

## Class 12 Chemistry

### NCERT Solutions for Chapter 3 – Electrochemistry

#### Exercises

**3.1. Arrange the following metals in the order in which they displace each other from their salts.**

Al, Cu, Fe, Mg and Zn

**Sol:** Mg, Al, Zn, Fe, Cu.

**3.2. Given the standard electrode potentials,  $K^+/K = -2.93$  V,  $Ag^+/Ag = 0.80$  V,  $Hg^{2+}/Hg = 0.79$  V,  $Mg^{2+}/Mg = -2.37$  V,  $Cr^{3+}/Cr = 0.74$  V.**

**Arrange these metals in their increasing order of reducing power.**

**Sol:** Higher the oxidation potential more easily it is oxidized and hence greater is the reducing power. Thus, increasing order of reducing power will be  $Ag < Hg < Cr < Mg < K$ .

**3.3. Depict the galvanic cell in which the reaction**

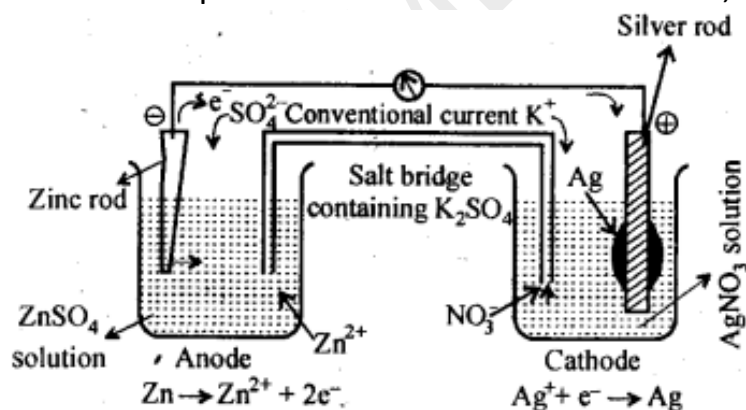
$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$  takes place. Further show:

(i) Which of the electrode is negatively charged?

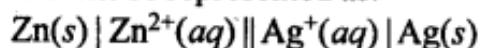
(ii) The carriers of the current in the cell.

(iii) Individual reaction at each electrode.

**Sol.** The set-up will be similar to as shown below,



The cell will be represented as:



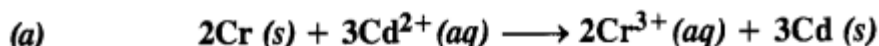
(i) Anode, i. e, zinc electrode will be negatively charged.

(ii) The current will flow from silver to copper in the external circuit.

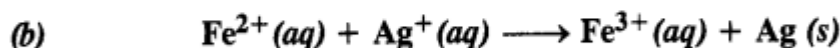
(iii) At anode:  $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

At cathode:  $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$

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



Given  $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$  ;  $E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.40 \text{ V}$



Given  $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}$  ;  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$

Also calculate  $\Delta G^\circ$  and equilibrium constant for the reaction. (C.B.S.E. Outside Delhi 2008)

Sol:

(a) Calculation of  $E^\circ_{\text{cell}}$ ,

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.40 - (-0.74) = +0.34 \text{ V}$$

Calculation of  $\Delta G^\circ$ ,

$$\begin{aligned} \Delta G^\circ &= -nF E^\circ_{\text{cell}} = -(6 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.34 \text{ V}) \\ &= -196860 \text{ CV} = -196860 \text{ J} = -196.86 \text{ kJ} \end{aligned}$$

Calculation of Equilibrium Constant ( $K_c$ )

$$\Delta G^\circ = -2.303 RT \log K_c$$

$$\log K_c = \frac{(-)\Delta G^\circ}{2.303 RT} = (-) \frac{(-)196860}{2.303 \times 8.314 \times 298} = 34.501$$

$$K_c = \text{Antilog}(34.501) = 3.17 \times 10^{34}$$

(b) Calculation of  $E^\circ_{\text{cell}}$ ,

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = (0.80 - 0.77) = 0.03 \text{ V}$$

Calculation of  $\Delta G^\circ$ ,

$$\begin{aligned} \Delta G^\circ &= -nF E^\circ_{\text{cell}} = -(1 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.03 \text{ V}) \\ &= -2895 \text{ CV} = -2895 \text{ J} = -2.895 \text{ kJ} \end{aligned}$$

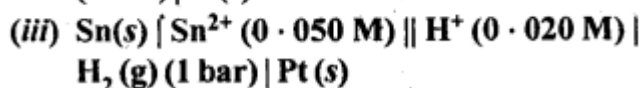
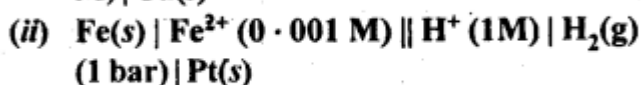
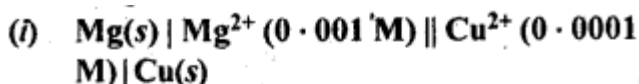
Calculation of Equilibrium Constant ( $K_c$ )

$$\Delta G^\circ = -2.303 RT \log K_c$$

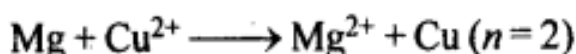
$$\log K_c = (-) \frac{(-)\Delta G^\circ}{2.303 RT} = (-) \frac{(-)2895}{2.303 \times 8.314 \times 298} = 0.5074$$

$$K_c = \text{Antilog}(0.5074) = 3.22$$

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



(i) Cell reaction:



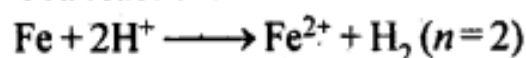
Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\therefore E_{\text{cell}} = 0.34 - (-2.37) - \frac{0.0591}{2} \log \frac{10^{-3}}{10^{-4}}$$

$$= 2.71 - 0.02955 = 2.68 \text{ V.}$$

(ii) Cell reaction:



Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^{+}]^2}$$

$$\therefore E_{\text{cell}} = 0 - (-0.44) - \frac{0.0591}{2} \log \frac{10^{-3}}{(1)^2}$$

$$= 0.44 - \frac{0.0591}{2} \times (-3)$$

$$= 0.44 + 0.0887 = 0.5287 \text{ V.}$$

Sol:

(iv)  $\text{Pt}(s) | \text{Br}_2(l) | \text{Br}^{-} (0.010 \text{ M}) || \text{H}^{+} (0.030 \text{ M}) | \text{H}_2(g) (1 \text{ bar}) | \text{Pt}(s)$

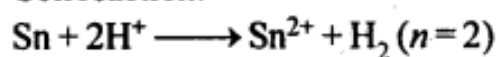
$$\text{Given } E_{\text{Mg}^{2+}, \text{Mg}}^{\circ} = -2.37 \text{ V,}$$

$$E_{\text{Cu}^{2+}, \text{Cu}}^{\circ} = +0.34 \text{ V, } E_{\text{Fe}^{2+}, \text{Fe}}^{\circ} = -0.44 \text{ V.}$$

$$E_{\text{Sn}^{2+}/\text{Sn}}^{\circ} = -0.14 \text{ V}$$

$$E_{1/2\text{Br}_2/\text{Br}^{-}}^{\circ} = +1.08 \text{ V}$$

(iii) Cell reaction:

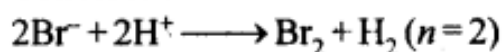


Nernst equation :

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2}$$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{0.05}{(0.02)^2} \\ &= 0 - (-0.14) - \frac{0.0591}{2} \log \frac{0.05}{(0.02)^2} \\ &= 0.14 - \frac{0.0591}{2} \log 125 \\ &= 0.14 - \frac{0.0591}{2} (2.0969) = 0.078 \text{ V.} \end{aligned}$$

(iv) Cell reaction:

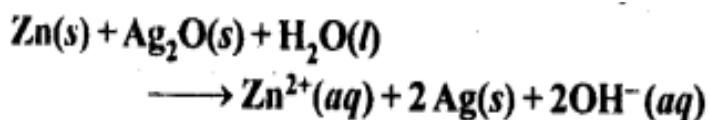


Nernst equation :

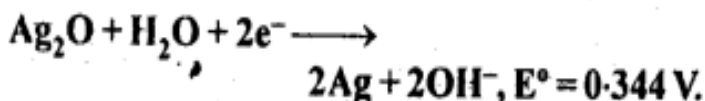
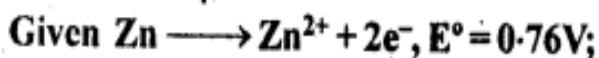
$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{1}{[\text{Br}^-]^2 [\text{H}^+]^2} \\ &= (0 - 1.08) - \frac{0.0591}{2} \log \frac{1}{(0.01)^2 (0.03)^2} \\ &= -1.08 - \frac{0.0591}{2} \log (1.111 \times 10^7) \\ &= -1.08 - \frac{0.0591}{2} (7.0457) \\ &= -1.08 - 0.208 = -1.288 \text{ V.} \end{aligned}$$

Thus, oxidation will occur at the hydrogen electrode and reduction will occur on  $\text{Br}_2$  electrode.

**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.



Sol:

Zn is oxidized and  $\text{Ag}_2\text{O}$  is reduced.

$$E_{\text{cell}}^\ominus = E_{\text{Ag}_2\text{O, Ag (reduction)}}^\ominus - E_{\text{Zn/Zn}^{2+} \text{ (oxidation)}}^\ominus \\ = 0.344 + 0.76 = 1.104\text{V}$$

$$\Delta G = -nFE_{\text{cell}}^\ominus = -2 \times 96500 \times 1.104\text{J} \\ = -2.13 \times 10^5\text{J}.$$

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

**Sol:** The reciprocal of resistivity is known as specific conductance or simply conductivity. It is denoted by  $\kappa$  (kappa). Thus, if  $\kappa$  is the specific conductance and  $G$  is the conductance of the solution, then

$$R = \frac{1}{G} \text{ and } \rho = \frac{1}{\kappa} \quad \therefore \frac{1}{G} = \frac{1}{\kappa} \times \frac{l}{A}, \quad \kappa = G \times \frac{l}{A}$$

Now, if  $l = 1\text{ cm}$  and  $A = 1\text{ sq.cm}$ , then  $\kappa = G$ .

Hence, conductivity of a solution is defined as the conductance of a solution of  $1\text{ cm}$  length and having  $1\text{ sq. cm}$  as the area of cross-section. Alternatively, it may be defined as conductance of one centimetre cube of the solution of the electrolyte.

Molar conductivity of a solution at a dilution  $V$  is the conductance of all the ions produced from  $1\text{ mole}$  of the electrolyte dissolved in  $V\text{ cm}^3$  of the solution when the electrodes are  $1\text{ cm}$  apart and the area of the electrodes is so large that the whole of the solution is contained between them. It is represented by  $\Delta_m$ .

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

Since  $l = 1 \text{ cm}$  and  $A = V$  (volume containing 1 mole of electrolyte)

$$\Lambda_m = \kappa V$$

Variation of conductivity and molar conductivity with concentration:

Conductivity always decreases with decrease in concentration, for both weak and strong electrolytes. This is because the number of ions per unit volume that carry the current in a solution decreases on dilution.

Molar conductivity increases with decrease in concentration. This is because that total volume,  $V$ , of solution containing one mole of electrolyte also increases. It has been found that decrease in  $\kappa$  on dilution of a solution is more than compensated by increase in its volume.

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

Sol:

$$\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{0.0248 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.20 \text{ mol L}^{-1}}$$

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

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

Sol:

$$\text{Cell constant} = \frac{\text{Conductivity}}{\text{Conductance}}$$

$$= \text{Conductivity} \times \text{Resistance}$$

$$= 0.146 \times 10^{-3} \text{ S cm}^{-1} \times 1500 \Omega$$

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

**3.10. The conductivity of NaCl at 298 K has been determined at different concentrations and the results are given below:**

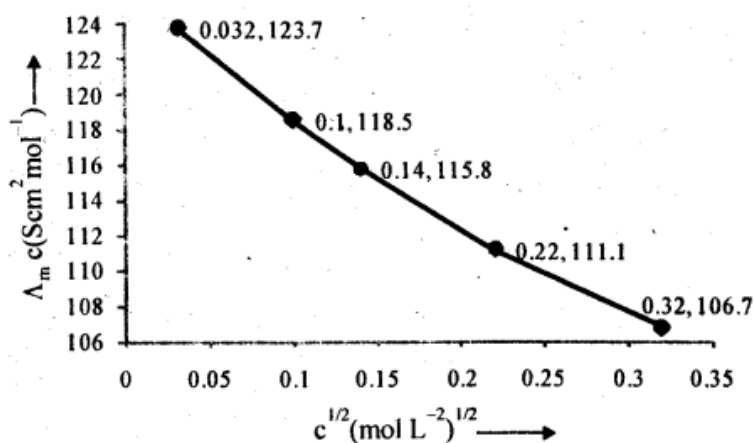
Concentration/M	0.001	0.010	0.020	0.050	0.100
$10^2 \times \kappa / \text{S m}^{-1}$	1.237	11.85	23.15	55.53	106.74

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

Sol:

$$\frac{1 \text{ S cm}^{-1}}{100 \text{ S m}^{-1}} = 1 \text{ (unit conversion factor)}$$

Concentration (M)	$\kappa$ (S m <sup>-1</sup> )	$\kappa$ (S cm <sup>-1</sup> )	$\Lambda_m = \frac{1000 \times \kappa}{\text{Molarity}}$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$c^{1/2}$ (M <sup>1/2</sup> )
10 <sup>-3</sup>	1.237 × 10 <sup>-2</sup>	1.237 × 10 <sup>-4</sup>	$\frac{1000 \times 1.237 \times 10^{-4}}{10^{-3}} = 123.7$	0.0316
10 <sup>-2</sup>	11.85 × 10 <sup>-2</sup>	11.85 × 10 <sup>-4</sup>	$\frac{1000 \times 11.85 \times 10^{-4}}{10^{-2}} = 118.5$	0.100
2 × 10 <sup>-2</sup>	23.15 × 10 <sup>-2</sup>	23.15 × 10 <sup>-4</sup>	$\frac{1000 \times 23.15 \times 10^{-4}}{2 \times 10^{-2}} = 115.8$	0.141
5 × 10 <sup>-2</sup>	55.53 × 10 <sup>-2</sup>	55.53 × 10 <sup>-4</sup>	$\frac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}} = 111.1$	0.224
10 <sup>-1</sup>	106.74 × 10 <sup>-2</sup>	106.74 × 10 <sup>-4</sup>	$\frac{1000 \times 106.74 \times 10^{-4}}{10^{-1}} = 106.7$	0.316



$\Lambda^\circ$  = Intercept on  $\Lambda_m$  axis = 124.0 S cm<sup>2</sup> mol<sup>-1</sup>, which is obtained by extrapolation to zero concentration.

3.11. Conductivity of 0.00241 M acetic acid is  $7.896 \times 10^{-5}$  S cm<sup>-1</sup>. Calculate its molar conductivity. If  $\Lambda_{m0}$ , for acetic acid is 390.5 S cm<sup>2</sup> mol<sup>-1</sup>, what is its dissociation constant?

Sol:

$$\begin{aligned}\Lambda_m^c &= \frac{\kappa \times 1000}{\text{Molarity}} \\ &= \frac{(7.896 \times 10^{-5} \text{ S cm}^{-1}) \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.00241 \text{ mol L}^{-1}} \\ &= 32.76 \text{ S cm}^2 \text{ mol}^{-1} \\ \alpha &= \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{32.76}{390.5} = 8.4 \times 10^{-2} \\ K_a &= \frac{C\alpha^2}{1-\alpha} = \frac{0.0024 \times (8.4 \times 10^{-2})^2}{1-0.084} = 1.86 \times 10^{-5}.\end{aligned}$$

**3.12. How much charge is required for the following reductions:**

(i) 1 mol of  $\text{Al}^{3+}$  to Al?

(ii) 1 mol of  $\text{Cu}^{2+}$  to Cu ?

(iii) 1 mol of  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$ ?

Sol: (i) The electrode reaction is  $\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$

$\therefore$  Quantity of charge required for reduction of 1 mol of  $\text{Al}^{3+} = 3F = 3 \times 96500 \text{ C} = 289500 \text{ C}$ .

(ii) The electrode reaction is  $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$

$\therefore$  Quantity of charge required for reduction of 1 mol of  $\text{Cu}^{2+} = 2F = 2 \times 96500 = 193000 \text{ C}$ .

(iii) The electrode reaction is  $\text{MnO}_4^- \longrightarrow \text{Mn}^{2+}$ .

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

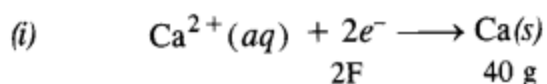
$\therefore$  Quantity of charge required =  $5F$   
 $= 5 \times 96500 \text{ C} = 482500 \text{ C}$ .

**3.13. How much electricity in terms of Faraday is required to produce :**

(i) 20.0 g of Ca from molten  $\text{CaCl}_2$

(ii) 40.0 g of Al from molten  $\text{Al}_2\text{O}_3$  ?

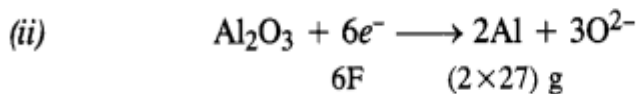
Sol:





To produce 40 g of  $\text{CaCl}_2$ , charge needed = 2F

To produce 20 g of  $\text{CaCl}_2$ , charge needed = 1F



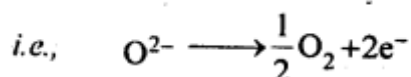
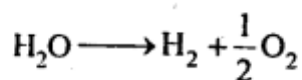
To produce 54 g of Al, charge needed = 6F

To produce 40 g of Al, charge needed =  $\frac{(40 \text{ g})}{(54 \text{ g})} \times (6F) = 4.44F$ .

3.14. How much electricity is required in coulomb for the oxidation of (i) 1 mol of  $\text{H}_2\text{O}$  to  $\text{O}_2$  (ii) 1 mol of  $\text{FeO}$  to  $\text{Fe}_2\text{O}_3$

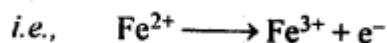
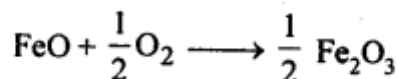
Sol:

(i) The electrode reaction for 1 mol of  $\text{H}_2\text{O}$  is



$\therefore$  Quantity of electricity required  
= 2F =  $2 \times 96500 \text{ C} = 193000 \text{ C}$ .

(ii) The electrode reaction for 1 mol of  $\text{FeO}$  is

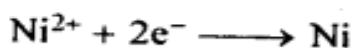


$\therefore$  Quantity of electricity required = 1F = 96500 C

3.15. A solution of  $\text{Ni}(\text{NO}_3)_2$  is electrolyzed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Sol:

Quantity of electricity passed  
= (5A)  $\times$  (20  $\times$  60 sec.) = 6000C



Thus, 2F, i.e.,  $2 \times 96500\text{C}$  of charge deposit

= 1 mole of Ni = 58.7 g

$\therefore$  6000 C of charge will deposit

$$= \frac{58.7 \times 6000}{2 \times 96500} = 1.825 \text{ g of Ni.}$$

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 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?

Sol:

Given:  $I = 1.5 \text{ A}$ ,  $W = 1.45 \text{ g of Ag}$ ,  $t = ?$ ,  $E = 108$ ,  $n = 1$

Using Faraday's 1st law of electrolysis  $W = ZIt$

$$\text{or, } W = \frac{E}{nF} It$$

$$\text{or, } t = \frac{1.45 \times 96500}{1.5 \times 108} = 863.73 \text{ seconds.}$$

Now for Cu,  $W_1 = 1.45 \text{ g of Ag}$ ,  $E_1 = 108$ ,  $W_2 = ?$ ,  $E_2 = 31.75$

From Faraday's 2nd law of electrolysis  $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

$$\frac{1.45}{W_2} = \frac{108}{31.75} \therefore W_2 = \frac{1.45 \times 31.75}{108}$$

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

Similarly, for Zn,  $W_1 = 1.45 \text{ g of Ag}$ ,  $E_1 = 108$ ,  $W_2 = ?$ ,  $E_2 = 32.65$

Using formula,  $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

$$\frac{1.45}{W_2} = \frac{108}{32.65}$$

$$\therefore W_2 = \frac{1.45 \times 32.65}{108} = 0.438 \text{ of Zn.}$$

3.17. Using the standard electrode potentials given in the table, predict if the reaction between the following is feasible.

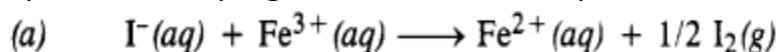
- (a)  $Fe^{3+}(aq)$  and  $I^{-}(aq)$
- (b)  $Ag^{+}(aq)$  and  $Cu(s)$
- (c)  $Fe^{3+}(aq)$  and  $Br^{-}(aq)$

**(d) Ag(s) and Fe<sup>3+</sup>(aq)**

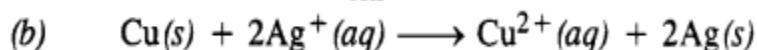
**(e) Br<sub>2</sub>(aq) and Fe<sup>2+</sup>(aq).**

**Sol:**

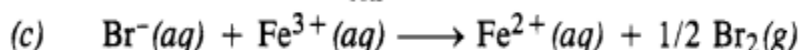
A particular reaction can be feasible if e.m.f. of the cell based on the E° values is positive. Keeping this in mind, let us predict the feasibility of the reactions.



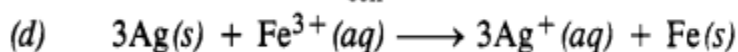
$$E_{\text{cell}}^{\circ} = 0.77 - 0.54 = \mathbf{0.23 \text{ V}} \quad (\text{feasible})$$



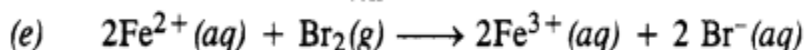
$$E_{\text{cell}}^{\circ} = (0.80 - 0.34) = \mathbf{0.46 \text{ V}} \quad (\text{feasible})$$



$$E_{\text{cell}}^{\circ} = 0.77 - (1.08) = \mathbf{-0.31 \text{ V}} \quad (\text{not feasible})$$



$$E_{\text{cell}}^{\circ} = (0.77 - 0.80) = \mathbf{-0.03 \text{ V}} \quad (\text{not feasible})$$



$$E_{\text{cell}}^{\circ} = 1.08 - 0.77 = \mathbf{0.31 \text{ V}} \quad (\text{feasible})$$

**3.18. Predict the products of electrolysis in each of the following.**

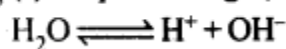
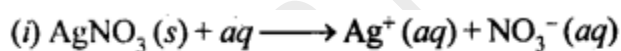
**(i) An aqueous solution of AgNO<sub>3</sub> with silver electrodes.**

**(ii) An aqueous solution of AgNO<sub>3</sub> with platinum electrodes.**

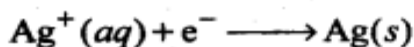
**(iii) A dilute solution of H<sub>2</sub>SO<sub>4</sub> with platinum electrodes.**

**(iv) An aqueous solution of CuCl<sub>2</sub> with platinum electrodes.**

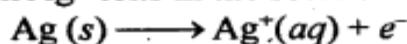
**Sol:**



At cathode:  $\text{Ag}^+$  ions have lower discharge potential than  $\text{H}^+$  ions. Hence,  $\text{Ag}^+$  ions will be deposited as Ag in preference to  $\text{H}^+$  ions:

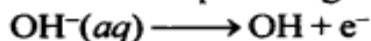


At anode: As Ag anode is attacked by  $\text{NO}_3^-$  ions, Ag of the anode will dissolve to form  $\text{Ag}^+$  ions in the solution.

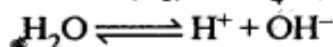


(ii) At cathode:  $\text{Ag}^+$  ions have lower discharge potential than  $\text{H}^+$  ions. Hence,  $\text{Ag}^+$  ions will be deposited as Ag in preference to  $\text{H}^+$  ions.

At anode: As anode is not attackable, out of  $\text{OH}^-$  and  $\text{NO}_3^-$  ions,  $\text{OH}^-$  ions have lower discharge potential. Hence,  $\text{OH}^-$  ions will be discharged in preference to  $\text{NO}_3^-$  ions, which then decompose to give out  $\text{O}_2$ .



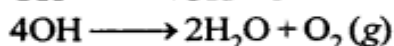
(iii)  $\text{H}_2\text{SO}_4(aq) \longrightarrow 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq)$



At cathode:  $\text{H}^+ + e^- \longrightarrow \text{H}$ ,

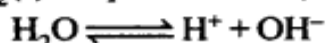


At Anode:  $\text{OH}^- \longrightarrow \text{OH} + e^-$

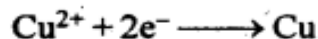


Thus,  $\text{H}_2$  gas is liberated at the cathode and  $\text{O}_2$  gas at the anode.

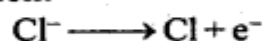
(iv)  $\text{CuCl}_2(s) + aq \longrightarrow \text{Cu}^{2+}(aq) + 2\text{Cl}^-(aq)$



At cathode:  $\text{Cu}^{2+}$  ions will be reduced in preference to  $\text{H}^+$  ions and copper will be deposited at cathode.



At anode:  $\text{Cl}^-$  ions will be discharged in preference to  $\text{OH}^-$  ions which remains in solution.



Thus, Cu will be deposited on the cathode and  $\text{Cl}_2$  gas will be liberated at the anode.