

NCERT SOLUTIONS

CLASS-XII CHEMISTRY

CHAPTER-3

ELECTROCHEMISTRY

Q 3.1:

In the order of their reactivity, i.e how they displace each other from their salt solutions, align the metals in decreasing order. Cu, Fe, Al, Zn and Mg.

Answer:

According to their reactivity, the given metals replace the others from their salt solutions in the said order: Mg, Al, Zn, Fe, Cu .

Mg : Al : Zn : Fe : Cu

Q 3.2:

Standard electrode potentials given as,

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

In the order of increasing of reducing power arrange the given metals accordingly.

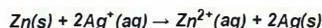
Ans:

The reducing power increases with the lowering of reduction potential. In order of given standard electrode potential (increasing order) : $K^+/K < Mg^{2+}/Mg < Cr^{3+}/Cr < Hg^{2+}/Hg < Ag^+/Ag$

Thus, in the order of reducing power, we can arrange the given metals as : $Ag < Hg < Cr < Mg < K$

Q 3.3 :

Represent the galvanic cell in which the following reaction takes place.



Also find :

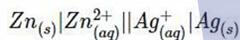
(i) *The negatively charged electrode ?*

(ii) *Current carriers in the cell.*

(iii) *At each electrode, the individual reaction.*

Ans :

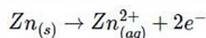
The galvanic cell in which the given reaction takes place is depicted as:



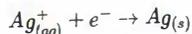
(i) The negatively charged electrode is the Zn electrode (anode)

(ii) The current carriers in the cell are ions. Current flows to zinc from silver in the external circuit.

(iii) Reaction at the anode is given by :

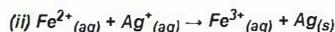
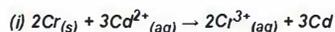


Reaction at the anode is given by :



Q 3.4:

With the following reactions given, find the standard cell potentials of galvanic cells with given reactions.



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

Ans :

(i) $E^\ominus_{Cr^{3+}/Cr} = 0.74 V$

$E^\ominus_{Cd^{2+}/Cd} = -0.40 V$

The galvanic cell of the given reaction is depicted as :



Now, the standard cell potential is

$$E^\ominus_{cell} = E^\ominus_g - E^\ominus_L$$

$$= -0.40 - (-0.74)$$

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

In the given equation, $n = 6$

$$F = 96487 \text{ C mol}^{-1}$$

$$E_{cell}^{\ominus} = +0.34 \text{ V}$$

$$\text{Then, } \Delta_r G^{\ominus} = -6 \times 96487 \text{ C mol}^{-1} \times 0.34 \text{ V}$$

$$= -196833.48 \text{ CV mol}^{-1}$$

$$= -196833.48 \text{ J mol}^{-1}$$

$$= -196.83 \text{ kJ mol}^{-1}$$

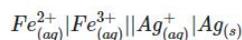
Again,

$$\Delta_r G^{\ominus} = -RT \ln K \quad \Delta_r G^{\ominus} = -2.303RT \log k = \frac{\Delta_r G}{2.303RT} = \frac{-196.83 \times 10^3}{2.303 \times 8.314 \times 298}$$

$$= 34.496$$

$$K = \text{antilog}(34.496) = 3.13 \times 10^{34}$$

The galvanic cell of the given reaction is depicted as:



Now, the standard cell potential is

$$E_{cell}^{\ominus} = E_g^{\ominus} - E_L^{\ominus}$$

Here, $n = 1$.

$$\text{Then, } \Delta_r G^{\ominus} = -nFE_{cell}^{\ominus}$$

$$= -1 \times 96487 \text{ C mol}^{-1} \times 0.03 \text{ V}$$

$$= -2894.61 \text{ J mol}^{-1}$$

$$= -2.89 \text{ kJ mol}^{-1}$$

$$\text{Again, } \Delta_r G^{\ominus} = -2.303RT \ln K$$

$$\ln K = \frac{\Delta_r G}{2.303RT} = \frac{-2894.61}{2.303 \times 8.314 \times 298}$$

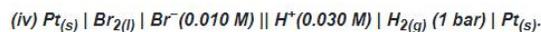
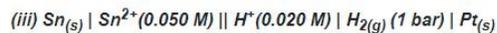
$$= 0.5073$$

$$K = \text{antilog}(0.5073)$$

$$= 3.2 \text{ (approximately)}$$

Q 3.5:

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



Answer

(i) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E_{cell}^{\ominus} - \frac{0.591}{n} \log \frac{[Mg^{2+}]}{[Cu^{2+}]} = 0.34 - (-2.36) - \frac{0.0591}{2} \log \frac{0.001}{0.0001} - 2.7 - \frac{0.0591}{2} \log 10$$

$$= 2.7 - 0.02955$$

$$= 2.67 \text{ V (approximately)}$$

(ii) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E_{cell}^{\ominus} - \frac{0.591}{n} \log \frac{[Fe^{2+}]}{[H^+]^2}$$

$$= 0 - (-0.14) - \frac{0.0591}{n} \log \frac{0.050}{(0.020)^2}$$

$$= 0.52865 \text{ V}$$

$$= 0.53 \text{ V (approximately)}$$

(iii) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E_{cell}^0 - \frac{0.591}{n} \log \frac{[Sn^{2+}]}{[H^+]^2}$$

$$= 0 - (-0.14) - \frac{0.591}{2} \log \frac{0.050}{(0.020)^2}$$

$$= 0.14 - 0.0295 \times \log 125$$

$$= 0.14 - 0.062$$

$$= 0.078 \text{ V}$$

$$= 0.08 \text{ V (approximately)}$$

(iv) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E_{cell}^0 - \frac{0.591}{n} \log \frac{1}{[Br^-]^2 [H^+]^2}$$

$$= 0 - 1.09 - \frac{0.591}{2} \log \frac{1}{(0.010)^2 (0.030)^2}$$

$$= -1.09 - 0.02955 \times \log \frac{1}{0.0000009}$$

$$= -1.09 - 0.02955 \times \log \frac{1}{9 \times 10^{-8}}$$

$$= -1.09 - 0.02955 \times \log(1.11 \times 10^7)$$

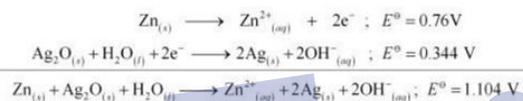
$$= -1.09 - 0.02955 \times (0.0453 + 7)$$

$$= -1.09 - 0.208$$

$$= -1.298 \text{ V}$$

Q 3.6:

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



For the given reaction calculate $\Delta_r G^{\ominus}$ and E^0 :

Ans:

$$E^0 = 1.104 \text{ V}$$

We know that,

$$\Delta_r G^{\ominus} = -nFE^{\ominus}$$

$$= -2 \times 96487 \times 1.04$$

$$= -213043.296 \text{ J}$$

$$= -213.04 \text{ kJ}$$

Q 3.7:

For the solution of an electrolyte describe its conductivity and molar conductivity. Also put some light on how they vary with concentration.

Answer

Conductivity of a solution is defined as the conductance of a solution of 1 cm in length and area of cross-section 1 sq. cm. Specific conductance is the inverse of resistivity and it is represented by the symbol κ . If ρ is resistivity, then we can write:

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

At any given concentration, the conductivity of a solution is defined as the unit volume of solution kept between two platinum electrodes with the unit area of cross-section at a distance of unit length.

$$G = k \frac{a}{l} = k \times 1 = k \text{ [Since } a = 1, l = 1 \text{]}$$

When concentration decreases there will be a decrease in Conductivity. It is applicable for both weak and strong electrolyte. This is because the number of ions per unit volume that carry the current in a solution decreases with a decrease in concentration.

Molar conductivity –

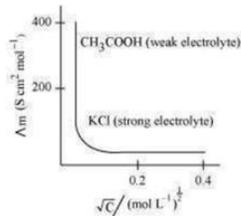
Molar conductivity of a solution at a given concentration is the conductance of volume V of a solution containing 1 mole of the electrolyte kept between two electrodes with the area of cross-section A and distance of unit length.

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

Now, $l = 1$ and $A = V$ (volume containing 1 mole of the electrolyte).

$$\Lambda_m = kV$$

Molar conductivity increases with a decrease in concentration. This is because the total volume V of the solution containing one mole of the electrolyte increases on dilution. The variation of Λ_m with \sqrt{c} for strong and weak electrolytes is shown in the following plot :



Q 3.8:

The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 Scm^{-1} . Find its molar conductivity.

Ans :

$$\text{Given, } \kappa = 0.0248 \text{ S cm}^{-1} \text{ c}$$

$$= 0.20 \text{ M}$$

$$\text{Molar conductivity, } \Lambda_m = \frac{k \times 1000}{c}$$

$$= \frac{0.0248 \times 1000}{0.2}$$

$$= 124 \text{ Scm}^2 \text{ mol}^{-1}$$

Q 3.9:

Considering the case of a conductivity cell having 0.001 M KCl solution at 298 K is 1500Ω . If given, conductivity of 0.001M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S}$, find the cell constant?

Answer

Given,

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

$$\text{Resistance, } R = 1500 \Omega$$

$$\text{Cell constant} = \kappa \times R$$

$$= 0.146 \times 10^{-3} \times 1500$$

$$= 0.219 \text{ cm}^{-1}$$

Q 3.10:

The conductivity of NaCl at 298 K has been found at different concentrations and the results are given below:

Concentration/M 0.001 0.010 0.020 0.050 0.100

$10^2 \times \kappa/\text{S m}^{-1}$ 1.237 11.85 23.15 55.53 106.74

for all concentrations and draw a plot between Λ_m and $c^{1/2}$. Find the value

Molar conductivity of

Calculate Λ_m of Λ_m^0

Ans:

Given,

$$\kappa = 1.237 \times 10^{-2} \text{ S m}^{-1}, c = 0.001 \text{ M}$$

$$\text{Then, } \kappa = 1.237 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.0316 \text{ M}^{1/2}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{1.237 \times 10^{-4} \text{ S cm}^{-1}}{0.001 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{\text{L}}$$

$$= 123.7 \text{ S cm}^2 \text{ mol}^{-1}$$

Given,

$$\kappa = 11.85 \times 10^{-2} \text{ S m}^{-1}, c = 0.010 \text{ M}$$

$$\text{Then, } \kappa = 11.85 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.1 \text{ M}^{1/2}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{11.85 \times 10^{-4} \text{ S cm}^{-1}}{0.010 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{\text{L}}$$

$$= 118.5 \text{ S cm}^2 \text{ mol}^{-1}$$

Given,

$$\kappa = 23.15 \times 10^{-2} \text{ S m}^{-1}, c = 0.020 \text{ M}$$

$$\text{Then, } \kappa = 23.15 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.1414 \text{ M}^{1/2}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{23.15 \times 10^{-4} \text{ S cm}^{-1}}{0.020 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{\text{L}}$$

$$= 115.8 \text{ S cm}^2 \text{ mol}^{-1}$$

Given,

$$\kappa = 55.53 \times 10^{-2} \text{ S m}^{-1}, c = 0.050 \text{ M}$$

$$\text{Then, } \kappa = 55.53 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.2236 \text{ M}^{1/2}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{106.74 \times 10^{-4} \text{ S cm}^{-1}}{0.050 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{\text{L}}$$

$$= 111.1 \text{ S cm}^2 \text{ mol}^{-1}$$

Given,

$$\kappa = 106.74 \times 10^{-2} \text{ S m}^{-1}, c = 0.100 \text{ M}$$

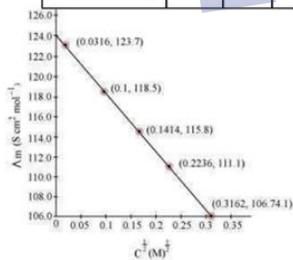
$$\text{Then, } \kappa = 106.74 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.3162 \text{ M}^{1/2}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{106.74 \times 10^{-4} \text{ S cm}^{-1}}{0.100 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{\text{L}}$$

$$= 106.74 \text{ S cm}^2 \text{ mol}^{-1}$$

Now, we have the following data :

$c^{1/2} / \text{M}^{1/2}$	0.0316	0.1	0.1414	0.2236	0.3162
$\Lambda_m (\text{S cm}^2 \text{ mol}^{-1})$	123.7	118.5	115.8	111.1	106.74



Since the line intercepts Λ_m at $124.0 \text{ S cm}^2 \text{ mol}^{-1}$, $\Lambda_m^0 = 124.0 \text{ S cm}^2 \text{ mol}^{-1}$

Q 3.11:

Find the molar conductivity of acetic acid if its conductivity is given to be 0.00241 M . Also, if the value of Λ_m^0 is given to be $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, calculate its dissociation constant?

Ans:

$$\text{Given, } \kappa = 7.896 \times 10^{-5} \text{ S m}^{-1} c$$

$$= 0.00241 \text{ mol L}^{-1}$$

$$\text{Then, molar conductivity, } \Lambda_m = \frac{\kappa}{c}$$

$$= \frac{7.896 \times 10^{-5} \text{ S cm}^{-1}}{0.00241 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$$

$$= 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

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

Again,

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0}$$

$$= \frac{32.76 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}}$$

Now,

$$= 0.084$$

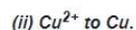
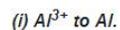
$$\text{Dissociation constant, } K_a = \frac{c\alpha^2}{(1-\alpha)}$$

$$= \frac{(0.00241 \text{ mol L}^{-1})(0.084)^2}{(1-0.084)}$$

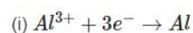
$$= 1.86 \times 10^{-5} \text{ mol L}^{-1}$$

Q 3.12:

How much charge is required for the following reductions of 1 mol of :



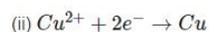
Ans :



Required charge = 3 F

$$= 3 \times 96487 \text{ C}$$

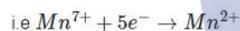
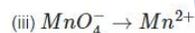
$$= 289461 \text{ C}$$



Required charge = 2 F

$$= 2 \times 96487 \text{ C}$$

$$= 192974 \text{ C}$$



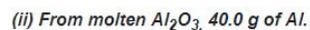
Required charge = 5 F

$$= 5 \times 96487 \text{ C}$$

$$= 482435 \text{ C}$$

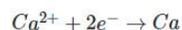
Q 3.13:

In the terms of Faraday, how much electricity is required to produce :



Ans:

(i) From given data,

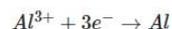


Electricity required to produce 40 g of calcium = 2 F

Therefore, electricity required to produce 20 g of calcium = $(2 \times 20) / 40$ F

$$= 1 \text{ F}$$

(ii) From given data,



Electricity required to produce 27 g of Al = 3 F

Therefore, electricity required to produce 40 g of Al = $(3 \times 40) / 27$ F

$$= 4.44 \text{ F}$$

Q 3.14:

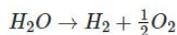
Calculate the amount of electricity required for the oxidation of 1 mol of the following in coulombs :

(i) H_2O to O_2 .

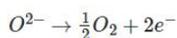
(ii) FeO to Fe_2O_3 .

Ans :

(i) From given data,



We can say that :

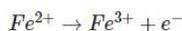


Electricity required for the oxidation of 1 mol of H_2O to $O_2 = 2 F$

$$= 2 \times 96487 \text{ C}$$

$$= 192974 \text{ C}$$

(ii) From given data,



Electricity required for the oxidation of 1 mol of FeO to $Fe_2O_3 = 1 F$

$$= 96487 \text{ C}$$

Q 3.15:

For 20 minutes, a current of 5 A is applied to between platinum electrodes to electrolyze a solution of $Ni(NO_3)_2$. Find the amount of Ni deposited at the cathode?

Ans :

Given,

$$\text{Current} = 5 \text{ A}$$

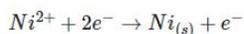
$$\text{Time} = 20 \times 60 = 1200 \text{ s}$$

$$\text{Charge} = \text{current} \times \text{time}$$

$$= 5 \times 1200$$

$$= 6000 \text{ C}$$

According to the reaction,



Nickel deposited by $2 \times 96487 \text{ C} = 58.71 \text{ g}$

$$\text{Therefore, nickel deposited by } 6000 \text{ C} = \frac{58.71 \times 6000}{2 \times 96487} \text{ g}$$

$$= 1.825 \text{ g}$$

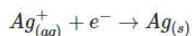
Hence, 1.825 g of nickel will be deposited at the cathode.

Q 3.16:

Solutions of 3 electrolytic cells are $ZnSO_4$, $AgNO_3$ and $CuSO_4$, cells are connected in series. Of the cells, A, B, C respectively, after passing a steady current of 1.5 amperes, 1.45 g of silver was found deposited at the cathode of cell B. How much time did the current flow? What amount of zinc and copper were deposited?

Ans :

According to the reaction:



i.e., 108 g of Ag is deposited by 96487 C.

$$\text{Therefore, } 1.45 \text{ g of Ag is deposited by} = \frac{96487 \times 1.45}{107} \text{ C}$$

$$= 1295.43 \text{ C}$$

Given,

$$\text{Current} = 1.5 \text{ A}$$

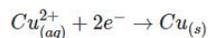
$$\text{Time} = 1295.43 / 1.5 \text{ s}$$

$$= 863.6 \text{ s}$$

$$= 864 \text{ s}$$

$$= 14.40 \text{ min}$$

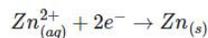
Again,



i.e., $2 \times 96487 \text{ C}$ of charge deposit = 63.5 g of Cu

$$\text{Therefore, } 1295.43 \text{ C of charge will deposit } \frac{63.5 \times 1295.43}{2 \times 96487}$$

$$= 0.426 \text{ g of Cu}$$



i.e., $2 \times 96487 \text{ C}$ of charge deposit = 65.4 g of Zn

$$\text{Therefore, } 1295.43 \text{ C of charge will deposit } \frac{65.4 \times 1295.43}{2 \times 96487}$$

$$= 0.439 \text{ g of Zn}$$

Q 3.17:

Using the standard electrode potentials given in Table 3.1, predict if the reaction between

the following is feasible:

(i)

$\text{Fe}^{3+}(\text{aq})$ and $\text{I}^-(\text{aq})$

(ii) $\text{Ag}^+(\text{aq})$ and $\text{Cu}(\text{s})$

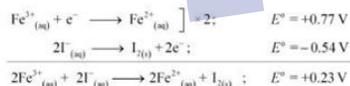
(iii) $\text{Fe}^{3+}(\text{aq})$ and $\text{Br}^-(\text{aq})$

(iv) $\text{Ag}(\text{s})$ and $\text{Fe}^{3+}(\text{aq})$

(v) $\text{Br}_2(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$.

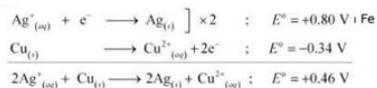
Ans :

(i)



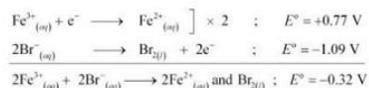
E° is positive, hence reaction is feasible.

(ii)



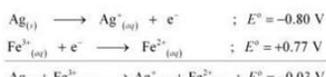
E° is positive, hence reaction is feasible.

(iii)



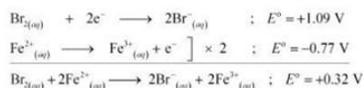
E° is negative, hence reaction is not feasible.

(iv)



E^0 is negative, hence reaction is not feasible.

(v)



E^0 is positive, hence reaction is feasible.

Q 3.18:

Predict the products of electrolysis in each of the following :

(i) An aqueous solution of AgNO_3 with silver electrodes.

(ii) An aqueous solution of AgNO_3 with platinum electrodes.

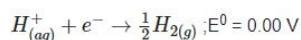
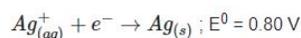
(iii) A dilute solution of H_2SO_4 with platinum electrodes.

(iv) An aqueous solution of CuCl_2 with platinum electrodes.

Ans:

(i) At cathode:

The following reduction reactions compete to take place at the cathode.



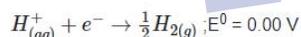
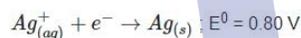
The reaction with a higher value of E^0 takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

At anode:

The Ag anode is attacked by NO_3^- ions. Therefore, the silver electrode at the anode dissolves in the solution to form Ag^+ .

(ii) At cathode:

The following reduction reactions compete to take place at the cathode.



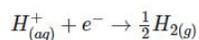
The reaction with a higher value of E^0 takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

At anode:

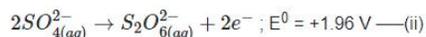
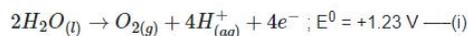
Since Pt electrodes are inert, the anode is not attacked by NO_3^- ions. Therefore, OH^- or NO_3^- ions can be oxidized at the anode. But OH^- ions having a lower discharge potential and get preference and decompose to liberate O_2 .



(iii) At the cathode, the following reduction reaction occurs to produce H_2 gas.



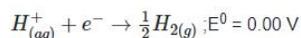
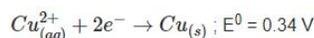
At the anode, the following processes are possible.



For dilute sulphuric acid, reaction (i) is preferred to produce O_2 gas. But for concentrated sulphuric acid, reaction (ii) occurs.

(iv) At cathode:

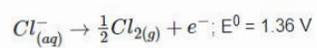
The following reduction reactions compete to take place at the cathode.



The reaction with a higher value of E^0 takes place at the cathode. Therefore, deposition of copper will take place at the cathode.

At anode:

The following oxidation reactions are possible at the anode.



At the anode, the reaction with a lower value of E^0 is preferred. But due to the over potential of oxygen, Cl^- gets oxidized at the anode to produce Cl_2 gas.

