

Q.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

Ans. Mg, Al, Zn, Fe, Cu, Ag

Q.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, $Cr^{2+} / Cr = -0.74$ V

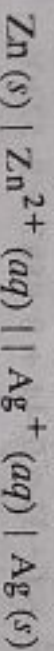
Arrange these metals in their increasing order of reducing power.

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

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

Ans. The set-up will be similar to that shown in Fig. 3.10. The cell will be represented as :



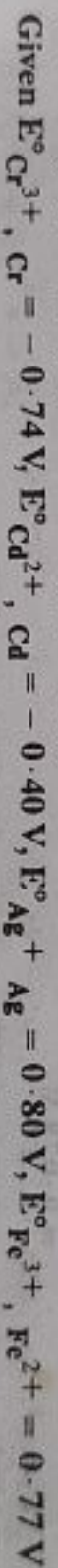
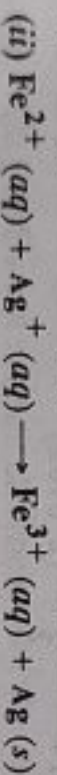
(i) Anode, i.e., zinc electrode will be negatively charged.

(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 : $Ag^+(aq) + e^- \rightarrow Ag$

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



Also calculate $\Delta_r G^\circ$ and equilibrium constants of the reactions.

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

$$\Delta_r G^\circ = -nFE^\circ_{cell} = -6 \text{ mol} \times 96500 \text{ C mol}^{-1} \times 0.34 \text{ V}$$

$$= -196860 \text{ CV mol}^{-1} = -196860 \text{ J mol}^{-1} = -196.86 \text{ kJ mol}^{-1}$$

$$-\Delta_r G^\circ = 2.303 RT \log K$$

$$196860 = 2.303 \times 8.314 \times 298 \log K \quad \text{or} \quad \log K = 34.5014$$

$$K = \text{Antilog } 34.5014 = 3.192 \times 10^{34}$$

(ii) $E^\circ_{cell} = +0.80$ V - 0.77 V = +0.03 V.

$$\Delta_r G^\circ = -nFE^\circ_{cell} = -(1 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.03 \text{ V})$$

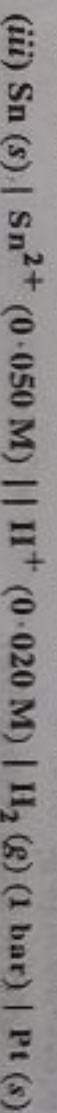
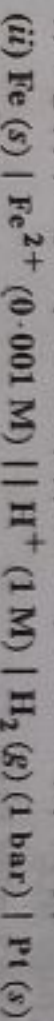
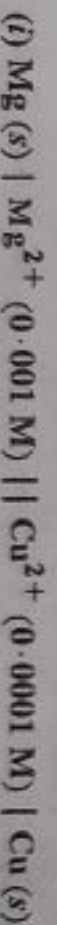
$$= -2895 \text{ CV mol}^{-1} = -2895 \text{ J mol}^{-1} = -2.895 \text{ kJ mol}^{-1}$$

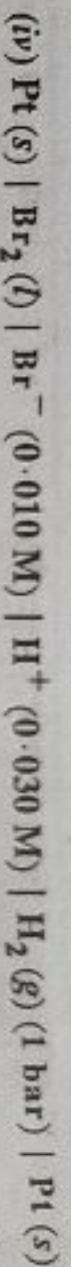
$$\Delta_r G^\circ = -2.303 RT \log K$$

$$-2895 = -2.303 \times 8.314 \times 298 \times \log K$$

$$\text{or} \quad \log K = 0.5074 \quad \text{or} \quad K = \text{Antilog}(0.5074) = 3.22.$$

Q.3.5. Write the Nernst equation and the e.m.f. of the following cells at 298 K :





Given $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37 \text{ V}$, $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$, $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$

$$E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14 \text{ V}, E^\circ_{1/2 \text{ Br}_2, \text{Br}^-} = +1.08 \text{ V}.$$

Ans. (i) Cell reaction: $\text{Mg} + \text{Cu}^{2+} \rightarrow \text{Mg}^{2+} + \text{Cu} (n = 2)$

$$\text{Nernst eqn. : } E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\therefore E_{\text{cell}} = 0.34 - (-2.37) - \frac{0.0591}{2} \log \frac{10^{-3}}{10^{-4}} = 2.71 - 0.02955 = 2.68 \text{ V}$$

(ii) Cell reaction: $\text{Fe} + 2 \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 (n = 2)$

$$\text{Nernst eqn. : } E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}$$

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

$$= 0.44 - \frac{0.0591}{2} \times (-3) = 0.44 + 0.0887 = 0.523 \text{ V}.$$

(iii) Cell reaction: $\text{Sn} + 2 \text{H}^+ \rightarrow \text{Sn}^{2+} + \text{H}_2 (n = 2)$

$$\text{Nernst eqn. : } E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2}$$

$$= 0 - (-0.14) - \frac{0.0591}{2} \log \frac{0.05}{(0.02)^2}$$

$$= 0.14 - \frac{0.0591}{2} \log 125 = 0.14 - \frac{0.0591}{2} (2.0969)$$

$$= 0.078 \text{ V}.$$

(iv) Cell reaction: $2 \text{Br}^- + 2 \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2$ (Note carefully)

$$\text{Nernst eqn. : } E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{1}{[\text{Br}^-]^2 [\text{H}^+]^2}$$

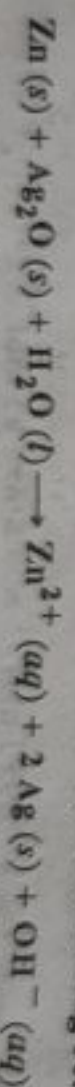
$$\therefore E_{\text{cell}} = (0 - 1.08) - \frac{0.0591}{2} \log \frac{1}{(0.01)^2 (0.03)^2}$$

$$= -1.08 - \frac{0.0591}{2} \log (1.111 \times 10^7) = -1.08 - \frac{0.0591}{2} (7.0457)$$

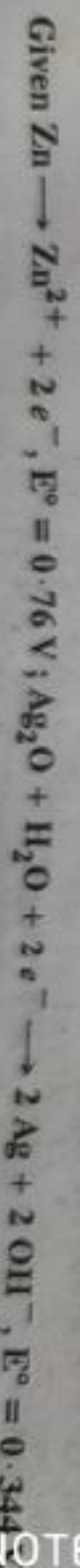
$$= -1.08 - 0.208 = -1.288 \text{ V}$$

Thus, oxidation will occur at the hydrogen electrode and reduction on the Br_2 electrode.
 $E_{\text{cell}} = 1.288 \text{ V}.$

Q.3.6. In the button cell widely used in watches and other devices, the following reaction takes place:



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



Ans. Refer to Solved Example 10, page 3/119.

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

(D.S.B. 2005, P.S.B. 2005, D.S.B. 2005, C.B. 2005)

Ans. Conductivity. Refer to sec. 3.6.1, page 3/12.

(A.I.S.B. 2007)

Molar conductivity. Refer to sec. 3.6.3, page 3/14.

Variation with concentration. Refer to sec. 3.8, page 3/21.

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

$$\text{Ans. } \Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{0.0248 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.20 \text{ mol L}^{-1}} = 124 \text{ S cm}^2 \text{ mol}^{-1}$$

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

$$\text{Ans. Cell constant} = \frac{\text{Conductivity}}{\text{Conductance}} = \text{Conductivity} \times \text{Resistance} = 0.146 \times 10^{-3} \text{ S cm}^{-1} \times 1500 \Omega = 0.219 \text{ cm}^{-1}$$

Q.3.10. Same as Solved Example on page 3/23.

Q.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 α for acetic acid is 390.5 $\text{S cm}^2 \text{ mol}^{-1}$, what is its dissociation constant?

$$\text{Ans. } \Lambda_m^c = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{(7.896 \times 10^{-5} \text{ S cm}^{-1}) \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.00241 \text{ mol L}^{-1}} = 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^o} = \frac{32.76}{390.5} = 8.4 \times 10^{-2}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.00241 \times (8.4 \times 10^{-2})^2}{1-0.084} = 1.86 \times 10^{-5}$$

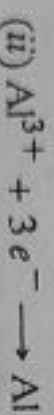
Q.3.12. Same as Solved Example 1 on page 3/8.

Q.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 .



Thus 1 mol of Ca, i.e., 40 g of Ca require electricity = 2 F

\therefore 20 g of Ca will require electricity = 1 F



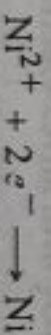
Thus, 1 mol of Al, i.e., 27 g of Al require electricity = 3 F

\therefore 40 g of Al will require electricity = $\frac{3}{27} \times 40 = 4.44 \text{ F}$.

Q.3.14. Same as Solved Example 2 on page 3/8.

Q.3.15. A solution of Ni (NO_3)₂ is electrolysed between platinum electrodes using a current of 5.0 ampere for 20 minutes. What mass of nickel will be deposited at the cathode? (At. mass of Ni = 58.7)

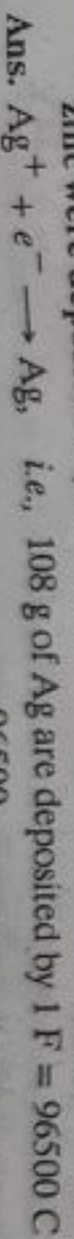
Ans. Quantity of electricity passed = (5 A) \times (20 \times 60 s) = 6000 C



Thus, 2 F, i.e., 2 \times 96500 C deposit Ni = 1 mole, i.e., 58.7 g

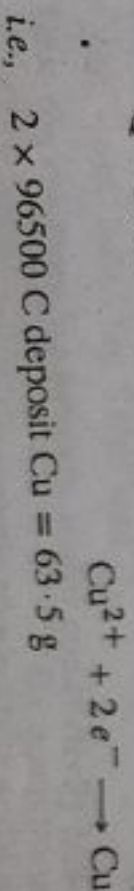
$$\therefore 6000 \text{ C will deposit Ni} = \frac{58.7}{2 \times 96500} \times 6000 \text{ g} = 1.825 \text{ g.}$$

Q.3.16. Three electrolytic cells A, B and C containing electrolytes ZnSO_4 , AgNO_3 and CuSO_4 respectively were connected in series. A steady current of 1.50 ampere was passed through them until 1.45 g of Ag were deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited? (At. wts. of Cu = 63.5, Zn = 65.3, Ag = 108)

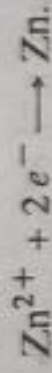


$$\therefore 1.45 \text{ g of Ag will be deposited by } \frac{96500}{108} \times 1.45 \text{ C} = 1295.6 \text{ C}$$

$$Q = I \times t \quad \text{or} \quad t = Q/I = 1295.6/1.50 = 863.7 \text{ s} = 14 \text{ min, } 24 \text{ sec.}$$

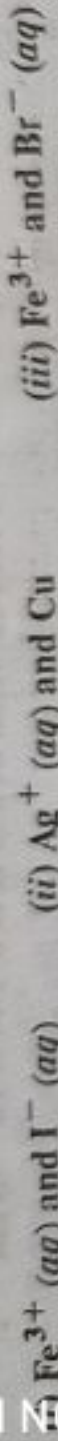


$$1295.6 \text{ C will deposit Cu} = \frac{63.5}{2 \times 96500} \times 1295.6 = 0.426 \text{ g}$$



$$\text{Zn deposited} = \frac{65.3}{2 \times 96500} \times 1295.6 = 0.438 \text{ g}$$

Q. 3.17 Predict if the reaction between the following is feasible :



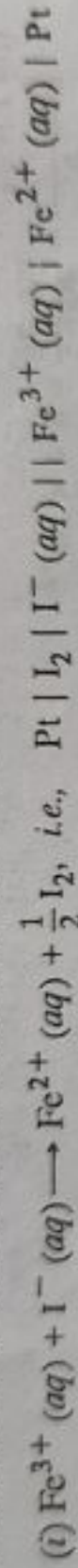
Given standard electrode potentials :

$$E^\circ_{1/2 \text{ I}_2, \text{I}^-} = 0.541 \text{ V}, \quad E^\circ_{\text{Cu}^{2+}, \text{Cu}} = 0.34 \text{ V}$$

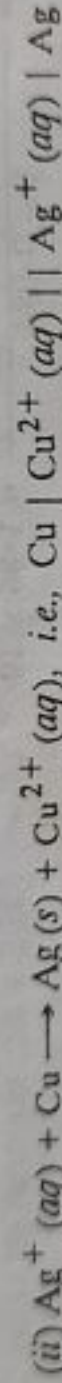
$$E^\circ_{1/2 \text{ Br}_2, \text{Br}^-} = 1.09 \text{ V}, \quad E^\circ_{\text{Ag}^+, \text{Ag}} = +0.80 \text{ V}$$

$$E^\circ_{\text{Fe}^{3+}, \text{Fe}^{2+}} = +0.77 \text{ V}$$

Ans. A reaction feasible if EMF of the cell reaction is +ve



$$\therefore E^\circ_{\text{cell}} = E^\circ_{\text{Fe}^{3+}, \text{Fe}^{2+}} - E^\circ_{1/2 \text{ I}_2, \text{I}^-} = 0.77 - 0.54 = 0.23 \text{ V (Feasible)}$$



$$E^\circ_{\text{cell}} = E^\circ_{\text{Ag}^+, \text{Ag}} - E^\circ_{\text{Cu}^{2+}, \text{Cu}} = 0.80 - 0.34 = 0.46 \text{ V (Feasible)}$$



Q. 3.18. Predict the products of electrolysis of the following :

(i) An aqueous solution of AgNO_3 with silver electrodes

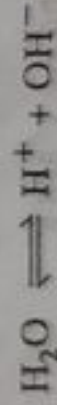
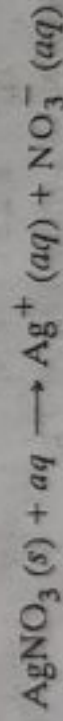
(ii) An aqueous solution of AgNO_3 with platinum electrodes

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

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

$$\text{(Given } E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V, } E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V)}$$

Ans. (i) Electrolysis of aqueous solution of AgNO_3 with silver electrodes.



At Cathode : Ag^+ ions have lower discharge potential than H^+ ions. Hence, Ag^+ ions will be deposited as Ag in preference to H^+ ions.

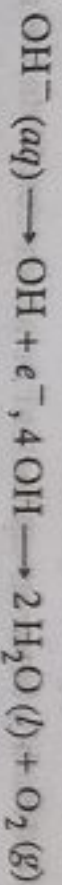
At Anode : As Ag anode is attacked by NO_3^- ions, Ag of the anode will dissolve to form Ag^+ ions in the solution.



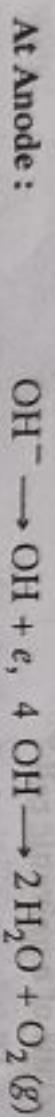
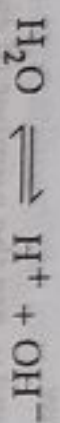
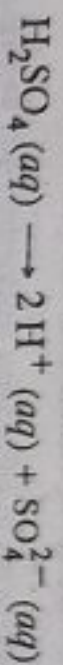
(ii) Electrolysis of aqueous solution of AgNO_3 using platinum electrodes.

At Cathode : Same as above.

At Anode : As anode is not attackable, out of OH^- and NO_3^- ions, OH^- ions have lower discharge potential. Hence, OH^- ions will be discharged in preference to NO_3^- ions, which then decompose to give out O_2 .

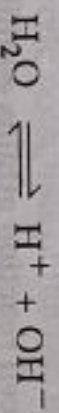
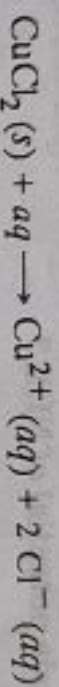


(iii) Electrolysis of dilute H_2SO_4 with platinum electrodes.

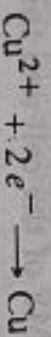


Thus, H_2 is liberated at the cathode and O_2 at the anode.

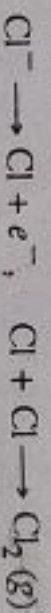
(iv) Electrolysis of aqueous solution of CuCl_2 with platinum electrodes



At Cathode : Cu^{2+} ions will be reduced in preference to H^+ ions



At Anode : Cl^- ions will be oxidized in preference to OH^- ions



Thus, Cu will be deposited on the cathode and Cl_2 will be liberated at the anode.

ADDITIONAL QUESTIONS

VERY SHORT ANSWER QUESTIONS

CARRYING 1 MARK

Q.1. How can you test whether the given electrolyte is a strong electrolyte or a weak electrolyte ?
Ans. If the aqueous solution of the electrolyte conducts electricity to a large extent, it is a strong electrolyte and if to small extent, it is a weak electrolyte.

Q.2. What is the effect of temperature on the electrical conduction of (i) metallic conductor
 (ii) electrolytic conductor ?
Ans. With increase of temperature, the electrical conduction of metals decreases whereas that of electrolytes increases.

Q.3. Define the following terms : Specific and equivalent conductance.
 (H.S.B. Sample Paper 1991 D.S.B. 1992)

Ans. Specific conductance is the conductance of 1 cm^3 of the solution whereas equivalent conductance is the conductance of a solution containing one gram equivalent of the electrolyte provided the distance between the electrodes is 1 cm and area of the electrodes is so large that the whole solution is contained between them. (A.I.S.B. 1994, H.S. 2011)

Q.4. What are the units of molar conductivity ?
Ans. $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ or $\text{S cm}^2 \text{mol}^{-1}$.

Q.5. Give the relationship between molar conductivity and specific conductivity.
Ans. $\Lambda_m = \kappa \times \frac{1000}{c}$ where κ is specific conductivity and c is the molar concentration.