \times 2} = 1.82 \times 10^{-3}$$

$$\begin{aligned} \text{Initial moles of Zn}^{2+} \text{ in the solution} &= 300 \times 10^{-3} \times 0.16 = 0.048 \text{ Moles of} \\ \text{Zn}^{2+} \text{ left in the solution} &= 0.048 - 1.82 \times 10^{-3} = 0.04618 \end{aligned}$$

$$\text{Zn}^{2+} \text{ solution molarity after deposition of Zn} = \frac{0.04618 \times 10^3}{300} = 0.154 \text{ M}$$

Example 7.

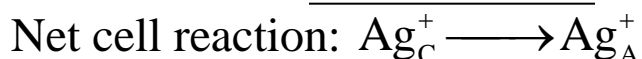
Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K, if the EMF of the cell,

$\text{Ag} \mid \text{Ag}^+ (\text{Satd. Ag}_2\text{CrO}_4 \text{ solution}) \parallel \text{Ag}^+ (0.1 \text{ M}) \text{ Ag}$

is 0.164 V at 298 K.

Solution:

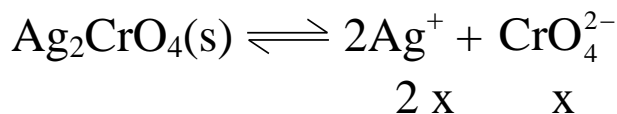
For the given cell, the reactions occurring at the anode and cathode are



Thus, it is an electrolyte concentration cell with $E_{\text{cell}}^{\circ} = 0$.

$$\therefore E_{\text{cell}} = \frac{0.059}{1} \log \frac{[\text{Ag}_A^+]}{[\text{Ag}_C^+]} = \frac{0.059}{1} \log \frac{[\text{Ag}_C^+]}{[\text{Ag}_A^+]}$$

The anode compartment have saturated solution of Ag_2CrO_4 , supplying Ag^+ ion concentration. Let the solubility of Ag_2CrO_4 be x moles/litre.



$$K_{\text{SP}} = [\text{Ag}_A^+]^2 [\text{CrO}_4^{2-}] = (2x)^2 x = 4x^3$$

$$\therefore [\text{Ag}_A^+] = 2x = 2 \times \sqrt[3]{\frac{K_{\text{SP}}}{4}}$$

$$\therefore E_{\text{cell}} = 0.164 = \frac{0.059}{1} \log \frac{0.1}{2 \times \sqrt[3]{\frac{K_{\text{SP}}}{4}}}$$

ELECTROCHEMISTRY

$$K_{SP} = 2.24 \times 10^{-12} \text{ M}^3$$

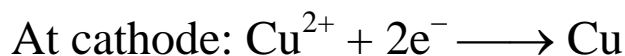
Example 8.

An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the Cu is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 ml and the current at 1.2 ampere. Calculate the volume of gases evolved at NTP during entire electrolysis.

Solution:

The problem does not mention about the acidic salt of Cu^{2+} i.e. what kind of acidic salt is this. Does the acidic salt have chloride, sulphate or nitrate as anion against the cation Cu^{2+} and the answer will solely depend on the assumption we make in the beginning about the acidic salt. First, let us assume that the salt is of cupric chloride (CuCl_2).

In the I part of electrolysis, the reactions occurring at the two electrodes are



[The reaction occurring at anode is the oxidation of Cl^- in preference to OH^- since the standard oxidation potential of $\text{Cl}^- > \text{OH}^-$]

$$\text{Mole of } \text{Cu}^{2+} \text{ reduced at cathode} = \frac{0.4}{63.5}$$

Mole of electrons required at cathode = $\frac{2 \times 0.4}{63.5}$ = Mole of electrons released at anode

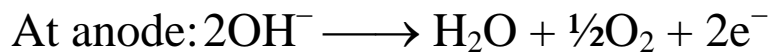
$$\text{Mole of } \text{Cl}_2 \text{ liberated at anode} = \frac{2 \times 0.4 \times 1}{63.5 \times 2} = \frac{0.4}{63.5}$$

$$\text{Volume of } \text{Cl}_2 \text{ liberated at STP at anode} = \frac{0.4}{63.5} \times 22400 = 141 \text{ ml}$$

In second part of electrolysis, when current is passed for 7 more minutes, the H^+ will be reduced at cathode since Cu^{2+} ions are discharged

ELECTROCHEMISTRY

completely and OH^- ions are oxidized at anode since Cl^- is also completely oxidized. The reactions occurring are



$$\text{Mole of electrons passed} = \frac{1.2 \times 7 \times 60}{96500}$$

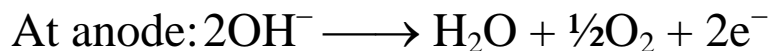
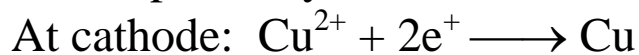
$$\text{Volume of H}_2 \text{ at STP released at cathode} = \frac{1.2 \times 7 \times 60}{96500 \times 2} \times 22400 = 58.49 \text{ ml}$$

$$\text{Volume of O}_2 \text{ at STP released at anode} = \frac{1.2 \times 7 \times 60}{96500 \times 4} \times 22400 = 29.245 \text{ ml}$$

Total volume of gases ($\text{Cl}_2 + \text{O}_2 + \text{H}_2$) liberated at STP during entire electrolysis = $141 + 59.49 + 29.245 = 228.735 \text{ ml}$

Second, let us assume that the salt is that of CuSO_4 .

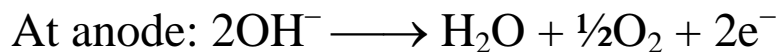
In part I of electrolysis, the ions discharged at cathode and anode are Cu^{2+} and OH^- respectively.



$$\therefore \text{Mole of O}_2 \text{ liberated at anode} = \frac{2 \times 0.4}{63.5 \times 4} = \frac{0.4}{63.5 \times 2}$$

$$\text{Volume of O}_2 \text{ at STP liberated at anode} = \frac{0.4}{63.5 \times 2} \times 22400 = 70.55 \text{ ml}$$

In part II of electrolysis, the H^+ and OH^- ions are discharged at cathode and anode respectively.



$$\text{Volume of H}_2 \text{ at STP released at cathode} = \frac{1.2 \times 7 \times 60}{96500 \times 2} \times 22400 = 58.49 \text{ ml}$$

$$\text{Volume of O}_2 \text{ at STP released at anode} = 29.245 \text{ ml}$$

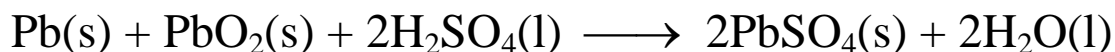
Total volume of gases ($\text{H}_2 + \text{O}_2$) released at STP during entire electrolysis
= $70.55 + 58.49 + 29.245 = 158.285 \text{ ml}$

ELECTROCHEMISTRY

[Note: If we assume the salt to be $\text{Cu}(\text{NO}_3)_2$, the volume of gases liberated (at STP) still remains same as in the case of CuSO_4 (158.235 ml) as NO_3^- is also resistant to oxidation (just like SO_4^{2-}) and OH^- oxidises in preference to NO_3^-].

Example 9.

A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 34.6% by weight (density 1.261 g ml^{-1} at 25°C) to one of 27% by weight. The original volume of electrolyte is one litre. Calculate the total charge released at anode of the battery. Note that the water is produced by the cell reaction as H_2SO_4 is used up. Over all reaction is



Solution:

Before the discharge of lead storage battery,

$$\text{Mass of solution} = 1000 \times 1.261 = 1261 \text{ g}$$

$$\text{Mass of H}_2\text{SO}_4 = \frac{1261 \times 34.6}{100} = 436.3 \text{ g}$$

$$\text{Mass of water} = 1261 - 436.3 = 824.7 \text{ g}$$

After the discharge of lead storage battery,

Let the mass of H_2O produced as a result of net reaction during discharge ($\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$) is $x \text{ g}$.

$$\text{Moles of H}_2\text{O produced} = \frac{x}{18} = \text{Moles of H}_2\text{SO}_4 \text{ consumed}$$

$$\text{Mass of H}_2\text{SO}_4 \text{ consumed} = \frac{x}{18} \times 98$$

Now, mass of solution after discharge = $1261 - \frac{98x}{18} + x$ % by mass of

$$\text{H}_2\text{SO}_4 \text{ after discharge} = \frac{\text{Mass of H}_2\text{SO}_4 \text{ left}}{\text{Mass of solution after discharge}} \times 100 = 27$$

$$= \frac{436.3 - \frac{98x}{18}}{1261 - \frac{98x}{18} + x} \times 100 = 27$$

$$\therefore x = 22.59 \text{ g}$$

From the reaction, it is evident that the moles of electron exchanged at anode or cathode is two and this is also the moles of H_2O produced or moles of H_2SO_4 consumed.

$$\text{Moles of electrons released at anode} = \frac{22.59}{18}$$

$$\text{Total charge released at anode} = \frac{22.59}{18} \times 96500 = 1.21 \times 10^5 \text{ Coulomb.}$$

Example 10.

For a saturated solution of AgCl at 25°C , specific conductance is $3.41 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ and that of water used for preparing the solution was $1.6 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. What is the solubility product of AgCl ? Given: $\Lambda_{\text{eqv}}^\infty(\text{AgCl}) = 138.3 \text{ ohm}^{-1} \text{ cm}^{-1} \text{ equiv}^{-1}$.

Solution:

Specific conductance of AgCl = Specific conductance of solution – specific conductance of H_2O .

$$= (3.41 - 1.6) \times 10^{-6} = 1.81 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}.$$

For saturated solution of sparingly soluble salt, $\Lambda_{\text{eq}} = \Lambda_{\text{eq}}^\infty$ and concentration of AgCl = solubility of AgCl .

$$\therefore \Lambda_{\text{eq}}^\infty = \frac{1000 \times \text{specific conductance of AgCl}}{\text{Solubility of AgCl}}$$

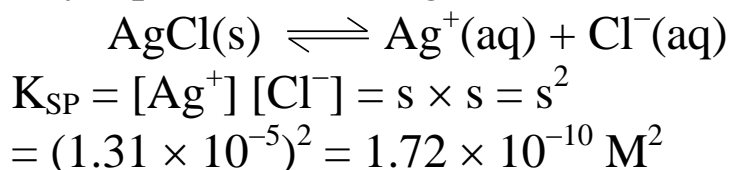
(since molarity = normality for AgCl)

$$\therefore 138.3 = \frac{1000 \times 1.81 \times 10^{-6}}{s}$$

ELECTROCHEMISTRY

$$\therefore s = \frac{1000 \times 1.81 \times 10^{-6}}{138.3} = 1.31 \times 10^{-5} \text{ mol/lit}$$

The solubility equilibrium of AgCl is shown as



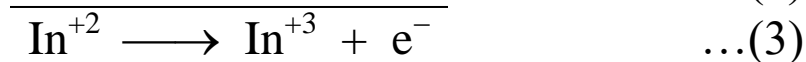
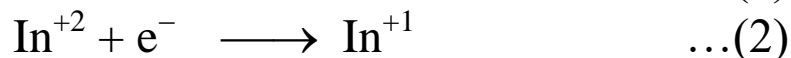
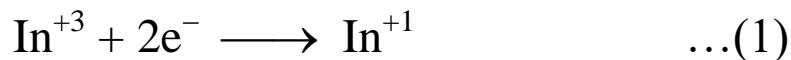
Example 11.

Find the equilibrium constant for the reaction,



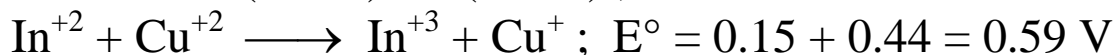
Given: $E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15 \text{ V}$; $E^\circ_{\text{In}^{3+}/\text{In}^+} = -0.42 \text{ V}$ & $E^\circ_{\text{In}^{2+}/\text{In}^+} = -0.40 \text{ V}$.

Solution:



$$(3) = (2) - (1)$$

$$-FE^\circ = -2F(-0.42) + F(-0.40) ; E^\circ = -0.84 + 0.4 = -0.44 \text{ V}$$



$$-n F E^\circ = -RT \ln K ; \frac{0.59}{0.059} = \log K ; K = 10^{10}.$$

Example 12.

In the cell,



a current of 40 mA is flowing from tin to thallium electrode. An external battery of 1.2 V emf is connected to the cell so that its polarity is opposite to the natural polarity of the cell. If 0.38 g of thallium is deposited in one hour at 25°C, determine efficiency of thallium electrode. (Tl = 204)

Solution:

For reversible cells, if an external voltage of opposing polarity is attached to the cell, a current flowing from thallium to tin electrode is given as:

$$I = \frac{E - E_b}{R} \quad \dots(i)$$

ELECTROCHEMISTRY

where E = Applied voltage = 1.2 V, E_b = Back emf (i.e. reversible emf of cell) and R = Cell resistance.

Calculation of R :

For cell : $\text{Tl} | \text{Tl}^+ (0.1 \text{ M}) || \text{Sn}^{+2} (0.01\text{M}) | \text{Sn}$

$$E_b = E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{1} \log \frac{[\text{Tl}^+]}{[\text{Sn}^{+2}]^{1/2}}$$
$$= (0.340 - 0.140) - 0.059 \log \frac{0.1}{(0.01)^{1/2}}$$

$$\Rightarrow E_b = 0.2 \text{ V}$$

$$= \frac{E_{\text{cell}}}{R} \Rightarrow R = \frac{E_{\text{cell}}}{I} = \frac{0.2}{40 \times 10^{-3}}$$

$$R = 5 \Omega$$

Using the value in equation (i),

$$I = \frac{1.2 - 0.2}{5} = 0.2 \text{ A.}$$

Charge passed for 1 hour = $0.2 \times 3600 \text{ C} = 720 \text{ Coulomb}$

$$\text{Equivalent of thallium deposited} = \frac{720}{96500}$$

$$\text{Weight of thallium deposited} = \frac{720}{96500} \times 204 = 1.52 \text{ g.}$$

$$\text{Efficiency of thallium electrode} = \frac{0.38}{1.52} \times 100 = 25\%.$$