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### (Chapter 3)(Electrochemistry) XII

**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,

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

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

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

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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 $Zn_{(s)} \left| Zn^{2+}_{(aq)} \right\| Ag^{+}_{(aq)} \left| Ag_{(s)} \right|$ 

(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,

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

**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) 
$$E_{Cr^{3+}/Cr}^{\Theta} = 0.74 \text{ V}$$
  
 $E_{Cd^{2+}/Cd}^{\Theta} = -0.40 \text{ V}$ 

The galvanic cell of the given reaction is depicted as:

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

Now, the standard cell potential is

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

In the given equation, n

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F = 96487 C mol<sup>-1</sup>  $E_{\text{cell}}^{\Theta}$  = +0.34 V Then,  ${}^{\Delta_{\mathbf{r}}G^{\Theta}}$ = -6 × 96487 C mol<sup>-1</sup> × 0.34 V = -196833.48 CV mol<sup>-1</sup> = -196833.48 J mol<sup>-1</sup>  $= -196.83 \text{ kJ mol}^{-1}$ Again,  $\Delta_{\rm r}G^{\rm e} = -{\rm R}T\ln K$  $\Rightarrow \Delta_r G^{\ominus} = -2.303 \text{ R}T \ln K$  $\Rightarrow \log K = -\frac{\Delta_r G}{2.303 \text{ RT}}$  $=\frac{-196.83\times10^3}{2.303\times8.314\times298}$ = 34.496K = antilog (34.496) =  $3.13 \times 10^{34}$ (ii)  $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\ominus} = 0.77 \text{ V}$  $E^{\Theta}_{\ Ag^*/Ag} = 0.80 \text{ V}$ 

The galvanic cell of the given reaction is depicted as:

$$\operatorname{Fe}_{(aq)}^{2+} \operatorname{Fe}_{(aq)}^{3+} \operatorname{Ag}_{(aq)}^{+} \operatorname{Ag}_{(s)}^{+} \operatorname{Ag}_{(s)}^{+}$$

Now, the standard cell potential is

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

Here, n = 1.

Then,  $\Delta_r G^{\ominus} = -n F E_{cell}^{\Theta}$ 

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

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= -2894.61 J mol<sup>-1</sup>

= -2.89 kJ mol<sup>-1</sup>

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) | Mg<sup>2+</sup>(0.001M) || Cu<sup>2+</sup>(0.0001 M) | Cu(s)

(ii) Fe(s) | Fe<sup>2+</sup>(0.001M) || H<sup>+</sup>(1M)|H<sub>2</sub>(g)(1bar) | Pt(s) (iii)

 $Sn(s) | Sn^{2+}(0.050 \text{ M}) || H^{+}(0.020 \text{ M}) | H_2(g) (1 \text{ bar}) | Pt(s)$ 

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

Answer

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

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

= 2.7 - 0.02955

= 2.67 V (approximately)

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



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

= 0.52865 V

= 0.53 V (approximately)

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

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

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

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

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

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**Question 3.6:** 

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

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{-}; E^{\Theta} = 0.76V$ $Ag_2O_{(s)} + H_2O_{(l)} + 2e^{-} \longrightarrow 2Ag_{(s)} + 2OH^{-}_{(aq)}; E^{\Theta} = 0.344 V$ $Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^{-}_{(aq)}; E^{\Theta} = 1.104 V$	$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^{-}(aq)$
$\therefore E^{\ominus}$	Determine
$\Delta_r G^{\odot}$ and $E^{\odot}$ for the reaction.	
Answer	

= 1.104 V

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

 $= -2 \times 96487 \times 1.04$ 

= -213.04 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.

$$G = \kappa \frac{a}{l} = \kappa \cdot 1 = \kappa$$
 i.e.,

(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.

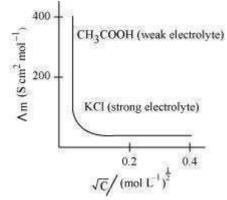
$$\Lambda_m = \kappa \frac{A}{l}$$

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

$$\therefore \Lambda_m = \kappa V$$

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  $\Lambda_m$  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 S cm<sup>-1</sup> c = 0.20 M  $\therefore$  Molar conductivity,  $\Lambda_m = \frac{\kappa \times 1000}{c}$  $= \frac{0.0248 \times 1000}{0.2}$ 

= 124 Scm<sup>2</sup>mol<sup>-1</sup>

#### **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 × 10<sup>-3</sup> S cm<sup>-1</sup>.

Answer Given, Conductivity,  $\kappa = 0.146 \times 10^{-3} \text{ S cm}^{-1}$ Resistance,  $R = 1500 \Omega$   $\therefore$  Cell constant =  $\kappa \times R$ = 0.146 × 10<sup>-3</sup> × 1500 = 0.219 cm<sup>-1</sup>

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

for all concentrations and draw a plot between  $\Lambda_m$  and c½. Find the value



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Calculate  $\Lambda_{_{\!M\!\!}}$  of  $\Lambda_m^0$ Answer Given,  $\kappa = 1.237 \times 10^{-2} \text{ S m}^{-1}, c = 0.001 \text{ M}$ Then,  $\kappa = 1.237 \times 10^{-4} \text{ S cm}^{-1}$ ,  $c\frac{1}{2} = 0.0316 \text{ M}^{1/2}$  $\therefore \Lambda_m = \frac{\kappa}{c}$  $=\frac{1.237\times10^{-4} \text{ S cm}^{-1}}{0.001 \text{ mol } \text{L}^{-1}}\times\frac{1000 \text{ cm}^{3}}{\text{L}}$ = 123.7 S cm<sup>2</sup> mol<sup>-1</sup> Given,  $\kappa = 11.85 \times 10^{-2} \text{ S m}^{-1}$ , c = 0.010M Then,  $\kappa$  = 11.85  $\times$  10  $^{-4}$  S cm  $^{-1}$ , c1/2 = 0.1  $M^{1/2}$  $\Lambda_m = \frac{\kappa}{c}$  $=\frac{11.85\times10^{-4} \text{ S cm}^{-1}}{0.010 \text{ mol } \text{L}^{-1}}\times\frac{1000 \text{ cm}^{3}}{\text{L}}$ = 118.5 S cm<sup>2</sup> mol<sup>-1</sup> Given,  $\kappa = 23.15 \times 10^{-2} \text{ S m}^{-1}, c = 0.020 \text{ M}$ Then,  $\kappa = 23.15 \times 10^{-4} \text{ S cm}^{-1}$ ,  $c^{1/2} = 0.1414 \text{ M}^{1/2}$  $\Lambda_m = \frac{\kappa}{c}$  $=\frac{23.15\times10^{-4} \text{ S cm}^{-1}}{0.020 \text{ mol } \text{L}^{-1}}\times\frac{1000 \text{ cm}^{3}}{\text{L}}$  $= 115.8 \text{ S cm}^2 \text{ mol}^{-1} \text{ Given},$  $\kappa = 55.53 \times 10^{-2} \text{ S m}^{-1}, \text{ c} = 0.050 \text{ M}$ Then,  $\kappa = 55.53 \times 10^{-4} \text{ S cm}^{-1}$ ,  $c^{1/2} = 0.2236 \text{ M}^{1/2}$ 



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

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

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

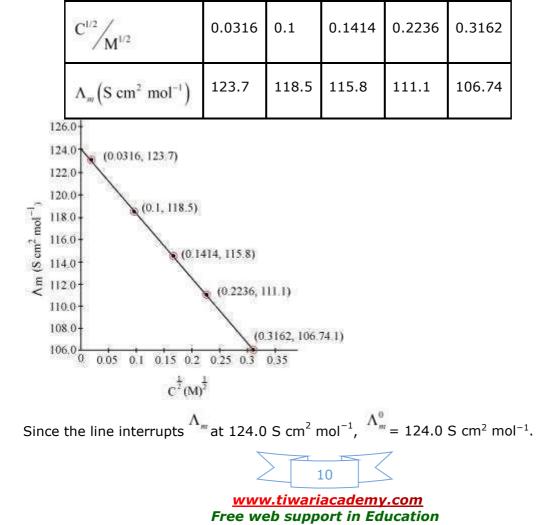
$$\kappa = 106.74 \times 10^{-2} \text{ S m}^{-1}, \text{ c} = 0.100 \text{ M}$$
Then,  $\kappa = 106.74 \times 10^{-4} \text{ S cm}^{-1}, \text{ c}^{1/2} = 0.3162 \text{ M}^{1/2}$ 

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

 $=\frac{106.74\times10^{-4} \text{ S cm}^{-1}}{0.100 \text{ mol } \text{L}^{-1}}\times\frac{1000 \text{ cm}^{3}}{\text{L}}$ 

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

have the following data:



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**Question 3.11:** 

Conductivity of 0.00241 M acetic acid is 7.896 × 10<sup>-5</sup> 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 constant?

Answer

Given,  $\kappa$  = 7.896 × 10<sup>-5</sup> S m<sup>-1</sup> c

= 0.00241 mol L<sup>-1</sup>

 $\Lambda_{m} = \frac{\kappa}{c}$ Then, molar conductivity,  $= \frac{7.896 \times 10^{-5} \text{ S cm}^{-1}}{0.00241 \text{ mol } \text{L}^{-1}} \times \frac{1000 \text{ cm}^{3}}{\text{L}}$   $= 32.765 \text{ cm}^{2} \text{ mol}^{-1}$   $\Lambda_{m}^{0} = 390.5 \text{ S cm}^{2} \text{ mol}^{-1}$ 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

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

$$\stackrel{\text{...}}{=} \frac{(0.00241 \text{ mol } \text{L}^{-1})(0.084)^2}{(1 - 0.084)}$$
$$= 1.86 \times 10^{-5} \text{ mol } \text{L}^{-1}$$

Question 3.12:

How much charge is required for the following reductions:

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

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(iii) 1 mol of  $MnO_4^-$  to  $Mn^{2+}$ . Answer (i)  $Al^{3+} + 3e^{-} \longrightarrow Al$  $\therefore$  Required charge = 3 F = 3 × 96487 C = 289461 C (ii)  $Cu^{2+} + 2e^{-} \longrightarrow Cu$  $\therefore$  Required charge = 2 F = 2 × 96487 C = 192974 C (iii)  $MnO_4^- \longrightarrow Mn^{2+}$ i.e.,  $Mn^{7+} + 5e^- \longrightarrow Mn^{2+}$ ... Required charge = 5 F= 5 × 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  $Al_2O_3$ .

Answer

(i) According to the question,

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

40 g

Electricity required to produce 40 g of calcium = 2 F

 $=\frac{2\times 20}{40}$  F

Therefore, electricity required to produce 20 g of calcium

= 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  $Fe_2O_3$ .

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 × 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 × 60 = 1200 s  $\therefore$  Charge = current × time = 5 × 1200 = 6000 C According to the reaction, Ni<sup>2+</sup><sub>(aq)</sub> + 2e<sup>-</sup>  $\longrightarrow$  Ni<sub>(s)</sub> 58.7 g Nickel deposited by 2 × 96487 C = 58.71 g Therefore, nickel deposited by 6000 C  $= \frac{58.71 \times 6000}{2 \times 96487}$ g = 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:

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

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

Therefore, 1.45 g of Ag is deposited by =  $\frac{96487 \times 1.45}{108}$  C = 1295.43 C Given, Current = 1.5 A

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 $=\frac{1295.43}{1.5}$ s - Time = 863.6 s = 864 s = 14.40 min Again,  $\operatorname{Cu}^{2+}_{(aq)} + 2e^{-} \longrightarrow \operatorname{Cu}_{(s)}$ 63.5 g i.e.,  $2 \times 96487$  C of charge deposit = 63.5 g of Cu  $=\frac{63.5\times1295.43}{2\times96487}$ g Therefore, 1295.43 C of charge will deposit = 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  $=\frac{65.4\times1295.43}{2\times96487}$ g Therefore, 1295.43 C of charge will deposit = 0.439 g 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)  $\operatorname{Fe}_{(aq)}^{3+} + e^{-} \longrightarrow \operatorname{Fe}_{(aq)}^{2+} ] \times 2;$   $E^{\circ} = +0.77 \text{ V}$  $\frac{2I_{(aq)}^{-} \longrightarrow I_{2(s)} + 2e^{-};}{2\operatorname{Fe}_{(aq)}^{3+} + 2I_{(aq)}^{-} \longrightarrow 2\operatorname{Fe}_{(aq)}^{2+} + I_{2(s)}^{-};}$   $E^{\circ} = +0.23 \text{ V}$   $\frac{1}{I_{(aq)}^{-} \operatorname{Since}_{(aq)}^{-} - 2\operatorname{Fe}_{(aq)}^{2+} + I_{2(s)}^{-};}$   $E^{\circ} = +0.23 \text{ V}$   $I_{(aq)}^{-} \operatorname{Since}_{(aq)}^{-} \operatorname{Since}_{(aq)}^{-} - 2\operatorname{Fe}_{(aq)}^{2+} + I_{2(s)}^{-};}$   $E^{\circ} = +0.23 \text{ V}$   $I_{(aq)}^{-} \operatorname{Since}_{(aq)}^{-} \operatorname{Since}_{(aq)}^{-} - 2\operatorname{Fe}_{(aq)}^{2+} + I_{2(s)}^{-};}$   $E^{\circ} = +0.23 \text{ V}$
- (ii)  $\operatorname{Ag}^{+}_{(aq)} + e^{-} \longrightarrow \operatorname{Ag}_{(s)} ] \times 2 ; E^{\circ} = +0.80 \text{ V } i \text{ Fe}$  $\frac{\operatorname{Cu}_{(s)} \longrightarrow \operatorname{Cu}^{2+}_{(aq)} + 2e^{-} ; E^{\circ} = -0.34 \text{ V}}{2\operatorname{Ag}^{+}_{(aq)} + \operatorname{Cu}_{(s)} \longrightarrow 2\operatorname{Ag}_{(s)} + \operatorname{Cu}^{2+}_{(aq)} ; E^{\circ} = +0.46 \text{ V}}$

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

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

$$\frac{2\operatorname{Br}_{(aq)}^{-} \longrightarrow \operatorname{Br}_{2(l)}^{-} + 2e^{-} ; E^{\circ} = -1.09 \text{ V}}{2\operatorname{Fe}_{(aq)}^{3+} + 2\operatorname{Br}_{(aq)}^{-} \longrightarrow 2\operatorname{Fe}_{(aq)}^{2+} \text{ and } \operatorname{Br}_{2(l)}^{-} ; E^{\circ} = -0.32 \text{ V}}$$

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

(iv) 
$$\operatorname{Ag}_{(s)} \longrightarrow \operatorname{Ag}_{(aq)}^{+} + e^{-}$$
;  $E^{\circ} = -0.80 \text{ V}$   
 $Fe^{3+}_{(aq)} + e^{-} \longrightarrow Fe^{2+}_{(aq)}$ ;  $E^{\circ} = +0.77 \text{ V}$   
(iv)  $\operatorname{Br}_{2(aq)}^{A} + 2e^{-} \longrightarrow 2Br_{(aq)}^{+} + Ee^{2+} + Ee^{2+} + Ee^{-} - 0.02 \text{ V}$   
 $\frac{Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^{-} \xrightarrow{} 2Br_{(aq)}^{-} + 2Fe^{-} + 1.09 \text{ V}$   
 $\frac{Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^{-} \xrightarrow{} 2Br_{(aq)}^{-} + 2Fe^{3+}_{(aq)}$ ;  $E^{\circ} = -0.77 \text{ V}$  en Ag (s) and Fe\_{3+(aq)} is  
 $\operatorname{Br}_{2(aq)} + 2Fe^{2+}_{(aq)} \longrightarrow 2Br_{(aq)}^{-} + 2Fe^{3+}_{(aq)}$ ;  $E^{\circ} = +0.32 \text{ V}$  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  $H_2SO_4$  with platinum electrodes.

(iv) An aqueous solution of  $\mbox{CuCl}_2$  with platinum electrodes.

Answer

(i) At cathode:

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

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

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<sup>+</sup>.

#### (ii) At cathode:

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

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

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<sup>-</sup> or  $NO_{3}^{-}$  ions can be oxidized at the anode. But OH<sup>-</sup> ions having a lower discharge potential and get preference and decompose to liberate O<sub>2</sub>.



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

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

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

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

At the anode, the following processes are possible.

$$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-; E^\circ = +1.23V$$
(i)  
$$2SO_4^{2-}_{(aq)} \longrightarrow S_2O_6^{2-}_{(aq)} + 2e^-; E^\circ = +1.96 V$$
(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.

$$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)} ; E^{\circ} = 0.34V$$
  
$$H^{+}_{(aq)} + e^{-} \longrightarrow \frac{1}{2}H_{2(g)} ; E^{\circ} = 0.00 V$$

 $E^{\circ}$  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  $CI^{-}_{(aq)} \longrightarrow \frac{1}{2}CI_{2(g)} + e^{-1}$ ;  $E^{\circ} = 1.36$  V  $2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-}$ ;  $E^{\circ} = +1.23$ V

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

overpotential of oxygen,  $CI^-$  gets oxidized at the anode to produce  $CI_2$  gas.

