# (Chapter 3)(Electrochemistry)

### Question 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

The following is the order in which the given metals displace each other from the solution of their salts.

Mg, Al, Zn, Fe, Cu

### Question 3.2:

Given the standard electrode potentials,

 $K^+/K = -2.93V$ ,  $Ag^+/Ag = 0.80V$ ,

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

 $Mg^{2+}/Mg = -2.37 \text{ V, } Cr^{3+}/Cr = -0.74 \text{V}$ 

Arrange these metals in their increasing order of reducing power.

#### Answer

The lower the reduction potential, the higher is the reducing power. The given standard electrode potentials increase in the order of  $K^+/K < Mg^{2+}/Mg < Cr^{3+}/Cr < Hg^{2+}/Hg < Ag^+/Ag$ .

Hence, the reducing power of the given metals increases in the following order: Ag < Hg < Cr < Mg < K

### Question 3.3:

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

- (i) Which of the electrode is negatively charged?
- (ii) The carriers of the current in the cell.
- (iii) Individual reaction at each electrode.

### Answer

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



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$$Zn_{(s)}\bigg|Zn^{^{2+}}_{\phantom{^{+}}(\mathit{aq})}\bigg|Ag^{^{+}}_{\phantom{^{+}}(\mathit{aq})}\bigg|Ag_{(s)}$$

- (i) Zn electrode (anode) is negatively charged.
- (ii) Ions are carriers of current in the cell and in the external circuit, current will flow from silver to zinc.
- (iii) The reaction taking place at the anode is given by,

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{-}$$

The reaction taking place at the cathode is given by,

$$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$$

### Question 3.4:

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

(i) 
$$2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd$$

(ii) 
$$Fe^{2+}(aq) + Ag^{+}(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$$

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

Answer

(i) 
$$E_{\text{Cr}^{3+}/\text{Cr}}^{\circ} = 0.74 \text{ V}$$

$$E_{Cd^{2+}/Cd}^{\ominus} = -0.40 \text{ V}$$

The galvanic cell of the given reaction is depicted as:

$$\operatorname{Cr}_{(s)} \left| \operatorname{Cr}^{3+}_{(aq)} \left| \operatorname{Cd}^{2+}_{(aq)} \left| \operatorname{Cd}_{(s)} \right| \right|$$

Now, the standard cell potential is

$$E_{\text{cell}}^{\Theta} = E_{\text{R}}^{\Theta} - E_{\text{L}}^{\Theta}$$
  
= -0.40 - (-0.74)  
= +0.34 V

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

In the given equation, n

= 6

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

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

Then, 
$$\Delta_{\rm r} G^{\rm e} = -6 \times 96487 \,{\rm C \, mol^{-1}} \times 0.34 \,{\rm V}$$

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

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

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

Again,

$$\Delta_{\mathbf{r}}G^{\scriptscriptstyle \Theta} = -\mathsf{R}T \ln K$$

$$\Rightarrow \Delta_r G^{\oplus} = -2.303 \text{ R} T \ln K$$

$$\Rightarrow \log K = -\frac{\Delta_{r}G}{2.303 \text{ R}T}$$
$$= \frac{-196.83 \times 10^{3}}{2.303 \times 8.314 \times 298}$$

$$= 34.496$$

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

(ii) 
$$E^{\oplus}_{Fe^{3+}/Fe^{2+}} = 0.77 \text{ V}$$

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

The galvanic cell of the given reaction is depicted as:

$$Fe^{2+}_{(aq)} | Fe^{3+}_{(aq)} | Ag^{+}_{(aq)} | Ag_{(s)}$$

Now, the standard cell potential is

$$E_{\text{cell}}^{\ominus} = E_{\text{R}}^{\ominus} - E_{\text{L}}^{\ominus}$$
  
= 0.80 - 0.77  
= 0.03 V

Here, n = 1.

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

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

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

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

Again, 
$$\Delta_r G^{\oplus} = -2.303 \text{ R} T \ln K$$

$$\Rightarrow \log K = -\frac{\Delta_r G}{2.303 \text{ R}T}$$

$$= \frac{-2894.61}{2.303 \times 8.314 \times 298}$$

= 0.5073

\*K = antilog (0.5073)

= 3.2 (approximately)

### Question 3.5:

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

(i) 
$$Mg(s) \mid Mg^{2+}(0.001M) \mid | Cu^{2+}(0.0001 M) \mid Cu(s)$$

(iv) 
$$Pt(s) | Br_2(I) | Br^-(0.010 M) | H^+(0.030 M) | H_2(g) (1 bar) | Pt(s)$$
.

Answer

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

$$\begin{split} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{\left[\text{Mg}^{2+}\right]}{\left[\text{Cu}^{2+}\right]} \\ &= \left\{0.34 - \left(-2.36\right)\right\} - \frac{0.0591}{2} \log \frac{.001}{.0001} \\ &= 2.7 - \frac{0.0591}{2} \log 10 \end{split}$$

$$= 2.7 - 0.02955$$

- = 2.67 V (approximately)
- (ii) For the given reaction, the Nernst equation can be given as:

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$$\begin{split} E_{\text{cell}} &= E_{\text{cell}}^{\Theta} - \frac{0.0591}{n} \log \frac{\left[\text{Fe}^{2+}\right]}{\left[\text{H}^{+}\right]^{2}} \\ &= \left\{0 - \left(-0.44\right)\right\} - \frac{0.0591}{2} \log \frac{0.001}{1^{2}} \\ &= 0.44 - 0.02955(-3) \end{split}$$

- = 0.52865 V
- = 0.53 V (approximately)

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

$$\begin{split} E_{\text{cell}} &= E_{\text{cell}}^{\oplus} - \frac{0.0591}{n} \log \frac{\left[\text{Sn}^{2+}\right]}{\left[\text{H}^{+}\right]^{2}} \\ &= \left\{0 - \left(-0.14\right)\right\} - \frac{0.0591}{2} \log \frac{0.050}{\left(0.020\right)^{2}} \end{split}$$

- $= 0.14 0.0295 \times log125$
- = 0.14 0.062
- = 0.078 V
- = 0.08 V (approximately)

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

$$\begin{split} E_{\text{cell}} &= E_{\text{cell}}^{\oplus} - \frac{0.0591}{n} \log \frac{1}{\left[\text{Br}^{-}\right]^{2} \left[\text{H}^{+}\right]^{2}} \\ &= \left(0 - 1.09\right) - \frac{0.0591}{2} \log \frac{1}{\left(0.010\right)^{2} \left(0.030\right)^{2}} \\ &= -1.09 - 0.02955 \times \log \frac{1}{0.00000009} \\ &= -1.09 - 0.02955 \times \log \frac{1}{9 \times 10^{-8}} \\ &= -1.09 - 0.02955 \times \log \left(1.11 \times 10^{7}\right) \\ &= -1.09 - 0.02955 \left(0.0453 + 7\right) \\ &= -1.09 - 0.208 \\ &= -1.298 \text{ V} \end{split}$$

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### Question 3.6:

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

$$\begin{split} Z n_{(s)} & \longrightarrow Z n^{2+}_{(aq)} + 2e^- \; ; \; E^\Theta = 0.76 V \\ & A g_2 O_{(s)} + H_2 O_{(l)} + 2e^- \longrightarrow 2 A g_{(s)} + 2 O H^-_{(aq)} \; ; \; E^\Theta = 0.344 \; V \\ \hline & Z n_{(s)} + A g_2 O_{(s)} + H_2 O_{(l)} \longrightarrow Z n^{2+}_{(aq)} + 2 A g_{(s)} + 2 O H^-_{(aq)} \; ; \; E^\Theta = 1.104 \; V \\ & \therefore E^\Theta \\ & \Delta_r G^\Theta \quad \text{and} \quad E^\Theta \text{ for the reaction.} \end{split}$$

Answer

$$= 1.104 V$$

We know that,

$$\Delta_{r}G^{\ominus} = -nFE^{\ominus}$$

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

$$= -213043.296 J$$

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

### Question 3.7:

Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation 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. The inverse of resistivity is called conductivity or specific conductance. It is represented by the symbol $\kappa$ . If  $\rho$  is resistivity, then we can write:

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

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The conductivity of a solution at any given concentration is the conductance (G) of one unit volume of solution kept between two platinum electrodes with the unit area of cross-section and at a distance of unit length.

$$G = \kappa \frac{a}{l} = \kappa \cdot 1 = \kappa$$

(Since a = 1, l = 1)

Conductivity always decreases with a decrease in concentration, both for weak and strong electrolytes. 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.

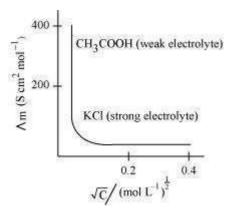
$$\Lambda_m = \kappa \frac{A}{I}$$

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

$$\Lambda_m = \kappa V$$

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  $^{\Lambda_{\rm m}}$  with  $^{\sqrt{c}}$  for strong and weak electrolytes is shown in the following plot:



### Question 3.8:

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The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 Scm<sup>-1</sup>. Calculate its molar conductivity.

Answer Given,  $\kappa$ 

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

= 0.20 M

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

Molar conductivity,

$$=\frac{0.0248\times1000}{0.2}$$

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

### Question 3.9:

The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500  $\Omega$ . What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146  $\times$  10<sup>-3</sup> S cm<sup>-1</sup>.

Answer

Given,

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

Resistance,  $R = 1500 \Omega$ 

 $\stackrel{\leftarrow}{\sim}$  Cell constant =  $\kappa \times R$ 

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

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

### Question 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

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

for all concentrations and draw a plot between  $^{\Lambda_m}$  and c1/2. Find the value

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Calculate 
$$\Lambda_{\scriptscriptstyle m}$$
 of

$$\Lambda_m^0$$

Answer Given,

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

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

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

$$= \frac{1.237 \times 10^{-4} \text{ S cm}^{-1}}{0.001 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{3}}{L}$$

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

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

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

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

$$= \frac{11.85 \times 10^{-4} \text{ S cm}^{-1}}{0.010 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$$

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

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

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

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

$$= \frac{23.15 \times 10^{-4} \text{ S cm}^{-1}}{0.020 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{L}$$

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

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

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

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

$$= \frac{55.53 \times 10^{-4} \text{ S cm}^{-1}}{0.050 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$$

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

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

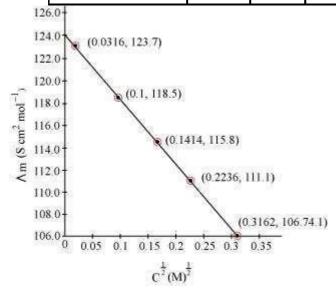
Then,  $\kappa = 106.74 \times 10^{-4} \,\mathrm{S} \,\mathrm{cm}^{-1}$ ,  $c^{1/2} = 0.3162 \,\mathrm{M}^{1/2}$ 

$$\Lambda_{m} = \frac{\kappa}{c}$$

$$= \frac{106.74 \times 10^{-4} \text{ S cm}^{-1}}{0.100 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{3}}{\text{L}}$$

= 106.74 S cm<sup>2</sup> mol<sup>-1</sup> Now, we have the following data:

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



Since the line interrupts  $\Lambda_m$  at 124.0 S cm<sup>2</sup> mol<sup>-1</sup>,  $\Lambda_m^0 = 124.0$  S cm<sup>2</sup> mol<sup>-1</sup>.

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#### Question 3.11:

Conductivity of 0.00241 M acetic acid is  $7.896 \times 10^{-5}$  S cm<sup>-1</sup>. Calculate its molar conductivity and if  $\Lambda_m^0$  for acetic acid is 390.5 S cm<sup>2</sup> mol<sup>-1</sup>, what is its dissociation

Answer

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

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

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

Then, molar conductivity,  $\Lambda_{m} = \frac{\kappa}{c}$ 

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

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

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

$$K_a = \frac{c\alpha^2}{(1-\alpha)}$$

$$\therefore \text{ Dissociation constant,}$$

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

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

### Question 3.12:

How much charge is required for the following reductions:

- (i) 1 mol of  $Al^{3+}$  to Al.
- (ii) 1 mol of Cu<sup>2+</sup> to Cu.

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(iii) 1 mol of 
$$MnO_4^-$$
 to  $Mn^{2+}$ .

Answer

(i) 
$$Al^{3+} + 3e^{-} \longrightarrow Al$$

$$= 3 \times 96487 C$$

= 289461 C

(ii) 
$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$

$$= 2 \times 96487 C$$

(iii) 
$$MnO_4^- \longrightarrow Mn^{2+}$$

i.e., 
$$Mn^{7+} + 5e^- \longrightarrow Mn^{2+}$$

....

Required charge = 5 F

### $= 5 \times 96487 C$

= 482435 C

### Question 3.13:

How much electricity in terms of Faraday is required to produce (i) 20.0 g of Ca from molten CaCl<sub>2</sub>.

(ii) 40.0 g of Al from molten Al<sub>2</sub>O<sub>3</sub>.

Answer

(i) According to the question,

$$Ca^{2+} + 2e^{-1} \longrightarrow Ca$$

Electricity required to produce 40 g of calcium = 2 F

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

(ii) According to the question,

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$$Al^{3+} + 3e^{-} \longrightarrow Al$$
27 g

Electricity required to produce 27 g of Al = 3 F

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

### Question 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<sub>2</sub>O<sub>3</sub>.

Answer

(i) According to the question,

$$H_2O \longrightarrow H_2 + \frac{1}{2}O_2$$

Now, we can write:

$$O^{2-}$$
  $\longrightarrow$   $\frac{1}{2}O_2 + 2e^-$ 

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

- $= 2 \times 96487 C$
- = 192974 C
- (ii) According to the question,

$$Fe^{2+}$$
  $\longrightarrow$   $Fe^{3+}$  +  $e^{-1}$ 

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

### Question 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

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Given,

Current = 5A

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

Charge = current × time

 $= 5 \times 1200$ 

= 6000 C

According to the reaction,

$$Ni^{2+}_{(aq)} + 2e^{-} \longrightarrow Ni_{(s)}$$

$$58.7$$

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

Therefore, nickel deposited by 6000 C =  $\frac{38.71 \times 6000}{2 \times 96487}$  §

= 1.825 g

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

### Question 3.16:

Three electrolytic cells A,B,C containing solutions of ZnSO<sub>4</sub>, AgNO<sub>3</sub> and CuSO<sub>4</sub>, 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

According to the reaction:

$$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$$
  
108 g

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

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

= 1295.43 C

Given,

Current = 1.5 A

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$$\therefore \text{Time} = \frac{1295.43}{1.5} \text{s}$$

= 863.6 s

= 864 s

= 14.40 min

Again,

$$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)}$$

$$63.5 g$$

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

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

= 0.426 g of Cu

$$Zn^{2+}_{(aq)} + 2e^{-} \longrightarrow Zn_{(s)}$$
65.4 g

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

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

= 0.439 q of Zn

### Question 3.17:

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

- (i)  $Fe^{3+}(aq)$  and  $I^{-}(aq)$
- (ii) Ag<sup>+</sup> (aq) and Cu(s)
- (iii)  $Fe^{3+}$  (aq) and  $Br^-$  (aq)
- (iv) Ag(s) and  $Fe^{3+}$  (aq)
- (v)  $Br_2(aq)$  and  $Fe^{2+}(aq)$ .

Answer

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(i) 
$$Fe^{3+}_{(aq)} + e^{-} \longrightarrow Fe^{2+}_{(aq)}$$
]  $\times$  2;  $E^{\circ} = +0.77 \text{ V}$ 

$$\frac{2I^{-}_{(aq)} \longrightarrow I_{2(s)} + 2e^{-}; \qquad E^{\circ} = -0.54 \text{ V}}{2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(s)} ; \qquad E^{\circ} = +0.23 \text{ V}}$$
Since
$$\frac{3+(aq)}{1-(aq)} = 1$$
Since
$$1-(aq) = 1$$
Sinc

(ii) 
$$Ag^{+}_{(\alpha q)} + e^{-} \longrightarrow Ag_{(s)} ] \times 2$$
;  $E^{\circ} = +0.80 \text{ V} \cdot \text{Fe}$ 

$$\frac{Cu_{(s)}}{2Ag^{+}_{(\alpha q)} + Cu_{(s)}} \longrightarrow 2Ag_{(s)} + Cu^{2+}_{(\alpha q)}$$
;  $E^{\circ} = +0.46 \text{ V}$ 

 $E^{o}$  for the overall reaction is positive, the reaction between Ag Since (aq) and Cu(s) is feasible.

(iii) 
$$\operatorname{Fe}^{3+}_{(\alpha q)} + \operatorname{e}^{-} \longrightarrow \operatorname{Fe}^{2+}_{(\alpha q)} \left[ \times 2 \right] \times 2$$
;  $E^{\circ} = +0.77 \text{ V}$   
 $2\operatorname{Br}^{-}_{(\alpha q)} \longrightarrow \operatorname{Br}_{2(l)} + 2\operatorname{e}^{-} : E^{\circ} = -1.09 \text{ V}$   
 $2\operatorname{Fe}^{3+}_{(\alpha q)} + 2\operatorname{Br}^{-}_{(\alpha q)} \longrightarrow 2\operatorname{Fe}^{2+}_{(\alpha q)} \text{ and } \operatorname{Br}_{2(l)} : E^{\circ} = -0.32 \text{ V}$ 

Since  $E^{\circ}$  for the overall reaction is negative, the reaction between Fe  $^{3+}$   $^{-(aq)}$  and Br  $^{(aq)}$  is not feasible.

(iv) 
$$Ag_{(s)} \longrightarrow Ag^{+}_{(aq)} + e^{-}$$
 ;  $E^{o} = -0.80 \text{ V}$   
 $Fe^{3+}_{(aq)} + e^{-} \longrightarrow Fe^{2+}_{(aq)}$  ;  $E^{o} = +0.77 \text{ V}$ 

(iv) 
$$Br_{2(aq)} + 2e^{-} \longrightarrow 2Br_{(aq)}^{-} + 2F^{3+}_{(aq)} \longrightarrow 2Br_{(aq)}^{-} + 2F^{3+}_{(aq)} \longrightarrow E^{0} = -0.77 \text{ V}$$
 en Ag (s) and  $Fe_{3+(aq)} = -0.77 \text{ V}$  is  $Br_{2(aq)} + 2Fe_{(aq)}^{2+} \longrightarrow 2Br_{(aq)}^{-} + 2Fe_{(aq)}^{3+} \longrightarrow 2Br_{(aq)}^{-} + 2Fe_{(aq)}^{3+} \longrightarrow E^{0} = -0.77 \text{ V}$  not feasible.

 $E^{\circ}$  for the overall reaction is positive, the reaction between Br Since  $_{2(aq)}$  and Fe<sub>2+(aq)</sub> is feasible.

**Question 3.18:** 

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Predict the products of electrolysis in each of the following:

- (i) An aqueous solution of AgNO<sub>3</sub> with silver electrodes.
- (ii) An aqueous solution of AgNO<sub>3</sub>with platinum electrodes.
- (iii) A dilute solution of H<sub>2</sub>SO<sub>4</sub>with platinum electrodes.
- (iv) An aqueous solution of CuCl<sub>2</sub> with platinum electrodes.

Answer

### (i) At cathode:

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

$$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$$
;  $E^{o} = 0.80 \text{ V}$   
 $H^{+}_{(aq)} + e^{-} \longrightarrow \frac{1}{2} H_{2(g)}$ ;  $E^{o} = 0.00 \text{ V}$ 

The reaction with a higher value of

 $E^{\circ}$  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.

$$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$$
;  $E^{o} = 0.80 \text{ V}$   
 $H^{+}_{(aq)} + e^{-} \longrightarrow \frac{1}{2} H_{2(g)}$ ;  $E^{o} = 0.00 \text{ V}$ 

The reaction with a higher value of  $E^{\circ}$  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<sub>2</sub>.

### (Chapter 3)(Electrochemistry)

XII

$$OH^- \longrightarrow OH + e^-$$

$$4OH^- \longrightarrow 2H_2O + O_2$$

(iii) At the cathode, the following reduction reaction occurs to produce H2 gas.

$$H^{+}_{(aq)} + e^{-} \longrightarrow \frac{1}{2}H_{2(g)}$$

At the anode, the following processes are possible.

$$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-; E^0 = +1.23V$$
 (i)

$$2SO_{4 (aq)}^{2-} \longrightarrow S_2O_{6 (aq)}^{2-} + 2e^-; E^o = +1.96 V$$
 (ii)

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.

$$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)}$$
;  $E^{0} = 0.34V$ 

$$H^{+}_{(aa)} + e^{-} \longrightarrow \frac{1}{2} H_{2(g)}$$
;  $E^{0} = 0.00 \text{ V}$ 

 $E^{\circ}$  The reaction with a higher value of 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

$$CI_{(aq)}^- \longrightarrow \frac{1}{2}CI_{2(g)} + e^{-1}; E^{\circ} = 1.36 \text{ V}$$

$$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(oq)} + 4e^-$$
;  $E^o = +1.23V$ 

 $E^{\circ}$  is preferred. But due to the

overpotential of oxygen, Cl<sup>-</sup> gets oxidized at the anode to produce Cl<sub>2</sub> gas.