

Electrochemistry - I

(Electrochemical Cells)

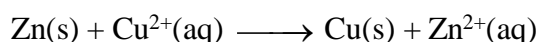
BASICS

Section - 1

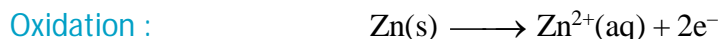
Electrochemistry deals with the inter-conversion of electrical energy and chemical energy. This part of Electrochemistry will deal with the conversion of chemical energy into electrical energy (Electrochemical Cells).

Electrochemical Cells :

Consider the following redox reaction :

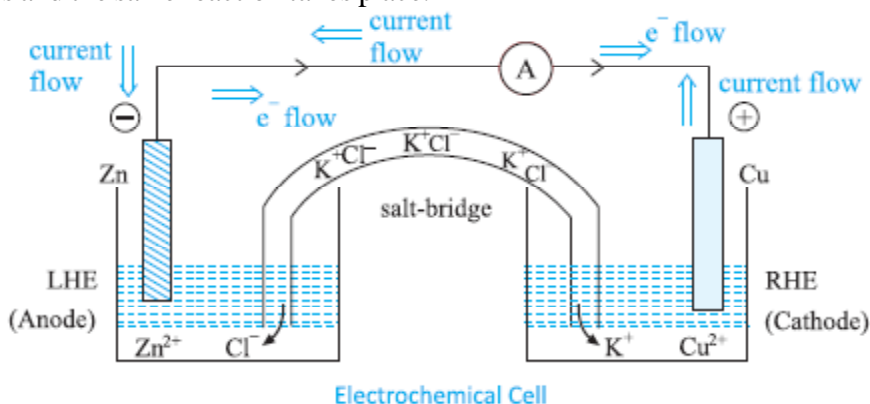


In the above reaction, Zn displaces copper ions (Cu^{2+}) from aqueous solution. This reaction can be achieved very easily in practice. Put a Zn rod into a solution of CuSO_4 (containing Cu^{2+} ions). It is observed that blue colour of CuSO_4 solution disappears after sometime. What happens actually? Zn loses $2e^-$ s per atom and Cu^{2+} ions in the solution accept them. Cu^{2+} ions from solution in this manner are deposited out in form of solid Cu and Zn goes into the solution as Zn^{2+} (colourless). The reaction can well be understood in terms of two half reactions :



- Note :**
- (i) In this reaction, Zn atoms are directly giving electrons to the copper ions.
 - (ii) Another aspect of this reaction is that it is an exothermic reaction. This means decrease in energy of the reacting system takes place which appears as heat.

Now, we can make the same reaction take place even if the copper ions and zinc rod are not in direct contact. If we put the Cu^{2+} ions and Zn rod in two separate containers and connect the two by a conducting metallic wire and introduce an inverted U shape instrument (called as **salt-bridge**), then electrons will still be transferred through the connecting wires. The electrons from Zn rod travel to Cu^{2+} ions through the connecting wires and the same reaction takes place.



In such an arrangement, the solution does not get heated up. The loss in energy now appears as the potential difference which is used to do the work in transferring the electrons from Zn to Cu^{2+} ions. Such an arrangement is called as **electrochemical cell** or Galvanic cell or Voltaic cell. The potential difference which drives the electrons from Zn to Cu^{2+} ions, is called as **electromotive force** (E.M.F.) of a cell.

An electrochemical cell (shown in diagram) mainly consists of two compartments : left hand electrode (LHE) and right hand electrode (RHE). In LHE, oxidation takes place and is called as anode. In RHE, reduction takes place and is called as cathode.

Anode is generally of that metal (or substance) which readily loses electrons (i.e., oxidised easily). A rod of that metal is prepared and put into one of its solution in LHE to get anode. In RHE, a rod of metal that loses electrons less easily as compared to the metal of LHE (in the diagram, Zn is taken in LHE and Cu is taken in RHE) is prepared and put into one of its solution to get cathode. LHE and RHE are also known as two half-cells. Now the electrons move from anode (LHE) to cathode (RHE) and hence a current flow is maintained in the external circuit.

The two half cells are connected by a inverted 'U' shaped tube called as **salt-bridge**. The salt-bridge contains solution of strong ionic salts like NaCl, NaNO_3 , KNO_3 and KCl, etc., (salts of most reactive alkali metals) soaked in a colloidal solution of agar-gel which allows only the movement of ions of salts, not water. The role of a salt-bridge is very important as it allows the continuous discharge of the cell (i.e., the supply of voltage from cell). The salt-bridge keeps the two solutions (i.e., in LHE and RHE) electrically neutral to each other. In the Zn- CuSO_4 cell, in left hand cell as Zn loses electrons, excess of positive charge (in form of Zn^{2+} ions) is collected near LHE and as Cu^{2+} ions gets discharged (accepting electrons from Zn) in right hand cell, excess of negative charge (in form of SO_4^{2-} ions) is accumulated near RHE. Now the salt-bridge provides positive charge to RHE (in form of K^+ , Na^+ ions) and negative charge to LHE (in form of Cl^- , NO_3^- etc) and thus bringing about the neutrality of two solutions. If this does not take place, a reverse potential difference is created in the two compartments and thus breaking the continuous supply of voltage (current), which is the purpose of the cell.

The efficiency of a cell is determined by the tendency of LHE to loose electrons and the tendency of RHE to accept electrons. A measure of cell efficiency is called as electromotive force (EMF) or the voltage or the difference in potentials of two electrodes. **EMF is defined as the difference in the potential across LHE and RHE due to which electrons from anode travel to cathode.**

EMF value of a cell made up of such two half-cells is a constant provided that the concentration of electrolyte, temperature and the pressure (if gases are involved) remains constant. It means that EMF values do change with concentration, temperature and pressure. EMF values are hence standardised at a temperature of 25°C (298 K), a pressure of 1 atm (if gases are involved) and at concentrations of 1.0 M for all solutes present as electrolytes. EMF value under these conditions is called as **standard EMF** and is denoted as E^0 .

EMF of a cell is measured as the difference of potentials of anode and cathode. The potential of a half-cell or EMF of a half-cell (i.e., a cathode or anode) is called as electrode potential. It is defined as the tendency of an electrode either to get oxidised or to get reduced i.e., to loose or gain electrons. electrode potentials are of two types :

Oxidation Potential :

It is the tendency of an electrode to get oxidised, i.e., to lose electrons.

Reduction Potential :

It is the tendency of an electrode to get reduced, i.e., to accept electrons.

Electrode potentials at standard conditions (1 atm, 298 K and 1.0 M) are called as **standard electrode potentials**.

- Note :**
- Anode is the negatively charged electrode in electrochemical cell and positively charged in electrolytic cell (to be discussed later) but it will always be the oxidation electrode (electrode on which oxidation takes place).
 - Cathode is the positively charged electrode in electrochemical cell and negatively charged in electrolytic cell (to be discussed later) but it will always be the reduction electrode (electrode on which reduction takes place).
 - We can also define cathode and anode electrodes as :

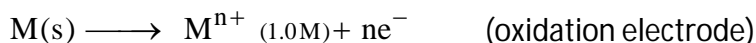
Anode : Electrode at which current enters.

Cathode : Electrode at which current leaves.
 - An important property for an ionic salt to act as a salt bridge is that ionic mobility (ease with which ions move in solution) of both cations and anion should be similar. Also, it should not react with the contents of either anode or cathode.

Types of Electrodes :**1. Metal in contact with its ions :**

Metal (M) in contact with its ion (M^{n+}) is represented as M/M^{n+} when it acts as oxidation electrode (anode) and M^{n+}/M when it acts as reduction electrode (cathode). Whether a given electrode acts as anode or cathode depends upon the other electrode with which it forms an electrochemical cell. So, it is necessary to define both oxidation and reduction potentials for an electrode.

M / M^{n+} is written as :



and its potential is called as oxidation potential and at standard state is represented as $E^0(M/M^{n+})$.

M^{n+} / M is written as :

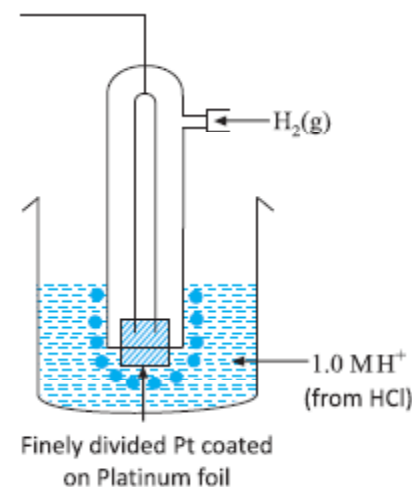


and its potential is called as reduction potential and at standard state is represented as $E^0(M^{n+}/M)$.

Note : Symbol “/” denotes the phase separation between the two substances.

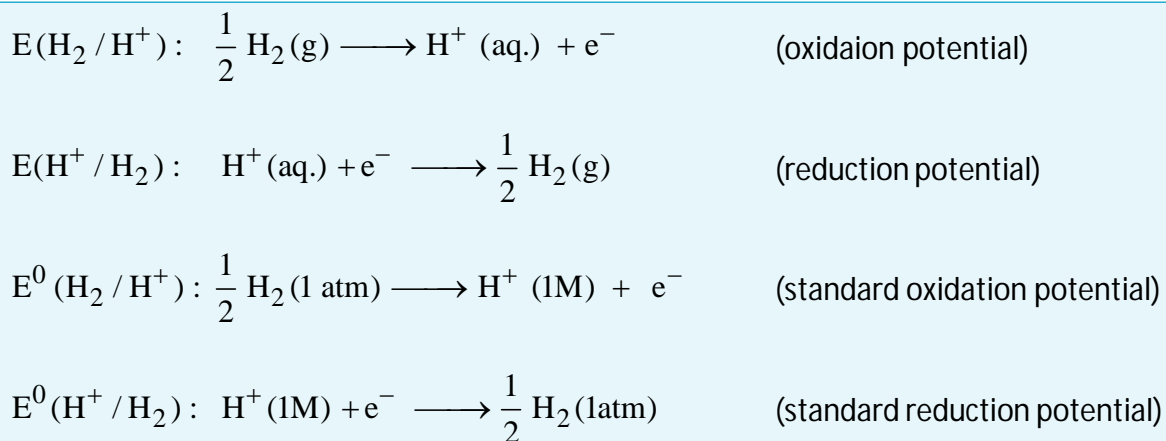
2. Gaseous electrode :

Gases like $\text{H}_2(\text{g})$ can loose electrons to form H^+ ions and hence can act as anode and also H^+ ion can add up electrons to form $\text{H}_2(\text{g})$ and hence can act as cathode. Similarly gases like $\text{Cl}_2(\text{g})$ can add electrons to form Cl^- ions and Cl^- ions can loose electrons to form $\text{Cl}_2(\text{g})$. The concentration of electrolytes is the value for $[\text{H}^+]$ ions and we take pressure of gas in atm. A hydrogen electrode is made by passing $\text{H}_2(\text{g})$ at 1 atm near an electric conductor made up of platinum (for conduction of e^- 's) dipped in an aqueous solution containing H^+ ions (generally HCl) as shown in figure.



Electrode representation : $\text{Pt}, \text{H}_2/\text{H}^+$
or $\text{H}^+/\text{H}_2, \text{Pt}$

Its electrode potentials are represents as :



Similarly, Cl_2/Cl^- electrode is prepared by passing Cl_2 gas and taking $\text{HCl}(\text{aq})$ or $\text{KCl}(\text{aq})$ as electrolyte.

3. Redox Electrodes :

In this type of electrode, an inert wire (e.g. Platinum) is placed in a solution (electrolyte) containing ions of an element in more than one oxidation states. e.g. Pt wire dipped in an electrolyte of Fe^{2+} and Fe^{3+} ions. The electrode (inert material wire) acts as a source / sink for electrons.

Electrode representation : $\text{Pt}/\text{Fe}^{3+}, \text{Fe}^{2+}$

Electrode reaction : As cathode : $\text{Fe}^{3+}(\text{aq.}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq.})$

As anode : $\text{Fe}^{2+}(\text{aq.}) \longrightarrow \text{Fe}^{3+}(\text{aq.}) + \text{e}^-$

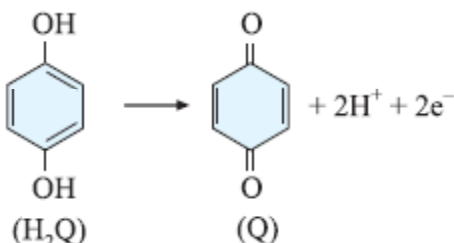
Another example : $\text{Pt}/\text{MnO}_4^-, \text{Mn}^{2+}, \text{H}^+$

As cathode : $\text{MnO}_4^-(\text{aq.}) + 8\text{H}^+(\text{aq.}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq.}) + 4\text{H}_2\text{O}(\ell)$

Redox electrodes can also be made using substances that exist in two different oxidation states. Quinhydrone is an equimolar mixture of benzoquinone (Q) and hydroquinone (H_2Q)

Electrode representation : $Pt/H_2Q, Q, H^+$

Electrode reaction : As anode :



Note : If two substances are in same solution then in the cell or electrode representation, they are separated by comma (',').

4. Calomel Electrode :

It consists of mercury covered with mercurous chloride (calomel) in contact with a solution of KCl :

Electrode representation : $Hg / Hg_2Cl_2 / Cl^-$

Electrode reaction : As cathode : $Hg_2Cl_2 (s) + 2e^- \rightleftharpoons 2Hg (\ell) + 2Cl^- (aq.)$

As anode : $2Hg (\ell) + 2Cl^- (aq.) \rightleftharpoons Hg_2Cl_2 (s) + 2e^-$

Most common calomel electrode is the saturated calomel electrode (SCE) in which the concentration of KCl is at its saturation (about 3.5 M). $E_{SCE}^0 \approx 0.24 \text{ V}$ (w.r.t. SHE)

5. Silver - Silver Chloride Electrode :

It consists of a pure silver wire in a solution of KCl saturated with solid silver chloride.

Electrode representation : $Ag/AgCl/Cl^-$

Electrode reaction : As cathode: $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq.)$ $E_{Reduction}^0 = 0.222 \text{ V}$

As anode : $Ag(s) + Cl^-(aq) \rightleftharpoons AgCl(s) + e^-$

If saturated KCl solution, $E_{reduction}^0$ become 0.197 V (w.r.t. SHE)

6. Mercury - Mercurous Sulphate Electrode :

In this electrode, the metal is mercury, the sparingly soluble compound is mercurous sulphate (Hg_2SO_4) and the source of SO_4^{2-} anions is H_2SO_4 or K_2SO_4 . It represented as :

Electrode representation : $\text{Hg} / \text{Hg}_2\text{SO}_4 / \text{SO}_4^{2-}$

Electrode reaction : As cathode : $\text{Hg}_2\text{SO}_4(\text{s}) + 2\text{e}^- \longrightarrow 2\text{Hg}(\ell) + \text{SO}_4^{2-}(\text{aq.})$

$$E_{\text{Reduction}}^0 = 0.616 \text{ V (w.r.t. SHE)}$$

As anode : $2\text{Hg}(\ell) + \text{SO}_4^{2-}(\text{aq.}) \longrightarrow \text{Hg}_2\text{SO}_4(\text{s}) + 2\text{e}^-$

Note: [1] Calomel electrodes, Silver - Silver Chloride electrodes and Mercury - Mercurous Sulphate electrodes are secondary reference electrodes. Silver - Silver electrodes and calomel electrodes are the most commonly used (practically) as a reference electrode rather than SHE / NHE due to practical difficulties associated with its (SHE) used and maintenance.

[2] The potential of metal - metal ion electrode and metal-metal insoluble salt-salt anion electrode is same while their standard potentials are not same. Standard potential are related by the following equation.

$$E_{\text{X}^-/\text{MX}/\text{M}}^0 = E_{\text{M}^+/\text{M}}^0 + \frac{2.303RT}{F} \log K_{\text{sp}}(\text{MX}) \quad [\text{Refer example - 4}]$$

7. Amalgam electrodes :

This is the modified version of Metal / Metal - ion electrode in which metal strip is replaced by metal amalgam.

e.g. $\text{Na (in Hg at } c_1 \text{ M)} / \text{Na}^+ (c_2 \text{ M})$

Electrode Potentials :

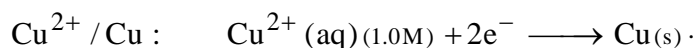
It is impossible to measure the absolute EMF's (electrode potentials) for half electrodes. This is done by arbitrarily selecting one half cell and setting its electrode potential as '0' volts. The electrode potentials of other half cells can then be measured by combining them with the standard reference electrodes in a cell arrangement.

The reference electrode against which all other half cells are generally measured is the hydrogen electrode half-cell at a concentration of H^+ ions equal to 1.0 M and $\text{H}_2(\text{g})$ at 1 atm pressure kept at 25°C (298 K). It is also known as SHE (standard hydrogen electrode) or NHE (normal hydrogen electrode). Its potential is taken as '0' volts.

$$E^0(\text{H}_2 / \text{H}^+) = 0 = E^0(\text{H}^+ / \text{H}_2)$$

Now other half cells can be divided into two categories : One which will act as anode and other which will act as cathode in a cell arrangement with SHE. Each type of cell arrangement will give an EMF value which will be actually the EMF value of known electrode as EMF value of SHE is 'zero' volts (whether SHE acts as anode or cathode).

For example : Cu electrode (half cell) acts as cathode with SHE, i.e., as :



The experimental measurement of EMF value for this cell arrangement give 0.34 volts. Since Cu electrode shows reduction with SHE, the given value of EMF represents the reduction potential of Cu half-cell.

$$E^0 (\text{Cu}^{2+} / \text{Cu}) = 0.34 \text{ volts}$$

The oxidation potential of Cu half-cell is just the negative of this value.

$$E^0 (\text{Cu}/\text{Cu}^{2+}) = -0.34 \text{ volts}$$

$$[\text{Note : } E_{\text{reduction}} = - E_{\text{oxidation}}]$$

Note : Reduction potential is taken as a standard potential i.e. if electrode potential is given (and nothing is mentioned whether it is oxidation or reduction), it is taken as the reduction potential, by default.

Rules for assigning sign (+ve or -ve) to electrode potentials :

1. The oxidation potential of half-cell (or an electrode) is given a positive sign if the given electrode acts as anode in a cell arrangement with SHE and its reduction potential is given a negative sign with the same magnitude. For example : oxidation potential of active metals like Na, Mg, Al, Zn, Fe etc. is given a positive sign.
2. The reduction potential of half-cell (or an electrode) is given positive sign if the given electrode acts as cathode in a cell arrangement with SHE and its oxidation potential is given a negative sign with the same magnitude.

For example : reduction potential of less active metals like Cu, Ag etc is given a positive sign.

Note : Electrode potential measured in this manner are called as standard hydrogen scale potentials.

Standard EMF of a Cell (E_{cell}^0) :

E_{cell}^0 can be defined in two ways as :

$$(i) \quad E_{\text{cell}}^0 = \left\{ \begin{array}{l} \text{standard reduction potential} \\ \text{of cathode} \end{array} - \begin{array}{l} \text{standard reduction potential} \\ \text{of anode} \end{array} \right\}$$

$$E_{\text{cell}}^0 = (E_{\text{reduction}}^0)_{\text{cathode}} - (E_{\text{reduction}}^0)_{\text{anode}}$$

$$(ii) \quad E_{\text{cell}}^0 = \left\{ \begin{array}{l} \text{standard oxidation potential} \\ \text{of anode} \end{array} - \begin{array}{l} \text{standard oxidation potential} \\ \text{of cathode} \end{array} \right\}$$

$$E_{\text{cell}}^0 = (E_{\text{oxidation}}^0)_{\text{anode}} - (E_{\text{oxidation}}^0)_{\text{cathode}}$$

Construction of a cell and writing cell representation :

It is clear that an electrochemical cell will be developed by two half-cells. If you arbitrarily select two half-cells for the purpose of constructing a galvanic cell, then always act in following manner :

Compare the reduction potentials of two electrodes. The electrode whose reduction potential has greater positive value is made the cathode and the other electrode is made the anode.

Note : (i) Constructing the cell in this manner will always give a positive EMF otherwise sometimes if an electrode is chosen wrongly, the EMF comes out to be negative. In that case, you should reverse the electrodes i.e., make anode the cathode and vice-versa.

(ii) It is now standardised to use the definition of EMF in terms of standard reduction potential.

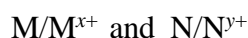
$$E_{\text{cell}}^0 = \left(E_{\text{reduction}}^0\right)_{\text{cathode}} - \left(E_{\text{reduction}}^0\right)_{\text{anode}}$$

Cell Representation :

The cell representation of a cell is written as :

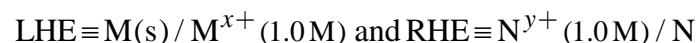


In general, if two electrodes at standard conditions are :



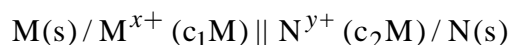
and let $E^0(\text{M}^{x+} / \text{M}) < E^0(\text{N}^{y+} / \text{N})$.

So M / M^{x+} is the anode and N / N^{y+} is the cathode. [\because Electrode having higher reduction potential has to be cathode.]

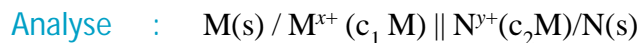


$\text{M(s)} / \text{M}^{x+} (1.0 \text{ M}) || \text{N}^{y+} (1.0 \text{ M}) / \text{N(s)}$ is the cell representation for a cell at standard state.

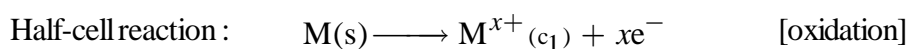
If the cell is not at standard state, then let c_1 be the concentration of anode and c_2 be the concentration of cathode. In that case, cell representation will be :



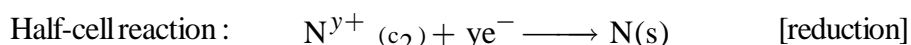
Analysis of a given cell representation :

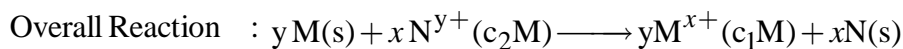


(i) Anode : $\text{M(s)} / \text{M}^{x+} (c_1 \text{ M})$



(ii) Cathode : $\text{N}^{y+} (c_2 \text{ M}) / \text{N(s)}$





[Balance the number of e^- s transferred at Cathode and Anode]

Electrochemical Series :

In this series, the standard reduction potential measured on hydrogen scale are arranged in increasing order.

Half Cell	Electrode reaction	Reduction Potentials (volts)
Li^+ / Li	$Li^+ (aq.) + e^- \longrightarrow Li (s)$	- 3.04
K^+ / K	$K^+ (aq.) + e^- \longrightarrow K(s)$	- 2.93
Ca^{2+}/Ca	$Ca^{2+}(aq.) + 2e^- \longrightarrow Ca(s)$	- 2.87
Na^+ / Na	$Na^+ (aq.) + e^- \longrightarrow Na(s)$	- 2.71
Mg^{2+} / Mg	$Mg^{2+} (aq.) + 2e^- \longrightarrow Mg(s)$	- 2.37
$Pt, H_2 / H^-$	$H_2 (g) + 2e^- \longrightarrow 2H^-(aq.)$	- 2.25
Al^{3+} / Al	$Al^{3+} (aq.) + 3e^- \longrightarrow Al(s)$	- 1.66
Mn^{2+}/Mn	$Mn^{2+} (aq.) + 2e^- \longrightarrow Mn(s)$	- 0.91
$OH^- / H_2, Pt$	$2H_2O (\ell) + 2e^- \longrightarrow H_2(g) + 2 OH^-(aq.)$	- 0.83
Zn^{2+} / Zn	$Zn^{2+} (aq.) + 2e^- \longrightarrow Zn(s)$	- 0.76
Cr^{3+} / Cr	$Cr^{3+} (aq.) + 3e^- \longrightarrow Cr(s)$	- 0.74
Fe^{2+} / Fe	$Fe^{2+} (aq.) + 2e^- \longrightarrow Fe(s)$	- 0.44
$Cr^{3+} / Cr^{2+}, Pt$	$Cr^{3+} (aq.) + e^- \longrightarrow Cr^{2+}(aq.)$	- 0.41
Cd^{2+} / Cd	$Cd^{2+} (aq.) + 2e^- \longrightarrow Cd(s)$	- 0.40
Co^{2+} / Co	$Co^{2+} (aq.) + 2e^- \longrightarrow Co(s)$	- 0.28
Ni^{2+}/Ni	$Ni^{2+} (aq.) + 2e^- \longrightarrow Ni(s)$	- 0.25
$I^- / AgI / Ag$	$AgI(s) + e^- \longrightarrow Ag(s) + I^-(aq.)$	- 0.15

Oxidising Power decreases

Reducing Power increases

$\text{Sn}^{2+} / \text{Sn}$	$\text{Sn}^{2+} (\text{aq.}) + 2\text{e}^{-} \longrightarrow \text{Sn}(\text{s})$	-0.14
$\text{Pb}^{2+} / \text{Pb}$	$\text{Pb}^{2+} (\text{aq.}) + 2\text{e}^{-} \longrightarrow \text{Pb}(\text{s})$	-0.13
$\text{Fe}^{3+} / \text{Fe}$	$\text{Fe}^{3+} (\text{aq.}) + 3\text{e}^{-} \longrightarrow \text{Fe}(\text{s})$	-0.04
$\text{H}^{+} / \text{H}_2, \text{Pt}$	$2\text{H}^{+} (\text{aq.}) + 2\text{e}^{-} \longrightarrow \text{H}_2(\text{g})$	0.00
$\text{Br}^{-} / \text{AgBr} / \text{Ag}$	$\text{AgBr}(\text{s}) + \text{e}^{-} \longrightarrow \text{Ag}(\text{s}) + \text{Br}^{-}(\text{aq.})$	0.10
$\text{Cu}^{2+} / \text{Cu}^{+}, \text{Pt}$	$\text{Cu}^{2+} (\text{aq.}) + \text{e}^{-} \longrightarrow \text{Cu}^{+}(\text{aq.})$	0.16
$\text{Sn}^{4+} / \text{Sn}^{2+}, \text{Pt}$	$\text{Sn}^{4+} (\text{aq.}) + 2\text{e}^{-} \longrightarrow \text{Sn}^{2+}(\text{aq.})$	0.15
$\text{SO}_4^{2-} / \text{H}_2\text{SO}_3$	$\text{SO}_4^{2-} (\text{aq.}) + 4\text{H}^{+} + 2\text{e}^{-} \longrightarrow \text{H}_2\text{SO}_3 (\text{aq.}) + \text{H}_2\text{O}(\ell)$	0.17
$\text{Cl}^{-} / \text{AgCl} / \text{Ag}$	$\text{AgCl}(\text{s}) + \text{e}^{-} \longrightarrow \text{Ag}(\text{s}) + \text{Cl}^{-} (\text{aq.})$	0.22
$\text{Cl}^{-} / \text{Hg}_2\text{Cl}_2 / \text{Hg}(\text{Pt})$	$\text{Hg}_2\text{Cl}_2 (\text{s}) + 2\text{e}^{-} \longrightarrow 2\text{Hg}(\ell) + 2\text{Cl}^{-} (\text{aq.})$	0.27
$\text{Cu}^{2+} / \text{Cu}$	$\text{Cu}^{2+} (\text{aq.}) + 2\text{e}^{-} \longrightarrow \text{Cu}(\text{s})$	0.34
$\text{Pt}, \text{O}_2 / \text{OH}^{-}$	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\ell) + 4\text{e}^{-} \longrightarrow 4\text{OH}^{-}(\text{aq.})$	0.40
$\text{Cu}^{+} / \text{Cu}$	$\text{Cu}^{+} (\text{aq.}) + \text{e}^{-} \longrightarrow \text{Cu}(\text{s})$	0.52
$\text{I}_2 / \text{I}^{-}, \text{Pt}$	$1/2\text{I}_2(\text{s}) + \text{e}^{-} \longrightarrow \text{I}^{-} (\text{aq.})$	0.54
$\text{Pt}, \text{O}_2 / \text{H}_2\text{O}_2$	$\text{O}_2(\text{g}) + 2\text{H}^{+} (\text{aq.}) + 2\text{e}^{-} \longrightarrow \text{H}_2\text{O}_2 (\text{aq.})$	0.68
$\text{Fe}^{3+} / \text{Fe}^{2+}, \text{Pt}$	$\text{Fe}^{3+} (\text{aq.}) + \text{e}^{-} \longrightarrow \text{Fe}^{2+} (\text{aq.})$	0.77
$\text{Hg}_2^{2+} / \text{Hg}(\text{Pt})$	$1/2\text{Hg}_2^{2+} (\text{aq.}) + \text{e}^{-} \longrightarrow \text{Hg}(\text{s})$	0.79
$\text{Ag}^{+} / \text{Ag}$	$\text{Ag}^{+} (\text{aq.}) + \text{e}^{-} \longrightarrow \text{Ag}(\text{s})$	0.80
$\text{Hg}_2^{2+} / \text{Hg}_2^{2+}$	$2\text{Hg}_2^{2+} (\text{aq.}) + 2\text{e}^{-} \longrightarrow \text{Hg}_2^{2+}(\text{aq.})$	0.92
$\text{NO}_3^{-} / \text{NO}, \text{Pt}$	$\text{NO}_3^{-} + 4\text{H}(\text{aq.}) + 3\text{e}^{-} \longrightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\ell)$	0.97
$\text{Pt}, \text{Br}_2 / \text{Br}^{-}$	$\text{Br}_2 (\ell) + 2\text{e}^{-} \longrightarrow 2\text{Br}^{-}(\text{aq.})$	1.09
$\text{MnO}_2 / \text{Mn}^{2+}$	$\text{MnO}_2(\text{s}) + 4\text{H}^{+}(\text{aq.}) + 2\text{e}^{-} \longrightarrow \text{Mn}^{2+}(\text{aq.}) + 2\text{H}_2\text{O}(\ell)$	1.23

Oxidising Power decreases

Reducing Power increases

$\text{H}^+ / \text{O}_2 / \text{Pt}$	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq.}) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}(\ell)$	1.23
$\text{Cr}_2\text{O}_7^{2-} / \text{Cr}^{3+}$	$\text{Cr}_2\text{O}_7^{2-}(\text{aq.}) + 14\text{H}^+(\text{aq.}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq.}) + 7\text{H}_2\text{O}(\ell)$	1.33
$\text{Cl}_2 / \text{Cl}^-$	$1/2 \text{Cl}_2(\text{g}) + \text{e}^- \longrightarrow \text{Cl}^-(\text{aq.})$	1.36
$\text{Au}^{3+} / \text{Au}$	$\text{Au}^{3+}(\text{aq.}) + 3\text{e}^- \longrightarrow \text{Au}(\text{s})$	1.40
$\text{MnO}_4^- / \text{Mn}^{2+}, \text{H}^+ / \text{Pt}$	$\text{MnO}_4^-(\text{aq.}) + 8\text{H}^+(\text{aq.}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq.}) + 4\text{H}_2\text{O}(\ell)$	1.51
$\text{Ce}^{4+} / \text{Ce}^{3+}, \text{Pt}$	$\text{Ce}^{4+} + \text{e}^- \longrightarrow \text{Ce}^{3+}(\text{aq.})$	1.72
$\text{H}_2\text{O}_2 / \text{H}_2\text{O}$	$\text{H}_2\text{O}_2(\ell) + 2\text{H}^+(\text{aq.}) + 2\text{e}^- \longrightarrow 2\text{H}_2\text{O}(\ell)$	1.78
$\text{Co}^{3+} / \text{Co}^{2+}, \text{Pt}$	$\text{Co}^{3+}(\text{aq.}) + \text{e}^- \longrightarrow \text{Co}^{2+}(\text{aq.})$	1.81
O_3 / O_2	$\text{O}_3(\text{g}) + 2\text{H}^+(\text{aq.}) + 2\text{e}^- \longrightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\ell)$	2.07
$\text{Pt}, \text{F}_2 / \text{F}^-$	$\text{F}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{F}^-(\text{aq.})$	2.87

- Lower the reduction potential, higher will be the tendency of forming positive ions. This is related to reactivity of metals. The order of reactivity of metals is : $\text{Li} > \text{K} > \text{Ca} > \text{Na} > \text{Mg} > \text{Al}$
- In this series oxidising character decreases and reducing character increases, e.g., the reducing character follow the order : $\text{Na} > \text{Mg} > \text{Zn} > \text{Fe} > \text{Ni} > \text{Cu} > \text{Ag}$

Illustration - 1

(a) If $E^0(\text{Ag}^+/\text{Ag}) = 0.8 \text{ V}$ and $E^0(\text{H}^+/\text{H}_2) = 0 \text{ V}$, in a cell arrangement using these two electrodes, which will act as anode and cathode? Also find the E^0_{cell}

(b) Construct a cell using given electrodes at 25°C . Find its standard EMF.

$$E^0(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V and } E^0(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$$

SOLUTION :

- (a) Note that reduction potentials are given. Comparing the two values, clearly

$$E^0(\text{H}^+/\text{H}_2) < E^0(\text{Ag}^+/\text{Ag})$$

⇒ Hydrogen electrode will act as anode and silver electrode will act as cathode. The cell representation of the cell will be :



$$E^0_{\text{cell}} = \left(E^0_{\text{reduction}}\right)_{\text{cathode}} - \left(E^0_{\text{reduction}}\right)_{\text{anode}}$$

$$E^0_{\text{cell}} = 0.8 - 0 = 0.8 \text{ V}$$

- (b) Note that $E^0(\text{Zn}^{2+}/\text{Zn}) < E^0(\text{Cu}^{2+}/\text{Cu})$

⇒ Zinc electrode will act as anode and Copper electrode will act as cathode.

The cell representation of the cell is :



$$E_{\text{cell}}^0 = 0.34 - (-0.76) = 1.1 \text{ V}$$

$$E_{\text{cell}}^0 = \left(E_{\text{reduction}}^0\right)_{\text{cathode}} - \left(E_{\text{reduction}}^0\right)_{\text{anode}}$$

Illustration - 2

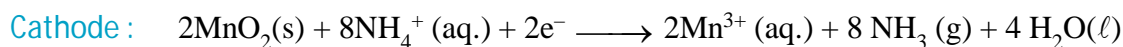
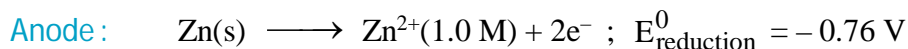
The dry cell (flash light battery) used to power flashlights, clocks, radios etc . follows



(a) Write anode and cathode reactions.

(b) Calculate the E_{cell}^0 of the dry cell if the electrode potential of cathode ($E_{\text{reduction}}^0$) varies between + 0.49 V and + 0.74 V and of anode ($E_{\text{reduction}}^0$) is -0.76 V.

SOLUTION :



$E_{\text{reduction}}^0$ of cathode varies between + 0.49 to +0.74 V

For $E_{\text{cathode}}^0 = 0.49 \text{ V}$

$$E_{\text{cell}}^0 = \left(E_{\text{reduction}}^0\right)_{\text{cathode}} - \left(E_{\text{reduction}}^0\right)_{\text{anode}} = 0.49 - (-0.76) = 1.25 \text{ V}$$

For $E_{\text{cathode}}^0 = 0.74 \text{ V}$

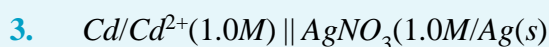
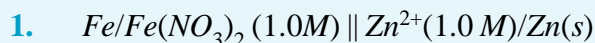
$$E_{\text{cell}}^0 = 0.74 - (-0.76) = 1.50 \text{ V}$$

$$\Rightarrow E_{\text{cell}}^0 \text{ cell varies between } 1.25 \text{ V to } 1.50 \text{ V.}$$

Note : A given electrode potential is to be taken as Reduction Potential. [as reduction potential is to be considered, “by default”.]

Illustration - 3 For each of the following cells :(a) Write the equation for cell process. (b) Find E^0 for each cell.

(c) Explain the significance of any negative answers in part (b).

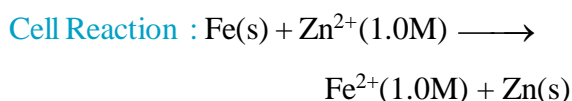
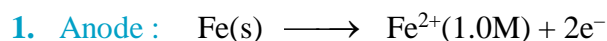


$$E^0(Fe) = -0.41 V ; \quad E^0(Cd) = -0.40 V ; \quad E^0(Zn) = -0.76 V$$

$$E^0(Cl^- / Cl_2) = -1.36V ; \quad E^0(Ag) = +0.80V ; \quad E^0(Hg / Hg_2Cl_2) = +0.27V$$

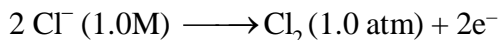
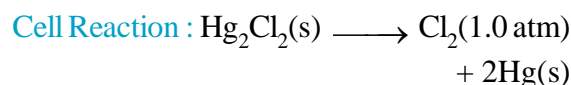
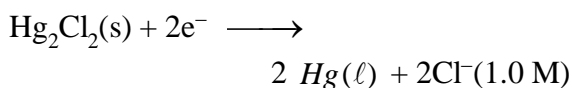
SOLUTION :

Use: $E_{cell}^0 = \left(E_{reduction}^0 \right)_{cathode} - \left(E_{reduction}^0 \right)_{anode}$



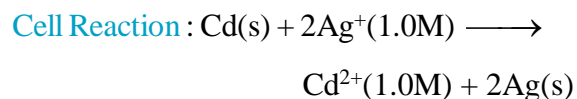
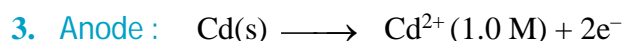
$$E_{cell}^0 = -0.76 - (-0.41) = -0.35 V$$

Negative EMF value means that the cell will not work in the manner shown i.e., Fe as anode and Zn as cathode. So reversing (interchanging) the anode and cathode i.e., making Zn as anode and Fe as cathode, can make the cell work.

2. **Anode :****Cathode :**

$$E_{cell}^0 = 0.27 - (1.36) = -1.36 V$$

Negative EMF value means that the cell will not work in the manner shown i.e., Cl^-/Cl_2 as anode and Hg_2Cl_2 as cathode. So reversing (interchanging) the anode and cathode i.e., making Hg_2Cl_2 (i.e., Hg/Hg_2Cl_2) as anode and Cl_2/Cl^- as cathode can make the cell work.

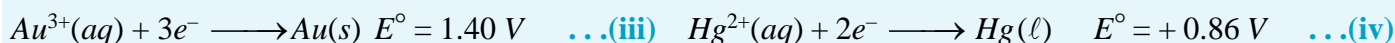


$$E_{cell}^0 = 0.8 - (-0.4) = 1.20 V$$

EMF value is positive, hence cell will function with Cd as anode and Ag as Cathode.

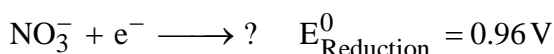
Illustration - 4

For the reduction of NO_3^- ion in an aqueous solution, E° is +0.96 V. Values of E° for some metal ions are given below :



The pair(s) of metals that is oxidized by NO_3^- in aqueous solution is (are) :

- (A) V and Hg (B) Hg and Fe (C) Fe and Au (D) Fe and V

SOLUTION : (ABD)

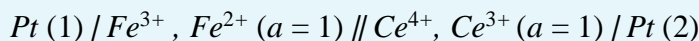
Check the reduction potential of the given metals and compare it with that of NO_3^- reduction.

$E_{\text{Reduction}}^0$ of (i), (ii) and (iv) is lesser than $E_{\text{Reduction}}^0$ for NO_3^- .

So, NO_3^- will be able to oxidise V, Fe and Hg. So, pairs are V and Fe, V and Hg, Fe and Hg.

Illustration - 5

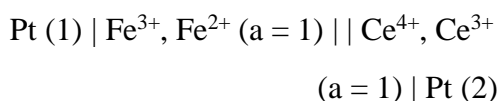
The following electrochemical cell has been set up :



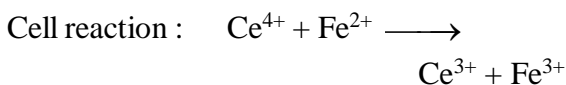
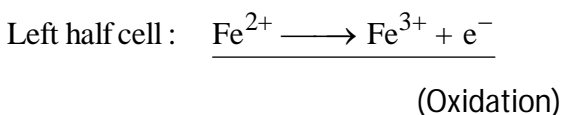
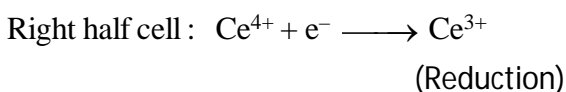
If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time ? ($E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 = 1.61 \text{ V}$; $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.77 \text{ V}$)

SOLUTION :

For the electrochemical cell :



The electrode reactions are as follows.



The net cell potential is :

$$E_{\text{cell}}^0 = (E_{\text{reduction}}^0)_{\text{cathode}} - (E_{\text{reduction}}^0)_{\text{anode}} \\ = 1.61 \text{ V} - 0.77 \text{ V} = 0.84 \text{ V}$$

Since E_{cell}^0 is positive, the cell reaction will be spontaneous.

The current in the circuit will flow from Pt (2) (which serves as cathode) to Pt (1), which serves as anode. With the passage of time, EMF of the cell will decrease and so is the current in the circuit.

Note : Current in an electrochemical cell flows from cathode to anode whereas the electron flow from anode to cathode.

NERNST EQUATION

Section - 2

Effect of concentration on EMF of half-cells and on EMF of a cell

(a) For an electrode $M(s)/M^{n+}(c M)$ c : concentration of electrolyte

- (i) If it acts as oxidation electrode (i.e., as anode) : $M(s) \longrightarrow M^{n+}(c M) + ne^{-}$, then its oxidation potential $E(M/M^{n+})$ at 25°C is given as :

$$E(M/M^{n+}) = E^{\circ}(M/M^{n+}) - \frac{2.303 RT}{nF} \log_{10} Q_{\text{oxidation}}$$

$$E(M/M^{n+}) = E^{\circ}(M/M^{n+}) - \frac{0.059}{n} \log_{10} Q_{\text{oxidation}} \quad (\text{at } 25^{\circ}\text{C}) \quad \dots (i)$$

(n : number of $e(s)$ transferred & F = charge on 1 mole electrons = 96500 C)

where $Q_{\text{oxidation}}$: reaction coefficient of oxidation half reaction and is given as :

$$Q_{\text{oxidation}} = \frac{a_{M^{n+}}}{a_M} = \frac{[M^{n+}]}{[M]} \quad \text{where } [] \text{ denotes concentration ; 'a' denotes activity}$$

- (ii) If it acts as reduction electrode (i.e., as cathode) : $M^{n+}(c M) + ne^{-} \longrightarrow M(s)$, then its reduction potential $E(M^{n+}/M)$ at 25°C is given as :

$$E(M^{n+}/M) = E^{\circ}(M^{n+}/M) - \frac{2.303 RT}{nF} \log_{10} Q_{\text{oxidation}}$$

$$E(M^{n+}/M) = E^{\circ}(M^{n+}/M) - \frac{0.059}{n} \log_{10} Q_{\text{reduction}} \quad (\text{at } 25^{\circ}\text{C}) \quad \dots (ii)$$

where $Q_{\text{reduction}}$: reaction coefficient of reduction half reaction and is given as :

$$Q_{\text{reduction}} = \frac{a_M}{a_{M^{n+}}} = \frac{[M]}{[M^{n+}]}$$

We can see that $E(M^{n+}/M) = -E(M/M^{n+})$

(b) For EMF of the cell : $M(s)/M^{x+}(c_1 M) || N^{y+}(c_2 M) / N(s)$

(i) Anode : $M(s) \longrightarrow M^{x+}(c_1 M) + xe^-$ [oxidation]

(ii) Cathode : $N^{y+}(c_2 M) + ye^- \longrightarrow N(s)$ [reduction]

Overall reaction : $yM(s) + xN^{y+}(c_2 M) \longrightarrow yM^{x+}(c_1 M) + xN(s)$

EMF (E_{cell}) of such a cell at 25°C is given is :

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n_{\text{cell}}} \log_{10} Q_{\text{cell}} \quad \dots \text{(iii)}$$

where Q_{cell} : reaction coefficient of overall reaction ; E_{cell}^0 : standard E.M.F. of the cell ;

n_{cell} : Number of e^- transfer in the cell reaction.

$$Q_{\text{cell}} = \frac{(a_{M^{x+}})^y \times (a_N)^x}{(a_M)^y \times (a_{N^{y+}})^x} = \frac{[M^{x+}]^y}{[N^{y+}]^x} \quad (a_N = a_M = 1 \text{ for solids})$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n_{\text{cell}}} \log_{10} \frac{[M^{x+}]^y}{[N^{y+}]^x}$$

Illustration - 6

Find the reduction potentials of the following electrodes :

(a) $Pt, H_2(1 \text{ atm}) / HCl(0.1 M),$

(b) $Pt, H_2(2 \text{ atm}) / H_2SO_4(0.01 M)$

SOLUTION :

(a) Writing half-cell reaction : $\frac{1}{2} H_2(1 \text{ atm}) \longrightarrow H^+(0.1M) + e^-$

$$\Rightarrow E(H_2/H^+) = E^0(H_2/H^+) - \frac{0.059}{1} \log_{10} \frac{[H^+]}{(p_{H_2})^{1/2}}$$

$$\Rightarrow E(H_2/H^+) = E^0(H_2/H^+) - \frac{0.059}{1} \log_{10} \frac{[0.1]}{(1)^{1/2}}$$

$$\Rightarrow E(H_2/H^+) = 0.059 \text{ V} \quad [\because E^0(H_2/H^+) = 0 \text{ V}] \quad \Rightarrow E(H^+/H_2) = -0.059 \text{ V}$$

Note : In the expression of Q , we put the value of partial pressure (for gases) in atmospheric units (atm.).

(b) Writing the half-cell reaction : $\frac{1}{2} \text{H}_2 (2 \text{ atm}) \longrightarrow \text{H}^+ (0.02 \text{ M}) + \text{e}^-$

$$\Rightarrow E(\text{H}_2/\text{H}^+) = E^0(\text{H}_2/\text{H}^+) - \frac{0.059}{1} \log_{10} \frac{[\text{H}^+]}{\sqrt{P_{\text{H}_2}}}$$

$$\Rightarrow E(\text{H}_2/\text{H}^+) = 0 - \frac{0.059}{1} \log_{10} \frac{0.02}{\sqrt{2}} \quad [\because E^0(\text{H}_2/\text{H}^+) = 0 \text{ V}]$$

$$\Rightarrow E(\text{H}_2/\text{H}^+) = 0.109 \text{ Volts} \quad \Rightarrow E^0(\text{H}^+/\text{H}_2) = -0.109 \text{ V}$$

Illustration - 7 For the cell : $\text{Zn(s)}/\text{Zn}^{2+}(x \text{ M}) \parallel \text{Ag}^+(y \text{ M})/\text{Ag(s)}$

(a) Write Nernst Equation to see how E_{cell} vary with concentration of Zn^{2+} and Ag^+ ions.

(b) Find E_{cell} for $[\text{Zn}^{2+}] = 0.01 \text{ M}$ and $[\text{Ag}^+] = 0.05 \text{ M}$. [$E^0(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$ $E^0(\text{Ag}^+/\text{Ag}) = 0.80$]

(c) For what value of Q will the cell EMF be :

(i) 0.97 V (ii) 0.0V

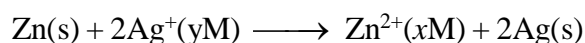
SOLUTION :

First writing the two half-reactions :

(a) Anode : $\text{Zn(s)} \longrightarrow \text{Zn}^{2+}(x \text{ M}) + 2\text{e}^-$

Cathode : $\text{Ag}^+(y \text{ M}) + \text{e}^- \longrightarrow \text{Ag(s)}$

The cell reaction is :



$$E_{\text{cell}}^0 = \left(E_{\text{reduction}}^0\right)_{\text{cathode}} - \left(E_{\text{reduction}}^0\right)_{\text{anode}} = 0.80 - (-0.76) = 1.56 \text{ V}$$

Now writing Nernst Equation :

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n_{\text{cell}}} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \quad (\text{Activity of Ag(s) and Zn(s)} = 1)$$

$$\Rightarrow E_{\text{cell}}^0 = E_{\text{cell}} - \frac{0.059}{n_{\text{cell}}} \log_{10} [\text{Zn}^{2+}] + \frac{0.118}{n_{\text{cell}}} \log_{10} [\text{Ag}^+]$$

$$\Rightarrow E_{\text{cell}}^0 \text{ will decrease when } [\text{Zn}^{2+}] \text{ increases and } [\text{Ag}^+] \text{ decreases.}$$

(b) If $[\text{Zn}^{2+}] = 0.01 \text{ M}$ and $[\text{Ag}^+] = 0.05 \text{ M}$

$$\Rightarrow E_{\text{cell}} = 1.56 - \frac{0.059}{2} \log \frac{0.01}{(0.05)^2} = 1.54 \text{ V}$$

(c) (i) $E_{\text{cell}} = 0.97 \text{ V}$; $E_{\text{cell}}^0 = 1.56 \text{ V}$

$$\Rightarrow E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n_{\text{cell}}} \log_{10} Q_{\text{cell}} \quad \Rightarrow \quad 0.97 = 1.56 - \frac{0.059}{2} \log_{10} Q_{\text{cell}}$$

$$\Rightarrow \log_{10} Q_{\text{cell}} = \frac{2 \times 0.59}{0.059} = 20 \quad \Rightarrow \quad Q_{\text{cell}} = 10^{20}$$

(ii) $E_{\text{cell}} = 0.0 \text{ V}$; $E_{\text{cell}}^0 = 1.56 \text{ V}$

$$\Rightarrow E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n_{\text{cell}}} \log_{10} Q_{\text{cell}} \quad \Rightarrow \quad 0.0 = E_{\text{cell}}^0 - \frac{0.059}{2} \log_{10} Q_{\text{cell}}$$

$$\Rightarrow \log_{10} Q_{\text{cell}} = \frac{2 \times 1.56}{0.059} = 52.88 \approx 53 - 0.15 = \log_{10} 10^{53} + \log \frac{1}{\sqrt{2}} = \log_{10} \left(\frac{1}{\sqrt{2}} \times 10^{53} \right)$$

$$\Rightarrow Q_{\text{cell}} = 7.07 \times 10^{52} \quad [\text{approximately}]$$

Illustration - 8

The solution of CuSO_4 in which copper rod is immersed is diluted to 10 times, the reduction electrode potential will :

(A) Increase by 0.030 V (B) Decrease by 0.030 V

(C) Increase by 0.059 V (D) Decrease by 0.059 V

SOLUTION : (B)



$$\text{Initially:} \quad \left(E_{\text{Cu}^{2+}/\text{Cu}} \right)_1 = E_{\text{Cu}^{2+}/\text{Cu}}^0 - \frac{0.059}{2} \log_{10} \left(\frac{1}{[\text{Cu}^{2+}]_1} \right) \quad (\text{Using Nernst equation.})$$

$$\text{After Dilution:} \quad \left(E_{\text{Cu}^{2+}/\text{Cu}} \right)_2 = E_{\text{Cu}^{2+}/\text{Cu}}^0 - \frac{0.059}{2} \log_{10} \left(\frac{1}{[\text{Cu}^{2+}]_2} \right) \quad (\text{Using Nernst equation.})$$

$$\left(E_{\text{Cu}^{2+}/\text{Cu}}\right)_2 - \left(E_{\text{Cu}^{2+}/\text{Cu}}\right)_1 = \frac{0.059}{2} \log_{10} \left(\frac{[\text{Cu}^{2+}]_2}{[\text{Cu}^{2+}]_1} \right) = \frac{0.059}{2} \log_{10} \left(\frac{1}{10} \right) = -0.03 \text{ V}$$

⇒ Reduction potential of the electrode decreases by 0.03 V

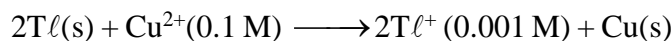
Illustration - 9

For the cell : $\text{Tl} \mid \text{Tl}^+ (0.001\text{M}) \parallel \text{Cu}^{2+} (0.1\text{M}) \mid \text{Cu}$, E_{cell} can be increased by :

(A) increasing $[\text{Cu}^{2+}]$ (B) increasing $[\text{Tl}^+]$ (C) decreasing $[\text{Cu}^{2+}]$ (D) decreasing $[\text{Tl}^+]$

SOLUTION : (AD)

First write the cell reaction :



Using : $E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n_{\text{cell}}} \log_{10} Q_{\text{cell}}$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^0 - \frac{0.059}{2} \log_{10} \left(\frac{[\text{Tl}^+]^2}{[\text{Cu}^{2+}]} \right) \\ &= E_{\text{cell}}^0 - 0.059 \log_{10} [\text{Tl}^+] + \frac{0.059}{2} \log_{10} [\text{Cu}^{2+}] \end{aligned}$$

⇒ E_{cell} can be increased by decreasing $[\text{Tl}^+]$ or increasing $[\text{Cu}^{2+}]$

Condition of equilibrium ($E_{\text{cell}} = 0.0 \text{ V}$)

When $E_{\text{cell}} = 0.0 \text{ V}$, i.e., no potential difference is obtained between the terminals of cell (battery), the cell reaction in such a state is said to be in equilibrium. So in such cases, when $E_{\text{cell}} = 0$, $Q = K_{\text{eq}}$ = equilibrium constant.

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^0 - \frac{0.059}{n_{\text{cell}}} \log_{10} Q_{\text{cell}} \\ \Rightarrow 0.0 &= E_{\text{cell}}^0 - \frac{0.059}{n_{\text{cell}}} \log_{10} K_{\text{eq}} \\ \Rightarrow E_{\text{cell}}^0 &= \frac{0.059}{n_{\text{cell}}} \log_{10} K_{\text{eq}} = \frac{2.303 RT}{n_{\text{cell}} F} \log_{10} K_{\text{eq}} = \frac{RT}{n_{\text{cell}} F} \ln K_{\text{eq}} \end{aligned}$$

Note : Refer to the illustration-7, part (c), when $E_{\text{cell}} = 0$ volts.

$$\Rightarrow Q_{\text{cell}} = K_{\text{eq}} = 7.07 \times 10^{52}$$

Illustration - 10 If excess of Zn is added to 1.0 M solution of CuSO_4 , find the concentration of Cu^{2+} ions at equilibrium. The standard reduction potentials of Zn and Cu at 25°C are -0.76 V and $+0.34\text{ V}$.

SOLUTION :

We know that at equilibrium, $E_{\text{cell}} = 0.0\text{ V}$ and the reaction coefficient $Q = K_{\text{eq}}$. So first let us calculate the value of K_{eq} as follows :

$$E^0 = \left(E_{\text{reduction}}^0\right)_{\text{Cathode}} - \left(E_{\text{reduction}}^0\right)_{\text{Anode}}$$

$$E^0 = 0.34 - (-0.76) = 1.10\text{ V}$$

$$\text{Now using } E_{\text{cell}}^0 = \frac{0.059}{n_{\text{cell}}} \log_{10} K_{\text{eq}}$$

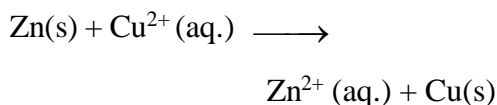
[At equilibrium]

$$\Rightarrow \log_{10} K_{\text{eq}} = \frac{E_{\text{cell}}^0 \times n_{\text{cell}}}{0.059} = \frac{1.10 \times 2}{0.059}$$

$$= 37.288 \approx 37.30 = \log_{10} 10^{37} + \log_{10} 2$$

$$\Rightarrow K_{\text{eq}} \approx 2.0 \times 10^{37}$$

Now writing the reaction at equilibrium :



Let x be the concentration of Cu^{2+} at equilibrium.

Zn	Cu^{2+}	Zn^{2+}	Cu	
Initial conc.	∞	1.0	0	0

Final conc.	∞	$1 - x$	x	x
-------------	----------	---------	-----	-----

(Zn is in excess, so $[\text{Zn}] = \infty$)

$$K_{\text{eq}} = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{x}{1-x} \approx \frac{1}{1-x} [\because x \approx 1]$$

(Look at the value of equilibrium constant. Too high)

$$\Rightarrow 1 - x = \frac{1}{K_{\text{eq}}} = \frac{1}{2.0 \times 10^{37}} = 5 \times 10^{-38}\text{ M}$$

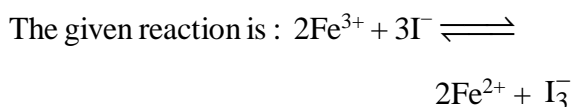
$$\Rightarrow [\text{Cu}^{2+}]_{\text{eq}} = 1 - x = 5 \times 10^{-38}\text{ M}$$

Note that $a_{\text{Zn(s)}} = a_{\text{Cu(s)}} = 1$

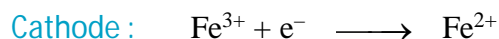
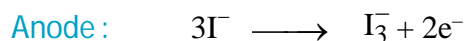
Illustration - 11 Calculate the equilibrium constant for the reaction: $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$. The standard reduction potentials in acidic conditions are 0.78 V and 0.54 V respectively for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and I_3^-/I^- couples.

$$[\text{Use : } 2.303 \frac{RT}{F} = 0.06 \text{ at } 298\text{ K}]$$

SOLUTION :



The electrodes reactions are :



$$\Rightarrow E_{\text{cell}}^0 = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - E_{\text{I}^-/\text{I}_3^-}^0$$

$$= 0.78 \text{ V} - 0.54 \text{ V} = 0.24 \text{ V}$$

Using the expression :

$$\log_{10} K_{\text{eq.}} = \frac{n_{\text{cell}} E_{\text{cell}}^0}{0.06} \quad (\text{at } 298 \text{ K}) \quad [n_{\text{cell}} = 2]$$

$$\Rightarrow \log_{10} K_{\text{eq.}} = \frac{(2)(0.24 \text{ V})}{(0.06 \text{ V})} = 8.0$$

$$\Rightarrow K_{\text{eq.}} = 10^8$$

CONCENTRATION CELLS

Section - 3

By difference in concentration of a given electrode, we can construct a cell from only one type of electrode as follows :

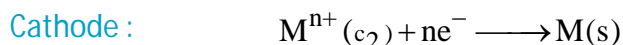
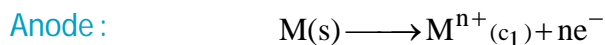
Let us take an electrode M/M^{n+} and take two different concentrations of it.



A cell made by using these two electrodes is called as concentration cell. Its cell representation is given as :



The two half-cell reactions are written as :



Using : $E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n_{\text{cell}}} \log_{10} Q_{\text{cell}}$

Now, clearly $E_{\text{cell}}^0 = 0$ volts and $Q_{\text{cell}} = \frac{[\text{M}^{n+} (c_1)]}{[\text{M}^{n+} (c_2)]}$ [For a concentration cell : $E_{\text{cell}}^0 = 0$ (always)]

$$E_{\text{cell}} = -\frac{0.059}{n_{\text{cell}}} \log_{10} \frac{[\text{M}^{n+} (c_1)]}{[\text{M}^{n+} (c_2)]}$$

Note : For a concentration cell made by using hydrogen electrodes, derive the EMF of cell in terms of pH of two electrodes. (Try yourself)

$$E_{\text{cell}} = 0.059 \left(\text{pH}_{\text{anode}} - \text{pH}_{\text{cathode}} + \frac{1}{2} \log_{10} \frac{(\text{pH}_2)_{\text{anode}}}{(\text{pH}_2)_{\text{cathode}}} \right)$$

Illustration - 12 Find the EMF of the concentration cell formed by coupling the following electrodes :

(a) $Pt, H_2(1 \text{ atm}) / HCl(0.1 \text{ M})$ (b) $Pt, H_2(2 \text{ atm}) / H_2SO_4(0.01 \text{ M})$

SOLUTION :

$$\text{Using } E_{\text{cell}} = 0.059 \left(pH_{\text{anode}} - pH_{\text{cathode}} + \frac{1}{2} \log_{10} \frac{(p_{H_2})_{\text{anode}}}{(p_{H_2})_{\text{cathode}}} \right)$$

Assume electrode (a) to be anode :

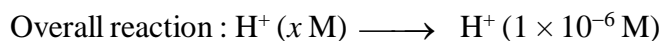
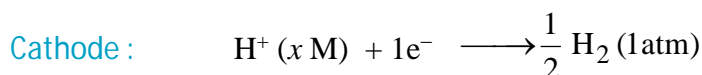
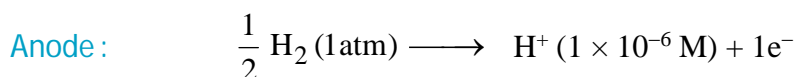
$$E_{\text{cell}} = 0.059 \left(1 + \log_{10} 0.02 + \frac{1}{2} \log_{10} \frac{1}{2} \right) \text{ Volts} = -0.05 \text{ Volts}$$

Note : E_{cell} is negative which means that electrode (a) is cathode and electrode (b) is anode.

Illustration - 13 A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of $10^{-6} \text{ M } H^+$ ions. The EMF of the cell is 0.118 V at 25°C . Calculate the concentration of hydrogen ions at the positive electrode.

SOLUTION :

The negative electrode is taken as anode and the positive electrode is as taken as cathode. Let the concentration of H^+ ions at positive electrode (i.e., at cathode) is $x \text{ M}$. Also, assume $p_{H_2} = 1 \text{ atm}$ at anode and cathode.



$$\text{Using : } E_{\text{cell}} = 0.059 \left(pH_{\text{anode}} - pH_{\text{cathode}} + \frac{1}{2} \log_{10} \frac{(p_{H_2})_{\text{anode}}}{(p_{H_2})_{\text{cathode}}} \right)$$

$$\Rightarrow 0.118 = 0.059 (6 - pH_{\text{cathode}} + 0)$$

$$\Rightarrow pH_{\text{cathode}} = 4 \Rightarrow [H^+]_{\text{cathode}} = 10^{-4} \text{ M}$$

E.M.F. vs WITH TEMPERATURE

Section - 4

Free Energy

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

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

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

$$-\Delta G = nFE$$

Similarly, maximum obtainable work from the cell at standard condition will be :

$$W_{\max} = nFE_{\text{cell}}^0 \quad \text{where } E_{\text{cell}}^0 = \text{standard emf of standard cell potential}$$

$$-\Delta G^\circ = nFE_{\text{cell}}^0$$

Variation of E.M.F. (E_{cell}) with Temperature

The temperature coefficient of e.m.f. of the cell is written as :

$$\Delta G = \Delta H + T \left(\frac{d(\Delta G)}{dT} \right)_{\text{Const. Pressure}} \quad \dots(i)$$

[This equation is known as **Gibbs - Helmholtz equation**. Learn this as a result]

$$\Rightarrow -nFE_{\text{cell}} = \Delta H + T \left(\frac{d(-nFE_{\text{cell}})}{dT} \right)_P \quad [\because \Delta G = -nFE_{\text{cell}}]$$

$$\Rightarrow \left(\frac{dE_{\text{cell}}}{dT} \right)_P = \frac{\Delta H}{nFT} + \frac{E_{\text{cell}}}{T} \quad \dots(ii)$$

Enthalpy change : From eq. (i) : $\Delta H = \Delta G - T \left(\frac{d}{dT}(\Delta G) \right)_P$

$$\Rightarrow \Delta H = -nF \left[E_{\text{cell}} - T \left(\frac{dE_{\text{cell}}}{dT} \right)_P \right] \quad \dots(iii)$$

Entropy change : Compare with equation : $\Delta G = \Delta H - T\Delta S$ with (i)

$$\Rightarrow \Delta S = - \left(\frac{d}{dT}(\Delta G) \right)_P = nF \left(\frac{dE_{\text{cell}}}{dT} \right)_P$$

Illustration - 14 For the standard electromotive force of the cell : $Fe | Fe^{2+}(aq) || Cd^{2+}(aq) | Cd$

If the temperature co-efficient of emf is -0.125 VK^{-1} , the value of ΔS at 25°C would be :

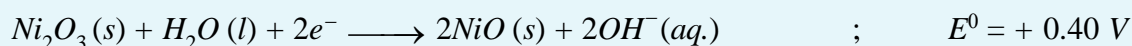
- (A) $-20.125 \text{ kJ K}^{-1}$ (B) $-24.125 \text{ kJ K}^{-1}$ (C) $-26.125 \text{ kJ K}^{-1}$ (D) $-22.125 \text{ kJ K}^{-1}$

SOLUTION : (B)

$$\text{Using : } \frac{dE_{\text{cell}}}{dT} = \frac{\Delta S}{nF}$$

$$\Rightarrow \Delta S = \left(\frac{dE_{\text{cell}}}{dT} \right) \times nF = -0.125 \times 2 \times 96500 = -24.125 \text{ KJ K}^{-1}$$

Illustration - 15 The Edison storage cell is represented as : $Fe(s) / FeO(s) || KOH(aq) || Ni_2O_3(s) / NiO(s)$
The half cell reactions are :

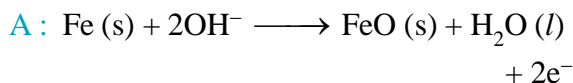
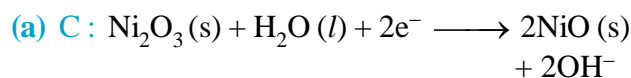


- (a) What is cell reaction ?
(b) What is the cell EMF ? How does it depend on the concentration of KOH ?
(c) What is the maximum amount of energy that can be obtained from one mole of Ni_2O_3 ?

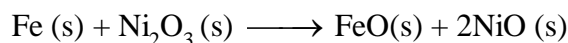
SOLUTION :

$FeO(s) / Fe(s)$ will be anode

and $Ni_2O_3(s) / NiO(s)$ will be cathode.



So cell reaction will be :



- (b) In the cell reaction, all the species are solid, so their activities will be equal to unity.

Hence $E_{\text{cell}} = E_{\text{cell}}^0$

$$E_{\text{cell}}^0 = \left(E_{\text{reduction}}^0 \right)_{\text{cathode}} - \left(E_{\text{reduction}}^0 \right)_{\text{anode}}$$

$$= 0.4 - (-0.87) = 1.27 \text{ volts}$$

As KOH does not effect cell reaction, so EMF does not depend on concentration of KOH

- (c) Energy obtained from the cell = magnitude of free energy (ΔG°)

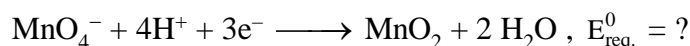
$$-\Delta G^0 = nFE_{\text{cell}}^0$$

$$\Rightarrow \text{amount of energy} = 2 \times 96500 \times 1.27 = 245.11 \text{ kJ.}$$

Illustration - 16 Find the standard electrode potential of $\text{MnO}_4^-/\text{MnO}_2$. The standard electrode potentials of $\text{MnO}_4^-/\text{Mn}^{2+} = 1.51 \text{ V}$ and $\text{MnO}_2/\text{Mn}^{2+} = 1.23 \text{ V}$

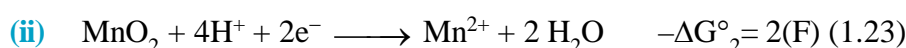
SOLUTION :

Use : $-\Delta G^0 = nFE^0$



$$-\Delta G_{\text{req.}}^0 = +3FE_{\text{req.}}^0$$

Given :



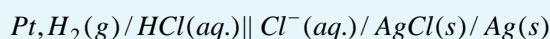
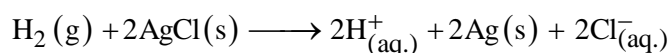
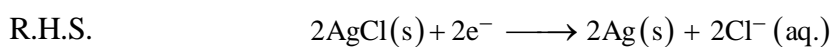
(i) – (ii) gives the required equation

$$\Delta G_{\text{req.}}^0 = \Delta G_1^0 - \Delta G_2^0 \quad (\Delta G \text{ is a state function})$$

$$-3FE_{\text{req.}}^0 = -5F(1.51) - [-2F(1.23)]$$

$$\Rightarrow E_{\text{req.}}^0 = 1.7 \text{ V}$$

Illustration - 17 E.M.F. of following cell is 0.265 V at 25°C and 0.26 V at 35°C . Calculate heat of the reaction taking place at 25°C .

**SOLUTION :**

$$\text{Use : } \Delta H = -nF \left[E_{\text{cell}} - T \left(\frac{dE_{\text{cell}}}{dT} \right)_P \right]$$

Put $n = 2$, $F = 96500 \text{ C}$

$$\frac{dE_{\text{cell}}}{dT} = \frac{0.260 - 0.265}{308 - 298} = -5.0 \times 10^{-4}, E_{\text{cell}} = 0.265 \text{ V (at } 298 \text{ K)}$$

to get : $\Delta H = -79.9 \text{ kJ}$.

BATTERIES

Section - 5

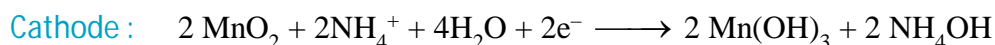
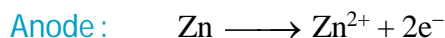
There are two types of batteries.

1. Primary Batteries

2. Secondary Batteries

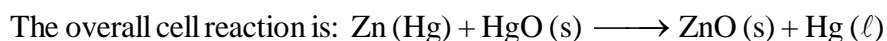
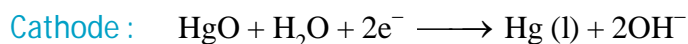
Primary Battery (Dry Cell) :

In this type of battery, the reaction occurs only once and battery then becomes dead after use over a period of time and cannot be then re-used. It is also called as a primary voltaic cell. It has a cathode consisting of carbon (graphite) rod surrounded by a paste consisting of MnO_2 and powdered graphite and an anode of zinc. The electrolyte is a moist paste of NH_4Cl . The electrode reactions are :



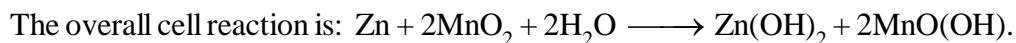
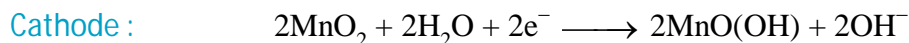
The cell potential is 1.6 V.

Another type of dry cell is Mercury cell which is suitable for the low current devices like hearing aids and watches, etc., consists of Zn – Hg amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions for the cell are :



The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

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

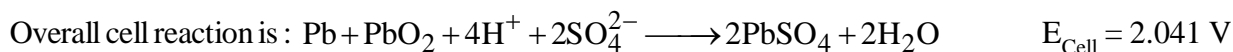
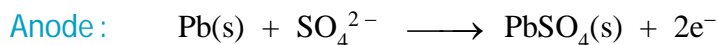


The cell potential is 1.5 volts.

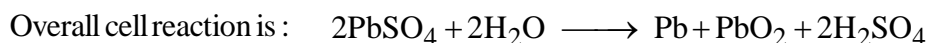
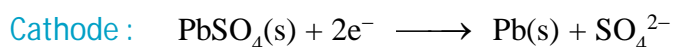
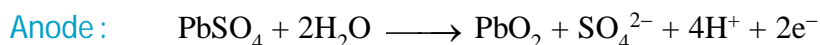
**Secondary Battery or Reversible Galvanic or Voltaic Cell :
(Lead Storage Battery) :**

A galvanic cell (or Voltaic cell) supplies a certain voltage. By imposing a higher voltage than the E.M.F. of cell (external voltage), one can reverse the cell reactions i.e. anode becomes cathode and the cathode becomes anode. The reversible lead storage battery is a typical example of it.

In a typical lead storage battery, the anode plates are made of lead, while the cathode plates are grids of lead packed with lead dioxide. A solution of sulphuric acid (H_2SO_4) surrounds the plates and acts as electrolyte. The half-cell reactions when the battery is being used up are :

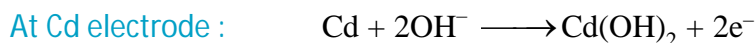


The battery is chargeable (reversible) since lead sulphate (product of both anode and cathode reactions) sticks to the plates. From cathode reaction, we see that as the battery is used up, the sulphuric acid is used up. Now we can determine the charge on the battery by measuring the concentration of H_2SO_4 in the cell. When the density of solution is between 1.25 g/m and 1.30 g/m, the cell is considered as fully charged. When its value goes down below 1.20 g/m, the battery is in need of charge. By applying external current we can charge the battery again. The charging follows following reactions :



After many repeated charging and discharging cycles, some of the Lead sulphate falls to the bottom of the container, the sulphuric acid concentration remains low and the battery cannot be recharged fully.

Another important secondary cell is the nickel-cadmium cell which has longer life than the lead storage cell but more expensive to manufacture. The discharging follows following reactions :



The overall reaction during discharge is:



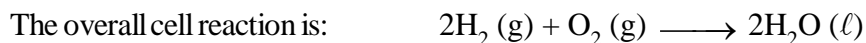
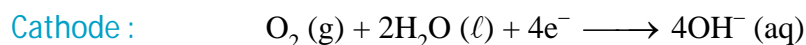
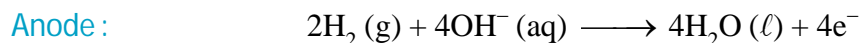
- Note :** ➤ Ni – cd cell has a cell potential of 1.2 V which changes a little as it discharges.
- Specific gravity of alkaline electrolyte remain same. So, it is not a guide to its change of state.

Other examples of rechargeable (secondary) cell are :

- | | |
|--|-----------------------------|
| (i) Nickel - Metal hydride (NiMH) | (ii) Lithium ion (Li - ion) |
| (iii) Lithium ion polymer (Li - ion polymer) | (iv) Iron - nickel |

Fuel Cell :

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

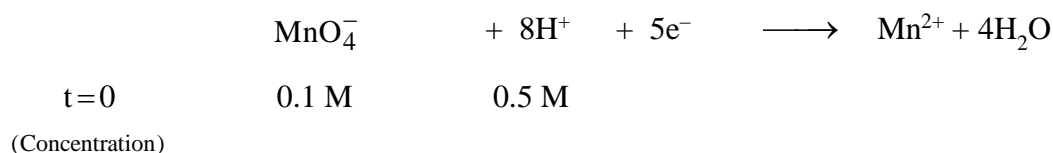


The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70% compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cell. These have been used in automobiles and space crafts. Fuel cells are pollution free and in view of their importance in future a variety of fuel cells have been fabricated and tried.

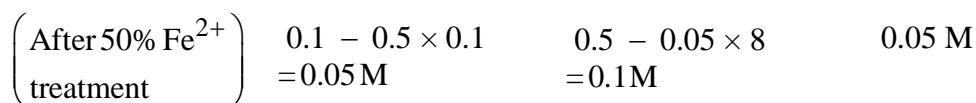
NOW ATTEMPT IN-CHAPTER EXERCISE-A BEFORE PROCEEDING AHEAD IN THIS EBOOK

SUBJECTIVE SOLVED EXAMPLES

Example - 1 Calculate the reduction potential of an electrode which was originally 0.1 M MnO_4^- and 0.5 M H^+ and has been treated with 50% of the Fe^{2+} required to reduce all the MnO_4^- to Mn^{2+} . ($E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51\text{ V}$)

SOLUTION :

$t = t_{\text{final}}$



Using: $E_{\text{MnO}_4^-/\text{Mn}^{2+}} = E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} - \frac{0.059}{n} \log_{10} Q_{\text{Reduction}}$

$$\begin{aligned} E_{\text{MnO}_4^-/\text{Mn}^{2+}} &= E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} - \frac{0.059}{5} \log_{10} \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8} \\ &= 1.51 - \frac{0.059}{5} \log_{10} \frac{0.05}{0.05 \times (0.1)^8} = 1.42 \text{ volts} \end{aligned}$$

Example - 2 Calculate the EMF of the following cell at 25°C .

**SOLUTION :**

Note that in this question, instead of H^+ ions in RHE, OH^- are given. Now, calculate $[\text{H}^+]$ from concentration of OH^- in the solution.

$$\text{pH}_{\text{Anode}} = -\log_{10} 0.09 = 1.05$$

Use: $E_{\text{cell}} = 0.059 (\text{pH}_{\text{Anode}} - \text{pH}_{\text{Cathode}})$

$$\begin{aligned} \text{pH}_{\text{cathode}} &= 14 - \text{pOH}_{\text{cathode}} &= 0.059(1.05 - 12.87) = -0.70 \text{ V} \\ &= 14 + \log_{10}(0.075) = 12.87 \end{aligned}$$

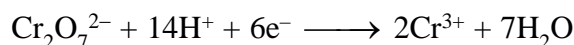
Note: The given cell is a Hydrogen concentration cell.

Example - 3

Calculate the reduction electrode potential at 25°C of $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ electrode at $\text{pOH} = 11$ in a solution of 0.01 M both in Cr^{3+} and $\text{Cr}_2\text{O}_7^{2-}$. $E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33\text{V}$. If this electrode is coupled with a hydrogen gaseous electrode at $\text{pH} = 3$, find the emf of the spontaneous cell.

SOLUTION :

Writing balanced equation for $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ electrode :



$$\text{pOH} = 11 \quad \Rightarrow \quad [\text{H}^+] = 10^{-3}\text{ M}$$

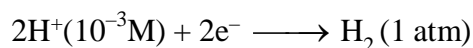
Using Nernst Equation :

$$E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} - \frac{0.059}{n} \log_{10} Q_{\text{reduction}}$$

$$\Rightarrow E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} - \frac{0.059}{n} \log_{10} \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}}$$

$$\Rightarrow E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 - \frac{0.059}{6} \log_{10} \frac{[0.01]^2}{[0.01][10^{-3}]^{14}} = 0.94\text{V}$$

Also, find the electrode potential of hydrogen electrode using Nernst Equation :



$$E_{\text{H}^+/\text{H}_2} = E^\circ_{\text{H}^+/\text{H}_2} - \frac{0.059}{2} \log_{10} \frac{1}{[\text{H}^+]^2}$$

$$E_{\text{H}^+/\text{H}_2} = 0 - \frac{0.059}{2} \log_{10} \frac{1}{[10^{-3}]^2} = -0.177\text{V}$$

\Rightarrow The hydrogen electrode will serve as anode and $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ will serve as cathode

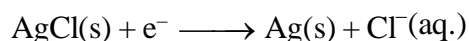
$$\text{So, } E_{\text{cell}} = (E_{\text{reduction}})_{\text{Cathode}} - (E_{\text{reduction}})_{\text{Anode}} = 0.94 - (-0.177) = 1.06\text{ V}$$

Example - 4

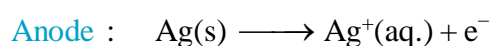
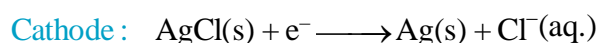
Find the K_{sp} of AgCl. The standard electrode potential of Ag/AgCl/Cl⁻ is 0.22 V and Ag⁺/Ag is 0.8 V.

SOLUTION :

The given electrode Ag/AgCl/Cl⁻ is visualized as :



It is now coupled with silver electrode as anode



⇒ Overall cell reaction is :



At saturation (i. e. at equilibrium), the above reaction gives the solubility of AgCl.

At equilibrium, $E_{\text{cell}} = 0$ V and $Q = K_{sp}$

$$\Rightarrow E_{\text{cell}}^0 = \frac{0.059}{n_{\text{cell}}} \log_{10} K_{sp}$$

$$E^0(\text{Ag} / \text{AgCl} / \text{Cl}^-) - E^0(\text{Ag}^+ / \text{Ag})$$

$$= \frac{0.059}{1} \log_{10} K_{sp}$$

$$\Rightarrow \log_{10} K_{sp} = \frac{0.22 - 0.8}{0.059} = -9.85$$

$$\Rightarrow K_{sp} = 1.4 \times 10^{-10}$$

Example - 5

The standard reduction potential of Ag⁺/Ag electrode at 298 K is 0.80 volts. K_{sp} of AgI = 1.0×10^{-16} . Find the electrode potential of Ag⁺/Ag in a saturated solution of AgI. Also, calculate standard reduction potential of I⁻/AgI/Ag electrode.

SOLUTION :

First calculate the concentration of Ag⁺ in a saturated solution of AgI.

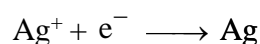


Let $[\text{Ag}^+] = x$

$$\Rightarrow K_{sp} \text{ of AgI} = [\text{Ag}^+][\text{I}^-] = x^2$$

$$\begin{aligned} \Rightarrow [\text{Ag}^+] = x &= \sqrt{K_{sp}} = \sqrt{1.0 \times 10^{-16}} \\ &= 1.0 \times 10^{-8} \text{ M} \end{aligned}$$

Now, calculate the reduction potential of silver electrode at $[\text{Ag}^+] = 10^{-8} \text{ M}$



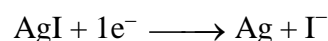
$$E(\text{Ag}^+ / \text{Ag}) = E^0(\text{Ag}^+ / \text{Ag}) -$$

$$\frac{0.059}{1} \log_{10} \frac{1}{[\text{Ag}^+]}$$

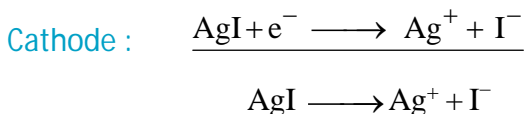
$$\begin{aligned} \Rightarrow E(\text{Ag}^+ / \text{Ag}) &= 0.80 - 0.059 \log_{10} \frac{1}{1.0 \times 10^{-8}} \\ &= 0.33 \text{ volts} \end{aligned}$$

$$E(\text{Ag}^+ / \text{Ag}) = 0.33 \text{ volts}$$

For E⁰ of I⁻/AgI/Ag, visualize the electrode as:



Now couple this electrode with Ag/Ag^+ as anode



At equilibrium:

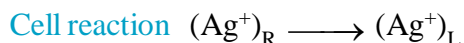
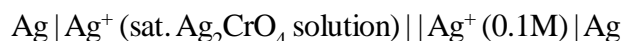
$$\begin{aligned}\Rightarrow E_{\text{cathode}}^0 - E_{\text{anode}}^0 &= 0.059 \log_{10} K_{\text{sp}} [\text{AgI}] \\ \Rightarrow E_{\text{cathode}}^0 &= E_{\text{anode}}^0 + 0.059 \log_{10} K_{\text{sp}} [\text{AgI}] \\ &= 0.8 + 0.059 \log_{10} 10^{-16} = -0.17 \text{ V}\end{aligned}$$

Example - 6

Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell: $\text{Ag} / \text{Ag}^+ (\text{saturated } \text{Ag}_2\text{CrO}_4 \text{ solution}) // \text{Ag}^+ (0.1\text{M}) / \text{Ag}$ is 0.177 V at 298 K.

SOLUTION:

The given cell is:



Using Nernst Equation, we get:

$$E_{\text{cell}} = 0 - \frac{RT}{F} \ln \frac{[\text{Ag}^+]_{\text{L}}}{[\text{Ag}^+]_{\text{R}}}$$

$$(E_{\text{cell}}^0 = 0 \text{ for concentration cells})$$

$[\text{Ag}^+]_{\text{R}} = 0.1 \text{ M}$. Let $[\text{Ag}^+]_{\text{L}} = 2x$ molar.

In the left half-cell, the concentration of Ag^+ will be related to the solubility product of Ag_2CrO_4 as follows:



If x is the solubility of Ag_2CrO_4 in solution, then:

$$[\text{Ag}^+] = 2x \quad \text{and} \quad [\text{CrO}_4^{2-}] = x$$

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

$$\text{or } x = (K_{\text{sp}}/4)^{1/3}$$

$$\Rightarrow [\text{Ag}^+]_{\text{L}} = 2x = 2(K_{\text{sp}}/4)^{1/3} = (2K_{\text{sp}})^{1/3}$$

Substituting the values in Nernst Equation, we have:

$$E_{\text{cell}} = -\frac{RT}{F} \ln \frac{(2K_{\text{sp}})^{1/3}}{[\text{Ag}^+]_{\text{R}}}$$

$$\Rightarrow 0.177 \text{ V} = - (0.059 \text{ V}) \log_{10} \frac{(2K_{\text{sp}})^{1/3}}{(0.1)}$$

$$\log_{10} \left[\frac{(2K_{\text{sp}})^{1/3}}{0.1} \right] = -\frac{0.177}{0.059} = -3$$

$$\Rightarrow \frac{(2K_{\text{sp}})^{1/3}}{0.1} = 10^{-3} \Rightarrow K_{\text{sp}} = 5 \times 10^{-13}$$

Example - 7

The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 35°C:



- (i) Write the cell reaction.
- (ii) Calculate ΔH° and ΔS° for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C.
- (iii) Calculate the solubility of AgCl at 25°C.

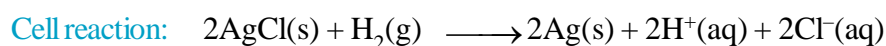
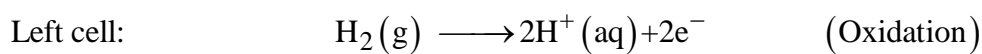
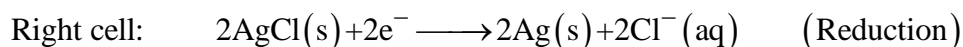
Given: The standard reduction potential of the $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ couple is 0.80 V at 25°C ;

$$2.303 \frac{RT}{F} \text{ at } 25^\circ\text{C} = 0.06 \text{ V}$$

SOLUTION :

The given cell is : $\text{Pt}, \text{H}_2(\text{g}) | \text{HCl}(\text{aq}) || \text{KCl}(\text{aq}) | \text{AgCl}(\text{s}) | \text{Ag}(\text{s})$

- (i) The cell reactions are as follows.



$$\begin{aligned} \text{(ii)} \quad -\Delta G_{15^\circ\text{C}}^0 &= nF E_{\text{cell}} = (2) (96500 \text{ C mol}^{-1}) (0.23 \text{ V}) \\ &= 44390 \text{ J mol}^{-1} \end{aligned}$$

$$\begin{aligned} -\Delta G_{35^\circ\text{C}}^0 &= nF E_{\text{cell}} = (2) (96500 \text{ C mol}^{-1}) (0.21 \text{ V}) \\ &= 40530 \text{ J mol}^{-1} \end{aligned}$$

$$\text{Now, } \Delta G_{15^\circ\text{C}}^0 = \Delta H^\circ - (288 \text{ K}) \Delta S^\circ = -44390 \text{ J mol}^{-1}$$

$$\text{and } \Delta G_{35^\circ\text{C}}^0 = \Delta H^\circ - (308 \text{ K}) \Delta S^\circ = -40530 \text{ J mol}^{-1}$$

[Using $\Delta G = \Delta H - T\Delta S$ and assuming ΔH and ΔS at 298 K and temperature independent i.e. $\Delta H_{15^\circ\text{C}} = \Delta H^\circ$ and $\Delta H_{35^\circ\text{C}} = \Delta H^\circ$]

Solving for ΔH° and ΔS° , we get,

$$\Delta H = -99974 \text{ J mol}^{-1} \quad \text{and} \quad \Delta S^\circ = -193 \text{ J K}^{-1} \text{ mol}^{-1}$$

- (iii) The value of ΔG° at 25°C is calculated as follows :

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - (298 \text{ K}) \Delta S^\circ = -99974 \text{ J mol}^{-1} - (298 \text{ K}) (293 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -42460 \text{ J mol}^{-1} \end{aligned}$$

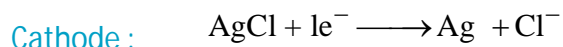
The value of $E^\circ_{\text{Cl}^- | \text{AgCl} | \text{Ag}}$ at 25°C will be :

$$E^\circ_{\text{cell}} = \frac{-\Delta G^\circ_{\text{cell}}}{nF} = \frac{-(-42460 \text{ Jmol}^{-1})}{(2)(96500 \text{ Cmol}^{-1})} = 0.22 \text{ V}$$

$$\Rightarrow E^\circ_{\text{Cl}^- / \text{AgCl} / \text{Ag}} - E^\circ_{\text{H}^+ / \text{H}_2} = 0.22 \text{ V}$$

$$\Rightarrow E^\circ_{\text{Cl}^- / \text{AgCl} / \text{Ag}} = 0.22 \text{ V} \left(\because E^\circ_{\text{H}^+ / \text{H}_2} = 0 \text{ V} \right)$$

For determination of K_{sp} , constructing the cell :



Now using the expression : $E^\circ_{\text{cell}} = E^\circ_{\text{Cl}^- / \text{AgCl} / \text{Ag}} - E^\circ_{\text{Ag}^+ / \text{Ag}} = \frac{RT}{F} \ln K_{\text{sp}}$ (at equilibrium)

$$\Rightarrow 0.22 \text{ V} - 0.80 \text{ V} = (0.06 \text{ V}) \log_{10} K_{\text{sp}}$$

$$\Rightarrow \log_{10} K_{\text{sp}} = \frac{(0.22 - 0.80) \text{ V}}{(0.06 \text{ V})} = -10.0$$

$$\Rightarrow K_{\text{sp}} = 1.0 \times 10^{-10}$$

Example - 8

Two Daniel cells contain the same solution of ZnSO_4 but differ in the CuSO_4 solution. The emf of the cell containing 0.5 M CuSO_4 is higher than the other cell by 0.06 V . Calculate the concentration of CuSO_4 in the other cell.

$$\left[\text{Use : } \frac{2.303 RT}{F} \approx 0.06 \right]$$

SOLUTION :

The reaction occurring in a Daniell cell is : $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$

The EMF of the cell is given as : $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$

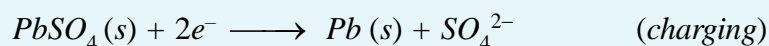
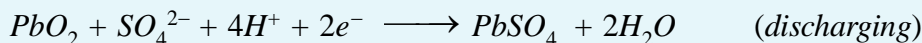
For the two cells, we have :

$$\left. \begin{aligned} (E_{\text{cell}})_1 &= E_{\text{cell}}^0 - \frac{RT}{2F} \ln \left(\frac{[\text{Zn}^{2+}]_1}{[\text{Cu}^{2+}]_1} \right) \\ (E_{\text{cell}})_2 &= E_{\text{cell}}^0 - \frac{RT}{2F} \ln \left(\frac{[\text{Zn}^{2+}]_2}{[\text{Cu}^{2+}]_2} \right) \end{aligned} \right\} \quad (E_{\text{cell}})_2 - (E_{\text{cell}})_1 = \frac{RT}{2F} \ln \left(\frac{[\text{Cu}^{2+}]_2}{[\text{Cu}^{2+}]_1} \right)$$

$$= 0.06 \text{ [Taking } [\text{Cu}^{2+}]_2 = 0.5 \text{ M]}$$

$$\Rightarrow \log_{10} \left(\frac{0.5}{[\text{Cu}^{2+}]_1} \right) = 2 \Rightarrow [\text{Cu}^{2+}]_1 = 0.5 \times 10^{-2} = 5 \times 10^{-3} \text{ M}$$

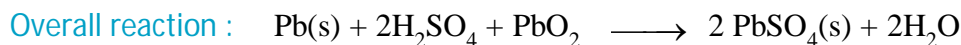
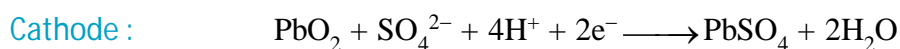
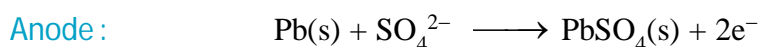
Example - 9 During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 g/ml to 1.139 g/ml. Sulphuric acid of density 1.294 g/ml was 39% H_2SO_4 by wt. while acid of density 1.139 g/ml contains 20% acid by wt. The battery holds 3.5 L of acid and the value remained practically same through the discharging. Calculate the number of amp/hr for which the battery must have been used. The charging and discharging reactions are :



SOLUTION :

Note that density of sulphuric acid has decreased, i.e discharging of battery takes place.

First write both the reaction for *discharging*.



\Rightarrow For the consumption of 2 molecules of H_2SO_4 , 2e^- are transferred

\Rightarrow For the consumption of 2 moles of H_2SO_4 , 2 moles of e^- s are transferred

\Rightarrow 2 mole of $\text{H}_2\text{SO}_4 \equiv 2\text{F}$ of electricity

(**Note:** $1\text{F} \equiv$ Charge on 1 mole of electrons)

Now let us calculate the decrease in moles of H_2SO_4 from the data given.

Volume of solution = 3.5 L = 3500 ml

Let the mass of H_2SO_4 before discharging = m_1

And the mass of H_2SO_4 after discharging = m_f

$$\Rightarrow m_i = \left(\frac{39}{100} \times 3500 \right) \times 1.294 = 1766.3 \text{ gm}$$

$$\Rightarrow m_f = \left(\frac{20}{100} \times 3500 \right) \times 1.139 = 797.3 \text{ gm}$$

$$\Rightarrow \Delta m (\text{the decrease in mass}) = 1766.3 - 797.3 = 969 \text{ gm}$$

$$\Rightarrow \text{moles of } \text{H}_2\text{SO}_4 \text{ consumed} = \frac{\Delta m}{98} = \frac{970}{98} = 9.89$$

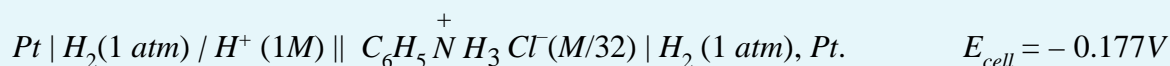
Now 1 mole of $\text{H}_2\text{SO}_4 \equiv 1 \text{ F of charge}$

$$\Rightarrow 9.89 \text{ moles} \equiv 1 \times 9.89 \text{ F of charge} \equiv 9.89 \times 96500 = 954385 \text{ C of charge}$$

$$\text{Now } Q = I t \Rightarrow I = \frac{Q}{t} \Rightarrow I = \frac{954385}{1 \times 60 \times 60} = 265 \text{ amp}$$

Example - 10

Determine the degree of hydrolysis and hydrolysis constant of aniline hydrochloride in $M/32$ solution of salt at 298 K from the following cell data at 298 K. :



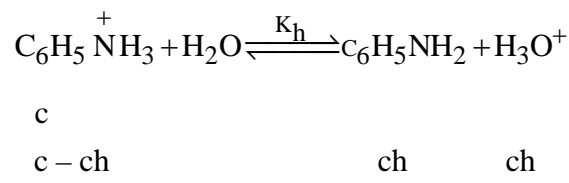
SOLUTION :

Note: Given cell is a Hydrogen Concentration cell.

$$\Rightarrow h = 32 \times 10^{-3} = 0.032$$

$$\begin{aligned} E_{\text{cell}} &= 0.059 (\text{pH}_{\text{Anode}} - \text{pH}_{\text{Cathode}}) \\ &= 0.059 (0 - \text{pH}_{\text{Cathode}}) = 0.059 \log_{10} [\text{H}^+]_{\text{Cathode}} \\ &= -0.177 \end{aligned}$$

$$\Rightarrow [\text{H}^+]_{\text{Cathode}} = 10^{-3} \text{ M}$$



$$K_h = \frac{ch \cdot ch}{c - ch} = \frac{10^{-3} \cdot 10^{-3}}{\frac{1}{32} - 10^{-3}} = 3.31 \times 10^{-5}$$

Note: Aniline Hydrochloride: $\text{C}_6\text{H}_5\text{N}^+\text{H}_3\text{Cl}^-$
[salt of SA – WB]

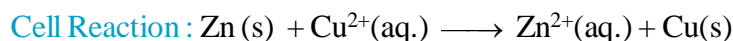
$$\Rightarrow [\text{H}^+]_{\text{Cathode}} = 10^{-3} = ch$$

$$(c = \frac{1}{32} \text{ M} ; h = \text{degree of hydrolysis})$$

Example - 11

Calculate the quantity of electricity delivered by a Daniel cell initially containing 1L, 1M Cu^{2+} ion and Zn^{2+} ion which is operated until its potential drops to 1.041 V.

$$(E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V} ; E^0_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V})$$

SOLUTION :

$t=0$	1	1
(concentration)		
$t = t_{\text{eq}}$	$1-x$	$1+x$

Using Nernst equation : $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{n_{\text{cell}}} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$

$$1.041 = 1.1 - \frac{0.059}{2} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \quad \left[\begin{array}{l} E^{\circ}_{\text{cell}} = 0.34 - (-0.70) = 1.1\text{V} \\ n_{\text{cell}} = 2 \quad \left(\begin{array}{l} \text{write half} \\ \text{cell reactions} \end{array} \right) \end{array} \right]$$

$$\Rightarrow 0.059 = \frac{0.059}{2} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\Rightarrow \log_{10} \frac{1+x}{1-x} = 2 \quad \Rightarrow \frac{1+x}{1-x} = 100 \quad \Rightarrow x = \frac{99}{101}$$

Moles of Cu^{2+} (initially) = $1 \times 1\text{L} = 1$

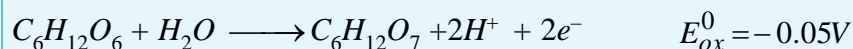
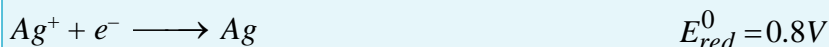
Moles of Cu^{2+} (left) = $1 - x = 1 - \frac{99}{101} = \frac{2}{101}$

For each ion of Cu^{2+} to Cu, $2e^-$ s are transferred.

Thus, no. of electrons transferred = $x \times 96500 = \frac{99}{101} \times 2 \times 96500 \text{ C} = 189178.2 \text{ C}$

Example 12 - 14**Read the following passage :**

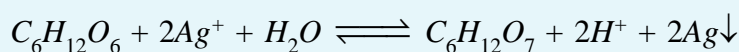
Tollen's test is used for detection of aldehydic group in organic compounds like glucose. The test is as follows : An aqueous solution of AgNO_3 is added to an aqueous solution of glucose in a test tube. When concentrated ammonia is added, silver is deposited. This is a redox reaction as Ag^+ is reduced to Ag and glucose is oxidized to gluconic acid. The following half-cell reactions and the standard half-cell potentials are given :



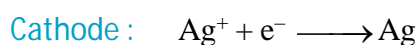
Given : $2.303 RT/F = 0.0592 \text{ V}$, $F/RT = 38.90 \text{ V}^{-1}$ at 298 K

Example - 12

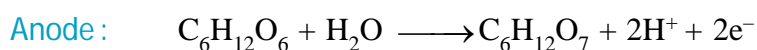
The logarithm of the equilibrium constant ($\ln K$) of the reaction is :

**(A)** 66.1**(B)** 29.2**(C)** 58.4**(D)** 116.8**SOLUTION : (C)**

Create cell as :



$$E_{\text{reduction}}^0 = 0.8\text{V}$$



$$E_{\text{reduction}}^0 = 0.05\text{V}$$



When the reaction reaches equilibrium, $Q_{\text{cell}} = K_{\text{eq}}$ and $E_{\text{cell}} = 0$

$$\text{Using : } \ln K_{\text{eq}} = E_{\text{cell}}^0 \cdot n_{\text{cell}} \cdot \frac{F}{RT} = 0.75 \times 2 \times 38.90 = 58.35 \quad (E_{\text{cell}}^0 = 0.8 - 0.05 = 0.75 \text{ V})$$

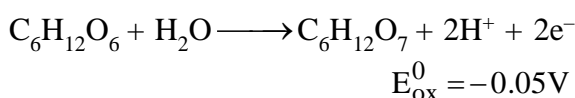
Example - 13

On the addition of conc. NH_3 , the pH of the solution rises to 11. Ignoring any changes in the concentration of glucose and gluconic acid, identify which of the half-cell electrodes will be sensitive to pH and the corresponding change in half-cell potential (E) relative to the standard half-cell potential (E^0)

- (A) an increase of E_{ox} over E_{ox}^0 by an amount 0.65 V (B) an increase of E_{red} over E_{red}^0 by an amount 0.65 V
 (C) decrease of E_{ox} over E_{ox}^0 by an amount 0.65 V (D) decrease of E_{red} over E_{red}^0 by an amount 0.65 V

SOLUTION : (AD)

Consider :



Using Nernst Equation :

$$E_{\text{ox}} = E_{\text{ox}}^0 - \frac{2.303RT}{nF} \log_{10} Q_{\text{oxidation}}$$

$$\Rightarrow E_{\text{ox}} = E_{\text{ox}}^0 - \frac{0.0592}{2} \log_{10} [\text{H}^+]^2$$

[Take other compounds activity to be unity]

$$\Rightarrow E_{\text{ox}} = E_{\text{ox}}^0 + 0.0592 \text{pH}$$

$$\Rightarrow E_{\text{ox}} - E_{\text{ox}}^0 = 0.0592 \times 11 = 0.65 \text{ V}$$

\Rightarrow There is an increase in E_{ox} over E_{ox}^0 by 0.65 V or decrease in E_{red} over E_{red}^0 by 0.65 V

Note: Only glucose electrode will be sensitive to pH changes as other electrodes do not depend on $[\text{H}^+]$.

Example - 14

The reaction does not proceed efficiently without addition of NH_3 . Moreover, addition of any other base is not recommended. Which of the following statements about the role of NH_3 must be incorrect ?

- (A) $\text{Ag}(\text{NH}_3)_2^+$ is weaker oxidizing agent than Ag^+
 (B) NH_3 complex Ag^+ efficiently
 (C) In absence of NH_3 , silver salts of gluconic acid would precipitate.
 (D) NH_3 alters the standard electrode potential of the glucose / gluconic acid electrode.

SOLUTION : (D)

(A) $E_{[\text{Ag}(\text{NH}_3)_2]^+ / \text{Ag}}^0 = 0.37 \text{ V}$ and $E_{\text{Ag}^+ / \text{Ag}}^0 = 0.8 \text{ V}$

$\Rightarrow \text{Ag}^+$ has a stronger tendency to get reduced than $[\text{Ag}(\text{NH}_3)_2]^+$. So, Ag^+ is a stronger oxidising agent than $[\text{Ag}(\text{NH}_3)_2]^+$.

- (B) NH_3 forms highly stable complex with Ag^+ .
- (C) NH_3 keeps most of Ag^+ in solution in the form of $[\text{Ag}(\text{NH}_3)_2]^+$. So, gluconate ion gets a very less chance to form silver salt of gluconic acid.
- (D) Standard electrode potential of the glucose / gluconic acid electrode is fixed and does not change with the addition of NH_3 in the solution.

Example - 15

(a) Calculate $\Delta_r G^0$ of the reaction : $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl}(\text{s})$

Given : $\Delta_f G^0(\text{AgCl}) = -109 \text{ kJ/mol}$; $\Delta_f G^0(\text{Cl}^-) = -129 \text{ kJ/mol}$; $\Delta_f G^0(\text{Ag}^+) = 77 \text{ kJ/mol}$

Represent the above reaction in the form of a cell. Also, calculate E_{cell}^0 and find $K_{\text{SP}[\text{AgCl}]}$.

(b) $6.539 \times 10^{-2} \text{ g}$ of metallic Zn was added to 100 mL of saturated solution AgCl. Calculate $\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$

Given that $\text{Ag}^+ + e^- \longrightarrow \text{Ag}$ $E^0 = 0.80 \text{ V}$

$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$ $E^0 = -0.763 \text{ V}$

Also find how many moles of Ag will be formed. [Given : $K_{\text{SP}[\text{AgCl}]} \approx 10^{-10}$]

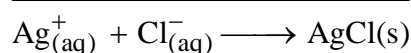
SOLUTION :

(a) $\text{Ag}^+(\text{aq.}) + \text{Cl}^-(\text{aq.}) \longrightarrow \text{AgCl}(\text{s})$

$$\Delta_r G^0 = \Delta_f G^0_{(\text{AgCl})} - \Delta_f G^0_{(\text{Cl}^-)} - \Delta_f G^0_{(\text{Ag}^+)} = -109 - (-129) - 77 = -57 \text{ kJ/mol}$$

Cathode : $\text{Ag}^+(\text{aq}) + e^- \longrightarrow \text{Ag}(\text{s})$

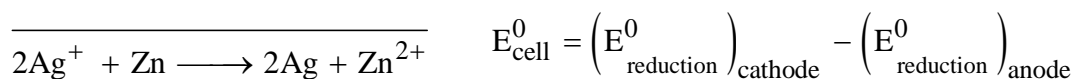
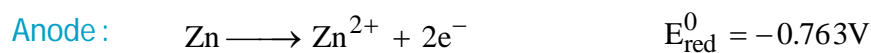
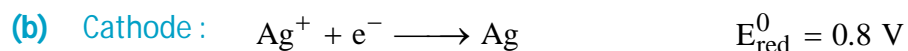
Anode : $\text{Ag}(\text{s}) + \text{Cl}^- \longrightarrow \text{AgCl}(\text{s}) + e^-$



$$\text{Using : } \Delta_r G^0 = -nFE_{\text{cell}}^0 = -1 \times 96500 E_{\text{cell}}^0 = -57 \times 10^3 \quad \Rightarrow \quad E_{\text{cell}}^0 = +0.59 \text{ volts}$$

$$\text{Using : } \log_{10} \frac{1}{K_{\text{sp}[\text{AgCl}]}} = \frac{E_{\text{cell}}^0 \cdot n_{\text{cell}}}{0.059} = \frac{0.59 \times 1}{0.059} = 10 \quad [\text{Note : } K_{\text{eq.}} = \frac{1}{K_{\text{SP}[\text{AgCl}]}}]$$

$$\Rightarrow K_{\text{sp}[\text{AgCl}]} \approx 10^{-10}$$



$$= 0.8 - (-0.763) = 1.563 \text{ V}$$

Initially 10^{-5} M 0.01 M

$$\text{At equilibrium: } \log_{10} \left[K_{\text{eq}} \left(\equiv \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \right) \right] = \frac{E_{\text{cell}}^0 \cdot n_{\text{cell}}}{0.059} = \frac{1.563 \times 2}{0.059} \approx 53$$

$$\Rightarrow K_{\text{eq}} = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = 10^{53} \quad (\text{i.e. whole of } \text{Ag}^+ \text{ is almost consumed.})$$

$$\text{Mmoles of Ag formed} = \text{Mmole of Ag}^+ \text{ used} = 10^{-5} \times 100 = 10^{-3}$$

$$\Rightarrow \text{Moles of Ag formed} = 10^{-6}$$

Electrochemistry - II

The process in which an electric current causes a chemical change (*conversion of electric energy to chemical energy*) is called as *electrolysis*. There are mainly two ways in which analysis is done in electrolysis :

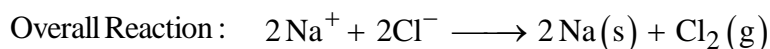
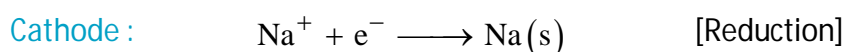
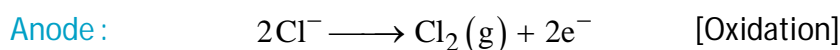
- (i) Qualitative Analysis : Study of possible products formed at cathode and anode during electrolysis.
- (ii) Quantitative Analysis : Study of amount /moles /volume of the products formed at cathode and anode during electrolysis.

QUANTITATIVE ANALYSIS

Section - 6

To understand the process of electrolysis more clearly, first let us consider electrolysis of molten salts (e.g., NaCl) and then aqueous solution of salts in an electrolytic cell shown.

Molten NaCl (an electrolyte) means free sodium ions (Na^+) and chloride ions (Cl^-), so it conducts current with the help of ions. As electric current is passed in the cell, Cl^- ions are attracted to anode (+ve electrode) and Na^+ ions to cathode (–ve electrode). Both ions are discharged at respective electrode as follows :



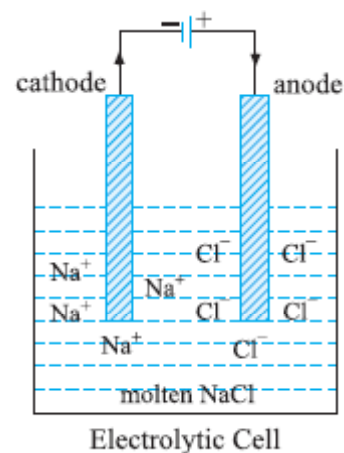
This type of cell is also called as electrolytic cell. The basic difference between an electrolytic cell and a galvanic (or voltaic) cell is that a voltaic cell produces electricity; an electrolytic cell consumes electricity.

The importance of electrolytic cell is that they are widely used in isolation and purification of various elements and gases.

Products of electrolysis depends mainly on the following factors :

- (i) Electrode potential of various possible reactions (deposition or liberation) at cathode or anode.
- (ii) Over potential of gases w.r.t. the electrode (material) at which they are liberating.
- (iii) Concentration of the ions (to be oxidised or reduced) in the solution.
- (iv) Type of electrodes [reacting or non-reacting (e.g. Pt, C (graphite))]

Now, we will discuss the products formed at cathode and anode for the most of the solutions as follows :



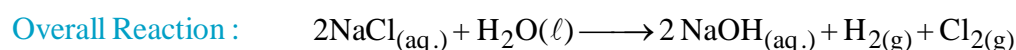
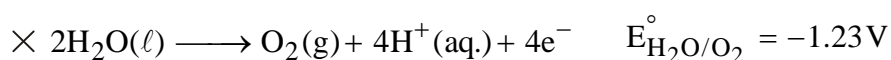
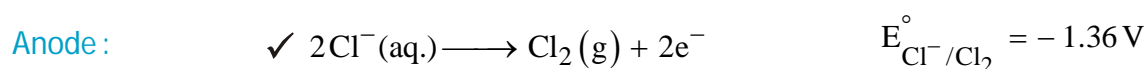
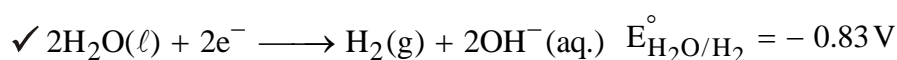
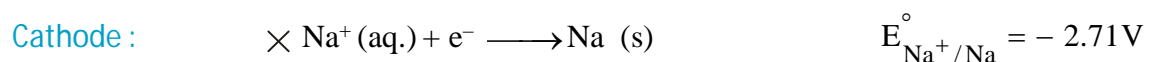
1. Aqueous NaCl solution :

Note : When electrode is not mentioned, assume it to be Pt.

In aqueous solution of NaCl, Na^+ , Cl^- , H^+ (from water) and OH^- (from water) ions are free to move for the conduction of electric current. When electric current is passed, Na^+ and H^+ ions are attracted to cathode and Cl^- and OH^- ions to anode.

The solution now contains four ions Na^+ , Cl^- (from NaCl), H^+ , OH^- (from water) and there is a race amongst them for their discharge at their respective electrodes.

The following electrode reactions are possible :



In this electrolysis, H_2 at cathode and Cl_2 at anode are given off. Now, question is, why Na^+ ions and OH^- ions are not discharged ? The reason lies in the reduction potential values. Clearly,

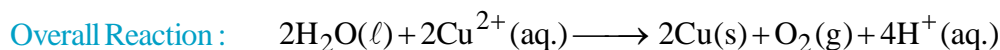
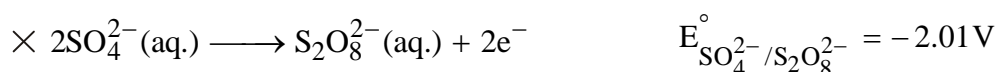
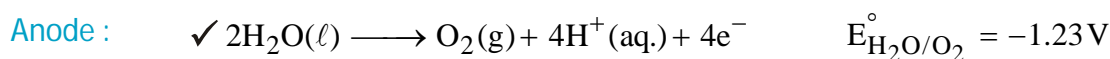
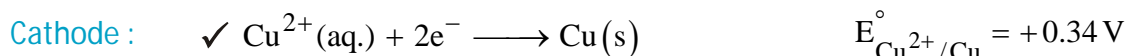
$$E_{\text{Na}^+/\text{Na}}^\circ < E_{\text{H}_2\text{O}/\text{H}_2}^\circ$$

- Although Cl^- has a lesser tendency to discharge (oxidize) [Cl^- will be at Anode where oxidation takes place] as compared to OH^- (Cl^- lies below OH^- in the Electrochemical series) at anode still OH^- will not be discharged (oxidize) due to the concept of *Overpotential* (Extra potential required to initiate a reaction at a required rate). Formation of O_2 from H_2O is kinetically very slow (i.e. low rate). Thus, OH^- ions will remain in the solution.
- The aqueous solution of NaCl will become alkaline (due to the presence of OH^- ions) after the electrolysis.
- In case of electrolysis of NaX (aq.) (where X^- is Br^- , I^-), X_2 will be liberated at anode. Using NaF, O_2 gas will be liberated at anode instead. Also, $E_{\text{Br}^-/\text{Br}_2}^\circ = -1.09 \text{ V}$ and $E_{\text{I}^-/\text{I}_2}^\circ = -0.54 \text{ V}$

but $E_{\text{F}^-/\text{F}_2}^\circ = -2.87 \text{ V}$

2. Aqueous CuSO_4 solution :

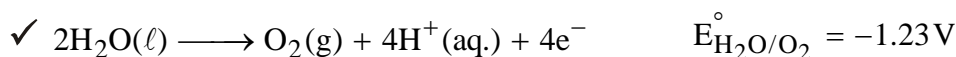
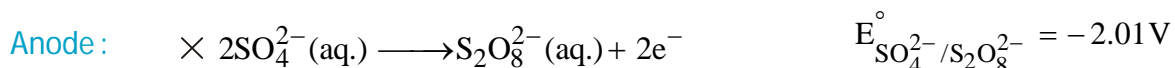
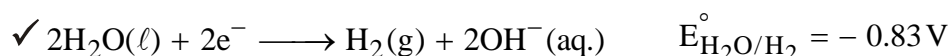
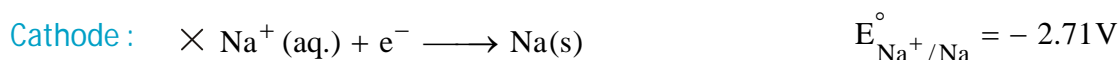
Possible reactions at :



In this electrolysis, Cu at cathode and O_2 at anode are produced. Also, the aqueous solution of CuSO_4 will become acidic (due to the presence of H^+ ions) after the electrolysis.

3. Aqueous Na_2SO_4 solution :

Possible reactions at :



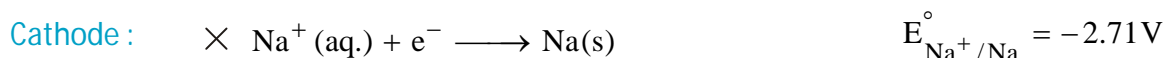
Clearly, at cathode, $\text{Na}^+(\text{aq.})$ ions will not be deposited due to their lower reduction potential than H_2O .

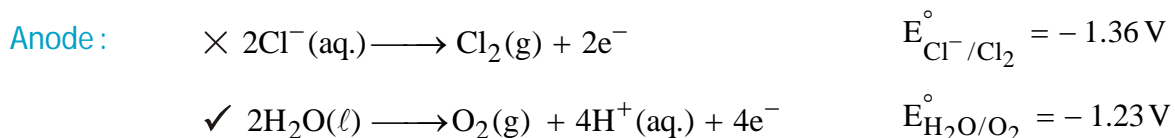
Similarly, SO_4^{2-} will not be oxidised due to their lower oxidation potential than H_2O .

Thus, electrolysis of $\text{Na}_2\text{SO}_4/\text{K}_2\text{SO}_4/\text{CaSO}_4/\text{MgSO}_4/\text{Li}_2\text{SO}_4$ etc. is actually equivalent of electrolysis of H_2O .

4. Aqueous NaCl solution(very dilute) :

Possible reactions at :





When NaCl is highly dilute, there is a very less chance of Cl^- (due to their less availability) getting oxidised. So, instead H_2O will get oxidised.

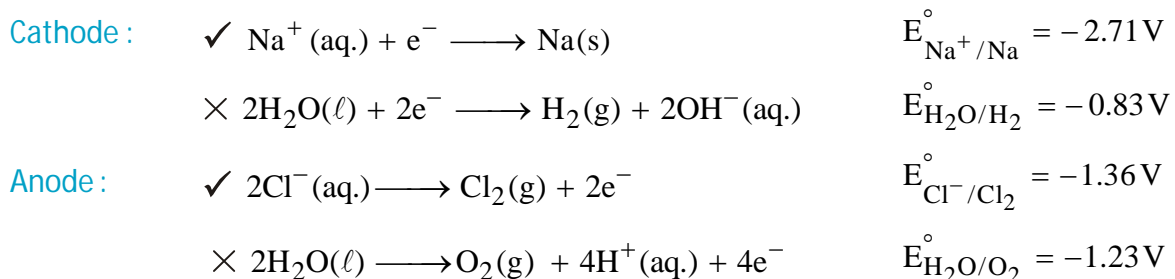
Note : $2\text{Cl}^-(\text{aq.}) \longrightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

$$E_{\text{Cl}^-/\text{Cl}_2} = E_{\text{Cl}^-/\text{Cl}_2}^\circ - \frac{0.059}{2} \log_{10} \frac{P_{\text{Cl}_2}}{[\text{Cl}^-]^2} = E_{\text{Cl}^-/\text{Cl}_2}^\circ - \frac{0.059}{2} \log_{10} P_{\text{Cl}_2} + 0.059 \log_{10} [\text{Cl}^-]$$

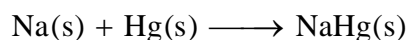
Thus, $E_{\text{Cl}^-/\text{Cl}_2}$ decreases as $[\text{Cl}^-]$ decreases making the oxidation of H_2O more favorable.

5. Aqueous NaCl solution (using Hg electrodes) :

Possible reactions at :



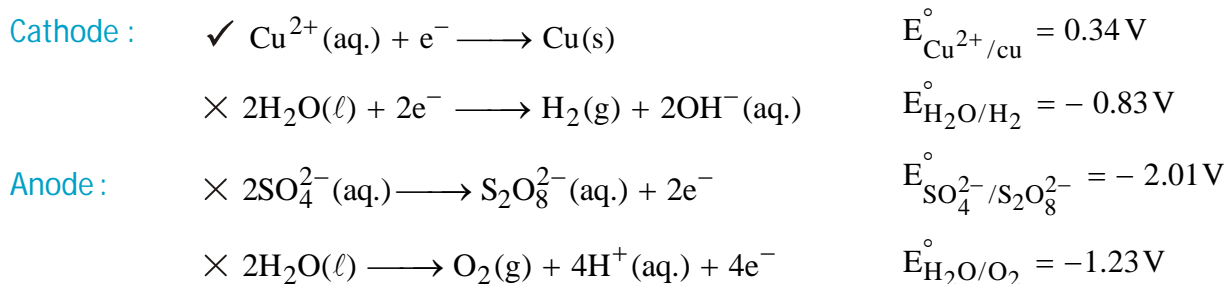
When Hg electrodes are used instead of Pt, $\text{Na}^+(\text{aq.})$ gets deposited which further reacts with Hg to form Sodium-Amalgam.



Thus, when $\text{NaCl}_{(\text{aq.})}$ is electrolyzed using Hg as electrode sodium amalgam is formed at cathode and $\text{Cl}_2(\text{g})$ is evolved at anode.

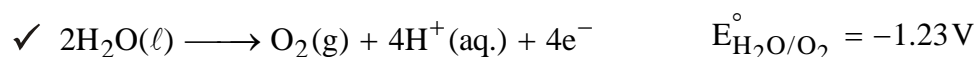
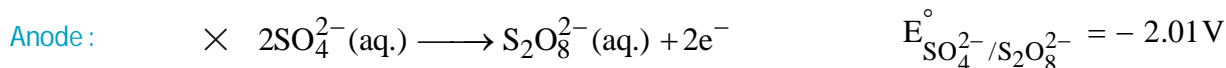
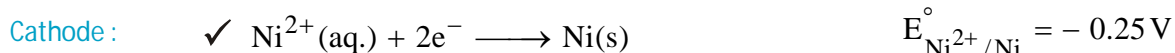
6. Aqueous CuSO_4 solution (using Cu electrodes) :

Possible reactions at :

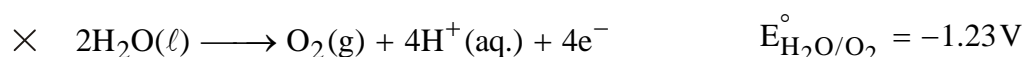
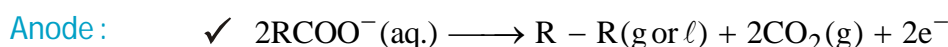
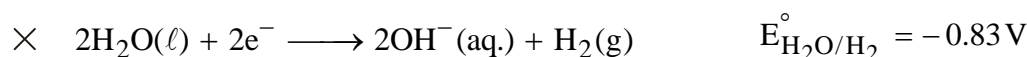
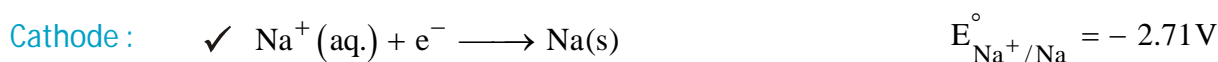


9. Aqueous NiSO₄ solution:

Possible reactions at :

In practice, it has been observed that H₂ gas also gets liberated at cathode along with Ni.**10. Aqueous RCOONa solution (Kolbe's Electrolysis):**

Possible reactions at :

**QUANTITATIVE ANALYSIS****Section - 7****Faraday's Law of Electrolysis (a quantitative analysis of electrolysis)**

Faraday proposed following two laws for the quantitative analysis for the product of electrolysis :

1st Law :

It states that "the amount of any substance that is deposited or liberated at an electrode is directly proportional to the quantity of electricity passing through the electrolytic cell".

The amount of electricity means quantity of charge (Q) in coulombs. If I is the current in amperes (A) and t is the time in seconds, then $Q = I t$.

If w is the amount of substance liberated or deposited, then

$$w \propto Q$$

$$w = Z Q$$

Z : electrochemical equivalent of a substance

$$\Rightarrow w = Z I t$$

IIInd Law :

It states that “when a given quantity of electricity is passed through different electrolytes, the amounts of different substances produced at the electrodes are directly proportional to the respective equivalent weights”.

For two substances A and B in two different electrolytic cells ;

$$\frac{w_A}{w_B} = \frac{E_A}{E_B}$$

Experimentally it is seen that 1 gm eq. of a substance is deposited by passing 1 Faradays of electricity.

Magnitude of charge carried by 1 mole of electrons is 96487 C ($6 \times 10^{23} \times 1.6 \times 10^{-19} = 96487$ C). It is also known as *one faraday* i.e., 1F = 96500 C. [96500 C is the widely accepted value of 1 F].

It can also be seen by combining Ist and IIInd Laws as follows :

$$w \propto Q \quad (\text{Ist Law})$$

$$w \propto E \quad (\text{IIInd Law})$$

$$\Rightarrow w = \frac{Q E}{F} \quad \left(\frac{1}{F} = \frac{1}{96500} \right) \quad \Rightarrow \quad \frac{w}{E} = \frac{Q}{F}$$

No. of gram equivalents = No. of Faradays of electricity

$$\Rightarrow 1 \text{ gm eq} = \text{any substance} = 1 \text{ F of electricity}$$

Now there are three approaches to solve a problem.

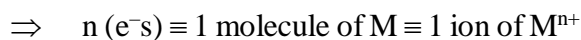
First calculate the number of faradays of electricity by using : No. of faradays = $\frac{Q}{F} = \frac{I t}{96500}$

(i) Now by using the definition : 1 gm. eq. of any substance \equiv 1 F of electricity passed

Calculate the number of gm. eq. and by using the definition of gm.eq. $\left(\text{gm.eq} = \frac{g}{E} \right)$, determine the amount of substance deposited.

(ii) Using anodic and cathodic reactions as follows :

Let us consider a typical cathode reaction : $M^{n+} + ne^- \longrightarrow M$



So in this approach, first write anodic and cathodic reactions and derive the *mole Vs faraday* relation.



(iii) Using the combined relation obtained from Ist and IInd Laws :

$$w = Z I t$$

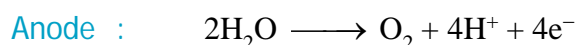
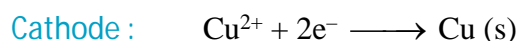
$$\Rightarrow w = \frac{E I t}{96500}$$

Illustration - 18

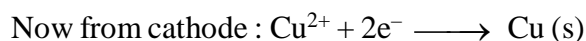
In the electrolysis of aq. $CuSO_4$, a current of 2.50 Amp is allowed to flow for exactly 3.0 hr. How many grams of Cu and lts of O_2 are produced at $25^\circ C$ and 1 atm. pressure?

SOLUTION :

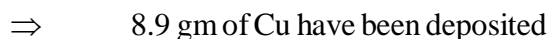
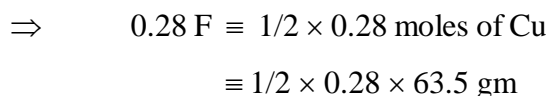
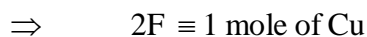
In the electrolysis of aqueous solution, following reactions will take place :



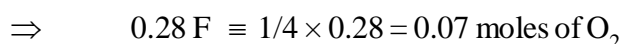
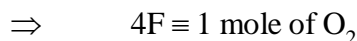
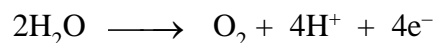
(Sulphate ions and H^+ ions remain in the solution to given an acidic solution)



$$\begin{aligned} \text{No. of faradays} &= \frac{I t}{96500} = \frac{2.5 \times 3 \times 3600}{96500} \\ &= 0.28 F \end{aligned}$$



Now from anode :



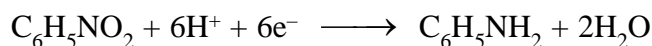
Now using gas equation : $PV = nRT$

$$V = \frac{nRT}{P} = \frac{0.07 \times 0.0821 \times 298}{1} = 1.71 \text{ L Of } O_2$$

Illustration - 19 Calculate the quantity of electricity required to reduce 12.3 gm of nitrobenzene to aniline if the current efficiency for the process is 50%. If the potential drop across the cell is 3.0 V, how much energy is consumed ?

SOLUTION :

Writing the half cell reaction for the reduction of nitro-benzene as follows :



\Rightarrow 1 mole of $\text{C}_6\text{H}_5\text{NH}_2 \equiv 6 \text{ F}$ of charge

Now, moles of nitro-benzene = $12.3/123$

= 0.1 moles

\Rightarrow 0.1 mole $\equiv 0.6 \text{ F}$

Hence, 0.6 F of electricity are used to reduce 12.3 gm of nitro-benzene if the current efficiency is 100 %. But it is given that current efficiency is 50 %, so

$$\text{No. of Faradays required} = \frac{0.6 \times 100}{50}$$

$$= 1.2 \text{ F} = 1.2 \times 96500 \text{ C}$$

Now potential difference = 3V

The energy (E) consumed is given by :

$$E = \text{charge} \times \text{potential difference}$$

$$\begin{aligned} \Rightarrow E &= (1.2 \times 96500 \times 3) = 347400 \text{ J} \\ &= 347.4 \text{ kJ} \end{aligned}$$

Illustration - 20 A potassium salt of ternary acid of Molybdenum (at. mass = 96) has the formula K_2MoO_n . When an acidified solution of K_2MoO_n is electrolysed, O_2 gas is liberated corresponding to a volume of 0.112 L at STP & 0.32 gm of Mo is deposited. Find the formula of salt.

SOLUTION :

The given situation in the question is possible only if MoO_n^{2-} ion gets dissociated to M_0^{x+} which moves towards cathode.

No. of faradays passed \equiv gmeq of $\text{O}_2 \equiv$ gmeq of Mo

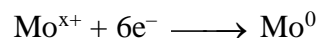
$$4\text{F} \equiv 1 \text{ mole of } \text{O}_2$$

$$\Rightarrow \text{gmeq of } \text{O}_2 = 4 \times \frac{0.112}{22.4} = 0.02$$

$$\Rightarrow \text{gmeq of Mo} = 0.02$$

$$\frac{g}{E} = \text{gmeq of Mo}$$

$$\Rightarrow 0.02 = \frac{0.32}{96/x} \Rightarrow x = 6$$



$$\Rightarrow \text{oxidation state of Mo} = 6$$

In K_2MoO_n , we have $2(+1) + 6 + n(-2) = 0$

$$\Rightarrow n = 4$$

$$\Rightarrow \text{molecular formula is } \text{K}_2\text{MoO}_4$$

SUBJECTIVE SOLVED EXAMPLES

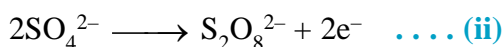
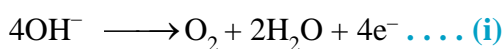
Example - 16 During an electrolysis of conc. H_2SO_4 , perdisulphuric acid ($H_2S_2O_8$) and O_2 form in equimolar amount. The moles of H_2 that will form simultaneously will be :

- (A) thrice that O_2 (B) twice that O_2 (C) equal to that O_2 (D) half of that O_2

SOLUTION : (A)

This is a special case of electrolysis where two products are being obtained at anode :

At anode :

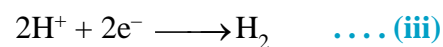


1 mole O_2 requires 4 F electricity and 1 mole $S_2O_8^{2-}$ ($\equiv H_2S_2O_8$) requires 2 F electricity.

So, if x moles of O_2 are being produced, electricity being passed at anode is :

$$4x \text{ (For } O_2) + 2x \text{ (3For } S_2O_8^{2-}) = 6x \text{ F}$$

At cathode :



2 F electricity \equiv 1 mole H_2 is produced

\Rightarrow 6x F electricity \equiv 3x mole H_2 is produced

\Rightarrow Moles of H_2 produced at cathode = 3 moles of O_2 produced at anode.

Example - 17 Assume that impure copper contains iron, gold and silver as impurities. In the purification of copper, after passing a current of 142 amperes for 482.5 seconds, the mass of anode decreased by 22.6 gm and that of cathode increased by 22.0 gm. Estimate % of iron and copper originally present.

SOLUTION :

Note: Silver and gold form the anode mud. Also, Impure Cu forms anode while pure Cu is made as cathode in the refining of impure Cu.

At Impure Cu electrode (\equiv anode in the Cu purification), both iron and Cu will go into the solution. So, mass of iron and Cu dissolved in solution is 22.6 gm.

At cathode (pure Cu electrode), mass of Cu deposited is 22.0 gm. So, amount of Cu in 22.6 gm dissolved at anode is 22.0 gm.

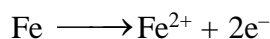
Thus, $22.6 - 22.0 = 0.6$ gm contains Fe, Au and Ag.

Now, No. of faradays passed at cathode
= Gm eq of Cu deposited

$$\frac{22}{63.5/2} = 0.69 = \text{No. of faradays passed at anode.}$$

$$\text{Total faradays passed} = \frac{It}{96500} = \frac{142 \times 482.5}{96500} = 0.71 \text{ (at anode and cathode)}$$

Thus, faradays taken up by Fe at anode
 $= 0.71 - 0.69 = 0.02$



\Rightarrow 2F electricity \equiv 1 mole Fe

$$\begin{aligned}\Rightarrow 0.02 \text{ electricity} &\equiv \frac{0.02}{2} \text{ Mole Fe} \\ &\equiv 0.01 \times 56 \text{ gm Fe} \\ &= 0.56 \text{ gm Fe}\end{aligned}$$

$$\Rightarrow \% \text{ Cu in the original sample} = \frac{22}{22.6} \times 100\%$$

$$= 97.3\%$$

$$\text{and } \% \text{ Fe in the original sample} = \frac{0.56}{22.6} \times 100\%$$

$$= 2.4\%$$

Example - 18

If 6.43×10^5 Coulombs of electricity are passed through an electrolytic cell containing NaClO_3 . 245 gm of NaClO_4 are produced at the anode at the end of electrolysis. Determine the anode efficiency.

SOLUTION :

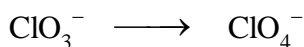
Anode efficiency

$$= \frac{\text{actual wt. of any substance deposited}}{\text{theoretical wt. deposited}} \times 100$$

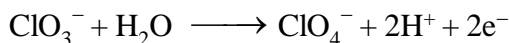
or Anode efficiency

$$= \frac{\text{actual No. of faradays used up}}{\text{total No. of faradays used}} \times 100$$

Let us write anode reaction first :



Balancing by ion electron method :



$$\Rightarrow 2\text{F} \equiv 1 \text{ moles of NaClO}_4$$

$$\Rightarrow 1 \text{ mole of NaClO}_4 \equiv 2 \text{ F of charge}$$

$$\Rightarrow \frac{245}{122.5} \text{ moles of NaClO}_4 \equiv 2 \times \frac{245}{122.5} = 4 \text{ F}$$

So for the production of 245 gm of NaClO_4 , 4F of electricity i.e., 4×96500 C of charge is actually consumed. But we are given that a total of 6.43×10^5 C of electricity is passed through the cell, so some of the charge is wasted.

$$\Rightarrow \text{Anode efficiency} = \frac{4 \times 96500}{6.43 \times 10^5} \times 100$$

$$\Rightarrow \text{Anode efficiency} = 60.03 \%$$

Alternative Method :

First calculate the theoretical amount of NaClO_4 produced by passing 6.43×10^5 C.

$$\Rightarrow 2 \text{ F} \equiv 1 \text{ mole of NaClO}_4$$

$$\Rightarrow \frac{6.43 \times 10^5}{96500} \text{ F} \equiv \frac{1}{2} \times \frac{6.43 \times 10^5}{96500}$$

moles of NaClO_4

$$\equiv \frac{1}{2} \times \frac{6.43 \times 10^5}{96500} \times 122.5$$

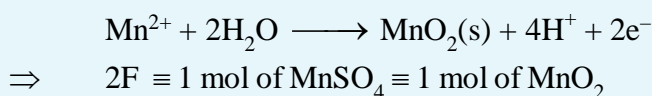
$$= 408.12 \text{ gm of NaClO}_4$$

But in actual only 245 gm of NaClO_4 are produced (some of the current is lost as heat and against the resistance to flow of ions).

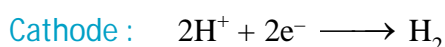
$$\Rightarrow \text{Anode efficiency} = \frac{245}{408.12} \times 100 = 60.03 \%$$

Note: Electro-synthesis

It is a method of producing chemical compounds through non-spontaneous reactions carried out by electrolysis. The above example is an illustration of electro-synthesis. Similarly, by electrolysis a solution of MnSO_4 in H_2SO_4 , MnO_2 may be produced at anode.

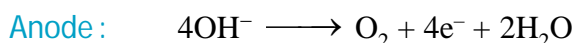
**Example - 19**

During the electrolysis of water, a total volume of 33.6 mL of hydrogen and oxygen gas was collected at STP. Find the amount of electricity that passed during electrolysis.

SOLUTION :

$$\Rightarrow 2\text{F} \equiv 1 \text{ mole of H}_2 \equiv 22400 \text{ mL}$$

$$\text{or } 1\text{F} \equiv 0.5 \text{ mole of H}_2 \equiv 11200 \text{ mL}$$



$$\Rightarrow 4\text{F} \equiv 1 \text{ mole of O}_2 \equiv 22400 \text{ mL}$$

$$\text{or } 1\text{F} \equiv 0.25 \text{ mole of O}_2 \equiv 5600 \text{ mL}$$

From two electrode reactions, it clear that hydrogen and oxygen are evolved in the mole ratio of 2 : 1, hence their volumes will also be in the same ratio.

$$\Rightarrow \text{volume of H}_2 = \frac{2}{3} (33.6) = 22.4 \text{ mL}$$

$$\text{As } 2\text{F} \equiv 22400 \text{ mL H}_2$$

$$\Rightarrow 0.002 \text{ F of charge is passed through the electrolytic cell.}$$

$$\Rightarrow \text{amount of electricity} = 0.002 \times 96500 \text{ C} \\ = 193.0 \text{ Coulombs.}$$

Example - 20

A current of 1.0 A is passed for 96.5 sec through a 200 mL solution of 0.05 M LiCl solution. Find :

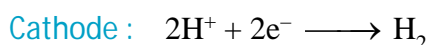
(a) the volume of gases produced at STP.

(b) the pH of solution at the end of electrolysis :

SOLUTION :

No. of faradays passed

$$= \frac{It}{96500} = \frac{1.0 \times 96.5}{96500} = 10^{-3} \text{ F}$$



(Li^+ will remain in solution)

$$\Rightarrow 2\text{F} \equiv 1 \text{ mole of H}_2$$

$$\text{or } 1 \times 10^{-3} \text{ F} \equiv 0.5 \times 10^{-3} \text{ mole of H}_2$$

$$\equiv 0.5 \times 10^{-3} \times 22400 \text{ mL H}_2 \text{ at STP}$$

$$\equiv 11.2 \text{ mL H}_2 \text{ STP}$$



[O_2 will not be liberated due to over potential]

$$\Rightarrow 2\text{F} \equiv 1 \text{ mole of Cl}_2$$

$$\text{or } 1 \times 10^{-3} \text{ F} \equiv 0.5 \times 10^{-3} \text{ moles of Cl}_2$$

$$\equiv 0.5 \times 10^{-3} \times 22400 \text{ mL Cl}_2 \text{ at STP}$$

$$\equiv 11.2 \text{ mL Cl}_2 \text{ at STP}$$

In solution, Li^+ and OH^- are left.

To calculate the pH of solution, first calculate the mmoles of H^+ ions electrolysed.

$$\begin{aligned}\Rightarrow \quad \text{mmoles of } \text{H}^+ \text{ ions electrolysed} &= \text{Meq. of } \text{H}^+ \text{ ions electrolysed} = \text{No. of faradays passed} \\ &= 10^{-3} \text{ F}\end{aligned}$$

Since H_2O produces equal no. of H^+ and OH^- ions, mmoles of OH^- ions left in excess = 10^{-3}

$$\Rightarrow \quad [\text{OH}^-] \approx \frac{10^{-3}}{200/1000} = 5 \times 10^{-3} \text{ M}$$

[Neglect OH^- from dissociation of H_2O]

$$\begin{aligned}\Rightarrow \quad \text{pOH} &= -\log_{10} (5 \times 10^{-3}) \\ &= 3 - \log_{10} 5 = 2.3\end{aligned}$$

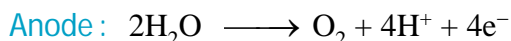
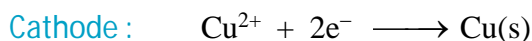
$$\Rightarrow \quad \text{pH} = 14 - \text{pOH} = 14 - 2.3 = 11.7$$

Example - 21

An acidic solution of Cu^{2+} salt containing 0.4 gm of Cu^{2+} is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 ml and the current at 0.965 amp. Calculate the volume of gases evolved at STP during the entire electrolysis.

SOLUTION :

Writing electrode reactions :



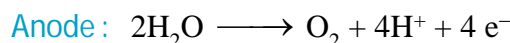
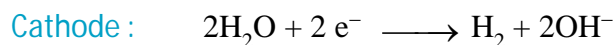
At Cathode : $2\text{F} \equiv 1 \text{ mole of Cu(s)}$

$$\Rightarrow \quad \frac{0.4}{63.5} \text{ moles of Cu} \equiv 2 \times \frac{0.4}{63.5} = 0.0125 \text{ F}$$

At Anode : $4\text{F} \equiv 1 \text{ mole of O}_2(\text{g})$

$$\begin{aligned}\Rightarrow \quad 0.0125 \text{ F} &\equiv \frac{1}{4} \times 0.0125 \\ &= 3.13 \times 10^{-3} \text{ moles of O}_2\end{aligned}$$

After all the copper ions are deposited as copper, electrolysis is continued for 7 minutes (for what ?). Now electrolysis of water is carried out to produce $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ at cathode and anode respectively as follows :



Numbers of faradays passed in 7 minutes are calculated as follows :

$$\begin{aligned}\text{No. of faradays} &= \frac{It}{96500} = \frac{0.965 \times 7 \times 60}{96500} \\ &= 4.2 \text{ mF}\end{aligned}$$

At Cathode : $2\text{F} \equiv 1 \text{ moles of H}_2(\text{g})$

$$4.2 \text{ mF} \equiv 1/2 \times 0.0042 = 2.1 \times 10^{-3} \text{ moles of H}_2$$

At Anode : $4\text{F} \equiv 1 \text{ mole of O}_2(\text{g})$

$$4.2 \text{ mF} \equiv 1/4 \times 0.0042 = 1.05 \times 10^{-3} \text{ moles of O}_2(\text{g})$$

During entire electrolysis, moles of all gases produced = moles of O_2 (with Cu) + (moles of H_2 + moles of O_2)

$$= 3.13 \times 10^{-3} + (2.1 \times 10^{-3} + 1.05 \times 10^{-3})$$

$$= 6.28 \times 10^{-3}$$

Volume of all gases at STP

$$= (6.28 \times 10^{-3}) \times 22400 \text{ ml} = 140.67 \text{ ml}$$

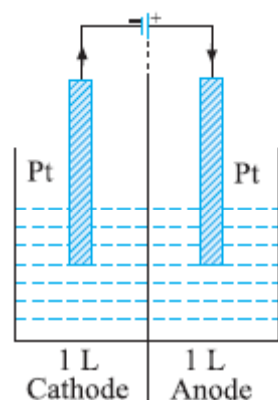
Example 22 - 23**Read the following passage :**

A student prepare 2L buffer solution of 0.3 M NaH_2PO_4 and 0.3 M Na_2HPO_4 . The solution is divided in half between the two compartment (each containing 1 L buffer) of an electrolysis cell, using Pt. electrodes. Assume that the only reaction is the electrolysis of water and electrolysis is carried out for 200 min with a constant current of 0.965 A.

$$\left[\text{Assume that } pK_a(\text{H}_2\text{PO}_4^-) = 7.2 \right]$$

Example - 22*pH at anode is :*

- (A) 7.2 (B) 6.83 (C) 7.57 (D) 7.0

SOLUTION : (C)

No. of faradays passed during electrolysis

$$= \frac{It}{96500} = \frac{0.965 \times 200 \times 60}{96500} = 0.12$$

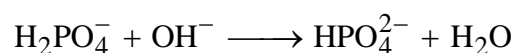


\Rightarrow 1 F electricity \equiv 1 mole H^+ consumed

\Rightarrow 0.12 Felectricity \equiv 0.12 mole H^+ consumed
 \equiv 0.12 mole OH^- left in excess

\Rightarrow After 200 min, $[\text{OH}^-] = \frac{0.12}{1} = 0.12\text{M}$

Now, these OH^- ions will react H_2PO_4^- with ions (\equiv Acid).

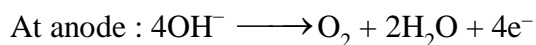


0.3 M	0.12 M	0.3 M
0.18 M	-	0.42 M

$$\begin{aligned} \Rightarrow \text{pH}_{\text{solution}} &= \text{pK}_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= 7.2 + \log_{10} \frac{0.42}{0.18} = 7.57 \end{aligned}$$

Example - 23 *pH at cathode is :*

- (A) 7.2 (B) 6.83 (C) 7.57 (D) 7.0

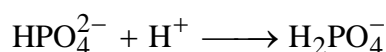
SOLUTION : (B)

\Rightarrow 1 F electricity \equiv 1 mole OH^- consumed

\Rightarrow 0.12 F electricity \equiv 0.12 mole OH^- consumed \equiv 0.12 mole H^+ left in excess

\Rightarrow After 200 min, $[\text{H}^+] = \frac{0.12}{1} = 0.12\text{M}$

Now, these H^+ ions will react HPO_4^{2-} with ions (\equiv Salt).



0.3 M 0.12 M 0.3 M

0.18 M - 0.42 M

\Rightarrow $\text{pH}_{\text{solution}} = \text{pK}_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]} = 7.2 + \log_{10} \frac{0.18}{0.42} = 6.83$

Note : In a buffer solution of $\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$, H_2PO_4^- will act as an acid and HPO_4^{2-} will act as a salt and this will behave as an acidic buffer.

Read the following passage :

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/ electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass : $\text{Na} = 23$, $\text{Hg} = 200$; 1 Faraday = 96500 coulombs).

Example - 24

(i) The total number of moles of chlorine gas evolved is :

- (A) 0.5 (B) 1.0 (C) 2.0 (D) 3.0

(ii) If the cathode is a Hg electrode, the maximum weight (g) of amalgam formed from this solution is :

- (A) 200 (B) 225 (C) 400 (D) 446

(iii) The total charge (coulombs) required for complete electrolysis is :

- (A) 24125 (B) 48250 (C) 96500 (D) 193000

SOLUTION : (i)-(B), (ii)-(D), (iii)-(D)Mole of NaCl in the solution = $4 \times 0.5 = 2$ At anode : $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$ Moles of Cl^- in the solution to be electrolysed = moles NaCl = 2
$$\Rightarrow \text{Moles of } \text{Cl}_2 \text{ produced} = 2 \times \frac{1}{2} = 1 \equiv 2 \text{ F electricity} \equiv 2 \times 96500 \text{ C} \equiv 193000 \text{ C}$$
At cathode : $\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$ (when Hg electrode) $\text{Na} + \text{Hg} \longrightarrow \text{NaHg}$ (Sodium Amalgam) $\Rightarrow 1 \text{ F electricity} \equiv 1 \text{ mole Na}$ $\Rightarrow 2 \text{ F electricity} \equiv 2 \text{ mole Na} \equiv 2 \text{ moles NaHg} \equiv 2 \times (23 + 200) = 446 \text{ gm}$

Electrochemistry - III

(Electrolytic Conductance)

In this chapter, we will deal with the Conductance of electricity (charge) through Electrolytic solutions (Electrolytic Conductance).

BASICS

Section - 8

Electrical conductors (materials/substances which conduct electricity) are of two types :

- (i) **Metallic or Electronic Conductors :** Conductors which transfer electric current by transfer of electrons, without transfer of any matter, are known as **metallic or electronic conductors**. These materials contain electrons which are relatively free to move. The passage of current through these materials has no observable effect other than a rise in their temperature.
- (ii) **Electrolytic Conductors :** Conductors like aqueous solutions of acids, bases and salts in which the flow of electric current is accompanied by chemical decomposition are known as **electrolytic conductors**. With the increase in temperature, the resistance decreases unlike in metallic conduction.
 - (a) The substances whose aqueous solutions allow the passage of electric current and are chemically decomposed are termed *electrolytes*. Solutions of NaCl, KCl, CH₃COOH etc. are examples of electrolytes.
 - (b) The substances whose aqueous solutions do not conduct electric current are called *non-electrolytes*. Solutions of cane sugar, glycerine, alcohol, etc., are examples of non-electrolytes.

Conductance

The conductance (G) is the property of the conductor (metallic as well as electrolytic) which facilitates the flow of electricity through it. It is equal to the reciprocal of resistance (R), i.e.

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

- It is expressed in the unit called reciprocal ohm (ohm⁻¹ or mho) or siemens (S) (S.I. unit).

The term **Conductance** can be further classified in the following ways :

(i) Conductivity (κ) :

The resistance of any conductor varies directly as its length (ℓ) and inversely as its cross-sectional area (A), i.e.,

$$R \propto \frac{\ell}{A} \quad \text{or} \quad R = \rho \frac{\ell}{A} \quad \dots \text{(ii)}$$

where ρ is called the **resistivity** or **specific resistance** (This name is now outdated as per IUPAC convention)

If $\ell = 1 \text{ cm}$ and $A = 1 \text{ cm}^2$, then $R = \rho$

The resistivity (ρ) is, thus, defined as the resistance of one centimeter cube of a conductor.

The reciprocal of resistivity (ρ) is termed the conductivity or it is the conductance of one centimeter cube of a conductor. It is denoted by the symbol κ (abbreviation for “Kappa”). Thus,

$$\kappa = \frac{1}{\rho}$$

Conductivity (κ) is also called as specific conductance (Outdated as per IUPAC convention).

From equation (ii), we have :

$$\rho = \frac{A}{\ell} \cdot R \quad \text{or} \quad \frac{1}{\rho} = \frac{\ell}{A} \cdot \frac{1}{R}$$

$$\kappa = \frac{\ell}{A} \times G \quad \left(\frac{\ell}{A} = \text{cell constant and is denoted by } G^* \right)$$

or Conductivity (κ) = Conductance (G) \times cell constant (G^*)

- Note :**
- The unit of conductivity (κ) is $\text{ohm}^{-1} \text{ cm}^{-1}$ or S cm^{-1} .
 - Conductivity can also be defined as the conductance of one centimeter cube of a conductor.
 - For the conductance measurement of a solution, ℓ is the distance between the electrodes and A is the area of the electrodes.
 - G^* is difficult to calculate using ℓ/A . It is calculated more precisely by using a solution having known values of κ at some concentration [Calibration Technique].

(ii) Molar conductance (Λ_m)

The molar conductance is defined as the conductance of all the ions produced by the ionisation of 1 g mole of an electrolyte when present in V ml of solution. It is denoted by Λ_m .

$$\text{Molar conductance } (\Lambda_m) = \kappa \times V$$

where V is the volume in ml containing 1 gm mole of the electrolyte.

If c is the concentration of the solution in g mole per litre, then :

$$\Lambda_m = \kappa \times \frac{1000}{c} \quad \text{where } c \text{ is the concentration of the solution in M}$$

Its units are $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ or $\text{S cm}^2 \text{mol}^{-1}$

Also, if $A_x B_y$ is an electrolyte dissociating as : $A_x B_y \rightleftharpoons xA^{y+} + yB^{x-}$

$$\Rightarrow \wedge_m A_x B_y = x \cdot \wedge_m (A^{y+}) + y \cdot \wedge_m (B^{x-})$$

For example : $\wedge_m \text{Al}_2(\text{SO}_4)_3 = 2\wedge_m(\text{Al}^{3+}) + 3\wedge_m(\text{SO}_4^{2-})$

(iii) Equivalent Conductance (\wedge_{eq})

One of the factors on which the conductance of an electrolytic solution depends is the concentration of the solution. In order to obtain comparable results for different electrolytes, it is necessary to take equivalent conductance.

- It is defined as the conductance of all the ions produced by one gram equivalent of an electrolyte in a given solution. It is denoted by \wedge_{eq} .

At concentration c (in gm-equivalent/L i.e., normality), equivalent conductance is denoted by \wedge_{eq} .

$$\Rightarrow \wedge_{\text{eq}} = \frac{1000 \times \text{conductivity} (\text{ohm}^{-1} \text{cm}^{-1})}{c [\text{or Normality}]} \times \frac{1000 \times \kappa}{N}$$

If 'V' is the volume in ml containing 1 gm equivalent of the electrolyte, the above equation can be written as :

$$\wedge_{\text{eq}} = \kappa \times V$$

Its units are $\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$ or $\text{S cm}^2 \text{equiv}^{-1}$.

Also, Equivalent conductance

$$= \frac{\text{Molar conductance}}{x} \text{ where } x = \frac{\text{Molecular mass}}{\text{Equivalent mass}} = n\text{-factor}$$

Also, if $A_x B_y$ is an electrolyte dissociating as : $A_x B_y \rightleftharpoons xA^{y+} + yB^{x-}$

$$\wedge_{\text{eq}} (A_x B_y) = \wedge_{\text{eq}} (A^{y+}) + \wedge_{\text{eq}} (B^{x-})$$

For example : $\wedge_{\text{eq}} \text{Al}_2(\text{SO}_4)_3 = \wedge_{\text{eq}} (\text{Al}^{3+}) + \wedge_{\text{eq}} (\text{SO}_4^{2-})$

Illustration - 21 Resistance of a decimolar solution between two platinum electrodes 0.02 m apart and 4cm^2 in area was found to be 40 ohms. Calculate : (a) cell constant (b) conductance (c) conductivity

SOLUTION :

(a) Cell constant (G^*)

$$= \frac{\ell}{A} = \frac{0.02}{4 \times 10^{-4}} \text{ m}^{-1} = 50 \text{ m}^{-1}$$

(b) Conductance (G) = $\frac{1}{R} = \frac{1}{40} \text{ S} = 0.025 \text{ S}$

(c) Conductivity (κ) = $G \cdot G^* = 50 \times 0.025 \text{ S/m}$
 $= 1.25 \text{ S/m}$

Illustration - 22 The resistance of 0.1 M solution of a salt (type : AB) is found to be $2.5 \times 10^3 \text{ ohm}$. The equivalent conductance of the solution is (Cell constant = 1.15 cm^{-1}) :

(A) 4.6 (B) 5.6 (C) 6.6 (D) 7.6

SOLUTION : (A)

Use :

$$\kappa = G \cdot G^*$$

$$= \frac{1}{2.5 \times 10^3} \times 1.15 = 4.6 \times 10^{-4} \quad \left[\because G = \frac{1}{R} \right]$$

$$\Lambda_{\text{eq}} = \frac{\kappa \times 1000}{N} = \frac{4.6 \times 10^{-4} \times 1000}{0.1}$$

$$= 4.6 \text{ S cm}^{-1} \text{ eq}^{-1}.$$

Illustration - 23 The conductivity of 0.02 M KCl solution at 25°C is $2.78 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of this solution at 25°C when measured with a particular cell was 250 ohms. The resistance of 0.01 M CuSO_4 solution at 25°C measured with the same cell was 8330 ohms. Calculate the molar conductivity of the copper sulphate solution

SOLUTION :

$$\text{Cell constant } (G^*) = \frac{\text{Conductivity } (\kappa) \text{ of KCl}}{\text{Conductance } (G) \text{ of KCl}} \text{ and Conductance of KCl } (G) = \frac{1}{R}$$

$$\Rightarrow \text{Cell constant } (G^*) = \frac{2.78 \times 10^{-3}}{1/250} = 2.78 \times 10^{-3} \times 250 \text{ cm}^{-1}$$

For 0.01 M CuSO_4 solution :

$$\text{Conductivity } (\kappa) = \text{Cell constant } (G^*) \times \text{conductance } (G)$$

$$= \left(2.78 \times 10^{-3} \times 250 \right) \times \frac{1}{8330} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\text{Molar conductance } (\Lambda_m) = \text{Conductivity } (\kappa) \times \frac{1000}{c} = \left(\frac{2.78 \times 10^{-3} \times 250}{8330} \right) \times \frac{1000}{0.01} = 8.3 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$$

EFFECT OF DILUTION

Section - 9

Effect on conductance

- (i) Conductance of a solution increases with increase in the number of solute molecules/ions and decreases with decreases in the number of solute molecules/ions.
- (ii) Conductance of a solution increases with dilution as the interactions between the molecules/ions decreases due to increase in the average distance between the molecules/ions.

Effect on degree of dissociation

- (i) **Strong electrolytes** : There is almost no change in the degree of dissociation (as it is already close to unity).
- (ii) **Weak electrolytes** : With dilution, degree of dissociation increases rapidly and thus, the number of molecules increases.

Effect on Molar and Equivalent conductance

Both \wedge_m and \wedge_{eq} increases with dilution as conductance increases with dilution.

For strong electrolytes, the increase in \wedge_m and \wedge_{eq} is relatively small as increase in the number of molecules/ions is very small.

For weak electrolytes, the increase in \wedge_m and \wedge_{eq} is large and rapid as ' α ' increases with dilution.

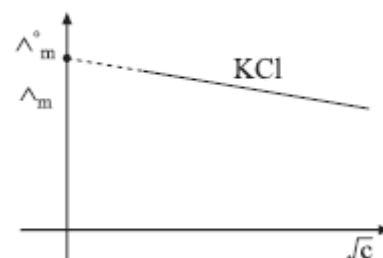
Effect on Conductivity

On dilution, number of molecules/ions per ml of the solution decreases. Since, conductivity is defined as the conductance of one ml of the solution, conductivity decreases with dilution (due to decrease in the conductance).

Infinite Dilution

When addition of water doesn't bring about any further change in the conductance of a solution, this situation is referred to as Infinite Dilution.

- (a) **Strong Electrolytes** : When infinite dilution is approached, the conductance of a solution of strong electrolyte approaches a limiting value and can be obtained by extrapolating the curve between \wedge_m and \sqrt{c} as shown: (Note: the behavior/variation is linear)



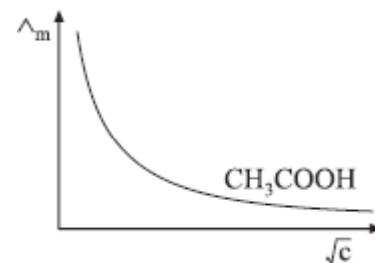
The molar conductivity of strong electrolytes is found to vary with concentration as :

$$\wedge_m = \wedge_m^0 - b\sqrt{c}$$

where b is a constant depending upon the type of electrolyte (e.g. AB, A_2B etc.), the nature of the solvent and the temperature.

This equation is known as **Debye Huckel–Onsager** equation and is found to hold good at low concentrations.

- (b) **Weak Electrolytes** : When infinite dilution is approached, the conductance of a solution of weak electrolyte increases very rapidly and thus, cannot be obtained through extrapolation. Also, the variation between \wedge_m and \sqrt{c} is not linear at low concentrations.



- Note:** (i) $\lim_{c \rightarrow 0} \wedge_m = \wedge_m^\circ$ and $\lim_{c \rightarrow 0} \wedge_{eq} = \wedge_{eq}^\circ$
- (ii) Conductance of a weak electrolyte at infinite dilution can be calculated by using Kohlrausch's law of Independent Migration of Ions.

Ionic Conductance

Conductance of an ion in the solution is inversely proportional to its size in the solution.

e.g. Li^+ ion has a very high charge to size ratio due to which it gets hydrated to a large extent, when dissolved in water. Thus, Size of $\text{Li}^+(\text{aq.}) \gg \text{Size of Li}^+(\text{g.})$.

- Note:** ➤ $r_{\text{K}^+(\text{g})} > r_{\text{Na}^+(\text{g})} > r_{\text{Li}^+(\text{g})}$ but $r_{\text{K}^+(\text{aq})} < r_{\text{Na}^+(\text{aq})} < r_{\text{Li}^+(\text{aq})}$
- $\Rightarrow \wedge_m \text{K}^+(\text{aq}) > \wedge_m \text{Na}^+(\text{aq}) > \wedge_m \text{Li}^+(\text{aq})$
- A heavily hydrated ion has to drag water molecules along with it when it moves in a solution which makes it less mobile (or less conducting).
- Size of $\text{H}^+(\text{g})$ and $\text{OH}^-(\text{g})$ ions are extremely small yet they have a very high conductance value in the solution (as opposed to what you might have expected). Infact, H^+ ion has the highest \wedge_m at any temperature followed by OH^- ions. This is due to the mechanism by which they travel in the aqueous solution.

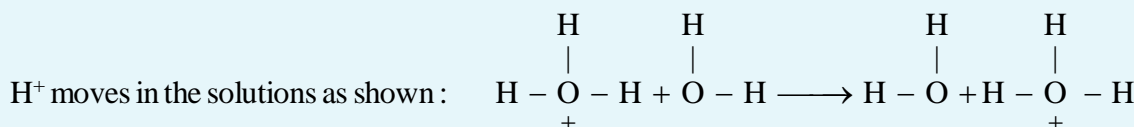


Illustration - 24 Arrange the following compounds in the orders of increasing conductionce. HCl , LiCl , NaCl , KCl .

SOLUTION :

Note that anion (Cl^-) is same in all the given compounds. So, look for the conductance values of cations only.

$$\text{Since, } \wedge_m \text{H}^+ > \wedge_m \text{K}^+ > \wedge_m \text{Na}^+ > \wedge_m \text{Li}^+$$

$$\text{So, } \wedge_m \text{HCl} > \wedge_m \text{KCl} > \wedge_m \text{NaCl} > \wedge_m \text{LiCl}$$

KOHLRAUSCH'S LAW OF INDEPENDENT MIGRATION OF IONS

Section - 10

As per Kohlrausch's Law of Independent Migration of Ions "At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of molar conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions, i.e., anions and cations".

As per Kohlrausch's law, at infinite dilution, the conductance of any ion is independent of its association with the other ion in the electrolyte i.e. $\Lambda_m^0(\text{K}^+)$ will be same in infinitely diluted solution of KCl or KBr or KNO_3 .

Illustration - 25 The equivalent conductance of sodium chloride, hydrochloric acid and sodium acetate at infinite dilution are 126.45, 426.16 and 91.0 $\text{S cm}^2 \text{equiv}^{-1}$, respectively, 25°C . Calculate the equivalent conductance of acetic acid at infinite dilution. If the equivalent conductance of N/100 solution of acetic acid is $3.9 \text{ S cm}^2 \text{eq}^{-1}$, calculate the degree of dissociation of acetic acid at this dilution.

SOLUTION :

According to Kohlrausch's law, $\Lambda_{\text{eq CH}_3\text{COONa}}^0 = \Lambda_{\text{eq CH}_3\text{COO}^-}^0 + \Lambda_{\text{eq Na}^+}^0 = 91.0 \quad \dots \text{(i)}$

Similarly, we have :

$$\Lambda_{\text{eq HCl}}^0 = \Lambda_{\text{eq H}^+}^0 + \Lambda_{\text{eq Cl}^-}^0 = 426.16 \quad \dots \text{(ii)}$$

$$\Lambda_{\text{eq NaCl}}^0 = \Lambda_{\text{eq Na}^+}^0 + \Lambda_{\text{eq Cl}^-}^0 = 126.45 \quad \dots \text{(iii)}$$

Adding Equations (i) and (ii) and subtracting (iii),

$$\begin{aligned} \text{we get : } & \left(\Lambda_{\text{eq CH}_3\text{COO}^-}^0 + \Lambda_{\text{eq Na}^+}^0 \right) + \left(\Lambda_{\text{eq H}^+}^0 + \Lambda_{\text{eq Cl}^-}^0 \right) - \left(\Lambda_{\text{eq Na}^+}^0 + \Lambda_{\text{eq Cl}^-}^0 \right) \\ & = 91.0 + 426.16 - 126.45 \end{aligned}$$

$$\Rightarrow \left(\Lambda_{\text{eq CH}_3\text{COO}^-}^0 + \Lambda_{\text{eq H}^+}^0 \right) = 390.7$$

$$\Rightarrow \Lambda_{\text{eq CH}_3\text{COOH}}^0 = 390.7 \text{ S cm}^2 \text{equiv}^{-1}$$

$$\text{Also, } \alpha = \frac{\Lambda_{\text{eq}}}{\Lambda_{\text{eq}}^0} = \frac{3.9}{390.7} = 0.01 = 1\%$$

Note : $\Lambda_{\text{eq Cl}^-}^0$ has been taken as same in equation (ii) and (iii). This is from the direct result of Kohlrausch's law.

Applications of Kohlrausch's law :

(i) Solubility Product of a Sparingly Soluble Salt :

If solute is sparingly soluble in a given solvent, its concentration is taken as its solubility in the saturated solution.

$$\text{Thus, } \Lambda_m^0 = \frac{1000 \times \text{conductivity}}{c} = \frac{1000 \times \kappa}{c}$$

Λ_m^0 can be computed using Kohlrausch's law:

Thus, c can be computed and can be used to calculate the solubility product.

$$\begin{aligned} \text{For example : For } \text{Al(OH)}_3 : K_{\text{SP}} &= [\text{Al}^{3+}](3[\text{OH}^-])^3 \\ &= (c)(3c)^3 \Rightarrow K_{\text{SP}} = 27c^4 \end{aligned}$$

(ii) Degree of dissociation :

At any dilution, the equivalent conductance is proportional to the degree of dissociation. Thus,

$$\begin{aligned} \text{Degree of dissociation } (\alpha) &= \frac{\Lambda_{\text{eq}}}{\Lambda_{\text{eq}}^0} = \frac{\text{Equivalent conductance at a given concentration}}{\text{Equivalent conductance at infinite dilution}} \\ &= \frac{\Lambda_m}{\Lambda_m^0} = \frac{\text{Molar conductance at a given concentration}}{\text{Molar conductance at infinite dilution}} \end{aligned}$$

Illustration - 26

The conductivity of a saturated solution of silver chloride is $2.30 \times 10^{-6} \text{ mho cm}^{-1}$ at 25°C . Calculate the solubility of silver chloride at 25°C if $\Lambda_{\text{mAg}^+}^0 = 61.9 \text{ mho cm}^2 \text{ mol}^{-1}$ and $\Lambda_{\text{mCl}^-}^0 = 76.3 \text{ mho cm}^2 \text{ mol}^{-1}$.

SOLUTION :

Let the solubility of AgCl be x gram mole per litre (i.e., mole/L). [Note : $N_{\text{AgCl}} = M_{\text{AgCl}}$]

Using :

$$\Lambda_m^0 = \frac{1000 \times \text{specific conductance}}{c} = \frac{1000 \times \kappa}{x}$$

Now find the equivalent conductance of AgCl at infinite dilution.

$$\Lambda_{\text{mAgCl}}^0 = \Lambda_{\text{mAg}^+}^0 + \Lambda_{\text{mCl}^-}^0$$

$$\Lambda_{\text{mAgCl}}^0 = 61.9 + 76.3 = 138.2 \text{ mho cm}^2 \text{ mol}^{-1}$$

$$\Rightarrow 138.2 = \frac{1000 \times 2.30 \times 10^{-6}}{x}$$

$$\Rightarrow x = \frac{2.30 \times 10^{-3}}{138.2} = 1.66 \times 10^{-5} \text{ mol/L}$$

$$\begin{aligned} \Rightarrow \text{Solubility in gm/L} &= 1.66 \times 10^{-5} \times 143.5 \\ &= 2.38 \times 10^{-3} \end{aligned}$$

(iii) Ionisation constant of weak electrolytes :

Let AB be a weak electrolyte of concentration c .



At $t = 0$	c	0	0
At equilibrium	$c - c\alpha$	$c\alpha$	$c\alpha$

Thus, Equilibrium Dissociation Constant = $K_d = \frac{[A^+][B^+]}{[AB]}$

$$K_d = \frac{c\alpha \cdot c\alpha}{c - c\alpha} = \frac{c\alpha^2}{1 - \alpha} \quad \dots (i)$$

For weak electrolytes, $\alpha \ll 1 \Rightarrow K_d \approx c\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_d}{c}}$

As concentration decreases, degree of dissociation increases.

Now, $\alpha = \frac{\frac{\wedge_m}{\wedge_m^0}}{\frac{\wedge_{eq}}{\wedge_{eq}^0}} = \frac{\wedge_{m}^{rq}}{\wedge_{eq}^0}$

Putting this value of α in (i) we get :

$$K_d = \frac{c \left(\frac{\frac{\wedge_m}{\wedge_m^0}}{\frac{\wedge_{eq}}{\wedge_{eq}^0}} \right)^2}{1 - \frac{\frac{\wedge_m}{\wedge_m^0}}{\frac{\wedge_{eq}}{\wedge_{eq}^0}}} = \frac{c \left(\frac{\wedge_{eq}}{\wedge_{eq}^0} \right)^2}{1 - \frac{\wedge_{eq}}{\wedge_{eq}^0}} \quad \dots (ii)$$

Equation (ii) is known as *Ostwald equation*.

Illustration - 27 Resistance of a solution (A) is 50 ohm and that of solution (B) is 100 ohm, both solutions being taken in the same conductivity cell. If equal volumes of solutions (A) and (B) are mixed, what will be the resistance of the mixture, using the same cell ? Assume that there is no increase in the degree of dissociation of (A) and (B) on mixing.

SOLUTION :

Let us suppose κ_1 and κ_2 are the specific conductance of solutions 'A' and 'B' respectively and cell constant is 'y'.

We know that :

Specific conductance = Conductance \times cell constant

Also, conductance = $\frac{1}{R}$

\Rightarrow For (A) : $\kappa_1 = \frac{1}{50} \times y$

and For (B) : $\kappa_2 = \frac{1}{100} \times y$

When equal volumes of (A) and (B) are mixed, the volumes becomes double. Then,

$$\Rightarrow \frac{1}{2} \left[\frac{y}{50} + \frac{y}{100} \right] = \frac{1}{R} \times y$$

$$\text{Specific conductance of mixture} = \frac{\kappa_1 + \kappa_2}{2}$$

$$\Rightarrow \frac{1}{100} + \frac{1}{200} = \frac{1}{R} \Rightarrow R = 200/3$$

$$\therefore \frac{\kappa_1 + \kappa_2}{2} = \frac{1}{R} \times y$$

$$= 66.66 \text{ ohm}$$

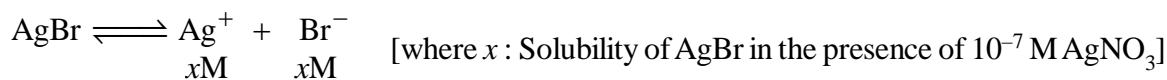
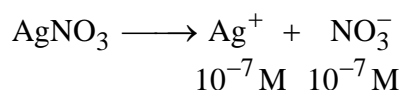
Illustration - 28 The solubility product of sparingly soluble $\text{AgBr}(s)$ is $12 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$. Calculate the conductivity in units of 10^{-7} Sm^{-1} of saturated solution of AgBr upon addition of $1 \times 10^{-7} \text{ mol dm}^{-3}$ aqueous AgNO_3 . The limiting ionic molar conductivity of Ag^+ , Br^- , and NO_3^- at infinite dilution are 6×10^{-3} , 8×10^{-3} and $7 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$, respectively. [Conductivity of pure water = $350 \times 10^{-7} \text{ S m}^{-1}$] (Neglect any effect due to concentration dependence of conductance)

- (A) 39 (B) 55 (C) 15 (D) 405

SOLUTION : (D)

$$K_{\text{SP}} \text{AgBr} = 12 \times 10^{-14} \left(\frac{\text{mol}}{\text{dm}^3} \right)^2 \equiv 12 \times 10^{-14} \text{ M}^2$$

When 10^{-7} M AgNO_3 is added into the saturated solution of AgBr :



At equilibrium :

$$K_{\text{SP AgBr}} = [\text{Ag}^+][\text{Br}^-] = (x + 10^{-7}) \cdot x = 12 \times 10^{-14}$$

$$\Rightarrow x^2 + 10^{-7}x - 12 \times 10^{-14} = 0$$

Solve to get : $x = 3 \times 10^{-7} \text{ M}$

$$\Rightarrow \text{At equilibrium, } [\text{Ag}^+] = x + 10^{-7} = 4 \times 10^{-7} \text{ M} = 4 \times 10^{-4} \text{ mol m}^{-3}; [\text{Br}^-] = x = 3 \times 10^{-7} \text{ M}$$

$$= 3 \times 10^{-4} \text{ mol m}^{-3}$$

$$[\text{NO}_3^-] = 10^{-7} \text{ M} = 10^{-4} \text{ mol m}^{-3}$$

$$[\text{Using : } 1 \text{ M} \equiv 1000 \text{ mol m}^{-3}]$$

$$\text{Total conductivity of solution} = \kappa_{\text{Ag}^+} + \kappa_{\text{Br}^-} + \kappa_{\text{NO}_3^-} + \kappa_{\text{H}_2\text{O}}$$

$$= \lambda_{\text{m}(\text{Ag}^+)}^0 \cdot [\text{Ag}^+] + \lambda_{\text{m}(\text{Br}^-)}^0 \cdot [\text{Br}^-] + \lambda_{\text{m}(\text{NO}_3^-)}^0 \cdot [\text{NO}_3^-] + \kappa_{\text{H}_2\text{O}}$$

$$= 6 \times 10^{-3} \times 4 \times 10^{-4} + 8 \times 10^{-3} \times 3 \times 10^{-4} + 7 \times 10^{-3} \times 10^{-4} + 350 \times 10^{-7}$$

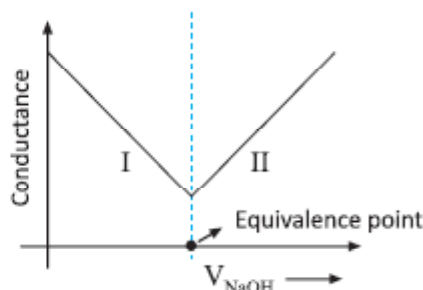
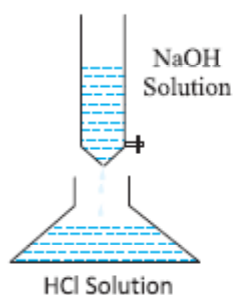
$$= 405 \times 10^{-7} \text{ S m}^{-1}$$

CONDUCTOMETRIC TITRATIONS

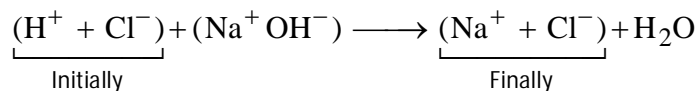
Section - 11

Measurement of conductance of resulting solution from an acid and base titration may be used to calculate the equivalence point if there is a regular change in the conductance and sharp change at the equivalence point.

CASE : I Strong Acid (HCl) vs. Strong Base (NaOH) :

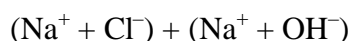


Region I : Initially the solution has the conductance due to the presence of H^+ and Cl^- ions. As NaOH is added, following reaction takes place :



Thus, highly conducting H^+ ions are replaced by lower conducting Na^+ ions, resulting in a decrease in the conductance of solution. As more and more NaOH is added (till the equivalence point), conductance goes on decreasing.

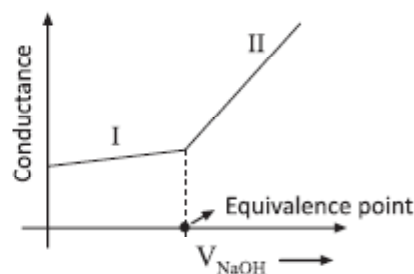
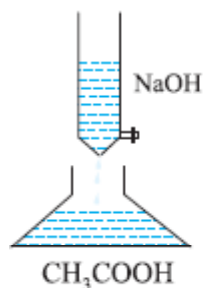
Region II : Just after the equivalence point, as more NaOH is added, now there are more ions (Nonneutralisation)



So, conductance will increase due to the presence of more number of ions in the solution.

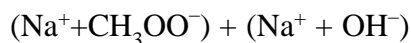
As we can see that equivalence point, there is a sharp change in the curve definition and we can easily calculate the equivalence point.

CASE : II Weak Acid (CH_3COOH) vs Strong Base (NaOH) :



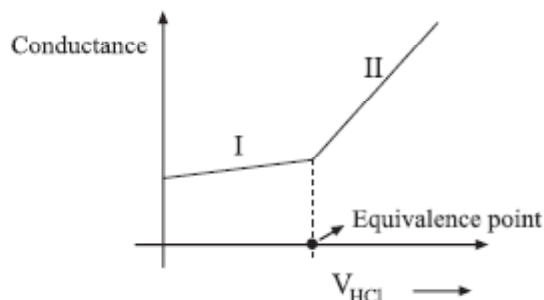
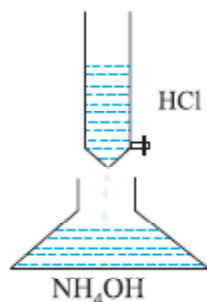
Region I : As more NaOH is added, it will directly react with CH_3COOH to form highly ionizable salt, $\text{CH}_3\text{COO}^- \text{Na}^+$. So, conductance will start increase (slowly as CH_3COO^- and Na^+ have low conductance)

Region II : Just after equivalence point, there will be an increase in the number of ions.



So, conductance will increase sharply (OH^- ions have highly conductance) and we can easily find the equivalence point required through the titration.

Case : III Strong acid (HCl) vs Weak Base (NH_4OH) :



Follows similar discussion as in [case II](#).

Illustration - 29 An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List I. The variation in conductivity of these reaction is given in List II. Match List I with List II.

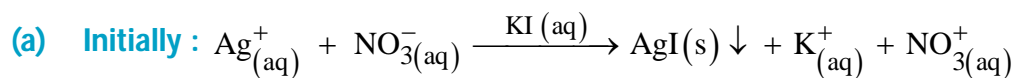
List I	List II
[P] $(C_2H_5)_3N + CH_3COOH$ X Y	1. Conductivity decreases and then increases.
[Q] $KI(0.1M) + AgNO_3(0.01M)$ X Y	2. Conductivity decreases and then does not change much
[R] $(CH_3COOH) + KOH$ X Y	3. Conductivity increases and then does not change much
[S] $NaOH + HI$ X Y	4. Conductivity does not change much and then increases

SOLUTION :

1. EtN in CH_3COOH solution

When Et_3N solution is added to CH_3COOH . ' α ' of CH_3COOH will increase, so through H^+ ions ions will be consumed by Et_3N , the overall number of ions in the solution will increase and hence conductivity increase initially. Once almost all of CH_3COOH is consumed, a lot of CH_3COOH^\ominus and Et_3NH^\oplus will be present in the solution and now further addition Et_3N doesn't cause much change in the total number of ions as Et_3N will not be able to extract H^+ ion from H_2O (because their will be suppression due to already present Et_3NH^\oplus ions) and hence conductivity will almost remain the same.

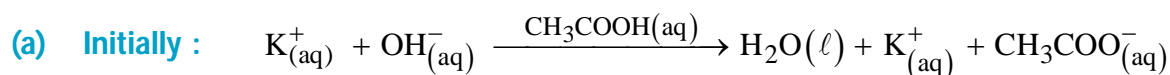
2. KI solution in $AgNO_3$ solution



\Rightarrow Number of ions remain the same \Rightarrow Conductivity does not change much.

(b) After all Ag^+ ions have been precipitated out, then the conductivity will increase because we are adding a more concentrated solution and consequently number of ions per unit volume will increase.

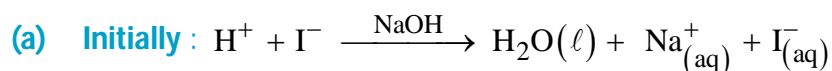
3. CH_3COOH in KOH



\Rightarrow Number of ions remains the same, but number of OH^- ions decrease \Rightarrow Conductivity decrease.

- (b) After all of OH^- ions have been consumed, then further addition of CH_3COOH will not have much effect as CH_3COOH will not break up much, as its dissociation will be suppressed by the already present $\text{CH}_3\text{COOH}^\ominus$ ions.

4. NaOH in HI



\Rightarrow Number of ions remains the same, but number of H^+ decrease \Rightarrow Conductivity decreases.

- (b) After all the H^+ ions have been consumed, then further addition of a strong electrolyte NaOH (which will give OH^\oplus ions in the solution) will increase conductivity.

ANSWER : [P-3] [Q-4] [S-1]

IN-CHAPTER EXERCISE - C

1. Given the following molar conductivities at 25°C ; HCl , $426\ \Omega^{-1}\text{cm mol}^{-1}$; NaCl , $126\ \Omega^{-1}\text{cm mol}^{-1}$; NaC (sodium crotonate) $83\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. What is the ionization constant of crotonic acid ?
- The conductivity of a $0.001\ \text{M}$ crotonic acid solution is $3.83 \times 10^{-5}\ \Omega^{-1}\text{cm}^{-1}$.

NOW ATTEMPT IN-CHAPTER EXERCISE C FOR REMAINING QUESTIONS

NOW ATTEMPT OBJECTIVE WORKSHEET BEFORE PROCEEDING AHEAD IN THIS EBOOK

THINGS TO REMEMBER

1. In an electrochemical cell, cathode is the electrode with higher reduction potential or lower oxidation potential.

$$\text{Also, } E_{\text{cell}}^{\circ} = \left(E_{\text{reduction}}^{\circ}\right)_{\text{cathode}} - \left(E_{\text{reduction}}^{\circ}\right)_{\text{anode}}$$

2. Electrode potential of an electrode or cell varies with concentration, partial pressure of the species involved and temperature.

$$E_{\text{reduction}} = E_{\text{reduction}}^{\circ} - \left[\frac{2.303 RT}{nF} \equiv \frac{0.059}{n} \text{ at } 25^{\circ}\text{C} \right] \log_{10} Q_{\text{reduction}}$$

$$\text{and } E_{\text{cell}} = E_{\text{cell}}^{\circ} - \left(\frac{2.303 RT}{n_{\text{cell}} F} \equiv \frac{0.059}{n_{\text{cell}}} \text{ at } 25^{\circ}\text{C} \right) \log_{10} Q_{\text{cell}}$$

3. For a concentration cell, $E_{\text{cell}}^{\circ} = 0$

$$\text{For a hydrogen concentration cell, } E_{\text{cell}} = 0.059 \left(\text{pH}_{\text{Anode}} - \text{pH}_{\text{cathode}} + \frac{1}{2} \log_{10} \frac{(\text{pH}_2)_{\text{anode}}}{(\text{pH}_2)_{\text{cathode}}} \right)$$

4. Gibbs Helmholtz equation :

$$\Delta G = \Delta H + T \left[\frac{d(\Delta G)}{dT} \right]_T \Rightarrow \Delta H = n_{\text{cell}} F \left[T \left(\frac{dE_{\text{cell}}}{dT} \right)_P - E_{\text{cell}} \right]$$

$$\text{and } \Delta S = n_{\text{cell}} F \left(\frac{dE_{\text{cell}}}{dT} \right)_P$$

5. In electrolysis, cations move towards cathode and anions move towards anode and the “chance” of their deposition/liberation depends on their electrode potential, concentration, overpotential etc.

6. Faraday's law : $W = ZIt$ (i)

$$\frac{W_A}{E_A} = \frac{W_B}{E_B} \quad \dots \text{ (ii)}$$

No. of Faradays supplied = $\frac{It}{96500}$ = No. of gm eq. of the substance deposited/liberated at the electrode.

7. Molar/ equivalent conductance and degree of dissociation of a electrolyte increases with dilution whereas conductivity decreases with dilution.

$$G \cdot G^* = \kappa ; \wedge_m = 1000 \times \frac{\kappa}{C} ; \wedge_{eq.} = 1000 \times \frac{\kappa}{C}$$

8. Molar/equivalent conductance of a strong electrolyte increases linearly with dilution whereas the change is very rapid for weak electrolytes at high dilutions.

To calculate the molar/equivalent conductance of a weak electrolyte at infinite dilution, use Kohlrausch's law of independent migration of ions.

$$\text{Also, } \alpha = \frac{\Lambda_m^\circ}{\Lambda_m} = \frac{\Lambda_{eq}^\circ}{\Lambda_{eq}}$$

9. For a smaller ion in gaseous state i.e. larger ion in aqueous, molar conductance is a small value. However, H^+ and OH^- ions are exceptions with high molar conductance values.

IN-CHAPTER EXERCISE-C

- C 1. 1.11×10^{-5}

SOLUTIONS TO IN-CHAPTER EXERCISE-C

1. Let crotonic acid be HC

$$\Lambda_{\text{HC}}^0 = \Lambda_{\text{NaC}}^0 + \Lambda_{\text{HCl}}^0 - \Lambda_{\text{NaCl}}^0 = 83 + 426 - 126 = 383$$

$$\Lambda_{\text{HL}}^c = \frac{3.83 \times 10^{-5} \times 10^3}{0.001} = 38.3 \quad \Rightarrow \quad \alpha = \frac{38.3}{383} = 0.1$$

$$K_a = \frac{C \alpha^2}{1 - \alpha} = \frac{0.001 \times 0.1^2}{1 - 0.1} = 1.11 \times 10^{-5}$$

My Chapter Notes

