

Class -XII

Chemistry

Chapter-3

Electrochemistry

### Solved Examples on NERNST Equation

1. Calculate the emf of the cell in which the following reaction takes place:  $\text{Ni(s)} + 2\text{Ag}^+ (0.002 \text{ M}) \rightarrow \text{Ni}^{2+} (0.160 \text{ M}) + 2\text{Ag(s)}$ . Given that  $E^\circ_{\text{cell}} = 1.05 \text{ V}$ .

**Solution:**

By using Nernst equation

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2} \\ &= 1.05 - \frac{0.059}{2} \log \frac{[0.160]}{[0.002]^2} \\ &= 1.05 - 0.02955 \log \frac{0.160}{0.000004} \end{aligned}$$

$$= 1.05 - 0.02955 \log 4 \times 10^4$$

$$= 1.05 - 0.02955 (\log 10000 + \log 4)$$

$$= 1.05 - 0.02955 (4 + 0.6021)$$

$$= 0.914 \text{ V}$$

2. The standard electrode potential of zinc ions is 0.76V. What will be the potential of a 2M solution at 300K?

**Solution:**

The Nernst equation for the given conditions can be written as follows;

$$E_{\text{Mn}^+/M} = E^\circ - \frac{2.303RT}{nF} \log \frac{1}{[M]^{n+}}$$

Here,

$$E^\circ = 0.76 \text{ V}$$

$$n = 2$$

$$F = 96500 \text{ C/mole}$$

$$[\text{Mn}^+] = 2 \text{ M}$$

$$R = 8.314 \text{ J/K mole}$$

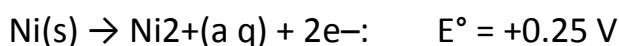
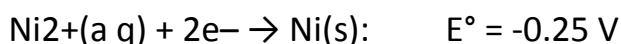
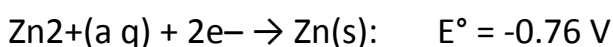
$$T = 300 \text{ K}$$

Substituting the given values in Nernst equation we get,

$$\begin{aligned} E_{\text{Zn}^{2+}/\text{Zn}} &= 0.76 - \frac{2.303 \times 8.314 \times 300}{2 \times 96500} \log \frac{1}{2} \\ &= 0.76 - [0.0298 \times (-0.301)] \\ &= 0.76 + 0.009 = 0.769 \text{ V} \end{aligned}$$

Therefore, the potential of a 2M solution at 300K is 0.769V.

**3.** From the following standard potentials, arrange the metals in the order of their increasing reducing power.



Reducing power of a metal increases with its ability to give up electrons i.e. lower standard potentials. Arranging the reduction potentials in the decreasing order gives the increasing order of reducing power of metals.

Increasing order of reduction potentials is Ni (-0.25V) < Zn (-0.76V) < Mg (-2.36V) < Ca (-2.87).

**4.** What is the Cell Potential of the electrochemical cell in which the cell reaction is:  $\text{Pb}^{2+} + \text{Cd} \rightarrow \text{Pb} + \text{Cd}^{2+}$ ; Given that  $E^\circ_{\text{cell}} = 0.277$  volts, temperature = 25°C,  $[\text{Cd}^{2+}] = 0.02\text{M}$ , and  $[\text{Pb}^{2+}] = 0.2\text{M}$ .

### Solution

Since the temperature is equal to 25°C, the Nernst equation can be written as follows;

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log_{10} Q$$

Here, two moles of electrons are transferred in the reaction. Therefore,  $n = 2$ . The reaction quotient (Q) is given by  $[\text{Cd}^{2+}] / [\text{Pb}^{2+}] = (0.02\text{M}) / (0.2\text{M}) = 0.1$ .

The equation can now be rewritten as:

$$E_{\text{cell}} = 0.277 - (0.0592/2) \times \log_{10}(0.1) = 0.277 - (0.0296)(-1) = 0.3066 \text{ Volts}$$

Thus, the cell potential of this electrochemical cell at a temperature of 25°C is 0.3066 volts.

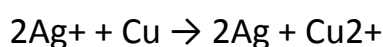
5. The  $\text{Cu}^{2+}$  ion concentration in a copper-silver electrochemical cell is 0.1M. If  $E^\circ(\text{Ag}^+/\text{Ag}) = 0.8\text{V}$ ,  $E^\circ(\text{Cu}^{2+}/\text{Cu}) = 0.34\text{V}$ , and Cell potential (at  $25^\circ\text{C}$ ) = 0.422V, find the silver ion concentration.

### Solution

Here, the silver electrode acts as a cathode whereas the copper electrode serves as the anode. This is because the standard electrode potential of the silver electrode is greater than that of the copper electrode. The standard electrode potential of the cell can now be calculated, as shown below.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.8\text{V} - 0.34\text{V} = 0.46\text{V}$$

Since the charge on the copper ion is +2 and the charge on the silver ion is +1, the balanced cell reaction is:



Since two electrons are transferred in the cell reaction,  $n = 2$ . Now, the Nernst equation for this electrochemical cell can be written as follows.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0592/2) \times \log(0.1/[\text{Ag}^+]^2)$$

$$0.422\text{V} = 0.46 - 0.0296 \times (-1 - 2\log[\text{Ag}^+])$$

$$\text{Therefore, } -2\log[\text{Ag}^+] = 1.283 + 1 = 2.283$$

$$\text{Or, } \log[\text{Ag}^+] = -1.141$$

$$[\text{Ag}^+] = \text{antilog}(-1.141) = 0.0722 \text{ M}$$

### NCERT INTEXT QUESTIONS

**Question 1:** How would you determine the standard electrode potential of the system  $\text{Mg}^{2+}/\text{Mg}$ ?

**Answer:** We know that it is not possible to measure the electrode potential of a half cell. We can only measure the difference between electrode potentials of two half cells, which gives the cell potential of the cell. For measuring the standard electrode potential of the given system, we need to use Mg as one electrode and a standard hydrogen electrode as the second electrode. Since, electrode potential of standard hydrogen electrode is zero, value of cell potential will give the value of standard electrode potential of the system  $\text{Mg}^{2+}|\text{Mg}$ .

**Question 2:** Can you store copper sulphate solutions in a zinc pot?

**Answer:** We know that zinc is more reactive metal than copper. Hence, zinc will displace copper from copper sulphate solution. So, keeping copper sulphate solution in a zinc pot will result in copper sulphate turning to zinc sulphate and the zinc pot getting corroded.

**Question 3:** Consult the table of standard electrode potentials and suggest three substances that can oxidize ferrous ions under suitable conditions.

**Answer:** Ferrous ion oxidizes to give ferric ions as follows:



Here,  $E^{\ominus} = -0.77 \text{ V}$

It is clear that a substance with reduction potential greater than 0.77 V can oxidize ferrous ion into ferric ion. Such elements are  $\text{Br}_2$ ,  $\text{Cl}_2$  and  $\text{F}_2$ .

**Question 4:** Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

**Answer:** For hydrogen electrode  $\text{H}^{+}_{(\text{aq})} + \text{e}^{-} \rightarrow 1/2 \text{H}_{2(\text{g})}$

Using Nernst Equation

$$E_{\text{H}^{+} / 1/2\text{H}_2} = E^{\ominus}_{\text{H}^{+} / 1/2\text{H}_2} + \frac{0.059}{1} \log [\text{H}^{+}]$$

$$= 0 + 0.059 \log [\text{H}^{+}]$$

$$= -0.0591 \times 10 = -0.591 \text{ V}$$

**Question 5:** Calculate the emf of the cell in which the following reaction takes place:



**Answer:**

Here Given:  $E^{\ominus}_{\text{cell}} = 1.05 \text{ V}$

$$[\text{Ni}] = [\text{Ag}] = 1$$

$$[\text{Ag}^{+}] = 0.002 \text{ M},$$

$$[\text{Ni}^{2+}] = 0.160\text{M}$$

$$n = 2$$

Using Nernst equation

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.059}{n} \log \frac{\text{Ni}^{2+}}{\text{Ag}^{+}}$$

$$= 1.05\text{V} - \frac{0.059}{2} \log \frac{0.160}{[0.002]^2}$$

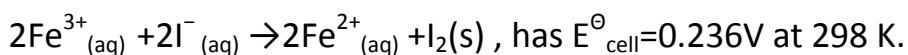
$$= 1.05 - \frac{0.059}{2} \log (4 \times 10^4)$$

$$= 1.05 - \frac{0.059}{2} (4.6021)$$

$$= 1.05 - 0.14 \text{ V}$$

$$= 0.914\text{V}$$

**Question 6:** The cell in which the following reaction occurs:



Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

**Answer:** For this cell,  $n=2\text{mol}$ ,  $E^{\ominus}_{\text{cell}}=0.236\text{V}$

**Calculation of  $\Delta G^{\circ}$**

$$\Delta G^{\circ} = -nFE^{\ominus}_{\text{cell}}$$

$$= -2 \times 96500 \times 0.236$$

$$= -45.55\text{kJ mol}^{-1}$$

Calculation of equilibrium constant ( $K_c$ )

$$\text{Moreover, } \Delta G^{\circ} = -2.303RT \log K_c$$

$$\text{Or, } \log K_c = -\Delta G^{\circ} / 2.303RT$$

$$= -45.55 / 2.303 \times 8.314 \times 298 = 7.983$$

$$\text{Or, } K_c = \text{antilog}(7.983) = 9.616 \times 10^7$$

**Question 7:** Why does the conductivity of a solution decrease with dilution?

**Answer:** We know that conductivity of a solution is the conductance of ions per unit volume of the solution. Number of ions per unit volume of solution decreases on dilution. Due to this, conductivity of a solution decreases with dilution.

### NCERT Exercises

**Question 1.**

Arrange the following metals in the order in which they displace each other from the solution of their salts.

Al, Cu, Fe, Mg and Zn.

**Ans:**

Mg, Al, Zn, Fe, Cu

**Question 2.**

Given the standard electrode potentials,

$$\text{K}^{+}/\text{K} = -2.93\text{ V}, \text{Ag}^{+}/\text{Ag} = 0.80\text{ V}, \text{Hg}^{2+}/\text{Hg} = 0.79\text{ V}, \text{Mg}^{2+}/\text{Mg} = -2.37\text{ V}, \text{Cr}^{3+}/\text{Cr} = -0.74\text{ V}$$

Arrange these metals in their increasing order of reducing power.

**Ans:**

Higher the oxidation potential, more easily it is oxidized and hence greater is the reducing

power. Thus, increasing order of reducing power will be  
 $\text{Ag} < \text{Hg} < \text{Cr} < \text{Mg} < \text{K}$ .

Question 3.

Depict the galvanic cell in which the reaction  $\text{Zn}_{(s)} + 2\text{Ag}^+_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + 2\text{Ag}_{(s)}$  takes place. Further show:

1. Which of the electrode is negatively charged?
2. The carriers of the current in the cell.
3. Individual reaction at each electrode.

Ans:

The cell will be represented as



(i) Anode, i.e., zinc electrode will be negatively charged.

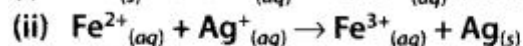
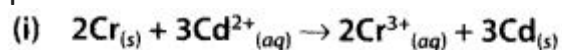
(ii) Electrons are current carriers. The current will flow from silver to zinc in the external circuit.

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

At cathode :  $\text{Ag}^+_{(aq)} + e^- \rightarrow \text{Ag}_{(s)}$

Question 4.

Calculate the standard cell potentials of galvanic cell in which the following reactions take place:



Calculate the  $\Delta_r G^\circ$  and equilibrium constant of the reactions.

Given :  $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$ ,  $E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.40 \text{ V}$

$E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}$ ,  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$

Solution:

$$\begin{aligned} \text{(i)} \quad E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= -0.40 \text{ V} - (-0.74 \text{ V}) = +0.34 \text{ V} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ_{\text{cell}} = -6 \times 96500 \times 0.34 \\ &= -196860 \text{ J mol}^{-1} = -196.86 \text{ kJ mol}^{-1} \\ -\Delta G^\circ &= 2.303 RT \log K \end{aligned}$$

$$196860 = 2.303 \times 8.314 \times 298 \times \log K$$

$$\text{or } \log K = 34.5014$$

$$K = \text{Antilog } 34.5014 = 3.172 \times 10^{34}$$

$$\text{(ii)} \quad E^\circ_{\text{cell}} = +0.80 \text{ V} - 0.77 \text{ V} = +0.03 \text{ V}$$

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ_{\text{cell}} = -1 \times 96500 \times 0.03 \\ &= -2895 \text{ J mol}^{-1} = -2.895 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta G^\circ = -2.303 RT \log K$$

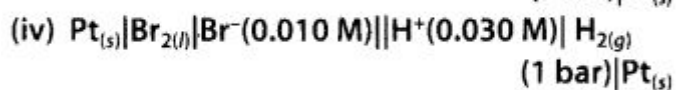
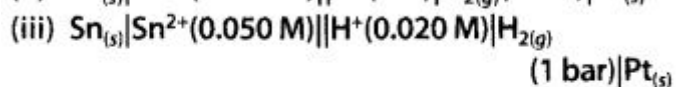
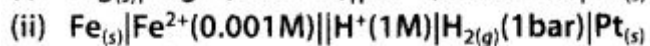
$$-2895 = -2.303 \times 8.314 \times 298 \times \log K$$

$$\text{or } \log K = 0.5074$$

$$K = \text{Antilog } (0.5074) = 3.22$$

Question 5.

Write the Nernst equation and emf of the following cells at 298 K :

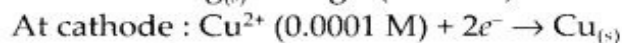
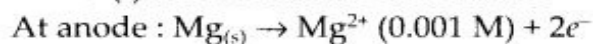


Given :  $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37 \text{ V}$ ,  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$

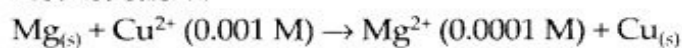
$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$ ,  $E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14 \text{ V}$

$E^\circ_{\text{Br}_2/\text{Br}^-} = +1.08 \text{ V}$

(i) The electrode reactions are



Net reaction :



The Nernst equation for this cell at 25°C

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

Where  $E_{\text{anode}}^{\circ} = -2.37 \text{ V}$ ;  $E_{\text{cathode}}^{\circ} = +0.34 \text{ V}$

$$\begin{aligned} \therefore E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \\ &= (+0.34 \text{ V}) - (-2.37 \text{ V}) = +2.71 \text{ V} \end{aligned}$$

The cell emf is then given by

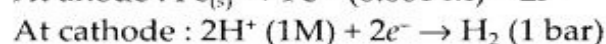
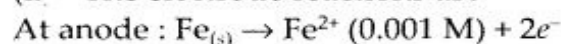
$$E_{\text{cell}} = 2.71 - \frac{0.0591}{2} \log \left( \frac{0.001}{0.0001} \right)$$

$$E_{\text{cell}} = \left( 2.71 - \frac{0.0591}{2} \log 10 \right) \text{ V}$$

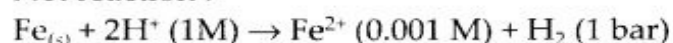
$$= \left( 2.71 - \frac{0.0591}{2} \right) \text{ V}$$

$$= 2.71 - 0.03 = 2.68 \text{ V}$$

(ii) The electrode reactions are



Net reaction :



The Nernst equation of this cell at 25°C

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}](\text{pH}_2)}{[\text{H}^+]^2}$$

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = E_{\text{H}^+|\text{H}_2}^{\circ} - E_{\text{Fe}^{2+}|\text{Fe}}^{\circ} \\ &= 0.000 \text{ V} - (-0.44 \text{ V}) = +0.44 \text{ V} \end{aligned}$$

The cell emf is then given by

$$E_{\text{cell}} = 0.44 - \frac{0.0591}{2} \log \frac{0.001 \times 1}{(1)^2}$$

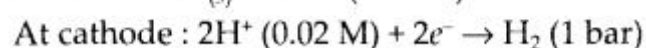
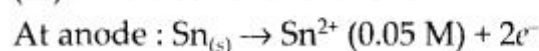
$$= 0.44 - 0.0296 \log \left( \frac{1}{1000} \right)$$

$$= 0.44 - 0.0296 \log(10^{-3})$$

$$= 0.44 + (3 \times 0.0296) = 0.44 + 0.0888$$

Therefore,  $E_{\text{cell}} = +0.53 \text{ V}$

(iii) The electrode reactions are



Net reaction :



The Nernst equation of this cell at 25°C



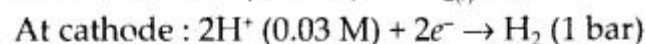
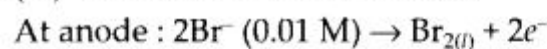
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Sn}^{2+}](\text{pH}_2)}{[\text{H}^+]^2}$$

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{H}^+|\text{H}_2}^{\circ} - E_{\text{Sn}^{2+}|\text{Sn}}^{\circ} \\ &= 0.000 \text{ V} - (-0.14 \text{ V}) = +0.14 \text{ V} \end{aligned}$$

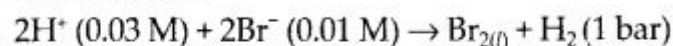
$$\begin{aligned} \text{or, } E_{\text{cell}} &= E_{\text{cell}}^{\circ} - 0.0296 \log \frac{0.05 \times 1}{(0.02)^2} \\ &= E_{\text{cell}}^{\circ} - 0.0296 \log \left( \frac{0.05}{0.0004} \right) \\ &= E_{\text{cell}}^{\circ} - 0.0296 (\log 125) \\ &= E_{\text{cell}}^{\circ} - 0.0296 \times 2.0969 = E_{\text{cell}}^{\circ} - 0.06 \end{aligned}$$

$$E_{\text{cell}} = 0.14 - 0.06 = 0.08 \text{ V}$$

(iv) The electrode reactions are



Net reaction :

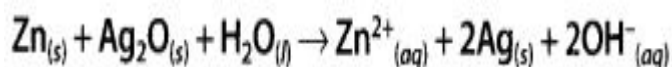


The Nernst equation of this cell at  $25^\circ\text{C}$  is

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Br}_{2(l)}](\text{pH}_2)}{[\text{H}^+]^2[\text{Br}^-]^2} \\ E_{\text{cell}}^{\circ} &= E_{\text{H}^+|\text{H}_2}^{\circ} - E_{\text{Br}_2|\text{Br}^-}^{\circ} = 0 - 1.08 \\ &= -1.08 - 0.0296 \times \log \frac{1}{(0.03)^2(0.01)^2} \\ &= -1.08 - 0.0296 \log \left[ \frac{1}{(9 \times 10^{-4})(1 \times 10^{-4})} \right] \text{ V} \\ &= -1.08 - 0.0296 \times \log \left( \frac{10^8}{9} \right) \\ &= -1.08 - 0.0296 (\log 10^8 - \log 9) \text{ V} \\ &= -1.08 - 0.0296 (8 - 0.9542) \text{ V} \\ &= -1.08 - 0.0296 (7.0457) \\ E_{\text{cell}} &= -1.08 - 0.21 = -1.29 \text{ V} \end{aligned}$$

### Question 6.

In the button cells widely used in watches and other devices the following reaction takes place:



Determine  $\Delta_r G^\circ$  and  $E^\circ$  for the reaction.

Given :  $E^\circ_{\text{Ag}_2\text{O}/\text{Ag}} = 0.344 \text{ V}$ ,  $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ ,

Solution:

Zn is oxidised and  $\text{Ag}_2\text{O}$  is reduced (as  $\text{Ag}^+$  ions change into Ag)

$$E^\circ_{\text{cell}} = E^\circ_{\text{Ag}_2\text{O}/\text{Ag}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} = 0.344 - (-0.76) \\ = 1.104 \text{ V}$$

$$\Delta_r G^\circ = -nFE^\circ_{\text{cell}} = -2 \times 96500 \times 1.104 \\ = -2.13 \times 10^5 \text{ J}$$

## Variation of conductivity and Molar conductivity with concentration

### Variation of conductivity with concentration

#### Conductivity or specific conductance:

Conductivity of a solution is equal to the conductance of a solution of 1 cm length and cross section area of 1 square cm. It may also be defined as the conductance of one centimetre cube of the conductor. It is represented by the symbol Kappa ( $\kappa$ ).

mathematically we can write

$$\kappa = 1/\rho$$

here  $\rho$  is resistivity

the unit of  $\kappa$  is  $\text{ohm}^{-1} \text{ cm}^{-1}$  or  $\text{S cm}^{-1}$

**Conductivity** always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution.

### Variation of Molar conductivity with concentration

#### Molar conductivity:

Molar conductivity of a solution at a given concentration is the conductance of the volume  $V$  of solution containing one mole of electrolyte kept between two electrodes with area of cross section  $A$  and distance of unit length. Therefore,

Distance is unit so  $l = 1$

Volume = area of base  $\times$  length

$$\text{So } V = A \times 1 = A$$

$$\Lambda_m = \kappa A/l$$

$$\Lambda_m = \kappa V$$

Molar conductivity increases with decrease in concentration. This is because the total volume,  $V$ , of solution containing one mole of electrolyte also increases. It has been found that decrease in  $\kappa$  on dilution of a solution is more than compensated by increase in its volume.

When concentration approaches zero, the molar conductivity is known as **limiting molar conductivity** and is represented by the symbol  $\Lambda^\circ_m$ . The variation in  $\Lambda_m$  with concentration is different for strong and weak electrolytes.

### Variation of molar conductivity with concentration

- **for strong electrolytes:**

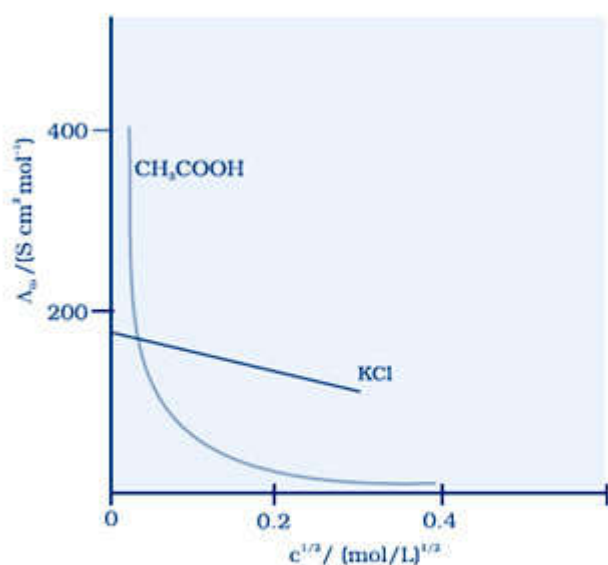
For strong electrolytes, the molar conductivity increases slowly with the dilution because on increasing dilution the ions move apart and inter-ionic attractions are decreased. As a result, the value of  $\Lambda_m$  increases. The mathematical relationship between  $\Lambda_m$  and  $\Lambda_m^0$  for strong electrolytes was developed by **Debye Huckel** and **Onsager** and is known after their names as **Debye Huckel Onsager** equation.

$$\Lambda_m = \Lambda_m^0 - A c^{1/2}$$

Where  $-A$  is a constant equal to the slope of the line. For a given solvent, the value of “ $A$ ” depends on the type of electrolyte at a particular temperature. The plot between the molar conductivity and  $c^{1/2}$  is a straight-line having y-intercept equal to

$\Lambda_m^0$ . Therefore, **limiting molar conductivity**,

$\Lambda_m^0$  can be obtained by extrapolation of molar conductivity to zero concentration.



*Molar conductivity versus  $c^{1/2}$  for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.*

- **for weak electrolyte:**

For weak electrolytes, the graph plotted between molar conductivity and  $c^{1/2}$  (where  $c$  is the concentration) is not a straight line. Weak electrolytes have lower molar conductivities and lower degree of dissociation at higher concentrations which increases steeply at lower concentrations. Therefore, **limiting molar conductivity**,  $\Lambda_m^0$  cannot be obtained by extrapolation of molar conductivity to zero concentration. Hence, we use **Kohlrausch law** of independent migration of ions for determining limiting molar conductivity,  $\Lambda_m^0$  of weak electrolytes.

## Kohlrausch's Law

It States that,

**"At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions", i.e., anions and cations. Thus**

$$\Lambda_m^\infty = v_+ \Lambda_+^\infty + v_- \Lambda_-^\infty$$

Where,  $v_+$  and  $v_-$  represent the number of positive and negative ions furnished by each formula unit of the electrolyte.

For example,

- i) One formula unit of NaCl furnished one  $\text{Na}^+$  and  $\text{Cl}^-$  ion, therefore,  
 $\Lambda_m^\infty (\text{NaCl}) = \Lambda_{\text{Na}^+}^\infty + \Lambda_{\text{Cl}^-}^\infty$
- ii) One formula unit of  $\text{BaCl}_2$  furnishes one  $\text{Ba}^{2+}$  and two  $\text{Cl}^-$  ions. Therefore,  
 $\Lambda_m^\infty (\text{BaCl}_2) = \Lambda_{\text{Ba}^{2+}}^\infty + 2\Lambda_{\text{Cl}^-}^\infty$
- iii) One formula unit of  $\text{Na}_2\text{SO}_4$  furnishes two  $\text{Na}^+$  and one  $\text{SO}_4^{2-}$  ions. Therefore,  
 $\Lambda_m^\infty (\text{Na}_2\text{SO}_4) = 2\Lambda_{\text{Na}^+}^\infty + \Lambda_{\text{SO}_4^{2-}}^\infty$

According to Kohlrausch's law. "conductivity of ions is constant at infinite dilution and it does not depend on nature of co-ions."

### Applications of Kohlrausch's law

- **Calculation of Molar Conductivity at Infinite Dilution for Weak Electrolytes**

As already mentioned, the molar conductivity of weak electrolytes at infinite dilution cannot be determined experimentally, firstly because the conductance of such a solution is low and secondly because dissociation of such an electrolyte is not completed even at high dilutions.

The molar conductivity of such an electrolyte at infinite dilution can be calculated using Kohlrausch's law.

For example, the value of  $\Lambda_m^\infty$  for acetic acid ( $\text{CH}_3\text{COOH}$ ) can be calculated from the knowledge of the limiting molar conductivities of strong electrolytes like  $\text{CH}_3\text{COONa}$ ,  $\text{HCl}$  and  $\text{NaCl}$ .

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

Now, add and subtract  $\Lambda_{\text{Na}^+}^\infty$  and  $\Lambda_{\text{Cl}^-}^\infty$  to the expression on right hand side and rearrange.

Thus,

$$\begin{aligned}
\Lambda_m^\infty(\text{CH}_3\text{COOH}) &= \Lambda_{\text{CH}_3\text{COO}^-}^\infty + \Lambda_{\text{H}^+}^\infty + \Lambda_{\text{Na}^+}^\infty - \Lambda_{\text{Na}^+}^\infty + \Lambda_{\text{Cl}^-}^\infty - \Lambda_{\text{Cl}^-}^\infty \\
&= [\Lambda_{\text{CH}_3\text{COO}^-}^\infty + \Lambda_{\text{Na}^+}^\infty] + [\Lambda_{\text{H}^+}^\infty + \Lambda_{\text{Cl}^-}^\infty] - [\Lambda_{\text{Na}^+}^\infty + \Lambda_{\text{Cl}^-}^\infty] \\
&= [\Lambda_m^\infty(\text{CH}_3\text{COONa})] + [\Lambda_m^\infty(\text{HCl})] - [\Lambda_m^\infty(\text{NaCl})]
\end{aligned}$$

### • Calculation of Degree of Dissociation

According to Arrhenius theory of electrolytic dissociation, the increase in the molar conductivity with dilution is entirely due to the increase in the dissociation of the electrolyte; the molar conductivity at infinite dilution being maximum because the dissociation is almost complete.

Thus, if  $\lambda_m^c$  is the molar conductivity of a solution at any concentration C and  $\lambda_m^\infty$  the molar conductivity at infinite dilution (i.e. zero concentration), we will have

$$\alpha = \frac{\text{no. of dissociated ions}}{\text{no. of total ions present}} = \frac{\lambda_m^c}{\lambda_m^\infty}$$

However, this relationship is found to hold good only for weak electrolytes. The value of  $\lambda_m^\infty$  for the weak electrolytes can be calculated, using Kohlrausch's law, as discussed already in the first application.

### • Calculation of Dissociation Constant for a Weak Electrolyte

Knowing the degree of dissociation (as calculated above) the dissociation constant (K) of the weak electrolyte at concentration C of the solution can be calculated

using the formula

$$K_c = \frac{C\alpha^2}{1-\alpha} \quad \text{also} \quad \alpha = \frac{\lambda_m^c}{\lambda_m^\infty}$$

$$K_c = \frac{C(\lambda_m^c)^2}{\lambda_m^c(\lambda_m^c - \lambda_m^\infty)}$$

### • Calculation of Solubility of Sparingly Soluble Salt

Salts such as AgCl, BaSO<sub>4</sub>, PbSO<sub>4</sub> etc which dissolve to a very small extent in water are called sparingly soluble salts.

As they dissolve very little; their solutions are considered as infinitely dilute. Further as their solutions are saturated, their concentration is equal to their solubility.

Thus, by determining the specific conductivity (K) and the molar conductivity of such solutions, we have

$$\lambda_m^o = \kappa \times \frac{1000}{\text{Molarity}} = \kappa \times \frac{1000}{\text{Solubility}}$$

$$\Rightarrow \text{Solubility} = \frac{\kappa \times 1000}{\lambda_m^0}$$

### Solved Example

Question:

From the given molar conductivities at infinite dilution, calculate  $\lambda_m^\infty$  for  $\text{NH}_4\text{OH}$ .

$\lambda_m^\infty$  for  $\text{Ba}(\text{OH})_2 = 457.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

$\lambda_m^\infty$  for  $\text{BaCl}_2 = 240.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

$\lambda_m^\infty$  for  $\text{NH}_4\text{Cl} = 129.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

Solution:

$$\lambda_m^\infty \text{ Ba}(\text{OH})_2 = \lambda_{\text{Ba}^{2+}}^\infty + 2\lambda_{\text{OH}^-}^\infty \dots (i)$$

$$\lambda_m^\infty (\text{BaCl}_2) = \lambda_{\text{Ba}^{2+}}^\infty + 2\lambda_{\text{Cl}^-}^\infty \dots (ii)$$

$$\lambda_m^\infty (\text{NH}_4\text{Cl}) = \lambda_{\text{NH}_4^+}^\infty + \lambda_{\text{Cl}^-}^\infty \dots (iii)$$

$$\therefore \lambda_m^\infty \text{ f } (\text{NH}_4\text{OH}) = \lambda_{\text{NH}_4^+}^\infty + \lambda_{\text{OH}^-}^\infty$$

$$= 1/2 \text{ eq. (i) + eq (iii) - } 1/2 \text{ eq (ii)}$$

$$= \frac{1}{2} \times 457.6 + 129.8 - \frac{1}{2} \times 240.6$$

$$= 238.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

### HOMEWORK

Solve 3.1 to 3.9 solved examples given in NCERT book in your note book.

### INTEXT QUESTIONS [ Continue....]

Ans 7.

**Conductivity** always decreases with decrease in concentration both, for weak and strong electrolytes because the number of ions per unit volume that carry the current in a solution decreases on dilution.

**Ans 8.**

Water is a weak electrolyte. Its  $\lambda_m^\infty$  value can be determined with the help of Kohlrausch's law.

$$\Lambda_m^0(\text{HCl}) = \Lambda_m^0(\text{H}^+) + \Lambda_m^0(\text{Cl}^-) \quad \dots \text{ (i)}$$

$$\Lambda_m^0(\text{NaOH}) = \Lambda_m^0(\text{Na}^+) + \Lambda_m^0(\text{OH}^-) \quad \dots \text{ (ii)}$$

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

Adding (i) and (ii) and subtracting (iii) we get

$$\begin{aligned} \Lambda_m^0(\text{H}_2\text{O}) &= \Lambda_m^0(\text{H}^+) + \Lambda_m^0(\text{OH}^-) \\ &= \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{NaOH}) - \Lambda_m^0(\text{NaCl}) \end{aligned}$$

**Solution 9.**

**Given:**

$$\lambda(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1} \text{ and}$$

$$\lambda(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\infty(\text{HCOOH}) = ?$$

From Kohlrausch's law

$$\begin{aligned} \Lambda_m^0(\text{HCOOH}) &= \lambda^0(\text{H}^+) + \lambda^0(\text{HCOO}^-) \\ &= 349.6 + 54.6 = 404.2 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

$$\alpha = \frac{\lambda_m}{\lambda_m^0} = \frac{46.1}{404.2} = 0.114 \Rightarrow \alpha = 11.4\%$$

$$\begin{aligned} K_a &= \frac{C\alpha^2}{1-\alpha} = \frac{0.025 \times (0.114)^2}{1-0.114} \\ &= \frac{0.025 \times 0.114 \times 0.114}{0.886} = 3.67 \times 10^{-4} \end{aligned}$$

### NCERT EXERCISE [Continue....]

**Ans 7.**

The reciprocal of resistivity is known as specific conductance or simply conductivity. It is denoted by  $\kappa$  (kappa). Thus, if  $\kappa$  is the specific conductance and  $G$  is the conductance of the solution, then

$$R = \frac{1}{G} \text{ and } \rho = \frac{1}{\kappa} \quad \therefore \frac{1}{G} = \frac{1}{\kappa} \times \frac{l}{A}, \quad \kappa = G \times \frac{l}{A}$$

Now, if  $l = 1 \text{ cm}$  and  $A = 1 \text{ sq.cm}$ , then  $\kappa = G$ .

Hence, conductivity of a solution is defined as the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section. Alternatively, it may be defined as conductance of one-centimetre cube of the solution of the electrolyte.

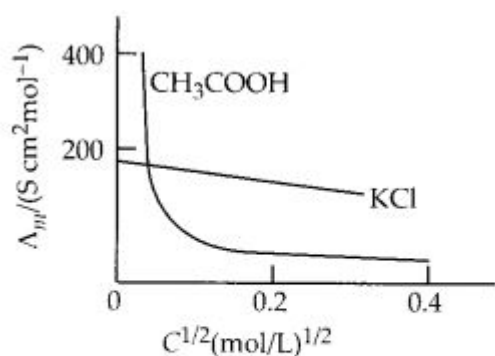
Molar conductivity of a solution at a dilution  $V$  is the conductance of all the ions produced from 1 mole of the electrolyte dissolved in  $V \text{ cm}^3$  of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole of the solution is contained between them. It is represented by  $\Delta_m$ .

$$\Lambda_m = \frac{\kappa A}{l}$$

Since  $l = 1 \text{ cm}$  and  $A = V$  (volume containing 1 mole of electrolyte)

$$\Lambda_m = \kappa V$$

Variation of conductivity and molar conductivity with concentration: Conductivity always decreases with decrease in concentration, for both weak and strong electrolytes. This is because the number of ions per unit volume that carry the current in a solution decreases on dilution.



Molar conductivity versus  $C^{1/2}$  for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.

Molar conductivity increases with decrease in concentration. This is because that total volume,  $V$ , of solution containing one mole of electrolyte also increases. It has been found that decrease in  $\kappa$  on dilution of a solution is more than compensated by increase in its volume.

**Ans 8.**

Given  $\kappa = 2.48 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ ,

$M = 0.20 \text{ mol L}^{-1}$

$$\begin{aligned} \Lambda_m &= \frac{\kappa \times 1000}{M} = \frac{1000 \times 2.48 \times 10^{-2}}{0.20} \\ &= 124 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

**Solution 9.**

**Given:**



Resistance (R) of the cell = 1500  $\Omega$

Conductivity ( $\kappa$ ) =  $0.146 \times 10^{-3} \text{ S cm}^{-1}$ .

We know that, cell constant = conductivity x Resistance

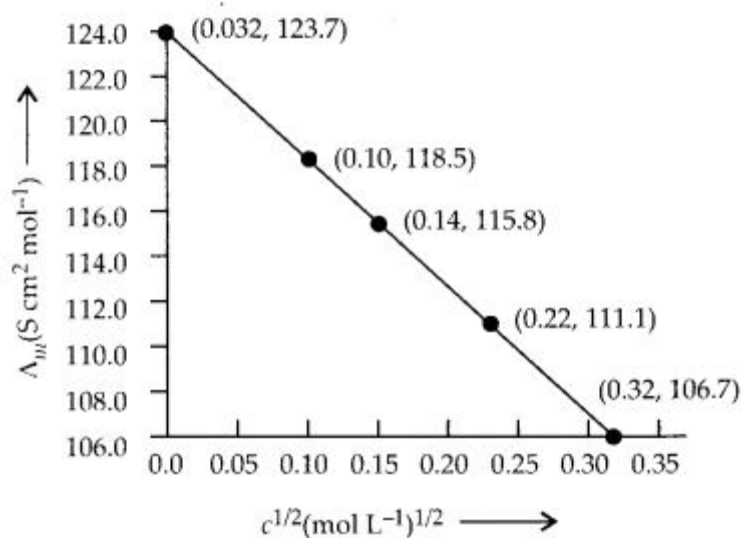
Cell constant =  $K \times R = 0.146 \times 10^{-3} \times 1500 = 0.219 \text{ cm}^{-1}$

### Solution 10.

$$1 \text{ S cm}^{-1} = 100 \text{ S m}^{-1}, \quad \frac{1 \text{ S cm}^{-1}}{100 \text{ S m}^{-1}} = 1$$

(unit conversion factor)

Conc. (M)	$\kappa (\text{S m}^{-1})$	$\kappa (\text{S cm}^{-1})$	$\Lambda_m = \frac{1000 \times \kappa}{\text{Molarity}} (\text{S cm}^2 \text{ mol}^{-1})$	$c^{1/2} (\text{M}^{1/2})$
$10^{-3}$	$1.237 \times 10^{-2}$	$1.237 \times 10^{-4}$	$\frac{1000 \times 1.237 \times 10^{-4}}{10^{-3}} = 123.7$	0.0316
$10^{-2}$	$11.85 \times 10^{-2}$	$11.85 \times 10^{-4}$	$\frac{1000 \times 11.85 \times 10^{-4}}{10^{-2}} = 118.5$	0.100
$2 \times 10^{-2}$	$23.15 \times 10^{-2}$	$23.15 \times 10^{-4}$	$\frac{1000 \times 23.15 \times 10^{-4}}{2 \times 10^{-2}} = 115.8$	0.141
$5 \times 10^{-2}$	$55.53 \times 10^{-2}$	$55.53 \times 10^{-4}$	$\frac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}} = 111.1$	0.224
$10^{-1}$	$106.74 \times 10^{-2}$	$106.74 \times 10^{-4}$	$\frac{1000 \times 106.74 \times 10^{-4}}{10^{-1}} = 106.7$	0.316



$\Lambda^0$  = Intercept on the  $\Lambda_m$  axis =  $124.0 \text{ S cm}^2 \text{ mol}^{-1}$   
(on extrapolation to zero concentration).

### Solution 11.

Given:

Conductivity ( $\kappa$ ) of acetic acid =  $7.896 \times 10^{-5} \text{ S cm}^{-1}$

Molarity (M) of acetic acid = 0.00241 M

molar conductivity ( $\Lambda_m^c$ ) = ?

$\Lambda_m^\infty$  for acetic acid =  $390.5 \text{ S cm}^2 \text{ mol}^{-1}$

dissociation constant ( $K_a$ ) = ?

$$\Lambda_m^c = \frac{\kappa \times 1000}{M} = \frac{(7.896 \times 10^{-5}) \times 1000}{0.00241}$$
$$= 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{32.76}{390.5} = 8.4 \times 10^{-2}$$

$$K_a = \frac{c\alpha^2}{1-\alpha} = \frac{0.00241 \times (8.4 \times 10^{-2})^2}{1-0.084}$$
$$= 1.86 \times 10^{-5}$$

## Electrolysis

The process of chemical decomposition of an electrolyte when electric current is passed through either its aqueous solution or molten state is called Electrolysis.

## Electrolytic cells

The phenomenon of chemical changes taking place by the passage of electrical energy from an external source is called electrolysis. The devices or cells used to carry out electrolysis are called electrolytic cells.

An electrolytic cell consists of:

- (i) Electrolytic tank, which is made of some non-conducting material like glass, wood etc.
- (ii) Electrolyte in its dissolved state or molten state.
- (iii) Source of electricity: an electrochemical cell or battery.
- (iv) Two metallic rods, suspended in the electrolyte and connected to the battery through conducting wires. These rods are called electrodes. The electrode connected to the negative terminal of battery is called cathode while the other one which is connected to the positive terminal is called anode.

## Mechanism of Electrolysis.

When an electrolyte is dissolved in water, it splits up into charged particles called ions. The positively charged ions are called cations while the negatively charged ions are called anions. The ions are free to move about in aqueous solution. When electric current is passed through the solution, the ions respond to the applied potential difference and their movement is directed towards the oppositely charged electrodes. The cations move

towards the negatively charged electrode while anions move towards the positively charged electrode. The formation of products at the respective electrodes is due to oxidation (loss of electrons) at the anode and reduction (gain of electrons) at the cathode.

### **Prediction of the Products of Electrolysis**

When an aqueous solution of an electrolyte is electrolysed, if the cation has higher reduction potential than water (-0.83 V), cation is liberated at the cathode (e.g. in the electrolysis of copper and silver salts) otherwise H<sub>2</sub> gas is liberated due to reduction of water (e.g., in the electrolysis of K, Na, Ca salts, etc.) Similarly, if anion has higher oxidation potential than water (- 1.23 V), anion is liberated (e.g., Br<sup>-</sup>), otherwise O<sub>2</sub> gas is liberated due to oxidation of water (e.g., in case of F<sup>-</sup>).

When two or more ions compete at the electrodes. the ion with higher reduction potential gets liberated at the cathode while the ion with lower reduction potential at the anode.

For metals to be deposited on the cathode during electrolysis, the voltage required is almost the same as the standard electrode potential. However, for liberation of gases, some extra voltage is required than the theoretical value of the standard electrode potential. The extra voltage thus required is called over voltage or bubble voltage.

Discharge potential is defined as the minimum potential that must be applied across the electrodes to bring about the electrolysis and subsequent discharge of the ion on the electrode.

### **Faraday's Laws of Electrolysis**

The relationship between the quantity of electricity passed and the quantity of a substance liberated at the electrode is given in the form of Faraday's Laws of Electrolysis.

#### **1. Faraday's First Law of Electrolysis**

The mass of the substance deposited or liberated at the electrode is directly proportional to the quantity of electricity passed through electrolyte.

$$W \propto Q$$

$$W \propto I \times t$$

$$W = Z \times I \times t$$

$$W = Q \times Z$$

Here, Q = quantity of charge (in coulomb)

I = current in amp,

t = time in sec,

Z is a proportionality constant known as electrochemical equivalent (ECE)

When I = 1 amp, t = 1 sec then Q = 1 coulomb, then w = Z.

Thus, electrochemical equivalent  $I''$  the amount of the substance deposited or liberated by passing 1A current for 1 sec (i.e. 1 coulomb,  $I \times t = Q$ )

## 2. Faraday's second Law of Electrolysis

When the same quantity of electricity is passed through different electrolytes. the amounts of the substance deposited or liberated at the electrodes are directly proportional to their equivalent weights.

OR

When same quantity of electricity is passed through different electrolytes connected in series then the masses of the substances liberated at the electrodes are in the ratio of their chemical equivalent masses or the ratio of their electrochemical equivalents. Thus,

$$\frac{\text{Mass of A}}{\text{Mass of B}} = \frac{\text{eq. wt. of A}}{\text{eq. wt. of B}}$$

$$\frac{w_1}{w_2} = \frac{E_1}{E_2} \Rightarrow \frac{Z_1 Q}{Z_2 Q} = \frac{E_1}{E_2}$$

Hence, electrochemical equivalent  $\propto$  equivalent weight.

### Problem:

Given the standard electrode potentials,

$$K^+ / K = - 2.93V,$$

$$Ag^+ / Ag = 0.80V,$$

$$Hg^{2+} / Hg = 0.79V$$

$$Mg^{2+} / Mg = - 2.37 V,$$

$$Cr^{3+} / Cr = - 0.74V$$

Arrange these metals in their increasing order of reducing power.

### Solution:

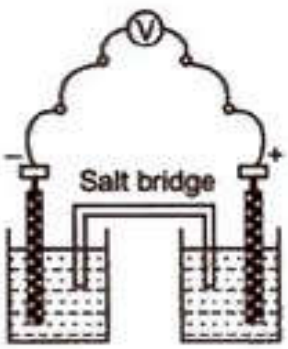
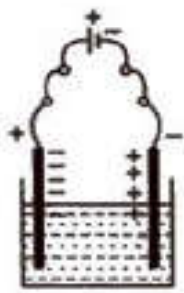
Lower the reduction potential leads to higher reducing power. The given standard electrode potentials increase in the following order:

$$K^+ / K < Mg^{2+} / Mg < Cr^{3+} / Cr < Hg^{2+} / Hg < Ag^+ / Ag.$$

Hence, reducing power of the given metals increases in the following order:

$$Ag < Hg < Cr < Mg < K.$$

## Differentiate Electrochemical Cell and Electrolytic cell

Characteristics	Electrochemical cell (Galvanic cell)	Electrolytic cell
	 <p> <math>M \rightarrow M^{n+} + ne^{-}</math>  Anode  <math>M^{n+} + ne^{-} \rightarrow M</math>  Cathode </p>	
1. Definition	A device used to convert chemical energy into electrical energy.	A device used to carry out non-spontaneous chemical reactions by electrical energy.
2. Assembly	It is a combination of two half-cells, containing the same or different electrodes in the same or different electrolytes.	It is a single cell containing the same electrodes present in the same electrolyte.
3. Nature of electrodes	Anode is negative, cathode is positive.	Anode is positive, cathode is negative.
4. Movement of electrons	From anode to cathode in external circuit.	Electrons enter through cathode and leave by anode.
5. Spontaneity	Cell reaction is spontaneous	Cell reaction is non-spontaneous.
6. Salt bridge	Salt bridge is required	Salt bridge is not required.

## NCERT INTEXT QUESTIONS

### Solution 10.

$$I = 0.5 \text{ A}$$

$$t = 2 \text{ hours} = 2 \times 60 \times 60 \text{ s} = 7200 \text{ s}$$

$$\text{Thus, } Q = It$$

$$= 0.5 \text{ A} \times 7200 \text{ s}$$

$$= 3600 \text{ C}$$

We know that  $96487 \text{ C} = 6.023 \times 10^{23}$  number of electrons.

Then,

$$3600 \text{ C} = \frac{6.023 \times 10^{23} \times 3600}{96487} \text{ number of electrons}$$

$$= 2.25 \times 10^{22} \text{ number of electrons}$$

Hence,  $2.25 \times 10^{22}$  number of electrons will flow through the wire.

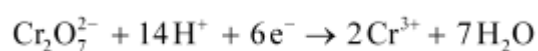
**Page No 87:**

**Ans 11.**

Metals that are on the top of the reactivity series such as sodium, potassium, calcium, lithium, magnesium, aluminium are extracted electrolytically.

**Solution 12.**

The given reaction is as follows:



Therefore, to reduce 1 mole of  $\text{Cr}_2\text{O}_7^{2-}$ , the required quantity of electricity will be:

$$= 6 \text{ F}$$

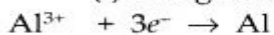
$$= 6 \times 96487 \text{ C}$$

$$= 578922 \text{ C}$$

### NCERT EXERCISE [ CONTINUE...]

#### Solution 12.

(i) The given reaction is



1 mole      3 mole

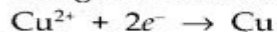
∴ 3 mole electrons are needed for reduction of 1 mole of  $\text{Al}^{3+}$  to Al.

$$3 \text{ mole electrons} = 3 \text{ Faraday}$$

$$= 3 \times 96500 \text{ coulombs}$$

$$= 2.895 \times 10^5 \text{ coulombs}$$

(ii) The given reaction is



1 mole    2 mole

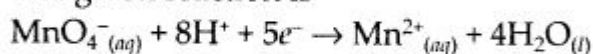
∴ 2 mole electrons are needed for reduction of 1 mole of  $\text{Cu}^{2+}$  to Cu.

$$2 \text{ mole electrons} = 2 \text{ Faraday}$$

$$= 2 \times 96500 \text{ coulombs}$$

$$= 1.93 \times 10^5 \text{ coulombs}$$

(iii) The given reaction is



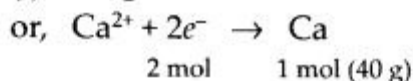
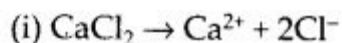
1 mole                      5 mole

∴ 5 mole electrons are needed for reduction of 1 mole of  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$ .

$$5 \text{ mole electrons} = 5 \text{ Faradays}$$

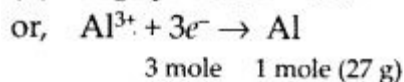
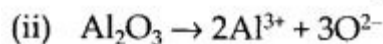
$$= 5 \times 96500 \text{ coulombs}$$

$$= 4.825 \times 10^5 \text{ coulombs}$$

**Solution 13.**

$\therefore$  40 g of calcium needs = 2 mole of electrons  
 $= 2 \times 96500$  coulombs

$\therefore$  20 g of calcium needs  
 $= 96500$  coulombs (1F).

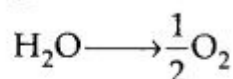


$\therefore$  27 g of aluminium needs = 3 mole of electrons  
 $= 3 \times 96500$  coulombs

$\therefore$  40.0 g of aluminium needs  
 $= \frac{3 \times 96500 \times 40.0}{27}$  coulombs  
 $= 4.28888 \times 10^5$  coulombs (4.44 F)

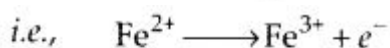
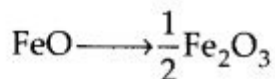
**Solution 14.**

(i) The electrode reaction for 1 mol of  $\text{H}_2\text{O}$  is given as

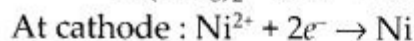
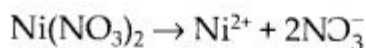


$\therefore$  Quantity of electricity required =  
 $2 \text{ F} = 2 \times 96500 \text{ C} = 193000 \text{ C}$

(ii) The electrode reaction for 1 mol of  $\text{FeO}$  is given as



$\therefore$  Quantity of electricity required =  
 $1 \text{ F} = 96500 \text{ C}$

**Solution 15.**

For getting 1 mole of Ni, we require 2 Faradays of electricity.

$$I = 5 \text{ A}, t = 20 \text{ min} = 20 \times 60 = 1200 \text{ sec},$$

$$(Q = I \times t = 5 \times 20 \times 60 = 6000 \text{ C})$$

$\therefore 2 \times 96500 \text{ C}$  of electricity will produce 58.7 g of nickel

$\therefore 6000 \text{ C}$  of electricity will produce

$$\frac{58.7 \times 6000}{2 \times 96500} = 1.825 \text{ g of nickel}$$

**Solution 16.**

Given :  $I = 1.5 \text{ A}$ ,  $W = 1.45 \text{ g Ag}$ ,  $t = ?$ ,

$$E = 108, n = 1$$

Using Faraday's 1<sup>st</sup> law of electrolysis,  $W = ZIt$

$$\text{or, } W = \frac{E}{nF} It$$

$$\text{or, } 1.45 \text{ g} = \frac{108}{1 \times 96500} \times 1.5t$$

$$\text{or, } t = \frac{1.45 \times 96500}{1.5 \times 108} = 863.73 \text{ seconds}$$

Now for Cu,  $W_1 = 1.45 \text{ g Ag}$ ,  $E_1 = 108$ ,  $W_2 = ?$ ,

$$E_2 = \frac{63.5}{2} = 31.75$$

From Faraday's 2<sup>nd</sup> law of electrolysis

$$\text{Using formula, } \frac{W_1}{W_2} = \frac{E_1}{E_2}$$

$$\frac{1.45}{W_2} = \frac{108}{31.75} \quad \therefore W_2 = \frac{1.45 \times 31.75}{108} = 0.426 \text{ g of Cu}$$

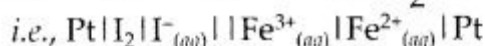
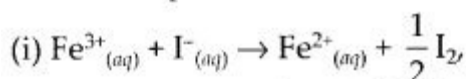
Similarly, for Zn,  $W_1 = 1.45 \text{ g Ag}$ ,  $E_1 = 108$ ,

$$W_2 = ?, E_2 = \frac{65.3}{2} = 32.65$$

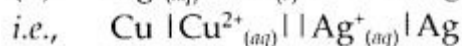
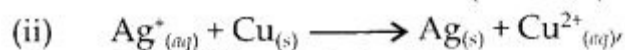


### Solution 17.

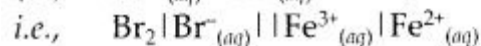
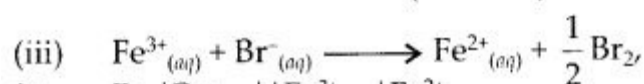
A reaction is feasible if EMF of the cell reaction is positive.



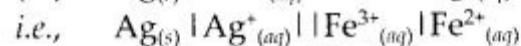
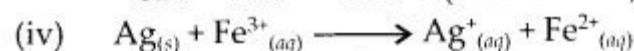
$$\begin{aligned} \therefore E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^{\circ}_{1/2\text{I}_2/\text{I}^{-}} \\ &= 0.77 - 0.54 = 0.23 \text{ V (Feasible)} \end{aligned}$$



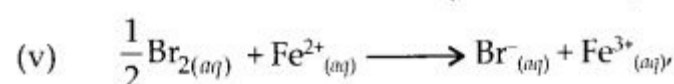
$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{Ag}^{+}/\text{Ag}} - E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} \\ &= 0.80 - 0.34 = 0.46 \text{ V (Feasible)} \end{aligned}$$



$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^{\circ}_{1/2\text{Br}_2/\text{Br}^{-}} \\ &= 0.77 - 1.09 = -0.32 \text{ V (Not feasible)} \end{aligned}$$



$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^{\circ}_{\text{Ag}^{+}/\text{Ag}} \\ &= 0.77 - 0.80 = -0.03 \text{ V (Not feasible)} \end{aligned}$$



$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{1/2\text{Br}_2/\text{Br}^{-}} - E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} \\ &= 1.09 - 0.77 = 0.32 \text{ V (Feasible)} \end{aligned}$$

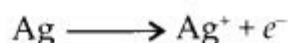
### Solution 18.

(i) Electrolysis of aqueous solution of  $\text{AgNO}_3$  with silver electrodes,



At cathode:  $\text{Ag}^+$  ions have lower discharge potential than  $\text{H}^+$  ions. Hence,  $\text{Ag}^+$  ions will be deposited as Ag in preference to  $\text{H}^+$  ions.

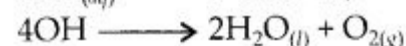
At anode: As Ag anode is attacked by  $\text{NO}_3^-$  ions, Ag of the anode will dissolve to form  $\text{Ag}^+$  ions in the solution.



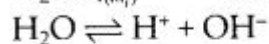
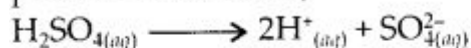
(ii) Electrolysis of aqueous solution of  $\text{AgNO}_3$  using platinum electrodes,

At cathode: Ag will be deposited.

At anode: As anode is not attacked, out of  $\text{OH}^-$  and  $\text{NO}_3^-$  ions,  $\text{OH}^-$  ions have lower discharge potential. Hence,  $\text{OH}^-$  ions will be discharged in preference to  $\text{NO}_3^-$  ions, and  $\text{OH}^-$  will then decompose to give out  $\text{O}_2$ .



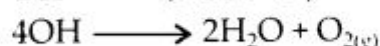
(iii) Electrolysis of dilute  $\text{H}_2\text{SO}_4$  with platinum electrodes,



At cathode:  $\text{H}^+ + e^- \longrightarrow \text{H}$ ,

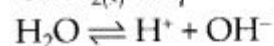
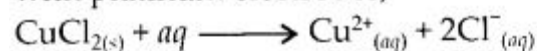


At anode:  $\text{OH}^- \longrightarrow \text{OH} + e^-$ ,

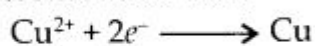


Thus,  $\text{H}_2$  is liberated at the cathode and  $\text{O}_2$  at the anode.

(iv) Electrolysis of aqueous solution of  $\text{CuCl}_2$  with platinum electrodes,



At cathode:  $\text{Cu}^{2+}$  ions will be reduced in preference to  $\text{H}^+$  ions.



At anode:  $\text{Cl}^-$  ions will be oxidized in preference to  $\text{OH}^-$  ions.



Thus, Cu will be deposited on the cathode and  $\text{Cl}_2$  will be liberated at the anode.