

## SOLVED EXAMPLES

## Example-1

Give the relationship between equivalent and molar conductance ?

**Sol.**  $\Lambda_m = \kappa \times \frac{1000}{\text{Molarity}}$  and  $\Lambda_{eq} = \kappa \times \frac{1000}{\text{Normality}}$

$$\therefore \frac{\Lambda_m}{\Lambda_{eq}} = \frac{\text{Normality}}{\text{Molarity}}$$

## Example-2

Can nickel spatula be used to stir a copper sulphate solution ? Support your answer with a reason

$$E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}, E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}.$$

**Sol.**  $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Ni}^{2+}/\text{Ni}} = +0.34 \text{ V} - (-0.25) = +0.59 \text{ V}$$

As  $E^\circ_{\text{cell}}$  is +ve,  $\Delta G = -ve$ , because  $\Delta G = -nE^\circ F$ , i.e., reaction will take place. Therefore, we cannot stir a copper sulphate solution with nickel spatula.

## Example-3

State two advantages of  $\text{H}_2\text{—O}_2$  fuel cell over ordinary cell.

**Sol.** The two advantages of  $\text{H}_2\text{—O}_2$  fuel cell over ordinary cell are :

- They do not cause any pollution.
- They have high efficiency of 60-70%.

## Example-4

What is galvanisation ?

**Sol.** The process of coating zinc over iron is called galvanisation.

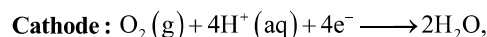
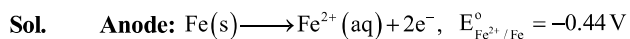
## Example-5

Which type of a metal can be used in cathodic protection of iron against rusting ?

**Sol.** A metal which is more electropositive than iron such as Al, Zn, Mg can be used in cathode protection of iron against rusting.

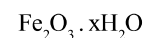
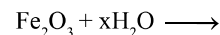
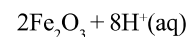
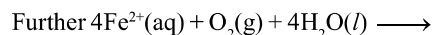
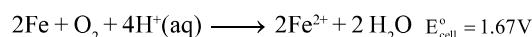
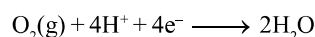
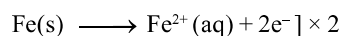
## Example-6

Write the chemical equations for all the steps involved in the rusting of iron, Give any one method to prevent rusting of iron.



$$E^\circ_{\text{H}^+/\text{O}_2/\text{H}_2\text{O}} = 1.23 \text{ V}$$

Overall reaction

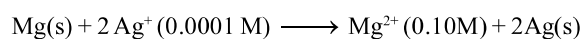


Hydrated ferric oxide (Rust)

Galvanisation is used to prevent rusting of iron.

## Example-7

The following chemical reaction is occurring in an electrochemical cell.



The  $E^\circ$  electrode values are

$$\text{Mg}^{2+}/\text{Mg} = -2.36 \text{ V}$$

$$\text{Ag}^+/\text{Ag} = 0.81 \text{ V}$$

For this cell calculate/write

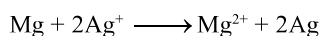
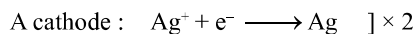
- (i)  $E^\circ$  value for the electrode  $2\text{Ag}^+/2\text{Ag}$ .
- (ii) Standard cell potential  $E^\circ_{\text{cell}}$ .
- (b) Cell potential ( $E_{\text{cell}}$ )
- (c) (i) Symbolic representation of the above cell.  
(ii) Will the above cell reaction be spontaneous ?

**Sol.** (a) (i)  $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.81 \text{ V}$

$$(ii) E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} + E_{\text{anode}}^{\circ}$$

$$= E_{\text{Ag}^{+}/\text{Ag}}^{\circ} + E_{\text{Mg}/\text{Mg}^{2+}}^{\circ} = 0.81 + 2.36$$

$$E_{\text{cell}}^{\circ} = 3.17 \text{ V}$$



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

$$= 3.17 - \frac{0.059}{2} \log \frac{0.1}{(10^{-4})^2}$$

$$= 3.17 - 0.0295 \log 10^7$$

$$= 3.17 - 0.0295 \times 7 = 3.17 - 0.21$$

$$E_{\text{cell}} = 2.96 \text{ V}$$



(ii) Yes, as the cell potential is positive.

#### Example—8

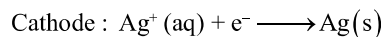
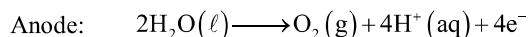
- (a) Current of 1.50 A was passed through an electrolytic cell containing  $\text{AgNO}_3$  solution with inert electrodes. The weight of Ag deposited was 1.50g. How long did the current flow ?
- (b) Write the reactions taking place at the anode and cathode in the above cell if inert electrodes are used.
- (c) Give reactions taking place at the two electrodes if these are made up of Ag.

**Sol.** (a) According to Faraday's first law, charge required to deposit 1.50 g.

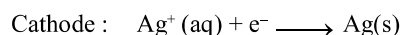
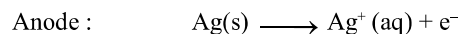
$$\text{Ag} = \frac{96500}{108} \times 1.50 = 1331.70 \text{ coulombs}$$

$$\text{Time taken} = \frac{1331.70}{1.50} = 893.5 \text{ s}$$

(b) Inert electrodes



(c) Ag electrodes



#### Example—9

Explain Kohlrausch's law of independent migration of ions. Mention one application of Kohlrausch's law.

**Sol.** **Kohlrausch's law of independent migration of ions:** The molar conductivity of an electrolyte at infinite dilution is the sum of the individual contributions of the anion and cation of the electrolyte.

$$\Lambda^{\circ} = \nu_{+} \lambda_{+}^{\circ} + \nu_{-} \lambda_{-}^{\circ}$$

where,  $\lambda_{+}^{\circ}$  and  $\lambda_{-}^{\circ}$  are the limiting molar conductivities of the cation and anion respectively and  $\nu_{+}$  and  $\nu_{-}$  are the number of cations and anions formed from a formula unit of the electrolyte. For example, one formula unit of  $\text{Al}_2(\text{SO}_4)_3$  gives two  $\text{Al}^{3+}$  ions and three sulphate ions. Therefore,

$$\Lambda_{\text{m}(\text{Al}_2(\text{SO}_4)_3)}^{\circ} = 2\lambda_{\text{Al}^{3+}}^{\circ} + 3\lambda_{\text{SO}_4^{2-}}^{\circ}$$

Application : It can be used to determine molar conductivity of weak electrolytes at infinite dilution :

Consider acetic acid as the example of a weak electrolyte.

$$\Lambda_{\text{m}(\text{CH}_3\text{COONa})}^{\circ} = \lambda_{\text{CH}_3\text{COO}^{-}}^{\circ} + \lambda_{\text{Na}^{+}}^{\circ}$$

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

$$\Lambda_{\text{m}(\text{NaCl})}^{\circ} = \lambda_{\text{Na}^{+}}^{\circ} + \lambda_{\text{Cl}^{-}}^{\circ}$$

From (i) + (ii) – (iii) we get

$$\lambda_{\text{CH}_3\text{COO}^{-}}^{\circ} + \lambda_{\text{Na}^{+}}^{\circ} + \lambda_{\text{H}^{+}}^{\circ} + \lambda_{\text{Cl}^{-}}^{\circ} - \lambda_{\text{Na}^{+}}^{\circ} - \lambda_{\text{Cl}^{-}}^{\circ} = \lambda_{\text{CH}_3\text{COO}^{-}}^{\circ} + \lambda_{\text{H}^{+}}^{\circ} = \Lambda_{\text{CH}_3\text{COOH}}^{\circ}$$

#### Example—10

The electrical resistance of a column of  $0.05 \text{ mol L}^{-1}$  NaOH solution of diameter 1 cm and length 50 cm is  $5.55 \times 10^3$  ohm. Calculate its resistivity, conductivity and molar conductivity.

**Sol.**  $A = \pi r^2 = 3.14 \times 0.5^2 \text{ cm}^2 = 0.785 \text{ cm}^2 = 0.785 \times 10^{-4} \text{ m}^2$ ,  
 $l = 50 \text{ cm} = 0.5 \text{ m}$

$$R = \frac{\rho \ell}{A} \text{ or } \rho = \frac{RA}{\ell} = \frac{5.55 \times 10^3 \Omega \times 0.785}{50 \text{ cm}} = 87.135 \Omega \text{ cm}$$

$$\text{Conductivity} = \kappa = \frac{1}{\rho} = \left( \frac{1}{87.135} \right) \text{ S cm}^{-1} = 0.01148 \text{ S cm}^{-1}$$

$$\begin{aligned} \text{Molar conductivity, } \Lambda_m &= \frac{\kappa \times 1000}{c} \\ &= \frac{0.01148 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.05 \text{ mol L}^{-1}} = 229.6 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

**Example – 11**

The measured resistance of a conductance cell containing  $7.5 \times 10^{-3} \text{ M}$  solution of KCl at  $25^\circ\text{C}$  was 1005 ohms. Calculate (a) specific conductance (b) molar conductance of the solution. Cell constant =  $1.25 \text{ cm}^{-1}$ .

**Sol.** Specific conductance ( $\kappa$ ) =  $\frac{1}{R} \times \text{cell constant}$

$$= \frac{1}{1005 \Omega} \times 1.25 \text{ cm}^{-1} = 0.001244 \Omega^{-1} \text{ cm}^{-1}$$

$$\begin{aligned} \text{Molar conductance } (\Lambda_m) &= \frac{\kappa \times 1000}{\text{Molarity}} \\ &= \frac{0.001244 \Omega^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{7.5 \times 10^{-3} \text{ mol L}^{-1}} \\ &= 165.87 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}. \end{aligned}$$

**Example – 12**

$\Lambda_m$  for NaCl, HCl and NaAc are 126.4, 425.9 and  $91.0 \text{ S cm}^2 \text{ mol}^{-1}$  respectively. Calculate  $\Lambda_m^0$  for HAc.

**Sol.**  $\Lambda_{m(\text{HAc})}^0 = \lambda_{\text{H}^+}^0 + \lambda_{\text{Ac}^-}^0 = \lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0 + \lambda_{\text{Ac}^-}^0 + \lambda_{\text{Na}^+}^0 - \lambda_{\text{Cl}^-}^0 - \lambda_{\text{Na}^+}^0$

$$= \Lambda_{m(\text{HCl})}^0 + \Lambda_{m(\text{NaAc})}^0 - \Lambda_{m(\text{NaCl})}^0$$

$$= (425.9 + 91.0 - 126.4) \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 390.5 \text{ S cm}^2 \text{ mol}^{-1}.$$

**Example – 13**

The conductivity of  $0.001028 \text{ mol L}^{-1}$  acetic acid is  $4.95 \times 10^{-5} \text{ S cm}^{-1}$ . Calculate its dissociation constant if  $\Lambda_m^0$  for acetic acid is  $390.5 \text{ S cm}^2 \text{ mol}^{-1}$ .

**Sol.**  $\Lambda_m = \frac{\kappa}{c} = \frac{4.95 \times 10^{-5} \text{ S cm}^{-1}}{0.001028 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$

$$= 44.88 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{44.88 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.115$$

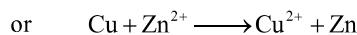
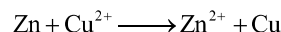
$$\begin{aligned} K &= \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028 \text{ mol L}^{-1} \times (0.115)^2}{0.115} \\ &= 1.65 \times 10^{-5} \text{ mol L}^{-1} \end{aligned}$$

**Example – 14**

A cell is prepared by dipping copper rod in 1 M copper sulphate solution and zinc rod in 1 M zinc sulphate solution. The standard reduction potentials of copper and zinc are 0.34 V and  $-0.76 \text{ V}$  respectively.

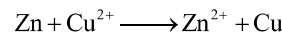
- What will be the cell reaction?
- What will be the standard electromotive force (EMF) of the cell?
- Which electrode will be positive?
- How will the cell be represented?

**Sol.** (i) The cell reaction can be



The EMF comes out to be positive for the 1st reaction.

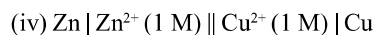
Hence, the cell reaction is



$$(ii) E_{\text{cell}}^0 = E_{\text{cathode}}^0 + E_{\text{anode}}^0 = E_{\text{Cu}^{2+}/\text{Cu}}^0 + E_{\text{Zn}/\text{Zn}^{2+}}^0$$

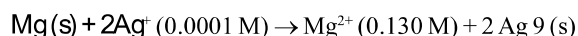
$$= 0.34 + 0.76 = 1.10 \text{ V}$$

(iii) reduction takes place on copper electrode. Hence it is positive



**Example – 15**

Represent the cell in which the following reaction takes place



Calculate its  $E_{(\text{cell})}$  if  $E_{(\text{cell})}^{\circ} = 3.17 \text{ V}$ .

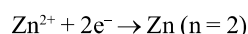
**Sol.** The cell can be written as  $\text{Mg} | \text{Mg}^{2+} (0.130 \text{ M}) || \text{Ag}^+ (0.0001 \text{ M}) | \text{Ag}$

$$\begin{aligned} E_{(\text{cell})} &= E_{(\text{cell})}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2} = E_{(\text{cell})}^{\circ} - \frac{2.303 RT}{2F} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2} \\ &= 3.17 \text{ V} - \frac{0.059 \text{ V}}{2} \log \frac{0.130}{(0.0001)^2} \\ &= 3.17 \text{ V} - 0.21 \text{ V} = 2.96 \text{ V} \end{aligned}$$

**Example – 16**

A zinc rod is dipped in 0.1 M solution of  $\text{ZnSO}_4$ . The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential ( $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$ ).

**Sol.** The electrode reaction written as reduction reaction is



Applying Nernst equation, we get

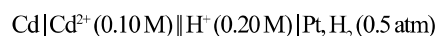
$$E_{\text{Zn}^{2+}/\text{Zn}} = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} - \frac{0.0591}{2} \log \frac{1}{[\text{Zn}^{2+}]}$$

As 0.1 M  $\text{ZnSO}_4$  solution is 95% dissociated, this means that in the solution,

$$\begin{aligned} [\text{Zn}^{2+}] &= \frac{95}{100} \times 0.1 \text{ M} = 0.095 \text{ M} \\ \therefore E_{\text{Zn}^{2+}/\text{Zn}} &= -0.76 - \frac{0.0591}{2} \log \frac{1}{0.095} \\ &= -0.76 - 0.02955 (\log 1000 - \log 95) \\ &= -0.76 - 0.02955 (3 - 1.9777) \\ &= -0.76 - 0.03021 \\ &= -0.79021 \text{ V} \end{aligned}$$

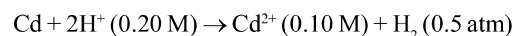
**Example – 17**

Calculate the potential (emf) of the cell



(Given  $E^{\circ}$  for  $\text{Cd}^{2+} / \text{Cd} = -0.403 \text{ V}$ ,  $R = 8.14 \text{ JK}^{-1} \text{ mol}^{-1}$ ,  $F = 96,500 \text{ C mol}^{-1}$ ).

**Sol.** The cell reaction is



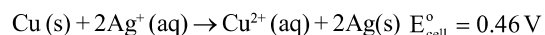
$$E_{\text{cell}}^{\circ} = E_{\text{H}^+ / 1/2\text{H}_2}^{\circ} - E_{\text{Cd}^{2+} / \text{Cd}}^{\circ} = 0 - (-0.403) = 0.403 \text{ V}$$

Applying Nernst equation to the cell reaction,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{2.303 RT}{nF} \log \frac{[\text{Cd}^{2+}] \times P_{\text{H}_2}}{[\text{H}^+]^2} \\ &= 0.403 - \frac{2.303 \times 8.314 \times 298}{2 \times 96,500} \log \frac{0.1 \times 0.5}{(0.2)^2} \\ &= 0.403 - 0.003 = 0.400 \text{ V} \end{aligned}$$

**Example – 18**

Calculate the equilibrium constant of the reaction



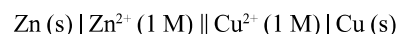
$$\text{Sol.} \quad E_{\text{cell}}^{\circ} = \frac{0.059 \text{ V}}{2} \log K_c = 0.46 \text{ V}$$

$$\text{or} \quad \log K_c = \frac{0.46 \text{ V} \times 2}{0.059 \text{ V}} = 15.6 \Rightarrow K_c = \text{Antilog } 15.6$$

$$K_c = 3.92 \times 10^{15}$$

**Example – 19**

Calculate the standard free energy change and maximum work obtainable for the reaction occurring in the cell : (Daniell cell).

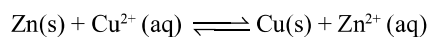


$$\begin{aligned} [\text{Given } E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} &= -0.76 \text{ V}, E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} \\ &= +0.34 \text{ V}, F = 96,500 \text{ C mol}^{-1}] \end{aligned}$$

Also calculate the equilibrium constant for the reaction.

$$\begin{aligned} \text{Sol.} \quad (i) \quad E_{\text{cell}}^{\circ} &= E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} + E_{\text{Zn}/\text{Zn}^{2+}}^{\circ} = 0.34 + 0.76 \\ &= 1.10 \text{ V} \end{aligned}$$

The reaction taking place in the Daniell cell is



For this reaction,  $n = 2$

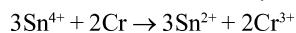
$$\begin{aligned}\Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ &= -2 \times 96500 \text{ C mol}^{-1} \times 1.10 \text{ V} \\ &= -212300 \text{ CV mol}^{-1} \\ &= -212300 \text{ J mol}^{-1} \quad (1 \text{ CV} = 1 \text{ J}) \\ &= -212.300 \text{ kJ mol}^{-1}\end{aligned}$$

Thus, the maximum work that can be obtained from the Daniel cell = 212.3 kJ.

$$\begin{aligned}\text{(ii)} \quad \Delta G^\circ &= -RT \ln K_c = -2.303 RT \log K_c \\ \therefore -212300 &= -2.303 \times 8.14 \times 298 \times \log K_c \\ \text{or} \quad \log K_c &= \frac{212300}{2.303 \times 8.314 \times 298} = 37.2704 \\ \therefore K_c &= \text{Antilog } 37.2704 = 1.6 \times 10^{37}\end{aligned}$$

#### Example – 20

Calculate the equilibrium constant,  $K_c$  for the reaction.



Given  $E^\circ = 0.885 \text{ V}$ .

**Sol.**  $E^\circ_{\text{cell}} = \frac{0.059}{n} \log K_c, n = 6$

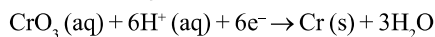
$$0.885 = \frac{0.059}{6} \log K_c$$

$$\log K_c = \frac{6 \times 0.885}{0.059}$$

$$K_c = \text{Antilog } 90 = 1 \times 10^{90}$$

#### Example – 21

Chromium metal can be plated out from an acidic solution containing  $\text{CrO}_3$  according to the following equation:



Calculate (i) how many grams of chromium will be plated out by 24,000 coulombs and (ii) how long will it take to plate out 1.5 g of chromium by using 12.5 amp current? (At. mass of Cr = 52).

**Sol.** (i)  $6 \times 96,500$  coulomb deposit Cr = 1 mole = 52 g

$$\therefore 24,000 \text{ coulomb deposit Cr} = \frac{52 \times 24000}{6 \times 96500} \text{ g} = 2.1554 \text{ g}$$

(ii) 52 g of Cr is deposited by electricity =  $6 \times 96500 \text{ C}$

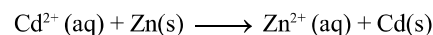
$$\therefore 1.5 \text{ g require electricity} = \frac{6 \times 96500}{52} \times 1.5 \text{ C} = 16071 \text{ C}$$

$\therefore$  Time for which the current is required to be passed

$$= \frac{16071.9}{12.5 \text{ A}} = 1336 \text{ s.}$$

#### Example – 22

(a) Calculate the equilibrium constant for the reaction

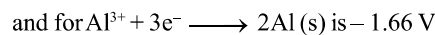
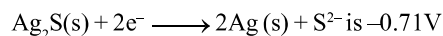


$$\text{If } E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.403 \text{ V}$$

$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.763 \text{ V}$$

(b) When a current of 0.75A is passed through a  $\text{CuSO}_4$  solution for 25 min, 0.369 g of copper is deposited at the cathode. Calculate the atomic mass of copper.

(c) Tarnished silver contains  $\text{Ag}_2\text{S}$ . Can this tarnish be removed by placing tarnished silver ware in an aluminium pan containing an inert electrolytic solution such as NaCl. The standard electrode potential for half reaction:



**Sol.** (a)  $E^\circ_{\text{cell}} = E^\circ_{\text{c}} + E^\circ_{\text{a}} = -0.403 + 0.763 = 0.360 \text{ V}$

$$\text{As } \log K_c = \left( \frac{nE^\circ_{\text{cell}}}{0.059} \right) = \left( \frac{2 \times 0.360}{0.059} \right)$$

$$= \left( \frac{0.720}{0.059} \right) = 12.20$$

$$K_c = \text{antilog } (12.20) = 1.585 \times 10^{12}$$

(b)  $M = Z I t$

$$0.369 = \frac{x}{2 \times 96500} \times 0.75 \times 25 \times 60$$

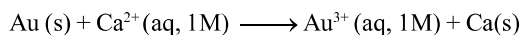
(x = molar mass of copper)

$$x = 63.3 \text{ g/mol}$$

- (c)  $E_{\text{cell}}^{\circ}$  for reaction of tarnished silver ware with aluminium pan is  $(-0.71 \text{ V}) + 1.66 \text{ V}$  i.e.,  $+0.95 \text{ V}$   
Tarnished silver ware, therefore, can be cleaned by placing it in an aluminium pan as  $E_{\text{cell}}^{\circ}$  is positive.

**Example–23**

- (a) Calculate the standard free energy change for the following reaction at  $25^{\circ}\text{C}$ .



$$E_{\text{Au}^{3+}/\text{Au}}^{\circ} = +1.50 \text{ V}, E_{\text{Ca}^{2+}/\text{Ca}}^{\circ} = -2.87 \text{ V}$$

Predict whether the reaction will be spontaneous or not at  $25^{\circ}\text{C}$ . Which of the above two half cells will act as an oxidizing agent and which one will be a reducing agent?

- (b) The conductivity of  $0.001 \text{ M}$  acetic acid is  $4 \times 10^{-5} \text{ S/cm}$ . Calculate the dissociation constant of acetic acid, if  $\Lambda_m^{\circ}$  for acetic acid is  $390.5 \text{ S cm}^2/\text{mol}$ .

**Sol.** (a)  $E_{\text{cell}}^{\circ} = (-2.87 \text{ V}) - (1.50 \text{ V}) = -4.37 \text{ V}$

$$\Delta G_{\text{cell}}^{\circ} = -6 \times 96500 \times -4.37 \text{ V} = +2530.230 \text{ kJ/mol}$$

Since  $\Delta_r G^{\circ}$  is positive, reaction is non-spontaneous.

$\text{Au}^{3+}/\text{Au}$  half cell will be a reducing agent,  $\text{Ca}^{2+}/\text{Ca}$  half cell will be an oxidising agent.

$$(b) \Lambda_m^c = K \times \frac{1000}{\text{molarity}}$$

$K = \text{Specific conductance}$

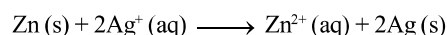
$$= \frac{4 \times 10^{-5} \text{ S/cm} \times 1000}{0.001} = 40 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}} = \frac{40}{390.5} = 0.103$$

$$K_c = \frac{C\alpha^2}{1-\alpha} = \frac{0.001 \times (0.103)^2}{1-0.103} = 1.19 \times 10^{-5}$$

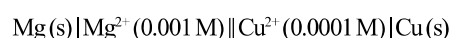
**Example–24**

- (a) Depict the galvanic cell in which the following reaction takes place :



Also indicate that in this cell

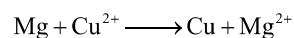
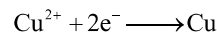
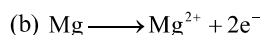
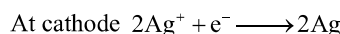
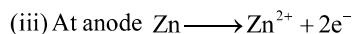
- which electrode is negatively charged.
  - what are the carrier of the current in the cell.
  - what is the individual reaction at each electrode.
- (b) Write the Nernst equation and determine the e.m.f. of the following cell at  $298 \text{ K}$ :



$$(\text{Given: } E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} = -2.375 \text{ V}, E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = +0.34 \text{ V})$$

**Sol.** (a)  $\text{Zn} | \text{Zn}^{2+}(\text{conc.}) || \text{Ag}^+(\text{conc.}) | \text{Ag}$

- Zn electrode is negatively charged.
- Current carriers of cell are
  - electrons in external wire
  - $\text{Zn}^{2+}$  ions in anodic half cell.
  - $\text{Ag}^+$  ions in cathodic half cell.
  - Ions of salt bridge, i.e.,  $\text{K}^+$  and  $\text{Cl}^-$ .



Nernst equation

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

$$E_{\text{cell}} = \left( E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} + E_{\text{Mg}/\text{Mg}^{2+}}^{\circ} \right) - \frac{0.059}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= 0.34 + (2.375) - \frac{0.059}{2} \log \frac{10^{-3}}{10^{-4}}$$

$$= 0.34 + 2.375 - 0.0295 \log 10$$

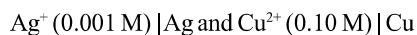
$$E_{\text{cell}} = 2.6855 \text{ V}$$

$$E_{\text{cell}} = 2.685 \text{ V}$$

**Example – 25**

- (a) Define molar conductivity of a substance and describe how weak and strong electrolytes' molar conductivity changes with concentration of solute. How is such change explained?

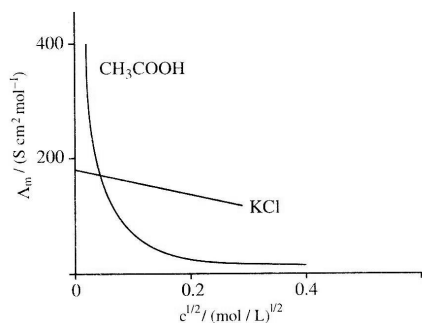
- (b) A voltaic cell is set up at 25 °C with the following half cells:



What would be the voltage of this cell ?

$$(E^\circ_{\text{cell}} = 0.46 \text{ V})$$

**Sol.** Molar Conductivity ( $\Lambda_m$ ): It may be defined as the conductance of a solution containing 1 mole of electrolyte such that the entire solution is placed in between two electrodes one centimetre apart.



$$\Lambda_m = k \times v$$

or

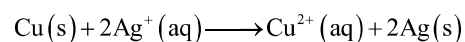
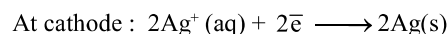
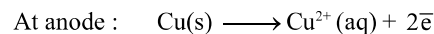
$$\Lambda_m = \frac{k \times 1000}{M}$$

Molar conductivity increases with decrease in concentration or increase in dilution as number of ions as well as mobility of ions increased with dilution.

For strong electrolytes, the number of ions do not increase appreciably on dilution and only mobility or ions increases due to decrease in interionic attractions.

Therefore,  $\Lambda_m$  increases a little as shown in graph by a straight line.

For weak electrolytes, the number of ions as well as mobility of ions increases on dilution which results in a very large increase in molar conductivity especially near infinite dilution as shown by curve in the figure.



$$\text{Here, } E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$\text{Here, } E^\circ_{\text{cell}} = 0.46 \text{ V, } n = 2$$

$$[\text{Ag}^+] = 0.001 \text{ M} = 1 \times 10^{-3} \text{ M, } [\text{Cu}^{2+}] = 0.1 \text{ M}$$

$$E_{\text{cell}} = 0.46 - \frac{0.0591}{2} \log \frac{0.1}{(10^{-3})^2}$$

$$E_{\text{cell}} = 0.46 - \frac{0.0591}{2} \log 10^5 = 0.46 - \frac{0.0591}{2} \times 5 \log 10$$

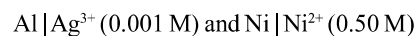
$$E_{\text{cell}} = 0.46 - 0.0591 \times 2.5 \times 1 = 0.46 - 0.14775 = 0.31225 \text{ V}$$

$$E_{\text{cell}} = 0.312 \text{ V}$$

**Example – 26**

- (a) State the relationship amongst cell constant of cell, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solute related to conductivity of its solution ?

- (b) A voltaic cell is set up at 25 °C with the following half-cells:



Calculate the cell voltage

$$[E^\circ_{\text{Ni}^{2+}|\text{Ni}} = -0.25 \text{ V, } E^\circ_{\text{Al}^{3+}|\text{Al}} = -1.66 \text{ V}]$$

**Sol.** (a)  $\kappa = \frac{1}{R} \times \left( \frac{l}{A} \right)$

where,  $\kappa$  = Conductivity

$$\frac{1}{A} = \text{Cell constant}$$

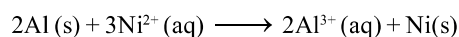
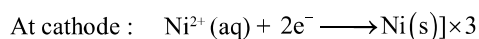
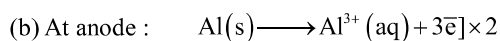
R = Resistance

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

where,  $\Lambda_m$  = Molar conductivity

$\kappa$  = Conductivity

M = Molarity of Solution



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3}$$

Here,  $n = 6$ ,  $[\text{Al}^{3+}] = 0.001 \text{ M} = 1 \times 10^{-3} \text{ M}$ ,

$[\text{Ni}^{2+}] = 0.5 \text{ M}$

$$E_{\text{cell}}^{\circ} = 1.41 \text{ V}$$

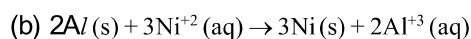
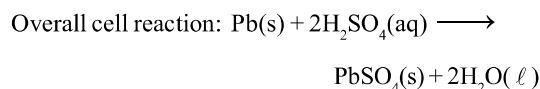
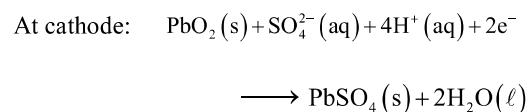
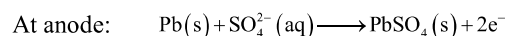
$$\begin{aligned} E_{\text{cell}}^{\circ} &= 1.41 \text{ V} - \frac{0.0591}{6} \log \frac{(10^{-3})^2}{(0.5)^3} = 1.41 - \frac{0.0591}{6} \log \frac{10^{-6}}{0.125} \\ &= 1.41 - \frac{0.0591}{6} \log (10^{-6} \times 8) = 1.41 - \frac{0.0591}{6} (\log 10^{-6} + \log 2^3) \\ &= 1.41 - \frac{0.0591}{6} (-6 \log 10 + 3 \log 2) = 1.41 - \frac{0.0591}{6} (-6 + 3 \times 0.3010) \\ &= 1.41 - \frac{0.0591}{6} (-5.097) = 1.41 + \frac{0.3012}{6} \\ &= 1.41 + 0.0502 = 1.4602 \text{ V} \\ E_{\text{cell}} &= 1.46 \text{ V} \end{aligned}$$

### Example–27

- (a) What type of a cell is the lead storage battery ? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery while operating.
- (b) A voltaic cell is set up at  $25^{\circ}\text{C}$  with the half-cells  $\text{Al} | \text{Al}^{3+} (0.001 \text{ M})$  and  $\text{Ni} | \text{Ni}^{2+} (0.50 \text{ M})$ . Write the equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.
- (Given :  $E_{\text{Ni}^{2+}|\text{Ni}}^{\circ} = -0.25 \text{ V}$ ,  $E_{\text{Al}^{3+}|\text{Al}}^{\circ} = -1.66 \text{ V}$ ).

**Sol.** (a) The lead storage battery is a secondary cell.

The cell reactions when the battery is in use are given below

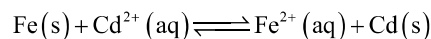


$$E_{\text{cell}}^{\circ} = 1.41 \text{ V}$$

$$\begin{aligned} E_{\text{cell}} &= 1.41 - \frac{0.0591}{6} \log \left[ \frac{(10^{-3})^2}{(0.5)^3} \right] \\ &= 1.46 \text{ V} \end{aligned}$$

### Example–28

- (a) Express the relationship amongst cell constant, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solute related to conductivity of its solution.
- (b) Calculate the equilibrium constant for the reaction.

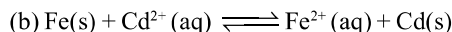


(Given :  $E_{\text{Cd}^{2+}|\text{Cd}}^{\circ} = -0.40 \text{ V}$ ,  $E_{\text{Fe}^{2+}|\text{Fe}}^{\circ} = -0.44 \text{ V}$ ).

**Sol.** (a) Conductivity ( $\kappa$ ) =  $\frac{1}{\text{Resistance (R)}} \times \text{Cell constant (G)}$



$$\Lambda_m = \frac{\kappa \times 1000}{M}, \text{ where, } \Lambda_m = \text{Molar conductivity}$$



$$\log k_c = n \frac{E_{\text{cell}}^{\circ}}{0.059}$$

Here,  $n = 2$

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} + E_{\text{anode}}^{\circ}$$

$$= E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} + E_{\text{Fe}/\text{Fe}^{2+}}^{\circ}$$

$$= -0.4 + 0.44$$

$$E_{\text{cell}}^{\circ} = 0.04 \text{ V}$$

$$\log k_c = \frac{2 \times 0.04}{0.059} = \frac{0.08}{0.059}$$

$$\log k_c = 1.3536$$

$$k_c = \text{Antilog } 1.3536$$

$$k_c = 22.57$$

### Example – 29

- (a) Define the term molar conductivity. How is it related to conductivity of the related solution?
- (b) One half-cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. Its other half-cell consists of zinc electrode dipping in 1.0 M solution of  $\text{Zn}(\text{NO}_3)_2$ . A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver nitrate solution used.

$$(E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}, E_{\text{Ag}^{2+}/\text{Ag}}^{\circ} = +0.80 \text{ V})$$

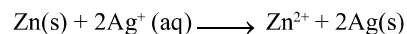
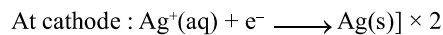
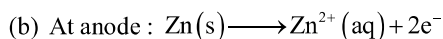
**Sol.**

- (a) **Molar conductivity** ( $\Lambda_m$ ): It may be defined as the conductivity of one molar electrolytic solution placed between two electrodes one centimetre apart and have enough area of cross section to hold entire volume.

$$\Lambda_m = \frac{\kappa}{c}$$

where,  $\kappa$  = Conductivity

$c$  = Concentration of solution in  $\text{mol L}^{-1}$



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^{+}]^2}$$

Here,  $n = 2$ ,  $[\text{Zn}^{2+}] = 1 \text{ M}$

$$E_{\text{cell}}^{\circ} = E_{\text{Ag}^{+}/\text{Ag}}^{\circ} + E_{\text{Zn}/\text{Zn}^{2+}}^{\circ} = 0.80 \text{ V} + 0.76 \text{ V}$$

$$E_{\text{cell}}^{\circ} = 1.56 \text{ V}$$

$$1.48 = 1.56 - \frac{0.0591}{2} \log \frac{1}{[\text{Ag}^{+}]^2}$$

$$-0.08 = -\frac{0.0591}{2} \log \frac{1}{[\text{Ag}^{+}]^2}$$

$$\log \frac{1}{[\text{Ag}^{+}]^2} = \frac{0.16}{0.0591} = 2.7072 = 2.7072$$

$$\log 1 - \log [\text{Ag}^{+}]^2 = 2.7072$$

$$0 - 2 \log [\text{Ag}^{+}] = 2.7072$$

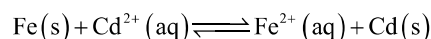
$$\log [\text{Ag}^{+}] = -1.3536 = \bar{2}.6464$$

$$[\text{Ag}^{+}] = \text{Anti log}(\bar{2}.6464) = 4.43 \times 10^{-2} \text{ M}$$

$$[\text{Ag}^{+}] = 0.044 \text{ M}$$

### Example – 30

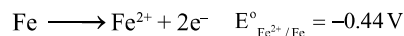
- (a) Corrosion is essentially an electrochemical phenomenon. Explain the reactions occurring during corrosion of iron kept in an open atmosphere.
- (b) Calculate the equilibrium constant for the equilibrium reaction.



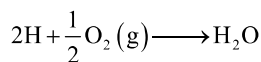
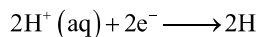
$$(\text{Given: } E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} = -0.40 \text{ V}, E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \text{ V})$$

**Sol.**

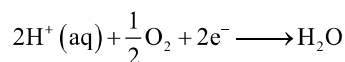
- (a) At anode : Oxidation of Fe atoms takes place



At cathode : Reduction of oxygen in the presence of  $\text{H}^{+}$  ions. The  $\text{H}^{+}$  ions are produced by either  $\text{H}_2\text{O}$  or  $\text{H}_2\text{CO}_3$  (formed by dissolution of  $\text{CO}_2$  in moisture)

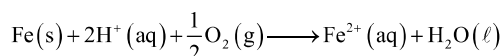


Net reaction at cathodic area



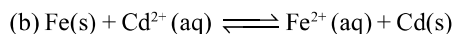
$$E^\circ_{\text{H}^+/\text{O}_2/\text{H}_2\text{O}} = 1.23 \text{ V}$$

The overall reaction



$$E^\circ_{\text{cell}} = 1.67 \text{ V}$$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ).



$$\log k_c = n \frac{E^\circ_{\text{cell}}}{0.059}$$

Here,  $n = 2$

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

$$= E^\circ_{\text{Cd}^{2+}/\text{Cd}} - E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -40 - (-0.44)$$

$$E^\circ_{\text{cell}} = 0.04 \text{ V}$$

$$\log k_c = \frac{2 \times 0.04}{0.059} = \frac{0.08}{0.059}$$

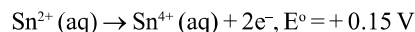
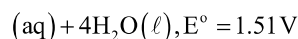
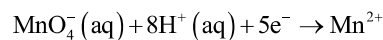
$$\log k_c = 1.3536$$

$$k_c = \text{Antilog } 1.3536$$

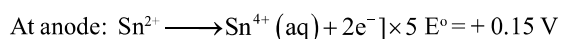
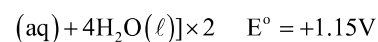
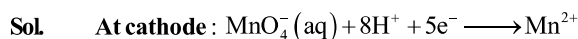
$$k_c = 22.57$$

### Example – 31

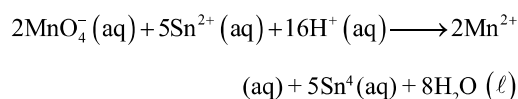
Two half cell reactions of an electrochemical cell are given below :



Construct the redox equation from the two half cell reactions and predict if this reaction favours formation of reactants or product shown in the equation



Overall reaction :



$$E^\circ_{\text{Sn}^{4+}/\text{Sn}^{2+}} = -E^\circ_{\text{Sn}^{2+}/\text{Sn}^{4+}} = -0.15 \text{ V}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} - E^\circ_{\text{Sn}^{4+}/\text{Sn}^{2+}} \\ = 1.51 - (-0.15)$$

$$E^\circ_{\text{cell}} = 1.66 \text{ V}$$

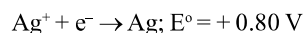
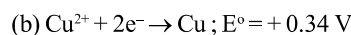
As  $E^\circ_{\text{cell}}$  is +ve therefore the reaction will take place in forward direction, i.e., favours the formation of products.

### Example – 32

(a) Account for the following

(i) Alkaline medium inhibits the rusting of iron

(ii) Iron does not rust even if the zinc coating is broken in a galvanized iron pipe.

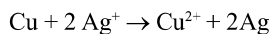


(i) Construct a galvanic cell using the above data.

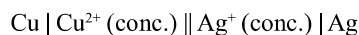
(ii) For what concentration of  $\text{Ag}^+$  ions will the emf of the cell be zero at  $25^\circ\text{C}$ , if the concentration of  $\text{Cu}^{2+}$  is  $0.01 \text{ M}$ ? [ $\log 3.919 = 0.593$ ]

**Sol.** (a) (i) The alkalinity of the solution prevents the availability of  $\text{H}^+$  ions.

- (ii) Zinc is more electropositive than iron. Therefore, zinc coating acts anode and the exposed iron portions act as cathode. If zinc coating is broken, zinc undergoes corrosion, protecting iron from rusting. No attack occurs on iron till all the zinc is corroded.



Cell representation



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

$$0 = (0.80 - 0.34) - \frac{0.059}{2} \log \left[ \frac{0.01}{x^2} \right]$$

$$15.59 = \log \left( \frac{0.01}{x^2} \right)$$

$$x = 1.597 \times 10^{-9} \text{ M}$$

$$[\text{Ag}^+] = 1.597 \times 10^{-9} \text{ M}$$

#### Example – 33

- (a) State advantages of  $\text{H}_2\text{-O}_2$  fuel cell over ordinary cell.
- (b) Silver is electrodeposited on a metallic vessel of total surface area  $500 \text{ cm}^2$  by passing a current of 0.5 amp for two hours. Calculate the thickness of silver deposited.

[Given: Density of silver =  $10.5 \text{ g cm}^{-3}$ , Atomic mass of silver = 108 amu,  $F = 9,500 \text{ C mol}^{-1}$ ]

**Sol.** (a) **Advantages Fuels Cells:**

1. It is a pollution-free device since no harmful products are formed.
2. This is very efficient cell. Its efficiency is about 75% which is considerably higher than conventional cells.

3. These cells are light in weight as compared to electrical generators to produce corresponding quantity of power.
4. It is a continuous source of energy if the supply of gases is maintained.

(b) **Mass of silver deposited**

$$m = z I t.$$

$$= \frac{108}{96500} \times 0.5 \times 2 \times 3600$$

$$m = 4.029 \text{ g}$$

$$d = \frac{m}{v} \Rightarrow v = \frac{m}{d}$$

$$V = \frac{4.029}{10.5} = 0.3837 \text{ cm}^3$$

Let the thickness of silver deposited be  $x \text{ cm}$ .

$$\therefore V = A \times x$$

$$\Rightarrow x = \frac{V}{A}$$

$$x = \frac{0.3837}{500}$$

$$\therefore x = 7.67 \times 10^{-4} \text{ cm}.$$

#### Example – 34

(a) Give reasons for the following:

- (i) Rusting of iron is quicker in saline water than in ordinary water.
- (ii) Resistance of a conductivity cell filled with 0.1 M KCl solution is 100 ohm. If the resistance of the same cell when filled with 0.02 M KCl solution is 520 ohms, calculate the conductivity and molar conductivity of 0.02 M KCl solution. (Conductivity of 0.1 M KCl solution is  $1.29 \text{ Sm}^{-1}$ ).

**Sol.** (a) (i) It is because in saline water, there is more  $\text{H}^+$  ions. Greater the number of  $\text{H}^+$  ions, quicker the rusting.

(ii) Due to higher reduction potential of hydrogen we get hydrogen at cathode.

$$(b) \quad \kappa = \frac{1}{R} \times \text{cell constant}$$

$$\Rightarrow \text{cell constant} = \kappa \times R$$

$$= 1.29 \text{ Sm}^{-1} \times 100 \text{ ohm}$$

$$= 129 \text{ m}^{-1} = 1.29 \text{ cm}^{-1}$$

For second solution

$$\kappa = \frac{1}{R} \times \text{cell constant}$$

$$\kappa = \frac{1}{520} \times 1.29 = 2.48 \times 10^{-3} \text{ S cm}^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

$$= \frac{2.48 \times 10^{-3} \times 1000}{0.02} = \frac{248}{2}$$

$$\Lambda_m = 124 \text{ S cm}^2 \text{ mol}^{-1}$$

### Example–35

- (a) Explain why electrolysis of aqueous solution of NaCl gives  $\text{H}_2$  at cathode and  $\text{Cl}_2$  at anode. Write overall reaction.

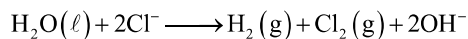
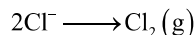
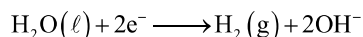
$$(E_{\text{Na}^+/\text{Na}}^\circ = -2.71 \text{ V}; E_{\text{H}_2\text{O}/\text{H}_2}^\circ = -0.83 \text{ V}, E_{\text{Cl}_2/2\text{Cl}^-}^\circ =$$

$$+1.36 \text{ V}; E_{\text{H}^+ + \text{O}_2/\text{H}_2\text{O}}^\circ = 1.23 \text{ V})$$

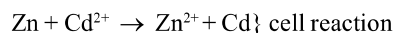
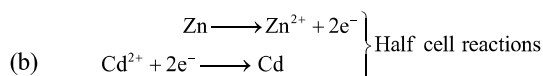
- (b) Calculate the emf of the cell of  $\text{Zn} / \text{Zn}^{2+} (0.1 \text{ M}) \parallel \text{Cd}^{2+} (0.01 \text{ M}) / \text{Cd}$  at 298 K,

$$[\text{Given } E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76 \text{ V and } E_{\text{Cd}^{2+}/\text{Cd}}^\circ = -0.40 \text{ V}]$$

**Sol.** (a) Because of higher reduction potential of water, water is reduced in preference to sodium at therefore instead of deposition of sodium metal, hydrogen is discharged at cathode.



At anode  $\text{Cl}_2$  gas is liberated because of overpotential of oxygen.



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ + E_{\text{anode}}^\circ$$

$$= 0.76 - 0.40 = 0.36 \text{ V}$$

$$E = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log Q$$

$$= 0.36 - \frac{0.0591}{2} \log \left[ \frac{\text{Zn}^{+2}}{\text{Cd}^{+2}} \right]$$

$$= 0.36 - \frac{0.0591}{2} \log \left[ \frac{0.1}{0.01} \right] = 0.33 \text{ V}$$

### Example–36

Three iron sheets have been coated separately with three metals A, B and C whose standard reduction potentials are given below.

metal	A	B	C	iron
$E_{\text{value}}^\circ$	-0.46 V	-0.66 V	-0.20 V	-0.44 V

Identify in which case rusting will take place faster when coating is damaged.

**Sol.** As iron (-0.44 V) has lower standard reduction potential than C (-0.20 V) only therefore when coating is broken, rusting will take place faster.