

Chapter.3 Electrochemistry Class-XII Subject-Chemistry

3.1 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

Answer 3.1

The order in which metal displaces each other from the solution of their salts is:
Mg, Al, Zn, Fe, Cu

3.2 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.

Answer 3.2

Lower the reduction potential, higher will be reducing power.

Therefore, the order of reducing power of the given metals increases as:

$Ag < Hg < Cr < Mg < K$

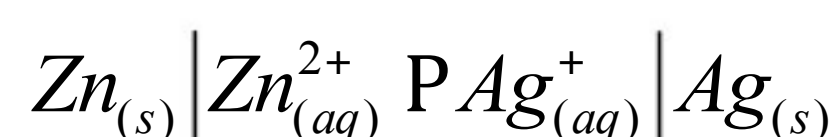
3.3 Depict the galvanic cell in which the reaction

$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place. Further show:

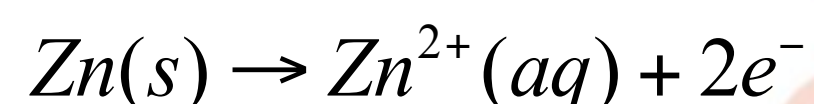
- Which of the electrode is negatively charged?
- The carriers of the current in the cell.
- Individual reaction at each electrode.

Answer 3.3

The galvanic cell of the given reaction can be represented as:



- Zn electrode is negatively charged.
- Ions are carriers of current in the cell. Current will flow from silver to zinc in the external circuit.
- The reaction takes place at the anode is:



The reaction takes place at the cathode is: $Ag^+(aq) + e^- \rightarrow Ag(s)$

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

- $2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd$
- $Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$

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

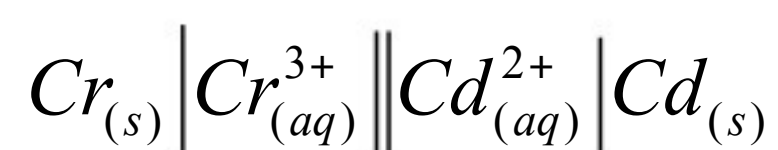
Answer 3.4

i.

$$E^\theta_{Cr^{3+}/Cr} = 0.74 \text{ V}$$

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

Galvanic cell of given reaction is:



Now,

$$\begin{aligned}
 E_{cell}^{\ominus} &= E_R^{\ominus} - E_L^{\ominus} \\
 &= -0.40 - (-0.74) \\
 &= 0.34 \text{ V}
 \end{aligned}$$

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

We know that,

$$n = 6$$

$$\begin{aligned}
 \Delta_r G^{\ominus} &= -nFE_{cell}^{\ominus} \\
 &= -6 \times 96487 \times 0.34 \\
 &= -196.83 \text{ KJ / mol}
 \end{aligned}$$

Also,

$$\Delta_r G^{\ominus} = -2.303RT \log K$$

$$\begin{aligned}
 \log K &= -\frac{\Delta_r G^{\ominus}}{2.303RT} \\
 &= -\frac{196.83 \times 1000}{2.303 \times 8.314 \times 298} = 34.496
 \end{aligned}$$

Thus,

$$K = \text{antilog}(34.496)$$

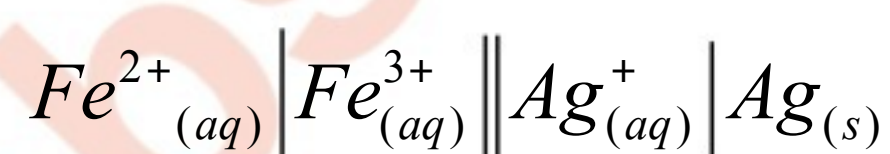
$$K = 3.13 \times 10^{34}$$

ii.

$$E_{Fe^{3+}/Fe^{2+}}^{\ominus} = 0.77 \text{ V}$$

$$E_{Ag^+/Ag}^{\ominus} = 0.80 \text{ V}$$

Galvanic cell of given reaction is:



Now,

$$\begin{aligned}
 E_{cell}^{\ominus} &= E_R^{\ominus} - E_L^{\ominus} \\
 &= 0.80 - 0.77 \\
 &= 0.03 \text{ V}
 \end{aligned}$$

We know that,

$$n = 1$$

$$\begin{aligned}\Delta_r G^\ominus &= -nFE_{cell}^\ominus \\ &= -1 \times 96487 \times 0.03 \\ &= -2.89 \text{ Kj / mol}\end{aligned}$$

Also,

$$\begin{aligned}\Delta_r G^\ominus &= -2.303RT \log K \\ \log K &= -\frac{\Delta_r G^\ominus}{2.303RT} \\ &= -\frac{2.89 \times 1000}{2.303 \times 8.314 \times 298} = 0.5073\end{aligned}$$

Thus,

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

$$K = 3.2$$

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

- i. $\text{Mg(s)} \mid \text{Mg}^{2+} (0.001\text{M}) \parallel \text{Cu}^{2+} (0.0001 \text{ M}) \mid \text{Cu(s)}$
- ii. $\text{Fe(s)} \mid \text{Fe}^{2+} (0.001\text{M}) \parallel \text{H}^+ (1\text{M}) \mid \text{H}_2(\text{g})(1\text{bar}) \mid \text{Pt(s)}$
- iii. $\text{Sn(s)} \mid \text{Sn}^{2+} (0.050 \text{ M}) \parallel \text{H}^+ (0.020 \text{ M}) \mid \text{H}_2 (\text{g}) (1 \text{ bar}) \mid \text{Pt(s)}$
- iv. $\text{Pt(s)} \mid \text{Br}_2 (\text{l}) \mid \text{Br}^- (0.010 \text{ M}) \parallel \text{H}^+ (0.030 \text{ M}) \mid \text{H}_2 (\text{g}) (1 \text{ bar}) \mid \text{Pt(s)}.$

Answer 3.5

- i. Nernst equation for the given equation is:

$$\begin{aligned}E_{cell} &= E_{cell}^0 - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} \\ &= [0.34 - (-2.36)] - \frac{0.0591}{2} \log \frac{0.001}{0.0001} \\ &= 2.7 - \frac{0.0591}{2} \log 10 \\ &= 2.67 \text{ V}\end{aligned}$$

- ii. Nernst equation for the given equation is:

$$\begin{aligned} E_{cell} &= E_{cell}^0 - \frac{0.0591}{n} \log \frac{[Fe^{2+}]}{[H^+]^2} \\ &= [0 - (-0.44)] - \frac{0.0591}{2} \log \frac{0.001}{1} \\ &= 0.44 - 0.0295 \times (-3) \\ &= 0.528V \end{aligned}$$

iii. Nernst equation for the given equation is:

$$\begin{aligned} E_{cell} &= E_{cell}^0 - \frac{0.0591}{n} \log \frac{[Sn^{2+}]}{[H^+]^2} \\ &= [0 - (-0.14)] - \frac{0.0591}{2} \log \frac{0.050}{(0.02)^2} \\ &= 0.14 - 0.0295 \times \log 125 \\ &= 0.14 - 0.062 \\ &= 0.078V \end{aligned}$$

iv.

Nernst equation for the given equation is:

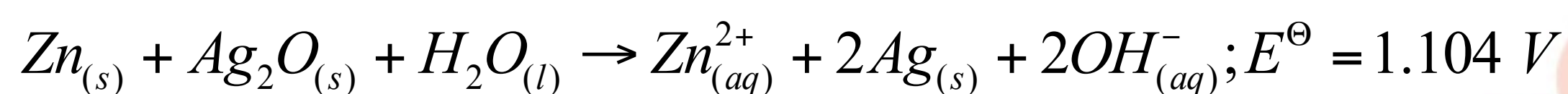
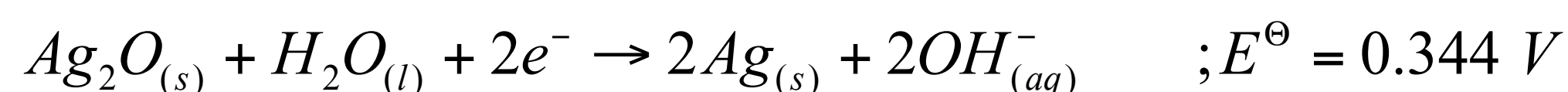
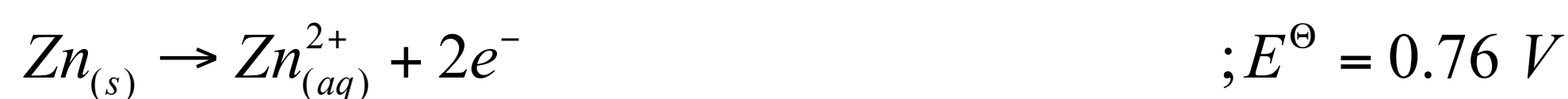
$$\begin{aligned} E_{cell} &= E_{cell}^0 - \frac{0.0591}{n} \log \frac{1}{[Br^-]^2 [H^+]^2} \\ &= [0 - 1.09] - \frac{0.0591}{2} \log \frac{1}{(0.01)^2 (0.03)^2} \\ &= -1.09 - 0.0295 \times \log \left(\frac{1}{9 \times 10^{-8}} \right) \\ &= -1.09 - 0.0295 \times 7.0453 \\ &= -1.298 V \end{aligned}$$

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



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

Answer 3.6



So, $E^\ominus = 1.104 \text{ V}$

Also,

$$\begin{aligned}
 \Delta_r G^\ominus &= -nFE^\ominus \\
 &= 2(96487)(1.04) \\
 &= -213.04 \text{ kJ}
 \end{aligned}$$

3.7 Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

Answer 3.7

Conductivity: - it is defined as the conductance of a solution of 1 cm in length and area of cross-section 1 sq. cm. The inverse of resistivity is called specific conductance or conductivity. It is represented by the symbol “ κ ”.

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

Where ρ is resistivity

Also,

At any given concentration if a solution is kept between two platinum electrodes having unit area of cross-section & with a distance of unit length, then, conductivity is equal to the conductance (G).

$$G = \kappa \frac{a}{l} = \kappa$$

As $a = 1$ & $l = 1$

Conductivity decreases with a decrease in concentration, for all the electrolytes weak and strong electrolytes. This happens because the number of ions that carry the current in a solution decreases with a decrease in concentration.

Molar conductivity: - at a given concentration, it can be defined as the conductance of volume V of a solution containing 1 mole of the electrolyte which is kept between two electrodes with the area A and distance of unit length.

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

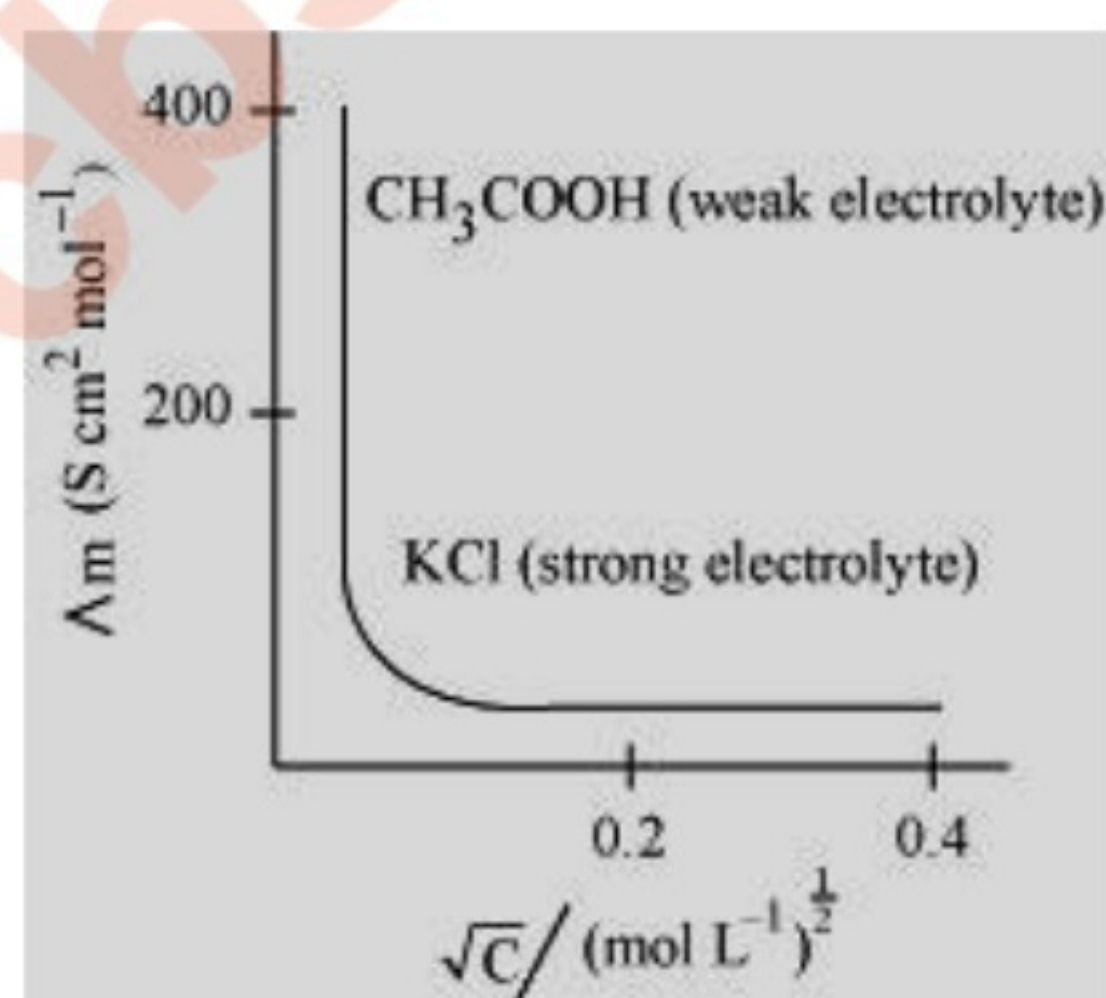
As $l = 1$, $A = V$

Hence,

$$\Lambda_m = \kappa V$$

It is inversely related to concentration thus it increases with a decrease in concentration. This happens 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:



3.8 The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1} . Calculate its molar conductivity.

Answer 3.8

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

$$c = 0.20 \text{ M}$$

$$\Lambda_m = \frac{\kappa \times 1000}{c} = \frac{0.0248 \times 1000}{0.2} = 124 \text{ S cm}^2 / \text{mol}$$

$$\therefore \text{Molar conductivity} = 124 \text{ S cm}^2 / \text{mol}$$

3.9 The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500Ω . What is the cell constant if conductivity of 0.001M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$?

Answer 3.9

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

$$R = 1500 \Omega$$

$$\begin{aligned} \therefore \text{cell constant} &= \kappa \times R \\ &= 0.146 \times 10^{-3} \times 1500 \\ &= 0.219 \text{ cm}^{-1} \end{aligned}$$

3.10 The conductivity of sodium chloride at 298 K has been determined 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

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{1/2}$. Find the value of Λ_m^0 .

Answer 3.10

1.

$$\kappa = 1.237 \times 10^{-2} \text{ S m}^{-1} = 1.237 \times 10^{-4} \text{ S cm}^{-1}$$

$$c = 0.001 \text{ M}, \sqrt{c} = 0.0316 \text{ M}^{1/2}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{1.237 \times 10^{-4} \times 1000}{0.001} = 123.7 \text{ Scm}^2 / \text{mol}$$

2.

$$\kappa = 11.85 \times 10^{-2} \text{ S m}^{-1} = 11.85 \times 10^{-4} \text{ S cm}^{-1}$$

$$c = 0.010 \text{ M}, \sqrt{c} = 0.1 \text{ M}^{1/2}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{11.85 \times 10^{-4} \times 1000}{0.010} = 118.5 \text{ Scm}^2 / \text{mol}$$

3.

$$\kappa = 23.15 \times 10^{-2} \text{ S m}^{-1} = 23.15 \times 10^{-4} \text{ S cm}^{-1}$$

$$c = 0.020 \text{ M}, \sqrt{c} = 0.1414 \text{ M}^{1/2}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{23.15 \times 10^{-4} \times 1000}{0.020} = 115.8 \text{ Scm}^2 / \text{mol}$$

4.

$$\kappa = 55.53 \times 10^{-2} \text{ S m}^{-1} = 55.53 \times 10^{-4} \text{ S cm}^{-1}$$

$$c = 0.050 \text{ M}, \sqrt{c} = 0.2236 \text{ M}^{1/2}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{55.53 \times 10^{-4} \times 1000}{0.050} = 111.11 \text{ Scm}^2 / \text{mol}$$

5.

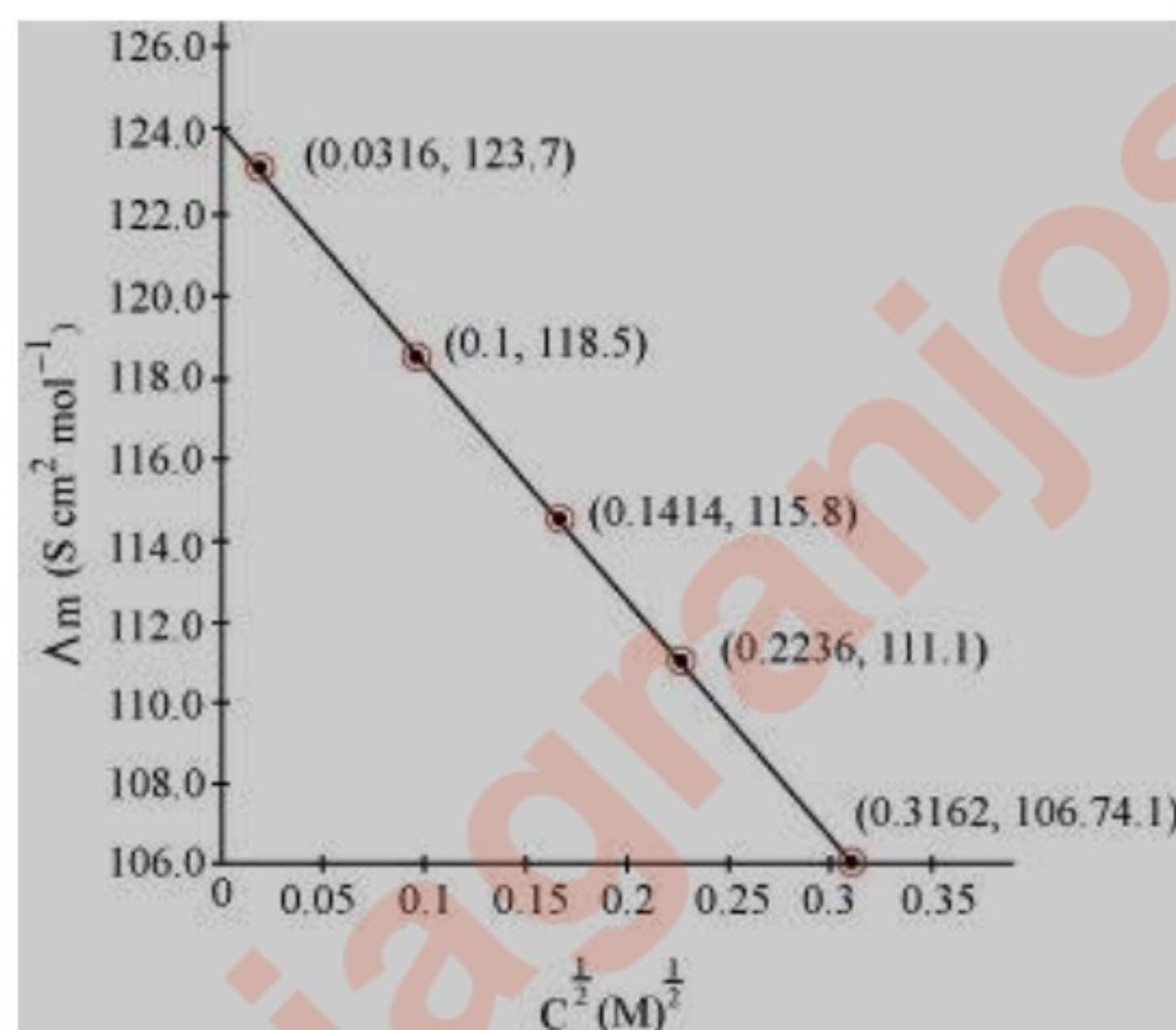
$$\kappa = 106.74 \times 10^{-2} \text{ S m}^{-1} = 106.74 \times 10^{-4} \text{ S cm}^{-1}$$

$$c = 0.100 \text{ M}, \quad \sqrt{c} = 0.3162 \text{ M}^{1/2}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{106.74 \times 10^{-4} \times 1000}{0.100} = 106.74 \text{ Scm}^2 / \text{mol}$$

Now, we have the following data:

\sqrt{c}	0.0316	0.1	0.1414	0.2236	0.3162
Λ_m	123.7	118.5	115.8	111.1	106.74



From the graph, $\Lambda_m^0 = 124 \text{ Scm}^2 / \text{mol}$

3.11 Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and if Λ_m^0 for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what is its dissociation constant?

Answer 3.11

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

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

$$\Lambda_m = \frac{\kappa}{c} = \frac{7.896 \times 10^{-5} \times 1000}{0.00241} = 32.76 \text{ Scm}^2 / \text{mol}$$

We have,

$$\Lambda_m^0 = 390.5 \text{ Scm}^2 / \text{mol}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{32.76}{390.5} = 0.084$$

$$\text{Dissociation constant, } \therefore K_a = \frac{c\alpha^2}{1-\alpha} = \frac{0.00241 \times 0.084 \times 0.084}{1-0.0084} = 1.86 \times 10^{-5} \text{ mol / l}$$

3.12 How much charge is required for the following reductions?

- i. 1 mol of Al^{3+} to Al.
- ii. 1 mol of Cu^{2+} to Cu.
- iii. 1 mol of MnO_4^- to Mn^{2+}

Answer 3.12

- i. Charge = 3 F

$$= 3 \times 96487 \text{ C} = 289461 \text{ C}$$

- ii. Charge = 2 F

$$= 2 \times 96487 \text{ C} = 192974 \text{ C}$$

- iii. $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$

Here, +7 oxidation state is converted into +2

Therefore, charge = 5 F

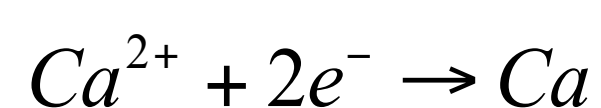
$$= 5 \times 96487 \text{ C} = 482435 \text{ C}$$

3.13 How much electricity in terms of Faraday is required to produce?

- i. 20.0 g of Ca from molten CaCl_2
- ii. 40.0 g of Al from molten Al_2O_3

Answer 3.13

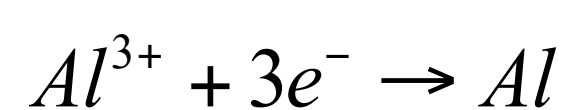
- i. As per the equation,



Electricity required to produce 40 g of calcium = 2 F

Hence, electricity required to produce 20 g of calcium = $\frac{2 \times 20}{40} \text{ F} = 1 \text{ F}$

- ii. As per the equation,



Electricity required to produce 27 g of Al = 3 F

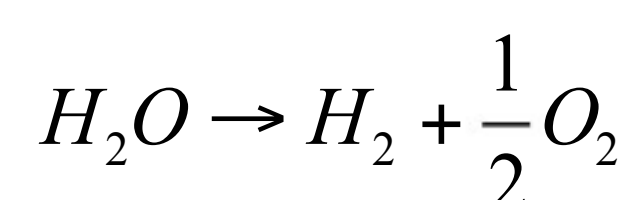
Hence, electricity required to produce 40 g of Al = $\frac{3 \times 40}{27} = 4.44 \text{ F}$

3.14 How much electricity is required in coulomb for the oxidation of?

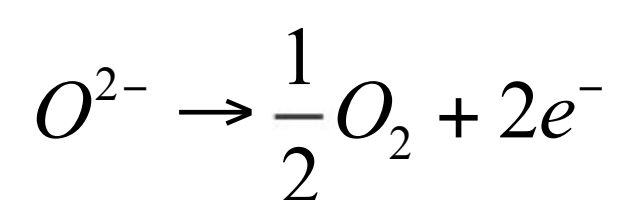
- i. 1 mol of H_2O to O_2 .
- ii. 1 mol of FeO to Fe_2O_3 .

Answer 3.14

- i. As per the equation,



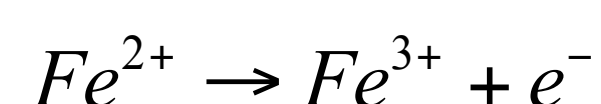
Now,



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. As per the equation,



Electricity required for the oxidation of 1 mol of FeO to $Fe_2O_3 = 1 F = 96487 \text{ C}$

3.15 A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Answer 3.15

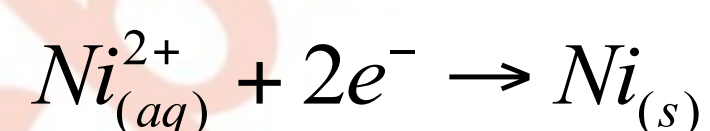
Current, $I = 5A$

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

Charge = current \times time

$$= 5 \times 1200 = 6000 \text{ C}$$

As per the equation,



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

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

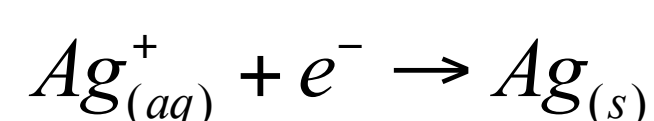
$$= 1.825 \text{ g}$$

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

- 3.16** Three electrolytic cells A, B, C containing solutions of ZnSO_4 , AgNO_3 and CuSO_4 , respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

Answer 3.16

As per the equation,



108 g of Ag is deposited by = 96487 C of charge

$$1.45 \text{ g of Ag is deposited by} = \frac{96487 \times 1.45}{108} \text{ C}$$

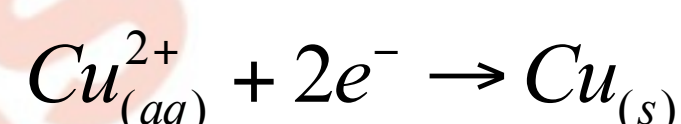
$$= 1295.43 \text{ C}$$

We have,

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

$$\text{Time} = \frac{1295.43}{1.5} \text{ s} = 863.6 \text{ s} = 864 \text{ s} = 14.40 \text{ min}$$

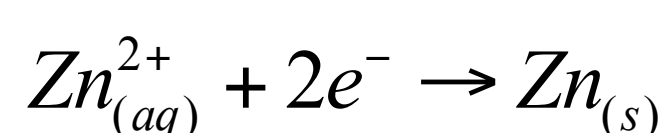
Now,



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

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

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



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

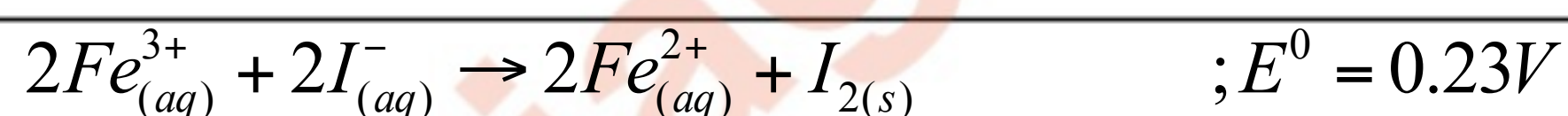
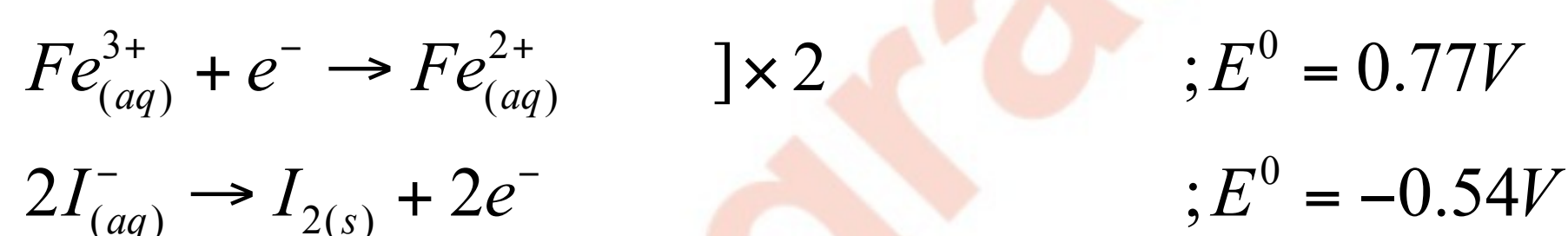
$$\begin{aligned}
 \text{Then, } 1295.43 \text{ C of charge will deposit} &= \frac{65.4 \times 1295.43}{2 \times 96487} \text{ g} \\
 &= 0.439 \text{ g of Zn}
 \end{aligned}$$

3.17 Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:

- i. $Fe_{(aq)}^{3+}$ & $I_{(aq)}^-$
- ii. $Ag_{(aq)}^+$ & $Cu_{(s)}$
- iii. $Fe_{(aq)}^{3+}$ & $Br_{(aq)}^-$
- iv. $Ag_{(s)}$ & $Fe_{(aq)}^{3+}$
- v. $Br_{2(aq)}$ & $Fe_{(aq)}^{2+}$

Answer 3.17

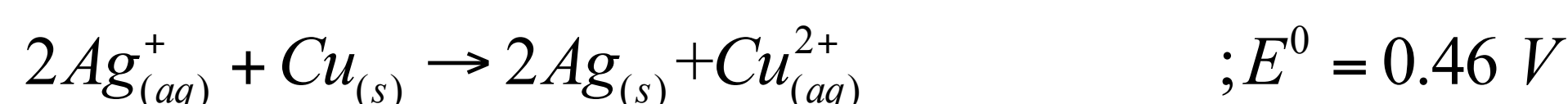
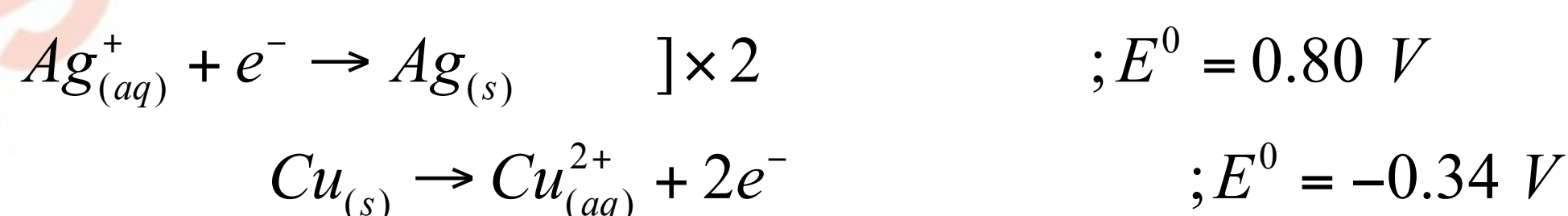
i.



$E^0 = \text{positive}$

\therefore Reaction is feasible

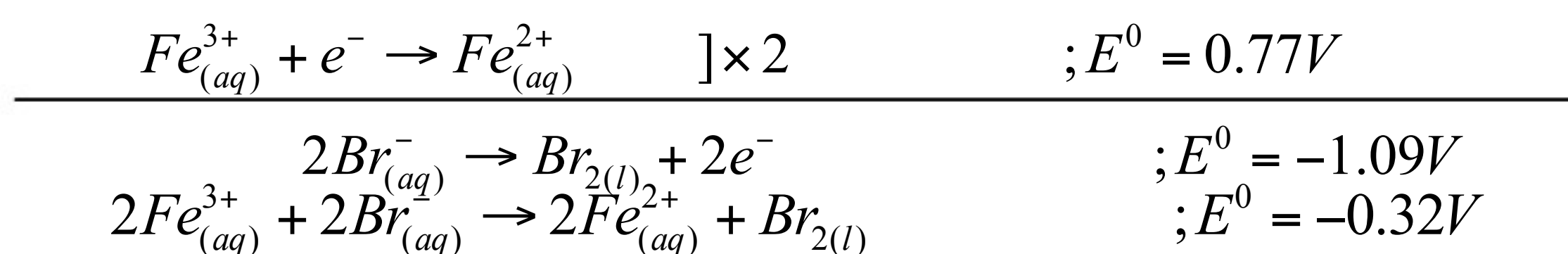
ii.



$E^0 = \text{positive}$

\therefore Reaction is feasible

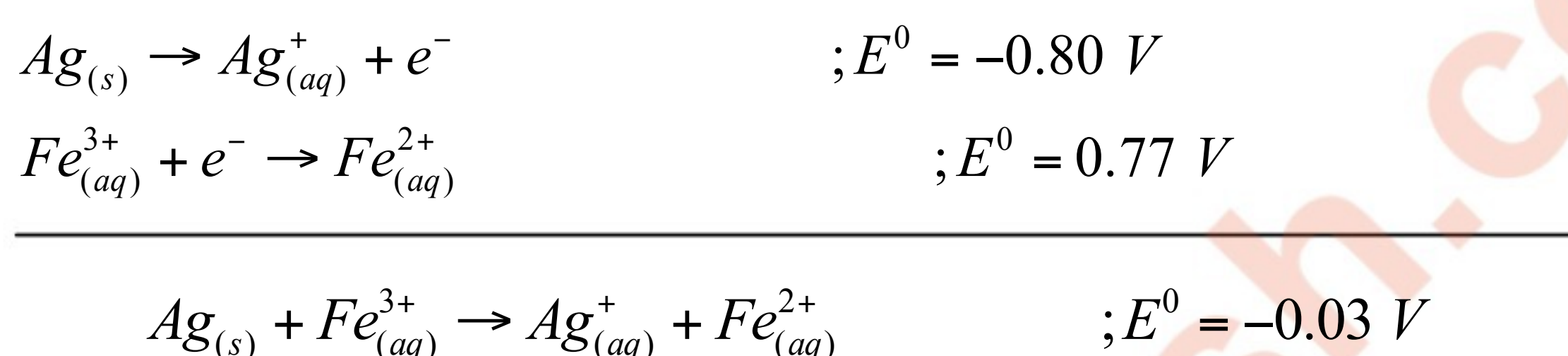
iii.



$E^0 = \text{negative}$

\therefore Reaction is not feasible

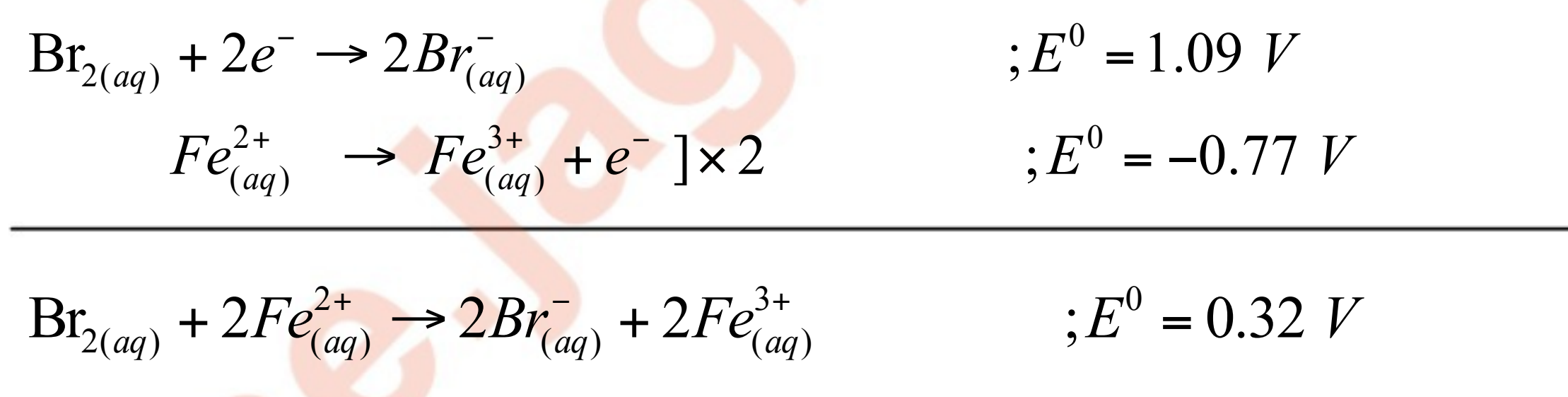
iv.



$E^0 = \text{negative}$

\therefore Reaction is not feasible

v.



$E^0 = \text{positive}$

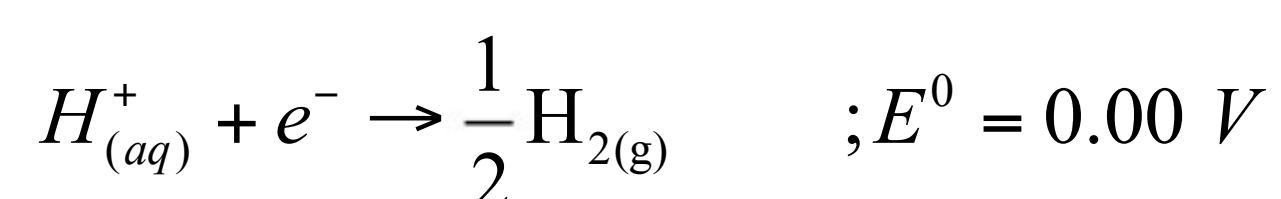
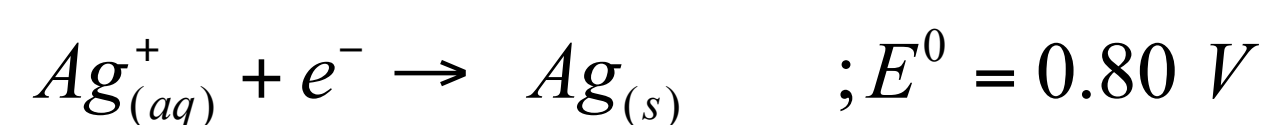
\therefore Reaction is feasible

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.

Answer 3.18

i. At cathode: reduction reaction

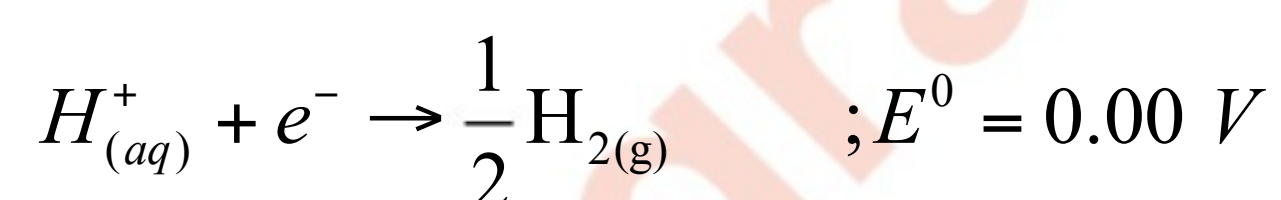
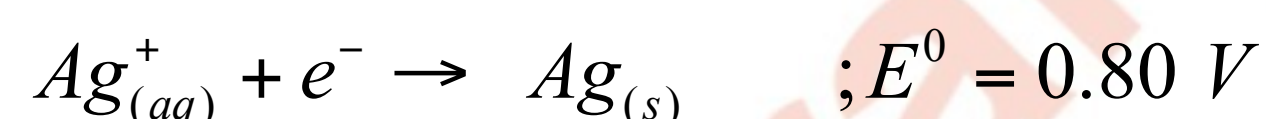


As we know that the reaction which has higher E^0 value, it will take place at cathode. Thus, deposition of silver will take place at the cathode.

At anode:

NO_3^- Ions will react with Ag anode. Thus, the silver electrode at the anode dissolves in the solution & form Ag^+ .

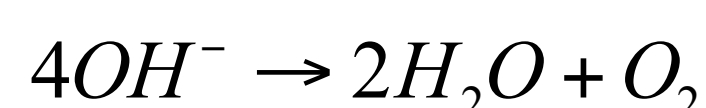
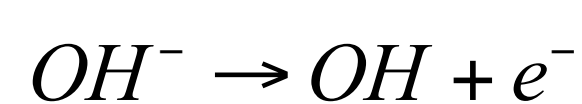
ii. At cathode: reduction reactions



As we know that the reaction which has higher E^0 value, it will take place at cathode. Thus, deposition of silver will take place at the cathode.

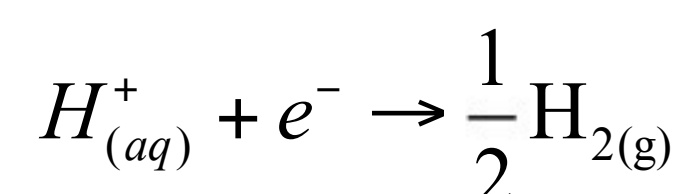
At anode:

NO_3^- Ions will not be able to react with Pt anode as Pt electrodes are inert in nature. Thus, OH^- or NO_3^- ions can be oxidized at the anode. But due to lower discharge potential, OH^- ions will get preference and it will decompose to liberate O_2 .

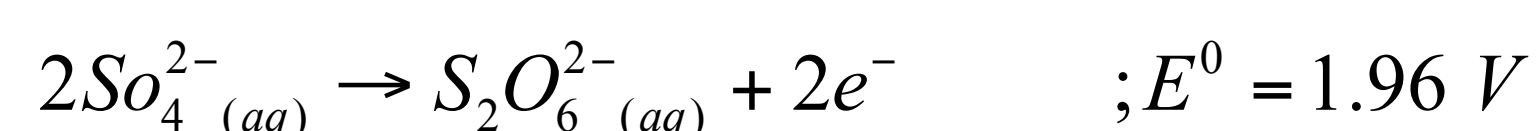
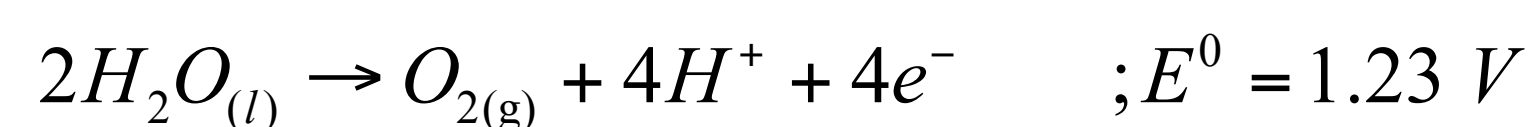


iii.

At the cathode: reduction reaction

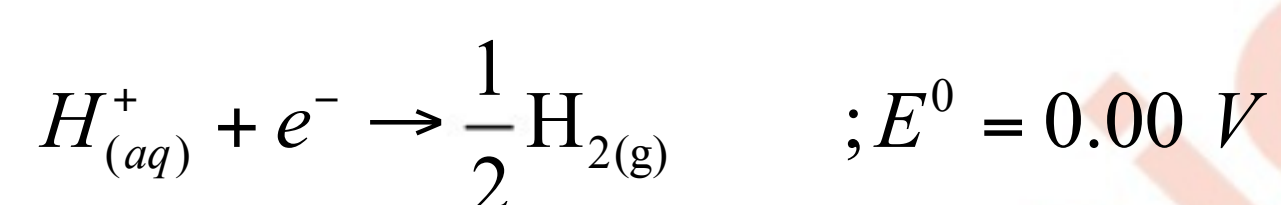
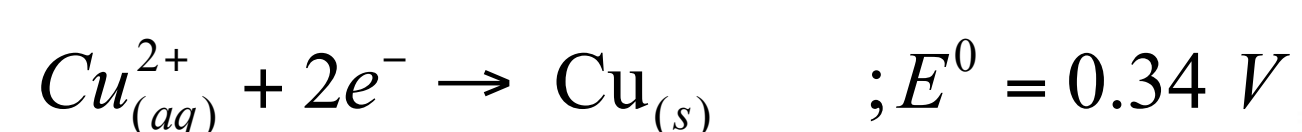


At the anode: following reactions can take place



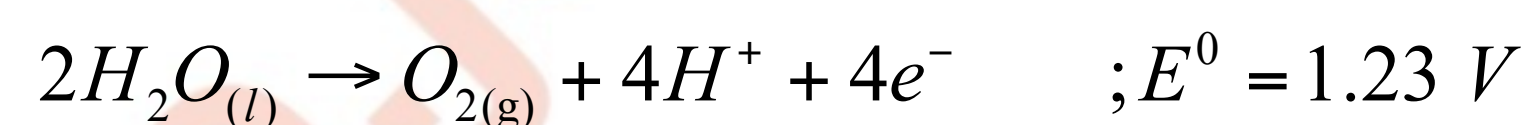
In case of dilute sulphuric acid, first reaction will be preferred & produce O_2 gas. But for concentrated sulphuric acid, second reaction will take place.

iv. At cathode: reduction reactions



As we know that the reaction which has higher E^0 value, it will take place at cathode. Thus, deposition of copper will take place at the cathode.

At anode: following oxidation reactions can take place



The reaction which has lower E^0 value, will take place at anode. Thus, deposition of copper will take place at the cathode. Due to the over-potential of oxygen, Cl^{-} gets oxidized at the anode to produce Cl_2 gas.